Dispersion of nano carbon black in cement paste using ultra sonication to improve the properties of concrete

Dr. Hitesh R. Ashani[1], Dr.J.H.Markna[2]
[1]Assistant Professor, Department of Civil Engineering, V.V.P. Engineering College, Rajkot, Gujarat, India
[2]Assistant Professor, V.V.P. Engineering College, Rajkot, Gujarat, India

***Abstract*— The scope of improvement in various mechanical and chemical properties of concrete by dispersion of nanomaterial in it, is immense importance of interest for the construction field specially in the vicinity of strength and quality. The carbon black isa revolutionary material with functional properties, especially in its nano structured form. To disperse them uniformly into cement paste, ultrasonic dispersion techniques were adopted to increase the packing density and strength of concrete. The effects of ultrasonic energy and surfactant concentration on the dispersion of nano carbon black at various amounts like 5%, 10%, and 15%incement-based material were investigated by the compressive strength test and ultrasonic pulse velocity test as well as the microstructural characterizations like scanning electron microscopy. Results of experimental data suggest that addition of nano carbon black in cement-based material, i.e., concrete with the testing age of 7, 14 and 28 days, densify the micro and nano structure, improved mechanical propertiesi.e., compressive strength and the quality of concrete.**

Index Terms: **nano material, ultra-sonication, scanning electron microscope, mechanical properties of concrete.**

1.INTRODUCTION

A significant portion of the recent civil infrastructure is partially or completely constructed out of cementious materials such as concrete[1]. Albeitconcrete is widely used cement-based material permeable to water and has poor mechanical properties. At the present, toughness, strength &sustainability is increasingly important in new concrete technology with the increasing demand for high-performance building materials, having smart and novel properties for economy &sustainability in construction province. We are witnessing a common phenomenon to improve the mechanical chattels of cement-based materials through very costly inert and additives, particularly at the nanoscale [2, 3].In cement matrix, Tri-calcium silicates, Di-calcium silicate, Tri-calcium Aluminate, Tetra-calcium alumina-ferrate are the main mineral constituents reacts chemically with water during hydration process. These four components are involved in PTO at various stages [4,6]. Tri-calcium silicate hydrates and hardens rapidly and is highly responsible for the initial setting and initial strength gained while the tri-calcium aluminate hydrates and cures the fastest, also releases a large amount of heat immediately and contributes to the initial resistance. The di-calcium silicate hydrates and hardens slowly and is responsible for the increase in long-term resistance [9]. This type of composite nanostructure result in remarkably high strength and toughness of the shell due to interlocking of nano blocks of calcium carbonate responsible for the crack arrest and dissipation of energy [7-8]. For the economical solution and to develop smart cement-based material, on the whole nanocarbon black has been highly appreciated and they have been studied for their extraordinary mechanical, thermal, and chemical properties. Several researchers have shown that nanocarbon black improves nano and micro-mechanical properties of cement-based material. [10]. In it was noted that nanocarbon black allows notable to improve in mechanical properties of cement-based material, but they must be appropriately treated and dispersed in cementitious material.

Nano carbon black is carbon ordered structure and have unique mechanical properties. The pH value of nano carbon black was found to be 6&specific gravity was determined by density bottle method and it was found to be 1.33[11]. Because of these outstanding mechanical properties, addition of nano carbon as reinforcement to cementitious materials can potentially improve their properties and has received much interest among researchers, due to their nano-scale diameter. Furthermore, the high nano carbon aspect ratio (length / diameter) combined with their flexibility causes highly entangled agglomerates in the liquid phase [12].

