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Performance on the Study of Nano Materials for the Development of Sustainable Concrete

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Abstract: This study focuses on the effect of incorporating nano particles such as nano Al_2O_3, nano Fe_2O_3 and nano SiO_2 on mechanical and durability properties of concrete. Nano particles were added in three different dosages of 0.5%, 1% and 1.5% of weight of the cementitious material into the concrete mixture. Experimental investigations on nano modified concrete were conducted after 28 days of water curing to obtain the mechanical properties such as compressive strength and split tensile strength of specimen. Also, Rapid Chloride Penetration Test (RCPT) and water absorption test were investigated for obtaining the durability properties of concrete specimen. Binary combination of nano Al_2O_3 + nano SiO_2 and nano SiO_2 + nano Fe_2O_3 were also considered to study the combined effect of the nano particles. Also, a micro-structural characteristic of nano modified concrete was done through the scanning electron microscope. Test results of the experimental study showed that incorporation of nano particles proved to increase the particle packing by reducing permeable pores and makes interfacial transition zone to be denser which enhanced the strength and durability properties of concrete. A significant performance was observed with the addition of nano silica in to the concrete when compared to the other nanoparticles.

Keywords: *Concrete, durability, nano modified, nano Al_2O_3, nano Fe_2O_3, nano SiO_2*

1. Introduction

The typical concrete consists of ordinary Portland cement (OPC), fillers such as sand, coarse aggregates, admixtures and water. This combination of materials allows concrete to be produced in a fluid form that can be pumped and molded. The complex chemistry and physical structure of cement hydrates in concrete however mean that issues of fundamental science still need to be resolved. Research at the nano scale has the potential to contribute to these debates and questions. Analysis at the nano scale may provide further insight into the nature of hydrated cement phases and their interaction with admixtures, nano fillers and nano fibers. These interactions offer the possibility of modifying cement reactions, creating new surface chemistries (referred to as Nano science), developing new products for the concrete industry (referred to as nanotechnology), and allowing more controlled and ecologically friendly manufacturing route to cement and concrete[1,2,3].

Nano particles have a high surface-area-to volume ratio. In this way, nano particles with 4-nm diameter have more than 50% of its atoms at the surface and are thus very reactive. The behavior of such materials is mainly influenced by chemical reactions at the interface, and by the fact that they easily form agglomerates. When higher surface area is to be wetted, it decreases free dispersant water in aqueous systems available in the mixture. Therefore, the use of nano particles in mortars and concretes significantly modify their behavior not only in the fresh, but also in the hardened conditions, as well as in the physical/mechanical and microstructure development [4]. The use of nano particles has recently been researched to overcome the deficiency of low early age compressive strength in concretes. Nano material is defined as a very small size particle in a scale of 10-9 meter, produced from modification of atoms and molecules in order to produce large surface area. Nano technology is developing at noticeable rate in recent years. Due to the new potential uses of nano particles there is a global interest in investigation of the influence of nano particles in construction materials especially in cement mortar and concrete. The use of some specific nano particles in concrete has commenced since the early 2000s. On the one hand some research studies were conducted investigating how these additives influenced the properties of pure cement; on the other hand the effects of the additives on behavior of the mortar and concrete were examined. From researchers' point of view, in general, nano-additives such as SiO_2 (NS), Al_2O_3 (NA), TiO_2 (TA) and Fe_2O_3 (NF) powders were mostly utilized in the studies [4, 5, 6, 7].

