Study and Development of Properties of Nano Concrete

Nikhil Srivastava[1] Mohammad Saif Asad[2] Surya Prakash Sharma[3] Ankur Kumar[4]
[1,2]UG Student [3,4]Assistant Professor
[1,2,3,4]Buddha Institute of Technology, India

Abstract— Nanotechnology is one of the most active research areas that include a number of disciplines including civil engineering and construction materials. Nano technology is the study of the control of matter nano atomic and molecular scale. It deals with the size 100 nanometers or smaller, and involves developing materials or devices within that size. Nanotechnology is being applied to paints and insulating properties, produced by the addition of nano-sized cells, pores and particles. This type of paint is used, at present, for corrosion protection under insulation since it is hydrophobic and repels water from the metal pipe and can also protect metal from salt water attack. TiO2 nano particles are also being used in coating material.
Keywords: Nano Concrete, Nano Technology

I. Introduction

Nanotechnology is one of the most active research areas that include a number of disciplines including civil engineering and construction materials. Nanotechnology is the understanding, control, and restructuring of matter on the order of nanometers (i.e., less than 100 nm) to create materials with fundamentally new properties and functions. Nanotechnology encompasses two main approaches:

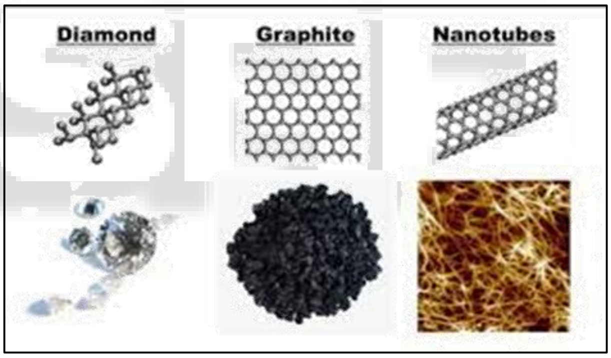
- The ‘‘top down” approach, in which larger structures are reduced in size to the nanoscale while maintaining their original properties or deconstructed from larger structures into their smaller, composite parts and
- The ‘‘bottom-up” approach, also called ‘‘molecular nanotechnology” or ‘‘molecular manufacturing,” in which materials are engineered from atoms or molecular components through a process of assembly or self-assembly. Traditionally nanotechnology has been concerned with developments in the fields of microelectronics, medicine and material sciences.

However the potential for applications of many developments in the nanotechnology field in the area of construction engineering is growing. The evolution of technology and instrumentation as well as its related scientific areas such as physics and chemistry is making the nanotechnology aggressive and evolutional. There are many potential areas where nanotechnology can benefit construction engineering like its applications in concrete, structural composites, coating materials and in nano-sensors, etc. Nanotechnology products can be used for design and construction processes in many areas. The nanotechnology generated products have unique characteristics, and can significantly fix current construction problems, and may change the requirement and organisation of construction process. The recent developments in the study and manipulation of materials and processes at the nanoscale offer the great prospect of producing new macro materials, properties and products. But till date, nanotechnology applications and advances in the construction and building materials fields have been uneven. Exploitation of nanotechnology in concrete on a commercial scale remains limited with few results successfully converted into marketable products. The main advances have been in the nanoscience of cementitious materials with an increase in the knowledge and understanding of basic phenomena in cement at the nanoscale. Improving concrete properties by addition of Nano particles have shown significant improvement than conventional concrete.

A. Nanotechnology and Concrete

Concrete is probably unique in construction in that it is the only material exclusive to the business and therefore is he beneficiary of a far proportion of the research and development money from industry. The following section describes some of the most promising applications of nanotechnology in construction that are being developed or are even available today.
Some of the applications of nanotechnology are:

