DURABILITY AND PORE STRUCTURE ANALYSIS OF HIGH PERFORMANCE CONCRETE WITH NANO SILICA

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When extra water in concrete evaporates, it leaves voids in the concrete element developing capillaries, which might be directly related to the porosity and permeability of concrete. By proper selection of components, and mix proportioning and following right construction practices, an almost impervious concrete can be obtained. The pores in cement paste consist of gel pores and capillary pores. The pores in concrete, because of incomplete compaction, are voids of large size which provide a honeycomb shape leading to concrete of low strength. In order to reduce the porosity, cement is partially substituted with nano silica in percent by weight and strive is made to examine durability homes of concrete composite. Since the water absorption test measures the response of concrete to pressure, which is rarely the driving force of fluids entering concrete, there is a need for another type of test. This test should measure the rate of absorption of water by capillary suction, and sorptivity of unsaturated concrete. By use of 0 to 4 % addition of nano silica, there is a considerable reduction in capillary absorption and there is an increase in the compression strength and modulus of elasticity of the concrete. Micro analysis was carried out by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS), and the studies indicate that nano silica is uniformly distributed by improving microstructure of concrete.

Keywords: *Nano silica, TEM, SEM, EDS.*

1. Introduction

Nano technology has attracted considerable scientific interest due to the new potential uses of particles in the order of nanometer (10^{-9} m) scale. The nano scale-size particles can result in dramatically improved properties in comparison with conventional grain-size of materials with the same chemical composition [1]. At some stage in the period of the second half of the previous century, the phrases ‘‘nano-science’’ and ‘‘nano-technology’’ were not familiarly used as nowadays. But, they had been certainly practiced and efficaciously implemented to development in the area of fabric technology. [2, 3] The combination of fly ash and nano materials can tightly bond the hydration product, which is regarded as an important factor for accelerating the pozzolanic reaction as it leads to the increased early strength development [4]. Main driving force in the construction for invention or adoption new technologies is to make energy efficient structures with an increased service lifetime [5]. In general, lime stone, marble, chalk produced artificially are by combining, Chemically, the presence of nano SiO_2 articles increases the rate of reaction of tricalcium aluminate to form carboaluminate complex, thereby increasing the total hydration products and consequently strength [6]. In recent years, the usage of nano concrete has increased because of its enhanced properties such as improved mechanical strength and durability [7].

2. Experimental program

2.1 Materials and Methods

The cement used for the study included 53 grade Ordinary Portland Cement (OPC) tested as per IS 12269 – 1989 and properties as shown in Table 1. The preliminary test on cement was conducted according to IS: 4031-1988. River sand passing through a 4.75 mm IS sieve conforming to grading zone III of IS 383 - 1970 [8] was used. The physical properties of the fine aggregate were determined as per IS 2386-1963 code of practice for test method for aggregates. Crushed natural aggregate with a maximum size of 12.5mm was used as coarse aggregate. The physical properties of coarse aggregate were determined as per IS: 2386 -1963 code of practices for methods of test for aggregates. Fly ash was used as a pozzolanic material with replacement of cement in high performance concrete. Fly ash is derived from burning coal and is an additive that makes concrete stronger, more durable and easier to work with; it aids formation of cementations compounds to enhance strength, impermeability and durability of concrete. Scanning Electron Micrographs (SEM) image and TEM analysis of nano silica are shown in Figures 1, 2 and properties as shown in Table 1.

