Nanoscience to Nanotechnology for Civil Engineering – Proof of Concepts

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Abstract: -Conventional concrete improved by applying nanotechnology aims at developing a novel, smart, eco- and environment- friendly construction material towards the green structure. In today's life, though utilization of cement based materials plays a vital role in the infrastructure development, it is polluting the environment by emitting CO_2. Based on this view, researchers have been pursuing to evolve new or alternate material towards a green and sustainable solution. This paper presents the possible role of nanotechnology for the construction applications. It also discusses the application of nanotechnology in the area of cement based materials, their composites. Further, the mechano-chemical activation process of cement based materials and their formation using nano based organo-mineral is also presented in brief. It has been observed that the inclusion of nano particles would improve the toughness, shear, tensile and flexural strength of cement based materials. Further, it is observed that the better understanding and engineering of complex structure of cement-based material at nano-level will definitely result in a new generation of construction materials with enhanced properties, viz., strength and durability.

Key words:- Construction materials, nano science, nano technology, civil application, metal oxide, crystalline, natural minerals, chemical reaction, challenges

1 Introduction

Nanotechnology is the re-engineering of materials and devices by controlling the matter at the atomic level [1]. Nanotechnology is not a new science or technology; rather it was first introduced by Richard P. Feynman in his famous lecture at the California Institute of Technology in 1959. However, the research on this topic has been very active only in recent two decades. Nevertheless, nanotechnology is still is one of the most active research areas with both novel science and innovative applications. The evolution of challenging technologies and sophisticated instrumentations as well as broadening of basic scientific knowledge are making the research on nanotechnology fast moving and evolutionary. The key in nanotechnology is the size of particles because the properties of materials are dramatically affected under a scale of nanometer [10^{-9} meter]. To better understand the difference among various scales, researcher have divided the area of science with the size of material, as presented in Table 1. In nano level, gravity becomes unimportant, electrostatic forces take over and quantum effects come in. Further, as particles become nano-sized, the proportion of atoms on the surface increases relative to those inside and this leads to novel properties. Current researchers dealing with nano-science and nano-technology are exploring these novel properties since at the nanoscale we can alter the macro-properties and produce significantly new materials and processes. Discussion on the application of nanotechnology in civil engineering; specifically in construction, is extremely important. According to a study by the Canadian Program on Genomics and Global Health (CPGGH), nanotechnology in civil engineering ranked 8 of 10 applications that most likely have impact in the developing world [2]. Nanotechnology can be applied for design and construction processes in many areas. Owing to many unique characteristics of nanotechnology derived products, newly developed nano based products can significantly reduce current civil engineering problems. Basically, construction deals with high-tech materials and processes that have been use in construction. Hence, there is huge scope to apply nanotechnology in construction materials, which can exhibit, probably one of the most prominent, societal impact.

Table 1: Size of material and related areas of study

Size (in meter)	Related science and technology
10^{-12}	Quantum mechanics
10^{-9}	Molecular Dynamics, Nanomechanics, Molecular Biology, Biophysics
10^{-6}	Elasticity, Plasticity, Dislocation
10^{-3}	Mechanics of materials
10^{-0}	Structural analysis

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2 Application of Nanotechnology in Construction

Many disciplines of civil engineering including design and construction processes can be benefited from nanotechnology. For example, new structural materials with unique properties, lighter and stronger composites, fire insulator, sound absorber, low maintenance coating, water repellants, nano-clay filled polymers, self-disinfecting surfaces, UN light protector, air cleaners, nano sized sensors, ultra thin- strong- conductive wafers, solar cells etc to name a few. This paper presents, in brief, the areas of application of nanotechnology in civil engineering and the science & technology behind the improved performance. Further, the existing challenges that the scientists and technologists facing towards exploiting the potentiality of nanotechnology is also brought out.

