

Role of Nano Oxides for Improving Cementitious Building Materials

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Abstract- Possible usage of nano oxides such as nano SiO₂, nano ZrO₂, nano Al₂O₃, nano Fe₂O₃ and nano TiO₂ for improving the mechanical properties of concrete has been explored in the present study. Action mechanisms proposed by various researchers for the enhancement of structural arrangement of cement at nano level by incorporating different oxides are discussed. It is observed that the reported studies on usage of nano oxides for construction material are scanty and scattered; and the findings are non convergent. To understand the structural configuration of the oxides at nano level, TEM and XRD studies on the oxides are carried out. In the present study, it is found that the mechanism behind the function of nano materials yet to be explored in detail, in order to gain the full effect of nano materials as intended. Enabling Form-Structure-Function properties of nano materials with cementitious materials can provide an excellent idea to use them in an effective way. Finally, it is concluded that to exploit the huge potentiality, a concerted effort from both science and engineering is required to engineer the available cement at nano level and develop smart cementitious building materials.

Keywords- Nano Particles; Cement; Concrete; Civil Engineering; C-S-H Structure; Mechanical Properties; Microstructure; Oxides; TEM; XRD

I. INTRODUCTION

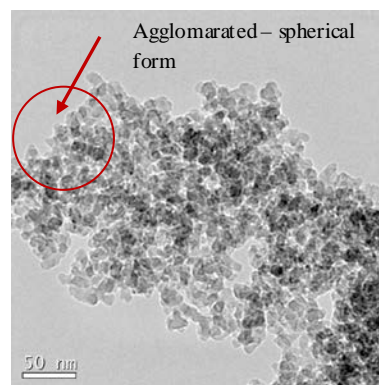
Due to the special property such as high surface to volume ratios, the nano particles have gained more attentions in all the fields and also in civil engineering field; they are stepping up slowly to create wonders for enhancement. Only few in-depth studies related to nano modifications of cement based materials and their enhanced performance on compressive and tensile strength properties are reported in literature. However, this field requires bottom-up approach to tailor, modify, replace, or include nano materials in the already available matrices such as cement or cement based materials. Due to the lack in understanding of scientific mechanism such as Form-Structure-Function on the reactivity of nano particles at molecular level, there is no clear cut knowledge about the intended role of nano materials in civil engineering field. The characteristic knowledge and behaviour of nano particles and their reactive mechanism with complex materials like cement have to be studied in detail, in order to utilize the full effect of nano materials for their greatest performance in construction materials. A perfect correlation of nano technology with cement chemistry will lead to a development of multi-functional materials with enhanced property. Only limited numbers of studies are reported in literature on usage of nano materials in construction applications. This paper discusses about the possible usage of various materials at their nano form in construction applications.

II. APPLICATION OF NANO SILICON DI OXIDE

Addition of nano-silica (nS) in cement paste and in concrete will results in different effects. There are many

discussions found in literatures on the mechanism of addition of the nS in cement paste. It was observed that only two ways of mechanism are possible when nano materials are used in cement or concrete. One is size effect i.e. based on their particle nature; it can be used as filler material and second is importing pozzolanic activity to the cluster compounds. To utilise these unique advantages, many researchers have attempted to improve the behaviour of cementitious matrix by incorporating nano silica. The productions of nano silica using various methods have been developed by several authors [1]-[13]. Types of methods used to synthesis nano silica are Sol-gel process [1], [2], [3], Electric-Arc-method [4], biological method [5], precipitation method [1], [2], [6]-[9], and alternative production method [4], [6], [10], [11]. Nano SiO₂ can be directly prepared from bio waste such as Rice Husk ash [9]-[22].

