

**Durability Studies in Concrete and Mortar Mixed with Supplementary
Materials- A Review**Bhawani Singh Bhati¹, Kapil Gandhi², Puneet Hiranandani³, Amit Purohit³, Kanika Mehta⁴¹Junior Engineer, Urban Improvement Trust, Barmer, Rajasthan, India²Consultant Engineer/Director, K.,G. Infrabuild, Jodhpur, Rajasthan, India³Lecturer, Department of Civil Engineering, Govt. Polytechnic College, Jodhpur, Rajasthan, India⁴Junior Engineer-Civil, North Western Railway, Jodhpur, Rajasthan, India

Abstract —Supplementary materials (SMs) have been widely used all over the world in ready-mixed concrete due to their economic and environmental benefits; hence, they have drawn much attention in recent years. Durability of concrete is defined as its ability to resist weathering action, chemical attack, abrasion or any other process of deterioration. It also includes the effects of quality and serviceability of concrete when exposed to sulphate and chloride attacks. Supplementary materials may contain fly ash (FA), silica fume (SF), Nano Silica, ground granulated blast furnace slag (GGBFS), rice husk ash (RHA), metakaolin (MK) and palm oil fuel ash (POFA), to name a few. In this reviewed paper we study on the concept how to enhance the durability of concrete and mortar mix with supplementary materials as additive and study about using supplementary materials and its applications and its effect on concrete properties. Paper discussed about Nano Silica used as supplementary material admixture in concrete.

Keywords-Durability; Nano Silica; Strength; Supplementary Materials

I. INTRODUCTION

The construction industry uses concrete to a large extent. About 14 billion ton concrete is used in infrastructure and buildings every year. It is composed of granular materials of different sizes and the size range of the composed solid mix covers wide intervals. The overall grading of the mix, containing particles size from 300 nm to 32 mm determines the mix properties of the concrete. The properties in fresh state (flow properties and workability) are for instance governed by the particle size distribution (PSD), but also the properties of the concrete in hardened state, such as strength and durability, are affected by the mix grading and resulting particle packing. One way to further improve the packing is to increase the solid size range, e.g. by including particles with sizes below 300 nm. Possible materials which are currently available are limestone and silica fines like silica fume (SF), silica fume (SF) and Nano-silica (NS). However, these products are synthesized in a rather complex way, resulting in high purity and complex processes that make them non-feasible for the construction industry.

Use of large quantities of cement produces large quantity of CO₂ which is prime gas causing the greenhouse effect. A method to reduce the cement content in concrete mixes is the use of mineral admixtures like fly ash, slag, silica fines etc. These are all waste products of different industries which is problem for disposal. Fly ash is waste product of thermal power plants. Silica fines are obtained as a waste product in manufacturing of silicon metals and ferro-silicon alloys which will be beneficial in making green concrete. However, presently Nano silica is produced by processes like vaporization of silica, sol-gel process, biological method, precipitation method, which are making its production little costly, also it affect health due to its small size which causes respiratory diseases. Addition of these materials improves the properties of concrete like durability, strength etc.

Basic structure of concrete include fine aggregate, coarse aggregate and cement which is the main strength making component. Voids of coarse aggregate are filled by fine aggregate; voids of fine aggregate are filled by cement and voids of cement remains open. But addition of finer particles like silica fume and Nano silica will fill voids of the cement and will improves different properties of concrete.

II. LITERATURE REVIEW

G.Quercia [1] he found out that with addition of nSilica, early strength of concrete as well as long term strength increases. He found beneficial effect of nSilica addition at a maximum level of 5% to 10% by weight of cement, Use of silica is almost compulsory in HPC (High Performance Concrete). Some researchers suggest that use of 1 Kg of silica fume reduces cement consumption by 4 Kg and use of nSilica reduced it further [1]. This reduces the Co₂ emission and support the theme of sustainable construction.

M.M. Reda [3] attempted to produce the UHPC mixtures with strength more than 200 MPa and examined them with SEM, XRD which showed very dense microstructures with some unique characteristics. The bond between the micro carbon fibers and the cement paste seems to be very good and the cement paste observed in the vicinity of the fibers was found to be very dense and homogeneous. They stated that the micro carbon fiber seems to govern the strength and post-cracking behavior of these materials.

