ISSN 0974-5904, Volume 10, No. 01

DOI:10.21276/ijee.2017.10.0102

International Journal of Earth Sciences and Engineering

www.cafetinnova.org

February 2017, P.P.05-10

Effects of Nanomaterial on Concrete

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Abstract: *Nanotechnology has made a vast progress in the field of construction as it has improved the characteristics of concrete such as mechanical properties and resistance to acidic and chloride attack. Nanotechnology is the use of nano sized particle of material to create a new material with improved properties. This experimental research compares the mechanical properties and durability of different nanomaterial concrete. Nanomaterial can be defined as those physical substances with at least one dimension between 1-150 nanometers. The nanomaterial properties can be very different from the properties of the same materials at micro or macro scale. Nanomaterial provides an exceptional surface area to volume ratio and changes the basic property and reactivity of the material. This in turn enhances the mechanical properties and durability of concrete. The effects of nano silica and nano alumina on M60 high performance concrete were discussed in this paper. The cement was replaced with 40% ground granulated blast furnace slag and different percentage of nanomaterial like 2% to 5% for preparing the concrete. Mechanical Properties like compressive strength, split tensile strength and flexural strength of these nanomaterial concrete were compared. Accelerated corrosion test in saline and acidic conditions was conducted to check the durability of concrete. From these test results the best nanomaterial concrete was determined.*

Keywords: *Nanotechnology, Nanomaterial, Nano Silica, Nano Alumina, Accelerated Corrosion Test*

1. Introduction

There has been a lot of development in the field of nanotechnology in the recent past years. The research in nanotechnology has introduced a new aspect in the field of science and technology. The properties of nanomaterial in concrete have not been completely explored and still there is a scope of research in the chemical reactivity of nanomaterial with concrete. The main reason for the use of nanomaterial in concrete is because of its higher surface area to volume ratio. The nano sized particle fills the interfacial transition zone which is present between the cement and aggregate. The nanomaterial densifies the cement matrix by increasing the C-S-H gel during the pozzolanic reaction of these materials with calcium hydroxide. A proper usage of nanomaterial with concrete leads to a new material with entirely different enhanced properties.

Nowadays the usage of cement in concrete is reduced due to the higher CO_2 emission from the cement producing industries. Many new materials have been introduced to partially replace cement and to attain better properties than ordinary Portland cement. In this experimental research the cement is replaced with ground granulated blast furnace slag (GGBS) and nanomaterial. GGBS was used because it mainly improves the pore structure of concrete and increases the impermeability to the external agencies. Moreover it attains mechanical properties much faster than Fly Ash and can be replaced for higher percentage of cement.

In this research, we focus on nano silica and nano alumina and compare their properties and chemical reactivity when used in concrete. According to M.S. Shetty et al. [18] silica and alumina are present in ordinary Portland cement at a percentage of 17-25 and 3-8 percentage respectively. These components are responsible for the higher heat of hydration and gain in early strength in concrete. Hence the incorporation of these materials in nano size in concrete was used for comparison. All these nanomaterials are used by replacing small percentage of cement from 2% to 5%.

This paper compares the results of mechanical properties, ultra-sonic pulse velocity (UPV) and durability by accelerated corrosion test in saline and acidic conditions of nanomaterial concrete.

2. Literature Review:

According to Said et al. [1] the permeability reduces with the addition of nano silica. They found that the overall performance of concrete with or without fly ash was significantly improved with the addition of variable dosage of nano silica. They concluded that nano silica led to significant consumption of portlandite (CH) in the pozzolanic reaction. On the other hand Shekari et al. [2] observed an improvement in the mechanical properties of high performance concrete by incorporating nano alumina in concrete. Nazari et al. [3] determined that nano titanium oxide act as nanofillers and improves the pore structure of self-compacting concrete. They also found that there is an increase in the compressive strength, split tensile strength and flexural strength of self-compacting concrete at a particular dosage and afterwards it

Received: July 31, 2016; Accepted: November 08, 2016; Published: February 22, 2017
International Journal of Earth Sciences and Engineering, 10(01), 05-10, 2017, DOI:10.21276/ijee.2017.10.0102

decreases. Bhuvaneshwari et al. [4] achieved improvement in mechanical properties of concrete by incorporating nano oxides. They observed that there is a delay in setting time of concrete when nano particles are blended in concrete. They further observed that nano oxides increases the density, reduces porosity and improves the bond between cement matrix and aggregate. Flores-Vivan et al. [5] found that the best performance was demonstrated with ground fly ash, 2% nano silica and 1.5% superplasticizer.