The TEM photograph of nano SiO₂ obtained by the present authors is shown in Fig. 1(a). The highly amorphous nature of the nano SiO₂ has been revealed from XRD studies as shown in Fig. 1(b). In this paper, nano SiO₂ shown in Fig. 1 was procured by the present authors from M/S Nanostructured and amorphous materials, USA. Nano silica in concrete or mortar will increase the density, reduces porosity, and improves the bond between cement matrix and aggregates [23]-[26] with higher compressive and flexural strength [27]. The compressive strength evaluation of cement mortar with nS and with silica fume was discussed for different w/c ratio [28]-[29]. The experimental result confirmed that the compressive strength of mortars with nS were higher than those of mortars containing silica fume at 7 and 28 days. It was proved from this study that the enhancement of strength mainly depends on nS addition rather than addition of silica fume. In line with the findings from other researchers, it was found that the nS behaves not only as a filler to improve the microstructure, but also as an activator to promote pozzolanic reactions and super-plasticiser plays an important role during mixing cement with nano particles.



(a)

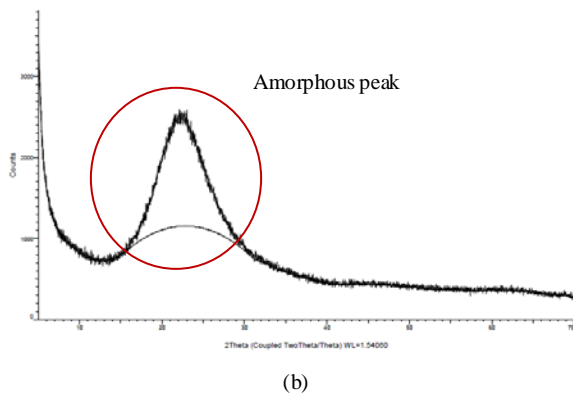


Fig. 1 (a) Nano SiO_2 particles observed using TEM; (b) XRD of nano SiO_2

The comparative studies on pozzolonic activity of nS and silica fume were carried out and the compressive, bond and bending strengths of hardened paste and concrete were also measured by Qing et.al [30]. Reported results indicated that cement paste containing $\text{Ca}(\text{OH})_2$ and nS improves the compressive strength, reaction rate and velocity of C-S-H gel with respect to the cement paste containing $\text{Ca}(\text{OH})_2$ with silica fume. Moreover, it was reported that with a small amount of nS, the $\text{Ca}(\text{OH})_2$ crystal at the interface between hardened cement paste and aggregate at early ages may be effectively

absorbed in high performance concrete. Bjornstrom et al. [31] investigated the hydration process of Ca_3SiO_5 cement and established the accelerating effects of colloidal silica and role of water during hydration. From their study, it was observed that colloidal silica accelerates dissolution of C3S phase thereby renders the rapid formation of C-S-H phase. Quercia and Brouwers [32] have studied the application of nano silica in mixtures. Gaiteroa et al [33] studied and proved the effect of silica nano particles on the reduction of calcium leaching rate of cement paste. The possibility to reduce the leaching rate by three ways such as reducing the porosity, transforming the portlandite into C-S-H gel by means of a pozzolonic reaction and modifying the internal structure of the C-S-H gel thereby increasing the average chain length of the silicate chains were discussed. Finally, it was concluded that addition of nS can control the C-S-H degradation due to calcium leaching and can increase the overall strength of cement-based materials at every stage. Also reported studies showed that the durability was increased by addition of nS and reduces the calcium leaching rate of cement pastes [23], [33]. Based on the reported studies, it is understood that proper filling of discrete and continuous pores in hydrates of cement matrix (as shown in Fig. 2 by using nS can lead to enhanced compressive strength of mortar, and concrete as a whole, which will facilitate to make durable concrete.

