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High performance concrete by nanophase modification and sodium nitrite inhibition

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ABSTRACT

The development of high performance concrete (HPC) through the additament of mineral and chemical admixtures to concrete opened up the opportunities of engineering a concrete commix with enhanced properties and meeting the intended performance requisites. Flyash, the waste product in coal based power plants is a commonly used supplementary cementitious material in concrete in order to reduce the usage of cement and to enhance its durability. Though studies have shown that flyash has superior properties, there are some early-age performance issues of flyash concrete like low early-age strength, delayed setting time, high calcium leaching, more stringent curing conditions etc. Hence, this study attempts to overcome these drawbacks of flyash concrete by addition of nanoparticles and inhibitor.

Four different mixes of concrete were prepared and designated as Control concrete (CC), Flyash concrete (CF), Flyash concrete with addition of 1% TiO_2 and 1% $CaCO_3$ nanoparticles (CFN) and Flyash concrete with addition of 1% TiO_2, 1% $CaCO_3$ nanoparticles and admixed with 2% sodium nitrite based corrosion inhibitor (CFNI). The samples were cured for 28 days in fresh water and the various mechanical properties such as compressive strength, split tensile strength and flexural strength were evaluated. Further, the durability properties like water sorptivity, penetration of chloride ions, water absorption capacity etc. were figured out. Scanning Electron Microscopy (SEM) was used to visualize the surface topography of the specimens. The results revealed that incorporation of nanoparticles together with inhibitor facilitated to overcome the shortfalls of flyash concrete and improved its early-age properties.

Keywords: *High performance concrete, nanoparticles, corrosion inhibitor, durability*

1.0 INTRODUCTION

Concrete is the most commonly used universal construction material as it is very strong and relatively cheap. It has been found that approximately 7% of the global CO_2 emission accounts from cement production alone. Thus, conventional concrete offers a threat to the harmony of the environment and looses its sustainability [1]. High Performance Concrete (HPC) is defined as concrete, which is specifically designed for enhanced performance and uniformity requirements that cannot be achieved using conventional materials and normal mixing practices [2]. The recent advancements in the field of HPC represent a giant step toward making concrete a high-tech material with enhanced characteristics and durability [3].

Fly ash is a by-product of the coal based power plants and consists mainly of SiO_2, Al_2O_3, Fe_2O_3, and CaO together with some impurities [4, 5]. It is also very economical and the desired properties in concrete can be obtained with large volume (>40%) of fly ash replacements [6, 7]. However, studies also showed that there are some drawbacks for FA concrete which needs improvement for a better performance. FA concrete exhibits high levels of calcium leaching even though the extent of weight loss and degradation is least [8]. Another major drawback is the delayed setting and lower initial strength development in concrete containing high concentrations of fly ash [9]. There are several researches carried out over the betterment of FA concrete by the incorporation of nanoparticles into concrete specimens in which most of them have focused on using SiO_2 nanoparticles, TiO_2 nanoparticles and nano $CaCO_3$ particles [10-12].

Corrosion of reinforcing steel in conventional concrete and HPC has become a major global problem, especially in buildings, bridges, tunnels and other buildings exposed to seawater or harmful chemicals. As a result of this deterioration process, the repair costs nowadays constitute a major part of the current spending on infrastructure [13]. The use of corrosion inhibiting admixtures is considered as one of the most cost effective solution to the widespread corrosion problem, due to their convenient and economical application to both new and existing structures [14]. But inhibitor and fly ash alone do not provide sufficient protection against corrosion, whereas the combination of the two provides a significant benefit in high performance concrete, increasing the resistance to chloride diffusion [15].

Thus, this work focuses on the development of a high performance green concrete by the incorporation of flyash and to further enhance its properties through nanophase modification and corrosion inhibition for marine applications. The mechanical and durability characteristics of the modified concrete will also be evaluated.