2.1 Nano cement

Portland cement is the most widely used construction material. It can be argued that concrete utilizes nanotechnology because it contains nano-particles as ingredients including nano-water particles and nano-air voids. But, it is not the application of the technology at nano level. If it is possible to create the technological tools and organize the amount and locations of these nano-ingredients in a scientific way, then concrete can experience the advances of nanotechnology. Concrete is, after all, a macro-material strongly influenced by its nano-properties and understanding it at nano level can provide the avenues for improvement of strength and durability. The particle size of cement can be reduced to nano-size or can be modified by adding nanotubes and reactive nano-size silica particles. A number of investigations have been carried out for developing smart concrete using carbon fibers [3] and it has been found that instead of carbon fibers, nano-carbon tubes added with nano-cement will be more effective. It is also envisaged that the micro-thick nano-cement with flexibility may not be an impossible task.

2.2 Nano composites

Nano-composites can be developed by using nano-tubes which can implant some of the outstanding properties of the nano-tubes. Alumino-silicates are being mixed with carbon nanotubes which can produce strong, durable conductive films. Further, the current sizes of alumino-silicates (50 to 100 nm) can further be reduced to 5 to 10 nm range and a little volume percent of nano-tubes ($\approx$ 0.5%) can produce extraordinary composites. Further, fibre wrapping commonly used for strengthening of existing concrete structures, has witnessed an advancement by using fibre sheet (matrix) containing nano-silica particles and hardeners [4]. These nanoparticles penetrate and close small cracks on the concrete surface and, in strengthening applications, the matrices form a strong bond between the surface of the concrete and the fibre reinforcement. A detailed discussion on different type of nano-cement composites is presented later.

2.3 Nano-Coatings for concrete

To protect the structures/components from abrasion, chemical attack and hydro-thermal variations, and to improve aesthetics, chemical coatings are generally and routinely used. Till date technology which limits the size of coating materials in micrometer, can enjoy the great advancement by using nano science and technology. Studies are being conducted on types of nanoparticles in various binders and their effectiveness on key properties related to concrete deterioration and it is reported that a solvent containing a low molecular weight epoxy resin and nano-clay particles has shown promising results. Nano-meter thick coatings are durable and could have self-cleaning and self-healing properties. Nano scale roughness of the coatings will have the property to repel water and dirt and can outdate the existing ‘non-stick’ technology. Self cleaning properties of a coating made using nano-particles would also help to keep the coated surface totally free of dirt and dust [5]. Nanocrystalline materials have considerable potential for energy storage applications also. This is owing to the highly reactive nature of nanosized grains. The nanosized materials such as nitrides, phosphors, nano Al_2O_3 can undergo reversible chemical reactions involving electron transfer, and simultaneously exhibit unique surface properties that enable them to adsorb charged species on the surface. This combination makes them ideal for storing charge.

2.4 Nano steel

Steel has played a major role in construction industry since past two centuries. Fatigue is a significant issue for the structures subjected to cyclic loading, such as in bridges, towers and off-shore platforms. Fatigue failure can occur at significantly low stresses than the yield stress of the material and lead to a significant reduction in service life. Stress concentration is responsible for initiating cracks which triggers fatigue failure and research [6] has shown that the addition of copper nano-particles reduces the surface unevenness of steel which then limits the number of stress risers and hence fatigue cracking. Further, it has been reported that vanadium and molybdenum nano-particles can improve the fracture problems associated with high strength bolts. The steel used for the fabrication of warships and aircrafts carriers requires special alloy chemistry containing Niobium, Vanadium, Titatium, Nickel and very low amount of hydrogen (maximum to 2ppm) to provide higher strength, superior low temperature toughness and improved ductility. Current research has shown that the refinement of the cementite phase of steel to a nano-size can produced stronger cables. High strength steel cables can pave the way for construction of long span prestressed bridges.

2.5 Nano glass

Extensive research is being carried out [7] on the application of nanotechnology to glass. It has been reported that Titanium dioxide (TiO_2) can be used in nano form to coat the glasses to import the sterilizing and anti-fouling properties of TiO_2 into glass. TiO_2 coating captures and breaks down organic and inorganic air pollutants by a photo-catalytic process. Further, TiO_2 is hydrophilic and this attraction to water forms sheets out of rain drops, and thus, self cleaning glass is present in the market. Recent literature shows that a considerable amount of works is being carried out to establish nano-technological solutions to block light and heat penetration through glass. Towards this, thermo-chromic, photo-chromic and electro-chromic coatings technologies are being explored. There is a possibility to use tungsten oxide layer in nano scale over glass cladding.