The incorporation of nano-carbon black in cement-based material, i.e., Concrete faces two major challenges: bonding and dispersion. In fact, during the last years, nano modification of cement based material i.e. concrete has an increasingly significant role and was done by the incorporation of several nanomaterials, including carbon nano tube (CNTs),nano silicon dioxide (SiO_2), nano titanium dioxide (TiO_2), and nano iron oxide (Fe_2O_3), nano aluminum oxide (Al_2O_3).Observing the use of nanotechnology in cement composites and describing the effect of hydrated cement phases, makes it easy to understand the relationship between structure and macro scale properties of materials[13].Thereby producing construction materials with improved mechanical, thermal and durable characteristics [14]. For the last decade, nanotechnology has been successfully applied to cement-based materials which can enhance some of the traditional properties or introduce new capabilities to the material. An addition of a CNT to cement leads to an increase in the amount of crystal hydrates formed in the cement paste and to changes in their morphological structure [15]. J. Eberhard Steiner etl. explored that the positive effect of carbon nanotubes on the elastic properties of cement stone is clearly visible at the microscopic scale by using an ultrasonic device. Saloma etl. Suggest that nano SiO_2 augment the performance of concrete [16-17]. N. Venkat Rao etl. Says that the nanomaterials in concrete will improve the pore structure of concrete, speed up the C-S-H gel formation and improve the concrete's mechanical properties [18].

Good dispersion can be achieved by using of ultrasonic mixer with surfactants in solution, with specific times and amount of energy. Zou et al. Obtained the simplest mechanical performance of CNTs/cement pastes with an ultra sonication energy of 20 J/ml per unit CNTs to cement (C/c) with 83% of maximum dispersion [19]. However, CNTs may dissolve into solution or tear into small pieces if excessive force is employed. Compatibility of surfactant with cement is also particularly important. The hydration, chemical reactions and hardening process of cement paste could be delayed or even stopped [20]. Chemical activation places functional groups on the surfaces of CNTs and facilitating dispersion, additionally, improve the bonding between CNTs and the matrix. Methods embody surface modification with exposure to ozone gas at high temperatures and the formation of carboxyl groups through acid treatment. The formation of the carboxyl groups on the surface improves the bonding by causing chemical reactions with hydraulic cementitious materials. Kang et al. used acid treatment to improve tensile and compressive strength by more than 30% without any surfactant [21].

2. EXPERIMENTALPROCESS

2.1 Synthesis and Sonication for preparation of Nano carbon black composite

Ultra-sonication is a common physical technique used to disperse nano material into base liquid. Nano carbon black is a strong, flexible &having superior mechanical properties, present challenges for usage as a reinforcement material because of its lack of adhesion with the cement matrix due to it disperse difficulties. The quality and yield of these composites have been found to depend on the reaction temperature. The best quality of nano carbon and cement composite is obtained at 1200°C reaction temperature. At lower temperatures, the structure quality deceases and the Nano carbon black start presenting many defects. Consequently, nano carbon black composite with 5%, 10% & 15% replacement by weight of cement in composite is commonly preparedby equally dispersing it in cement paste providing energy for the chemical reaction by the ultra-sonication process as shown in figure 1. For the same, the Carbonyl Carboxylate ether solution is used as a surfactant for the preparation of an aqueous solution. Super plasticizer (polycarboxylate 8H) is used at a rate of 0.25% by weight of cement to bring down water content and mixed for 30 minutes to complete the sonication process. Then after, the sample is kept under magnetic stirring for another half hour to obtain a uniform mixture. Superplasticizer adsorbs to the cement particles and releases the trapped water van der Waals forces. This phenomenon improves the workability of the mixture while facilitating the dispersion of nanoparticles through the mixture as well[22].

