NANOTECHNOLOGY AND CONCRETE: RESEARCH OPPORTUNITIES

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Abstract

Nanotechnology is one of the most active research areas that encompass a number of disciplines including civil engineering and construction materials. The most active fields are: electronics, bio-mechanics and coatings. Interest in nanotechnology concept for portland cement composites is steadily growing. Currently, the most active research areas dealing with cement and concrete are: understanding of the hydration of cement particles and the use of nano-size ingredients such as alumina and silica particles. There are also a limited number of investigations dealing with the manufacture of nano-cement. If cement with nano-size particles can be manufactured and processed, it will open up a large number of opportunities in the fields of ceramics, high strength composites and electronic applications. This will elevate the status of portland cement to a high tech material in addition to its current status of the most widely used construction material. Very few inorganic cementing materials can match the capabilities of portland cement in terms of cost and availability. The main objective of this paper is to outline promising research areas. Basic background information on nanotechnology research, state of the art on use of this technology in concrete, opportunities and challenges are discussed.

Keywords: nano portland cement, carbon, nano-tubes, composites

1. INTRODUCTION

Nanotechnology is a very active research field and has applications in a number of areas. Currently this technology is being used for the creation of new materials, devices and systems at molecular, nano- and micro-level [1-8]. Various government agencies in the United States of America are supporting nanotechnology exceeding billion dollars per year. National Science Foundation (NSF) is one of the active participants with a major share of research funding.
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Dr. Ken Chong is Engineering Advisor and Program Director in Engineering Directorate of National Science Foundation (NSF). Over the last two decades Dr. Chong initiated and directed a large number of initiatives to further the state of the art in concrete, reinforced concrete and prestressed concrete. His direction support resulted in development of high strength and durable concrete and self-healing concrete. He was one of the pioneers at NSF to initiate research in the area of nanotechnology. His focus on materials was a boon for researchers in the area on nano-concrete. He is an active researcher with a number of publications including books and made a large number of presentations including Key-Note and Plenary Lectures.

Areas of investment for the fiscal year 2006 were:

- Fundamental Nano-scale Phenomena and Processes;
- Nano-materials;
- Nano-scale Devices and Systems;
- Instrumentation Research, Metrology, and Standards for Nanotechnology;
- Nano-manufacturing;
- Major Research Facilities and Instrumentation Acquisition;
- Societal Dimensions.

Program emphases for fiscal year 2007 are:

- Increased focus on complex large nano-systems. Research on nano-scale devices and system architecture, dynamic and emerging behavior, and their respective fabrication, will be emphasized;
- Increased focused on three-dimensional measurements of domains of engineering relevance with good time resolution;
- Converging science, engineering and technology from the nano-scale, by integrating nano-systems into applications (in manufacturing, information systems, medicine, environment, etc.);
- Expanded joint research program addressing potential implications of nanotechnology with other federal agencies;
- Earlier educational programs and teaching materials, including for K-12, by using remote access to NSF educational networks; and
- Expand partnerships of academic researchers with industry, medical facilities and states.
As of 2007, there are more than 700 active research projects supported by NSF. The primary objective of this paper is to present the possibilities of using nanotechnology for portland cement-based composites including nano- and micro-concrete.

Portland cement is the most common and widely used construction material and its current production is estimated as 6 billion cubic meters per year [18]. The major advantages of this material are: availability of raw materials for production all over the world, low cost, room temperature setting, ease of construction, readily available properties and performance data for design and construction. In addition modern day concrete has a very good performance record for a period of more than 175 years. Portland cement is typically used as cementing materials with fine and coarse aggregates to create products that are a few mm to several meters thick. Average size of portland cement particle is about 50 microns. In applications that require thinner final products and faster setting time, micro cement with a maximum particle size of about 5 microns is being used [10]. Therefore the particle size has to be reduced by an order of magnitude to obtain nano-portland cement. If these nano-cement particles can be processed with nanotubes and reactive nano-size silica particles; conductive, strong, tough and room temperature processed ceramics can be developed both for electronic applications and coatings. Since carbon oxidizes at temperatures above 400 °C, room temperature processing will be a boon to retain the mechanical properties of carbon nano-tubes. Since most ceramics are processed at temperatures much higher than 400 °C, carbon fibers can not be used with these processes.

