TRANSPORTATION RESEARCH

CIRCULAR

Number E-C170 December 2012

Nanotechnology in Concrete Materials

A Synopsis

TRANSPORTATION RESEARCH BOARD
OF THE NATIONAL ACADEMIES

Transportation Research Circular E-C170

Nanotechnology in Concrete Materials

A Synopsis

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Transportation Research Board
500 Fifth Street, NW
Washington, D.C.
www.TRB.org

TRANSPORTATION RESEARCH CIRCULAR E-C170
ISSN 097-8515

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500 Fifth Street, NW
Washington, D.C.
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Javy Awan, Production Editor; Jennifer Correro, Layout and Proofreading

Preface

The mechanical behavior of concrete materials depends to a great extent on structural elements and phenomena which are effective on a micro- and nanoscale. The ability to target material modification at the nanostructural level promises to deliver the optimization of material behavior and performance needed to improve significantly the mechanical performance, volume change properties, durability, and sustainability of concrete.

This synopsis is written to assist in the identification of promising new research and innovations in concrete materials using nanotechnology that can result in improved mechanical properties, volume change properties, durability, and sustainability. This publication was developed both for the practitioner who wants a general knowledge of how nanotechnology can shape—and is shaping—the future and for the academician who is interested in a compilation of the latest research including detailed references related to nanotechnology in concrete.

Parts 1, 3, and 4 are on a level that can be comprehended by a reader who has no background in nanotechnology. Part 1 is a general overview for practitioner and academician alike. Part 3 highlights some of the current implementation case studies, and Part 4 identifies some of the challenges and sets a course for future direction.

In Part 2, at the front of each of the main sections is a general description for the practitioner. The body of the section details the state of the art in research and technology in nanotechnology. This synergy of practical needs and future vision will change the future of concrete construction in the transportation industry.

—Bjorn Birgisson
Chair, Task Force on Nanotechnology-Based Concrete Materials

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PART 1

Nanotechnology for Concrete

Overview

Nanotechnology is an emerging field of science related to the understanding and control of matter at the nanoscale, i.e., at dimensions between approximately 1 and 100 nm (www.nano.gov). At the nanoscale, unique phenomena enable novel applications. Nanotechnology encompasses nanoscale science, engineering, and technology that involve imaging, measuring, modeling, and manipulating matter at this length scale.

Just how small is "nano"? In the serviceability index system of units, the prefix "nano" means 1-billionth or 10^{-9}. Therefore 1 nm is 1-billionth of a meter. It's difficult to imagine just how small that is, so here are some examples (www.nano.gov):

- A sheet of paper is about 100,000-nm thick.
- A strand of human DNA is 2.5 nm in diameter.
- There are 25,400,000 nm in 1 in.
- A human hair is approximately 80,000 nm wide.
- On a comparative scale, if the diameter of a marble was 1 nm, then diameter of the Earth would be about 1 m.

Nanoscale particles are not new in either nature or science. Recent developments in visualization and measurement systems for characterizing and testing materials at the nanoscale have led to an explosion in nanotechnology-based materials in areas such as polymers, plastics, electronics, car manufacturing, and medicine.

Matter can exhibit unusual physical, chemical, and biological properties at the nanoscale, differing in important ways from the properties of bulk materials and single atoms or molecules. Some nanostructured materials are stronger or have different magnetic properties compared to other forms or sizes of the same material. Others are better at conducting heat or electricity. They may become more chemically reactive or reflect light better or change color as their size or structure is altered.

Nanotechnology is not simply working at ever-smaller dimensions; rather, working at the nanoscale enables scientists to utilize the unique physical, chemical, mechanical, and optical properties of materials that naturally occur at that scale.

Of particular relevance for concrete is the greatly increased surface area of particles at the nanoscale. As the surface area per mass of a material increases, a greater amount of the material can come into contact with surrounding materials, thus affecting reactivity.

Nanotechnology considers two main approaches: (*a*) the ‘‘top down” approach in which larger structures are reduced in size to the nanoscale while maintaining their original properties without atomic-level control (e.g., miniaturization in the domain of electronics) or deconstructed from larger structures into their smaller composite parts and (*b*) the ‘‘bottom-up” approach, also called ‘‘molecular nanotechnology” or ‘‘molecular manufacturing” (example: www.nano.gov) in which materials are engineered from atoms or molecular components through a process of assembly or self-assembly (Figure 1).

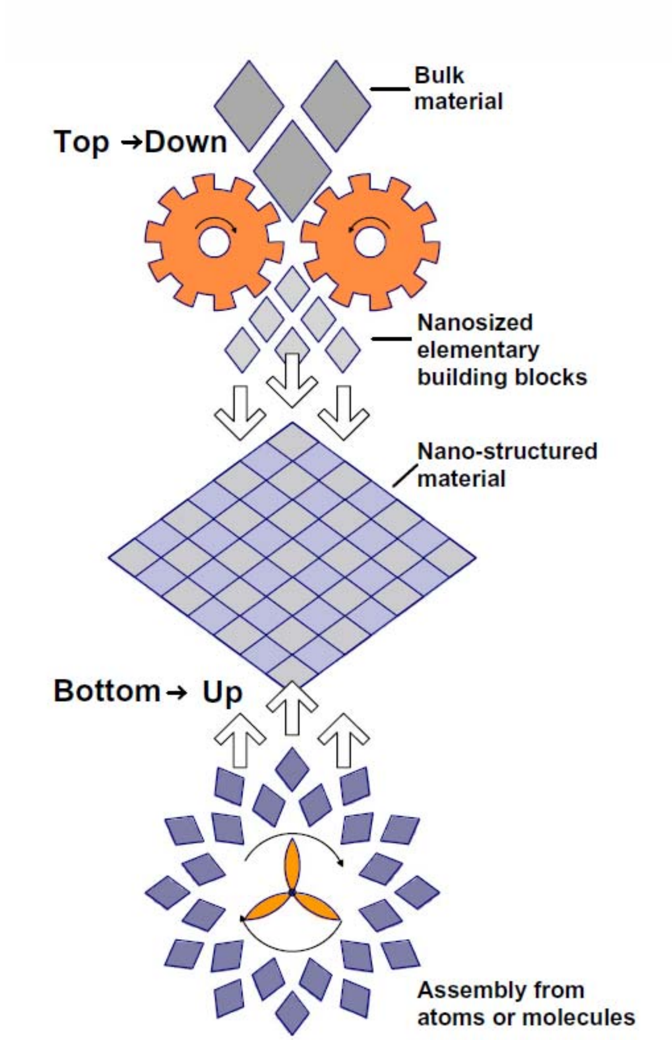

FIGURE 1 The top-down and bottom-up approaches in nanotechnology (*1*) (Sanchez and Sobolev, 2010).

Thus the basic concept behind nanomodification of materials is that of bottom-up engineering, starting with engineered modifications to the molecular structure with an aim to affect the bulk properties of the material. Conceptually, this is simply an imitation of nature. In practice, the introduction of nanotechnology represents a revolution that is allowing for the development of high-performance and long-lasting products and processes within an ideal context of sustainable development.

The 2000 Presidential Commission on Nanotechnology likened the potential impact of nanotechnology on society to that of the Industrial Revolution. The report (www.nano.gov) by the commission identified economic and safe transportation as one of the nine grand challenges where nanotechnology had the greatest potential for pay-off. Concrete-based materials are considered by the National Nano Initiative as examples where nanotechnology may have a particularly large impact in the future.

Concrete, the most ubiquitous material in the world, is a nanostructured, multiphase, composite material that ages over time (Sanchez and Sobolev, 2010). It is composed of an amorphous phase, nanometer- to micrometer-size crystals, and bound water. The properties of concrete exist in, and the degradation mechanisms occur across, multiple length scales (nano to micro to macro) where the properties of each scale derive from those of the next smaller scale (Figure 2, page 5). Nanoengineering of concrete can take place in one or more of the three locations such as (*a*) in the solid phases, (*b*) in the liquid phases, or (*c*) at the interfaces between liquid–solid and solid–solid (Garboczi, 2009).

The mechanical behavior of concrete materials depends to a great extent on structural elements and phenomena that are effective on a micro- and nanoscale. The size of the calcium silicate hydrate (C-S-H) phase, the primary component responsible for strength and other properties in cementitious systems, lies in the few nanometers range (Taylor, 1997). The structure of C-S-H is much like clay, with thin layers of solids separated by gel pores filled with interlayer and adsorbed water (Mehta, 1986). This has significant impact on the performance of concrete because the structure is sensitive to moisture movement, at times resulting in shrinkage and consequent cracking if accommodations in element sizes are not made (Jennings et al., 2007). Hence, nanotechnology may have the potential to engineer concrete with superior properties through the optimization of material behavior and performance needed to significantly improve mechanical performance, durability, and sustainability.

The development of nanotechnology-based concrete materials requires a multidisciplinary approach, consisting of teams of concrete materials experts: civil engineers, chemists, physicists, and materials scientists. Porro et al. (2010) presented an overview of how nanotechnology could be applied to concrete technology, emphasizing the multidisciplinary approach needed for successful breakthroughs leading to ultra high-performance materials and new multiscale models that enable the prediction of bulk material properties from composition and processing parameters. Grove et al. (2010) identified opportunities for nanotechnology leading to new concrete products and materials, and also for improving the sustainability and reducing the environmental footprint of concrete-based materials in the future. Finally, Birgisson et al. (2010) identified the following key breakthroughs in concrete technology that are most likely to result from the use of nanotechnology:

- Development of high-performance cement and concrete materials as measured by their mechanical and durability properties;
- Development of sustainable concrete materials and structures through engineering for different adverse environments, reducing energy consumption during cement production, and enhancing safety;
- Development of intelligent concrete materials through the integration of nanotechnology-based self-sensing and self-powered materials and cyber infrastructure technologies;
- Development of novel concrete materials through nanotechnology-based innovative processing of cement and cement paste; and
- Development of fundamental multiscale model(s) for concrete through advanced characterization and modeling of concrete at the nano-, micro-, meso-, and macroscales.

PART 2

Nanotechnology-Based Research in Concrete to Date

HIGH-PERFORMANCE CEMENT AND CONCRETE MATERIALS

The addition of nanofine particles can improve the properties of concrete due to the effect increased surface area has on reactivity and through filling the nanopores of the cement paste. Nanosilica and nanotitanium dioxide are probably the most reported additives used in nanomodified concrete. Nanomaterials can improve the compressive strength and ductility of concrete. Carbon nanotubes or nanofibers (CNT-CNF) have also been used to modify strength, modulus and ductility of concretes. CNFs can act as bridges across voids and cracks that ensure load transfer in tension. Ultra high-performance concretes (UHPC) used in current practice and found in the research literature have mainly been developed using some type of nanomodification or the use of an admixture developed using nanotechnology methods. Some of the ways nanotechnology can be used to affect concrete include modifying the cement properties through nanomodification, modifying the cement paste itself through admixtures, or affecting the concrete mixture using nanoporous thin film (NPTF) coatings for the aggregates themselves.

Durability of concretes can also be improved through reduced permeability and improved shrinkage properties. These effects can be accomplished through nanomodified cements or the use of nanodeveloped additives to the paste.

Mechanical Properties

Incorporation of nanomaterials into the matrix to improve concrete mechanical properties has emerged as a promising research field. Nanoscale particles are characterized by a high surface area-to-volume ratio and many are highly reactive (Figure 2). Most of the concrete-related research to date has been conducted with nanosilica (nano-SiO_2) (Bjornstrom et al., 2004; Flores, 2010; Ji, 2005; Jo, 2007; Li, 2004, 2006, 2007; Qing, 2007; Lin KL, 2008; Lin DF, 2008; Sobolev, 2005, 2009; Sanchez, 2010; Qing, 2008; Kuo, 2006) and nanotitanium oxide (nano-TiO_2) (Li, 2006, 2007). A few studies on incorporation of nanoiron (nano-Fe_2O_3) (Li, 2004), nanoalumina (nano-Al_2O_3) (Li, 2006), and nanoclay particles (Chang, 2007; Kuo, 2006) have also been reported. Manufacture of nanosized cement particles and the development of nanobinders (Lee, 2005; Sobolev, 2005) is another area where limited numbers of investigations have been carried out (Figure 3).

