Nanoengineering Concrete for Sustainable Built Environment: A Review

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Abstract

The construction industry is a major consumer of material and energy sources in the world. Among all the materials used in construction, concrete, which is the most widely used, can have a significant impact. Meanwhile, nanotechnology is one of the most influential technologies in this century and it has significantly impacted the construction sector. Better understanding and engineering cementitious materials at nanometer scale can result in novel construction materials which are more strong and durable than conventional materials. Engineering concrete at the nano meter scale includes the incorporation of nano sized particles into concrete at suitable proportions and methods. Nano Silica is one such nano material which has shown to enhance the overall performance of concrete. Incorporation of nano Silica at smaller volume fractions has shown to result in higher compressive and flexural strengths at early ages, improved hydration characteristics and reduced porosity and water absorption when compared with conventional cementitious materials. The impacts of other nano materials such as CNTs, nano TiO_2, nano Al_2O_3 and nano TiO_2 on concrete are also promising. While nano materials acts as fillers and provide nucleation sites for cement hydration, nano SiO_2 also acts as a pozzolanic material, increasing the amount of stiff CSH within the hydrated cement paste, resulting an improved microstructure. Nanomaterials can also pave the path to reduce the cement content in concrete than in conventional mixes while maintaining same strength characteristics, which will lead into the production of a ‘greener’ concrete. Numerical models of the composite material validated with experimental results can be used to come up with optimum nano material contents and performance.

This paper reviews the efforts, current status and effects of nano modification of cementitious materials and numerically modelling strength properties. These innovative materials will be of high performance and less energy consuming, which will lead towards sustainable construction practices.

Keywords: Concrete, Cement Paste, Nano Silica, Strength, Modelling

1. Introduction

Concrete is considered to be the most widely used construction material worldwide. The present consumption rate of concrete is estimated to be around 20000 million metric tons per year(Mehta and Meryman, 2009). With large scale constructions carried out across the globe, concrete with higher performance was in greater demand. This led to the introduction of high strength and high performance concrete, with the inclusion of several other pozzolanic materials into conventional concrete including silica fume and fly ash. Yet, there are many areas where concrete should be improved for better performance in renewal and expansion of infrastructure such as higher tensile strength, reduced brittleness, increased toughness and higher durability. High performance concrete at present does not address these issues in greater extent. It has also been noted that the action of silica fume and fly ash in concrete is very slow at early ages, reducing the early age strength of high performance concrete. On the other hand, cement is the main constituent of concrete. Production of cement releases very high amounts of CO_2 into the atmosphere, thereby, increasing global warming issues. The abilities of reducing the cement content in concrete while maintaining its strength and durability aspects are of great interest as well.

Nanotechnology and nano materials have the potential of solving many of these issues. The insight of nanotechnology was first introduced by Physics Nobel Laureate Richard Feynman at a lecture entitled "There's a plenty of room at the bottom" at California Institute of Technology(Feynman, 1960). A dramatic development in the fields of nanotechnology and nano materials has occurred especially in the last two decades since, with the development of other facilitating sciences such as physics and chemistry as well as the developments in instrumentation and experimenting techniques.

The definition of "nanotechnology" depends on the field which it is talked about. But basically it is defined as 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(NSTC). Nanotechnology and nano materials deals with particle sizes at the nanometer (i.e.10^{-9}m) scale.

The significance of nanotechnology has impacted various fields including medical, automotive, electronics and telecommunication, military, textile, information technology and biotechnology as well as food packaging industries. Nano science and nano technology has open up the possibility of a wide range of innovative introductions. A few examples include strong but lightweight bullet stopping armor, miniaturization of aircrafts, self healing systems, high performance materials under extreme pressure and temperature conditions, nano motors, artificial bone composites, cellular implants, high performance solar cells, tear resistant cloth fibers and self cleaning materials(Karkare, 2008).

Impacts of nano technology and nano materials are comparatively low for the construction sector when compared with other industries. With its large scale of material and energy usage, advances in construction materials and techniques can have a huge impact on global economy and sustainability. Present research has found out ways of using nano materials in enhancing and converting conventional materials to be more effective, smart and sustainable. These include products for strong but light structural composites, low maintenance coating, enhancing properties of cementitious materials, better insulating materials, increasing sound absorption of acoustic absorbers, self cleaning products etc(Ge and Gao, 2008).