2.2 Preparation Sulphate Concentration

In this study, an experimental method was developed for the accelerated corrosion by a sulfate solution in a dry-wet cycle to study,

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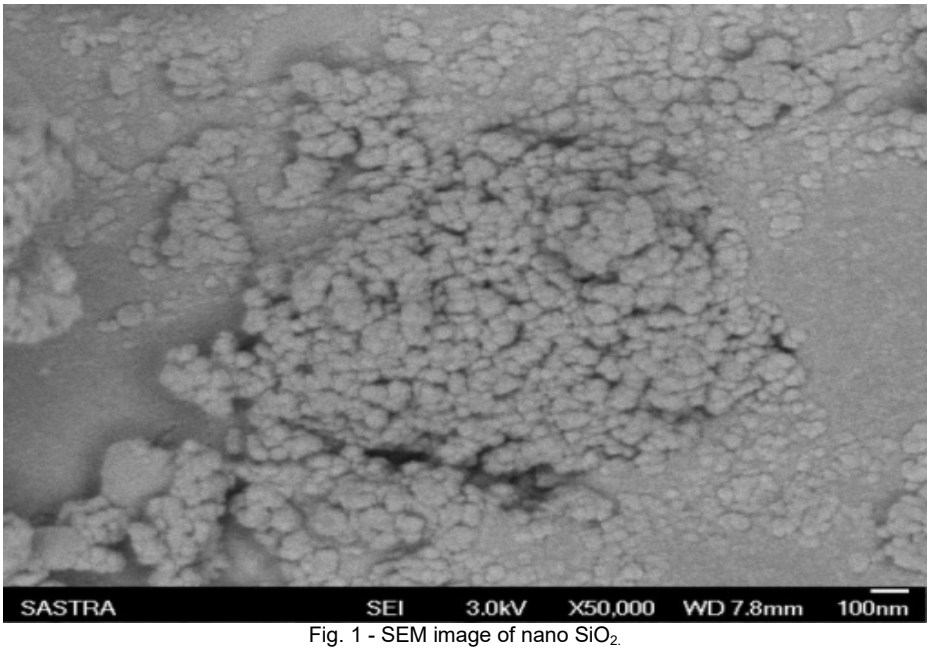

Fig. 1 - SEM image of nano SiO_2.

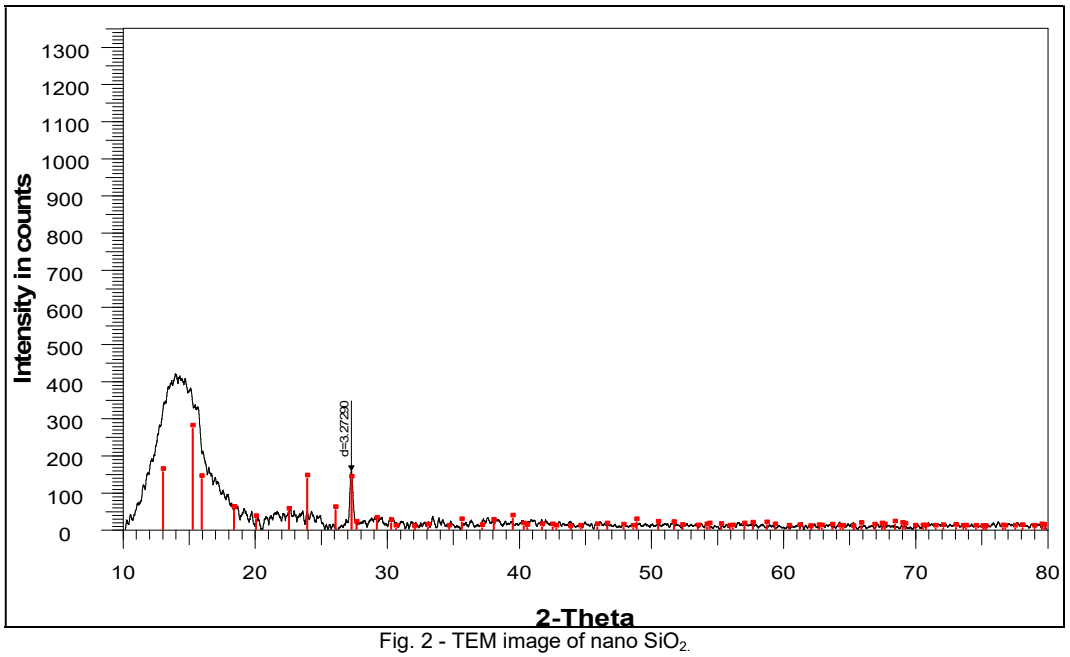

Fig. 2 - TEM image of nano SiO_2.