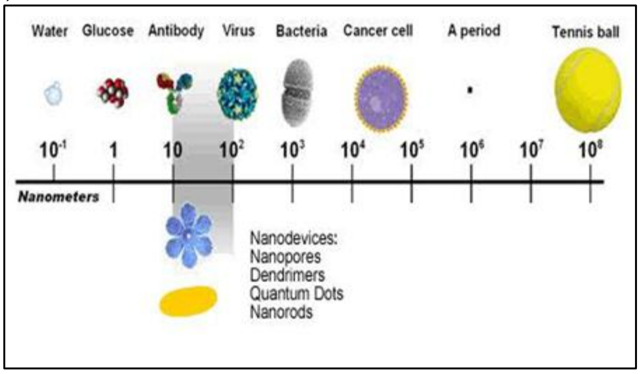
- Cuore concrete- nano silica
- Titanium dioxide
- Carbon nanotubes
- Polycarboxylates
- Nano-sensors



1) What Is Nano?

The word “NANO” come from Greek and it means “very small”.
1nm = 0.000000001m.
500000 smaller than a pen line.
50000 smaller than a hair.
100 smaller than the DNA molecules.

2) Nano Scale



II. NANO TECHNOLOGY FOR CONCRETE

Nanotechnology is an emerging field of science related to the understanding and control of matter at the nanoscale, i.e., at dimensions between approximately 1 and 100 nm (www.nano.gov). At the nanoscale, unique phenomena enable novel applications. Nanotechnology encompasses nanoscale science, engineering, and technology that involve imaging, measuring, modeling, and manipulating matter at this length scale. Just how small is "nano"? In the serviceability index system of units, the prefix "nano" means 1-billionth or 10–9.

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

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1) Improves the material's bulk properties.
2) Ability to control or manipulate material at the atomic scale. NANOSCALE ATTACK ON ASR (ALKALI SILICATE REACTION).

The alkali–silica reaction (ASR), more commonly known as "concrete cancer", is a swelling reaction that occurs over time in concrete between the highly alkaline cement paste and the reactive non-crystalline (amorphous) silica found many common aggregates, given sufficient moisture.

This reaction causes the expansion of the altered aggregate by the formation of a soluble and viscous gel of sodium silicate ($Na_2SiO_3 \cdot n\ H_2O$, also noted $Na_2H_2SiO_4 \cdot n\ H_2O$, or N-S-H (sodium silicate hydrate), depending the adopted convention). This hygroscopic gel swells and increases in volume when absorbing water: it exerts an expansive pressure inside the siliceous aggregate, causing spalling and loss of strength of the concrete, finally leading to its failure.

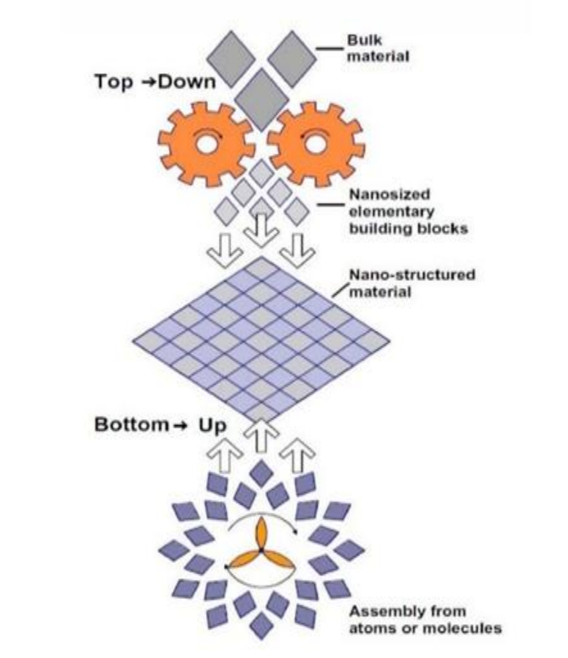


FIGURE 1 The top-down and bottom-up approaches in nanotechnology (*1*) (Sanchez and Sobolev, 2010).

Typical crack pattern of the alkali-silica reaction (ASR). The gel exudations through the concrete cracks have a characteristic yellow color and a high pH.

