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Review Article

Influence of Nano Materials on the Characteristics of Ternary Mixes for Cement Mortar and Concrete for Urban High-Rise Structures

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ABSTRACT: Due to urbanization urban population increases, to accommodate this huge population in a constraint city/area is not possible therefore high-rise buildings are the better solution to avoid space constraint. To build such high-rise buildings and large construction strength of concrete play a crucial role. from last two decades extensive research had been done and still going on the nano materials incorporating in cement to overcome the limitations of conventional concrete. The nano materials are Nano silica (NA), Nano Alumina (NA), Graphene Oxide (GO), TiO_2 etc. Due its nano size and high surface area it increases the rate of reactions in cement thereby achieve high early strength. But this nano material has some disadvantages such as poor dispersion, high amount heat of hydration, workability etc. these problems can be overcome by going to ternary mixes. The aim of this paper is to review the effect of the microstructural behaviour of cement composites by using ternary mixes (cement + Nano materials + mineral admixtures) or (cement + two different nano materials). Further explains the effect of this ternary mix on workability, pore structure, interfacial transition zone (ITZ), mechanical strength and durability. Finally illustrate the research gap and conclusions.

KEYWORDS: Dispersion, Interfacial transition zone, Nano silica, Nano Alumina, Ternary mix.

INTRODUCTION

Due to urbanization concrete consumption increase across the world and stood at 2nd place in consumption after the water [1]. Every year cement production increases to fulfil the requirement of construction but cement production generates the environmental issues because one ton of cement production releases one ton of CO_2 gas which contributes to global warming [2]. Every year urban population increases, because people migrating villages, towns to cities. To accommodate this huge population city needs expansion its area by deforesting or by converting fertile land in to a concrete land, thus this will may create a social, environmental and ecological imbalance. Because of place is a constraint instead expansion in horizontal a vertical expansion is the better solution; thus, high-rise buildings will play a key role in future to avoid the problem of area constraint [3]. To build such a high-rise buildings and mass construction involves large money spending and environmental concerns therefore using only

cement-based concrete though we can satisfy the structural requirements but from economic and environmental point of view may not be good solution. Therefore, one should promote incorporation of advance materials and industrial by product (which are pozzolanic in nature) in concrete to make strong, durable and sustainable structures [4]. From durability aspects conventional concrete shows poor performance. In cement during hydration C_3S and C_2S reacts with water and form calcium silicate hydrate (C-S-H gel) and calcium hydroxide (CH). This calcium hydroxide does not contribute any strength in cement paste instead generates the porosity when external chemical agents attack and creates durability issues in concrete. But helps in maintaining the pH of concrete high which somehow positive aspects for steel rebar in RC structures. This paper is to review the influence of the ternary blended cement composites on the mechanical and durability properties and also illustrate the addition of significance of nano materials as ternary material in cement. Ternary mixes are adding two different mineral admixture or nanoparticles or combined in cement [5] as shown in Figure 1.

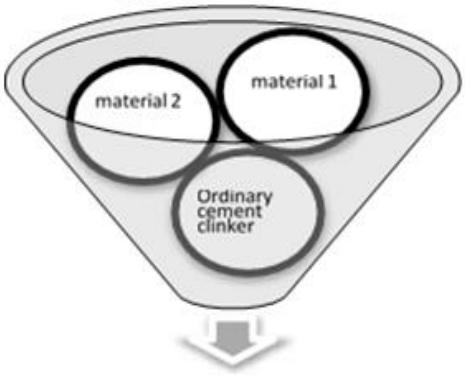

Figure 1: Illustration of Ternary Mix

SUPPLEMENTARY CEMENTITIOUS MATERIALS

From last few decades research had been done to upgrade the concrete strength and durability properties and also reduce the impact of carbon foot print on environment by replacing cement partially by industrial by products which are commonly called as supplementary cementitious material (SCM) or mineral admixtures such as GGBFS, fly ash, silica fume, rice hush ash (RHA), calcined clay, lime stone etc [6,7]; Figure 2: represents the different SCMs and their functions. According to ASTM C595 the pozzolans are the siliceous or aluminous materials, which possess little or no cementitious properties, but in finely divided form react with Ca $(OH)_2$ to form compounds which possess cementitious properties [8].