The experimental investigation on the influence of nano particles like nano-ZrO_2 nano-Fe_2O_3, nano-TiO_2 and nano- Al_2O_3 on durability and mechanical properties of high performance concrete. Nano Al_2O_3 particles contributed higher compressive strength and Nano Fe_2O_3 particles contributed higher tensile strength when compared to other nano particles [9,10]. Nano alumina increases compressive strength of mortars by 16% and enhances residual properties. Incorporating nano alumina into mortars cannot significantly affect the compressive strength of mortar. The main reason is that the porosity of cement matrix cannot be significantly decreased under the experimental condition of this literature. There exists big room to improve preparation technology .Nano SiO2 has found application very close to cement degradation by controlling the leaching of calcium. Nano SiO_2 is also used as a resistance to water penetration and improving concrete workability and strength [11]. Reduced setting time was observed by many researchers on the incorporation of nano silica in concrete which is same as observed for paste and mortar. The role of nano particles of silica act as fillers in the voids or empty spaces. The well dispersed NS act as a nucleation or crystallization centres of the hydrated products, thereby increasing the hydration rate, i.e., nano silica assisted towards the formation of smaller size CH crystals and homogeneous clusters of C-S-H composition. Moreover, they found that NS improved the structure of the transition zone between aggregates and paste. With regard to the influence of nano-silica on the mechanical strength development of cementitious materials, the addition of nano silica to Portland cement (PC) pastes was found to increase the compressive strength to an extent that was dependent on the nano-silica content, water-to-binder weight ratio (w/b), and curing time. Experimental study showed that nano Fe_2O_3 particles blended concrete had significantly higher compressive strength compare to that of the concrete without nano Fe_2O_3 particles. It is found that the cement could be advantageously replaced with nano Fe_2O_3 particles up to maximum limit of 2.0% with average particle sizes of 15 nm. Fe_2O_3 nanoparticles can improve the filler effect and also the high pozzolanic action of fine particles increases substantially the quantity of C—F—H gel. If this phenomenon joints with low water-to-cement ratio, it can improve the microstructure in the interfacial transition zones and thus the value of C—F—H gel results in decreasing the water permeability. The results also show that the workability and setting time of fresh concrete were decreased by increasing the content of Fe_2O_3 nanoparticles. The effect of Fe_2O_3 nano particles was investigated and reported that nano Fe_2O_3 particles increase the compressive strength of concrete. Nano Fe_2O_3 particles can significantly reduce the water absorption of concrete. It also enhances tensile strength of concrete[12].

The aim of the application of ultra-fine additives (nano particles) in cementitious systems is to improve the characteristics of the plastic and hardened material. The Nano-scaled Al_2O_3, TiO_2 and Fe_2O_3 particles have a filler effect by filling up the voids between the cement grains [12,13,14].With the right composition, the higher packing density results in a lower water demand of the mixture and it. It also contributes to strength enhancement due to the reduced capillary porosity. Also accounting for its durability properties, results show that addition of nano particles improves durability performance of the same. Nano modified green concrete is defined as a concrete which integrates nano particles such as Al_2O_3, SiO_2 and Fe_2O_3 in the concrete mix of three different percentages 0.5%, 1% and 1.5% and the optimum dosage results in higher performance and lifecycle sustainability. Developing of nano modified green concrete will result in higher performance in terms of strength, stiffness, durability and sustainability [15]. The partial replacement of cement by a mineral admixture called Metakaolin will obtain both higher performance and economy. Concrete mixes are modified with addition of admixtures and nano particles, which improve the microstructure as well as decrease the calcium hydroxide concentration by consuming it through a pozzolanic reaction. The subsequent modification of the microstructure of cement composites improves the mechanical properties, durability and increases the service life properties contributing to sustainably built environment.

2. Material Properties

Nano modified concrete consists of nano metal oxide powders, cement, metakaolin, fine aggregate and coarse aggregate. Apart from this poly carboxylate ether solution was also used in the study in order to enhance the flow property of nano modified concrete.

2.1 Nano Particles Details

Nano Al_2O_3 and nano Fe_2O_3 powders were produced from micro powder to nano size by ball milling process and synthesis of nano Al_2O_3 and nano Fe_2O_3 were also carried out by sol gel process and co-precipitation process respectively. Nano SiO_2 was procured from ASTRA chemicals supplier.

2.1.1 Ball milling technique for size reduction

Ball milling is a process where the powdered mixture is placed inside the ball mill and subjected to high-energy collision from the balls. A ball mill works on the principle of impact and attrition where the size reduction is done by impact as the balls drop from near of the top of shell. The ball mill equipment is shown in figure 1. In this technique, micro powders of alumina and ferric oxide were separately put inside the container having ball mills of different sizes in 1:10 ratio so that grinding force is high. Toluene solution was used so as to avoid burning of the powder during grinding. Usually balls of sizes 2 mm to 20 mm were used and the ball mill was set to run at 250 rpm for 8-12 hrs. The obtained wet powder is kept for oven drying between 70 – 80 °C to evaporate any organic impurities and to get particles in nano scale.