3. Experimental Program:

3.1 Materials

53 grade Ordinary Portland Cement was used in this experimental research. M60 grade high performance concrete was adopted in this experiment. GGBS was used as partial replacement of cement. It was found that 40% GGBS was giving better mechanical properties compared to other percentage of replacement. Moreover higher percentage of GGBS may lead to segregation. 12.5mm coarse aggregate was used. The fine aggregate used confirms to Zone 2. The superplasticizer used belongs to polycarboxylate ether based family. The nano oxides used are nano silica (SiO_2) and nano alumina (Al_2O_3). The physical properties of these nano oxides are shown in Table 1 and chemical compositions of nano SiO_2 and nano Al_2O_3 are shown in Table 2 and Table 3 respectively.

Table 1: *Physical Properties of Nanomaterials*

Properties	**Nano SiO_2**	**Nano Al_2O_3**
Morphology	Porous	Spherical
Color	White	White
Purity	99.5%	99.5%
Particle Size	50-80 nm	30-50 nm
Specific Gravity	2.1	3.9

Table 2: *Chemical Compositions of Nano SiO_2*

SiO_2	Al	Fe	Mg	Ca
> 99.5%	< 0.02%	< 0.05%	< 0.1%	<0.08%

Table 3: *Chemical Compositions of Nano Al_2O_3*

Al_2O_3	CaO	Fe_2O_3	MgO	SiO_2
>99.5%	<0.017%	<0.035%	<0.001%	<0.05%

3.2 Procedure

The materials for preparing the concrete were mixed properly in a pan mixer. The coarse aggregate used for the mix was thoroughly sieved and was in saturated surface dry condition. The nanomaterial used was in powder form. The superplasticizer and nanomaterial was thoroughly mixed in water by using a stirrer for 5 minutes. The nanomaterial was mixed along with superplasticizer to avoid the chances of agglomeration. The superplasticizer induces electrostatic dispersion and reduces the chances of agglomeration. First the coarse aggregate was fed into the pan mixer. Small quantity of water was poured and the aggregate was mixed until it was completely wet. Before pouring the water with superplasticizer and nanomaterial each time into the mix, it should be stirred properly. Next the binding materials (cement and GGBS) were introduced into the mixer and again a little quantity of water was poured. The mixing was done until the binding material was coated properly on to the coarse aggregate. The binding material coated aggregate was wetted with water and thoroughly sieved dry fine aggregate was fed into the mixer machine. After 2 minutes of mixing the remaining water with superplasticizer and nanomaterial was stirred and poured into the pan mixer. The mixing was done until a homogeneous mixture of concrete was obtained.

A total of 10 mixes were prepared for the tests. The first one was a control mix, in second mix the cement was replaced by 40 % GGBS and in rest of the mix it was replaced by 40% GGBS and 2% to 5% nano silica (SiO_2) and nano alumina (Al_2O_3). For each mixes 6 cubes, 3 cylinders and 3 prisms were made. 6 cylinders with steel rebar were made for corrosion test for control mix, 40% GGBS and for optimum dosage of two nanomaterials.

3.3 Tests conducted on Specimens

3.3.1 Destructive Tests

The cubes cast for the compressive test were of 100x100x100 mm. The cylinders made for split tensile test were of 100mm diameter and 200mm height. The prisms cast for flexural test were of 500x100x100 mm. The cubes were tested for 7 days and 28 days compressive strength. The split tensile test and flexural test was conducted for 28 days.

3.3.2 Non-Destructive Tests

Apart from destructive tests a non-destructive test was performed. Ultra-Sonic Pulse velocity test (UPV) was conducted to know the quality of concrete. The UPV test was done on the cubes. The test was done as per IS 13311 (Part 1): 1992 and the results of different nanomaterial concrete were compared.

3.3.3 Durability Tests

The durability test conducted in this research was accelerated corrosion test. The specimen used for these test were concrete cylinders of 100mm diameter and 200mm height. The cylinders consist of a 12mm diameter and 200mm height Fe415 steel rebar embedded in it. The initial weight of the steel rebar was taken before placing it in the concrete cylinder. The steel rebar was placed at the center of the cylinder. A cover of 50mm was provided at the bottom of the cylinder. The steel rebar projects 50mm out of the concrete cylinder. 6 cylinders were cast for 4 mixes as mentioned before. The cylinders were cured for 28 days. The cured cylinders were transferred to the solution of accelerated corrosion setup. 3 cylinders were tested in 5% NaCl solution and 3 cylinders were tested in 5% H_2SO_4 solution.