2.0 MATERIALS AND METHODS

2.1 MATERIALS

Ordinary Portland Cement (OPC 43 grade PENNA) with a specific gravity of 3.12 and a fineness module of 5.0 confirming to IS 8112-2013 was used for casting the concrete specimens. Class F Flyash (Siliceous type) procured from Ennore Thermal Power Plant, Chennai confirming to IS 3812 was used as the partial (40%) cement replacement material. Crushed river sand with a maximum size of 4.75 mm and specific gravity of 2.83 was used as the fine aggregates. Crushed black granite with a maximum size of 20 mm and 12 mm with a specific gravity of 2.85, were used in equal proportions as the coarse aggregates. The selection of the aggregates was in agreement with IS 383 standards. RheoBuild 1125, a sulphonated Naphthalene based high range water reducing admixture was used in this study as the superplasticizer confirming to BIS 9103:1999/ASTM C494 type F. Corrosion inhibitor used in this study is sodium nitrite based compound which can inhibit the corrosion rate. The laboratory grade nano-titania and nano-calcium carbonate (Merck, Germany) were purchased from the market with a size of 400-500 nm and subjected to ball milling to break down its size up to 100-120 nm. The ball milled samples were characterized with a Scanning Electron Microscope (Nano-eye Desktop Mini SEM, Korea) to confirm the size and distribution of the particles.

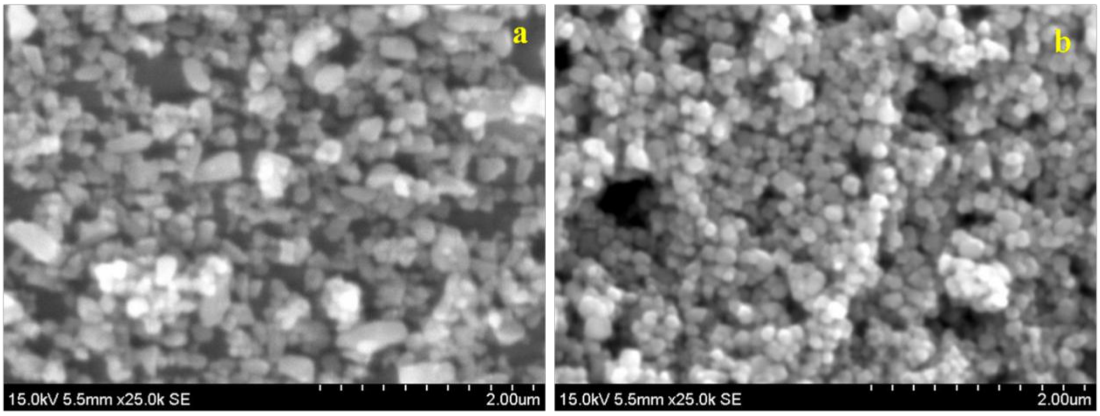

Figure 1: SEM images of (a) nano-$CaCO_3$ (b) nano-TiO_2

2.2 MIX DESIGN AND PROPORTIONING

The mix proportion for HPC was designed based on the recommendations given in IS 10262: 2009. Four different mixes of concrete of M45 grade were prepared and designated as Control concrete (CC), Flyash concrete (CF), Flyash concrete with addition of 1% TiO_2 and 1% $CaCO_3$ nanoparticles (CFN) and Flyash concrete with addition of 1% TiO_2, 1% $CaCO_3$ nanoparticles and admixed with 2% sodium nitrite based corrosion inhibitor (CFNI). The mix design details are given in the table 1 below. The FANI mix had a reduced w/c ratio of 0.32 confirming to the requirements of high performance concrete.