2.6 Nano Particles for fire protection

Application of Portland cement based coatings for fire protection of steel structures is limited since it is thick, tend to be brittle and polymer additions are needed to improve adhesion with steel surface. It has been found that nano-cement mixing with carbon nanotubes (CNT) with the cementious material to fabricate fibre composites has outstanding properties of high strength [8] and fire resistance.

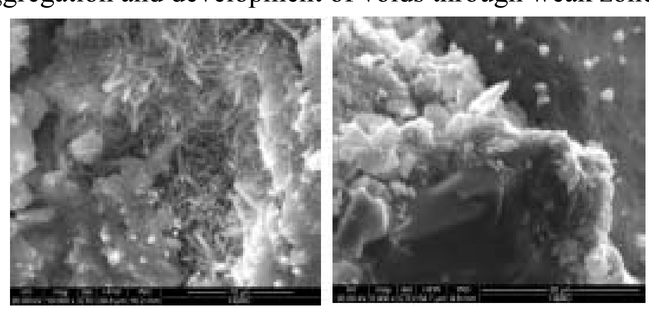
2.7 Nano Sensors for Concrete Structures

Possibilities of using smart aggregates as wireless sensors are being attempted by researchers [9]. It is envisaged that these wireless sensors can be embedded in concrete during construction itself. Thus, these sensors can be used for remote health monitoring and nondestructive condition assessment of existing structures. From effective applications of micro-electromechanical (MEM) devices into concrete, nanoscale “smart nano-dust” is being developed that can be sprinkled on the surface of the structure or can be incorporated into the mix. It is reported that nanotechnology-based sensors have great potential to use in concrete structures for quality control and health monitoring by using the information on changes in density and viscosity, shrinkage, moisture, chlorine concentration of concrete.

3 Science and technology behind the improved performance of nano-particles obtained from natural source

3.1 Nature nano-mineral - Clay

Due to exponential growth of population and availability of limited natural resources, extensive scientific explorations have been carried out to find out available raw materials those can be engineered and utilized. It has been found that the most available raw mineral such as clay has a huge potential to be used in the construction industry both as a building material and as a foundation for structures. The tremendous developments in the area of “wet” colloid chemical synthesis of nano-sized and nano-structured materials, which was mimicked by “biomineralization and hierarchically organized self-assembly” [10], is giving a new gateway to solve the environmental and energy problem to maintain social sustainable development in construction sector. The alternating layer-by-layer (LBL) deposition process was the basic principle behind the wet synthesis. A variety of nano-structured materials with improved properties have been further developed by Isayama and Kunitake[11]. Gupta and Maharsia [12] reported the enhancement of energy absorption in synthetic foams by using nano-clay for sandwich core application. The study towards the changes in mechanical and micro-structural properties of cement mortar due to the effect of nano-clay is conducted by Morsy et al [13]. The Nano-fiber nature of NMK (only cement mortar containing 4% and 8 % NMK, due to their high strength) and their filler effect in cement mortar was revealed by morphological study through SEM as reported in Fig. 1. In the control specimen, a needle like hydrates were formed around the CSH gel and deposited CH crystals were distributed in the cement paste. The texture of hydrate products was found to be denser, compact and with uniform microstructure. It indicates the uniform distribution of nano-particles in the cement mortar due to their high surface energy during hydration. The reported study has also cautioned on non-uniform dispersion of nano-particles which could lead to particles aggregation and development of voids through weak zone.