Formation of Dense Microstructure and More Efficient Cement Hydration

Scanning electron microscopy (SEM) microstructural studies of mortar specimens with and without nanoparticles have revealed the mechanisms for improved performance with nano-SiO_2 (Figure 3). When a small quantity of nanoparticles is uniformly dispersed in a cement paste, the hydrated products of cement deposit on the nanoparticles due to their higher surface energy, i.e., act as

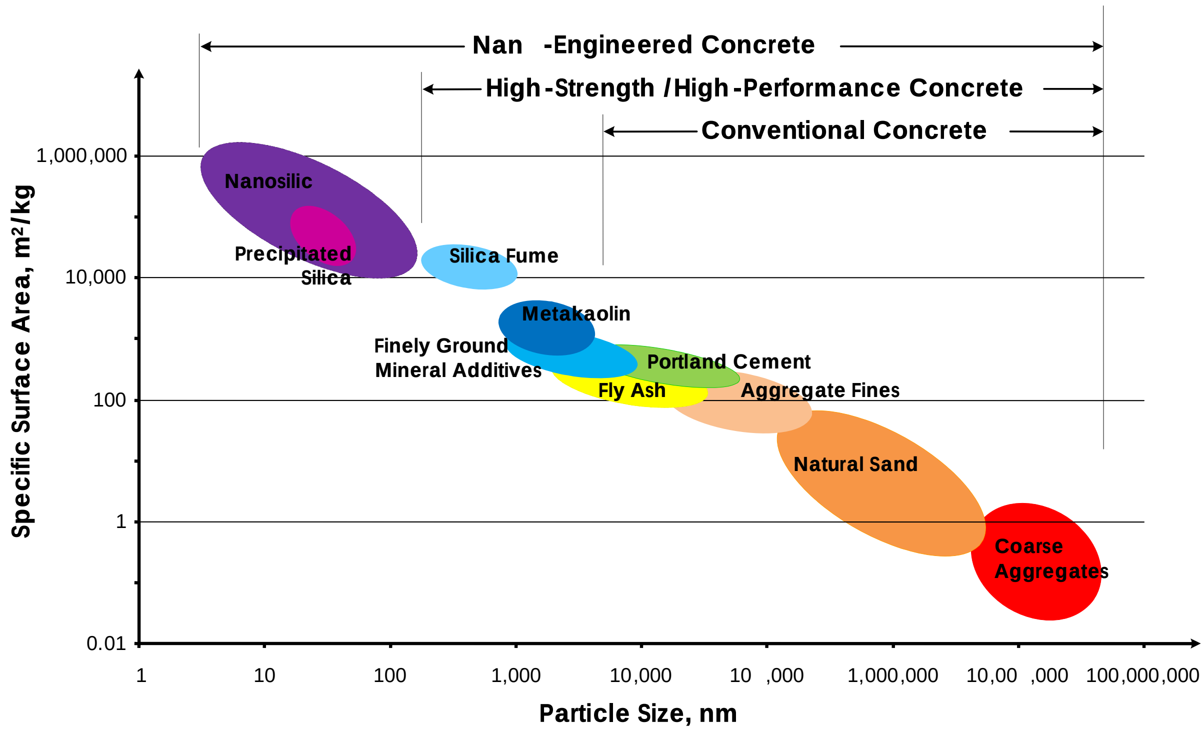

FIGURE 2 Particle size and specific surface area related to concrete materials (adapted from Sobolev, 2005).

nucleation sites. Nucleation of hydration products on nanoparticles further promotes and accelerates cement hydration (Bjornstrom et al., 2004; Lin, 2008). The addition of colloidal silica resulted acceleration of C_3S dissolution and rapid formation of C-S-H phase in cement paste (Bjornstrom et al., 2004).

The other mechanisms of improved performance are that: (*a*) nanoparticles fill the nanosize pores of the cement paste, and (*b*) nano-SiO_2 reacts with $Ca(OH)_2$ (i.e., pozzolanic reaction) and generates additional C-S-H (Sobolev, 2005; Jo, 2007). Both processes are influenced by the particle size and the proper dispersion of the nanoparticles within the cement paste, with colloidal dispersions being more effective than the powder (Gaitero et al., 2010). A reduction in $Ca(OH)_2$ content and increase in C-S-H content in cement mortar as a result of nano-SiO_2 addition was noticed through DTA and XRD testing (Tang et al., 2003). With the addition of 3% (by weight) of nano-SiO_2, significant improvement of early-age interfacial transition zone (ITZ) structure with respect to reduction in content, crystal orientation degree, and crystal size of portlandite crystals was reported by (Qing et al., 2003). An increase of chemically combined water content and heat of hydration and a decrease of CH content in presence of nanometer-sized SiO_2 powder was reported by Lu et al. (2006). The microstructural studies by NMR, BET, and MIP indicated that portland cement composites with nanosilica produce more solid, dense, and stable bonding framework (Shih et al., 2006). In another study (Dolado et al., 2005), it is reported that the improvement in strength due to nanosilica addition was not related to pozzolanic reaction, but due to the formation of denser microstructures through growth of silica chains in C-S-H.

The addition of silica nanoparticles has important implications for the hydration kinetics and the microstructure of the paste such as (*a*) an increase in the initial hydration rate, (*b*) an increase of the amount of C-S-H gel in the paste through pozzolanic reaction, (*c*) reduction of porosity, (*d*) improvement in the mechanical properties of the C-S-H gel itself (e.g., greater alumina-content, longer silicate chains) (Gaitero et al., 2010). Sum of these factors resulted in pastes with 30% more compressive strength. Nanoindentation studies have shown that the volume fraction of the high stiffness C-S-H gel increased significantly with addition of nanosilica (Mondal et al., 2010), which significantly improves concrete durability. Samples with nanosilica showed almost twice the amount of high-stiffness C-S-H as the sample with silica fume. The addition of nanosilica particles (5 to 70 nm, synthesized by using sol-gel method) along with superplasticizing admixture in portland cement mortar resulted compressive strength to reach up to 63.9 MPa and 95.9 MPa at the ages of 1 day and 28 days, respectively (Flores et al., 2010) and flexural strength of 23.5 MPa at 28 days. Silica nanoparticles modify the ITZ of cement mortar in four different ways, i.e., (*a*) acting as nucleation site, (*b*) generating more C-S-H through pozzolanic reaction that is also more dispersed through a nucleation effect, (*c*) controlling crystallization, and (*d*) improving the microfilling effect (Hosseini et al., 2010). The effect of nanoparticles at early ages (especially in the first 3 days) is more noticeable than with other curing ages. The ultra high reactivity of nanosilica particles contributes to the promotion of hydration reaction and also expedites the pozzolanic reaction.

A combined effect of the above mechanisms produces a uniform dense microstructure with improvement not only in the cement paste but also in the ITZ.

A few studies have shown that nano-TiO_2 can accelerate the early-age hydration of portland cement (Jayapalan et al., 2010), improve compressive and flexural strengths (Li H et al., 2007).

Conduction calorimeter based test results (Sato and Diallo, 2010) indicated that the addition of nano-$CaCO_3$ significantly accelerated the rate of heat development and shortened the induction period of C_3S hydration. It was proposed that nano-$CaCO_3$ either broke down the protective layer on C_3S grains during hydration to shorten the induction period, or accelerated C-S-H nucleation (i.e., seeding effect).

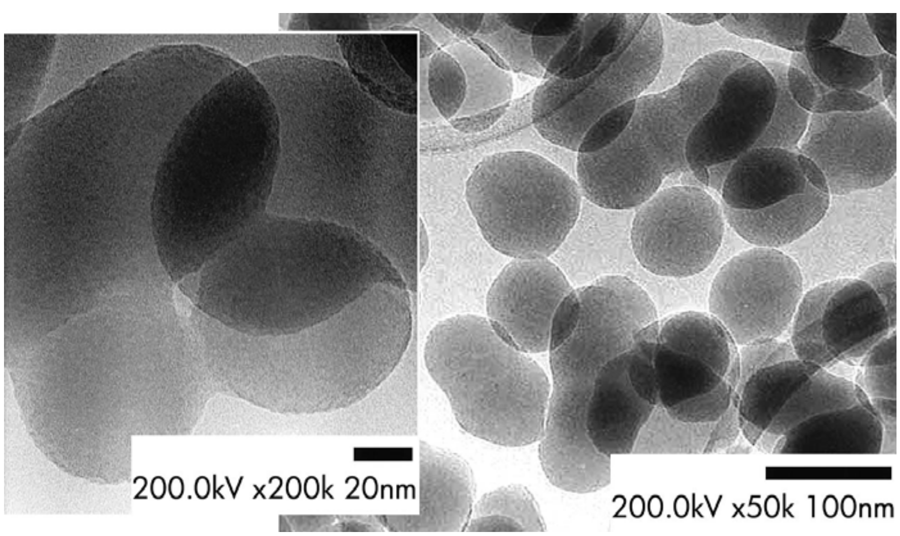

FIGURE 3 Spherical nano-SiO_2 particles of uniform distribution observed using TEM (Sanchez and Sobolev, 2010).

Higher Compressive Strength Concrete

Research showed that the compressive and flexural strengths of cement mortars containing SiO_2 and Fe_2O_3 nanoparticles were both higher than those of plain cement mortar (Li et al., 2004; L. Hui, 2004). The experimental results show that the compressive strengths of mortars with nanosilica (NS) were all higher than those of mortars containing silica fume at 7 and 28 days. An addition of 10% nano-SiO_2 with dispersing agents resulted in a 26% increase of 28-day compressive strength whereas the increase was 10% with 15% silica fume (H. Li et al., 2004) without dispersing agents. Other research showed that the addition of small amounts of NS (i.e., 0.25%) caused 10% increase of compressive strength and 25% increase of flexural strength at 28 days (Sobolev et al., 2009). Nanofume, a new ultrafine, powder admixture of amorphous SiO_2 produced from fly ash, was used to prepare high-strength concrete based on normal portland cement. Compressive strength of the concrete increased with increasing specific surface area of nanofume (20 m^2/g to 130 m^2/g). Nanofume with a specific surface area between 30 m^2/g to and 50 m^2/g was recommended for the preparation of a concrete with compressive strength of 120 MPa.

NanoAl$_2$O$_3$ was found to be very effective in increasing the modulus of elasticity of cement mortar. With 5% of nanoAl$_2$O$_3$ (approximately 150 nm average particle size), the elastic modulus increased by 143% at 28 days, whereas the increase of compressive strength was not very obvious (Zhenhua et al., 2006). A proper mixing procedure was selected in order to ensure adherence of nanoAl$_2$O$_3$ particles on the sand surfaces. It is believed that during cement hydration, these nanoalumina particles were available to fill the pores at the sand–paste interfaces and created a dense ITZ with less porosity. With an increase in nanoAl$_2$O$_3$ content, the elastic modulus of mortars increases when nanoAl$_2$O$_3$ content is less than 5%. At higher replacement level (e.g., >5%), agglomeration of nanoparticles caused ineffective densification of ITZ and as a result, the elastic modulus of mortars decreases.

The effect of synthetic nano-ZrO_2 powder addition in cement on the strength development of portland cement paste was studied by Fan et al. (2004). Reduction in porosity and permeability, enhancement in compressive strength, and improvement in microstructure of cement paste were observed due to the addition of nano-ZrO_2 powder in cement. Both pore filling and bridging action were identified as possible mechanisms for improvement.

The effect of incorporating nanometer-sized franklinite ($ZnFe_2O_4$) particles obtained from electric–arc–furnace dust (EAFD) on strength properties of portland cement paste was studied by Balderas et al. (2001). The powder obtained after acid treatment of the EAFD consisted basically of nanometer-sized particles of franklinite. Incorporation of the EAFD in a portland cement paste caused a retardation in the setting time. Nevertheless, after 7 days, the compressive strength of the portland cement–EAFD pastes was superior to portland cement alone, and, after 28 days, the extent of hydration of the portland cement–EAFD paste was equivalent to portland cement alone. A compressive strength of 72 MPa was attained after 42 days for OPC doped with 10 wt% EAFD.

Improvement in flexural strength in mortar and concrete due to the addition of calcium carbonate particles with surface area $\geq 10\ m^2/g$ was observed by Cervellati et al. (2006).

The organo-modified montmorillonites (OMMT) particles are hydrophobic and thus can be utilized to improve the strength and permeability of cement mortar and concrete. The compressive and flexural strengths of cement mortars can be increased up to 40% and 10%, respectively, by the addition of OMMT particles.

Higher Tensile Strength, Ductile, and Tougher Concrete

CNTs-CNFs are potential candidates for use as nanoreinforcements in cement-based materials. CNTs-CNFs exhibit extraordinary strength with moduli of elasticity of the order of TPa and tensile strength in the range of GPa, and they have unique electronic and chemical properties (Ajayan, 1999;, Salvetat et al., 1999; Srivastava et al., 2003). Cementitious materials (e.g., concrete) typically behave as brittle materials with low tensile strength and are prone to cracking. Incorporation of fibers into cementitious materials is a common practice to increase tensile strength and ductility and improve durability. The interfacial interactions between CNTs and cement hydrates produce high bond strength. CNTs act as bridges across cracks and voids, which ensures load-transfer in tension (Makar, 2005; G. Li et al., 2005).

Research has shown that flexural strength and stiffness of cementitious materials can be increased by adding low concentration (e.g., 0.025% by weight of cement) of homogeneously dispersed multiwall CNTs (MWCNTs). It is reported that adding small amounts of CNTs (1%) by weight could increase both compressive and flexural strength (Mann, 2006).

Research has revealed that incorporation of macrofibers and microfibers in cementitious system can control cracking through bridging and load transfer across cracks and pores (Makar 2005). Although, microfibers delay the propagation of microcracks, they do not stop their initiation. CNFs are able to bridge nanocracks and pores and achieve good bonding with the cement hydration products. In one study incorporation of an optimal amount of CNFs (close to 0.048 wt%) was shown to improve flexural strength of the cementitious matrix significantly (Metaxa et al., 2010). To develop high-performance nanofiber–cement nanocomposites, a homogeneous distribution of the nanofibers in cementitious matrices must be achieved. Segregation of CNF in cement paste due to improper distribution of CNF fibers is a common concern.

The effect of CNTs in cement mortar at different types and dosage rates of multiwall nanotubes was studied by Manzur and Yazdani (2010). The initial results are encouraging but depend largely on the mixing techniques and workability issues. A sonication technique was adapted to ensure uniform dispersion of CNTs. MWCNT was added in sequence and was sonicated for 5 min for each addition. An increase in mean strength is observed up to 0.5 wt% MWNT addition compared with the control sample of both types of MWNT; addition of 0.3 wt% MWNT provided the highest mean compressive strengths. A smaller-sized MWNT results higher compressive strength as small MWNTs are distributed at a much finer scale and therefore fill the nanopore space more effectively. Some of the challenges are (*a*) achieving proper dispersion; (*b*) high water demand to achieve satisfactory workability in nanotube-reinforced cement composites; and (*c*) reduction in strength due to formation of large voids.