2.3 PREPARATION OF TEST SPECIMENS

The concrete designed for high performance concrete requires proper selection of materials, optimum dosage, mixing, compaction and curing to achieve homogenous mixing. Initially cementitious materials such as cement and fly ash were thoroughly mixed with water in a concrete mixer machine and subsequently fine and coarse aggregates were added into it and allowed to mix for 3-5 minutes. The nanoparticles were mixed with 70% of total water content using a handheld mixer for one minute and the remaining 30% of water was mixed with superplasticizer and added in the later stage to disperse the agglomerates. Slumps of the fresh concrete were determined immediately to assess the workability. The concrete was mixed thoroughly and then placed in the standard moulds. The specimens were cast as per the procedure laid in IS 516 and thereafter cured for 28 days in a laboratory curing tank filled with water at room temperature.

Table 1. Mix proportion of concrete

Nomenclature	Materials								
	Cement (kg/m^3)	Fly Ash (kg/m^3)	F.A (kg/m^3)	C.A (kg/m^3)	Water (kg/m^3)	SP (kg/m^3)	TiO_2 (kg/m^3)	$CaCO_3$ (kg/m^3)	SN (kg/m^3)
CC	450	-	797	1090	162	3.6	-	-	-
CF	270	180	744	1017	166	4.5	-	-	-
CFN	270	180	733	1010	166	5.4	4.5	4.5	-
CFNI	261	180	724	1003	144	5.4	4.5	4.5	9.0

2.4 TESTING OF CONCRETE SPECIMENS

Compressive strength test was carried out as per BIS: 516(Method of test for strength of concrete) on concrete cubes of size 100 mm at the age of 7 and 28 days of the specimens. The test was conducted in a 3000kN capacity digital compressive testing machine. Totally 24 cubes were subjected to compression test. The evaluation of split tensile strength was carried out as per BIS 5816 (Method of Test for Split tensile strength of concrete) on cylindrical specimens of 150 mm diameter and 300 mm height after 28 days of aging. Totally 9 cylinders were subjected to split tensile strength test using a 150 tones compression testing machine. The flexure strength test was conducted in accordance with BIS 519(Method of test for Flexure strength of concrete) on a normal standard specimen of size 100 x 100 x 500 mm using a Universal Testing Machine of 40 tones capacity at two point loading condition. A total of 9 beams were used for flexure testing.

Durability properties of the HPC were ascertained using the Rapid Chloride Penetration Test (RCPT), water absorption test and the water sorptivity test. RCPT was conducted as per ASTM C1202 by monitoring the amount of electrical current that passes through the sliced cylindrical core sample of 50 mm thickness and 100 mm diameter in 6 hours. The characteristics of the pore structure of the concrete were determined using a simple water absorption test on standard test specimens as per ASTM-C642-81. The tendency of the concrete to absorb and transmit water by capillary action was evaluated using water sorptivity test as per ASTM C1585 – 13. Both the tests were conducted on test specimens of size 100 mm diameter and 50 mm height. The surface topography of the fractured surface of the concrete specimens was investigated using SEM.

3.0 RESULTS AND DISCUSSIONS

3.1 Compressive Strength of Concrete

The observations on the compressive strength of the concrete specimens after 7 and 28 days of curing in fresh water are listed in table 2. It can be observed that a significant increase in strength was attained for CC concrete specimens when compared to CF and CFN mixes at the age of 7 days. However, for CFNI specimens the strength was comparable to that of the control concrete mix. For CC and CFNI mix, almost 65% of target strength was attained in the early age whereas for CF and CFN mix, only 40% of strength was attained in their early age. It is also observed that for CC specimens, expected target mean strength of about 53.25 MPa was attained at the end of 28 days curing period. For CF and CFN specimens, a little reduction in the target mean compressive strength was observed when compared to CC and CFNI mix. But, for CFNI concrete specimens, the obtained compressive strength was more than that of the CC control specimens. Figure 2 shows the comparison of compressive strength results for the curing period of 7 and 28 days.

