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EMERGING TRENDS IN APPLICATION OF NANOTECHNOLOGY FOR CEMENT BASED MATERIALS – A PRE-PROOF OF CONCEPT

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***Abstract**: This paper presents the pre-proof of concept played for the role of nanotechnology towards the construction applications, specifically on materials. It includes the application of nanotechnology in the area of cement based materials, their composites, and scope of usage of one of the most natural nano mineral, namely clay as a construction material. It can be clearly understood that the mechano-chemical activation of cement with developed grinding modifiers is found to be very effective method to tailor the cement behavior in fresh and hardened state. Based on the review, it is observed that the inclusions of nano particles 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. Further, due to improved mechanical properties, lesser requirement of cement in construction activities will immensely reduce the emission of CO_2.*

***Keywords**: Nanotechnology, Civil Engineering, Natural Mineral, C-S-H, Bottom-up.*

INTRODUCTION

Conventional concrete improved by applying nanotechnology aims at developing a novel, smart, eco- and environment- friendly construction material towards realization of green structure. In today's life, utilization of cement based materials plays a vital role in the development of technology such as high performance concrete (HPC), self compacting concrete (SCC), high strength concrete, reactive powder concrete (RPC) etc. On one hand, these advanced concrete technologies are promoting the development of a country through smart and eco-construction; on the other hand it is polluting the environment by emitting CO_2 due to the "rapid utilization" of cement in construction based works. Researchers have been pursuing to evolve new or alternate material for the replacement or reduction of CO_2 emitting entity for cement composites, and also to make them as smart materials. Nanotechnology is the re-engineering of materials and devices by controlling the matter at the atomic level. Nanotechnology is one of the most active and attractive research areas with both novel science and innovative applications. The evolution of challenging technology and sophisticated instrumentation 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 due to their size (**Fig. 1**). As particles become nano-sized,

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the proportion of atoms on the surface increases relative to those inside and this leads to novel properties.

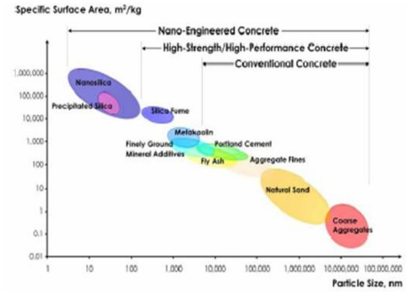


Fig. 1: The particle size and specific surface area of concrete materials [Sobolev and Gutierrez 2005]

APPLICATION OF NANOTECHNOLOGY IN CONSTRUCTION

Nanotechnology is interdisciplinary in nature and it has already inter-connected medical science to mechanical engineering, chemical science and metallurgical engineering to civil/structural engineering. 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, self-healing and self-cleaning coatings, UN light protector, air cleaners, nano sized sensors, ultra thin- strong- conductive wafers, solar cells etc to name a few. This paper presents the possible areas of application of nanotechnology in improving materials used in civil engineering.

Nano cement and composites

Portland cement is the most widely used construction material. Average size of Portland cement particle is about 50 microns. Therefore, concrete is a macro-material strongly influenced by its nano-properties and understanding it at nano level can provide the changes 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. If Portland cement can be formulated with nano-size cement particles, it will open up a large number of opportunities. It may also impart the new properties like conductivity, improved strength, enhanced toughness etc. It is envisaged that the micro-thick nano-cement with improved properties may not be an impossible to achieve. Several types of nano-cement are currently being investigated by the researchers, viz., (*i*) high energy milling of ordinary portland cement to improve strength of concrete, (*ii*) addition of SiO_2 nanoparticles part of the cement to enhance strength to weight ratio, (*iii*) addition of TiO_2 in cement to provide an excellent reflective coating with sterilizing properties, and, (*iv*) addition of small amounts of carbon nano tube (CNT) to improve the mechanical properties of ordinary cement.

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, fiber wrapping commonly used for strengthening of existing concrete structures, has witnessed an advancement by using fiber sheet (matrix) containing nano-silica particles and hardeners (Ge and Gao, 2008). 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 fiber reinforcement. A detailed discussion on different type of nano-cement composites are presented later.