Strong attraction among nanoscale fibers (CNFs-CNTs) due to van der Waals forces makes uniform distribution of fibers in the matrix difficult. With the use of superplasticizer, CNFs can be uniformly dispersed in water by ultrasonic processing. But mixing a water-superplasticizer-CNF dispersion with cement doesn’t ensure uniform distribution of CNFs in cement paste. To achieve better fiber dispersion in paste, either functionalized or highly dispersible CNFs should be used. The CNFs can be implanted or grown on cement particles (Nasibulina et al., 2010). An investigation on the relationship between cement particle size and the dispersion of CNFs-CNTs in paste revealed that large cement particles prevent a uniform distribution, when fibers are very small or used in high dosages. It is advisable to use fresh cement with minimal amount of large grains and clumps for making CNF-CNT reinforced cementitious composites (Yazdanbakhsh et al., 2010).

Time-consuming steps are required in purifying and functionalizing the carbon nanomaterials in order to obtain a good dispersion. A novel cement-hybrid material (CHM) was synthesized in which CNTs and CNFs are attached to the cement particles by two different methods: screw feeder and fluidized bed reactors (Nasibulina et al., 2010). CHM has been proved to increase the compressive strength by two times and the electrical conductivity of the hardened paste by 40 times.

Micro- and nanoscale characterization of ITZ of UHPC revealed that an enhanced fiber-matrix interfacial region, created by thermal treatment, contributes significantly to the reductions in tensile-creep deformation measured for UHPC subjected to early curing at 90°C and 60°C. The results suggest that a more moderate but longer period of thermal curing may be appropriate and may offer a practical alternative for the curing of prestressed UHPC elements. This has relevance to the development of guidelines for optimizing practical curing regimes for fiber-reinforced UHPC and demonstrates the necessity to perform tensile-creep tests in cases in which satisfactory long-term tensile performance is desired (Garas et al., 2010).

Similarly, the reinforcement of combined nanocellulose and microcellulose fibers in reactive powder concrete (RPC) was found to be effective in increasing the toughness of an otherwise brittle material. Preliminary results show that the addition of up to 3% micro- and nanofibers in combination increased the fracture energy by more than 50% relative to the unreinforced material (Peters et al., 2010).

Use of polycarboxylate-based HRWR proved successful in disaggregating the CNFs in solution and improved the dispersion of CNFs in the cement paste at the individual fiber level but inhomogeneous distribution (i.e., areas of high and low CNF density) of the fibers cannot be avoided. Addition of 0.2 wt% CNF resulted in increased splitting tensile strength of 22% in portland cement composites. Migration of CNFs along the bleed water (depending on the water-binder ratio used) sometimes creates a porous layer of agglomerated CNFs intermixed with cement paste at the upper surface of the composite (Gay and Sanchez, 2010).

Improved Aggregate–Paste Bond Strength

With the addition of 3% of nano-SiO_2, significant improvement of early age ITZ structure with respect to reduction in content, crystal orientation degree, and crystal size of portlandite crystals was reported by Qing et al. (2003). It is believed that during cement hydration, the nanoalumina particles fill the pores at the aggregate–paste interfaces and created a dense ITZ with less porosity, which was mainly responsible for significant increase of elastic modulus of mortars (Z. Li et al., 2006).

Improved Concrete Performance Using Nanoporous Thin Film Technology

As discussed above, most nanotechnology research has focused on characterizing concrete when nanosilica particles are dispersed in the cement paste. Nanoparticles added during mixing affect only the microstructure of the paste without making any significant improvement in the strength of the interfacial transition zones (ITZ). The addition of nanoparticles as NPTF on aggregate surface before concrete mixing was found to be an effective way to improve the ITZ and thereby the performance of concrete (Munoz and Meininger 2010). Water suspended nanoparticles (i.e., colloidal suspension) are used to coat aggregates through dip- or spray-coating methods. The technology necessary to apply NPTF on aggregates is already available in the market. This is a cost-effective method as small quantify of nanoparticulate additives is needed to obtain significant results as opposed to conventional powder addition method. Improvements in compressive, tensile, and flexural strengths and reduction in drying shrinkage have been observed through the incorporation of NPTFs in mortar and concrete. The overall modulus of elasticity increase in mortars with nanosilica coated aggregates is believed to be due to the improvements in the ITZ. Meininger and Munoz (2010) showed how the addition of NPTFs resulted in 8% to 22% reduction in relative porosity in the ITZ. This improvement in performance can ameliorate longitudinal and transverse cracking, corner breaks, punchouts, and D-cracking in concrete pavement. Research on NPTF additions in concrete is in an early stage. Further work is needed to understand the mechanisms and the full-scale impact of this technology.

The addition of nano-SiO_2 into concrete as thin films on aggregate surfaces has a high potential for improving the overall performances of concrete. Mortar made with a nano-SiO_2-cement ratio of 0.0032 deposited as a surface coating of just one-third of the total fine aggregates showed an average 35% improvement in compressive strength, flexural strength, and tensile strength at early ages along with a reduction in chloride permeability (Sanfilippo et al., 2010).

Self-Healing of Microcracks Through Use of Chemistry and Microbes

Self-healing polymers, which include a microencapsulated healing agent and a catalytic chemical trigger (Kuennen 2004), could be especially applicable to fix the microcracking in bridge piers and columns. When the microcapsules are broken by a crack, the healing agent is released into the crack along with a catalyst. Subsequent polymerization bonds the crack faces.

Preliminary work on assessing the self-healing performance of cementitious composite using microcapsules (PSMs) with oil core and silica gel shell (Yang et al., 2010) is very promising. The microcapsules were dispersed in fresh cement mortar along with carbon nanofibers and silica fume. EIS (electrochemical analyses) was used to characterize microstructural properties and self-healing effect of the fiber-reinforced cement mortars. The EIS data suggested that the inclusion of PSMs enabled the mortar composite to heal at least part of the artificially induced microcracks (Yang et al., 2010).

Nanomaterials for Electrical Conductivity and Stress-Sensing of Concrete

The addition of CNTs treated with a mixed solution of H_2SO_4 and HNO_3 or untreated CNTs to cement paste results in a considerable decrease in electrical resistivity and a distinct enhancement in compressive strength. The cement paste with treated CNT reinforcement showed higher mechanical strength, higher compressive sensitivity and lower electrical conductivity than those with untreated CNT (G. Li et al., 2007).

Concrete with nano-Fe_2O_3 can have self-diagnostic ability of stress as well as improvement of compressive and flexural strengths (Li et al., 2004; Xiao and Ou, 2004). It was observed that the volume electric resistance of cement mortar changes with the applied load in presence of nano-Fe_2O_3 (30-nm particle size). On the other hand the plain cement mortar is poor in monitoring its stress. The resistance linearly decreased with the increase of the compressive loading for mortars with nano-Fe_2O_3 more sharply with 5% nano-Fe_2O_3. Based on this observation, it is logical to postulate that concrete with nanoFe_2O_3 should be capable to sense its own compressive stress. This property can be used for structural health monitoring in real time without the use of any embedded or attached sensors, which can be considered as a potential application in constructing smart structures.

Han et al. (2004) studied change of specific resistance under compression for cement paste containing two types of nano-TiO_2 particles (i.e., anatase and rutile based) and nanocarbon fiber. They observed that the cement paste containing anatase TiO_2 shows pressure-sensitivity property whereas paste containing rutile-based nano-TiO_2 does not show that property. Cement paste containing carbon fiber shows the best pressure-sensing property with lowest specific resistance. The rate of reduction of specific resistance for paste with anatase nano-TiO_2 was 7% to 10% whereas it was 17% to 35% for paste with carbon fiber.

Durability Properties

Reduced Permeability

It is expected that permeability (with respect to gas, liquid, ionic movement) of concrete with nano-SiO_2 should be low enough to increase its durability and service life (Sobolev, 2005). Incorporation of 1.5% of nanosilica with average particle size of 15 nm has caused a decrease in water penetration depth, gas permeability, and diffusion depth (Wagner et al., 1994). The water permeability test showed that the nano-SiO_2 concrete has lower water permeability than the normal concrete (Tao Ji, 2005).

Reactive nanoparticles can be electro-kinetically transported to reduce the permeability of hardened cement paste (Cardenas et al., 2006) through some kind of chemical reactions. Nanosilica (20-nm size) and nanoalumina (2-nm size) particles dispersed in simulated pore fluids were used to make colloidal nanoparticles. It was observed that 5-min treatment using 5 V of potential applied over a span of 0.15 m is sufficient to drive nanoparticles into the pore system. The coefficients of permeability for each paste were reduced by 1 to 3 orders of magnitude.

Use of calcium carbonate particles with surface area $\geq$10 m^2/g in mortar and concrete to improve hardened properties such as high permeability to water vapor but low permeability to liquid water was observed (Cervellati et al., 2006).

Nanoclay particles have shown promise in enhancing the mechanical performance, the resistance to chloride penetration, and the self-compacting properties of concrete and in reducing permeability (Chang et al., 2007; Kuo et al., 2006; Morsy et al., 2009; He and Shi, 2008). OMMT, which have been widely used in polymer–clay nanocomposites (PCN), are employed as fillers and reinforcements in cement mortars (Kuo et al., 2006). The hydrophilic montmorillonite (MMT) nanoparticles cannot be directly used as reinforcements in cement and concrete because (*a*) water absorbed in the interlayer regions between silicate sheets will cause detrimental expansion and (*b*) the interlayer alkali cations of MMT nanoparticles are harmful to the durability of cement mortar and concrete. The OMMT nanoparticles modified by a cationic-exchange reaction become hydrophobic and thus can be utilized to improve the strength and permeability of cement mortar and concrete. The coefficients of permeability of cement mortars could be 100 times lower if an optimal dosage (less than 1%) of OMMT nanoparticles is added. The OMMT nanoparticles around capillary pores can obstruct the diffusion of pore solution and aggressive chemicals and thus reduce the permeability of cement mortar and concrete. MIP results showed that the accessible pore volume is significantly reduced due to the obstruction of OMMT micro-particles around capillary pores. The optimal dosage of OMMT nanoparticles approximately increases with the water-to-cement (w/c) ratio in a mix design. Clusters of OMMT micro-particles were observed from SEM micrographs when the dosage of OMMT micro-particles is larger than 1%. Addition of nanoMMT composite (liquid form with planar diameter of about 100 nm) in cement paste (0.4 and 0.6 wt%) causes increase of compressive strength (~ 13.24%) and decrease of permeability coefficient (~ 49.95%) with more dense solid materials and stable bonding framework in the microstructure (Chang et al., 2007). Additionally, nonmodified, nanosized smectite clays were observed to act as nucleation agents for C–S–H and to modify the structure of C–S–H (Lindgreen et al., 2008; Kroyer et al., 2003).

Improved Shrinkage Properties

Nanoclay particles have shown promise in reducing shrinkage of concrete (Chang et al., 2007; Kuo et al., 2006; Morsy et al., 2009; He and Shi, 2008).

The moisture and drying resistance of a novel cement-based nanocomposite, polymer intercalated–exfoliated (PIE) cement, has been studied by Qiao et al. (2006). The effects of the post-processing treatment procedure and the nanofiller content are discussed in this study. The experimental results indicate that the flexure strength of the PIE cement is higher than that of ordinary portland cements by more than an order of magnitude and is quite insensitive to the humidity level.

Alkali–aggregate reactions have been studied at nanoscale (Bernabeu et al., 2005). In-situ and ex-situ experiments on the alkali dissolution of mica have been carried out with an atomic force microscope (AFM). The cleavage properties of mica make it extremely suitable for nanoscale surface evolution studies. Crystal growth on the basal [001] surface of muscovite has been quantitatively monitored in order to gain insights on the kinetics and mechanisms of silicate dissolution and precipitation reactions in an alkali environment.

The nanoindentation study showed that the volume fraction of the high-stiffness C–S–H gel increased significantly with addition of nanosilica (Mandal et al., 2010). Volume fractions of high-stiffness C-S-H were 38% and 50% for samples with 6% and 18% nanosilica, respectively. This has significance to the durability of concrete. Gaitero et al. (2008) reported that high stiffness C-S-H is more resistant to calcium leaching. Using ^{29}Si magic-angle spinning–nuclear magnetic resonance (MAS-NMR) spectroscopy of cement paste with nanosilica showed that nanosilica increases the average chain length of C-S-H gel.

Sustainable and Safe Concrete Materials and Structures

Sustainable Cements

Belite cement is an environment friendly (reduced CO_2 emissions) and energy-efficient cement and offers superior durability. Although, long-term strength gain of belite cement can be either comparable or even better than ordinary portland cement, low early strength due to slow hydration rate is a limitation for its widespread use. Addition of nanoparticles to accelerate belite hydration at early ages was studied by different researchers (Dolado et al., 2007; Campillo et al., 2007). Different nanoparticles were added to belite cement and both the early-age mechanical properties and microstructure modification were studied. The results showed that the addition of nanoparticles can overcome the drawback of this type of eco-friendly cements, which will enable them to be competitive to OPC.