cylindrical concrete specimen of 100mm diameter by 50 mm height is subjected to a DC voltage of 70 v applied for 6.3 hours using the six cell apparatus arrangement. Reservoir one has 3.0% sodium chloride (NaCl) solution and the other a 0.3 M sodium hydroxide (NaOH) solution. The total charge passed is determined and used to rate the concrete.

2.3 Mix proportions and test specimens

For proportioning HPC mix, ACI 211 method modified by Aitcin, was used and the final mix proportion was obtained by trial and error with different combinations of materials. The experimental investigation consisted of casting and testing of 413 specimens for mechanical determinations and 17 specimens for micro analysis. The main variables considered in this study are four different percentages of nano silica added with volume fraction of cement. Mixing operation was continued till a good uniform and homogeneous concrete was obtained. During mixing, casting and compaction, it was observed that the nano silica is uniformly distributed. The well mixed concrete was then poured into moulds of cubes of size of 150x150x150 mm for compression testing and density of concrete, cylinders of size 150x300 mm for determination of the elasticity modulus. An external vibrator was used for compaction. For micro analysis, 17 prism specimens of size 20 x 20 x 50 mm were also cast and tested. The casting specimens and SEM sample are shown in Figures 3 and 4.

Fig. 3 - Casting of specimens.

Fig. 4 - SEM and EDS samples.

Table1

Chemical composition and Physical properties of cementitious materials

Items	Chemical compositions (%)		
	OPC	**Silica fume**	**Nano SiO_2**
SiO_2	22.0	90-96	99.9
Al_2O_3	6.6	0.5-3	-
Fe_2O_3	2.8	0.2-0.8	-
CaO	60.1	0.98	-
MgO	3.3	0.5-15	-
SO_3	2.1	0.1-2.5	-
LOI	2.6	0.7-2.5	0.1
Physical properties			
Specific gravity	3.1	2.34	-
Avg. particle size	13µm	0.1µm	15nm (TEM)
SSA(m^2/g)	0.38	20	60.08

2.4 Sorptivity determination

The durability test for the specimen was conducted by performing sorptivity. It is a measure of the capacity of the medium to absorb or desorb the is performed on cylindrical specimens of size 50 mm × 100 mm which were initial cured in water for 28 days. After that they were kept in water in a state such that by 1/10th of the height of the specimen was immersed in water. The amount of absorbed water depends on the characteristic of the concrete surface layer. Initial weight and final weight of the specimen after it was immersed in water for certain specified period of time are noted periodically. Finally the sorptivity of the tested specimens were calculated using the equation (1).

$$I = \frac{\Delta m}{a \times d} \quad \ldots\ldots\ldots (1)$$

Where, I = absorption
m= Change in specimen mass
a = Exposed area of specimen, in mm^2
d = density of water in g/mm^3

2.5 Porosity determination

ASTM standard procedure was employed to determine the porosity using 100 mm × 50 mm cylinder specimens. The specimens were dried in the oven at 105 ± 5ºC for 24 h to determine the oven-dry mass. In order to determine the saturated surface-dry mass in cold water saturation method, the specimens were simply immersed in cool water at approximately 21ºC for more than 48hr. During boiling water saturation, the specimens were impressed in a receptacle for 5 h and then allowed to cool for 19 hr to a final temperature of 20 - 25ºC. Now the apparent mass of the specimen in water was found by suspending it through a wire mesh with spring balance. The following equation is used to determine the porosity of the concrete specimens as per ASTM C642 [8].

Volume of permeable pore space (voids)
%= C-A / B-D x 100
Where,
A= mass of oven-dried sample in air;
B= mass of surface-dry sample in air after immersion;
C= mass of surface-dry sample in air after immersion and boiling;
D=apparent mass of sample in water after immersion and boiling.