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 concrete (HSC), high performance concrete (HPC) **(**Nazari et.al 2010 a,b**)** and self compacting concrete (SCC) **(**Collepardi et.al 2002, 2007**)** 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 tensile 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 **(**Akkaya et al 2003**)**. This microfiber inclusion will help to delay the development of micro-cracks but it will not help to stop or terminate their initiation **(**Makar and Beaudoin 2003**)**. This obstacle can be overcome by the development of nanotechnology by the inclusion of 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*"**(**Konsta-Gdoutos et al 2010 and Shah et al 2009**)**. This type of concrete have 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 healing 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 (1999). To understand the mechanism of the C-S-H hydrates, studies conducted on the pure cement paste and on cement-silica fume paste. It is reported that the microstructure of the cement paste greatly affected by calcium leaching. Also it was noted that the leaching test as it was performed is very severe and leads to the loss of the advantageous effects brought by the application of nano-silica fume. It has been found that 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 to change its structures at micro level has been investigated using Thermogravimetric Analysis, X-ray diffraction analysis and Mercury Intrusion Porosimetry analysis. Granulometry and heat treatment were optimized to obtain excellent mechanical and durability properties. It was clearly depicted from the studies made 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 C-S-H hydrates and pozzolonic activity were also noticed. Mercury Intrusion Porosimetry analysis demonstrated the very low porosity of RPC which can reduce the chances of leaching.

NATURE NANO-MINERAL - CLAY

Due to exponential growth of population and limitation of 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 minerals 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. Natural clays such as clay stone or mudstone comprise several clay minerals with one or more impurities. The most common impurities are, free iron oxide minerals, amorphous silica and alumina, quartz grain, limestone, gypsum and other more soluble salts. These impurities affect largely clay characteristics and may affect adversely its use in specific applications. Clay minerals can be categorized in four subgroups in natural environments: (*i*) kaolinite group, (*ii*) smectite group, (*iii*) illite group, and (*iv*) chlorite group. Since they occur with metal-oxides, they naturally acquire colors. They may also contain organic matter. When the amount of kaolinitic is more than 50 % **(**Chandrasekhar and Ramaswamy, 2002**)** then the rock is considered as kaolin. The color clays deposits become white to beige in the middle and top parts. Clays become brown to red brown depending on top and middle parts **(**Felhi et al., 2008**)**. Clays inherently absorb water, thus they are always wet. Physical and chemical properties of the clays make them adequate material for different purposes in different fields. Clay-organic complex structures have been a research subject particularly since 1930’s.

Understanding the crystallography of clay minerals was possible due to the extensive progress in materials research. The properties of clay at normal temperatures are determined only during the reaction with water. The tremendous developments in the area of “wet” colloid chemical synthesis of nano-sized and nano-structured materials 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 (Fendler, 1996**).** A variety of nano-structured materials with improved properties or enhanced functionalities, including inorganic or hybrid organic-inorganic composites, have been developed using this technique **(**Chen et al 2008, Morgan et al., (2010)**)**. The major advantage of this process was relative ease of preparation, low cost, and high versatility. The study towards the colloidal state clay research is of fundamental importance to soil mechanics

Thermographic study of meta-kaolinite

The exothermic effect of meta-kaolinite was discussed by Lemaitre et al, 1975, stating that the exothermic effect had a double origin: (a) direct formation of mullite, promoted by CaO, and (b) formation of a segregated spinel-type phase, i.e. y-Al_2O_3, promoted by MgO. Attempts were made to correlate modifications of the exothermic peak characteristics with the nature of the various crystalline phases which develop after prolonged heating in the presence of chemical additives. From this study, it was stated that, it is possible to classify mineralizers into three categories depending on the selectivity regarding the formation of new phases at 900°C: i.e., (*i*) mineralizers with no definite selectivity: Li_2O, Na_2O, K_2O; (*ii*) mineralizers promoting the formation of a spinel type phase: MgO, ZnO; and (*iii*) mineralizers promoting the formation of mullite: CaO, CuO. It was found that the exothermic effect of metakaolinite does not have a single origin. Moreover this effect was due to both the formation of a cubic-type phase, for instance, λ-Al_2O_3, and the nucleation of mullite. By using selective mineralizers, it was possible to enhance either the formation of λ-alumina or mullite. The physico-chemical measurement such as crystallinity of the metakaolinite and role of mineralizers and their dispersion method was studied by Bulens (Bulens and Delmon, 1977). The thermal transformation of metakaolinite into mullite was proposed, as shown in **Fig. 2**.

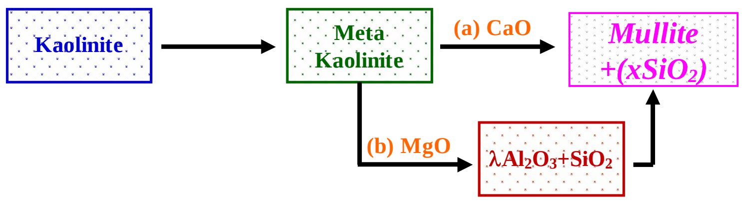
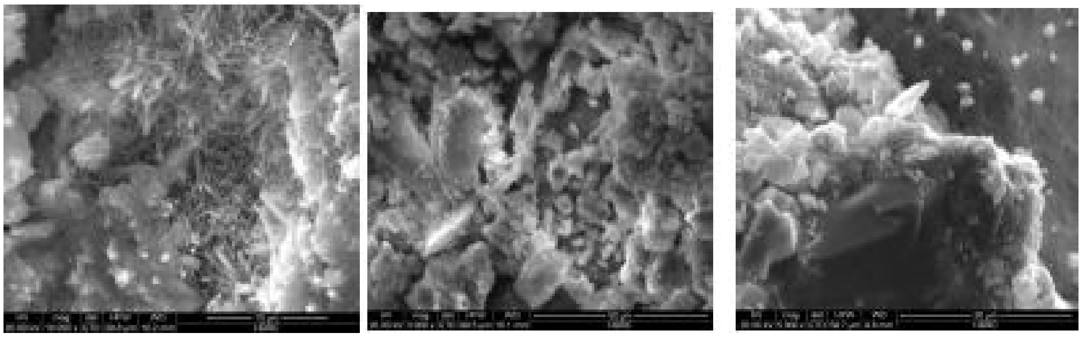