At the micro level, there is also a very good analogy between reinforced concrete and fiber composites. The lessons learned on fiber reinforced concrete can also be effectively used for composites made using short discrete fibers, both at micro and nano-level. For example, considerable amount of fiber reinforced concrete containing 0.5% of steel fibers are being used in actual construction. The enhancement of properties provided by this 0.5% of steel fibers to concrete matrix are not that much different from the enhancement provided by 0.5% of carbon nano-tubes in high performance composites [9-10]. Note that carbon fibers provide enhancement to both mechanical and electrical properties.

2. DEFINITION OF NANO-CONCRETE

For discussions presented in this paper, nano-concrete is defined as a concrete made with portland cement particles that are less than 500 nano-meters as the cementing agent. Currently cement particle sizes range from a few nano-meters to a maximum of about100 micro meters. In the case of micro-cement the average particle size is reduced to 5 micro meters. An order of magnitude reduction is needed to produce nano-cement.
3. IS THERE A NEED FOR NANO-CONCRETE?

The authors believe that the answer is Yes. Certain unique properties of portland cement such as: room temperature processing, low shrinkage, temperature resistance up to 600 °C, compatibility with a number of fiber types including carbon fibers, reaction capability with currently available nano-materials such as nano-silica and non toxic characteristics can be effectively used to create unique products. It can also be molded to complex shapes; heat cured and coated with other nano-materials.

If processable nano-cement is synthesized, micro-meter thick plates and other shapes such as cylinders can be manufactured for various applications including electronic components and high temperature sensors. Carbon nano-tubes can be used for both strengthening and creating electric circuits. Another major large volume application is in the area of coatings. Current portland cement-based coatings are not popular because they need to be thick and polymer additions are needed to improve adhesion. Nano-cement will create a new paradigm in this area of application. Crack free decks will be a reality instead of a dream.

4. STATE-OF-THE-ART

4.1. Concrete and Nanotechnology

One can claim that concrete utilizes nanotechnology because it contains nano-particles as ingredients including nano-water particles and nano-air voids. However, to claim the use of nanotechnology, we should be able to control the amount and the locations of these nano-ingredients inside the final products. The scales of various constituent materials of concrete are shown in Fig. 1. If we can create chemical or mechanical tools to control nano-scale pores and the placement of calcium-silicate hydration products then concrete becomes a product of nanotechnology.

![Fig. 1: Scales of various constituents of concrete and a typical application [7]](image-url)
Current research activities of nanotechnology in concrete include: characterization of cement hydration, influence of the addition of nano-size silica to concrete, synthesis of cement using nano-particles and coatings (that contain nano-size particles) applied to protect concrete. These activities are briefly described in the following sections.

4.2. Cement Reactivity Nano-Structure

A collaborative research activity supported by Federal Highway Administration (FHWA) and NSF is being conducted at University of Connecticut to study cement hydration at a nano-scale level. In this study US and German scientists are using nuclear resonance reaction analysis (NRRA) to investigate what takes place on the surface of the cement particle as it hydrates. A beam of nitrogen atoms is used to probe a reacting cement grain to locate hydrogen atoms, a necessary component of water, or reaction by-products. Location of these hydrogen atoms are used to create a hydrogen depth profile, which shows the rate of water penetration as well as the arrangement of various surface layers formed during the reaction.