3. Results and Discussion

3.1 Compressive Strength

It can be seen that the compressive strength of specimens with nano silica after 28 days and 90 days as shown in Figure 5, were higher than that of control concrete. The effectiveness of nano silica in enhancing the strength is increased with the increase of nano silica content. Replacement of cement with silica fume improved compressive strength up to 8.2% while replacement of the same amount of cement with nano silica improved compressive strength up to 44.3%.

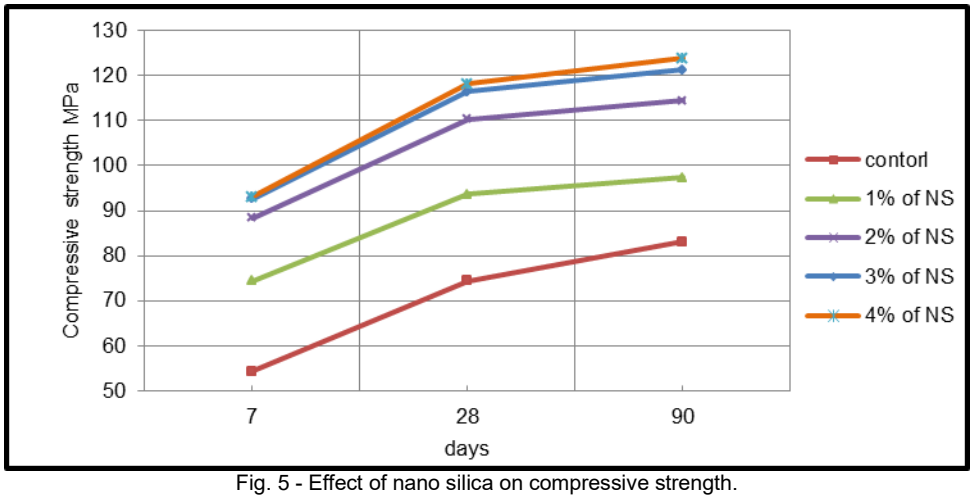

Fig. 5 - Effect of nano silica on compressive strength.

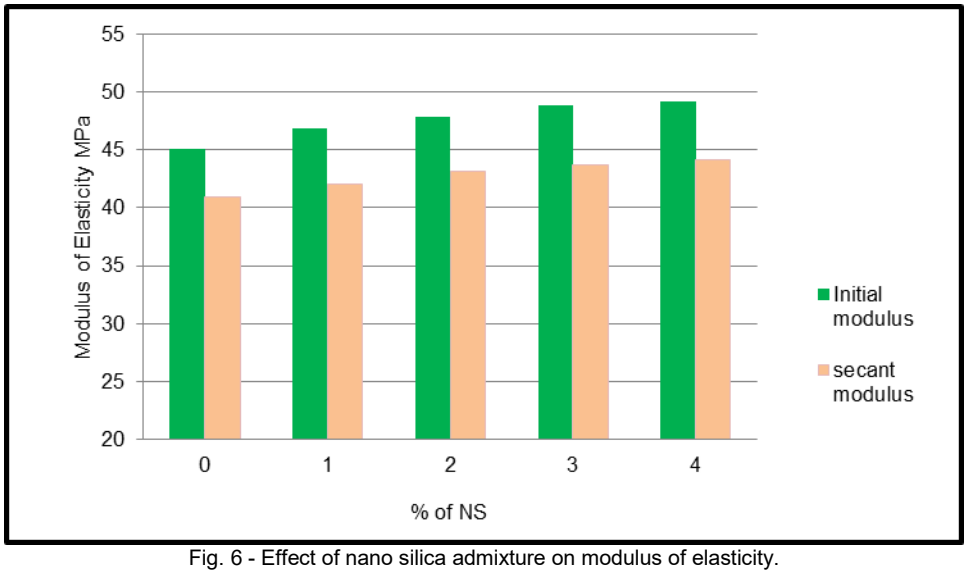

Fig. 6 - Effect of nano silica admixture on modulus of elasticity.