Fig. 2: Schematic flow chart of thermal transformation of metakaolinite into mullite

It was found that the direct mullite formation path (*a*) occurs readily at 900°C in well-ordered kaolinite, but not in poorly ordered samples, even when fired with CaO. On the other hand, path (*b*) can be promoted in all samples using MgO as a mineralizer. When the indirect reaction path (*b*) occurs, a second exothermic effect is observed at approximately 1200°C, indicating secondary mullite formation by recombination of segregated silica and alumina phases. The production of porous mullite from kaolinitic clays has been studied by Esharghawi et al (2009). Lee et al (2008) carried out an extensive study on review of recent studies of mullite formation in clays and clay-based vitreous ceramic systems.

Nano-meta kaolin as a substitute in cemetitious matrix

The study towards the changes in mechanical and micro-structural properties of cement mortar due to the effect of nano-clay has been conducted by Morsy et al (2009). The nano-kaolin was used as a clay source. It was subjected to heat for 2 hours at 750°C to get a nano-meta kaolin (NMK). The replacement level of OPC by NMK has led to higher compressive (8%) and tensile strength (49%) of the cement mortars. The Nano-fiber nature of the NMK (only cement mortar containing 4% and 8 % NMK, due to their high strength) and their filler effect in cement mortar after 28 days hydration and their corresponding control specimen was revealed by morphological study through SEM as reported in **Fig. 3**. From this figure, it is found in control specimen, a needle like hydrates were formed around the CSH gel and deposited CH crystals were distributed in the cement paste, where as, in mortar containing 4% and 8% NMK, the texture of hydrate products were found to be denser and compact, and good microstructure uniformity. It was indicating the uniform distribution of nano-particles in the cement mortar even at small quantity, and due to their high surface energy during hydration, the product hydrates were deposited on it. Moreover, it is significant to mention that the hydrates contain nano-particles, prevents the growth of CH and AFm fine crystals, which favors the cement-paste strength also. Reported research has also confirmed that nano-particle acts as an activator to promote and accelerate hydration process due to their high activity. The reported study has also cautioned on non-uniform dispersion of nano-particles which could lead to particles aggregation and generation of voids through weak zone.



(a) (b) (c)

Fig. 3: SEM micrographs of hydrated NMK mortar hydrated for 28 days, a) 0% NMK, b) 4% NMK, c) 8 % NMK (*Reproduced with kind permission from M.S. Morsy*)

Gupta and Maharsia (2005) reported the enhancement of energy absorption in synthetic foams by using nano-clay incorporation for sandwich core application. This study has depicted the changes in compressive properties of synthetic foam due to the incorporation of nano-clay particles. Replacement of cement by metakaolin was studied by Guneyisi et al (2008) and reported the strength improvement, drying shrinkage and pore structure of concrete using metakaolin. Results report clearly depicted that inclusion of metakaolin remarkably reduced the drying shrinkage strain, but increased the strengths of the concretes in varying magnitudes, depending on the replacement level and water/cement ratio also with respect to age of testing and ultra fine particles of metakaolin has effectively reduced the harmful large pores at 20% replacement level. Mohsen and Maghraby (2010) conducted the studies on characterisation and assessment of Saudi clays raw material at different area. From this conducted study, he reported clays have adequate characteristics for ceramics wall, floor, roof tiles, tableware, and earthenware and brick fabrication.

Chemistry of Clay/Polymer nano- composites

Clay/Polymer nano-composites are a typical example and good demonstration of nanotechnology **(**Gao, 2004**)**. The basic phenomena behind this technique are “bottom-up and top-down approach”. In the bottom-up approach, the nano-materials are made from atoms or molecules. In this method, stabilization of the nano-particles is generally achieved by lowering the surface free energy through bonding with organic molecules that passivate the surface atoms. The micro-composite arrangement of this clay is shown in **Fig. 4**. Based on the nature of the bonding between these atoms, the layers would exhibit excellent mechanical properties. But the exact mechanical properties of the layers are yet to be established. 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 **(**Wang et al (2001), Brune and Bicerano (2002), Fornes and Paul (2003), Manevitch and Rutledge, (2004), Luo and Daniel (2003)**)**. Weak Van Der Waals forces help in the formation of clay particles by arranging thousands of these layers together.