(a) (b)

Fig. 1 SEM micrographs of hydrated NMK mortar a) with 0% NMK, b) with 8 % NMK (Courtesy : Morsy [13])

3.2 Clay/Polymer nano composites

One of the most interesting interdisciplinary areas in civil engineering discipline is clay/polymer composites. This technology has received great attention in the area of nano-composites research. It offers tremendous improvement in a wide range of physical and engineering properties for polymers with lower percentage of filler. This nano composite approach has advantages over the so called fiber reinforced composites in the low filler loading range, but still it needs more research for further applications to overtake the traditional composites.

3.2.1 Chemistry of Clay/Polymer nano- composites

Clay/Polymer nano-composites are a typical example and good demonstration of nanotechnology [14]. The basic phenomenon behind this technique is “bottom-up and top-down approach”. In the bottom-up approach, the nano-materials are made from atoms or molecules (small to big) and by adopting this principle, molecules can be made to arrange themselves automatically into useful shapes and structures. In the later case, nano-objects are made from large objects (big to small), sincere attention needs to be paid to get a controlled particle size. In general, the goal is to produce stable nano-particles of uniform size, shape, and properties. This category of material uses smectite-type clays, such as hectorite, montmorillonite, and synthetic mica as fillers to enhance the properties of polymers. Smectite type clays have layered structure and each layer is constructed from tetrahedrally co-ordinated Si atoms fused into an edge-shared octahedral plane of either $Al(OH)_3$ or $Mg(OH)_2$. Based on the nature of the bonding between these atoms, the layers exhibit excellent mechanical properties. The recent modeling work has illustrated that the young’s modulus in the layer direction is 50 to 400 times higher than that of a typical polymer [15]. But the exact mechanical properties of the layers are yet to be established. It is expected that, using nano composite approach, it is possible to make functioning of individual clay layers effectively to get excellent mechanical property.

3.2.2 Properties and Uses

Clay/polymer nano composites have improved physical and engineering properties include fire retardancy, barrier resistance and ion conductivity [16]. This polymer composite technique can also be useful for water-soluble hydrophilic/hydrophobic functional monomer [17] systems for the preparation of polymer/silicate hybrid nano-materials.

3.3 Mechano-chemical Activation

As discussed in the preceding section, top down approach method is useful for the synthesis of nano-materials at an industrial scale but the bottom up approach is useful for the basic and fundamental research application. In the top-down process, special type of admixture-modifiers containing an effective surfactant are inter-grinded with cement, to get high strength concrete with reduced water cement ratio It is known that, the formation of nano-thick organo-mineral layers on the surface of the cement particles promotes the development and stabilization of highly reactive dislocation centers and defectives site during the cement grinding process, and hence high strength has obtained. But, this process needs to have lot experience and trials to get a controlled particle size shape. But using molecular recognition approach, one can control the size and shapes of the atoms effectively as it’s intended to work. It will help to investigate the cement, modifiers and its effects on nano-structure and hydration of cement based materials. Sobolev *et al* [18] has reported the mechanism for the formation of nano-layer on the surface of cement. Three type of modifiers such as sulphonated naphthalene formaldehyde (SNF), sulphonated melamine formaldehyde (SMF), and polycarboxylate (PC) have been used in the experimental program. Portland cement clinker and natural gypsum were used as the ingredients of mechano-chemically activated (MCA) cements. The modifiers were mixed with complex admixture by intermixing and granulating with silica fume at a ratio of 1:10, by weight. In the study a significant amorphization on the surface of the cement was noted. From this conducted study, it was reported that the SNF based modifiers effectively reduces the particle size of the cement and also increases the surface area, but it is not the case where PC is involved. The difference in early hydration between MCA and NPC (portlandite) cements were observed by SEM studies, indicates the absence of C-S-H and portlandite due to stable dormant period at early hydration of MCA cements. The study underlines that the fine tuning of cement system at nano level is able to control the workability loss and prevent intensive strength development.