Nano-SiO_2 could significantly increase the early-age compressive strength of high-volume fly ash concrete, which has early age strength gain characteristics similar to that of belite cement concrete (Li, 2004). Significant increase (i.e., 81%) of 3 days compressive strength was observed in nano-SiO_2 added high-volume fly ash concrete (HVFC) in comparison with HVFC without any nano addition. The addition of fly ash alone leads to higher porosity at early ages, while nano-SiO_2 actually lowers the concrete porosity through pore size refinement at early ages. The enhancement of pozzolanic activity of the fly ashes due to the presence of nano-SiO_2 was observed from heat of hydration test data. The maximum temperature due to heat of hydration was 61°C for the concrete with 50% fly ash incorporating 4% nano-SiO_2 whereas it was 65°C for plain portland cement concrete (PCC) and 51°C for HVFC. The benefits of using HVFC in terms of better durability and long-term mechanical properties had already been established but low early-age strength of HVFC is a drawback. The addition of nano-SiO_2 has a great potential to overcome this drawback of HVFC. The composite addition of nano-SiO_2, fly ash, and silica fume was found to be very effective way to achieve good performance and an economic way to use nano-SiO_2 (Feng et al., 2004).

Degradation of Pollutants and Self-Cleaning Concrete

Concrete containing nano-TiO_2 has proven to be very effective for the self-cleaning of concrete as well as converting some pollutants to innocuous forms. Nano-TiO_2 triggers a photocatalytic degradation of pollutants (e.g., NOx, carbon monoxide, volatile organic compounds, chlorophenols, and aldehydes from vehicle and industrial emissions) (Vallee et al., 2004; Murata et al., 1999; Chen, 2009). Photocatalytic concrete pavement blocks were found to be very effective in removing NO_x through photocatalytic reaction of TiO_2 (Kamitani et al., 1998; Murata et al., 2002). The surface reactions have been explored using X-ray photoelectron and Raman spectroscopy (Dalton et al., 2002). In Europe and Japan, nano-TiO_2–based "self-cleaning" concrete products are commercially available for use in the building facades and in concrete paving materials. The performance is confirmed in laboratory settings under an ultraviolet light with intensity similar to natural levels, however, long-term performance under outdoor exposure condition is yet to be established.

Pollution-reducing photocatalytic performance of a series of premix products containing nano-TiO_2 mineral pigments was evaluated by Enea and Guerrini (2010). The tested products are hydraulic binders (natural hydraulic lime and cement) and pigments (inorganic) with a wide range of color selection. These materials seemed to be particularly interesting as finishing coatings for new buildings or for the renovation of historic buildings, which can guarantee better maintenance of building surfaces and provide a valid contribution to the reduction of pollution in urban environments.

Concrete with Nonconventional Aggregates

The possibility of using incinerator bottom ash as a substitute for natural aggregates was investigated (Park et al., 2007). The rough, porous surfaces typical of bottom ash particles, which diminishes the strength of solidified products, was modified by the introduction of colloidal silica, resulting in a significant increase of mechanical strength was accomplished by a slight amount of silica (<1 wt% to total). Moreover, a pozzolanic reaction was induced during initial cement hydration due to the nanoparticle size of about 20 nm in colloidal silica solution. Cylindrical specimens and bricks were prepared from bottom ash added to a colloidal silica (SiO_2) solution and cement, and then their compressive strengths were evaluated. Cylindrical specimens showed an increase of approximately 60% in compressive strength when a colloidal solution containing 4 wt% silica particles was sprayed onto the bottom ash. The strength of bricks containing colloidal silica was in excess of 20 MPa, which is suitable for a wide range of applications. Results of leaching tests based on toxicity characteristic leaching procedure (TCLP) proved that the solidified bottom ash possessed good chemical stability.

Reactive Powder Concrete for Optimized Design

A process for synthesis of cement with nanoscale particle sizes has recently been developed. These nanocements can be tailored with varying phase compositions. Addition of nanocement in RPC systems has the potential to further enhance the properties of an already optimized system. The replacement of a small fraction of the conventional cement with these nanocements causes faster cement hydration reaction and reduces the induction period (Dham et al., 2010). The additional benefit of use of nanocement is creating denser microstructure which causes higher compressive and tensile strength. A reduction in permeability through the improvement of ITZ is expected to be a potential merit of nanocement additions in RPC. The improvement in strength was not accompanied by an increase of elastic modulus. Further research is needed to analyze the effect of nanocement additions on the long-term durability of the RPC systems.

The leaching of calcium from a hydrated cement matrix is of vital importance for structures like water containers, dams, bridges, etc., which have to be in contact with water during their lifetime. Characterization techniques such as ^{29}Si MAS NMR, X-ray diffraction, mercury intrusion porosimetry, and EDX–microanalysis have been used to evaluate the effect of the nanoparticles in the cement matrix nanostructure and their impact on the evolution of the Ca leaching throughout time (Gaitero et al., 2005). Subsequent analysis of the results indicates that silica nanoparticles can reduce Ca leaching by decreasing the amount of portlandite in the matrix and reducing the degradation rate of the C-S-H gel.

Building construction takes time, in part because the binding process of cement is based on the slow recrystallization and precipitation of calcium silicate species. Since the material reactivity is controlled by surface area, a reduction in particle size of portland cements has been used to prepare faster binding formulations. The present work investigates a new and direct, one-step preparation of calcium silicate-based nanoparticles of a typical portland cement composition by flame spray synthesis. Isothermal calorimetry revealed that the hardening of this new nanocement corroborated a more than tenfold increase of initial reactivity with different reaction kinetics if compared to conventionally prepared cements. At present, the unfavorably high porosity of nanocements, however, underlines the need for additional improvements of chemical composition and formulation to make these highly reactive materials applicable to modern construction work, where load-bearing strength is of importance (Halim et al., 2007).

MULTISCALE CHARACTERIZATION AND MODELING OF CONCRETE

Nanoindentation is a method where the mechanical properties of a material are measured at nano level. A nanosize needle is inserted into a material and load-displacement curves are developed based on the resulting force and movement of the needle. The slope of the curve and the maximum load is used to characterize the material at a nanoscale. SEMs (scanning electron microscope) are high-magnification micropscopes that are used in nanoindentation to identify the movement and also to identify the spatial relation of particles to each other, which is important at a nano level.

Modeling of the C-S-H gel is done through nano indention type methods, and using these type methods two distinct C-S-H forms have been identified. The amount and type of C-S-H in a mix can be used to predict the resulting properties of the cement pastes. It is difficult to investigate the nanostructure of C-S-H with typical methods. Nanotechnology tools can also be used to monitor the progress of the cement hydration reaction, which can be useful in evaluating admixtures or processes such as thermal degradation and enhance the knowledge of developmental properties of concrete. Being able to see the cement reaction over time also has the potential to provide for the development of new materials for controlled delivery of admixtures in concrete.

Nanoindentation and Atomic Force Microscopes for Characterizing Concrete

Nanoindentation includes a variety of indentation hardness tests applied to small volumes. Indentation is perhaps the most commonly applied means of testing the mechanical properties of materials. Small loads and tip sizes are used, so the indentation area may only be a few square micrometers or even nanometers. Typically, an indenter with a geometry known to high precision is used. During the course of the indentation process, a record of the depth of penetration is made, and then the area of the indent is determined using the known geometry of the indentation tip. While indenting, various parameters such as load and depth of penetration can be measured. A record of these values can be used to extract mechanical properties of the material (e.g., Poon et al., 2008).

The ability to conduct nanoindentation studies with nanometer depth, and sub-nanonewton force resolution is also possible using a standard AFM setup. AFM is a type of scanning probe microscopy where the sample is scanned under the probe by a piezoelectric translator in order to get information on surface properties. The probe has a very sharp tip, often less than 50Å; when the tip is approached to the sample surface, interaction forces between the tip and the surface cause a deflection of the cantilever. This deflection is detected by an optical lever technique. The AFM allows for nanomechanical studies to be conducted alongside topographic analyses, without the use of dedicated instruments. Load-displacement curves can be collected similarly for a variety of materials, and mechanical properties can be directly calculated from these curves (e.g., Kurland et al., 2011).

Measuring of mechanical properties of cementitious materials at the nanoscale is still an emerging science. Considering the sizes of ITZ and capillary pores, a spatial resolution of about 1 μm, which was thought to be the minimum for nanoindentation, is required (Kim et al., 2010). Ultrasonic AFM (AFAM) was used to characterize the cement paste in order to achieve this resolution. AFAM gives a more concentrated probability of the modulus than nanoindentation. Considering the contact and indent sizes, AFAM is a more promising means of measuring mechanical properties at the nanoscale.

The influence of internal curing by water filled lightweight aggregates (LWAs) on the microstructure of mortars was studied by scanning AFM and SEM (Peled et al., 2010). The differences and similarities that exist at both the microscale and nanoscale of conventionally cured mortars and internally cured mortars were studied. It was found that LWAs can be used for internal curing to provide a greater degree of hydration in a small region around the aggregate interface, which results in a microstructure that is denser and more homogeneous and that contains less CH.

TEM and SEM studies have revealed the presence of nanosized hydration products embedded in a cross-linked polymer matrix (Bortzmeyer et al., 1995). The nanoscale composite structure of the cement is thought to play an important part in the mechanical properties.

TEM studies of C-S-H gels in portland cement indicated large fluctuations in the local calcium–silicon ratio (Viehland et al., 1996). Lattice imaging studies have revealed the presence of nanocrystalline regions within an amorphous matrix. The local composition within the nanocrystalline regions is believed to be homogeneous. Optical diffractograms taken from individual nanocrystalline regions demonstrated the coexistence of both jennite and 1.4-nm tobermorite structural elements, supporting the essential features of the Taylor nanophasic model (Taylor, 1993).

NMR spectroscopy [cross-polarization (CP) technique in combination with MAS] was used to investigate the hydration of alkali-activated slag (Wang and Scrivener, 2003). The NMR study provides information on the polymerization of silicates, the role of aluminates in cement hydration and the nanostructure of C-S-H gel.

Recent progress in experimental and theoretical nanomechanics opens new venues in materials science for the nanoengineering of cement-based composites. Some recent results obtained by nanoindentation technique have been reviewed (Constantinides, Ulm, and Van Vliet, 2003), which reveal that the C-S-H gel exists in two different forms: a low-density form and a high-density form. These two C-H-H types have different mean stiffness and hardness values and different volume fractions. While the volume fractions of the two phases depend on mix proportions, the mean stiffness and hardness values do not change from one cement-based material to another; instead they are intrinsic properties of the C-S-H gel.

It has long been recognized, in cement chemistry, that two types of C-S-H exist in cement-based materials, but less is known about how the two types of C-S-H affect the mechanical properties. By means of nanoindentation tests on nondegraded and calcium-leached cement paste, the existence of two types of C-S-H was confirmed and the distinct role played by the two phases on the elastic properties of cement-based materials was investigated (Constantinides and Ulm, 2004). It was found that (*a*) high-density C-S-H is less affected by calcium leaching than low density C-S-H and (*b*) the volume fractions of the two phases in the C-S-H is not affected by calcium leaching. The nanoindentation results also suggest that the elastic properties of the C-S-H phase are intrinsic material properties that do not depend on mix proportions of cement-based materials. The material properties and volume fractions are used in a novel two-step homogenization model that predicts the macroscopic elastic properties of cement pastes with high accuracy. In particular, from an application of the model to decalcified cement pastes, it is shown that that the decalcification of the C-S-H phase is the primary source of the macroscopic elastic modulus degradation that dominates over the effect of the dissolution of portlandite in cement-based material systems.

Nanoindentation was employed (1 µm resolution) for the characterization of N-A-S-H gel in alkali (Na-silicate solution) activated low-calcium fly ash (AAFA) cured both at ambient and elevated temperatures (Nemecek et al., 2010). The intrinsic Young's modulus of the N-A-S-H gel was found to be around 17.7 GPa, irrespective of the curing procedure. N-A-S-H gel can be considered mechanically similar to low-density C-S-H gels in cement paste. Therefore, AAFA binder can be successfully used as an alternative binder for partial replacement of portland cement.

In the presence of high concentrations of NaOH, fresh C-S-H gels deteriorated in short reaction times. High alkaline contents led to polymerization with a rise in the mean chain length in the original gel. The inclusion of soluble silica, in addition to aluminum (the situation alkali-activated SCM) and alkalis, in the C-S-H gels favored the precipitation of a silicon-rich gel, with aluminum and calcium in its composition. This was a product of the direct reaction between the portlandite and the soluble Si and Al added. The soluble Si and Al in the medium, taken up by the original C-S-H gel, modified gel structure and chemical composition (Garcia-Loderio et al., 2010).

Characterization of the Hydration Process

The poorly crystalline C-S-H phases that form near room temperature have a broad similarity to the crystalline minerals tobermorite and jennite, but are characterized by extensive imperfections and structural variations at the nanometer scale. Both new and previously published data show that these phases generate a family of solubility curves in the CaO-SiO_2-H_2O system at room temperature. As demonstrated by ^{29}Si MAS NMR data and by charge balance calculations, the observed solubility differences arise from systematic variations in Ca-Si ratio, silicate structure, and $Ca(OH)_2$ content. Based on this evidence, the solubility curves are interpreted as representing a spectrum of metastable phases whose structures range from purely tobermorite-like to largely jennite-like. These findings give an improved understanding of the structure of these phases and reconcile some of the discrepancies in the literature regarding the structure of C-S-H at high Ca-Si ratios (Chen, Thomas, Taylor, Jennings, and Hamlin, 2004). Similarly, a new technique has been proposed to rationally assess the nanomechanical behavior of C-S-H based on a statistical analysis of hundreds of nanoindentation tests. Two structurally distinct but compositionally similar C-S-H phases, i.e., low density (LD) C-S-H and high-density (HD) C-S-H, or outer and inner products, have been identified. Both the phases exhibit a unique nanogranular behavior which is driven by particle-to-particle contact forces rather than by mineral properties (Constantinides and Ulm, 2007).