The reaction can be compared to the pozzolanic reaction which would be catalysed by the undesirable presence of too high concentrations of alkali hydroxides (NaOH and KOH) in the concrete. It is a mineral acid-base reaction between NaOH or KOH, calcium hydroxide, also known as Portlandite, or ($Ca(OH)_2$), and silicic acid (H_4SiO_4, or $Si(OH)_4$). When complete and to simplify, this reaction can be schematically represented as following:

1) $Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2\ H_2O \rightarrow CaH_2SiO_4 \cdot 2\ H_2O$
2) $Na(OH) + H_4SiO_4 \rightarrow Na_2H_2SiO_4 \cdot 2\ H_2O$
   $Na_2H_2SiO_4 \cdot 2\ H_2O + Ca(OH)_2 \rightarrow CaH_2SiO_4 \cdot 2\ H_2O + 2\ NaOH$
   $Ca(OH)_2 + H_4SiO_4 \rightarrow CaH_2SiO_4 \cdot 2\ H_2O$
3) To obtain thinner final products and faster setting time.
4) Cost effectiveness.
5) Lowered levels of environmental contamination.

III. NANO CONCRETE

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 micrometers. An order of magnitude reduction is needed to produce Nano-cement.

Nano concrete is one of the most active research are as the at encompass a number of disciplines including civil engineering and construction materials, 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 titanium oxide, silica, carbon nano cubes, and nano-sensors. if cement with nano-size particles can be manufactured and processed, it will open up a large number of opportunities in the field of ceramics, high strength composites etc. it will elevate the status cement to a high tech material in addition to its current status of most widely used construction material .The main objective of this paper is to outline some of the applications of nanotechnology in concrete and comparing this concrete with the ordinary concrete.

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

IV. NANO MATERIALS

Nanomaterials describe, in principle, materials of which a single unit is sized (in at least one dimension) between 1 to 1000 nanometres (10^{-9} meter) but usually is 1 to 100 nm (the usual definition of Nano scale).

Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties. Nanomaterial is defined as a "material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale", with nanoscale defined as the "length range approximately from 1 nm to 100 nm". This includes both nano-objects, which are discrete pieces of material, and nanostructured materials, which have internal or surface structure on the nanoscale; a nanomaterial may be a member of both these categories

Some of main NANO material used in concrete:

1) Carbon Nanotubes.
2) Nano-silica.
3) Polycarboxylates.

V. CARBON NANO TUBES

Nano tubes are the members of the fullerene structural family. They align themselves into "ropes" held together by vander Waals forces.

Carbon nano tubes are molecular-scale tubes of graphitic carbon with outstanding properties.

They can be several millimeters in length and they can have one "layer" or wall (single walled Nano tube) or more than one wall (multi walled Nano tube).

The addition of Nano fine particles can improve the properties of concrete due to the effect increased surface area has on reactivity and through filling the Nano pores of the cement paste. Nano silica and Nano titanium dioxide are probably the most reported additives used in Nano modified concrete. Nano materials can improve the compressive strength and ductility of concrete. Carbon Nano tubes or Nano fibers (CNT-CNF) have also been used to modify strength, modulus and ductility of concretes. CNFs can act as bridges across voids and cracks that ensure load transfer in tension. Durability of concretes can also be improved through reduced permeability and improved shrinkage properties. These effects can be accomplished through Nano modified cements or the use of Nano developed Dimension additives to the paste.

A. *Single Walled Carbon Nano Tubes:*

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 Newton's and the displacements are measured in fractions of Nano meters.

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 50nm. The typical length varies from 100 to 1000nm. Single layer tube has a much smaller diameter (1 to 3 nm) and length (about 300)