2. Effects of Nanotechnology in Concrete

When comparing with the advancement of other materials through nanotechnology, concrete, which is the most widely used material in the construction sector, shows a lag in its development. According to E.J. Garboczi (Garboczi, 2009), this is due to two main reasons. The first reason is due to the lack of understanding of the physical and chemical properties of concrete as well as its structure at the nano mater length scale. The second reason is the lack of understanding of what nano modification means for specifically concrete. There is an immense opportunity of enhancing performance of concrete using nano materials, but further research is required so that these innovative materials will be used practically within the construction sector. Most of the work carried out in this novel area of research is still at the preliminary stages, and has many issues to be addressed.

Concrete is a nano composite material. The CSH gel which is the most important phase which defines the underlying performance of concrete is itself a nano material, along with nano sized pores and water filled volumes. As a result, manipulations done at the nano meter level in concrete can result in significant impacts at macro level properties. In other words, alterations carried out at nanometer level affect engineering properties of the bulk material (Scrivener and Kirkpatrick, 2008, Jennings et al., 2008, Garboczi and Bentz, 1998, Garboczi and Bentz, 1996).

Nano modification of concrete can be done through incorporation of suitable nano particles or nano tubes into concrete, thereby producing concrete with improved mechanical, thermal and durability characteristics. Literature available shows that there are possibilities of improving concrete performance through incorporation of several nano materials including nano silica, nano TiO_2, nano Fe_2O_3, nano Al_2O_3, nano clay as well as Carbon Nano Tubes(CNTs) in suitable proportions and mixing methods with suitable dispersing agents. This paper emphasizes the potential effects of nano silica on concrete.

When comparing with the other nano materials such as CNTs and nano TiO_2, nano silica is a pozzolanic material. The pozzolanic reaction can increase the ability of strength development of concrete more than the other non-pozzolanic nano materials discussed. On the other hand, Silica fume, which is another form of silica, is used in the construction industry at large scales for the production of high performance concrete at present. As nano silica also belongs to the same material family and has a similarity with silica fume, the practical applicability of using nano silica in the construction industry is far higher than for other nano materials.

Figure 1 below shows the size distribution of the particle sizes present in Conventional concrete compared with that of High Strength/High Performance concrete and nano engineered concrete containing nano silica(Sobolev and Gutiérrez, 2005). High Strength/High Performance concrete is an outcome of gradually refining the structure of hydrated cement paste through the incorporation of silica fume as a pozzolanic material into conventional concrete, so, the particle size distribution of high strength/high performance concrete ranges from the millimeter range up to about 100nm. The figure also shows the range at which nano engineered concrete falls in; it can be seen that nano silica particles which has a very high specific surface area, increases the range of the particle size distribution of concrete up to about 5nm level.

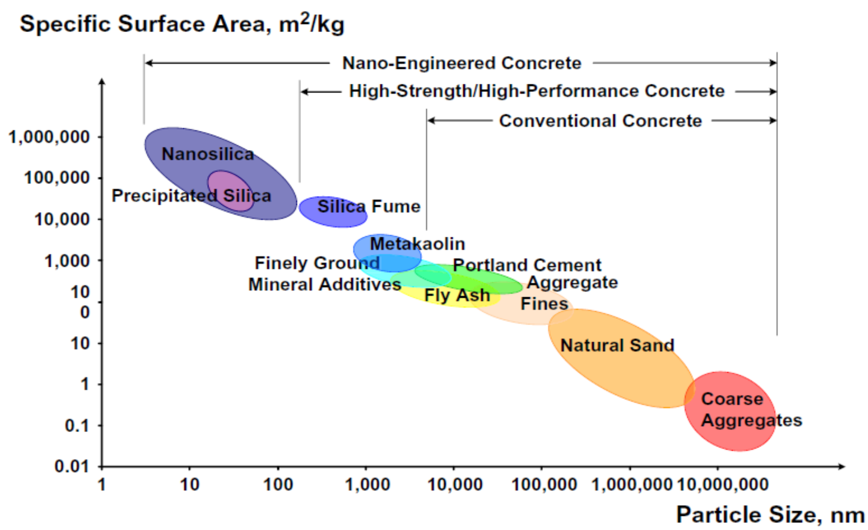

Figure 1: Particle sizes and specific surface area related to concrete materials(Sobolev and Gutiérrez, 2005)

Silica fume is a byproduct of manufacturing of Silicon and ferrosilicon alloys. The degree of purity of silica fume can depend on its origin, thereby, its effects on concrete can vary. Another important consideration is that the particle size of silica fume also depends on the manufacturer and the method of production, usually having a mean diameter of 100nm. In contrast to silica fume, nano silica is not an industrial byproduct. It is manufactured under special conditions making nano silica to have a high degree of purity and a well defined range of diameter for the particles (Usually within 10-50nm). Nano silica can be obtained either in powder form or in a colloidal solution. The former has a higher chance of forming agglomerates within concrete rather than being well dispersed as separate particles. But still, the surface areas of the particles are larger than that of silica fume. It is also important to state that nano silica and silica fume have different reaction kinetics and produce different hydration products.