Early hydration (1, 7, 14, and 28 days) of five ordinary portland cement pastes with different w/c ratios (0.3, 0.4, 0.5, 0.6, and 1.0 wt.) was investigated through positron annihilation lifetime spectroscopy and compared with the results obtained from thermogravimetric analyses (Consolati, Dotelli, and Quasso, 1999). This technique allows to separate gel pores from the capillary pores which facilitates to monitor the evolution of pores with aging time. It is found that the concentration of gel pores increases with aging time and w/c ratio. However, the pore sizes do not show any significant variations with aging time or w/c.

It is difficult to investigate nanostructure of C-S-H with conventional instrumental methods. Neutron scattering methods possess unique capabilities to characterize cementitious materials. Quasi-elastic neutron scattering is used to monitor the progress of the cement hydration reaction and to determine the distribution of the water content among the various states, i.e., free, chemically bound, or physically trapped water in the gel network. Small-angle neutron scattering (SANS) proves to be well suited to determine the surface and volume fractal dimensions of the gel as a function of time and as a function of additives such as fly ash or silica fume (Livingston et al., 1995).

The mechanism of deterioration of mechanical properties (stiffness, strength) due to thermal degradation of C-S-H is still an enigma. A new experimental technique was introduced that allows one to rationally assess the evolution of the nanomechanical behavior of cement paste at elevated temperatures. Specifically, the thermal degradation of the two distinct C-S-H phases, i.e., LD C-S-H and HD C-S-H is assessed based on a statistical analysis of hundreds of nanoindentation tests. From a combination of nanoindentation, thermogravimetry and micromechanical modeling, a new mechanism has been identified (DeJong and Ulm, 2007). The thermally induced change of the packing density of the two C-S-H phases is the dominant mechanism that drives the thermal degradation of cementitious materials. The loosening of the packing density was explained due to the shrinkage of C-S-H nanoparticles that occurs at high temperatures, most probably due to the loss of chemically bound water.

The addition of TiO_2 nanoparticles can be used to increase the rate of hydration and potentially the rate of strength development of cement pastes but the addition of nano-TiO_2 particles increases the shrinkage in cement paste (increase of shrinkage is proportional to the replacement level). Hence, an optimum dosage or particle size distribution of nanoparticles could be used to avoid or reduce the undesirable effects. Thus, it is proposed that the setting behavior, strength development, and permeability of photocatalytic and other portland cement mixes can be optimized by controlling compositional variables and particles size (Jayapalan et al., 2010).

In situ studies of the microstructures of fresh cement paste can greatly enhance knowledge of the development properties of concrete at an early age (e.g., setting and hydration), which can be helpful for improvement of the quality of concrete (Venkiteela et al., 2010). The use of quantomix capsuling system in conventional SEM can be very effective for observing the evolution of the actual microstructure of the cement paste. There was no significant development of dynamic shear modulus (G_{WR}) before the initial setting. Furthermore, the same shear modulus level was observed at the time of initial setting irrespective of w/c ratios. G_{WR} increases significantly after the initial setting time and a better correlation between the solid phase and its corresponding elastic modulus was possible from 6- to 8-h age.

The complex rheological behavior of cement paste is basically related to the interactions at the molecular level, which, unfortunately are poorly understood. The rheological behavior of cement-based materials is directly linked to the aggregation, deaggregation, reaggregation, and dispersion of the solid particles. Characterization of the internal structure of fresh cement paste has been obtained through in situ particle chord length distribution measurements. The chord size evolution depends on the rate of aggregation of particles forming flocs and the rate of floc breakage from shear-induced forces. The results showed that mixtures designed with the same initial slump flow can have significantly different internal structures and that these internal structures are highly sensitive to the shearing conditions. The strength and the stability of the internal structure decrease as the average size of the flocs increases (Ferron and Shah, 2010).

An extremely small amount of C-S-H nuclei (0.3%) significantly increases the degree of hydration by promoting the growth of C-S-H clusters into the pore solution instead of around the C_3S or cement grains. Although, the early growth occurs in the pore solution, the mechanical properties of the cement pastes are preserved and use of seeding consequently accelerates the strength developments of mortars (Nicoleau, 2010).

Studying the structural and chemical composition of C-S-H after carbonation is critical for determining the durability and serviceability of concrete. Recent studies showed that the mechanical properties are likely to be enhanced when mineral admixture and polymer are introduced but no molecular-level studies have been conducted on carbonated C-S-H yet. Scanning transmission X-ray microscopy (STXM) was used to study C-S-H modified by two organic polymers (HDTMA and PEG 200) and exposed to different reaction times with CO_2 (Ha et al., 2010). No calcite formed in the presence of HDTMA, even though the C-S-H sample reacted with an intense concentration of CO_2. It seems polymers interfere with CO_2 penetration into the C-S-H layer structure and hinder the formation of $CaCO_3$. The CO_2 reaction strongly depends on the types of organic polymers incorporated within the C-S-H structure as the mineral phase formed within the C-S-H varies with the types of polymers used. Further work in terms of more experiments and careful analysis is needed in order to make recommendation on practical use of polymers as additives to arrest carbonation.

Nanoscale Model of Portland Cement Concrete

The innovations in concrete technology which are currently being applied in the field such as high and ultra high performance (strength), and self-consolidating concrete have been discussed (Scrivener et al., 2007). They discussed the factors which have enabled these developments and ongoing needs in these areas. The importance of sustainability as the major driver for future innovations and prospects for development of new cementitious materials with lower environmental impact is briefly discussed. Finally the importance of innovation in research is examined. The dramatic development in experimental and computational techniques over recent years opens up wide-ranging possibilities for understanding the micro- and nanoscale chemical and physical processes which underlie performance at a macroscopic level. The example of computational approaches at the atomic and molecular scale is presented in detail. In order to take advantage of the opportunities presented by such new techniques, there needs to be greater efforts to structure interdisciplinary, multi-group research.

The measurement of elastic properties at the nanoscale is a prerequisite to building a foundation for nanomechanics applications. Nanoindentation is widely used to measure the properties of elasticity (Kim et al., 2010). It is supposed that a low modulus (10 to 20 GPa) corresponds to C-S-Hs and that a high modulus (40 to 50 GPa) corresponds to CH. AFAM more effectively demonstrates the differentiation of nanoparticles than nanoindentation. The nanoindentation results give an effective (average) modulus for the indented area of about 1 μm whereas AFAM can measures modulus of a small contact area with a diameter of about 30 nm. AFAM is expected to differentiate two types of C-S-H at the nanoscale effectively because of its improved resolution. AFAM measures the modulus directly at the nanoscale whereas nanoindentation evaluates the modulus of each nanocomposite by applying an inversion technique on the measured effective moduli.

The discrete element method (DEM) was used to model nanoindentation of C-S-H (Chandler et al., 2010). It is assumed that the particles are spherical with diameters of ~ 5 nm. Both modulus and hardness, calculated from the DEM, were much smaller than the results from nanoindentation experiments. The effects of interparticle forces on the elastic modulus and hardness were studied to explore possible reasons for the differences. The DEM simulations give insight into the morphology of C-S-H nanoparticles and the interparticle forces between C-S-H nanoparticles. The nature of the interparticle forces and their effects on the bulk properties of C-

S-H were explored to assess the plausibility of various mechanisms contributing to C-S-H behavior.

It is known that increasing the tensile strength in cement paste can minimize the shrinkage cracking potential of concrete. To enhance macroscopic mechanical properties (e.g., tensile strength), it is necessary to understand the structure and behavior of C-S-H gel at the atomic level. Derivation of tensile and compressive strengths of C-S-H structure by using molecular dynamics simulations from uniaxial stress-strain data was conducted by Murray et al. (2010). A plausible atomic structure of C-S-H gel is proposed. The results showed that the maximum strengths (compressive and tensile) for the proposed C-S-H structures are three orders of magnitude higher than the strength at the macrolevel. The young's modulus values of the C-S-H unit with dimer silicate chains and the C-S-H unit with continuous silicate chains in the b direction were found to be 70 and 96 GPa, respectively. However, the strength of the proposed C-S-H gel is 23% of the compressive strength. This research also concludes that elastrostatic forces and bond forces in the silicate chains are the main contributors to cement strength at the atomic level and that breakage in silicate chains leads to low tensile strength in C-S-H gel.

INTELLIGENT CONCRETE MATERIALS THROUGH INTEGRATION OF NANOTECHNOLOGY-BASED SENSING TECHNOLOGIES

Nanoelectronic mechanical systems (NEMS) combine electrical and mechanical materials together at the nanoscale. NEMS are being developed in the health care arena to develop drug delivery systems that deliver the drugs right to the source of the infection or cancer. NEMS in transportation has the capability of providing for measurement of hydration in the plastic state while also providing the future stress strain properties of the hardened concrete. NEMS can be designed to be used as part of quality assurance for construction materials. They can be designed to measure material properties of the concrete during hydration. These sensors can also be designed to provide for measurement of long-term degradation by continuous monitoring of the stress and strains in the final structure. This information can be used to maintain performance models for structures or pavements, or it can have safety implications to prevent unforeseen failures by sending out a warning when stress levels are excessive.

Self-Sensing and Self-Powered Materials

Concrete can be transformed into a self-sensing device by properly embedding a network of CNTs. By measuring changes in the electrical resistance of this network of CNTs wirelessly, the initiation and propagation of damage in concrete structures can be detected and monitored. In a proof of concept study, Saafi (2009) embedded wireless cement–CNT sensors in concrete beams, and then subjected the beams to monotonic and cyclic loading. These sensors were responsive to loading induced damages, and capable of detecting damages at early stages of loading.

Calcium carbonate particles with surface area ≥ 10 m^2/g were used to improve the sound absorption of mortar and concrete (Cervellati et al., 2006).

Nanotechnology-Based Devices

NEMS can be used for better quality control of concrete, which indirectly helps to improve its durability. NEMS are wireless nanomachines designed to measure (*a*) density and viscosity of green concrete during mixing and pumping, (*b*) strength development, (*c*) shrinkage stress, and (*d*) parameters affecting concrete durability such as temperature, moisture, chloride, pH, and carbon dioxide (McCoy et al., 2005).

Researchers at Alabama A&M University's Center for Transportation Infrastructure Safety and Security (TIS2) have explored the use of nanotechnology-based devices for in-place measurement of concrete density and viscosity. A wireless densitometer–viscometer, which was originally developed by Sandia National Laboratories to measure the density and viscosity of oil, was miniaturized and modified for use in fresh concrete. The device consisted of smooth and textured nanoresonators, a microresistance temperature detector, and a power source-free radio frequency communication system. It was envisioned that with proper packaging and sealing, the device could be mixed with fresh concrete, allowing in-place workability measurements remotely and online (Saafi and Romine, 2005).

Microelectromechanical systems (MEMS) has been used to measure temperature and internal relative humidity of concrete by utilizing microcantilever beams and moisture-sensitive thin polymer (Norris et al., 2008). MEMS were found to be (*a*) effective and sensitive in measuring concrete temperature and moisture and (*b*) durable under corrosive environment and internal–external stresses. Monitoring temperature and moisture is very important in order to (*a*) monitor setting and hardening characteristics of concrete and (*b*) predict the possibility of occurrence of concrete chemical distresses such as corrosion of steel reinforcement, freeze–thaw distress, carbonation, and alkali-aggregate reaction. The areas that need further investigation are (*a*) long-term behavior and repeatability of MEMS embedded into concrete and (*b*) wireless interrogation such as signal processing, powering, communication, location, orientation, data storage, and computation capabilities.

ENHANCED CONCRETE PAVEMENT DESIGN AND CONSTRUCTION

The abrasion resistance of concrete containing nanoparticles (both nano-TiO_2 and nano-SiO_2) for pavement is experimentally studied (H. Li et al., 2006). The abrasion resistance of concrete containing nano-TiO_2 is better than that containing the same amount of nano-SiO_2. The effectiveness of nano-TiO_2 (NT) in enhancing abrasion resistance increases in the order: 5% NT < 3% NT < 1% NT (with the decrease on NT content).

The flexural fatigue performance of concretes containing nanoparticles is significantly improved and the sensitivity of their fatigue lives to the change of stress is also increased. The concrete containing nano-TiO_2 (1 wt%) showed the best flexural fatigue performance (better than concrete containing polypropylene fibers), which has been extensively used in paving concrete (H. Li et al., 2007).

PART 3

Implementation Case Studies

If nanoparticles are integrated with traditional building materials, the new materials would possess outstanding properties for the construction of super high-rise, long-span or intelligent civil infrastructure systems (Li, 2004). However, even though, in some ways, nanotechnology is an integral part of every concrete mixture, in other ways it's application is still limited. Calcium silicate hydrate is fundamentally a nano system and work is continuing to develop tools to better observe and model the material. In addition, modern chemical admixtures are designed and prepared by manipulating the molecular structure of complex organic compounds, and such materials are used in virtually every batch of concrete prepared in the United States.

On the other hand, usage of nanomaterials such as CNTs has yet to find acceptance for everyday use. Products such as RPCs are commercially available and are aimed at improving structural performance and have been used in bridge construction in several states. However, a recent review of state departments of transportation (DOTs) in the United States showed that none of the respondents reported using nanoproducts to date except for the use of TiO_2 for photocatalytic concrete. This dichotomy suggests that although nanotechnology materials may be in use, they are not recognized as such by the practitioner.