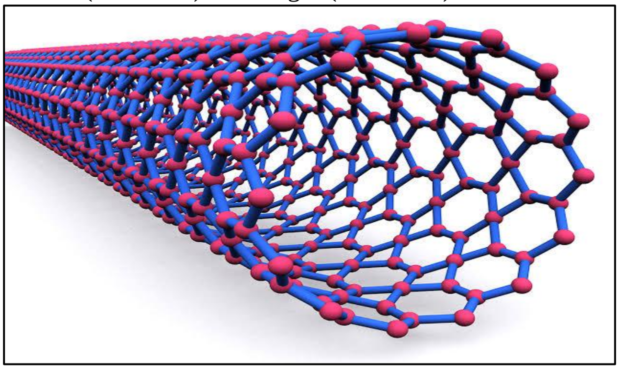


Fig. 6: Single Walled Carbon Nano Tube

B. *Multi Walled Carbon Nano Tubes:*

Multi walled carbon nano tube (MWNTs) consist of multiple rolled layers (concentric tubes) of graphene. There are two models that can be used to describe the structures of multi-walled nano tubes. The interlayer distance in multi-walled nano tubes is close to the distance between graphene layers in graphite, approximately. The Russian Doll structure is observed more commonly. Its individual shells can be described as SWNTs, which can be metallic or semiconducting. Because of statistical probability and restrictions on the relative diameters of the individual tubes, one of the shells, and thus the whole MWNT, is usually a zero-gap metal.

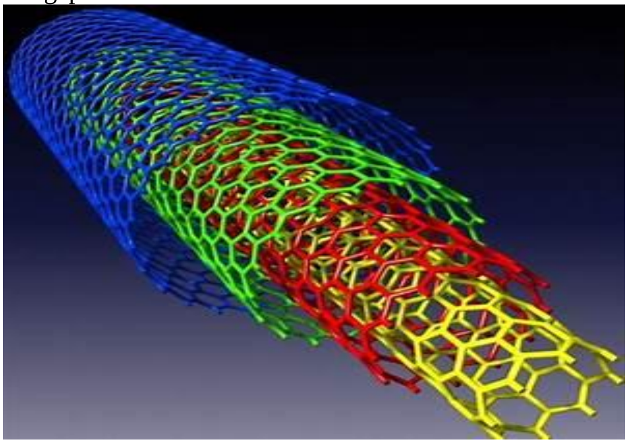


Fig. 7: Multi Walled Carbon Nano Tubes.

C. Properties

1) CNTs Electrical Conductivity

There has been considerable practical interest in the conductivity of CNTs. CNTs with particular combinations of N and M (structural parameters indicating how much the Nano tube is twisted) can be highly conducting, and hence can be said to be metallic. Their conductivity has been shown to be a function of their chirality (degree of twist), as well as their diameter. CNTs can be either metallic or semi-conducting in their electrical behavior.

The conductivity and resistivity of ropes of SWNTs has been measured by placing electrodes at different parts of the CNTs. The resistivity of the SWNT ropes was in the order of 10–4 ohm-cm at 27°C. This means that SWNT ropes are the most conductive carbon fibers known. The current density that was possible to achieve was 107 A/cm2.

2) CNTs Strength and Elasticity

The carbon atoms of a single (graphene) sheet of graphite form a planar honeycomb lattice, in which each atom is connected via a strong chemical bond to bonds, the basal-plane elastic modulus of graphite is one of the largest of any known material. For this reason, CNTs are expected to be the ultimate high-strength fibers. SWNTs are stiffer than steel, and are very resistant to damage from physical forces. Pressing on the tip of a Nano tube will cause it to bend, but without damage to the tip. When the force is removed, the tip returns to its original state.

3) CNTs Thermal Conductivity and Expansion

New research from the University of Pennsylvania indicates that CNTs may be the best heat-conducting material man has ever known. Ultra-small SWNTs have even been shown to exhibit superconductivity below 20oK. Research suggests that these exotic strands, already heralded for their unparalleled strength and unique ability to adopt the electrical properties of either

D. Nano Silica

Is the first Nano product that replaced the micro silica. The Nano silica powder is one of the blended material. Studies have shown the existence of silica powder, in the early cement hydration product Ca (OH) 2 content along with the growth of the age becoming less and less, even complete reacted, generate new material which will jam channel, big pores will less, cohesion between aggregate and plaster will be strengthen, compactness will be improved.

Advancement made by the study of concrete at Nano scale have proved Nano silica much better than silica used in conventional concrete, but engineering experience shows that as with silicon powder, also bring two problems, on the one hand is the cohesiveness increase of concrete to construction cause certain difficult, on the other hand is shrinkage rate increases can lead early crack.