3.2 Modulus of elasticity

Replacement of cement with silica fume ensured modulus of elasticity improvement by 9.75%, 17.35% at 28 days and 90 days respectively while replacement of the same amount of cement with nano silica improved modulus by 20.13%, 31.74% at the same ages. Investigated and proved that the modulus of elasticity will increase to a certain percentage and then decrease as shown in Figure 6. This is due to the fact that concrete with nano material attains greater stiffness than concrete without nano material [9]. This value of stiffness is due to the compactness of the past bond with the aggregates. That mechanical strength will be greater for concrete with nano material than for that without nano material was specified.

3.3 Sorptivity

The results of sorptivity test for concrete are shown in Figure 7, depending on the distance from the upper surface of the element. The mean values of sorptivity for concrete with 4 % NS for concretes, which was tested after 28 and 90 days since the specimens were made, are shown in the figures dashed lines. Dependencies of sorptivity, measured on cores, on the distance x to element's upper surface, had been approximated with linear functions, where control concrete is a parameter approximately equivalent to concrete sorptivity on element's upper surface and coefficient is a measure of the intensity of sorptivity which decreases, Also the coefficients 'y' of correlation between the results of measurements and values of approximating functions that had been determined. Calculation results shown in Figure 8 present graph the correlation of experimentally obtained values with the ones calculated from the adjusted function dependency can be noticed for those particular series. The differences in the compressive strength of the core specimens of diameter and height equal to 65 mm, between the upper and lower layer of concrete amounted decrease 3.2% of series NS 4 %.

3.4 Adsorption of water

In Figure 8, permeability and porosity are considered. In order to analyze the changes in pore size, pore diameter are evaluated. Capillary pores which are closely related to mass transport