The corrosion test was carried out for 1 week. Figure 1 shows the acceleration corrosion setup in 5% NaCl and 5% H_2SO_4 solution. The corrosion was carried out using an AC-DC convertor of 5A and 24V.

Fig.1. *Accelerated Corrosion of Cylinders*

The positive terminal of the AC-DC convertor was connected to the steel rebar of the cylinder and the negative terminal was connected to the steel rod dipped in the solution as shown in Figure 1. The first row of buckets consists of 5% NaCl solution and the second row of buckets consists of 5% H_2SO_4 solution. The setup was kept undisturbed for 1 week. After 1 week the cylinders were taken out and the steel rebar was taken out of the cylinders by breaking it. The final weight of the rebar was taken after cleaning the bar properly with emery paper and distilled water. There will be a weight loss due to corrosion in the bar. According to ASTM G1-03 the corrosion rate can be calculated from weight loss by using the below given formula.

$$CR = 3.45 \times 10^{6} W/DAT \quad (1)$$

Where, CR – Corrosion Rate in mpy
W – Weight Loss in g
D – Density of Steel in g/cm^2
A – Area of steel plate in cm^2
T – Duration of corrosion in hours

The pH of the saline and acidic solution before corrosion and after corrosion has been taken to notice the reaction of nanomaterial concrete with these solutions.

4. Results and Discussions:

Table 4 shows the test result for destructive tests such as compressive strength for 7 and 28 days, split tensile strength and flexural strength for 28 days and non-destructive test such as UPV which was conducted on 100x100x100mm cubes cured for 28 days. CM indicates control mix of M60 grade concrete and CMG stands for 40% replacement of cement with GGBS. Concrete with nano silica (CNS) and concrete with nano alumina (CNA) for 2% to 5% replacement of cement and 40% replacement of cement with GGBS are shown in Table 4.

From Table 4 it can be seen that the compressive strength of CMG for 7 days has increased by 23.46% than CM and it has been increased by 4.78% for 28 days. This shows that the initial rate of hydration is increased by addition of GGBS.

The optimum dosage of nano SiO_2 and nano Al_2O_3 is at 3% i.e. CNS3 and CNA3 respectively. From Fig.2, Fig.3, Fig.4 and Fig.5 it can be observed that the compressive strength, split tensile strength and flexural strength is giving the same optimum dosages. From Table 4 and Fig.3 it can be deduced that the compressive strength of CNS3 for 28 days has increased by 24.25% than CMG and 30.18% than CM whereas compressive strength of CNA3 for 28 days has increased by 17.06% than CMG and 22.65% than CM. Therefore it can be clearly stated that CNS3 gives the maximum percentage of increase in compressive strength, split tensile strength and flexural strength when compared to CMG and CM than CNA3. The high mechanical property of nano SiO_2 is due to the increase in the quantity of C-S-H gel in the paste through pozzolanic reaction, increase in initial hydration rate, reduction of porosity and improvement in mechanical property of C-S-H gel itself.

The UPV velocity criterion for concrete quality grading is based on IS: 13311 – Part 1. From Table 4 it can be observed that CNS3 have the maximum velocity. This is contributed to the dense packing of CNS3 due to which the ultrasonic pulse can pass through the cube with high velocity. It can also be noticed that for all nanomaterial concrete the quality grading is good. Hence nanomaterial when mixed along with concrete results in less porous and impermeable concrete.

The decrease in mechanical properties after the optimum dosage is mainly due to the excess quantity of nanomaterial present in the concrete than the quantity which is required for combining with liberated lime produced during hydration and therefore the excess silica leaches out leading to the decrease in strength of concrete.

Table 5 shows the result for accelerated corrosion of the cylinders. The corrosion rate was measured using weight loss method and using the formula (1). The table also shows the pH of the solution before and after the corrosion process. The accelerated corrosion tests were conducted for 4 mixes as shown in the table. The optimum dosage of two nanomaterial concrete was taken for the corrosion test to determine the most durable concrete among the two. From Table 5 it can be observed that more corrosion takes place in saline condition i.e. 5% NaCl solution than in acidic condition i.e. 5% H_2SO_4. The corrosion rate of CNS3 has decreased by 64.31% than CM and 50.07% than CMG whereas for CNA3 it has been decreased by 60.66% and 44.97% than CM and CMG respectively in 5% NaCl solution. In 5% H_2SO_4 solution the corrosion rate of CNS3 has decreased by 50.19% and 42.91% than CM and CMG respectively and for