E. Properties

1) Physical and Chemical Properties

a) Fresh Properties

Reduced setting times were observed by various researchers on incorporation of Nano-silica in concrete which is same as observed for pastes and mortar. Also, decrease in initial and final setting time was observed on incorporation of nS in various quantities, with increase in viscosity and yield stress reported.

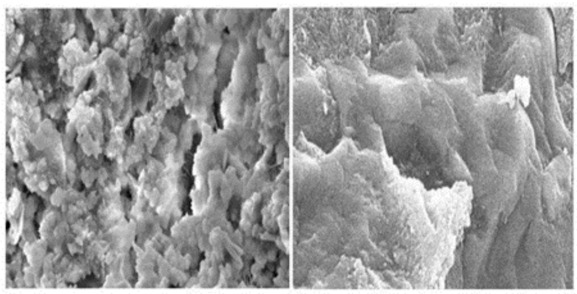
b) Mechanical Properties

Concrete strength is influenced by lots of factors like concrete ingredients, age, ratio of water to cement materials, etc. Nano-silica incorporation into concrete resulted in higher compressive strength than that of normal concrete to a considerable level. Li et al. (2004) reported 3-day compressive strength increase by 81% and also at later stages, same trend was observed with 4% Nano-silica in high volume fly ash concrete. Naji Givi, Abdul Rashid, Aziz, and Salleh (2010) also reported higher compressive strength at all ages, for Nano-silica blended concretes up to maximum limit of 2% with average particle size of 15 and 80 nm. Same results were obtained for split tensile and flexural strength. An increase of about 23–38% and 7–14% at 7 days and 28 days, respectively, in compressive strength of Nano-silica concrete was reported, whereas low increase of 9.4% (average) was reported for flexural strength.

c) Durability properties

Durability properties of concrete include aspects such as permeability, pore structure and particle size distribution, resistance to chloride penetration, etc. Investigations on

Nano-silica concrete for its permeability characteristics showed that the addition of Nano-silica in concrete resulted in reduction in water absorption, capillary absorption, rate of water absorption, and coefficient of water absorption and water permeability than normal concrete. The pore structure determines the transport properties of cement paste, such as permeability and ion migration. Reduction in water absorption, capillary absorption, rate of water absorption and water permeability has been observed by various researchers (Li, 2004; Zhang & Li, 2011; Zhang et al., 2012).



a. Concrete without nanosilica   b. Concrete with 5% nanosilica

Comparison of the concrete density with and without nanosilica

F. Applications

1) High compressive strength concretes.
2) High workability with reduced water/content ratio.
3) Use of super plasticizing additives is unnecessary.
4) Fills up all the micro pores and micro spaces.
5) Cement saving up to 35-40%.
6) As an additive for rubber and plastics
7) As a strengthening filler for concrete and other construction composites

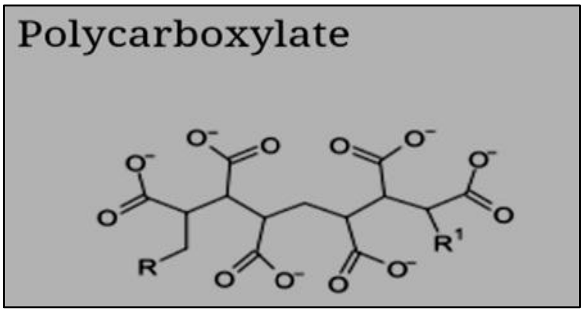
MATERIAL	MIX 1	MIX 2	MIX 3	MIX 4	MIX 5
Cement (kg/m^3)	600	585	570	555	540
Nanosilica (kg/m^3)	0	15	30	45	60
Water (kg/m^3)	120	120	120	120	120
Quartz sand (kg/m^3)	652,4	652,4	652,4	652,4	652,4
Quartz powder (kg/m^3)	279,6	279,6	279,6	279,6	279,6
Coarse aggregate 0 - 15 mm	748	748	748	748	748
Superplasticizer (kg/m^3)	12	12	12	12	12

Table 1: Mix Proportion of Nano Silica

VI. Polycarboxylates

Polycarboxylates or polymer based concrete admixtures are high range water reducing admixture (HRWR) without affecting workability. Superplasticizers, also known as high range water reducers, are chemical admixtures used where well-dispersed particle suspension is required. These polymers are used as dispersants to avoid particle segregation (gravel, coarse and fine sands), and to improve the flow characteristics (rheology) of suspensions such as in concrete applications.