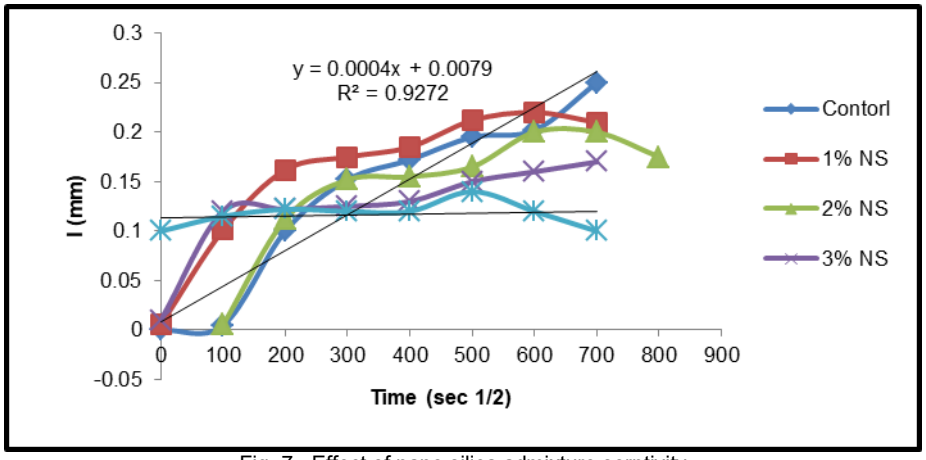

Fig. 7 - Effect of nano silica admixture sorptivity

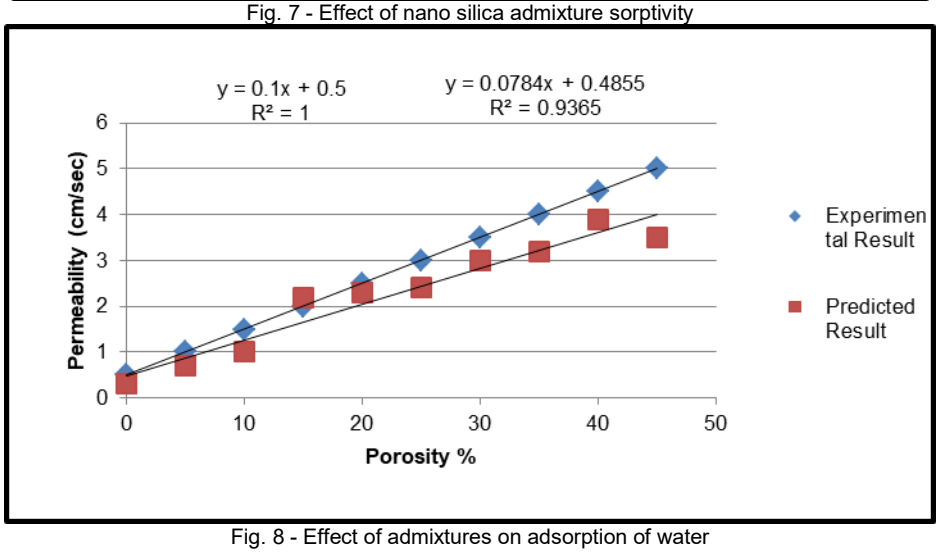

Fig. 8 - Effect of admixtures on adsorption of water

are reported to be within the size of 10^{-8} - 10^{-4} m, and the results from 0.25 to 0.1 ranges can cover this range. In each NS by volume of weight region, measured porosities are averaged as one value and they are compared with control concrete. By doing so, the changes in porosity with different % ratios can be easily evaluated. Analysis on durability characteristics in function of the porosity performed with control concrete may be practical but have no consideration of physical properties [10]. Total porosity measure through Mercury intrusion porosimetry (MIP) is normalized by the case of NS 4% and compared with normalized durability test results.

3.5 Microstructure and discussion

The Scanning Electron Microscope (SEM) Images can be used to study the ITZ are given in Figures 9, 11 and 13 and Energy Dispersive Spectroscopy (EDS) are shown in Figures 10, 12 and 14. This is seen in the topographical surface at 10 µm level at 4% of NS, smaller voids were visible but very little improvement was seen compared to the control specimen. When 2% of weight fraction of nano silica is present in specimen, more than 7 % void reduction was achieved at 10 µm level compared to the control specimen [11].

At the 10 µm level, a few additional silica atoms enter voids compared to the control specimen. The experimental results show that CSH gel hydrates hydration of C-H-S gel surface becomes denser than conventional concrete mix. Nano silica acts as filler and improving the physical structure, which will probably improves the paste aggregate bond. The positions of the peak are characteristic of particular element, so identification is made by examination of peak positions and relative intensities.

The microstructures of cement paste at the ITZ were captured by SEM, as seen in Figures 9, 11, and 13. The porous paste structures at ITZ in conversional concrete are shown in Figure 9, where crystalline CH, needle-shaped ettringite, and amorphous calcium–silicate–hydrates (C–S–H) can be clearly recognized. Among the solids, pores of varying sizes are also noticeable. In contrast, the pozzolanic reaction densified the microstructures by turning CH into secondary C–S–H, and produced a more homogeneous microstructure, as shown in Figure 11 and 13 No large pores were easily found. Therefore, it is expected that the mechanical and durable properties of concrete could be improved due to this densified ITZ, which is normally the weakest phase in concrete composites (compared to