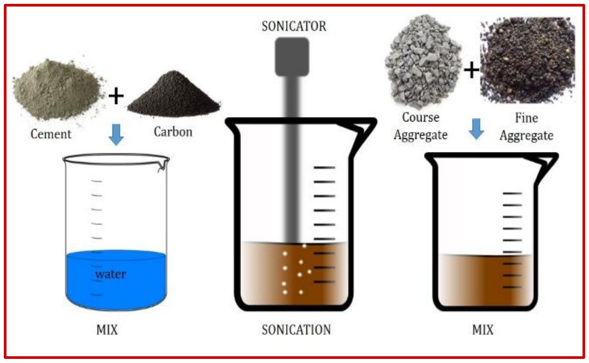

Fig.1: - Ultra sonication process

2.2Preparation of concrete specimen:

The grade of concrete used is M25 and concrete mix design is as per IS-10262-2009[29].Cube of size 150 mm x 150 mm x 150 mm as per IS:10086-198 were used to prepare concrete cube specimens[30]. Total 27 nos. of Concrete cubes were casted in three layer and compaction of specimen is done by vibrating table for necessary duration to achieve top smooth surface and upto removal of air bubbles for 5%, 10% & 15% of nano carbon black with a testing age of 7,14 and 28 days. The casted cubes were covered with wet straw or gunny sacking & stored under protection at a temperature of 22^0C to 33^0C & a place free from the vibration for 24 hours. After 24 Hrs cubes were removed from mould and immersed in clean water at a temperature 24^0C to 30^0C till the age of testing.

3. RESULT AND DISCUSSION

3.1Study of Characterization: -

The scanning electron microscopy can provide the topographic and morphological composition of nano carbon and cement which was particularly useful for analyzing the nano carbon and cement mixer prepared by ultra-sonication method. Effective dispersion of the nanocarbon was obtained by applying ultrasonic energy and in combination with the use of a surfactant or superplasticizer [23]in the cement matrix resulted in the reduction of the particle free area in the material and in an increase in the mechanical performance of the nanocomposite [24].

Cementitious product consistsof calcium–silica–hydrate (C–S–H) (as a chief ingredient) and aggerates. The size and number of particles, chemical bonding, homogeneous distribution, consistency, orientation of grains, porosity and micro-crepes are believed to be responsible for the mechanical properties of the cemented product. Considering various scanning electron microscope images, the phases were indicated studying the literature available [Lea's [41], Yazici [60]]. It was assumed that he bright and dark matter in the images stands for C–S–H gel/paste and inert aggregates, respectively.

In fact, the C-S-H gel phase formation has been extensively investigated due to its admixture based complexity and other chemical bonding based issues. Due to mention reason, SEM characterization paly very decisive role to study such microstructure and related properties of the concrete. Due to SEM micrographs, it became possible to study the role of various nanostructured additive and its bonding with C-S-H phase and aggregate in the concrete mixer. Such observations were reported by many researchers and shown that nano additives were mainly acting as filler materials as well as enhance the hydration process resulting into enhanced microstructure when it was dispersed in a good manner in the concreted matrix, resulting in batter physics strength. But till date, there is no systematic study performed on the correlation of microstructure, strength and packing density of nano additive added concreated with various concentrations. Figure X shows the typical SEM images (black and white color) of concrete without and with nano additive in the ration of 5, 10 and 15%, respectively. While figure XX show the detailed algorithm used to produce above image for the analysis point of view. While in the same figure, in the next part, images are generated through image processing to get the detailed analysis of porosity and packing density of concrete. Images clearly indicated, nano carbon act as nanofiller as result surface morphology gradually increase with respect to the amount of nano additive carbon black the white color region in images are porosity while other granular portions were formed C-S-H. From figure:2 and table one, clearly indicate, nano additive paly very crucial role in concrete matrix and reduce the porosity and increase the packing density of material. It is also noted that the number of voids and porosity is very less in the concrete, synthesized by adding 15% carbon black.