CNA3 it has been decreased by 37.46% and 28.32% than CM and CMG respectively. Therefore CNS3 shows less corrosion rate compared to CNA3 in saline as well as in acidic conditions as shown in Table 5. The less corrosion rate of CNS3 in saline and acidic conditions can be mainly due to the dense packing of the concrete, reduction in porosity and increase in impermeability of concrete. The pH of water used for curing the concrete cylinders for corrosion was 7.9. From table 5 it is clear that there is a drastic variation in pH before and after 7 days corrosion in 5% NaCl solution whereas there is only a slight variation in pH before and after 7 days in 5% H_2SO_4 solution. Due to this high variation in pH of saline solution before and after the corrosion, the corrosion rate of specimen in saline solution is greater than in acidic solution. Again from Table 5 it can be observed that higher the difference between pH before and after corrosion of saline and acidic solution, greater will be its corrosion rate. The corrosion rate depends upon the high solubility of oxygen and high conductivity of the solution used for corrosion.

Table 4: *Destructive and Non-destructive Tests Results*

Specimen	Compressive Strength (MPa)		Split Tensile Strength (MPa)	Flexural Strength (MPa)	UPV (28 Days)	
	7 Days	28 Days	28 Days	28 Days	Velocity(km/s)	Quality
CM	38.15	61.76	3.20	8.20	3.7	Good
CMG	47.10	64.71	3.50	9.00	4.3	Good
CNS2	51.20	72.60	3.82	10.50	4.1	Good
CNS3	56.80	80.40	4.36	12.50	4.6	Excellent
CNS4	53.60	77.30	4.23	12.13	4.1	Good
CNS5	52.40	75.21	4.02	11.00	4.0	Good
CNA2	48.80	71.40	3.62	9.50	3.8	Good
CNA3	52.20	75.75	3.98	10.13	4.0	Good
CNA4	50.20	73.10	3.80	10.00	4.0	Good
CNA5	49.90	72.30	3.75	9.75	3.9	Good