Zain [4] explored the possibility of developing high performance concrete (HPC) using silica fume (SF) at relatively high water-binder ratios (0.45 and 0.50). Test specimens were air and water cured and exposed to a medium temperature range of 20°C to 50°C. Test results indicated that concrete under water curing offers the best results. The highest level of compressive strength and modulus of elasticity and the lowest level of Initial Surface Absorption (ISA) were produced by SF concrete under water curing and at temperature of 35°C. They have concluded that, under controlled curing conditions, it is possible to produce HPC at relatively high water-binder ratios.

P. K. Chang [6] have conducted tests on hydration properties of high strength concrete and have concluded that Alite decreases with the increase of the W/B ratio and the age. The hydration rate of C3A is extremely high. As the age advances, the strength of C3A declines. The amount of CSH increases proportionally to the W/B ratio and the age. By adding the slag to consume CSH, the pozzolanic reaction proceeds obviously. But ettringite is mostly formed by the hydration before the age of the 7th day, and there is no obvious increase of the radiation strength from the 7th to 60th days.

Jian Yin [7] have succeeded in producing HPC by adopting ordinary Portland cement (minimum content 273 kg/m³, maximum content 392 kg/m³), river sand, broken gravel, pulverized fly ash composites, with excellent workability (slump: 200 mm) and high strength (28-day compressive strength: 95.2–114.9 MPa) at a water-binder ratio of 0.20. The double effects of PFAC and super plasticizer give concrete a series of excellent performances, such as excellent workability, lower drying shrinkage, better durability, higher mechanical properties, etc.

M. Lachemi [8] studied the performance of new viscosity modifying admixtures in enhancing the rheological properties of cement paste and concluded that mini slump value increases with the increase of dosages of VMA from 0.025% to 0.075% for a fixed dosage of SP. The apparent viscosity of the cement paste is increased with the increase of dosages of VMA from 0.025% to 0.075%. The mini slump test results correlate roughly with the yield stress of the cement paste even if there is a scatter of data. General trend shows a decrease in yield stress of the paste with the increase in slump. A correlation between viscosity and mini slump of paste shows a decrease in mini slump with the increase in viscosity of the paste.

S. Chandra [9] have worked to find out the influence of cement and superplasticizers type and dosage on the fluidity of cement mortars and have concluded that the addition of a lingo-sulfonic acid (LS)-based superplasticizer resulted in higher fluidity of the mortar compared to when a melamine sulfonic acid (SMF) -based SP was used. This is because the variation of lime saturation rate in the case of LS is smaller than that in the case of SMF. Further SMF is much more unevenly adsorbed than LS on the clinker minerals of cement. Higher fluidity was observed with white cement for both LS and SMF than in the case of low alkali cement and OPC cements. This is attributed to the lower C3A+C4AF and alkali content and higher sulfate content in white cement compared to the low alkali cement and OPC.

Pierre-Claude Aitcin [11] in their work on superplasticizers found that superplasticizers are essentially surface active agents and their performance in cement – water system results in reduction in surface tension of water, adsorption on the C3A and C3S phases of cement thereby inhibiting the surface hydration reactions, induces electrical repulsion between particles, causes dispersion and deflocculation.

Mullik [12] studied on cement superplasticizer compatibility and there methods of evaluation. He found that at higher dosages of superplasticizers in concrete mixes of low water – cementitious ratio, unexpected behavior is sometimes experienced such as strong retardation, unusual rapid stiffening of concrete, low fluidification effect, rapid loss of slump and aggressive segregation and bleeding. He explained the Marsh cone method for determining the rheological properties of any given combination of superplasticizer and cement.

Yogendran [15] in their study determined that optimum replacement of cement by silica fume in high strength concrete of compressive strength 50 to 70 MPa at 28 day is 15%. Furthermore, the effects of silica fume decreases with increase in cement content and decreasing water to cementitious ratio.

III. SUPPLEMENTARY MATERIALS

In its most basic form, concrete is a mixture of Portland cement, sand, coarse aggregate and water. The principal cementitious material in concrete is Portland cement. To-day, most concrete mixtures contain supplementary cementitious materials that make up a portion of the cementitious component in concrete. These materials are generally byproducts from other processes or natural materials. They may or may not be further processed for use in concrete. Some of these materials are called pozzolans, which by themselves do not have any cementitious proper-ties, but when used with Portland cement, react to form cementitious compounds. Other materials, such as slag, do exhibit cementitious properties.