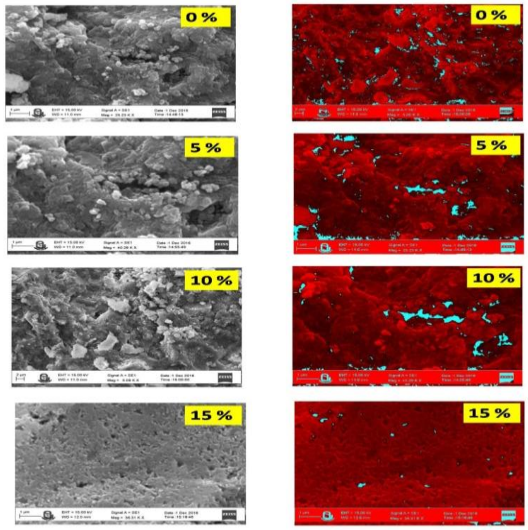

Fig. 2 SEM image of concrete , pristine and with nano carbon as 5%,10% & 15% addative respectively

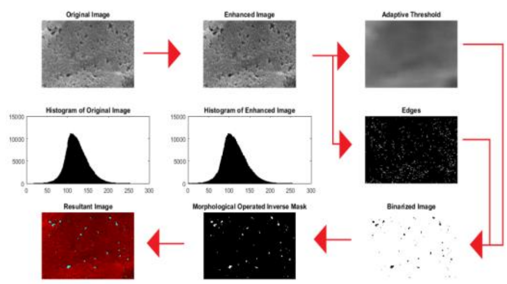

Fig. 3: SEM images after image processing, including blue regions corresponding to pores, while other represent C-S-H gel phase

3.2 X- Ray Diffraction study:-

Composition, structure, and shape of the material can be determined by advanced characterization technique like as X-ray Diffraction (XRD), Energy-dispersive X-ray spectroscopy EDX, Fourier transform infrared spectroscopy (FTIR) and many more [25]. In the present case, XRD was used to ensure the phase purity and size of the carbon black as shown in figure 4.

The grain size, was calculated from the full-width at half maximum (FWHM) of XRD lines by using the Debye–Scherrer formula

$$P = \frac{K\lambda}{\beta\ cos\theta}$$

Where, P = Mean size of the ordered domains, which smaller or equal to the grain size,

k = Dimensionless shape factor, with a value closer to unity. The shape factor is having a typical value about0.9 and varies with the actual shape of the crystallite,λ = X-Ray wavelength (1.54 A °), β= Full width half maxima, θ = Bragg Angle. We achieved the grain size 45 nm using the Debye–Scherrer formula.

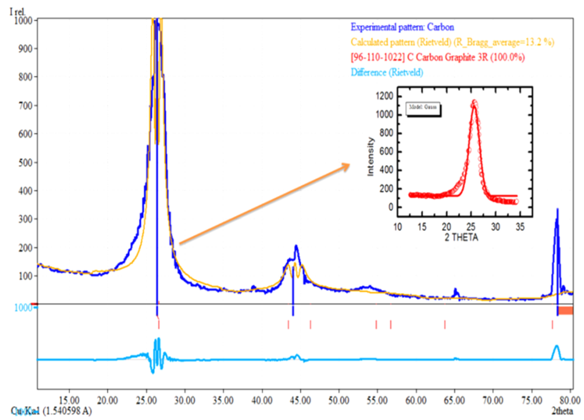

Fig. 4: X-ray diffraction pattern of nano carbon with rietveld analysis, while inset shows the Gaussian fitting of main XRD peak

3.3Compressive Strength:-

The tool used for testing for compressive strength is C.T.M. (compression testing machine) as per IS:14858-2000 [31] of 2000 kN capacity Specimes were tested as per IS 516:1959 for the different age of concrete[32].The result of concrete specimens at the ages of 7, 14 and 28 days as presented below suggest the significant improve in concrete strength because due to reduction in pore size due to filling of the pores between the cement particle by nano carbon black in concrete.