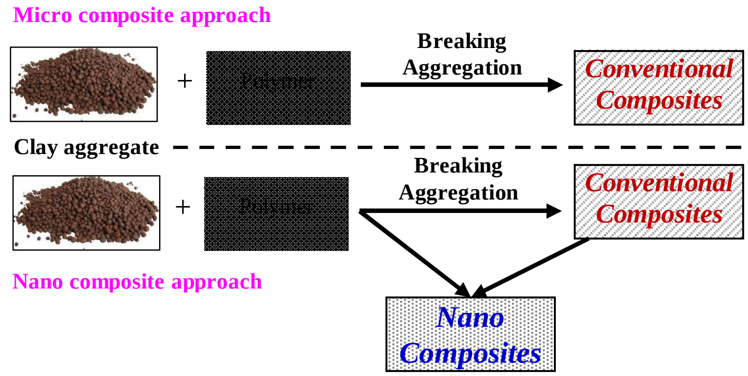


Fig. 4: Fabrication of conventional micro- and nano-composites

It has been observed by the researchers that the excellent mechanical properties of each individual layers are not functioning effectively. The weak interlayer bonding may leads to damage initiation sites. The strength and toughness of the polymers are reduced, during high clay loading to achieve adequate improvement of the modulus of it. But, in the principle use in the nano-composite approach, is to separate not only clay aggregates but also individual silicate layers in a polymer. It is expected that, by doing this, it is possible to make functioning of individual clay layers effectively to get excellent mechanical property.

Properties and Uses

This type of composites has improved physical and engineering properties include fire retardancy **(**Hussain and Simon (2003), Zhao et.al (2009)), barrier resistance (Nah, et al., (2002), Gorrasi (2003)**)** and ion conductivity **(**Meneghetti and Qutubuddin (2006), Shakoor, et.al., (2008)). Specific advantage of clay/polymer nano-composites is that the optical properties of the polymer are not significantly affected. Due to the smaller thickness of individual clay layers (smaller than the wavelength of visible light), the well exfoliated clay/polymer composites were optically clear. This polymer composite technique can also be useful for water-soluble hydrophilic/hydrophobic functional monomer (Zakir et.al 2011) systems for the preparation of polymer/silicate hybrid nano-materials. Another interesting aspect is utilization of hybrids as reactive compatibilizer/nano-fillers for the immiscible thermoplastic polymer blends and their in situ melt processing by a reactive extrusion system and in-line nano-coating technology to improve the barrier properties by surface modification of the conventional multilayered polymer thin films. Moreover this type of composite nanostructure leads to high strength and toughness of the cement-concrete matrix because of interlocking of nanoblocks of calcium carbonate responsible for crack arrest and energy dissipation.

Challenges

Though a huge and alluring potential of nanotechnology to engineer materials used in civil engineering has been envisaged and enormous efforts throughout the world are being taken up, still few of the grey areas need to be explored to make the technology more acceptable. These are: (i) understanding cement-chemistry at nano level, (ii) understanding and exploring new experimental and analytical tools, in order to study the complete spectrum of *Form-Structure-Function* of materials, (iii) handling of materials (preparation, synthesis, and characterization) in nano level is extremely difficult and expensive, (iv) most of the cases, theoretical developments are lacking from proper experimental validation, (v) advancements in science is still in pre-proof stage which need to be applied in practice. Further, developing standard methods and practices to explore the possibilities of nanoscience to nanotechnology is utmost important. By exploiting the advances of nanotechnology and being fully aware of the limitations, authors of the present paper are engaged in developing suitable cementitious material which can be a potential substitute (fully or partially) of conventional cement and it would lead to a sustainable, efficient and green construction practice.

CONCLUSIONS

The present paper discusses the present and futuristic applications of nanotechnology in cement based materials for civil engineering applications. A brief on different cement based materials developed/being developed for construction industry which can not only revolutionarise conventional use of raw materials, specifically cemetitious material, in civil engineering, it would have probably the greatest positive impact on society and environment as well. Nano cement and composites, use of nano-materials in cement, possibility of use of clay as a cementitius material, thermographic study of metakaolinite, chemistry of clay/polymer nano- composites and their properties and uses are discussed in this paper. Finally, the challenges which the researchers have to address at the earliest are briefly pointed out. Construction materials, mainly cement, is one of the most responsible source of green house gas emission, there is an alarming demand to find for its substitute to save the nature. To engineer the materials at atomic level to obtain the desired properties, it is required to employ a well conceived, concerted and intensive inter-disciplinary effort.

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