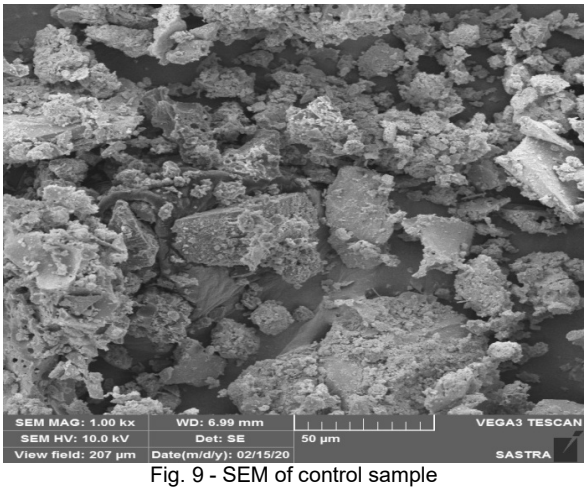

Fig. 9 - SEM of control sample

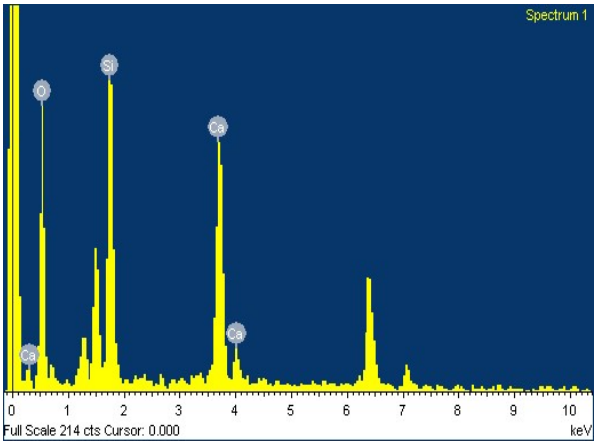

Fig. 10 - EDS of control sample

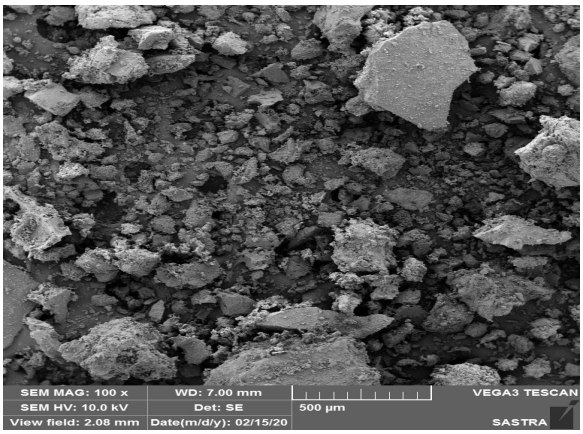

Fig. 11 - SEM of sample with 2% NS

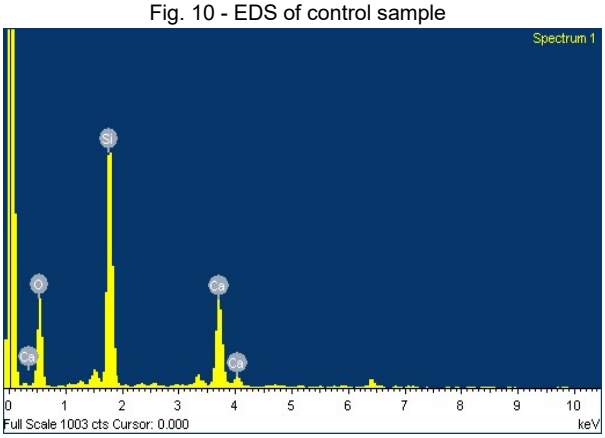

Fig. 12 - EDS of sample with 2% NS

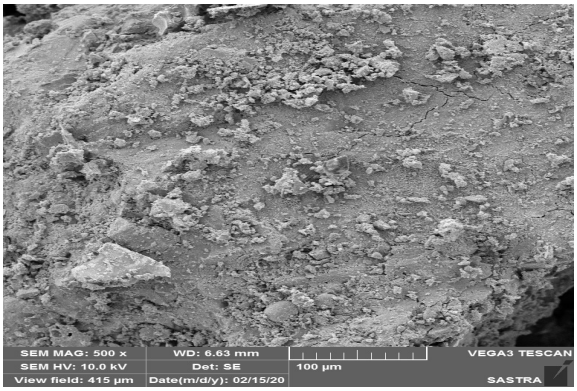

Fig. 13 - SEM sample with 4% NS

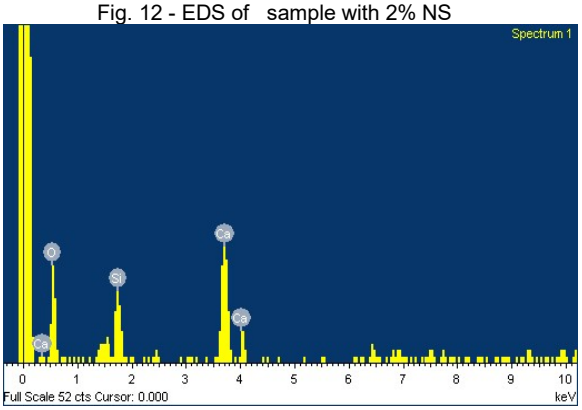

Fig. 14 - EDS Composition of 4% NS

aggregates and bulk paste). A second-order chemical reaction between penetrating sulfates consumed by reacting with calcium aluminates is considered. The general format of the equation is based on the formation of ettringite from an aluminate phase and the potential expansions associated with that. Three compounds may react with ingressing sulfates represented in the form of gypsum according to one of the following reactions represents the weighted average proportion of the aluminate phase taking part in the reaction, and NaOH represents the stoichiometric sulfate required for the reaction. It must be emphasized that no expansion occurs until the capillary pores are totally filled with ettringite.The effect of pore

Filling with ettringite will be addressed in subsequent sections [12]. The EDS analysis identifies the existence of sodium, aluminum, silicon, calcium and sulfur. According to the EDS results, it is supposed that these white blocky crystals are gypsum and mirabilite, and the fine granular crystals are thenardite, and the bar-like particles are ettringite. In the EDS image of conversional concrete sample in Figure 10, there are abundant white blocky crystals with the fine granular crystals on the surface, as well as the occurrence of fine cracks [13]. The SEM analysis, together with the EDS analysis, confirms that the white blocky crystals are gypsum and mirabilite, and the fine granular crystals are thenardite.

Low Al peak in the EDS image signifies the little amount of ettringite.