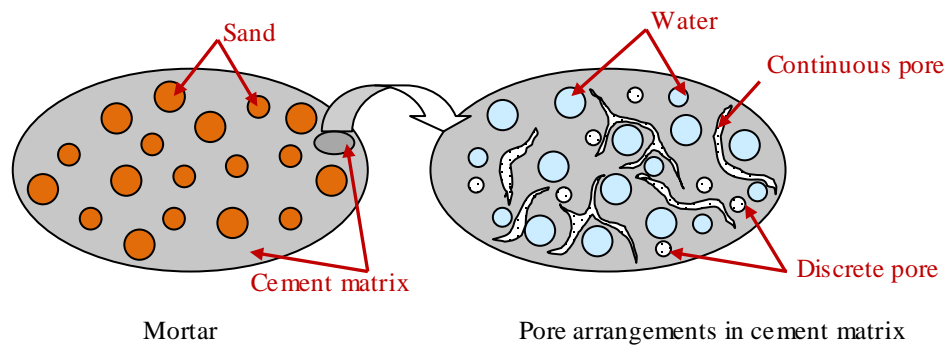


Fig. 2 Schematic arrangements of pore in cement paste

An indirect method for measuring viscosity change such as rheology study of cement paste and mortars was shown to be helpful to predict the accelerating effect of inclusion of nS [25], [34]. From the result, it was proved that cement paste and mortar with nS addition requires more water in order to keep the workability of mixtures constant, and it was concluded that nS shows stronger tendency for adsorption of ionic species in aqueous medium and the formation of agglomerates is also expected. Moreover, it is important to note that it is necessary to use a dispersing additive or plasticizer to reduce the agglomeration effect. The production of nS from olivine was reported and further their addition in concrete was discussed. Researchers ([34], [35]) have reported that due to the acceleration effect of nS in the cement paste, strength and durability of concrete can be improved. The accelerating effect of nS in cement paste was well documented ([23], [31], [34]). It was clear from the studies that the mechanism of working principle is related to high surface area of nS as it works as nucleation site for precipitation of the C-S-H gel. Elaborate discussion on this can be found in [32]. The effect of water permeability and microstructure of concrete in presence of nS was studied by Ji [36] and results showed that nS can improve the microstructure and reduce the water permeability of hardened concrete. Moreover, it was concluded that due to larger

specific area of nS, it imparts sticky nature to the concrete and it can react with $\text{Ca}(\text{OH})_2$ crystals and thus, making the interfacial transition zone (ITZ) more stronger. It was also pointed out that this type of phenomenon will be helpful to fill voids of the C-S-H gel structure and act as nucleus to tightly bond with CSH-gel particles. Hence, long term-mechanical and durability properties of concrete are expected to be increased. Lin et al. [24] observed the effect of nS addition on permeability and compressive strength of ash-cement mortar (eco-concrete). From the mercury porosimetry analysis it was reported that the relative permeability and pores sizes of concrete were decreased and also the compressive strength of ash-cement was increased by adding more nS. A pore filling effect of nS was addressed. Lin et al [26] described the improvements on sludge/ fly ash mortar in presence of nS and improvement in cement hydration products of cement to the finer size was discussed. A significant improvement of compressive strength of nS added sludge/mortar was noticed. Several authors have conducted studies on microstructural properties of nS added concrete. It was clear that the inclusion of nS will accelerate the more uniform and compact microstructure of concrete [23]-[25], [31], [34], [36]-[37]. Many attempts have been made to control the effect of self-desiccation of nS and development of cracks in concrete due to autogenous shrinkage at high concentration by using

different types of superplasticisers [25], [31]. Jo et al [38] reported the investigations on the development of powder concrete with nS particles. Various physical, mechanical and chemical characteristics such as heat evolution, compressive strength and microstructure of nS incorporated cement have been investigated and positively reported which are in well agreement with [23]. It has been well established that by using superplasticisers, agglomeration of nS in cement paste can be efficiently avoided.

