Opportunities & Challenges for Use of Nanotechnology in Cement-Based Materials

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Exploring and manipulating inner characteristics at nano-meter scale of matter in order to obtain exceptional properties and performance of materials is one of the most active research areas of the present time. The potential for application of nanotechnology in cement-based materials is huge. Currently, applications of nanotechnology in cement-based materials in several areas including construction of concrete roads are being explored. Nanotechnology has immense potential to result in a new generation of concrete, stronger and more durable, with desired stress-strain behavior and possibly with the whole range of newly introduced properties. Enhanced flexural behavior of the concrete may lead a reduction in the concrete slab thickness used in the construction of concrete pavements. This paper presents brief information on nanotechnology research opportunities and challenges in cement-based materials.

Introduction

Nanotechnology has immense potential and abilities to control the materials world including cement-based materials. It is the science of extremely tiny particle that deals with the study and use of materials and devices that operate at unimaginable nanometer scale i.e. one billionth, or 10"9, of a meter. A nanometer is so small that we cannot see something of this size without the use of very powerful microscopes. It is used to measure things that are very tiny i.e. atoms and molecules. Another way of putting it: a nanometer is the amount an average man's beard grows in the time it takes him to raise the razor to his face [1]. It is more about taking advantage of novel properties that arise solely due to the nano-scale and producing useful or functional components. Materials at this scale behave very differently from when they are in larger form. This technology offers better built, long lasting, cleaner, safer and smarter products for the home, for medicine, for agriculture, for communication and for industry in general. It is the synthesis and application of ideas from science and engineering towards the understanding and production of new materials and devices with enhanced properties and capabilities.

Nanoscience & Nanotechnology

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; while nanotechnology describes design, characterisation, production and application of materials and systems by controlling the size at nanometre scale. The term "Nanotechnology" was invented by Taniguchi in 1974, and it was first popularized in the 1980 by scientist and visionary K. Eric Drexler [2] in his book "Engines of Creation." Nanotechnology is the creation and utilization of materials, devices, and systems through the control of matter on the nanometre scale. It is more about taking advantage of novel properties that arise solely due to the nano-scale and producing useful or functional components with new or enhanced properties. Some of the important fields where nanotechnology applications are being actively explored are shown in Fig.1.

Why Do Materials at Nano-Scale Behave Differently?

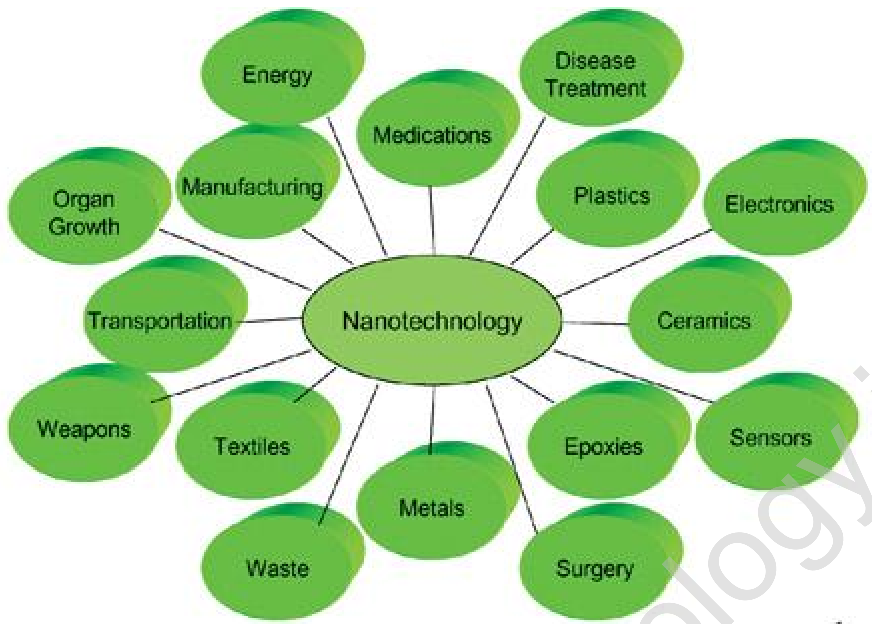

Figure 1: Current active fields where nanotechnology applications are being explored

When the dimensions of a material are decreased from macro size to nano size, significant changes in electronic conductivity, optical absorption, chemical reactivity and mechanical properties occur. Materials with the size range from 100 nm down to the atomic level can have different or enhanced properties compared with the same materials at a larger size. The two main reasons for the change in behavior are an increased relative surface area and the dominance of quantum effects [1-3]. An increase in surface area will result in a corresponding increase in chemical reactivity and making some nanoparticles useful as catalysts too. As size of the matter is reduced to tens of nanometers or less, quantum effects can begin to play a role, and these can significantly change materials optical, magnetic or electrical properties.