$$Ca(OH)_2 + \text{reactive silica/aluminates} + H_2O \longrightarrow \text{C-S-H (or C-A-H)}$$

The above reaction called as pozzolanic reaction. It involves lime consuming, pore refining, and improvement of ITZ in concrete. The fly ash (pozzolanic character), GGBFS (possess cementitious + pozzolanic character) shows slow pozzolanic reaction in concrete which can suitably use in mass construction such as dams, retaining walls etc, where low heat concrete is preferred. The Silica fume, rice husk ash (controlled burning) is highly pozzolanic materials contains >95% of reactive amorphous silica which accelerates the hydraulic reaction and forms C-S-H gel these contributes in early age strength gain. But these SCM require adequate and long period of curing to achieve good benefits of it [9]. The limitation using of SCM in concrete are slow early strength gaining, long period of curing, and variability of quality because these are by products obtained from different manufacturing industries therefore, we cannot ensure the same quality every time [10].

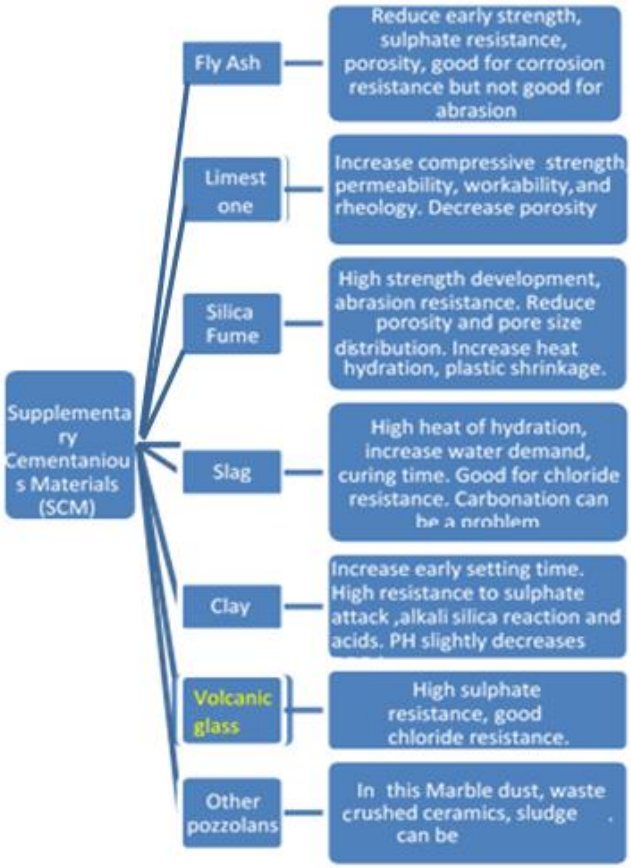

Figure 2: Schematic representation of different possible ternary mixes

NANO MATERIALS

Nanomaterials are new advance material, from last two to three decades of rigorous research had been done by incorporating this advance material in concrete. The nanomaterials are Nano silica (NA), Nano Alumina (NA), Graphene Oxide (GO), TiO_2, carbon nano tubes (CNT) etc. These nano size materials possess high surface area which increases the rate of hydration reactions in cement thereby achieve high early strength and due to its ultra-fine particle size, it can fill up micro and capillary pores which yields higher compressive, flexural, split tensile strength and also improves the durability properties. Due to pore refinement the water sorptivity, chloride ion penetration and other chemical agents' diffusion can effectively stops penetrating in to the concrete. But this nano material has some disadvantages such as handling of these materials because of fine size, poor dispersion that leads to agglomeration which can alter the kinetics of hydration process, and poor workability. The problem of dispersion counter by using good surfactant to separate the nanoparticles and good dispersant technique such as sonication process [11].