Dolado et al [39] investigated the effect of nano silica additions on the mechanical properties and the microstructure changes of fly ash belite cement pastes held in sulfate solutions for 28, 90, and 180 days. Results found that although at 28 and 90 days the compressive strength of the samples without nano silica additions exceeds the values found in samples with nano silica additions, at 180 days, the behavior is reversed. The XRD studies showed clear correlation between the mechanical properties (compressive strengths) and the Mean Chain Lengths of silicate chain. Baomin et al [40] studied the freezing resistance of HPC with nS and found that nS was capable of improving the microstructure of cement, and consequently improving the freezing resistance of concrete materially. Moreover, it was noticed that a micro shape and appearance of C-S-H gel were more uniform, compact and orderly than the reference mix. Hosseini et al [41] reported the influence of nS addition on microstructure and mechanical properties of cement mortars for ferrocement. The results concluded that cement mortars containing nano particles have a reasonably higher strength and denser interfacial transition zone than do ordinary portland cement ferrocement mortars, while the flowability of mortars with and without nano particles is considered as equal. Influence of nS particles on the mechanical properties (compressive and tensile strength) and durability (in terms of water absorption and the depth of chloride penetration) of concrete has been studied in [42] and concluded that due to pozzolonic activity of nS, superior properties had been achieved. Pozzolonic reaction improvement by the addition of nS addition in High-Volume Fly Ash Concrete (HFC) is reported by Yazdi et al [43].

Nano Silica was mostly used in making Self Compacting Concrete and High Performance Concrete. Normally those two concrete can be named as eco-concrete. Eco-concretes are mixtures where cement is replaced by waste materials mainly sludge ash, incinerated sludge ash, fly ash or other supplementary waste materials. The main problem in these types of eco-concrete is segregation. However it will be overcome by adding nS in the corresponding mixtures and accelerates setting time and compressive strength of concrete. Nano silica application includes a preparation of rock-matching grouting, gypsum particle board, additives in tile, workability increaser, anti bleeder etc. Li et.al [37] demonstrated the effect of addition of nS in high volume fly ash concrete and the results are compared with control concrete. It was reported that activation of pozzolanic property of fly ash based concrete with nS was increased considerably. A study report showed the decrement in permeability even with small addition of nS in fly ash concrete and also it leads to gaining high strength in short term as well as in long term. Sadrmomtazi and Barzegar [44] reported the experimental investigation on the effect of nS on properties of self-compacting concrete with and without rice husk ash (RHA). Results showed the improvement in physical and mechanical properties of self-compacting concrete by

adding nS. The pore filling property and hydration acceleration were discussed. Importance of superplasticisers for nano particle dispersion was also addressed. The splitting tensile strength assessments, thermal behaviour and microstructure of concrete containing different amounts of ground granulated blast furnace slag and nS as binder were investigated by Nazari and Riahia [45]. It was emphasized that beyond the percentage level of 3% nS replacement would cause reduction in splitting tensile strength due to the formation of dense C-S-H at early stage.

Qing et al [46] demonstrated the influence of nS addition on properties of hardened cement paste (hcp) as compared with silica fume through measurement of compressive and bond strengths of hcp. Results showed that both nS and silica fume are in the amorphous state, but the influence of nS and silica fume on consistency and setting time are different. nS makes cement paste thicker and accelerates the cement hydration process and increases the compressive strength of hcp especially at early stage. By increasing the nS content, the rate of bond strength increased and much greater the pozzolonic activity of nS was observed than that of silica fume. Finally it was concluded that nS consumes calcium hydroxides (CH) crystals and resulted in decreases the orientation and reduces the size of CH crystals at the interface. It was important to note that the improvement in the interface structure was more effectively with nS than with silica fume. The experimental investigation on damping ability of concrete materials and its members with nS was carried out by Zou et al [47] using the method of 3-point bending beam damping measurement and cantilever beam free vibration respectively. From the experimental results it was observed that the damping effect was achieved best with the 4% mixture ratio of nS, but the optimal adulteration quantity of nS was 3% of cement weight by the comprehensive consideration of cost, workability, strength and dynamic properties. It was noticed that nano materials as a mixture increase interfaces, and the non-uniform stress distribution under external force improves frictional damping energy consumption ability of concrete.