Carbon Nanotubes (CNTs)

Carbon nanotubes are among the most extensively researched nano-materials today. CNTs are tubular structures of nano meter diameter with large aspect ratio. These tubes have attracted much attention in recent years not only for their small dimensions but also for their potential applications in various fields. A single sheet of graphite is called grapheme. A CNT can be produced by curling a graphite sheet. Carbon sheets can also curl in number of ways. CNT can be considered as the most superior carbon fiber ever made. Addition of small amount (1% by wt) of CNT can improve the mechanical properties consisting of the main Portland cement phase and water. A CNT can be singled or multi walled. CNTs are the strongest and most flexible molecular material with Young's modulus of over 1 TPa. The approximate diameter is 1 nm with length to micron order. CNTs have excellent flexibility. These are essentially free from defects. Nanotubes are highly resistant to chemical attack and have a high strength to weight ratio (1.8g/ cm3 for MWNTs & 0.8G/cm3 for SWNTs). CNT has maximum strain of about 10% which is higher than any other material. Fig.2 shows the flexible behaviour of CNTs. Electrical conductivity of CNTs are six orders of magnitude higher than copper, hence, have very high current carrying capacity. Hence, carbon nano tubes have excellence potential for use in the cement composites.

Opportunities in the Fields of Cement-Based Composites

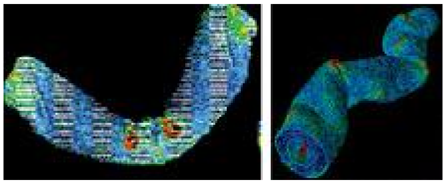

Figure 2: Flexible behavior of CNTs

Nanotechnology is being used for the creation of new materials, devices and systems at molecular, nano- and micro-level [4-9]. Interest in nanotechnology concept for portland cement composites is steadily growing. The most reported research work regarding application of nanotechnology in cement-based materials is either related to coating or enhancement of mechanical and electrical properties. Some of the widely reported nanoparticles in cement concrete industries are Titanium dioxide (TiO_2), Nanosilica (SiO_2), Alumina (Al_2O_3), Carbon nanotube (CNT) etc. 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 [4-7]. A typical scale of various constituent of a normal concrete is given in Fig. 3.

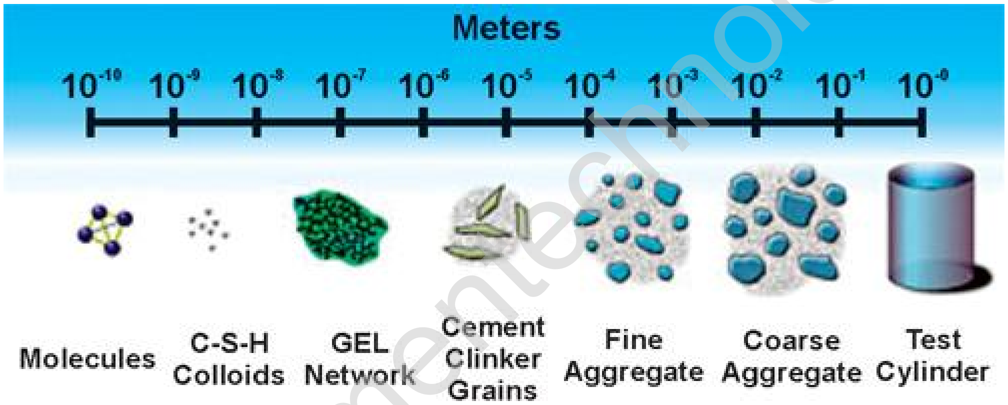

Figure 3: Scales of various constituents of concrete [7]

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 [4]. Knowledge at the nanoscale of the structure and characteristics of materials will promote the development of new applications and new products to repair or improve the properties of construction materials. For example, the structure of the fundamental calcium-silicate-hydrate (C-S-H) gel which is responsible for the mechanical and physical properties of cement pastes, including shrinkage, creep, porosity, permeability and elasticity. C-S-H gel can be modified to obtain better durability. Cement-based materials containing carbon nanotubes can be used for both strengthening and enhancing electrical and electronic properties of the concrete besides their mechanical properties. Development of smart concrete using carbon nano tubes would be easier. If nano-cement particles can be processed with nanotubes and nano-size silica particles; conductive, strong, tough, more flexible, cement-based composites can be developed with enhanced properties, for electronic applications and coatings.