Nano-Silica

The commonly used nano material in cement composites is nano silica which can replace the micro-silica or silica fume. Nano silica contains 99% of reactive amorphous silica which instant start reacting calcium hydroxide formed during cement hydration to form C-S-H gel that may enhance mechanical strength and durability properties of cement mortar/concrete. Higher specific surface area of nano silica in cement composites accelerates the cement hydration reaction and also helps in fast dissolution of C_3S and C_2S in cement paste, but decreases the workability. Good dispersion of nano silica can effectively fill up the pore and voids in cement composites on the other hand poor dispersion of NS leads to agglomeration. Generally, from

previous research study the preferred dosage of nano silica may range from 1.5% to 6%, the dosage may vary due particle size and materials used in cement composite [12].

Nano Titanium Oxide

Another novel nano material is Nano-Titanium oxide (n-TiO_2), the coating of concrete with n-TiO_2 provide self-cleaning properties and degradation of pollutants such as aldehydes, CO, NOx, VOCs, organic matter and chlorophenols which are generated from automobile and chemical or manufacture industries by undergoing photocatalytic process in presences of UV rays. However, the efficiency of n-TiO_2 coating decreases with aging due to carbonation effect. Incorporation of n-TiO_2 in cement composite improves the strength and durability properties. S Ehsan Mohsen et al. observe that n-TiO_2 shows better workability than that of all NS and NA [13].

Nano Alumina

Nano Alumina has its applications in many fields medicine, engineering, AI applications, electronics and electrical, it also plays crucial role in many industries such as petroleum, gas, optics, steel industries, aero plane and construction industries. From the point of construction Nano Alumina use to enhance the properties of concrete by incorporation in cement partially. Nano Alumina (NA) contains > 99% of Al_2O_3 composition because high purity of Al_2O_3 chemical compound in NA setting time of cement composite decreases. High aluminates composition in concrete is advantage for chloride environment. Yang et al. studied the influence of Al_2O_3 on the chloride binding capacity of cement paste. Nano-Al_2O_3 dosages of 0.5% to 5% with increment of 0.5% added in cement paste this are exposed to NaCl solution at different mol/L. 5% dosage of nano-Al_2O_3 shows good chloride binding capacity. Resistance concrete. Al_2O_3 bend the chloride ions. NA accelerates the hydration process of cement composites and fasten the formation C-S-H-gel by consuming calcium hydroxide, fill up the micro pores, and improve the bond between aggregates and cement paste i.e., interfacial transition zone (ITZ). Due its fine size and large surface area which demands large amount of water thereby workability of cement paste decreases [14].

Graphene Oxide

Graphene oxide is made of carbon, oxygen, and hydrogen. These belong to graphene family nanosheets (GFN), among GFN graphene oxide is preferred material in cement composites. This nano material has excellent property such as electrical, thermal, mechanical, durability, it modulus of elasticity far greater than steel modulus, also it allows the self-cleaning and self-sensing ability. It has two-dimensional network of carbon atoms. This is a new nano material boon in a concrete technology because which has strongest, high modulus elasticity and thinnest sheet material. It has two-dimensional network of carbon atoms. From last two decades rigorous research has been done to know its effect on cement composite material by incorporation with different percentages to make high strength and high performable concrete. But still lot of research yet to be done with GO in concrete especially very limited research had done in SCC. This GO added in a very small percentage, but still, it modifies the concrete properties from micro scale, refinement of pore structure results in good mechanical and durability properties. GO accelerates hydration process in cement composites. GO nucleates the flower like semi crystalline component which has large surface area which fill up all the pores and voids in concrete make concrete dense, thus concrete produced will be strong and durable [15].