The researchers identified four components that are active during cement hydration, Fig. 2. The following section provides a short summary of their observations. The 20-nanometer-thick semi-permeable surface layer allows water to enter the cement grain and leaches out calcium ions. The larger silicate ions in the cement are trapped behind this layer. As the reaction continues, a silicate gel forms there, causing swelling within the cement grain. This leads to eventual breakdown of the outermost layer. The surface disintegration then releases accumulated silicate into the surrounding solution. The silicate reacts with calcium ions to form a calcium-silicate hydrate gel, which binds cement grains together and sets the concrete.

![Fig. 2. Details of hydrating cement grain at nano-scale](image-url)
The evolution of the hydrogen profile shows the timing of the surface layer's breakdown. This information can be used to study the concrete setting process as a function of time, temperature, cement chemistry, and other factors. For example, researchers used NRRA to determine that in cement hydrating at 30°C (86°F); the breakdown occurs at 1.5 hours [7].

4.3. Nano-Scale Silica Fume for Improving Concrete Performance

Ultra-fine amorphous colloidal silica was found to be much more efficient than micron sized silica for improving the performance such as permeability, and subsequently, durability [5]. In addition, reduced amount of about 15 to 20 kg of nano-silica was found to provide same strength as 60 kg of regular or micro silica.

4.4. Alkali-Silicate Reaction (ASR) Studies

ASR results in the formation of alkali/silica gel, which expands and causes significant material damage. The gel is formed due to the reaction between cement alkalis and a reactive form of silica from aggregates or supplementary additions. FHWA researchers are using neutron scattering and positron annihilation spectroscopy to measure nano-scale changes in gel microstructure as a function of gel chemistry, temperature and relative humidity [7].

4.5. Fly Ash Reactivity Characterization

FHWA is also funding a research study to examine interactions between fly ash and portland cement gel nano-structure. Small-angle neutron scattering is being used to quantify the changes on a nano-scale as a function of time and fly ash composition.

4.6 Cement Hydration Kinetics

Conventional analytical methods are unable to provide an accurate model for the rate of cement's reaction with water as a function of temperature, water/cement ratio, and grain size because the reactions occur in the nano-scale pores of the cement gel. Therefore, scientists from National Institute for Standards & Technology's (NIST) Center for Cold Neutron Research and FHWA are using neutron scattering methods to measure motions and reactions of water at a nano-scale. This study is expected to explain the effects of various factors on the rate of development of cement's fractal nano-scale structure.

4.7 Synthesis of Cement Using Nano-Particles

In a project supported by National Science Foundation, it has been synthesized the components of portland cement Type I using nano-particles and compared their properties with that of commercial cement. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) equipment were used to evaluate the morphology and structure of
synthesized tricalcium silicate ($\text{C}_3\text{S}$) components. Conglomerated nano-particles with crystalline structures containing quantities of tri- and di-calcium silicate compounds as well as copper oxide were found to be present in the synthesized cement. Hydration tests indicated that the nano-cement had a more rapid hydration rate than portland cement Types I and III. Compressive strength of the cement synthesized using nano-particles was found to be less than that of ordinary portland cement. The authors attributed this reduction to a number of factors including: particle aggregation, rapid hydration, a high water to cement ratio, and the lack of gypsum [14].

4.8. Carbon Nano-Tubes

Since carbon nano-tubes have excellent potential for use in cement composites, basic mechanical properties of these tubes are presented in the following sections [4-6]. More details can be found in reference 4.

4.8.1. General Description

The most popular nano-tubes are carbon nano-tubes, discovered by the Japanese Scientist Sumio Iijima in 1991 [6]. Within a short period, arc-evaporation techniques were used to produce bulk quantities of nano-tubes. These tubes were multilayered structures. A single layer nano-tube was synthesized in 1993 by adding metals such as Cobalt to Graphite electrodes. In 1996, Smalley’s group in Texas, USA developed a method that resulted in high yield of single walled tubes with unusually uniform diameters. These uniform tubes had a tendency to form aligned bundles compared to those prepared using arc-evaporation. The bundled nano-tubes are sometimes referred to as nano “ropes”.