Nano Concrete and Nano Ingredients

Nano concrete is defined as a concrete made with portland cement particles with sizes ranging from a few nanometer to a maximum of about 100 micrometers [4]. Nano ingredients are ingredients with at least one dimension of nano meter size. Therefore the particle size has to be reduced in order to obtain nano-portland cement. If these nano-cement particles can be processed with nanotubes and

reactive nano-size silica particles; conductive, strong, tough, more flexible, cement-based composites can be developed with enhanced properties, for electronic applications and coatings. There is also limited information 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 cement-based composites. Current research activity in concrete using nano cement and nano silica includes:

- **Characterization of cement hydration**
- **Influence of the addition of nano-size silica to concrete**
- **Synthesis of cement using nano particles and coatings (applied to protect concrete).**

The characteristics of nano concrete can be effectively used to create unique products, which can be also molded to complex shapes. Nano concrete containing carbon nanotubes can be used for both strengthening and creating electric circuits. Recently, Wang et al. [10] has demonstrated the use of nanoclays in the making of self compacting concrete for improve it for slipform paving for the construction of concrete road.
The NIST researchers have claimed that the service life of concrete could be doubled by using a nano-sized additive that slows down aggressive ion transport in concrete (http://www.nanowerk.com/news/newsid=9054.php). Rather than change the size and density of the pores in concrete, they reasoned, it would be better to change the viscosity of the solution in the concrete to reduce the speed at which chlorides and sulfates enter the concrete. The basic is "Swimming through a pool of honey takes longer than making it through a pool of water. The NIST researchers have demonstrated that the nanotechnology additives can be blended directly into the concrete with current chemical admixtures, but that even better performance is achieved when the additives are mixed into the concrete by saturating absorbent, lightweight sand [8]
It has been claimed that all the samples showed a unique nanosignature for the C-S-H material regardless of the sample origin. This is known as the material's genomic code and means that the strength of cement paste is not a function of specific minerals but relates to the way the nanoparticles are arranged. "If everything depends on the organizational structure of the nanoparticles that make up concrete, rather than on the material itself, we can conceivably replace it with a material that has concrete's other characteristics—strength, durability, mass availability and low cost—but does not release so much CO2 into the atmosphere during manufacture." said Professor Franz-Josef Ulm from civil and environ- mental engineering at MIT [11].

Nano Silica Fume for Improving Concrete Performance

Nano silica is most common nano additive to concrete. It is reported that nano silica was found to be much effective than micron sized silica for improving the performance such as permeability, and subsequently, durability. 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. Fig.4 presents a typical SEM of nanosilica particles.
Nano-silica is effective additives to polymers and concrete, a development realized in high-performance and self–compacting concrete with improved workability and strength. Nano-silica addition to cement based materials control the degradation of the fundamental C-S-H (Calcium-silicate-hydrate) reaction in water as well as block water penetration and leads to improvement in durability. The addition of nano SiO_2 particles enhances the density and strength of concrete. The results indicate that nanosilica behaves not only as a filler to improve microstructure, but also as an activator to promote pozzolanic reaction for fly ash concrete as a result strength of the fly ash concrete improves particularly in the early stages.