IMPORTANCE AND APPLICATION OF TERNARY MIX IN CEMENT COMPOSITES

From the early 20th century onwards, the cement was experimented with incorporation of different materials usually called as SCM to improve the strength and durability properties that results to a idea of binary mix and ternary mix cement composites. Ternary mix cement composites yield better results than binary mix cement composites because individual SCM has its own limitation for example fly ash exhibits only pozzolanic character whereas GGBFS exhibits both pozzolanic and cementitious character. Combination of these both (fly ash + GGFS) in proper proportion in cement exhibits good results than that of binary mix. Mala Kanchan et al. [22] determined the effects on strength properties of concrete by replacing cement partially with fly ash and silica fume. The results obtained shows silica fume in concrete accelerates the formation of secondary C-S-H gel that leads to early strength of concrete and the fly ash due its slow pozzolanic reaction it starts forming C-S-H gels in later stages. Aldred, J. [23] in the construction of Burj Khalifa 13-20% fly ash and 5 to 10% silica fume added in cement. From last two to three decades good research had been done to enhance the mechanical and durability properties of concrete by adding nano materials. Nano materials due its fine particle size and has high specific surface area which speed up reaction, pore refinement of ITZ hence we can achieve high strength and high durability concrete. Manank Shah investigated the effect on strength properties of ternary cementitious composite by using GGBFS and nano silica as partial replacement of cement. The results show nano silica helps in gaining early and high strength of concrete. The incorporation of nanomaterials in concrete with this SCM in concrete in a suitable proportion, one can achieve high early strength, higher long term mechanical strength, pore structure refinement and higher durability, which will decrease their maintenance requirements. Thus, we can make thinner section of concrete than that of conventional concrete for same given load which leads to economic and also reduces the cement quantity production thereby curtailment of CO_2 emission.

P. Mondal et al. [24] work on comparative study between silica fume and nano silica effects on the strength and durability properties of concrete. They found that nano silica due its ultra-fine particle size and higher specific surface area shows higher strength and durability than silica fume. Thus, nano silica can used as a replace material of silica fume in cement composite. These nano materials still not achieved its mature stage in research; thus, a lot of scope have for the researchers to work on these nano materials.

LITERATURE SURVEY

Amin Nazerigivi and Alireza Najigivi: The authors studied the effect of two different sizes of Nano Silica (NS) particles which are 15 nm and 80 nm on ternary blended concrete. Sixteen (16) different proportion of mixes prepared by replacing cement with different sizes(15nm and 80nm) of nano silica particles at different percentages. The percentage replacement is 0.5%, 1%, 1.5%, 2% wt of cement. The specimens are cured in a lime solution, but earlier researchers reported that lime curing on binary blended concrete with silica nano particle decreases the compressive strength after 28 days due to the formation of Ca $(OH)_2$. But in spite in the present experiment lime curing shows beneficial effects with ternary mix concrete. The ultra-fine nano silica particle 15nm size reacts fast with Ca $(OH)_2$ forms C-S-H gels and later the 80 nm silica nano particles reacts with $Ca(OH)_2$ which are formed in lime curing process, thus 80nm NS ensures the continuous formation C-S-H gel in the system till 90 days. The mechanical test that are compressive strength, flexural strength, and split tensile strength were tested after 7, 28, 90 days. The results show better improvement in mechanical strength at all mix proportions with incorporation of different sizes of nano silica particles than that of control mix. The mixes with 2% of 15nm plus 1.5% of 80nm nano silica particles combination gave the (high)peak mechanical strength. Therefore, concluded that different size NS particles in cement concrete nucleates the strengthening gels and fill up all the void in the system results into dense and

strong concrete [25].

Alireza Naji Givia et al. The author studied the effect of strength properties using ternary blended mix. The cement is replaced by different percentages of RHA and silica nano particles. Twenty four (24) ternary mixes were prepared with rice husk ash (RHA) and two different sizes of nano silica particles 15nm and 80nm replacing in cement partially. The percentage replacement of cement partially by RHA are 10%, 15%, 20% and nano silica by 0.5%, 1%, 1.5% and 2% and cured for 7, 28, 90 days under a lime solution The results showed the mechanical strength tests were performed at 7, 28, 90 days, it shows better improvement of strength properties at all curing days than that of control mix. The nano silica majorly contribute to increase of early strength of concrete after 28 days there is no significant increase of strength, however addition of RHA improved the later (after28 days) strength since RHA starts significant reaction after 28 days, therefore results in continues increment of strength properties. The optimum percentage of mix which give maximum Compressive strength is (cement + 20% of RHA + 2% of 80nm silica nano particles) at all curing days [26].