2.1.2 Synthesis of Nano Al_2O_3

Synthesis of nano alumina was done from a base material of 1M aluminium monohydrate and 0.5M of glycine. This solution was sonicated for 15 minutes for uniform dispersion and stirred for two hours maintaining 50°C followed by drop wise addition of ammonia solution to form a gel. This gel formed was then dried at 60°C for overnight at the oven, followed by calcination at 1100°C for two hours in muffle furnace. The white colour precipitate was collected and grained for obtaining fine nano particles as shown in figure 2.

Figure 1.*Ball mill equipment*

Figure 2.*Grained of Al_2O_3 precipitate by mortar and pestle*

2.1.3 Synthesis of Nano Fe_2O_3

In this method 1 $FeCl_2$.$4H_2O$: 2 $FeCl_3.6H_2O$ was taken in a beaker containing double distilled water. This solution was kept in sonication for 10 mins followed by stirring for half an hour at 60 °C. Light red colour solution was obtained to which 0.5M NaOH solution was added to maintain pH at 9. After addition of NaOH, a dark brown colour precipitated was formed, this was collected in petri dish and oven dried at 60 °C. The obtained particles were grinded still finer with mortar and pestle assembly to nano scale as shown in figure 3.

Figure 3.*Grained of Fe_2O_3 precipitate by mortar and pestle*

2.1.4 Nano particles properties

The properties of nano particles such as appearance, particle size, specific surface area and density are shown in table 1.

Table 1: *Properties of nano particles*

Nano particles	Appearance	Particle size (nm)	Specific surface area (m^2/g)	Density (g/L)
Nano-Fe_2O_3	Reddish Brown	90-100	150	90
Nano-Al_2O_3	White	90-100	150	90
Nano-SiO_2	White	20	202	44

2.2 Cement

Ordinary Portland Cement (OPC) of 53 grade was used in this experimental investigation. The basic properties of cement such as fineness, specific gravity, consistency, initial setting time and final setting time have been investigated as per BIS 4031:1996 and is presented in Table 2.

Table 2: *Properties of 53 grade ordinary Portland cement*

Property	Test results
Specific Gravity	3.15
Standard Consistency	32%
Initial Setting Time	50 min
Final Setting Time	430 min

2.3 Metakaolin

Pinkish white coloured metakaolin of specific area 150000 to 180000 cm^2 /gm having specific gravity of 2.5 and mean grain size 2.54 µm was used in this study.

2.4 Super plasticizer

Light brown colour poly carboxylate ether based super plasticizer was used having pH of 6.5 and volumetric mass of 20°C – 1.06 kg/L was used as a chemical admixture.

2.5 Aggregates

Fine aggregate passing through 4.75mm IS sieve with fineness modulus 3.07 and specific gravity 2.31 was adopted for the study. Coarse aggregate less than 20 mm size with fineness modulus 4.06 and specific gravity 2.54 were used after testing. The testing was conducted as per BIS 2386: 1963.

3. Experimental Work

3.1 Mix Proportioning

Mix proportion for the control specimen was designed as per IS 10262-2009 with ordinary portland cement, metakaolin, coarse aggregate, fine aggregate, super plasticizer and water. The nano series specimens were prepared by addition of nano particles such as nano Al_2O_3, nano Fe_2O_3 and nano SiO_2 from 0.5% to 1.5% of the weight of total cementitious materials (cement and metakaolin). Also binary combinations of nano SiO_2 + nano Al_2O_3 and nano SiO_2 + nano Fe_2O_3 were prepared to study the combined effect on nano particles. The different mixtures used in the investigation and their proportions are presented in the Table 3.

Table 3: *Mix proportions for specimens*

Specimen designation	Cement +Metakaolin (Kg/m^3)	Nano-Al_2O_3 (%)	Nano-Fe_2O_3 (%)	Nano-SiO_2 (%)
CO	388.82	-	-	-
NA1	388.82	0.5	-	-
NA2	388.82	1	-	-
NA3	388.82	1.5	-	-
NF1	388.82	-	0.5	-
NF2	388.82	-	1	-
NF3	388.82	-	1.5	-
NS1	388.82	-	-	0.5
NS2	388.82	-	-	1
NS3	388.82	-	-	1.5
NSA	388.82	1	-	1
NSF	388.82	-	1	1

The cementitious material in each sample was replaced by weight of 15% of metakaolin. The super plasticizer (SP) poly carboxylate ether solution with a dosage of 1% of the weight of cementitious materials was added to the total mixture for enhancing the flow property of the concrete specimen. The water to cement ratio of 0.38, fine aggregate of 727.23 Kg/m^3 and coarse aggregate of 1245.82 Kg/m^3 were used for all the mixes.