A. Functions



Their addition to concrete or mortar allows the reduction of the water to cement ratio, not affecting the workability of the mixture, and enables the production of self-consolidating concrete and high performance concrete. The strength of concrete increases when the water to cement ratio decreases. High range water reducing (HRWRA)/ superplasticizing admixtures are synthetic, water-soluble organic chemicals, usually polymers, which significantly reduce the amount of water required to achieve a given consistency in plastic concrete. This effect can be utilized in two ways:

1) To reduce water content to achieve increased strength and reduced permeability/improved durability.

2) To achieve increased workability at the same water content.

With a slightly higher admixture dosage, both these effects can often be achieved in the mix. When high range water reducing admixtures are used to increase the workability or consistency of the concrete they are usually termed 'Superplasticizing admixtures' but these names are frequently interchanged.

High range water reducing admixtures function in a similar way to 'Normal Water Reducing Admixtures' but are more powerful in their cement dispersing action and can be used at higher dose without unwanted side effects such as air entrainment or retardation of set.

B. Chemical Structure

PCEs (Polycarboxylate ether superplasticizer) are composed by a methoxy-polyethylene glycol copolymer (side chain) grafted with methacrylic acid copolymer (main chain). The carboxylate group -COO-Na+ dissociates in water, providing a negative charge along the PCE backbone. The polyethylene oxide (PEO or MPEG) group affords a not uniform distribution of electron cloud, which gives a chemical polarity to the side chains. The number and the length of side chains are flexible parameters that are easy to change. When the side chains have a huge amount of EO units, they lower with their high molar mass the charge density of the polymer, which enables poor performances on cement suspensions. To have both parameters on the same time, long side chain and high charge density, one can keep the number of main-chain-units much higher than the number of side-chain-units.

C. Working Mechanisms

PCE's backbone, which is negatively charged, permits the adsorption on the positively charged colloidal particles. As a consequence of PCE adsorption, the zeta potential of the suspended particles changes, due to the adsorption of the COO- groups on the colloid surface. This displacement of the polymer on the particle surface ensures to the side chains the possibility to exert repulsion forces, which disperse the particles of the suspension and avoid friction. These forces can be directly detected by the use of the atomic force microscopy (AFM), working with model substances in liquid environment.

Fig. 11: Polycarboxylate Concrete

D. *Application of Nano Concrete*

1) The Jubilee Church , formally known as Chiesa di Dio Padre Misericordioso (Italian for Church of God the Merciful Father), is a Roman Catholic church and community center in Tor Tre Teste in Rome. According to Richard Meier, its architect, it is "the crown jewel of the Vicariato di Roma's (Archdiocese of Rome) Millennium project". The Church serves eight thousand residents of the Tor Tre Teste area and was meant to socially "revive" Tor Tre Teste.Meier was selected as the architect as winner of a competition that included famous architects such as Frank Gehry, Santiago Calatravaand Tadao Ando in 1996.

Fig. 12: The Jubilee Church

2) The Gartnerplatzbrucke, across Kassel (German pronunciation spelled Cassel until 1928) is a city located at the Fulda River in northern Hesse, Germany. It is the administrative seat of the Regierungsbezirk Kassel and the Kreis of the same name and had 200,507 inhabitants in December 2015.

Fig. 13: The Gartnerplatzbrucke Bridge

VII. Scope

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. 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. 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.

A. *Future Directions*

Some of the potential areas of applications of Nano-based products as well as future direction are listed below:

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

VIII. Conclusion

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.

1) Well dispersed Nano particles increase the viscosity of the liquid phase, improves the segregation resistance and workability of the system.
2) Accelerates the hydration.
3) Better bond between aggregates and cement paste.
4) Improves the toughness, shear, tensile strength and flexural strength of concrete.

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