3.4 Use of nano-materials in cement

A small quantity of nano material is sufficient to enhance the performance of nano-composites. In cement composites, inclusion of nano particles such as nano SiO_2, Al_2O_3, TiO_2, quartz were used to make High Strength (HSC), High Performance (HPC) [19] and Self Compacting concrete (SCC) [20] for the past years. Nowadays researchers are looking for ultra high performance concrete with the improved mechanical properties. Basically cementitious materials are quasi-brittle materials with low tensile strength and low strain capacity. In order to overcome these weaknesses, fibers are incorporated into cementitious matrix, and the use of this microfiber reinforcement leads to the improvement of mechanical properties of cement based materials [21]. This microfiber inclusion will help to delay the development of micro-cracks but it will not help to stop or terminate their initiation [8]. This obstacle can be overcome by using nano sized fibers or nano-particles into the cement matrix. It has opened a new pathway for evolving "nano-engineered ultra high performance material" and to create a new generation of a "crack free material" [22]. This type of concrete has many advantages including low-environmental impact, high strength and light weight structures with low CO_2 emissions, also enhances mechanical property, vibration damping capacity, air void content, low permeability, steel rebar corrosion resistance, and workability as well as alkali-silica mitigations because this nano-particle will act as mechanical rebar in between the interfacial transition zone, thereby suppresses the alkali-silica reaction. It will reform the traditional concrete into crack-resistant self monitoring multifunctional smart material.

Reactive Powder concretes are used for storage of nuclear waste due to their excellent micro-structural property such as very low porosity. One of the common problems of HPC is durability (lead to water leaching) has been investigated by Matte and Moranville [23]. It is reported that the microstructure of the cement paste greatly affected by calcium leaching and leads to the loss of the advantageous effects brought by the application of nano-silica fume. Due to leaching of anhydrous clinker, it cannot be hydrated and therefore no more pozzolanic reaction is possible. Application of silica fume in cementitious material in RPC [24] to change its structures at micro level has been investigated using analytical tools. It was clearly depicted that the presence of crystal such as hydrate, xonotlite was observed at high temperatures and based on their heat treatment conditions the changes in microstructure of CSH hydrates and pozzolonic activity were also noticed. Mercury Porosimetry analysis demonstrated the very low porosity of RPC which can reduce the chances of leaching. The addition of small amounts (1% wt) of carbon nano tube (CNT) can improve the mechanical properties of ordinary cement. Oxidized multi-walled nanotubes (MWNT's) show the best improvements both in compressive strength and flexural strength compared to ordinary cement.

4 Challenges

Though a huge and alluring potential of nanotechnology in civil engineering has been envisaged and enormous efforts throughout the world are being taken up to use nanotechnology in civil engineering applications, still few of grey areas need to be explored to make the technology more applicable. These are: (i) manufacture nano-size cement particles [25], (ii) heat of hydration, (iii) Influence of water-cement ratio, (iv) performance of the (coating) and the interface between the film and the parent material , (v) analytical models to predict the initiation and growth of cracks and their contribution to final degradation, (vi) agglomeration of nano tubes, (vii) lack of cohesion between nano-tubes with concrete matrix, (viii) optimum values of nano-tubes and dispersing agents in concrete mix design, (ix) high strength material with high ductility, (x) deterioration in mechanical properties and insufficient thermal stability of nano-composites due to high concentrations of organic surfactants for modification of nano-clay, and (xi) development of multi-functional material towards green construction.

To bring the advances of nanotechnology in civil engineering applications, authors of the present paper are engaged in developing a green and sustainable cementitious material which can be a potential substitute (fully or partially) of conventional cement.

5 Conclusions

The present paper discusses the present and futuristic applications of nanotechnology in civil engineering. A brief on different materials developed/being developed for construction industries which will not only revolutionaries conventional civil engineering and low tech construction materials; it would have probably the greatest positive impact on society as well. Further, mechano-chemical activities in nano level of the materials responsible for the changes in properties are discussed to provide the science behind change of material properties. It is found that the natural minerals can also be treated as nano particles for producing nano cement. Though the field is enormous, promising and extremely fast moving, there are some challenges, as pointed out in this paper, need to be addressed by the scientists and solutions should be found at the earliest to elevate nanotechnology from high tech stature to the one of biggest graces to the society in general, to the engineers, in particular.

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