3.2 Preparation of Concrete Specimens

Concrete specimens containing nano particles were prepared by initial dry mixing of cement, sand and metakaolin for about 2 minutes in pan mixer. The super plasticizer was dissolved in 30% of water and nano particles were added and stirred at a rate of 350 rpm for about 5 minutes for uniform dispersion without any coagulation. Then, this solution was added to the dry mixture with the remaining 70% of water followed by continuous mixing for about another 3 minutes in pan mixer. The control specimen was prepared in the similar way as described above, but without any addition of nano particles. Cubes of 100 mm x 100 mm x 100 mm in dimension and cylinders of 100 mm in diameter and 200 mm in height were cast in steel mold and compacted. The cubes and cylinders were removed from the molds 24 hours after casting, and were allowed to cure in water. The 100 mm cubes were used for the determination of compressive strength, 100 mm x 200 mm cylinders were used for the determination of the split tensile strength and discs of size 100mm x 50 mm were used for determination of water absorption and rapid chloride permeability tests.

4. Results and Discussions

4.1 Compressive Strength Test

Compressive strength test was performed in accordance with IS 516-1959 on cube specimen of size 100 mm x 100 mm x 100 mm after 28 days of water curing. The test results of compressive strength are shown in figure 4 which was the average of three samples. The results showed that the specimens containing nanoparticles showed an increase in concrete compressive strength when compared with the control specimen. The results showed that concrete containing 1.5% of NS, 1% NF and 1% NA respectively of 54.6%, 34.2% and 27.1% enhanced in compressive strength with that of control specimen. The comparison of results showed that in case of NF and NA up to 1% there was an increase in compressive strength thereafter fall in the values. This may be due to the fact that the quantity of nano particles present in the mix was higher than the amount required to combine with the liberated lime during the process of hydration thus leading to excess silica leaching out and causing a deficiency in strength. But in contrary optimum dosage for nano silica was found to be 1.5%. For binary combination NSA and NSF there is 54.1% and 57.6% increase in compressive strength with that of control. The enhancement of the compressive strength of concrete can be attributed to that the nano particles act as nuclei in promoting cement hydration and filling up of pores to increase the compressive strength.

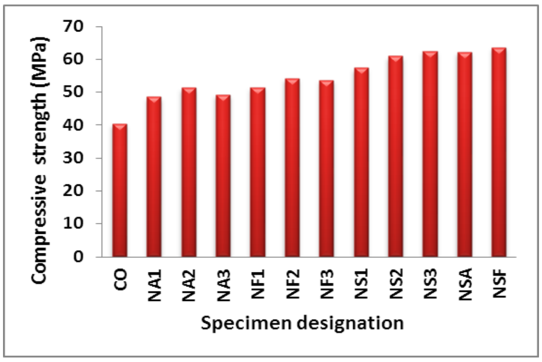

Figure 4 *Compressive strength of examined specimens*

4.2 Splitting Tensile Strength Test

Splitting tensile strength was performed in accordance with IS 5816-1999 on cylinder specimens of size 100 mm x 200 mm after 28 days of water curing. The figure 5 shows the indirect tensile strength values. Similar trend in the test result values were observed in splitting tensile strength as in case of compressive strength values. About 58.8%, 44.1% and 35.9% enhancement in splitting tensile strength were observed in specimen containing NS3, NF2 and NA2 respectively at their optimum level addition. This could be due to more C–S–H gel formation in the presence of nanoparticles in concrete and denser packing of material at their interfacial transition zone. Binary combination NSA and NSF showed 70.6 % and 76.8% increase in splitting tensile strength with that of control.