High Performance Concrete, as mentioned above, is an outcome of refining the structure of the hydrated cement paste through the incorporation of silica fume into conventional concrete. As a pozzolanic material, it is supposed to react with the CH formed during cement hydration and produce more CSH. But, literature revels that the activity of silica fume is low at early ages. Mitchell et.al(Mitchell et al., 1998) studied the XRD patterns of silica fume in a saturated $Ca(OH)_2$ solution and has concluded that there are only minor changes in the samples up to 7 days, and extensive formation of CSH begins only after 120 days . According to Li et.al(Li et al., 1985) silica fume consumption even after 90 days of hydration is only 75%. The influence of nano silica addition on the properties of hardened cement paste were demonstrated by Ye et.al.(Ye et al., 2007). The outcomes were compared with the performance of silica fume on cement paste as well. Cement pastes with replacement of cement content with nano silica by 1%, 2% 3% and 5% were experimented and compared with the performance of cement pastes with the cement content replaced with silica fume by 2%, 3% and 5%. With the increase of nano silica content, paste strengths have shown to increase. The paste with 5% replacement of cement with nano silica has increased its strength when compared with the control mix by 8%, 41%, 25% and 15% at 1day, 3days, 28 days and 60 days after hydration respectively. The performance of silica fume with same amount of cement replacement, especially at early ages, has been lower. Moreover, the flexural strength of the nano modified pastes was found out to be higher than the control samples and the samples with silica fume. The same mix (i.e. 5% replacement of cement with nano silica) showed an increase of the flexural strength by 43% and 88% at 7 days and 28 days respectively when compared with the control mix. It was concluded that the flexural strength enhancement of nano modified cement pastes is higher than that of the enhancement of compressive strength. Through observing the XRD patterns of the hydrated cement paste, Ye et.al(Ye et al., 2007) also demonstrated that nano silica consumes more CH than silica fume, and that the pozzolanic reaction degree of nano silica is much greater than that of silica fume.

Ye e.al(Ye et al., 2007) also studied the SEM micrographs of the paste-aggregate interface. It was found that the largest crystal size of CH particles present in the samples reduced from 10μm (for the control paste) to 4μm (for paste with 3% nano silica). The CH crystal size of the sample with 3% silica fume was 7μm. It was concluded that nano silica reduces the CH crystals at the interface more effectively than silica fume, and that the pozzolanic reaction of nano silica is greater.

Several other researches also give indication of increasing strength characteristics of cementitious materials when nano silica is used as a replacement for cement and that the performance is higher when compared with silica fume (Jo et al., 2007, Li et al., 2004b). The Study by Jo et.al(Jo et al., 2007) reported that compressive strength of mortar increases significantly with addition of nano silica than with silica fume.

Li et.al(Li et al., 2004b) performed experiments on the effects of nano particles on cement mortar and reported that the compressive and the flexural strengths can be increased. Through analyzing SEM micrographs of cement pastes, they have concluded that nano silica improves the microstructure of the cement paste. Figure 2 (a) and figure 2 (b) are the micrographs of the hydrated cement paste without and with nano silica respectively, extracted from Li et.al (Li et al., 2004b). These figures indicate that clusters of CSH are stand-alone structures connected by many needle like hydrates. The amount of hydrates and sizes of the pores are higher for the sample without nano silica. Cement paste with nano silica incorporated shows a more compact, denser structure and has interconnected CSH clusters. Large CH crystals are absent in the sample, and the pore size is reduced. The pozzolanic reaction of nano silica has led the microstructure to be denser. Very highly reactive nano silica particles react with CH quickly and produce CSH. As a result, the size and amount of CH and the porosity are reduced and additional CSH is produced(Li et al., 2004b).