III. APPLICATION OF NANO TITANIUM DI OXIDE

Similar to investigations on nano SiO₂ in cementitious matrix, many researchers have discussed the possible methodologies and observed advantages by using nano TiO₂ in cement matrix. Nazari et al [48, 49] conducted the studies on the compressive-, split tensile- and flexural, strength, and workability and setting time of concrete by partial replacement of cement with nano-phase TiO₂ particles. A significant achievement in high compressive- and flexural-strength has been obtained. Similar to other nano particles, decrease in workability and delay in setting time was found in presence of nano particle blended concrete. Nazari [50] conducted studies on the effect of lime water on flexural strength and water permeability of TiO₂ nano particles blended concrete. A significant achievement in flexural strength and water permeability of concrete with nano particle in lime water curing was observed but there was no considerable improvement in compressive strength. The filler effect and pozzolonic activity of TiO₂ was also discussed.

The effect of chemically nonreactive anatase TiO₂ nanoparticles on early-age hydration of cement was investigated by Jayapalan [51]. The effects of different percentage rates of added TiO₂ to portland cement on early-age behavior were examined, and influence of TiO₂ on hydration of C3S phase were conducted to determine whether

the influence of TiO_2 could be adequately described by a kinetic model based on boundary nucleation theory. From the comparison of experimental results and the modeling, it was showed that (a) an increase in addition rates of TiO_2 accelerates the rate of cement hydration and (b) the heterogeneous nucleation effect rather than the dilution effect was dominant. Based on the concept of the heterogeneous nucleation effect, boundary nucleation model resulted in increased rate of hydration in presence of TiO_2 due to large surface area. Finally, it was concluded that the above conducted research could be used for future studies towards optimizing photocatalytic and other nanoparticle-containing cements.

The strength assessments and percentage of water absorption of self compacting concrete containing different amounts of ground granulated blast furnace slag and TiO_2 nanoparticles as binder were investigated by Nazari and Riahi [52]. Cement replaced with 45% of ground granulated blast furnace slag and up to 3.0 wt% TiO_2 nanoparticles was able to increase the compressive strength due to the presence of increased crystalline $\text{Ca}(\text{OH})_2$ by formation of dense C-S-H at early stage and was able to improve the permeability of the matrix. Flores and Dominguez [53] studied the characterization and properties of portland cement composites with electric arc furnace dust (EAFD). The results indicated that a compressive strength of 72 MPa can be attained after forty-two days for OPC doped with 10 wt% of EAFD but a small retardation in setting time was observed.

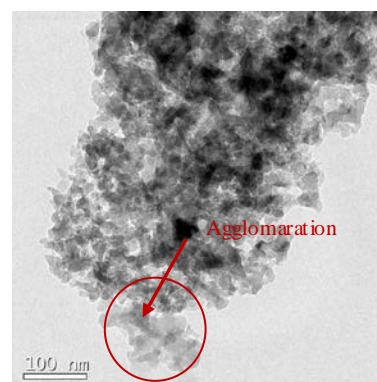
The flexural fatigue performance of concrete containing both nS and nano TiO_2 as an additive were studied separately and results were compared with concrete containing polypropylene (PP) fibers [54]. The enhanced flexural fatigue performance of concrete was proved experimentally as well as theoretically. Especially the result conveyed that concrete containing nano TiO_2 increased the fatigue behaviour in comparison with the normal concrete and concrete with polypropylene (PP) fibers. The abrasion resistance of concrete containing both nS and nano TiO_2 as an additive was studied separately and results were compared with concrete containing PP fibers [55]. Improvement in abrasion resistance was observed in all the mixtures. Even then the indices of abrasion resistance of concrete containing nano-particles are much larger than that of concrete containing PP fibers. A more pronounced effect of nano TiO_2 was compared with nS. Finally, it was concluded that compressive strength of the corresponding mixes were increased when abrasion resistance was more.