Coatings for Concrete

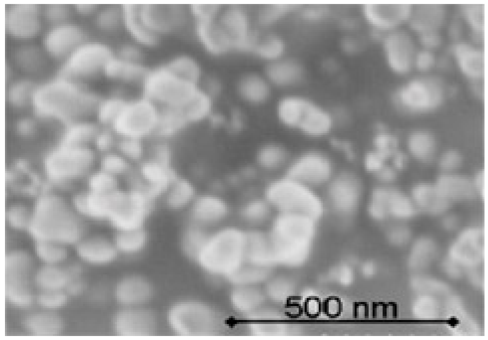

Figure 4: SEM of a typical nanosilica particles

Another major large volume application of nano powder in cement-based materials is the area of coatings. The attractive colouring on ancient Czech glasses is found to contain nanoparticles. This shows that nanotechnology was used for coating surfaces i.e. spraying and making a product look attractive from ancient time. Nano-powders have a remarkable surface area. The surface area imparts a serious change of surface energy and surface morphology. The change in properties causes improved catalytic ability, tunable wavelength-sensing ability and better designed pigments and paints with self-cleaning and self-healing feature. One promising area of application of nanoparticle for cement based materials is development of self-cleaning coating. Titanium oxide is commonly used for this purpose. It is incorporated, as nano particles to block UV light. It is added to paints, cements and windows for its sterilizing properties as TiO2 breaks down organic pollutants, volatile organic compounds, and bacterial membrane through powerful catalyst reactions and can reduce airborne pollutants applying to outer surfaces. Additionally it is hydrophilic and therefore gives self-cleaning properties to surface to which it is applied.

Challenges for the Application of Nanotechnology in Cement-Based Materials

The primary challenge is to manufacture nano-size cement particles. The second challenge is the heat of hydration. Due to many folds increase in specific surface areas the nano cement particle are very reactive and results in enormous amount of heat of hydration. Special organic and inorganic additives are needed to be developed to control the setting and heat of hydration. For the nano-coatings, the properties of the coatings themselves need extensive investigation. Durability of coatings under various exposure conditions, abrasion resistance, friction resistance, high temperature resistance, failure modes, and electrical characteristics need to be proven by using exhaustive experiments. Furthermore, huge amount of expenditure is needed for the equipments to study the behaviour of nano cement and nano additive in cement based materials.

Conclusion

There is wide scope for the use of nanotechnology including nano ingredients for harnessing improved mechanical and electrical properties such as higher strength, toughness, flexibility, stability, conductivity, besides self-cleaning property of cement-based composites. The challenges are also huge that includes health hazards working with dry nanoparticle, huge expenditure for procuring equipment for study at nano level. Currently, limited availability/Non-availability of nano cement, sand etc. makes it difficult to apply to use this technology in cement-based material. Current studies are mostly confined to laboratory stage. Therefore, a lot more extensive studies are required before the application of nanotechnology becomes viable and economical way for enhancing the important properties of cement-based materials.

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References:

- **Kahn, J. (2006). "Nanotechnology". National Geographic 2006 (June): 98–119**
- **Drexler, K. E. (1986). "Engine of creation." Anchor Book Edition, N.Y.**
- **Deb, B-Woods. (2008). "Nanotechnology: Ethics and Society." Taylor and Francis Group, N.Y.**
- **Balaguru, P., and Chong, K. "Nanotechnology and concrete: Research opportunities." Proceedings of ACI Session on "Nanotechnology of Concrete: Recent Developments and Future Perspectives" November 7, 2006, Denver, USA, 16-27.**
- **Boresi, Arthur P.; Chong, Ken P.; Saigal, Sunil. Approximate Solution Methods in**
- **Engineering Mechanics, John Wiley, New York, 2002, 280 pp.**
- **Chong, K.P. "Research and Challenges in Nanomechanics" 90- minute**
- **Nanotechnology Webcast, ASME, 2002; archived in www.asme.org/nanowebcast**
- **Collepardi, M.; Collepardi, S.; Troli, R.; and Skarp, U. "Combination of Silica Fume,**
- **Fly Ash and Amorphous Nano-Silica in Superplasticized High-performance**
- **Concretes", Proceeding of First International Conference on Innovative Materials and**
- **Technologies for construction and Rehabilitation, Lecce, Italy, 2004, 459-468.**
- **http://www.nanowerk.com/news/newsid=9054.php. "Nanotechnology to double the lifetime of concrete." Accessed on 2 Dec. 2010.**
- **Sobolev, K., and Gutierrez, M. F. (2005). "How nanotechnology can change the concrete word." American Ceramic Society Bulletin, Vol.84, No.10, pp.14-18.**
- **Wang, K., Shah, S. P., and Voigt, T. (2007). "A novel self-consolidating concrete for slip-form application." TRB 2007 Annual Meeting.**
- **http://www.azonano.com/Details.asp?ArticleID=1873. "Cement and concrete combined with nanotechnology may hold key to reducing greenhouse gases and climate change." Accessed on 6 Dec. 2010.**