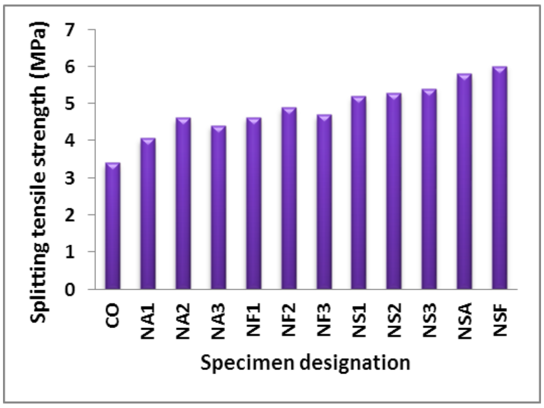

Figure 5 *Splitting tensile strength of examined specimens*

4.3 Water Absorption Test

Water absorption test was carried out as per ASTM C 642-06 on discs of size 100 mm x 50 mm after 28 days of water curing. Figure 6 shows the results of water absorption test. From the values of test results it was evident that NS3 had greater reduction in water permeation amongst addition of individual nano particles. This could be due to lesser size of particles (<20nm) in effective filling of gel pores present in the concrete specimen. It could be inferred from the test values that NA3,NF3,NS3 significantly reduced the water absorption by 30.6%, 35.8% and 54.2% in comparison to control specimen, which was due to filling of pores at nano scale and densification resulting in reduction of permeable pores present in the concrete specimen. Also NSA and NSF showed resistance to water absorption by 58.9% and 64.2% declination in water absorption values compared to control. Thus from the figure 6 it was evident that binary combination NSF has better water resistance ability amongst all the specimens.

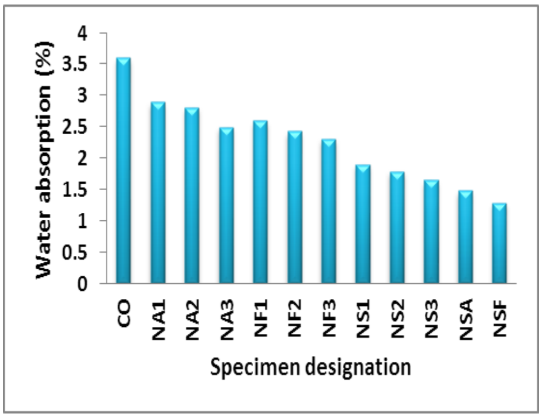

Figure 6 *Water absorption of examined specimens*

4.4 Rapid Chloride Permeability Test

Rapid chloride permeability test was carried out as per ASTM C-1202 on discs of size 100 mm x 50 mm after 28 days of water curing. Figure 7 shows the results of rapid chloride permeability test. In case of the specimen containing addition of nano particles from 0.5% to 1.5% showed better improvements in terms of resistance to permeation of chloride ions. Table 3 shows the chloride ion penetrability based on charge passed (ASTM C1202). From the records it was noted that NA3, NF3, NS3, NSA and NSF had 24.3%, 25.8%, 56.1%, 58.3% and 60.4% respectively with lower charge passage than the control. It indicates that chloride permeability of the mixtures with addition of nanoparticles mostly declined due to less number of voids. It was also noted that NFS drastically reduced the passage of current in the specimen which was due to effective filling up of microstructure by all the three nano particles in the concrete. Thus it can be reported that addition of nano particles reduces the chloride permeability thereby increasing the durability of the concrete.

Table 3: *Chloride ion penetrability based on charge passed (ASTM C1202)*

Charge passed(coulomb)	Chloride ion penetrability
> 4000	High
2000 – 4000	Moderate
1000 – 2000	Low
100 -1000	Very low
< 100	Negligible