Other forms of carbon nano-tubes are: nano-horns, nano-test tubes and nano-fibers. Nano-horns are single walled carbon cones with remarkable adsorptive and catalytic properties. They have excellent potential for use in fuel cells. Nano test tubes have potential for use in a number of applications, including medical fields. These tubes can be filled with materials including biological molecules. Nano-fibers could become the ultimate carbon fibers because of their very high strength, stiffness, aspect ratio and purity.

Single layer nano-tube can be considered as the perfect thin walled cylinder because of the uniformity in thickness, accurate geometry and linear elastic material behavior. The challenge is to test them to obtain strength, stiffness and stability properties. A number of techniques are being developed to use electro-mechanical devices to induce force and measure responses. The forces are measured in nano Newtons and the displacements are measured in fractions of nano meters. Structural properties of single walled (single layered) tubes, multi walled tubes and single wall bundled tubes are needed for effective utilization of these materials in electronic and bio applications and development of nano/micro composites. The following sections provide some basic information on geometric dimensions and mechanical properties of carbon nano-tubes. Since this is a
very active research area, the reader is advised to refer to latest journals for up to date information.

4.8.2. Dimensions of Carbon Nano-Tubes

The first nano-tubes discovered were multi-walled tubes [11]. Transmission electron microscopy studies indicate that these tubes look like nested shells with an interlayer spacing of about 0.34 nm. The equivalent diameter of the tubes is in the range of 10 to 50 nm. The typical length varies from 100 to 1000nm. Single layer tube has a much smaller diameter (1 to 3 nm) and length (about 300 nm). The single layer tubes are often manufactured in “rope” or “bundled” form, where many individual tubes are close-packed in parallel.

4.8.3. Mechanical Properties of Nano-Tubes

The basic information needed for analysis are elastic modulus, stress-strain behavior, strain capacity in compression and tension, shear modulus and strengths in various modes. These values can be obtained using either experimental techniques or theoretical formulations. The small dimensions of the tubes impose a tremendous challenge for experimental study. Various types of high-resolution microscopes with the recent innovative developments in the area of nano manipulation have helped to obtain quantitative results. However, the numbers reported on strengths and modulus values vary widely. The modulus values reported range from 270 to 3600 GPa. Theoretical predictions indicate that the modulus can be as high as 5000 GPa. Typical stress-strain plots reported two investigators are shown in Fig. 3 [10]. The stresses were estimated assuming a uniform thickness of 0.34 nm for the single tube. The strains reported are engineering strains.

In tension mode, the reported strain at failure is as high as 12% and the strengths vary from 10 to 63 GPa. The strengths of very long (about 2 mm) ropes were found to be in the range of $1.72 \pm 0.64$ GPa [12].

4.9. Nano Composites

Nano-tubes can be used to fabricate fiber composites that can inherit some of the outstanding properties of the nano-tubes. For example, carbon nano-tubes can be mixed with alumino-silicates to produce very thin wafers that are very strong and highly conductive. The composite can also be used as a tough, durable, high temperature and low-friction coating. Current alumino-silicate formulations consist of silica particles in the range of 50 to 100 nm [8]. It is possible to refine the process to reduce the maximum particle size in the matrix to 5 or 10 nm. These matrices can be reinforced with as low as 0.5% of nano-tubes and still produce extraordinary strength and electrical conductivity improvements.
Researchers at NIST and university of Pennsylvania have been building nano-clay filled polymers that can improve fire resistance as well as mechanical properties [15]. Metal oxide nano-particles have also been used in coatings for protection of UV light, self-disinfecting surfaces, solar cells, indoor air cleaners, etc. Other nano-composites have superior structural performance.

4.10. Nano Sensors for Concrete Structures

The feasibility of Cyberliths, or Smart Aggregates, as wireless sensors embedded in concrete is being evaluated [16]. In the future these micro sensors might be reduced to dust-particle size, with the ability to coat an entire bridge with Smart Dust for optimum monitoring capabilities via a smart sensor net. These sensors can be used to remotely monitor the condition of the concrete and reinforcement without damaging the structures.