Figures 12 and 14 show the EDS images for the conversional and 4% of NS sample. There are large quantities of needle-like crystals, as well as some white crystals with the fine granular particles on the surface. According to the SEM and EDS analysis, these needle-like crystals are ettringite, and the white crystals are gypsum and mirabilite, and the fine granular particles are thenardite [14]. This produces various corrosive products, which is determined by the composition of the cementitious materials. The portlandite in the cement paste is mainly converted to gypsum by reaction with sulfates for conversional concrete while for the conversional concrete, a large quantity of portlandite reacts with sodium sulfate to form gypsum and ettringite. These expansive products accumulate to cause the occurrence of cracks in the structure, leading to the destruction of concrete.

4. Conclusions

1. It can be concluded that the compressive strength of the concrete exhibits an increase in extensometer readings with increased nano silica (NS) content at all load levels compared to silica fume (SF) concrete.
2. The modulus of elasticity for nano silica and silica fume showed good results over the control specimen for all ages (i.e. 28 and 90 days). In nano silica, modulus of elasticity in high performance concrete varied from 4.65% to 28.56%, but in silica fume variations are less compared to nano silica, which is 3.55 to 10.32%.
3. Sorptivity tested on the upper surface of the element in comparison to the result of the test on specimens after 90 days was lower from 4.7% for series conversional concrete to 96.1% for series NS.
4. The second order investigated micro level analysis of Scanning Electron Microscope (SEM) of topographical surface analyzer and Energy Dispersive Spectroscopy (EDS) chemical characterization analyzer were used to find the structural behaviour of nano silica and silica fume at the nano level. Nano silica with its microscopic grains makes concrete more compact and improves infiltration resistance of concrete.

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