Table 1 - Test results and different % of nano carbon black for compressive strength (7 days)

% Carbon black	load observed at failure of specimen	Compressive strength N/mm²	% Increase in compressive strength
	7 days	7 days	
0%	399	17.74	-
5%	421	18.73	5.58
10%	455	20.22	13.24
15%	490	21.76	19.88

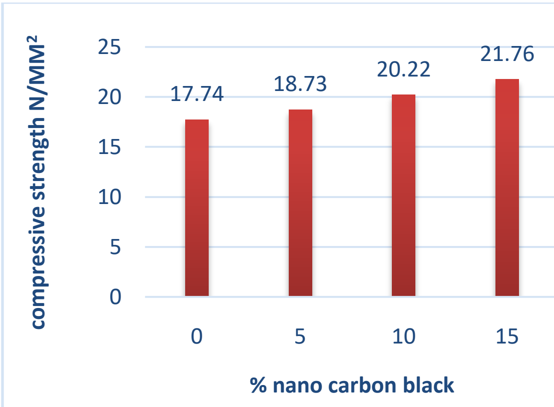

Fig.5 - Test results and different % of nano carbon black for compressive strength (7 days)

The compressive strength of M25 grade of concrete after 7 days age with replacement of 5%, 10%, 15% nano carbon black was increased gradually by 5.58 %, 13.24% and 19.88% respectively compared to normal concrete specimen.

Table 2 - Test results and different % of nano carbon black for compressive strength(14 days)

% Carbon black	Load observed at failure of specimen	Compressive strength N/mm²	% Increase in compressive strength
	14 days	14 days	
0%	513	22.79	-
5%	528	23.46	2.94
10%	578	25.67	12.28
15%	604	26.86	15.86

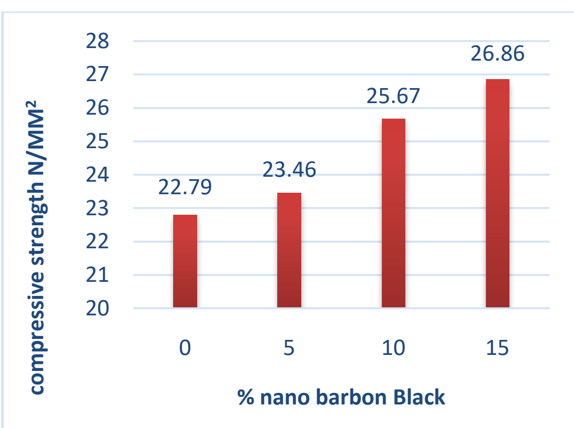

Figure 6:- Test results and different % of nano carbon black for compressive strength (14 days)

The compressive strength of M_{25} grade of concrete after 14 days age with replacement of 5%, 10%, 15% nano carbon black was increased gradually by 2.94 %, 12.28% and 15.86% respectively compared to normal concrete specimen.

Table 3- Test results and different % of nano carbon black for compressive strength (28 days)

% Carbon black	Load observed at failure of specimen	Compressive strength N/mm²	% Increase in compressive strength
	28 days	28 days	
0%	599	26.64	-
5%	629	27.96	4.95
10%	662	29.44	10.01
15%	684	30.38	12.70

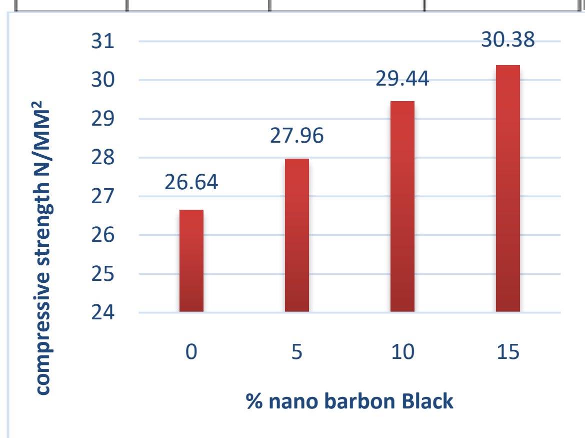

Figure 7:- Test results and different % of nano carbon black for compressive strength (14 days)

The compressive strength of M_{25} grade of concrete after 28 days age with replacement of 5%, 10%, 15% nano carbon black was increased gradually by 4.95 %, 10.01 % and 12.70% respectively compared to conventional concrete specimen.