PHOTOCATALYTIC CONCRETE

White cement containing TiO_2 nanoparticles can have photocatalytic properties, which allow the maintenance of the aesthetic characteristics of architectural and decorative concretes over time (Cassar et al., 2003) along with removal of pollutants as an additional benefit. White cement containing photocatalytic self-cleaning nanoparticles has been used in the construction of the modernistic "Dives in Misericordia" church in Rome. TiO_2 coatings (15 nm thick) have been applied to glass windows to photocatalytically decompose dirt and smut particles that adhere to the glass (Skarendahl et al., 2003). Other applications of nanotechnology in the building sector include thin film solar cells, coatings with embedded nanoparticles to provide infrared and ultraviolet screening on windows, tailored molecules to improve cement, colloidal silica (10 nm particle size) for improving polymer-based floor coatings, improved insulation materials with a porosity of the order of 10 to 100 nm, nanofilters to purify water, improved paint coatings, and asphalt blends with better oxidation resistance.

Currently, there are several trial photocatalytic pavements sections that have been either built or are being planned. One such section using TiO_2 is in St. Louis, MO. This pavement is a new highway constructed in 2011. The nanomodification product used contains the anatase form of TiO_2 that acts as a very reactive catalyst that helps to break down NO_x when exposed to UV light. Trials in Europe have shown that the material helps to reduce smog in urban areas. The trial in Missouri is in a semi-urban environment. The trial section will be monitored and compared to similar data collected over a full year at an adjacent section of the roadway that does not contain the compound. Air quality will be monitored at and near the highway at more than one level. Another section of the roadway used TXActive in the pervious shoulders, and the quality of the water passing through it will be monitored to assess the effectiveness of the compound in treating pollutants in the water.

Another example of the application of nanotechnology based photocatalytic concrete is in Baton Rouge, Louisiana where an approximately ¼ mile of a concrete roadway was sprayed with a photocatalytic coating, with an objective to demonstrate the ability of ultrafine TiO_2 to trap and degrade nitrogen oxides in the environment. The performance of the coated test section was compared with untreated sections by measuring NO_x in the air and the nitrates deposited on the concrete pavement surface. The results of initial monitoring indicated that the coating was effective in photocatalytic degradation of NO_x. A number of factors were identified that affect the performance of the photocatalytic coating. These include relative humidity, light intensity, solar radiation, and wind speed and direction (Dylla et al., 2012).

NANOMODIFIED CONCRETE FOR SELF-COMPACTING CONCRETE AND IMPROVED SLIPFORM PAVING

The dispersion–slurry of amorphous nanosilica was used to improve segregation resistance for self-compacting concrete by Bigley and Greenwood (2003). Addition of nanoparticles such as silica in concrete has been realized an effective way to develop high-performance and self-compacting concrete with improved workability and strength.

Another near-implementation ready application of nanotechnology includes the use of nanoclays for producing self-consolidating concrete for slip form paving. The key to slipform paving is that the material must be workable enough to be consolidated, yet stiff enough to stand without formwork after the paver moves on at the end of the processing. Therefore, concrete slip form pavement construction typically uses dry stiff concrete with slump of less than 5 cm (2 in.). A slipform paving machine processes the fresh concrete, including placement, leveling, casting, consolidation, and finishing. Equally spaced vibrators in the paving machine introduce extensive internal vibration to consolidate and compact the fresh concrete (pack the materials and remove larger sized trapped air voids). These internal vibrators may cause overvibration of the stiff concrete if the vibration frequency is set incorrectly or the paving machine moves too slowly. Overvibration leads to segregation of aggregates and significant reduction of smaller-sized entrained air in the concrete along the path of the vibrators. When such a pavement is subjected to heavy traffic loading or freeze–thaw weather cycles during its service life, so-called vibrator trails (surface defects indicating segregation of aggregates, leaving a cement-rich layer) can occur, or longitudinal cracks can form.

To eliminate the need for internal vibration in the paving process, Shah et al. (2008) and Tregger et al. (2010) collaborated with the National Concrete Pavement Technology Center at Iowa State University to extend self-consolidating concrete technology to slipform pavement applications. The challenge to develop SF-SCC is that the material must change from very fluid to very stiff during the slipform process. The development of SF-SCC required changing the microstructure by combining concepts from particle packing (how particles of different sizes are arranged and how that affects compressive strength), admixture technology (the combination of different mineral and chemical admixtures), and rheology (the study of how materials flow). Specifically, the addition of a nanoclay consisting of highly purified magnesium aluminosilicate in very small dosages (1 percent by weight of cement) and Class C fly ash to the composition made it possible to maintain a balance between flowability during compaction and stability after compaction. For this research, the Iowa State team developed a model minipaver that simulates the slipform paving process without the application of internal or external vibration. At the end of the process, concrete slabs of modified mix with fly ash and nanoclay showed much better shape stability and surface smoothness than the slab with a standard sliporm concrete mix, as well as the greatest increase in green strength and compressive yield stress of the paving concrete.

ULTRA-HIGH-PERFORMANCE BRIDGE ELEMENTS

Reactive powder concretes or ultra-high-performance concretes (UHPC) are nano to microstructure optimized materials that have already been used in several states for bridge construction. The Iowa DOT and Wappelo County, Iowa built the first UHPC Bridge in North America in Wappelo County, Iowa in 2006. It was a joint project between Wappelo County and the DOT, with the IHRB (Iowa Highway Research Board) and FHWA a part of the funding and the Bridge Engineering Center at Iowa State doing the research. This bridge used a standard I-shaped girder section constructed using UHPC. Compressive strengths of 18,000 to 30,000 psi have been achieved in the construction of UHPC bridge beams. Different types of structural shapes are also being researched. Further research in Iowa developed a pi-shaped girder that takes advantage of the improved ductility properties of UHPC. New York State and Virginia have also built bridges with UHPC components. Other states are researching the use of these materials in beams and in prestressed concrete piling. Both Iowa and Georgia have performed research on UHPC substructure elements. A unique concrete h-pile shape was developed in Iowa for IHRB Project TR-558 (Figure 4). The pile was driven and load tested along with a steel H-pile for comparison. The weights of the piles were approximately equal but the axial and vertical load capacity of the UHPC concrete pile was greater than the H-pile.

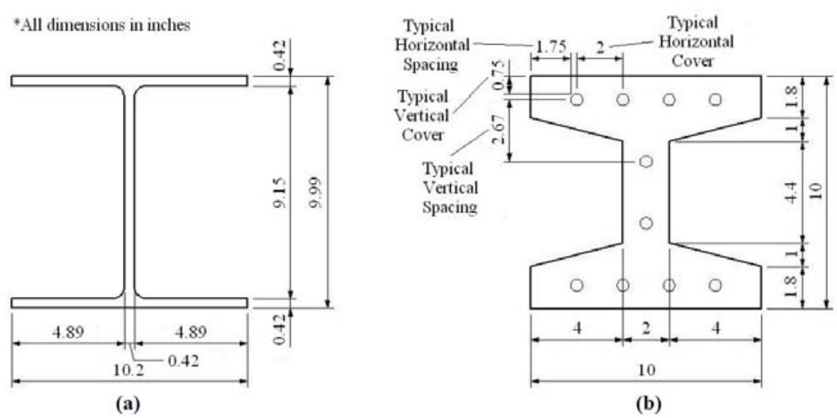

Figure 3.7. Dimensions of (a) an HP 10×57 steel pile and (b) a UHPC tapered H-shaped pile

FIGURE 4 IHRB Project TR-558.

PART 4

Future Challenges and Directions

Some of the potenial areas of applications of nano-based products as well as future direction are listed below.

1. Engineered materials using nanotechnology that will allow maximum use of locally available materials and avoid unnecessary transport. Design ductile, flexible, breathable, permeable, or impermeable concrete properties on demand.
2. Design concrete mix that is resistance to freeze–thaw, corrsion, sulfate, ASR, and other environmental attacks.
3. Develop speciality products such as products with blast resistance and conductive properties as well as temperature-, moisture-, and stress-sensing abilities.

While nanotechlogy-based construction products provide many advantages to the design and construction process as identified in the National Roadmap for Nanotechnology in Concrete (Birgisson et al., 2010), the following can be considered as future challenges.

1. Production of nanomaterials may in some cases require relatively high energy. Given the desire of the construction industry for their materials to be sustainable as well as cost- and-energy effective, the use of nanotechnology may in certain cases create an environmental challenge to the construction industry. For example, the production of nanosilicate materials by grinding requires high energy, which runs counter to the construction industry's continual efforts to make their materials sustainable as well as cost and energy effective. However, Birgisson and Dham (2011) described how nanosilicate platelets can be produced through chemical processing of montmorillonite clays, with minimal use of energy. In summary, the net sustainability impact should be investigated.
2. Developing a better procedure to ensure proper dispersion of nanomaterials in large-scale field applications. Effective dispersion of nanoparticles is key to achieving the full benefits of adding nanoparticles in cementitious system. Self aggregation, especially at high dosages of nanoparticles, is a common concern (Ozyildirim and Zegetosky, 2010), which sometimes leads to nonhomogeneous microstructure development and poor performance. The application of superplasticizer and high-speed mixing were found to be effective in proper dispersion of nanosilica particles (Flores et al., 2010). This is consistent with the observations by other researchers that high-intensity, high-shear mixing with the use of a proper dispersant would be helpful in thorough mixing with minimal clumping (Ozyildirim and Zegetosky, 2010).
3. With more research and practice efforts, smart design, and planning, construction projects can be made sustainable and avoid damages to environment.
4. Lack of adequate research and development funding.
5. Slow adoption rates of new technologies.
6. Low level of collaboration for multidisciplinary problems.
7. Inadequacy of quality control technologies.
8. The imaging of cement-based materials need further enhancement.

Finally, any potential health safety concerns for nanomaterials are not completely investigated, even though the typically small addition rates of nanoparticles in concrete may act to reduce the likelihood of adverse negative health and environmental effects. Human exposure to nanoparticles is inevitable as nanoparticles become more widely used and, as a result, nanotoxicology research is now gaining attention. However, while the number of nanoparticle types and applications continues to increase, studies to characterize any health effects are few in comparison. In the medical field in particular, nanoparticles are being utilized in diagnostic and therapeutic tools to better understand, detect, and treat human diseases. A review (Lewinski et al., 2008) states that even though nanoparticles may not be inherently safe, it is premature to state that they are inherently dangerous. This uncertainty is a significant factor influencing the decisions of industry and government leaders, as exhibited in the amended version of the national nanoinitiative in 2008, intended to strengthen research efforts on the environmental, health and safety issues related to the use of nanotechnology.

References

Ajayan, P. M. Nanotubes from Carbon. Chemistry Review, Vol. 99, 1999, pp. 1787–1799.

Bentz, D. P., K. A. Snyder, L. C. Cass, and M. A. Peltz. Doubling the Service Life of Concrete. *Reducing Ion Mobility Using Nanoscale Viscosity Modifiers*. Submitted to Cement and Concrete Composites. 2008.

Bernabeu, J., and I. Casanova. Real-Time Alkali-Silicate Dissolution Experiments with an Atomic Force Microscope. *Proc., 2nd International Symposium on Nanotechnology in Construction*, 2005, pp. 169–177.

Bjornstrom J., A. Martinelli, A. Matic, L. Borjesson, and I. Panas. Accelerating Effects of Colloidal Nanosilica for Beneficial Calcium-Silicate-Hydrate Formation in Cement. *Chemical Physics Letters*, Vol. 392, No. 1–3, 2004, pp. 242–248.

Bigley, C., and P. Greenwood. Using Silica to Control Bleed and Segregation in Self-Compacting Concrete. *Concrete*, Vol. 37, No. 2, 2003, pp. 43–45.

Birgisson, B., J. Armaghani, and S. Shah. First Workshop on Nanomodification of Cementitious Materials. NSF Award No. CMS-0529884, Final Report, 2006.

Birgisson, B., P. Taylor, J. Armaghani, and S. P. Shah. American Road Map for Research for Nanotechnology-Based Concrete Materials. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 130–137.

Birgisson, B., and M. Dham. Optimization of Clay Addition for Enhancement of Pozzolanic Reaction in Nanomodified Cement Paste. *Nanotechnology in Civil Infrastructure: A Paradigm Shift*, Springer Verlag (K. Gopalakrishnan, B. Birgisson, P. C. Taylor, and N. O. Attoh-Okine, eds.), Berlin Heidelberg, 2011, pp. 223–236.

Bortzmeyer, D., L. Frouin, Y. Montardi, and G. Orange. Microstructure and Mechanical Properties of Macro-Defect-Free Cements. *Journal of Materials Science*, Vol. 30, No. 16, 1995, pp. 4138–4144.

Campillo, I., A. Guerrero, J. S. Dolado, A. Porro, J. A. Ibanez, and S. Goni. Improvement of Initial Mechanical Strength by Nanoalumina in Belite Cements. *Materials Letters*, Vol. 61, No. 8–9, 2007, pp. 1889–1892.

Cardenas, H. E., and L. J. Struble. Electrokinetic Nanoparticle Treatment of Hardened Cement Paste for Reduction of Permeability. *Journal of Materials in Civil Engineering*, Vol. 18, No. 4, 2006, pp. 554–560.

Cassar, L., C. Pepe, G. Tognon, G. L. Guerrini, and R. Amadelli. White Cement for Architectural Concrete, Possessing Photocatalytic Properties. *International Congress on the Chemistry of Cement*, 2003.

Chandler, M. Q., J. F. Peters, and D. Pelessone. Modeling Nanoindentation of Calcium Silicate Hydrate. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 67–74.

Chang, T.-P., J.-Y. Shih, K.-M. Yang, and T.-C. Hsiao. Material Properties of Portland Cement Paste with Nano-Montmorillonite. *Journal of Material Science*, Vol. 42, No. 17, 2007, pp. 7478–7487.