Table 2. Compressive Strength at the age of 7 days and 28 days

Sl.No	Type Of Mix	7 days compressive strength (MPa)	28 days compressive strength (MPa)
1	CC	34.7	53.5
2	CF	21.9	49.5
3	CFN	29.3	50.5
4	CFNI	33.5	55.6

3.2 SPLIT TENSILE STRENGTH TEST

The observations on split tensile strength of concrete after the curing age of 28 days are shown in table 3. It is inferred from the results that for CC concrete specimens, the ultimate tensile strength was found to be 2.51 MPa whereas for CF and CFN specimens the obtained tensile strength was found to be 2.5 and 2.55 MPa. Out of all the four mixes, maximum tensile strength was obtained for CFNI specimen reaching up to 2.62 MPa. The above results indicate that there is a marginal increase in the tensile strength of concrete in all fly ash mixes compared to control mix and the maximum strength was observed for CFNI specimen. The figure 2 shown below compares the split tensile strength and compressive strength of the four concrete mixes for a curing period of 7 days and 28 days.

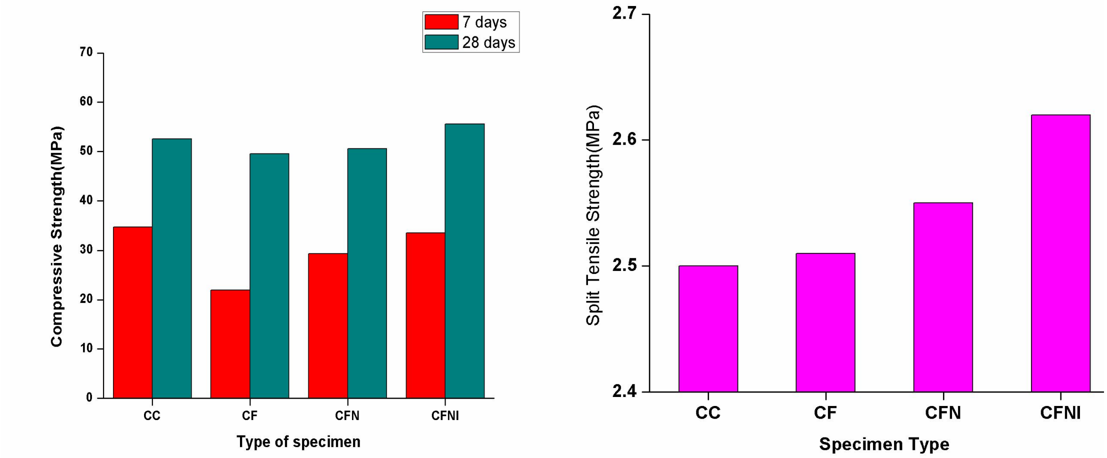

Figure 2: Compressive strength and split tensile strength of concrete specimens

3.3 FLEXURAL STRENGTH OF CONCRETE

Beam specimens of size 500 x 100 x 100 mm were subjected to two point loading using a Universal Testing Machine and loaded upto failure. All cracks were developed in the middle third region which indicates that the specimen undergoes pure bending during testing. No shear cracks were developed in any specimens. Table 3 summarizes the observations on flexural strength test on different concrete specimens. It is observed from the results that for CC concrete specimens, the modulus of rupture value was found to be 8.96 MPa whereas for CF and CFN specimens the flexural strength was found to be 9.27 and 9.51 MPa respectively. For CFNI mix, the flexural strength was observed as 9.71 MPa. The above results indicate that for flexural strength also, there is a gradual increase observed in all fly ash mixes compared to control mix and the maximum strength was obtained for CFNI specimen.