Manank Shah et al. Author explained the influence of ternary blended mix made by GGBS and nano silica incorporated in cement partially at different percentages. 7 mixes are made one with control mix (OPC) and other 6 mixes by the GGBS replacing the cement by 50 percent and nano silica by 1%, 2%, 3%, 4%, and 5% wt of cement. Tests were conducted at 7, 28, 56, and 90 days. Replacement of cement with GGBS along with nano silica would improve the strength then the only GGBS in cement. GGBS shows slow reaction in cement during hydration therefore have low early strength but addition of NS to cement + GGBS would increase the hydration thereby fasten the CSH gel formation results in early high strength and different range of particle size makes concrete dense and strong. The test conducted are compression test, Pull Out test, Split Tensile test and Flexural test. All the test shows good results than normal control concrete. Addition of higher quantity of nano silica leads to agglomeration and poor dispersion [27].

S Ehsan Mohsen et al. studied individual and combined effect of nano alumina (NA), nano silica (NS) and nano TiO_2 (NT) on fresh, strength, and durability properties of self-compacting concrete. The percentage replacement of cement with different nano materials partially were 1%, 3%, and 5% and constant 25%wt of cement with fly ash. The fresh properties were decreases by combination of nano particles than control mix for slump flow, whereas improved for V-funnel. The strength properties show that among individual incorporation of nano materials at 5%NS, 1% NA, 5%NT give better strength at 90 day and among all 5% NT shows maximum strength. In double combination mixes the mix 5%(NS +NT) in cement shows high compressive strength and In triple mixes 5%(NS + NA + NT) in cement shows maximum compressive strength. Further durability properties were studied [28].

Anas Al Khatib et al. The author used Electric arc furnace dust (EAFD) and cement kiln dust (CKD) are the two industrial waste materials as a replacement of cement at different percentages along with constant 5% nano silica to make high performance concrete. Binary mixture of CKD with cement obtained a poor result then a control concrete due to CKD replacement in cement decreases the C_3S, C_2S content in cement and low SiO_2 content in CKD leads to poor pozzolanic reaction and also increases of free lime content contributed by CKD this free lime reacts with water produce a $Ca(OH)_2$ which expand the cement paste and develops pores in cement. By incorporating nano silica to this binary mix improves the strength because SiO_2 particles develops additional CSH gels by consuming $Ca(OH)_2$ and pore filling effect. Whereas the binary mix of EARD with cement improves compressive strength than that of control concrete because EARD contains more Zn under hydration reaction obtain a Z-S-H gel. This ZSH gel stronger than that of CSH gel. However, by adding nano silica to binary mix

of EARD + cement further increment of compressive strength can be seen. Therefore, addition of nano silica with this industrial waste in cement increases the compressive strength and decreases the chloride penetration [29].

Supit and Shaikh et al. Investigated the durability properties of OPC and high-volume fly ash (HVFA) containing nano silica. They replaced 38% and 58% wt of cement partially with fly ash along with nano silica at 2% for both mixes and 2%, 4% cement replaced with only nano silica. The test conducted were compressive strength, and durability test such as chloride permeability, water sorptivity, porosity, and volume of permeable voids (VPV). The results obtained with only nano silica replacement are superior than OPC in all the aspects. Nano silica accelerates hydration reaction and due to its ultrafine particle size makes concrete dense. Whereas 38% fly ash with 2% nano silica shows better results for all durability properties than OPC, but no such improvement seen with compressive strength [30].

Faiz Uddin Ahmed Shaikh et al. the author studied the influence of ternary mix on compressive strength and microstructural behaviour of cement paste. 70%, 80% and 90% of cement replaced partially by high volume blast furnace slag (HVBFS) and combined (BFS)Blast furnace slag (70%) and (FA) class F fly ash (30%). 1 to 4% of nano alumina partially replaced in HVBFS and BFS-FA. The obtained results shows that strength increased from 2% to 16% by addition of NA in HVBFS and BFS-FA and also reduces capillary pores which are greater than 0.1 micro meter. Mix with (69% BFS+30% cement+1% NA) shows compressive strength greater than control cement paste and all other mixes didn't cross the strength of control OPC. From micro structural analysis of the paste done by SEM, TGA and EDS shows that low strength is due to high volume of cement replacement reduce the formation calcium hydroxide thereby decrease in production of secondary C-S-H gel [31].