IV. APPLICATION OF NANO ALUMINIUM DIOXIDE

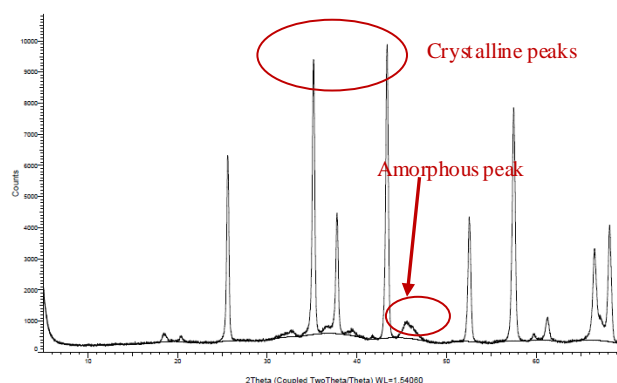
Research on nano Al_2O_3 in increasing the mechanical properties of cement has been carried out by few researchers. Most of them attempted to evaluate the improvement in compressive and tensile strength of nano Al_2O_3 incorporated cement. The TEM photograph of nano Al_2O_3 obtained by the present authors is shown in Fig. 3(a). The crystalline nature of the nano Al_2O_3 has been found from XRD studies as shown in Fig. 3(b). In this paper, nano Al_2O_3 as shown in Fig. 3 was procured by from M/S Nanostructured and amorphous materials, USA. Split tensile and flexural strength together with the setting time of concrete by partial replacement of cement with nano-phase Al_2O_3 particles were investigated by Nazari et al [56]. By adding nano Al_2O_3 , a significant achievement in high compressive strength was reported [57]. Similar to the observations made on using nS and nano Fe_2O_3 ,

it was reported that workability decreases and setting time delays in presence of nano particle blended concrete. The optimized level of usage of nano particles to attain the ultimate strength was reported. The effect of curing medium on microstructure together with physical, mechanical and thermal properties of concrete containing Al_2O_3 nano particles was explored by Nazari and Riahi [58]. It was noted that strength of the concrete was increased due to strengthening of gel for nano particle mixed lime water than lime water without nanoparticle.

Campillo et al [59] emphasized the potential of nano materials for activation of the initial strength of belite cements. In this study two types of Al_2O_3 based nano materials such as an agglomerated dry alumina (ADA) with an average grain size ranging from 0.1 μm (100 nm) to 1 μm and colloidal alumina (CA) composed of 50 nm alumina nanoparticles dispersed in water was used for the activation of early strength of belite cements. The study concluded that an addition of nano particles notably increases the early strength (7 days) and the nano particle can be used as an agent for activating hydraulic properties of belite cement thereby changes in microstructure causes improved mechanical property. The effect of nano Al_2O_3 on elastic modulus and compressive strength of the cement composites was brought out by Li et al [60]. The role of nano particles as a fine aggregate was confirmed through SEM and EDS study stating that the nano Al_2O_3 fill the ITZ of cement- sand and some capillary in the matrix and hence the elastic modulus and compressive strength of mortars were increased. But, no significant improvement in compressive strength was noticed due to insufficient filling of pores in the cement matrix under experiment condition.



(a)



(b)