Table 3. Flexural Strength at the age of 28 days

Sl.No	Type of Mix	Ultimate Load (kN)	Crack Length (cm)	Ultimate Strength (MPa)
1	CC	16.10	19.5	8.96
2	CF	16.10	19.8	9.27

3	CFN	16.85	20.4	9.51
4	CFNI	17.9	18.8	9.71

3.4 RAPID CHLORIDE PENETRATION TEST

Figure 3 shows the observations of the Rapid Chloride Penetration Test for the four different concrete mixes. The CC control mix has a current value of 1033 coulombs and for the other three mixes the observed values were 559, 433 and 303 coulombs respectively. As per ASTM C1202, the chloride ion permeability in CC control mix comes under the low category and for all three fly ash mixes the permeability was found to be very low. CFNI mix showed an excellent result having least value among all the mixes.

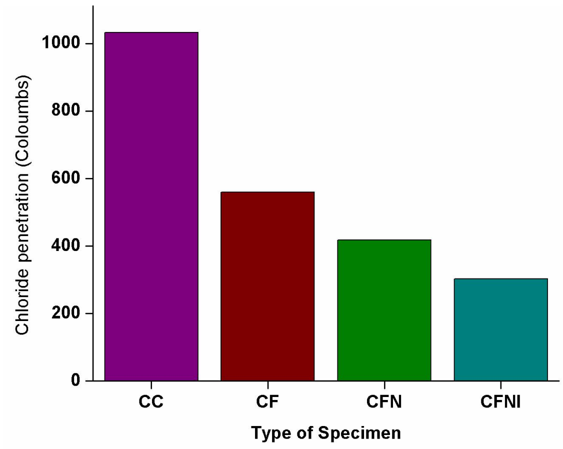

Figure 3: RCPT values of the concrete specimens

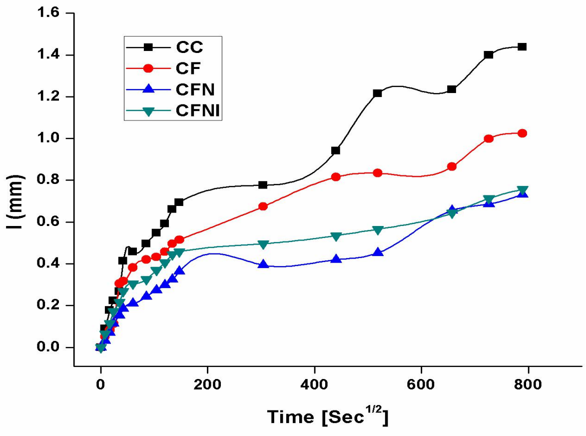

Figure 4: Absorption, I for all specimens

3.5 WATER SORPTIVITY TEST

The water sorptivity test was conducted on all the different concrete mixes at different time intervals for 7 days. It is observed that the water absorbed through capillary action in all fly ash concrete mixes was found to be marginally lesser than control mix in which the least value was observed for nanophase modified mixes. This indicates that the addition of fly ash and nanomaterials enhance the density of concrete by occupying all the minor pores present in the interfacial transition zone. The figure 4 shown above is the interaction curve obtained by plotting the absorption values of various mixes at different time intervals.

3.6 WATER ABSORPTION TEST

The percentage increase in weight of various concrete mixes measured for 6 hours continuously at various time intervals and measured after 24 hours are presented in figure 5. When the concrete or mortar specimens are immersed in water for a longer period, as time passes the water is absorbed by the concrete or mortar thereby gradually increasing its weight It is observed from the study that the process of absorption continues to happen for a particular period of time say 8 hours or so and thereafter the weight of the specimens remain unchanged. The results of the test shows that the water absorbed in the all fly ash concrete specimens were found to be lesser than control specimens among which CFN and CFNI showed excellent results. This indicates that partial replacement of cement with fly ash consistently improves the density of the concrete and addition of nanomaterials and inhibitor in the same mix further densifies the concrete by occupying the remaining pores in it.