Chen, J., and C.-S. Poon. Photocatalytic Construction and Building Materials: From Fundamentals to Applications. Building and Environment, Vol. 44, No. 9, 2009, pp. 1899–1906.

Chen, J. J., J. J. Thomas, H. F. W. Taylor, and H. M. Jennings. Solubility and Structure of Calcium Silicate Hydrate. *Cement and Concrete Research*, Vol. 34, No. 9, 2004, pp. 1499–1519.

Consolati, G., G. Dotelli, and F. Quasso. Investigation of Nanostructures in Ordinary Portland Cement Through Positron Annihilation Lifetime Spectroscopy. *Journal of Applied Physics*, Vol. 86, No. 8, 1999, pp. 4225–4231.

Constantinides, G., F. Ulm, and K. Vliet. On the Use of Nanoindentation for Cementitious Materials. *Materials and Structures*, Vol. 36, No. 257, 2003, pp. 191–196.

Constantinides, G., and F.-J. Ulm. The Effect of Two Types of C-S-H on the Elasticity of Cement-Based Materials: Results from Nanoindentation and Micromechanical Modeling. *Cement and Concrete Research*, Vol. 34, No. 1, 2004, pp. 67–80.

Constantinides, G., and F.-J. Ulm. The Nanogranular Nature of C-S-H. *Journal of the Mechanics and the Physics of Solids*, Vol. 55, No. 1, 2007, pp. 64–90.

Dalton, J. S., P. A. Janes, N. G. Jones, J. A. Nicholson, K. R. Hallam, and G. C. Allen. Photocatalytic Oxidation of NOx Gases Using TiO_2: A Surface Spectroscopic Approach. *Environmental Pollution*, Vol. 120, No. 2, 2002, pp. 415–422.

DeJong, M. J., and F.-J. Ulm. The Nanogranular Behavior of C-S-H at Elevated Temperatures (up to 700 C). *Cement and Concrete Research*, No. 37, No. 1, 2007, pp. 1–12.

Dham, M., T. S. Rushing, R. Helferich, T. Marth, S. Sengupta, R. Revur, C. A. Weiss, and K. Cummins. Enhancement of Reactive Powder Concrete Via Nanocement Integration. In *Transportation Research Record: Journal of Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 18–24.

Dolado, J. S., I. Campillo, E. Erkizia, Y. R. de Miguel, Y. S. de Ibarra, A. Porro, and A. Ayuela. Effects of Nanosilica Additions on Cement Pastes. *Proc., International Conference on Applications of Nanotechnology in Concrete Design*, 2005, pp. 87–96.

Dolado, J. S., I. Campillo, A. Porro, J. A. Sanchez, S. Goni, A. M. Guerrero, and A. Moragues. A Study on the Acceleration of Belite Cement Hydration. *Cemento-Hormigon*, Vol. 78, No. 897, 2007, pp. 24–30.

Dylla, H., M. M. Hassan, and D. Osborn. Field Evaluation of Ability of Photocatalytic Concrete Pavements to Remove Nitrogen Oxides. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2290*, Transportation Research Board of the National Academies, Washington, D.C., 2012, pp. 154–160.

Enea, D., and G. L. Guerrini. Photocatalytic Properties of Cement-Based Plasters and Paints Containing Mineral Pigments. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 52–60.

Fan, J.-J., J.-Y. Tang, L.-Q. Cong, and I. J. Mcolm. Influence of Synthetic Nano-ZrO2 Powder on the Strength Property of Portland Cement. *Jianzhu Cailiao Xuebao*, Vol. 7, No. 4, 2004, pp. 462–467 (in Chinese).

Feng, Q., C. D. Liang, and G.-M. Liu. Experimental Study on Cement-Based Composites with Nano-SiO_2. *Cailiao Kexue Yu Gongcheng Xuebao*, Vol. 22, No. 2, 2004, pp. 224–227 (in Chinese).

Ferron, R. D., and S. P. Shah. The Fresh State: From Macroscale to Microscale to Nanoscale. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 89–91.

Flores, I., K. Sobolev, L. M. Torres-Martinez, E. L. Cuellar, P. L. Valdez, and E. Zarazua. Performances of Cement Systems with Nano-SiO_2 Particles Produced by Using the Sol-Gel Method. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 10–14.

Garboczi, E. J. Concrete Nanoscience and Nanotechnology: Definitions and Applications. *Nanotechnology in Construction: Proceedings of the NICOM3 (3rd International Symposium on Nanotechnology in Construction)* (Z. Bittnar, P. J. M. Bartos, J. Nemecek, V. Smilauer, and J. Zeman, eds.), Prague, Czech Republic, 2009. pp. 81–88.

Gaitero, J. J., I. Campillo, and A. Guerrero. Reduction of the Calcium Leaching Rate of Cement Paste by Addition of Silica Nanoparticles. *Cement and Concrete Research*, Vol. 38, No. 8–9, 2008, pp. 1112–1118.

Gaitero, J. J., I. Campillo, P. Mondal, and S. P. Shah. Small Changes Can Make a Great Difference. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 1–5.

Garas, V. Y., A. R. Jayapalan, L. F. Kahn, and K. E. Kurtis. Micro-and Nanoscale Characterization of Effect of Interfacial Transition Zone on Tensile Creep of Ultra-High-Performance Concrete. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 82–88.

Garcia-Lodeiro, I., A. Fernandez-Jimenez, D. E. Macphee, I. Sobrados, J. Sanz, and A. Palomo. Stability of Synthetic Calcium Silicate Hydrate Gels in Presence of Alkalis, Aluminum, and Soluble Silica. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 52–57.

García-Lodeiro, A., and D. R. Bernal. High Strength Micro/Nano Fine Cement. *Proc., RILEM PRO 45 (2nd International Symposium on Nanotechnology in Construction)*, 2005, pp. 285–291.

Gay, C., and F. Sanchez. Performance of Carbon Nanofiber–Cement Composites with a High-Range Water Reducer. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 109–113.

Grove, J., S. Vanikar, and G. Crawford. Nanotechnology: New Tools to Address Old Problems. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 47–51.

Ha, J., S. Chae, K. W. Chou, T. Tyliszczak, and J. M. Monteiro. Scanning Transmission X-Ray Microscopic Study of Carbonated Calcium Silicate Hydrate. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 83–88.

Han, B., X. Guan, and J. Ou. Specific Resistance and Pressure-Sensitivity of Cement Paste Admixing with Nano-TiO_2 and Carbon Fiber. *Guisuanyan Xuebao*, Vol. 32, No. 7, 2004, pp. 884–887 (in Chinese).

He, X., and X. Shi. Chloride Permeability and Microstructure of Portland Cement Mortars Incorporating Nanomaterials. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2070,* Transportation Research Board of the National Academies, Washington, D.C., 2008, pp. 13–21.

Hosseini, P., A. Booshehrian, and S. Farshchi. Influence of Nano-SiO_2 Addition on Microstructure and Mechanical Properties of Cement Mortars for Ferrocement. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 15–20

Hui, L., X. Hui-Gang, and O. Jinping. A Study on Mechanical and Pressure-Sensitive Properties of Cement Mortar with Nanophase Materials. *Cement and Concrete Research*, Vol. 34, 2004, pp. 435–438.

Hui, L., X. Hui-Gang, Y. Jie, and O. Jinping. Microstructure of Cement Mortar with Nano-Particles. *Composites Part B: Engineering*, Vol. 35, No. 2, 2004, pp. 185–189

Jennings, H. M., J. W. Bullard, J. J. Thomas, J. E. Andrade, J. J. Chen, and G. W. Scherer. Characterization and Modeling of Pores and Surfaces in Cement Paste: Correlations to Processing and Properties. *Journal of Advanced Concrete Technology*, Vol. 6, No. 1, 2008, pp. 5–29.

Jayapalan, A. R., B. Y. Lee, S. M. Fredrich, and K. E. Kurtis. Influence of Additions of Anatase TiO_2 Nanoparticles on Early-Age Properties of Cement-Based Materials. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 41–46.

Jennings, H. M., J. J. Thomas, J. S. Gevrenov, G. Constantinides, and F.-J. Ulm. A Multi-Technique Investigation of the Nanoporosity of Cement Paste. *Cement and Concrete Research*, Vol. 37, 2007, pp. 329–336.

Ji, T. Preliminary Study on the Water Permeability and Microstructure of Concrete Incorporating Nano-SiO_2. *Cement and Concrete Research*, Vol. 35, No. 10, 2005, pp. 1943–1947.

Jo, B.-W., C.-H. Kim, G.-H. Tae, and J.-B. Park. Characteristics of Cement Mortar with Nano-SiO_2 Particles. *Construction and Building Materials*, Vol. 21, No. 6, 2007, pp. 1351–1355.

Jo, B.-W., C.-H. Kim, and J.-H. Lim. Characteristics of Cement Mortar with Nano-SiO_2 Particles. *ACI Materials Journal*, Vol. 104, No. 4, 2007, pp. 404–407.

Kamitani, K., Y. Murata, H. Tawara, and K. Takeuchi. Air Purifying Pavement: Development of Photocatalytic Concrete Blocks. *Proc., International Symposium on Cement and Concrete* (Z. Wu, ed.), International Academic Publishers, Beijing, 1998, pp. 751–755.

Kantro, D. L. Influence of Water-Reducing Admixtures on Properties of Cement Pastes: A Miniature Slump Test. *Cement and Concrete Research*, Vol. 2, No. 2, 1980, pp. 95–102.

Khan, M. I. Nanostructure and Microstructure of Cement Concrete Incorporating Multicementitious Composites. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 21–27.

Kim, J. H., O. Balogun, and S. P. Shah. Atomic Force Acoustic Microscopy to Measure Nanoscale Mechanical Properties of Cement Pastes. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 102–108.

Kroyer, H., H. Lindgreen, H. J. Jacobsen, and J. Skibsted. Hydration of Portland Cement in the Presence of Clay Minerals Studied by 29Si and 27Al MAS NMR Spectroscopy. *Advanced Cement Research*, Vol. 15, 2003, pp. 103–112.

Kuennen, K. Small Science Will Bring Big Changes To Roads. *Better Roads*, 2004.

Kuo, W.-Y., J.-S. Huang, and C.-H. Lin. Effects of Organo-Modified Montmorillonite on Strengths and Permeability of Cement Mortars. *Cement and Concrete Research*, Vol. 36, No. 5, 2006, pp. 886–895.

Kurland, N. E., Z. Drira,and V. K. Yadavalli. Measurement of Nanomechanical Properties of Biomolecules Using Atomic Force Microscopy. *Micron*, Oxford, England, 2011.

Lee, S. J., and W. M. Kriven. Synthesis and Hydration Study of Portland Cement Components Prepared by the Organic Steric Entrapment Method. *Materials and Structures*, Vol. 38, No. 1, 2005.

Li, G. Properties of High-Volume Fly Ash Concrete Incorporating Nano-SiO_2. *Cement and Concrete Research*, Vol. 34, 2004, pp. 1043–1049.

Li, G. Y., P. M. Wang, and X. Zhao. Mechanical Behavior and Microstructure of Cement Composites Incorporating Surface-Treated Multi-Walled Carbon Nanotubes. *Carbon*, Vol. 43, No. 6, 2005, pp. 1239–1245.

Li, G. Y., P. M. Wang, and X. Zhao. Pressure-Sensitive Properties and Microstructure of Carbon Nanotube Reinforced Cement Composites. *Cement and Concrete Composites*, Vol. 29, No. 5, 2007, pp. 377–382.

Li, H., M.-H. Zhang, and J.-P. Ou. Abrasion Resistance of Concrete Containing Nano-Particles for Pavement. *Wear 260*, 2006, pp. 1262–1266.

Li, H., H. Zhang, H. Mao, and J.-P. Ou. Flexural Fatigue Performance of Concrete Containing Nano-Particles for Pavement. *International Journal of Fatigue*, Vol. 29, No. 7, 2007, pp. 1292–1301.

Li, H., H.-G. Xiao, J. Yuan, and J.-P. Ou. Microstructure of Cement Mortar with Nano-Particles. *Composites Part B: Engineering*, Vol. 35, No. 2, 2004, pp. 185–189.

Li, H., H.-G. Xiao, and J.-P. Ou. A Study on Mechanical and Pressure-Sensitive Properties of Cement Mortar with Nanophase Materials. *Cement and Concrete Research*, Vol. 34, No. 3, 2004, pp. 435–438.

Li, Z., H. H. S. Wang, and Y. W. M. Lu. Investigations on the Preparation and Mechanical Properties of the Nano-Alumina Reinforced Cement Composite. *Materials Letters*, Vol. 60, No. 3, 2006, pp. 356–359.

Lindgreen, H., M. Geiker, H. Krøyer, N. Springer, and J. Skibsted. Microstructure Engineering of Portland Cement Pastes and Mortars Through Addition of Ultrafine Layer Silicates. *Cement and Concrete Composites*, Vol. 30, No. 8, 2008, pp. 686–699.

Lin, D. F., K. L. Lin, W. C. Chang, H. L. Luo, and M. Q. Cai. Improvements of Nano-SiO_2 on Sludge/Fly Ash Mortar. *Waste Management*, Vol. 28, No. 6, 2008, pp. 1081–1087.

Lin, K. L., W. C. Chang. D. F. Lin, H. L. Luo, and M. C. Tsai. Effects of Nano-SiO_2 and Different Ash Particle Sizes on Sludge Ash-Cement Mortar. *Journal of Environmental Management*, Vol. 28, No. 6, 2008, pp. 708–714.