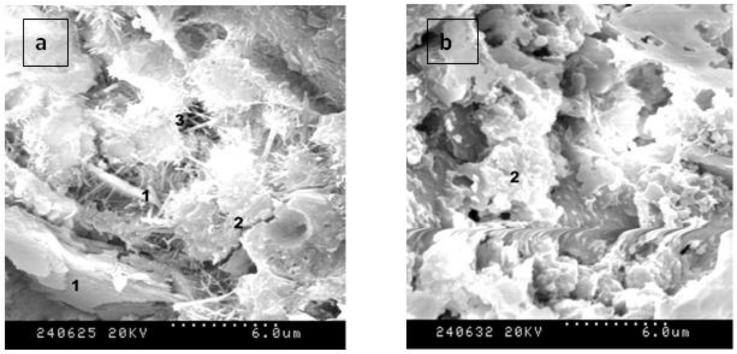

Figure 2: Microstructure of cement paste without(a) and with(b) nano silica(Li et al., 2004b). (1, 2, 3 indicate CH crystals, CSH clusters and pores respectively)(Li et al., 2004b)

Literature reveals that two types of CSH are formed during cement hydration, high density CSH and low density CSH(Jennings et al., 2008). Through advanced nanoindentation techniques, it has been shown that the stiffness of the higher density CSH is larger than that of lower density CSH(Constantinides and Ulm, 2004). As a result, the formation of more high density CSH is preferred from the point of strength and stiffness of concrete. The influence of nano silica on the formation of these two types of CSH has been performed by Mondal et.al(Mondal et al., 2010). It was concluded that nano silica does not have an effect of changing the elastic moduli and hardness of the two types of CSH. However, it was found that the volume fraction of high stiffness CSH is increased up to 50% when nano silica was incorporated at a replacement of 18% weight of cement. This results in a stronger and more durable cement paste (Gaitero et al., 2010, Mondal et al., 2010).

Porosity is a parameter which has high influence of the strength as well as the durability of cement paste. Lesser the porosity of the cement paste, higher the resistance to chemical attack and stronger it is. The effects of various types of nano silica in colloidal dispersion form and in powder form on cement paste properties including the porosity was investigated by Gaitero et.al.(Gaitero et al., 2010). It was confirmed that the samples with nano silica in whatever form had less porosity when compared with the control sample, along with higher compressive strength and hydration characteristics. The reduction of the porosity was attributed to the fact that nano silica acting as an ultrafine filler to fill in the voids present in the cement paste. Although their sizes are relatively small to fill in the voids, they act as nucleation sites for growth of hydration products around them, thus, reducing the porosity.

Jo et.al (Jo et al., 2007)demonstrated that addition of nano silica increased the amount of heat evolved during setting and hardening of cement. This study included experiments for various amounts of nano silica contents with different amounts of superplasticizer for each mix so that no bleeding or segregation occurred. Even when the high amount of superplasticizer content can have a negative effect on the heat of hydration characteristics, nano modified mixes showed improved hydration characteristics.

Water permeability and water absorption of concrete are two main characteristics affecting its durability aspects. Water permeability characteristics of concrete incorporating nano silica was studied by Ji (Ji, 2005). The experimental results demonstrated that nano silica improved water permeability resistance capacity of concrete. The mixes with nano silica withstood high water pressure (3.2MPa) than for normal concrete (0.5MPa) without showing water penetration phenomena. Ji(Ji, 2005) used SEM micrographs to verify his results. Khanzadi et.al(Khanzadi et al., 2010) investigated the influence of nano silica on mechanical properties and water absorption of concrete. With 1.5% weight replacement of cement with nano silica, the compressive as well as the split tensile strengths of concrete showed to increase. Nano modified concrete also demonstrated less amount of water absorption percentage when compared with the control mix. Due to the greater pozzolanic reactivity of nano silica the amount of CH crystals present is reduced and denser and uniform CSH is formed, thereby reducing the porosity of the paste. These effects resulted in fewer amounts of water absorption and higher strength characteristics.

Based on available literature, the factors affecting improved performance of concrete with nano silica when compared with conventional concrete can be described as follows.