Jalal et al. Investigated the fresh, strength, thermal and durability properties of high strength self-compacting concrete (HSSCC) containing fly ash and TiO_2. 5%, 10% and 15% replacement of cement content with fly ash and the mix of TiO_2 used in cement was 1 to 5%. The results shows that addition of fly ash improved the rheological properties of SCC and at 15% replacement of fly ash reduces water absorption, chloride penetration, and capillary absorption. At 4% replacement of cement by TiO_2 shows better properties in all aspects than that of all the mixes prepared expect workability. At 4% TiO_2 fasten the formation of C-S-H gel and improve microstructure of concrete and at above dosage of 4% TiO_2 decreases the mechanical properties because at higher dosage stops formation of C-S-H gels due to shortage of Ca $(OH)_2$. fine particles of TiO_2 improves the pore structure that leads to decreases in water absorption, chloride penetration, and capillary absorption and fast hydration reaction shows peak curve in calorimetric [32].

CHALLENGES

Using of ternary blend with different nano materials has not achieved a matured stage at present. From literature survey identified significant research gaps that need to be addressed to achieve the useful outcomes. The following are some recommendations given:

- Using of nano materials in cement still not achieved its matured state, therefore comprehensive research is required.
- Only few nano materials are research extensively, yet more research has to be done on other nano materials.
- There is a need to determine the optimal dosage of the nano materials to achieve required mechanical and durability properties. Extensive research needs to be required about effects of different nano materials on the properties of mortar/concrete. The studies should also address the effect of these nano materials in combination with other cementitious

materials.

- Dispersion of nano materials in cement composite play a significant role, poor dispersion leads to agglomeration of particles. Poor dispersion of nano silica in cement composites may leads to alkali-silica reaction.
- Nano materials are very expansive, because of that commercial application in cement composites is limited. In case of graphene oxide its fabrication process is very expansive. For instance, production of nano silica is relatively low cost. Therefore, in future reduction of production cost of these nano materials is a challenge, thus it can be used commercially in cementitious material.

CONCLUSIONS

From research survey on importance/benefits of ternary mix can concluded as follows:

- The incorporation of nanomaterials in binary mix cement concrete can improve the mechanical properties, denser microstructure, reduction in pores, decreasing water absorption. Nanomaterials add in a very small amount to the concrete.
- Addition of Nano-TiO_2 in concrete provides a self-cleaning property to the structures from environmental pollutants by undergoing photocatalytic degradation process.
- The binary mix made of cement plus nano materials shows poor workability because of its high surface area and high reactivity of nanomaterials. By adding admixtures such as GGBS, fly ash to the nano material cement composite improves the workability.
- Due to large surface area of Nano particles in cement produces high amount heat during hydration which may develops micro cracks in cement paste. The high amount of heat reduced by adding mineral admixtures to the binary mix of nano-cement composites.
- Incorporation of nano materials in cement reduces the setting time (initial and final) which lead to a problem especially regarding initial setting time such as placing, transportation of cement paste. By addition of mineral admixture can increase the setting time.
- Ternary mix i.e., cement plus nano material plus GGBS/fly ash/RHA in proper proportion shows continuous improvement in strength. The fact that nano materials provide high early strength due to fast production of C-S-H gel, and after 28 days GGBS/fly ash/RHA will start formation of additional C-S-H gel actively along with nano particles in cement concrete, thereby we obtain a continuous increase in the strength at all curing days.
- Ternary mix shows better reduction of pores in ITZ, Gel pores, capillary pores of concrete because ternary mix contains wide range particles sizes distribution which provides good filling effect in concrete therefore obtain a dense and compact concrete.
- High volume of cement replacement that is 80 to 90% by admixtures (GGBS/fly ash) will reduce the strength of concrete, but by addition of nano materials, one can achieve the strength as equal to the normal OPC concrete. From durability point of view can achieve higher than OPC concrete and decreases the CO_2 contribution by cement in environment.
- This high-volume blended cement concrete with nanomaterials can use for the structures where strength is less important.

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