Livingston, R. A., D. A. Neumann, A. Allen, and J. J. Rush. Application of Neutron Scattering Methods to Cementitious Materials. *Proc., Materials Research Society Symposium (Neutron Scattering in Materials Science II)*, Vol. 376, 1995, pp. 459–469.

Lu, Z.-Y., and X. Xu. Effect of Nanometer SiO_2 on Hydration Character of Portland Cement. *Jianzhu Cailiao Xuebao*, Vol. 9, No. 5, 2006, pp. 581–585 (in Chinese).

Makar, J. M., J. Margeson, and J. Luh. Carbon Nanotube/Cement Composites – Early Results and Potential Applications. *Proc., 3rd International Conference on Construction Materials: Performance, Innovations and Structural Implications*, Vancouver, B.C., Aug. 22–24, 2005. p. 1–10.

Mann, S. Nanotechnology and Construction. Nanoforum Report, 2006. Available at www.nanoforum.org. Accessed May 30, 2008.

Manzur, T., and N. Yazdani. Strength Enhancement of Cement Mortar with Carbon Nanotubes: Early Results and Potential. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 102–108.

McCoy, M., J. Betts, A. Norris, and M. Saafi. Nanotechonology in Construction: Nano Materials and Devices Offer Macro Improvements in Concrete Materials. *Proc., RILEM PRO 45 (2nd International Symposium on Nanotechnology in Construction*, 2005, pp. 223–231.

Mehta, P. K. *Concrete Structure, Properties and Materials*, Prentice-Hall, Engelwood Cliffs, N.J., 1986.

Metaxa, Z. S., M. S. Konsta-Gdoutos, and S. P. Shah. Carbon Nanofiber-Reinforced Cement-Based Materials. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 114–118

Mondal, P., S. P. Shah, L. D. Marks, and J. J. Gaitero. Comparative Study of the Effects of Microsilica and Nanosilica in Concrete. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 6–9.

Morsy, M. S., H. A. Aglan, and M. M. Abd El Razek. Nanostructured Zonolite-Cementitious Surface Compounds for Thermal Insulation. *Construction and Building Materials*, Vol. 23, No. 1, 2009, pp. 515–521.

Munoz, J. F., R. C. Meininger, and J. Youtcheff. New Possibilities and Future Pathways of Nanoporous Thin Film Technology to Improve Concrete Performance. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 34–41.

Murata, Y., and K. Tobinai. Influence of Various Factors on NOx Removal Performance of Permeability Interlocking Block Based on Photocatalysis. *Journal of Structural and Construction Engineering*, Vol. 555, 2002, pp. 9–15 (in Japanese).

Murata, Y., T. Obara, and K. Takeuchi. Air Purifying Pavement: Development of Photocatalytic Concrete Blocks. *Journal of Advanced Oxidative Technologies*, Vol. 4, No. 2, 1999, pp. 227–230.

Murray, S. J., V. J. Subramani, R. P. Selvam, and K. D. Hall. Molecular Dynamics to Understand the Mechanical Behavior of Cement Paste. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 75–82.

Nasibulina, L. I., I. V. Anoshkin, S. D. Shandakov, A. G. Nasibulin, A. Cwirzen, P. R. Mudimela, K. Habermehl-Cwirzen, J. E. M. Malm, T. S. Koltsova, Y. Tian, E. S. Vasileva, V. Penttala, O. V. Tolochko, M. J. Karppinen, and E. I. Kauppinen. Direct Synthesis of Carbon Nanofibers on Cement Particles. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 96–101.

Nemecek, J., V. Smilauer, L. Kopecky, and J. Nemeckova. Naoindentation of Alkali-Activated Fly Ash. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 36–40.

Nicoleau, L. New Calcium Silicate Hydrate Network. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 42–51.

Norris, A., M. Saafi, and P. Romine. Temperature and Moisture Monitoring in concrete Structures Using Embedded Nanotechnology/Microeletronic Mechanical Systems Sensors. *Construction and Building Materials*, Vol. 22, No. 2, 2008, pp. 111–120.

North American Cement Industry. Annual Yearbook 2006. Portland Cement Association, ER365, Skokie, Ill., 2007.

Ozyildirim, C., and C. Zegetosky. Exploratory Investigation of Nanomaterials to Improve Strength and Permeability of Concrete. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 1–8.

Park, J. S., Y. J. Park, and J. Heo. Solidification and Recycling of Incinerator Bottom Ash Through the Addition of Colloidal Silica (SiO_2) Solution. *Waste Management*, Vol. 27, No. 9, 2007, pp. 1207–1212.

Peled, A., J. Castro, and J. Weiss. Atomic Force Microscopy Examinations of Mortar Made by Using Water-Filled Lightweight Aggregates. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 92–101.

Peters, S. J., T. S. Rushing, E. N. Landis, and T. K. Cummins. Nanocellulose and Microcellulose Fibers for

Concrete. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 25–28.

Poon, B., D. Rittel, and G. Ravichandran. An Analysis of Nanoindentation in Linearly Elastic Solids. *International Journal of Solids and Structures*, Vol. 45, No. 24, 2008, p. 6018.

Qiao, Y., J. K. Deliwala, S. S. Chakravarthula, and X. Kong. Moisture and Drying Resistance of a Nanointerphase Reinforced Cement. *Cement and Concrete Composites*, Vol. 28, No. 9, 2006, pp. 800–802.

Qing, Y., Z. Zenan, K. Deyu, and C. Rongshen. Influence of Nano-SiO_2 Addition on Properties of Hardened Cement Paste as Compared with Silica Fume. *Construction and Building Materials*, Vol. 21, No. 3, 2007, pp. 539–545.

Qing, Y., Z. Zenan, S. Li, and C. Rongshen. A Comparative Study on the Pozzolanic Activity Between Nano-SiO_2 and Silica Fume. *Journal of Wuhan University of Technology–Materials Science Edition*, Vol. 21, No. 3, 2008, pp. 153–157.

Raki, L., J. J. Beaudoin, and L. D. Mitchell. Layered Double Hyroxides-Like Materials: Nanocomposites for Use in Concrete. *Cement and Concrete Research*, Vol. 34, 2004, pp. 1717–1724.

Raki, L., and J. J. Beaudoin. Controlled Release of Chemical Admixtures. Canadian Patent #CA 2554347, U.S. Patent Application US 2007/0022916 A1, 2007.

Saafi, M., and P. Romine. Nano- and Microtechnology: Wireless Devices in Concrete for Monitoring Quality and Durability. *Concrete International*, Vol. 27, No. 12, 2005, pp. 28–34.

Saafi, M. Wireless and Embedded Carbon Nanotube Networks for Damage Detection in Concrete Structures. *Nanotechnology*, Vol. 20, No. 39, 2009, pp. 28–34.

Salvetat, J.-P., J.-M. Bonard, N. H. Thomson, A. J. Kulik, L. Forro, W. Benoit, and L. Zuppiroli. Mechanical Properties of Carbon Nanotubes. *Applied Physics A: Materials Science and Processing*, Vol. 69, 1999, pp. 255–260.

Sanchez, F., and K. Sobolev. Nanotechnology in Concrete: A Review. *Construction And Building Materials*, Vol. 24, No. 11, 2010, pp. 2060–2071.

Sanchez, F., L. Zhang, and C. Ince. Multi-Scale Performance and Durability of Carbon Nanofiber/Cement Composites. *Nanotechnology in Construction: Proceedings of the NICOM3 (3rd International Symposium on Nanotechnology in Construction)* (Z. Bittnar, P. J. M. Bartos, J. Nemecek, V. Smilauer, and J. Zeman, eds.), Prague, Czech Republic, 2009, pp. 345–350.

Sanchez, F., and C. Ince. Microstructure and Macroscopic Properties of Hybrid Carbon Nanofiber/Silica Fume Cement Composites. *Composites Science and Technology*, Vol. 69, No. 7–8, 2009, pp. 1310–1318.

Sanchez, F. Carbon Nanofiber/Cement Composites: Challenges and Promises as Structural Materials. *International Journal of Materials and Structural Integrity*, in press.

Sanfilippo, J. M., J. F. Munoz, M. I. Tejedor, M. A. Anderson, and S. M. Cramer. Nanotechnology to Manipulate the Aggregate-Cement Paste Bond Effects on Mortar Performance. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 29–33.

Sato, T., and F. Diallo. Seeding Effect of Nano-$CaCO_3$ on the Hydration of Tricalcium Silicate. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 61–67.

Shah, S., P. Mondal, R. P. Ferron, N. Tregger, and Z. Sun. News on Nanotechnology. *Public Roads*, Vol. 71, No. 6, 2008.

Shih, J.-Y., T.-P. Chang, and T.-C. Hsiao. Effect of Nanosilica on Characterization of Portland Cement Composite. *Materials Science and Engineering A: Structural Materials: Properties, Microstructure and Processing*, Vol A424, No. 1–2, 2006, pp. 266–274.

Skarendahl, A. Nanotechnology Developments for Building and Protection. *Vbyggaren* (Swedish Society of Civil and Structural Engineers), Vol. 6, 2003, pp. 8–11.

Sobolev, K., and M. Ferrada-Gutiérrez. How Nanotechnology Can Change the Concrete World. *American Ceramic Society Bulletin*, No. 10, 2005, pp. 14–17.

Sobolev, K., I. Flores, L. M. Torres-Martinez, P. L. Valdez, E. Zarazua, and E. L. Cuellar. Engineering of SiO_2

Nanoparticles for Optimal Performance in Nano Cement-Based Materials. Nanotechnology in Construction. *Proc., NICOM3 (3rd International Symposium on Nanotechnology in Construction)* (Z. Bittnar, P. J. M. Bartos, J. Nemecek, V. Smilauer, and J. Zeman, eds.), Prague, Czech Republic, 2009, pp. 139–148.

Srivastava, D., C. Wei, and K. Cho. Nanomechanics of Carbon Nanotubes and Composites. *Applied Mechanics Review*, Vol. 56, 2003, pp. 215–230.

Tang, M., H. Ba, and Y. Li. Study on Compound Effect of Silica Fume and Nano-SiOx for Cementing Composite Materials. *Guisuanyan Xuebao*, Vol. 31, No. 5, 2003, pp. 523–527 (in Chinese).

Tregger, N., M. Pakula, and S. P. Shah. Influence of Micro- and Nano-Clays on Fresh State of Concrete. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 68–74.

Taylor, H. F. W. Nanostructure of C-S-H: Current Status. Advanced Cement Based Materials, Vol. 1, No. 1, 1993, pp. 38–46.

Taylor, H. F. W. *Cement Chemistry*, 2nd ed., Thomas Telford, London, 1997.

Taylor, P., E. Cackler, and B. Birgisson. Second Workshop on Nanotechnology for Cement and Concrete. NSF Grant CMMI 074949. Final Report. September 5, 2007.

Vallee, F., B. Ruot, L. Bonafous, L. Guillot, N. Pimpinelli, L. Cassar, A. Strini, E. Mapelli, L. Schiavi, C. Gobin, H. Andre, N. Moussiopoulos, A. Papadopoulos, J. Bartzis, T. Maggos, R. McIntyre, C. Lehaut-Burnouf, A. Henrichsen, P. Laugesen, R. Amadelli, D. Kotzias, and P. Pichat. Cementitious Materials for Self-Cleaning and Depolluting Facade Surfaces. *Proc., PRO 41 (RILEM International Symposium on Environment-Conscious Materials and Systems for Sustainable Development*, 2004, pp. 337–346.

Venkiteela, G., Z. Sun, and S. P. Shah. Observation of Cement Paste Microstructure Evolution. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2141*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 75–81.

Viehland, D., J.-F. Li, L.-J. Yuan, and Z. Xu. Mesostructure of Calcium Silicate Hydrate (C-S-H) Gels in Portland Cement Paste: Short-Range Ordering, Nanocrystallinity, and Local Compositional Order. *Journal of the American Ceramic Society*, Vol. 79, No. 7, 1996, pp. 1731–1744.

Wang, S.-D., and K. L. Scrivener. ^{29}Si and ^{27}Al NMR Study of Alkali-Activated Slag. *Cement and Concrete Research*, Vol. 33, No. 5, 2003, pp. 769–774.

Wille, K., and K. J. Loh. Nanoengineering Ultra-High-Performance Concrete with Multiwalled Carbon Nanotubes. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 119–126.

www.nano.gov, 2007.

Yang, Z., J. Hollar, X. He, and X. Shi. Laboratory Assessment of a Self-Healing Cementitious Composite. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 9–17.

Yazdanbakhsh, A., Z. Grasley, B. Tyson, and R. K. Abu Al-Rub. Distribution of Carbon Nanofibers and Nanotubes in Cementitious Composites. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2142*, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 89–95.

Ye, Q., Z. Zhang, R. Chen, and C. Ma. Interaction of Nano-SiO_2 with Portlandite at Interface Between Hardened Cement Paste and Aggregate. *Guisuanyan Xuebao*, Vol. 31, No. 5, 2003, pp. 517–522 (in Chinese).

Yohanis, Y. G., and B. Norton. Life-Cycle Operational and Embodied Energy for a Generic Single-Storey Office Building in the U.K. *Energy*, Vol. 27, No. 1, 2002, pp. 77–92.

Zhi, G., and G. Zhili. Applications of Nanotechnology and Nanomaterials in Construction. First International Conference on Construction in Developing Countries (ICCIDC–I): Advancing and Integrating Construction Education, Research, and Practice, Karachi, Pakistan, Aug. 4–5, 2008.

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