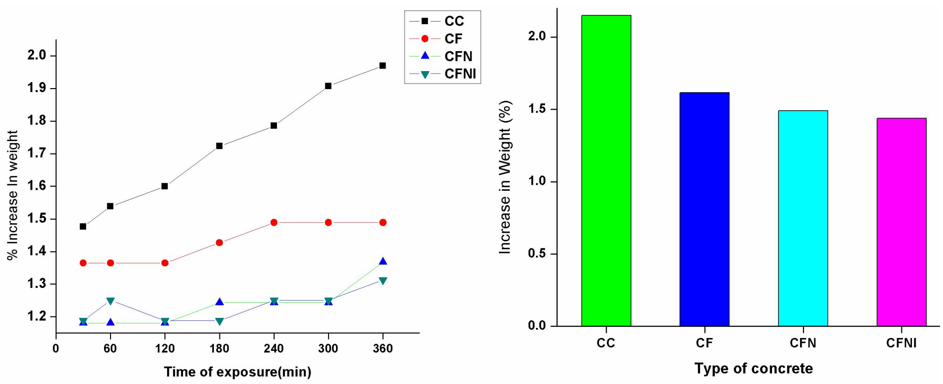

Figure 5: Percentage increase in weight observed for different time intervals and after 24 h

3.7 SCANNING ELECTRON MICROSCOPY ANALYSIS

Figure 6. Shows the micrographs of various concrete mixes taken using a scanning electron microscope. On looking at microscopic level, it can be clearly inferred that CFN and CFNI mixes have a dense homogeneous structure. The addition of nanoparticles and inhibitor to the concrete

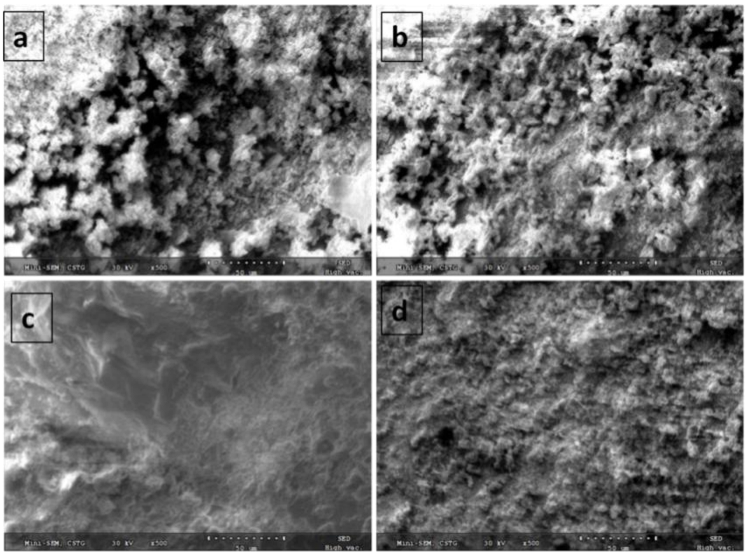

Figure 6: Micrographs of different concrete mixes after 28 days a) CC b) CF c) CFN d) CFNI

has greatly reduced the pore structure of the concrete. This is the reason for the superior mechanical and durability characteristics of the nanophase modified flyash concrete specimens when compared to control concrete.

4.0 CONCLUSIONS

- The addition of flyash, nanoparticles and inhibitor to conventional concrete has greatly enhanced its properties. Among all the different mixes, inhibitor admixed concrete mix (CFNI) has emerged as the superior one.

- Water/cement ratio was reduced to 0.32 which clearly indicates that SN inhibitor not only mitigates the corrosion rate but also acts a superplasticizer by reducing the water content.

- The compressive strength, split tensile and flexural strength of CFNI mix were found to be higher than control mix.

- RCPT results obtained for various mixes highlights that all fly ash mixes have very low permeability property compared to control mix among which CFNI mix showed an excellent resistance indicating that the corrosion inhibitor added in the mix mitigates the corrosion process.

- Water absorption and water sorptivity results shows that the amount of water absorbed in CFNI mix is found to have lesser value compared to other mixes showing its improved resistance to permeability.

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