- Being a pozzolanic material, nano silica participates in the pozzolanic reaction consuming CH crystals and producing more high stiffness CSH. This results in stronger concrete with higher chemical resistance (Li et al., 2004a, Mondal et al., 2010, Gaitero et al., 2010, Ji, 2005, Khanzadi et al., 2010, Ye et al., 2007, Li et al., 2004b, Jo et al., 2007).
- Nano particles act as a filler for the voids, resulting reduced porosity (Li et al., 2004a, Ji, 2005, Khanzadi et al., 2010).
- Nano particles act as nucleation sites allowing to form small sized uniform clusters of CSH while favoring the formation of small sized crystals(of CH and AF_m). It also promotes further hydration, resulting increase of strength (Li et al., 2004a, Khanzadi et al., 2010, Li et al., 2004b)
- With their smaller particle size and greater surface energy, nano silica has higher amount of free and unsaturated bonds resulting it to be in an unstable state of thermodynamics. Coupled up with the increase in the area for chemical reaction, nano silica shows higher performance in concrete/cement paste when compared with the performance of silica fume (Ye et al., 2007, Sobolev et al., 2006, Sobolev et al., 2009).
- Nano particles if well dispersed can increase the viscosity of the fresh cement paste, which will lead to improved segregation resistance. Nano silica makes the cement paste thicker as well(Ye et al., 2007, Sobolev et al., 2006, Sobolev et al., 2009)

According to literature, when the nano silica particles are not well dispersed within the cement paste, they tend to form agglomerates or clusters. This may be due to extensive amount of nano particle content or not using proper dispersion techniques. These nano particle clusters can create weak zones within the material, leading to low strength and high porosity (Li et al., 2004a, Li et al., 2004b). Further research should be carried out to find out optimum nano silica contents which can be mixed, and the best available mixing methods.

3. Modelling the Performance of Nano Engineered Concrete

As discussed earlier, experimental investigations have verified that Nano silica improves the mechanical and durability aspects of concrete. However, when considering studies on analytical modeling of concrete modified with nano materials, a significant research gap exists. So far, work carried out on modelling the performance of nano modified concrete is limited. With the complex nature of concrete and unclear nature of its behavior at smaller scales, analytically modeling its performance is a challenge. However, with the improvements in instrumentation and analyzing techniques, the understanding of the fundamental properties of hydrated cement paste has been revealed. Following is an overview of modelling the performance of ordinary cement paste and concrete, without the incorporation of any sort of nano materials. Appropriate modifications should be carried out on these models to reflect the behavior of nano silica in concrete.

3.1. Upscaling technique

Due to this vast difference of scales of the constituent materials of concrete, modelling the performance directly at the macro scale is inefficient. It will not capture the behavior of the material at smaller length scales. Scale separation principal is considered as an effective method of modelling concrete; i.e. to analyze the performance of concrete at different scales; cement paste (at micro scale), mortar (at meso scale) and concrete (at macro scale). When modeling properties of concrete, according to literature, the most effective way used to corporate with the different scales is to use the upscaling technique. The smaller levels are first modeled at the properties desired are computed, and the resulting material properties are used as inputs in modeling the next scale.

Literature reveals that there are two distinct methods of modelling concrete, Theory of Homogenization and the Finite Element Approach. In the following sections, a review will be given based on these two approaches. In either case, the heterogeneous material is replaced by an equivalent homogeneous medium at a particular length scale. The analysis is done on an equivalent homogeneous sample which statistically represents the heterogeneous material which is known as a Representative Unit Volume (RVE) or a material unit cell.

3.2. Theory of Homogenization

Theory of homogenization is the method of obtaining the macroscopic behavior of concrete based on its microstructure. Concrete, which is a heterogeneous material, is replaced by an equivalent homogenous continuum. The analysis is performed on a statistically representative sample of the material, which is known as the Representative Volume Element (RVE) with characteristic length of the element satisfying the scale separation requirement(Pichler and Hellmich).

Various theories based on advanced homogenization techniques have been proposed to model the performance of composite materials. These include models of Eshelby(Eshelby, 1957), Hashin(Hashin, 1962), Mori and Tanaka(Mori and Tanaka, 1973) and self-consistent approach of Hill(Hill, 1965). When reviewing existing analytical models based on the theory of homogenization, some of models give estimates for macroscopic properties whereas some of the models give boundaries of the properties(Gal and Kryvoruk). For example, the models predicted by self-consistent scheme and Mori Tanaka scheme gives estimates of elastic moduli of a material. The self-consistent scheme is applied when modeling polycrystalline microstructures, when inclusions are of elliptical shape and are of low concentrations(Kurukuri, 2005, Sanahuja et al., 2007). The Mori Tanaka scheme is used when a continuous matrix phase surrounds all the other phases(Sanahuja et al., 2007). Some examples of models predicting boundaries for elastic properties are Voigt and Reuss method and Hashin-Shtrikman(Kurukuri, 2005).