Supplementary cementitious materials such as fly ash, slag and silica fume enable the concrete industry to use hundreds of millions of tons of byproduct materials that would otherwise be land filled as waste. Furthermore, their use reduces the consumption of Portland cement per unit volume of concrete. Portland cement has high energy consumption and emissions associated with its manufacture, which is conserved or reduced when the amount used in concrete is reduced.

Some examples of these materials are listed below.

3.1. Fly Ash

Fly Ash is a byproduct of coal-fired furnaces at power generation facilities and is the non-combustible particulates removed from the flue gases. Fly ash used in concrete should conform to the standard specification, ASTM C 618. The amount of fly ash in concrete can vary from 5% to 65% by mass of the cementitious materials, depending on the source and composition of the fly ash and the performance requirements of the concrete. Characteristics of fly ash can vary significantly depending on the source of the coal being burnt. Class F fly ash is normally produced by burning anthracite or bituminous coal and generally has a low calcium content. Class C fly ash is produced when sub bituminous coal is burned and typically has cementitious and pozzolanic properties.

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3.2. Silica Fume

Silica Fume is a highly reactive pozzolanic material and is a byproduct from the manufacture of silicon or ferrosilicon metal. It is collected from the flue gases from electric arc furnaces. Silica fume is an extremely fine powder, with particles about 100 times smaller than an average cement grain. Silica fume is available as a densified powder or in a water-slurry form. The standard specification for silica fume is ASTM C 1240. It is generally used at 5 to 12% by mass of cementitious materials for concrete structures that need high strength or significantly reduced permeability to water. Due to its extreme fineness special procedures are warranted when handling, placing and curing silica fume concrete.

3.3. Natural Pozzolans

Natural Pozzolans Various naturally occurring materials possess, or can be processed to possess pozzolanic properties. These materials are also covered under the standard specification, ASTM C 618. Natural pozzolans are generally derived from volcanic origins as these siliceous materials tend to be reactive if they are cooled rapidly. In the US, commercially available natural pozzolans include metakaolin and calcined shale or clay. These materials are manufactured by controlled calcining (firing) of naturally occurring minerals. Metakaolin is produced from relatively pure kaolinite clay and it is used at 5% to 15% by mass of the cementitious materials. Calcined shale or clay is used at higher percentages by mass. Other natural pozzolans include volcanic glass, zeolitic trass or tuffs, rice husk ash and diatomaceous earth.

3.4. Ground Granulated Blast Furnace Slag (GGBFS)

Ground Granulated Blast Furnace Slag (GGBFS) is a non-metallic manufactured byproduct from a blast furnace when iron ore is reduced to pig iron. The liquid slag is rapidly cooled to form granules, which are then ground to fineness similar to Portland cement. Ground granulated blast furnace slag used as a cementitious material should conform to the standard specification, ASTM C 989. Three grades - 80, 100, and 120 are defined in C 989, with the higher grade contributing more to strength potential. GGBFS has cementitious properties by itself but these are enhanced when it is used with Portland cement. Slag is used at 20% to 70% by mass of the cementitious materials.

IV. EFFECT ON CONCRETE PROPERTIES

4.1. Fresh Concrete

In general, supplementary cementitious materials improve the consistency and workability of fresh concrete because an additional volume of fines is added to the mixture. Concrete with silica fume is typically used at low water contents with high range water reducing admixtures and these mixtures tend to be cohesive and stickier than plain concrete. Fly ash and slag generally reduce the water demand for required concrete slump. Concrete setting time may be retarded with some supplementary cementitious materials used at higher percentages. This can be beneficial in hot weather. The retardation is offset in winter by reducing the percentage of supplementary cementitious material in the concrete. Because of the additional fines, the amount and rate of bleeding of these concretes is often reduced. This is especially significant when silica fume is used. Reduced bleeding, in conjunction with retarded setting, can cause plastic shrinkage cracking and may warrant special precautions during placing and finishing.

4.2. Strength

Concrete mixtures can be proportioned to produce the required strength and rate of strength gain as required for the application. With supplementary cementitious materials other than silica fume, the rate of strength gain might be lower initially, but strength gain continues for a longer period compared to mixtures with only Portland cement, frequently resulting in higher ultimate strengths. Silica fume is often used to produce concrete compressive strengths in excess of 70 MPa. Concrete containing supplementary cementitious material generally needs additional consideration for curing of both the test specimens and the structure to ensure that the potential properties are attained.