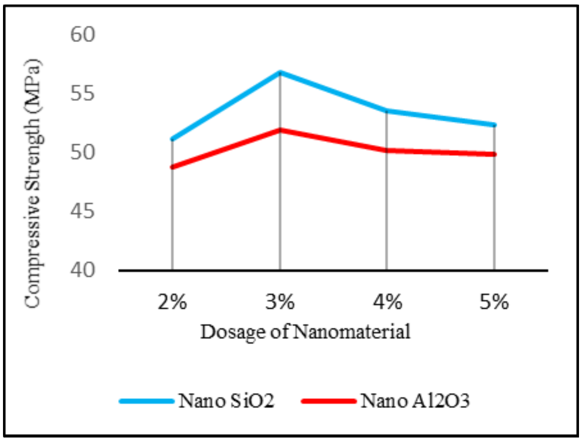

Fig.2. *7 Days Compressive Strength of Nanomaterial Concrete*

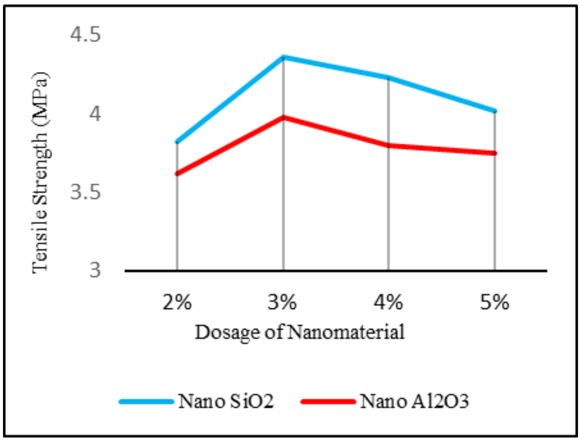

Fig.4. *28 Days Tensile Strength of Nanomaterial Concrete*

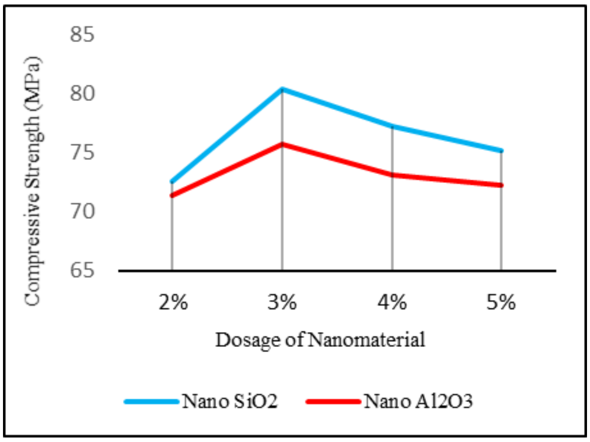

Fig.3. *28 Days Compressive Strength of Nanomaterial Concrete*

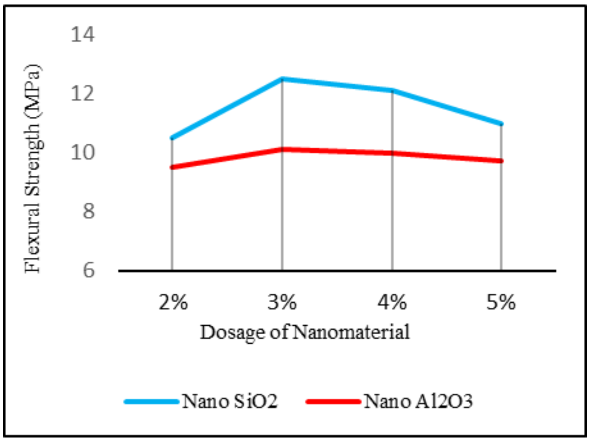

Fig.5. *28 Days Flexural Strength of Nanomaterial Concrete*

In Fig 6, pores can be noticed in CMG which results in low strength and less durable concrete as shown in Table 4 and Table 5 respectively. From Fig 7 it can be clearly observed that the nanomaterial fills the pores present in between cement and aggregate and makes it tightly packed causing it to be less porous which results in better mechanical properties and better durability.

Table 5: *Accelerated Corrosion Test Results for 5% NaCl and 5% H_2SO_4 solution*

Solution	Specimen	Weight Loss (gms)	Corrosion Rate (mpy)	pH of solution before corrosion	pH of solution after corrosion
5% NaCl	CM	9.33	313.89	8.4	11.8
	CMG	6.67	224.39	8.4	11.6
	CNS3	3.33	112.03	8.4	11.5
	CNA3	3.67	123.47	8.4	11.5
5% H_2SO_4	CM	2.67	89.83	0.2	1.5
	CMG	2.33	78.38	0.2	1.2
	CNS3	1.33	44.74	0.2	0.6
	CNA3	1.67	56.18	0.2	0.6

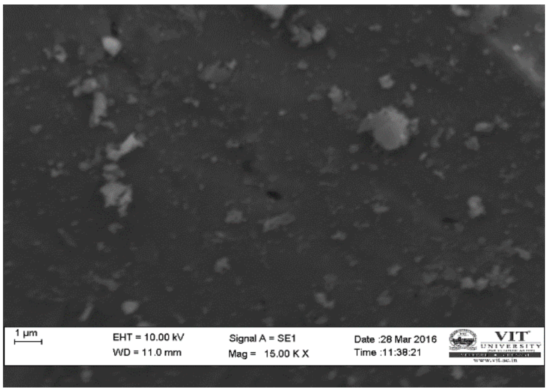

Fig.6. *SEM of CMG*

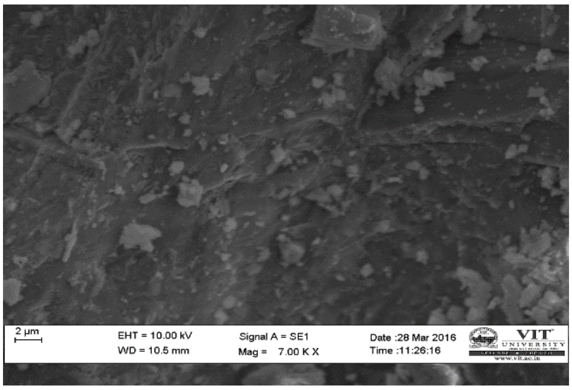

Fig.7. *SEM of CNS3*

5. Conclusion:

From all of the above results it can be concluded that CNS3 is having better mechanical properties than CNA3 and CNS3 is also more durable compared to CNA3. When 3% of cement is replaced with nano SiO_2 there is a significant change in the early interfacial transition zone structure. Moreover there is a decrease of CH content due to the presence of nano SiO_2. Nano Al_2O_3 is having less mechanical properties compared to nano SiO_2 but the corrosion rate of nano Al_2O_3 is near to that of nano SiO_2. This is due to the almost same particle size of nano SiO_2 and nano Al_2O_3 as shown in Table 1. Therefore nano SiO_2 is preferred over nano Al_2O_3 for construction of concrete structures exposed to sea water and structures susceptible to chemical attack like those near chemical factories.

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