Fig. 3 (a) Nano Al_2O_3 particles observed using TEM; (b) XRD of nano Al_2O_3

V. APPLICATION OF NANO ZIRCONIUM DIOXIDE

Research on usage of nano ZrO_2 in increasing the mechanical property of concrete is quite uncommon and only a particular group of researchers attempted to bring out the possibility of the same. Possibility of increasing split tensile strength of self compacting concrete (SCC) by adding ZrO_2 nano particles were conducted by Nazari and Riahi [61]. Reported results showed that inclusion of ZrO_2 up to 4 wt% was able to increase the split tensile strength of SCC due to the formation of more hydrated products in presence of ZrO_2 nano particles and improvement in pore structure was indicated. Further, Nazari et al [62] investigated the compressive strength and workability of concrete by partial replacement of cement with nano-phase ZrO_2 particles. It was observed that the addition of nano- ZrO_2 particles decreased the fluidity and increased the water demand for normal consistency. Therefore, the use of super-plasticisers was insisted while adding ZrO_2 nano particles. A significant improvement in compressive strength was achieved. Same researchers [63] studied the split tensile- and flexural-strength together with the setting time of concrete by partial replacement of cement with nano- ZrO_2 particles. The optimized level of usage of nano particles to attain an ultimate strength was identified. A delay in setting time was observed in nano particles blended concrete. Further, it was suggested that by using needle like nano particles, split tensile strength of concrete can be achieved.

VI. APPLICATION OF NANO FERROUS OXIDE

Similar to the investigations on possible uses of nano ZrO_2 in cement, the behaviour of nano Fe_2O_3 incorporated cement is very scanty. Nazari et al [64] conducted studies on the compressive strength and workability of concrete by partial replacement of cement with nano-phase Fe_2O_3 particles and results were compared with control specimen. A significant achievement in high compressive strength has been obtained and also decrease in workability has been seen in presence of nano particle blended concrete. As an extension of the study, investigations on the improvement in split tensile- and flexural- strength together with the setting time of concrete by partial replacement of cement with nano-phase Fe_2O_3 particles were carried out and positive results were reported [65]. A delay in setting time was observed in nano particles blended concrete. The optimized level of usage of nano particles to attain the ultimate strength was reported. Mechanical properties such as compressive- and flexural- strengths of cement mortar containing nano particles such as nS and nano Fe_2O_3 (hybrid incorporation) were studied and their impressive results (improvement in both compressive and tensile strength) were reported by Li et.al [66] and the smart behaviour of nano Fe_2O_3 in self stress sensing was also observed which can lead to a paradigm shift in techniques for health monitoring of structures.

VII. OBSERVATIONS FROM THE PRESENT STUDY AND WAY FORWARD

The role and mechanism of the nano particles of various oxides with cementitious materials have been reviewed and discussed in detail. Most of the authors concluded that inclusion of nano particles will impart more uniform and compact microstructure inside the concrete. The improvement in mechanical properties such as compressive-, flexural- and split- tensile strength of concrete containing nano particles have been reviewed by several researchers. One of the most

common findings was the delay in setting time of concrete when nano particles are blended in concrete. One important suggestion was made to use a de-agglomerating or dispersive agent while mixing the nano particle with cementitious material. The issue of decrease in workability by using nano materials in cementitious matrix has immensely constrained the advantages of usage of nano blending in construction materials. Although, several studies are reported, there is no clear mechanism on the Form-Structure-Function of materials as it's intended to use them in cement or concrete. Further studies based on the assessment of nano particles with respect to their high surface to volume ratio, stability and their structural elucidation when combined with other cementitious materials have to be studied in detail.

From the reported research works, it has been found that though many researchers had reported positive change in mechanical and chemical properties of cement after inclusion of nano particles as discussed above, the exact mechanism responsible for enhancement of properties of nano concrete is not clear. Further, the role (physical, chemical and mechanical) of nano particles in different phases of cement matrix has not been revealed yet. There is no established or proven mechanism to describe the conceptual path between nano particles and their reaction with cementitious phases such as C3S, C2S, C3A and C4AF and have been attempted by many researchers. Main issue on C-S-H modification by the inclusion of nano particles is still a grey area and it needs a strong collaboration between computational and characterisation studies. As part of the ongoing project on use of nanotechnology for engineering sustainable materials, the structural form of the materials at nano levels are being explored at CSIR-Structural Engineering Research Centre, India, using various computational and instrumental techniques to correlate the behaviour of nano engineered cementitious materials at various levels such as nano, micro and macro levels and to link the chemistry of binders (different cementitious composites) to concrete technology.

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