4.3. Durability

Supplementary cementitious materials can be used to reduce the heat generation associated with cement hydration and reduce the potential for thermal cracking in massive structural elements. These materials modify the microstructure of concrete and reduce its permeability thereby reducing the penetration of water and water-borne salts into concrete. Watertight concrete will reduce various forms of concrete deterioration, such as corrosion of reinforcing steel and

chemical attack. Most supplementary cementitious materials can reduce internal expansion of concrete due to chemical reactions such as alkali aggregate reaction and sulfate attack. Resistance to freezing and thawing cycles requires the use of air entrained concrete. Concrete with a proper air void system and strength will perform well in these conditions.

V. INVESTIGATIONS MADE ON APPLICATION OF NANO SILICA

Nanotechnology was first introduced in famous lecture of Nobel Laureate Richard P. Feynman "There's Plenty of Room at the Bottom" given in 1959 at the California Institute of Technology. From then number of development are done in Nanotechnology in field of electrical, electronics, mechanical and materials. It has been found by number of researchers that due to introduction of Nano particles properties of the cementitious system increases. Nano particles are difficult to produce, costly and also have health hazards [1]. But if used in proper proportions and way can have reduction in cost.

According to the investigations made by [1] a special type of Nano-silica and new Nano-silica is produced from olivine. This NS, as well as commercially available NS, will be applied and tested. In addition, a mix design tool used for self compacting concrete (SCC) will be modified to take into account particles in the size range of 10 to 50 nm. The following results were obtained according to their studies and it is as follows:

5.1. Production Method of NS

Nowadays there are different methods to produce Nanosilica concrete. One of the production methods is water route method at room temperature. In this process the starting materials (mainly Na_2SiO_4 and organometallics like TMOS/TEOS) are added in a solvent, and then the PH of the solution is changed, reaching the precipitation of silica gel. The produced gel is aged and filtered to become a xerogel. This xerogel is dried and burned or dispersed again with stabilized agent (Na, K, NH_3 , etc.) to produce a concentrated dispersion (20 to 40% solid content) suitable for use in concrete industry.

An alternative production method is based on vaporization of silica between 1500 to 2000°C by reducing quartz (SiO_2) in an electric arc furnace. Furthermore, NS is produced as a byproduct of the manufacture of silicon metals and ferrosilicon alloys, where it is collected by subsequent condensation to fine particles in a cyclone. Nano-silica produced by this method is a very fine powder consisting of spherical particles or microspheres with a main diameter of 150 nm with high specific surface area (15 to 25 m^2/g).

Estevez et al. developed a biological method to produce a narrow and bimodal distribution of NS from the digested humus of California red worms (between 55 nm to 245 nm depending of calcinations temperature). By means of this method, Nanoparticles having a spherical shape with 88% process efficiency can be obtained. These particles were produced by feeding worms with rice husk, biological waste material that contain 22% of SiO_2 .

Finally, NS can also be produced by precipitation method. In this method, NS are precipitated from a solution at temperatures between 50 to 100 °C (precipitated silica). It was first developed by Iller in 1954. This method uses different precursors like sodium silicates (Na_2SiO_3), burned rice husk ash (RHA), semi-burned rice straw ash (SBRSA), magnesium silicate and others.

In addition, Nano-silica (NS) is being developed via an alternative production route. Basically, olivine and sulphuric acid are combined, whereby precipitated silica with extreme fineness but agglomerate form is synthesized (Nano-size with particles between 6 to 30 nm), and even cheaper than contemporary micro-silica. The feasibility of this process has been proven in two preceding PhD theses and published data. Currently, parallel PhD project focuses on the process to produce NS on industrial scale in large quantities for concrete production. Furthermore, the combination of raw materials and process parameters on production will be examined.