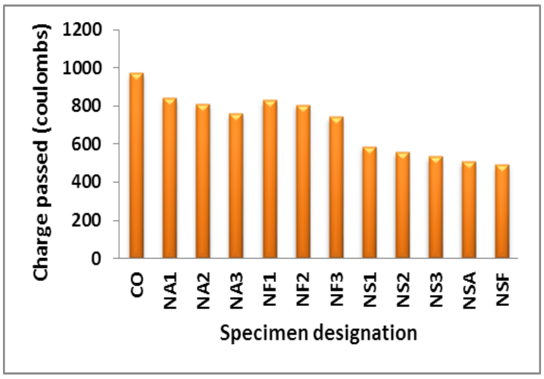

Figure 7 *Chloride ion penetrations of examined specimens*

4.5 Micro Characteristic Study

In order to study the microstructure of the concrete specimens with and without the addition of nanoparticles SEM (scanning electron microscope) analysis was adopted. The samples for SEM were taken from the broken fragments obtained after testing for the compressive strength of the specimens. These fragments were dried at room temperature and then examined at accelerating voltages ranging from 20 to 25 kV by a SEM analysis through higher magnification. The figure 8 and figure 9 shows the micrographs of specimens without and with the addition of nano particles respectively. From the micrograph images it could be seen that the concrete specimen without any addition of nano particles was fibrous matrix which has large number of voids and lean microstructure. But whereas in the specimen containing nano particles denser microstructure was seen with most of the voids being filled up by the nano particles due to rapid processing of C-S-H gel in presence of disparate nanoparticles. Also the $Ca(OH)_2$ crystals was decreased and a compact formation of hydration products was observed by utilizing this micrograph.

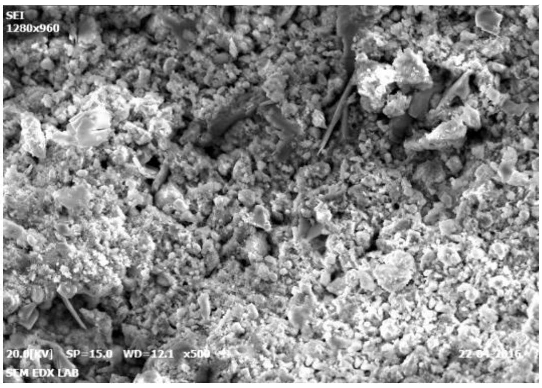

Figure 8 *SEM micrograph of concrete without nanoparticles*

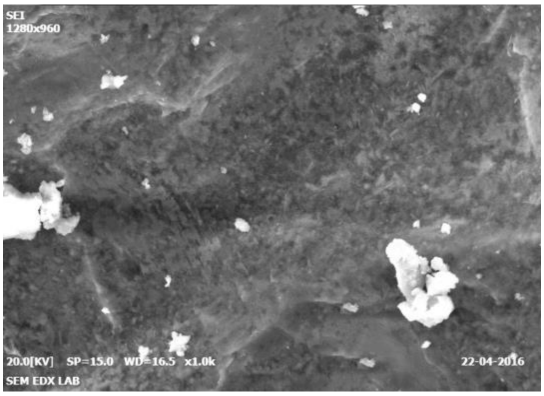

Figure 9 *SEM micrograph of nano modified concrete*

5. Conclusion

After investigation on influence of nano particles such as nano Al_2O_3, nano Fe_2O_3 and nano SiO_2 on strength and durability properties of concrete the following conclusion are drawn:

1) From the experimental evaluation of strength properties of nano modified concrete with addition of nano particles, it has been found that the compressive strength increased to a maximum value of 54.6% and 57.6% with 1.5% addition of nano SiO_2 and binary combination NSF respectively with respect to control specimen.
2) The split tensile strength increased to a maximum value of 76.8% for NSF and 58.8% for NS3 with respect to control mix.
3) There is a 64.2% reduction in water absorption for specimen with addition of 1% of binary combination NSF as compared to control specimens based on 24 hours water absorption test thus showing better resistance to water absorption.
4) RCPT results suggest that control specimen and nano modified concrete specimens are under low chloride permeability. But there was up to 60.4% reduction in current passage for addition of nanoSiO_2 and nano Fe_2O_3 particles in concrete specimens as compared to control specimen which reveals improved durability.
5) Also with addition of 1% of nano Al_2O_3,1% nano Fe_2O_3 and 1.5% nano SiO_2 there was noticeable improvement in strength properties of concrete with that of control and thus 1% and 1.5 % will be their optimum level for nano Al_2O_3, nano Fe_2O_3 and nano SiO_2 respectively. But for durability properties 1.5% addition is found to the optimum level for all the nano particles.
6) The contribution of individual nano silica and tertiary combinations was significant in enhancement of strength and durability properties which could be due to large specific surface area of 20nm particle size of nano silica.
7) Also there was a noticeable positive effect in addition of each of the individual nano particles in improving the strength and durability properties of concrete.
8) Microstructure analysis using SEM analysis confirmed that there was denser packing of C-S-H gel, reduction in $Ca(OH)_2$ crystals and improved pore structure of concrete specimen with the addition of nano particles.

6. Acknowledgement

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