5. FUNDAMENTAL CEMENT HYDRATION CONCEPTS RELATED TO NANO-CEMENT

A large and in-depth knowledge base has been developed regarding the behavior of concrete over the past 150 years [8]. Possible issues related to nano-size cement particles are discussed in this section. The first and major issue is the synthesis of nano-cement. As mentioned earlier the particle size has to be reduced by an order of magnitude. Possible
avenues are chemical synthesis and separation of nano-size particles from micro cement using mechanical means. Attempts have been made in both fronts but published information is not available in the open literature.

The second major issue is the structure of hydrated cement. Heat of hydration and fabrication techniques are related to this subject area. The following facts that we learned from cement hydration will play an important role in understanding the hydration of nano-cement paste:

- One cubic mm of cement occupies about 2 cubic mm of space after complete hydration.
- Three major solid components of hydrated cement paste are: Calcium Silicate Hydrate (CSH), Calcium Hydroxide crystals (CH or portlandite) and Calcium Sulfo-Aluminates (CS or ettringite). CSH occupies about 50 to 60 percent of the volume whereas CH and CS occupies 20 to 25 percent and 15 to 20 percent respectively.
- The size of CSH sheet is less than 2 nm and the space between the sheets vary from 0.5 to 2.5 nm. Aggregation of poorly crystalline CSH particles could occupy 1 to 100 nm. Inter-particle spacing within an aggregation vary from 0.5 to 3 nm.
- CSH has a large surface area (100 to 700 m²/g) and the strength of this material is attributed to van der Waals forces.
- CH products are typically large with a width of about 1000 nm.
- CS has needle type structure and is unstable.
- Hydrated cement paste can contain adsorbed water. Up to six molecular layers of water, about 1.5 nm thick can be held by hydrogen bonding. Major part of this water can be removed by drying at 30 percent relative humidity.
- Size of capillary voids range from 10 to 1000 nm. However in well hydrated paste with a low water-cement ratio the pore size is typically less than 100 nm.
- Small CSH crystals, hexagonal calcium aluminate hydrates and calcium sulfoaluminates possesses large surface areas and adhesive capability. They also adhere to un-hydrated cement grains and aggregate particles.
- Pozzolanic reaction results in reduced capillary voids and replacement of calcium hydroxide with CSH.
- Heat of hydration is strongly influenced by particle size of cement. Blaine of cement varies from 320 m²/kg for normal cement to 900 m²/kg for ultra high early strength cement.
- C₃A generates the most heat and C₂S generates the least amount of heat.
- Heat of hydration has two peaks, one occurs during the dissolution stage and the second occurs during the formation of compounds.
- Active hydration zone is about 2000 nm thick, [Fig. 2].
- Of the two mechanisms of hydration through-solution hydration is more suitable for nano-cements. In this mechanism, complete dissolution of anhydrous compounds to their ionic constituents and eventual precipitation of hydrates are assumed to take place.
Aluminates hydrate much faster than silicates. Silicates, which make up about 75 percent of cement, play a dominant role on strength development.

5.1. Possible Performance and Fabrication Techniques

A careful review of the aforementioned facts and figures on portland cement can be used to envision the performance of nano-cement:

• Irrespective of the mode of manufacturing, the gypsum content has to be engineered to control the heat of hydration and strength development.
• It is possible to mix nano-carbon tube bundles in nano-cement slurry. For certain applications even regular carbon whiskers can be used.
• Only nano-size pozzolans and fillers should be used for nano-cement composites. Note that silica fume and titanium oxide are readily available in nano-sizes.
• The techniques used to manufacture asbestos cement sheets can be used to fabricate micro-meter thick carbon-cement sheets. Filtering technique of asbestos sheet manufacturing needs to be combined with vacuum bagging technique used for fabrication of aircraft structural components.