5.2. Role of Nano Silica

Byung-Wan Jo et al [20] have conducted experiments to explore the characteristics of cement mortar with Nanosilica particles. They have found out that amorphous or glassy silica, which is the major component of a pozzolana, reacts with calcium hydroxide formed from calcium silicate hydration. The rate of the pozzolanic reaction is proportional to the amount of surface area available for reaction. Therefore, it is plausible to add Nanosilica particles in order to make high-performance concrete. The experimental results show that the compressive strengths of mortars with Nanosilica particles were all higher than those of mortars containing silica fume at 7 and 28 days. It is demonstrated that the Nano-particles are more effective in enhancing strength than silica fume. In addition, the continuous hydration progress was monitored by scanning electron micrograph (SEM) observation, by examining the residual quantity of $\text{Ca}(\text{OH})_2$ and the rate of heat evolution. The results of these examinations indicate that Nanosilica behaves not only as a filler to improve microstructure but also as an activator to promote pozzolanic reaction.

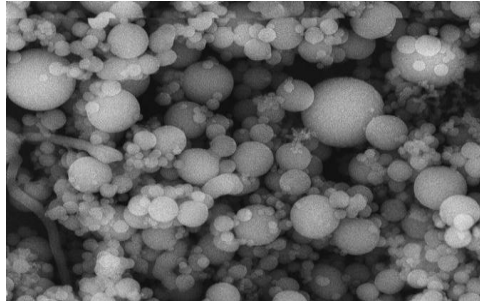


Fig: 1 SEM image of silica fume

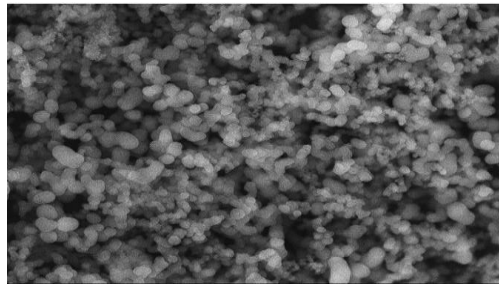


Fig: 2 SEM image of Nanosilica

5.3. Effect of NS Addition in Concrete and Mortars

In concrete, the Micro-silica (Sf and SF) works on two levels. The first one is the chemical effect: the pozzolanic reaction of silica with calcium hydroxide forms more CSH-gel at final stages. The second function is physical one, because micro-silica is about 100 times smaller than cement. Micro-silica can fill the remaining voids in the young and partially hydrated cement paste, increasing its final density. Some researchers found that the addition of 1 kg of micro-silica permits a reduction of about 4 kg of cement, and this can be higher if NS is used. Another possibility is to maintain the cement content at a constant level but optimizing particle packing by using stone waste material to obtain a broad PSD. Optimizing the PSD will increase the properties (strength, durability) of the concrete due to the acceleration effect of NS in cement paste. Nano-silica addition in cement paste and concrete can result in different effects. The accelerating effect in cement paste is well reported in the literature. The main mechanism of this working principle is related to the high surface area of NS, because it works as nucleation site for the precipitation of CSH gel.

However, according to Bjornstrom it has not yet been determined whether the more rapid hydration of cement in the presence of NS is due to its chemical reactivity upon dissolution (pozzolanic activity) or to their considerable surface activity. Also the accelerating effect of NS addition was established indirectly by measuring the viscosity change (rheology) of cement paste and mortars. The viscosity test results shown that cement paste and mortar with NS addition needs more water in order to keep the workability of the mixtures constant, also concluded that NS exhibits stronger tendency for adsorption of ionic species in the aqueous medium and the formation of agglomerates is expected. In the latter case, it is necessary to use a dispersing additive or plasticizer to minimize this effect.

Ji studied the effect of NS addition on concrete water permeability and microstructure. Different concrete mixes were evaluated incorporating NS particles of 10 to 20 nm (160 m²/g), fly ash, gravel and plasticizer to obtain the same slump time as for normal concrete and NS concrete. The test results show that NS can improve the microstructure and reduce the water permeability of hardened concrete. Lin et al. demonstrated the effect of NS addition on permeability of eco-concrete. They have shown with a mercury porosimetry test that the relative permeability and pores sizes decrease with NS addition (1 and 2% bwoc). Decreasing permeability in concrete with high fly ash content (50%) and similar NS concentrations (2% of NS power) was reported by. Micro structural analysis of concrete by different electronic microscope techniques (SEM, ESEM, TEM and others) revealed that the microstructure of the NS concrete is more uniform and compact than for normal concrete. Ji demonstrated that NS can react with Ca (OH)₂ crystals, and reduce the size and amount of them, thus making the interfacial transition zone (ITZ) of aggregates and binding cement paste denser. The NS particles fill the voids of the CSH-gel structure and act as nucleus to tightly bond with CSH-gel particles. This means that NS application reduces the calcium leaching rate of cement pastes and therefore increasing their durability.