There are several existing models for concrete developed based on these fundamental models. The models are appropriately combined to predict the Elastic properties (Bulk moduli, shear moduli) of cement paste (Constantinides and Ulm, 2004, Sanahuja et al., 2007, Pichler and Hellmich, Gal and Kryvoruk, Smilauer and Bittnar, 2006). Resulting homogenized elastic properties are used as inputs to the next level of modelling, i.e. modelling performance of mortar and concrete. However, so far, the performance of nano modified concrete has not been investigated using this approach.

3.3. Finite Element Method

The Finite Element Method is another option available to predict mechanical characteristics of concrete. Though not much implemented for modelling cement paste, the performance of mortar and concrete have been modeled using this approach(Kamali-Bernard and Bernard, 2009, Kurukuri, 2005). Though it is a less applied method of obtaining the mechanical properties of a heterogeneous material, it is an efficient method due to the ability of analyzing the structure in 2D as well as in 3D forms, provided that the structure and the boundary conditions are modeled with adequate degree of accuracy and precision. Unlike the homogenization method which ends up with the computation of elastic properties, the FEM approach can be used to predict the complete stress strain behavior of the material. When comparing with the application of the homogenization theory in modelling, the FEM has the advantage as a numerical method where the macroscopic properties are computed through volumetrically averaging the numerical solutions obtained for a Representative Unit Cell (RVE). It should also be born in mind that the homogenization method provides estimates or boundaries for the macroscopic properties and that the assumptions made during modeling can result in variations of the computed properties with the exact values(Gal and Kryvoruk). But FEM requires more computational power and time.

Nano modification of concrete using nano silica is a novel approach, and is still not implemented at large scales in construction. Though experimentation techniques on the effects of nano silica on mechanical properties of concrete have been widely performed, numerically modelling the performance is still at preliminary stages. Kim et.al(Kim et al., 2010) suggested a model for cement paste incorporating nano silica to predict the strength and stiffness. Through calculating the volume fractions of different phases of the hydrated cement paste and adjusting the quantities to reflect the performance of nano silica, the stress strain curves for the nano modified cement paste has been obtained. The performance of Nano silica was modeled considering the equivalent amount of silica fume having the same surface area, and applying existing theories for the performance of silica fume. However, it is noteworthy to mention that the pozzolanic activity of nano silica and silica fume is different(Mondal et al., 2010). The volume fractions of high stiffness CSH and low stiffness CSH created is not similar for the two materials. If the authors had considered this aspect when incorporating the performance of nano silica, the validity of the model would have greatly improved.

4. Conclusion

Through reviewing the available literature, it can be seen that the effects of nano silica on mechanical properties have been tested. However, the performance of different types of nano silica (in powder form, colloidal form, and nano silica produced under different conditions) has not been comparatively analyzed in great detail. Investigations of suitable mixing methods and dispersing agents for the nano silica to be well dispersed within the cement paste should also be carried out further. Well dispersed nano particles are crucial for optimal performance of the nano material in concrete. But with the tendency of nano materials to cluster together instead of firmly dispersing within the matrix material, the performance of nano modified concrete can be reduced. Methods of effective dispersion of the material should be further analyzed to enhance the practical applicability of nano engineered concrete.

With the expected higher reactivity of nano silica and its pozzolanic behavior, nano silica has the potential to be used as a cementitious material in concrete. Nano modified concrete has the potential of higher strength especially compressive and tensile strengths and higher durability. But its applicability and success depends largely on correct dispersing methods and mixing techniques as well as correct proportions. Further research is needed to fulfill the research gaps so that the possibility of practically using nano silica in concrete for construction is enhanced. While aiming improved strength characteristics of concrete through nano modification, integrating nano materials into conventional concrete widens the possibilities of reducing the cement content in concrete as well. As cement production releases a huge amount of green house gases to the atmosphere, reduction of the cement content in concrete can have a significant impact on environmental friendly concrete. Modelling the performance of nano modified concrete can be of great value as well. The lack of analytical investigations on the behavior of nano modified concrete is a significant research gap when analyzing available literature. Improving analytical investigations can result in predictions of the strength aspects of nano modified concrete, which will be a valuable source for engineers to seek the possibilities of implementing this novel material in their designs, thereby enhancing its practical applicability.

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