If the nano-carbon is not properly dispersed, there may be no increase in the mechanical properties of the concrete. Nano carbon having a larger surface area which, in turn, improves the stress concentration in the interface of mortar aggregates [26]. Hence this enormity of nano-carbon in concrete is to have the ability to be favorable and profitable. The compression resistance, thrust shows that the agglomeration of the nano-carbon in the cementitious product has been minimized due to the good dispersion of the nano-carbon in the cement concrete [27]. Agglomeration is counteracted by a sonication and magnetic stirring process.

3.4 Quality of Concrete: -

An ultrasonic pulse velocity (UPV) test is an in-situ, nondestructive test applied as per IS-13311(part-1)-1992to establish the consistency of the concrete and to determine the existence of the fissure, crater another deficiency[33]. A pulse of ultrasonic wave from side-to-side concrete to be tested and assessed the time taken by pulse to get through the specimen structure. Higher velocities point toward good quality and continuity of the material, while lower velocities may point toward concrete with fissures or cavity. The process stands on the set of laws that the velocity of an ultrasonic pulse all the way through any material depends upon the Poisson's ratio, density & modulus of elasticity of the material. Comparatively higher velocity is obtained when the concrete quality is good [28].

UPV test was conducted on concrete cubes after 28 days to analyst Quality of concrete in terms of strength, homogeneity, trapped air, inner defect, fracture, separation, honeycombing, compaction, workmanship, and robustness of nano carbon black concrete. Ultrasonic testing tools includes a pulse generation circuit, consisting of electronic circuit for generating pulses and a transducer for transforming electronic pulse into mechanical pulse having an oscillation frequency in range of 40 kHz to 50 kHz, and a pulse reception circuit that receives the signal. After calibration to a standard sample of material with known properties, the transducers are placed on opposite sides of the material. Pulse velocity is measured by a simple formula:

Velocity of pulse = structure's width / time taken by pulse. The results of the ultrasonic pulse velocity test are shown in the Table as below.

Table 4: Result of ultrasonic pulse velocity test for different % of carbon black

% Of carbon black	Time (micro second)	Distance Travelled (m)	Velocity (km/s)	% Increase in velocity
0%	33.55	0.15	4.45	-
5%	31.65	0.15	4.64	4.74
10%	30.65	0.15	4.79	4.89
15%	29.87	0.15	4.97	5.02

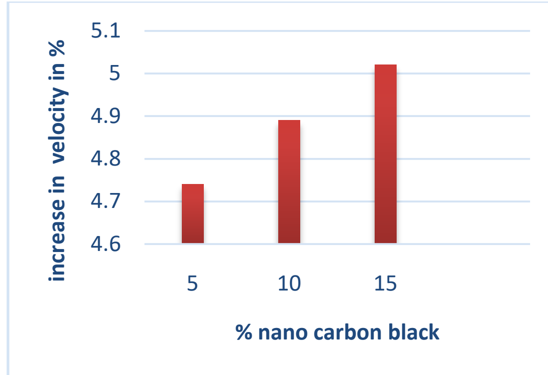

Fig. 8: % increase in velocity with respect to different % of nano carbon black in concrete specimen.

4.CONCLUSION

Based on the above experimental investigations, we have concluded that increasing the proportions of functional nano carbon into concrete increases the compressive strength. The compressive strength of the concrete with a proportion of 5%, 10%, 15% nanostructured nano carbon increases by about 5.58%, 13.24% & 19.88% for 7day, 2.94%, 12.28% & 15.86% for 14 days, & 4.95%, 10.01% & 12.70% for 28 days compared to conventional concrete, respectively. The quality of concrete in terms of density, homogeneity & uniformity with a proportion of 5%, 10%, 15% functional nano carbon increases as velocity increases by about 4.47%, 4.89% & 5.02%, more compared to conventional concrete for the duration of 28 days

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