The most reported effect of NS addition is the impact on the mechanical properties of Concrete and mortars. As it was explained before, the NS addition increases density, reduces porosity, and improves the bond between cement matrix and aggregates. This produces concrete that shows higher compressive and flexural strength. Also, it was observed that the NS effect depends on the nature and production method (colloidal or dry powder). Even though the beneficial effect of NS additions reported, its concentration will be controlled at a maximum level of 5% to 10% bwoc, depending on the author or reference. At high NS concentrations the autogenous shrinkage due to self-desiccation increases, consequently resulting in higher Cracking potential. To avoid this effect, high concentration of super plasticizer and water has to be added and appropriate curing methods have to be applied.

5.4. Applications of NS

At present Sf, SF and NS, because of their price, are only used in the so-called high performance concretes (HPC), eco-concretes and self compacting concretes (SSC). For the last types of special concretes (eco-concrete and SCC), the application of these materials is a necessity. Also, some explorative applications of NS in high performance well cementing slurries, specialized mortars for rock-matching grouting, and gypsum particleboard [39] can be found, but NS is not used in practice yet. The application of these concretes can be anywhere, both in infrastructure and in buildings.

Nano-silica is applied in HPC and SCC concrete mainly as an anti-bleeding agent. It is also added to increase the cohesiveness of concrete and to reduce the segregation tendency. Some researchers found that the addition of colloidal ns (range 0 to 2% bwoc) causes a slight reduction in the strength development of concretes with ground limestone, but does not affect the compressive strength of mixtures with fly ash or ground fly ash (GFA). Similarly, Sari et al. used colloidal NS (2% bwoc) to produce HPC concrete with compressive strength of 85 MPa, anti-bleeding properties, high workability and short demolding times (10 h). Another application of NS well documented and referred in several technical publications, is the use as additive in eco-concrete mixtures and tiles.

Eco-concretes are mixtures where cement is replaced by waste materials mainly sludge ash, incinerated sludge ash, fly ash or others supplementary waste materials. One of the problems of these mixtures is their low compressive strength and long setting period. This disadvantage is solved by adding NS to eco-concrete mixes to obtain an accelerated setting and higher compressive strength. Roddy et al. applied particulate NS in oil well cementing slurries in two specific ranges of particles sizes, one between 5 to 50 nm, and a second between 5 and 30 nm. Also they used NS dry powders in encapsulated form and concentrations of 5 to 15% bwoc. The respective test results for the slurries demonstrate that the inclusion of NS reduces the setting time and increases the strength (compressive, tensile, Young's modulus and Poisson's ratio) of the resulting cement in relation with other silica components (amorphous 2.5 to 50 μm , crystalline 5 to 10 μm and colloidal suspension 20 nm types silica) that were tested.

V. CONCLUSION

In study of various investigations in this paper, it is found that Cement replacement up to 12% with silica fume leads to increase in compressive strength, splitting tensile strength and flexural strength, for high strength concrete. Beyond 12% there is a decrease in compressive strength, tensile strength and flexural strength for 28 days curing period of high strength concrete.

A new Nano-silica (NS) can be produced in high quantities and for low prices that allows for a mass application in concrete. It may replace cement in the mix, which is the most costly and environmentally unfriendly component in concrete. The use of NS makes concrete financially more attractive and reduces the CO₂ footprint of the produced concrete products. The NS will also increase the product properties of the concrete: the workability and the properties in hardened state, enabling the development of high performance concretes for extreme constructions.

The highest compressive strength at the ages of 7 and 28 days was attained when the mixtures contain 6% micro silica and 1.5% Nanosilica considerable increase in electric resistant of Nano-micro silica specimens was observed compare to reference ones and the highest value was corresponding to the specimens who contain totally 7.5% Nano and micro silica. In general we can conclude that micro silica and Nano-silica replace cement in some percentages results in improved compressive strength, to quite an extent tensile strength is also improved. We can also notice that incorporation of colloidal Nano-silica and micro silica as partial replacements of cement have got advantageous effect on overall concrete performance.

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