5.2. Fundamental Questions

Some of the fundamental questions that need to be answered are:

• Is the influence of water-cement ratio same for nano-cement?
• Will the strength and strain capacity remain same?
• Is it possible to use metallic nano-fibers?
• Will it be possible to dry process the cement-filler-fiber mix and cure using steam impregnation?

6. SOME OPPORTUNITIES AND CHALLENGES

6.1. Cement composites

If portland cement can be formulated with nano-size cement particles, it will open up a large number of opportunities. For example, the cement can be used as an inorganic adhesive with carbon fibers. Currently the micron size cement particles are not conducive for use with 7 micron diameter carbon fibers. The cement will not only be more economical than organic polymers but also will be fire resistant. In addition it will not emit any volatile organic compounds (voc) and the composites can be attached to parent concrete substrate using a compatible adhesive. It will be also very competitive with current inorganic composites because they have to be processed at high temperature.

A number of investigations have been carried out for developing smart concrete using carbon fibers [17]. This will become a reality with nano-cement because nano-carbon
tubes are much more effective than carbon fibers. The thickness of the composite can be reduced to microns and hence flexible and smart cement composite can be manufactured.

The primary challenge is to manufacture nano-size cement particles. Chemical vapor deposition shows promise [14]. Other avenue is high tech grinding. The second challenge is the heat of hydration. Special organic and inorganic additives need to be developed to control the setting and heat of hydration. Even though this is a risky and tough venture, the authors believe that the risk is worth taking.

6.2. Coatings for Concrete

Coatings are routinely used as protective barriers against abrasion, chemical attack, hydro-thermal variations and to improve aesthetics. Currently, most of these coatings are in the micrometer range. New materials and techniques are being developed to develop nano-meter thick coatings that are durable and generate less heat due to reduced friction. Coatings could be self-cleaning and self-healing. In most cases the performance of these coatings are evaluated using experimental techniques. The major parameters evaluated are: durability of coatings under various exposure conditions, abrasion resistance, friction resistance, high temperature resistance and electrical characteristics. Performance of the (coating) film and the interface between the film and the parent material play important role in the overall durability of the system. The authors believe that analytical models are needed to predict the performance of various types of coatings, so that optimum design approaches can be developed. The models could become quite complex because of the interaction of the coating-film with the parent material through the interface. For most cases, the mechanical properties of parent surfaces and some of the available coating materials are known. But very little is known about the performance of the interface under mechanical, hygrothermal and magnetic forces. For the nano coatings, the properties of the coatings themselves need investigation.

Brittle coatings usually fail by cracking, delaminating and spalling rather than “wearing out”. Robust analytical models are needed to predict the initiation and growth of cracks and their contribution to final degradation. We believe that the knowledge-base developed to analyze the thin walled structures can be effectively used to develop the aforementioned analytical models. Most existing coatings tend to accumulate grime reducing aesthetics. The deposited materials also degrade the parent surface over time. Coatings with a nano-scale of roughness that will repel water and dirt, modeled after the coating of the lotus leaf are being created. The lotus leaf has extraordinary ability to keep itself clean and dry. Now nanotechnology is being used to mimic the lotus leaf surface and create new products that outperform existing no-stick products. Typically, on a hydrophobic or water-repellent surface, particles of dirt are removed by moving water. But on a Lotus simulated surface, dirt particles are collected by water drops and rinsed off. Fig. 4 shows self cleaning properties of a coating made using nano-particles. It can be seen that the coated surface is totally free of mold that is present adjacent to the coated surface [13].
7. CONCLUSIONS

Large amounts of funds and effort are being utilized to develop nanotechnology. Even though cement and concrete may constitute only a small part of this overall effort, research in this area could pay enormous dividends in the areas of technological breakthroughs and economic benefits.

Current efforts are focused on understanding cement particle hydration, nano-size silica and sensors. Unique opportunity exists for the development of nano-cement that can lead to major long standing contributions.

REFERENCES