

Effect of Nanosilica and Carbon Nanotubes Addition on Mortar Mechanical and Durability Properties

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Received: 27 May 2022; Accepted: 5 August 2022; Available online: 25 September 2022

Abstract: Nowadays, nanomaterials are being extensively used in civil engineering works for improving their quality. Improved compressive strength, flexural strength, modulus of elasticity, and good durability performance of nanocomposites attracted the researcher's interest in understanding these nanomaterials' behavior in cementitious composites. In the present paper, mechanical and durability properties of 1.0 wt% nanosilica (NS) and four different types of 0.3 wt% carbon nanotubes (CNTs) admixed cement mortar was assessed at 28, 56, 90 and 120 days under sulphate water curing. The outside diameters of CNTs are 10-20 nm and 30-50 nm, each type are un-treated and treated with COOH group, respectively. Results showed that flexural and compressive strength was improved for mortar sample admixed with nanomaterials than normal one. Also, nanomaterials came up as a good solution against abrasion and sulphate attacks. The durability is also enhanced for such mortar samples as the density increases, reducing the porosity and water absorption capacity. Resistivity results indicated negligible to low risk of corrosion, thus increasing the durability of these mortar samples. Overall, the sample formed with treated CNTs and 30nm – 50nm outside diameter gave better results than control specimen and other admixed mortar. Scanning Electron Microscopic images were in strong correlation with the experimental results.

Keywords: Nanotechnology; Mechanical and durability properties; Multi-walled carbon nanotubes; Nanosilica; Length expansion; Porosity; Observable deterioration; Abrasion resistance.

1. Introduction

Cementitious composites like mortar and concrete are the primary materials used in the construction industry from the past centuries and will continue to do so in future. The major problem in cement production is the emission of CO₂, leading to the environmental pollution. Approximately 90% CO₂ is released per 100% cement production. This is the biggest threat to the environment in this era. Worldwide, researchers have proposed many alternatives to overcome this problem leading to sustainable development. One such solution to overcome this problem is the advantageous use of nanomaterials in cementitious composites. The addition of nanomaterials in cementitious composites improves its strength properties. Further, nanomaterials makes cementitious composites more durable by retarding the degrading effect of aggressive elements like chlorides and sulphates. This degrading effect due to aggressive elements are advantageously mitigated by using nanomaterials like carbon nanotubes (CNTs), nano-TiO₂, nano-Al₂O₃, nano-Fe₂O₃, nano-SiO₂ and others as nanofiller in the production of cementitious composites by improving the strength and microstructure [1–10], but these particles were found to be expensive, limiting large scale application.

The formation of nano cracks under small tensile loads is the common problem seen in cementitious composites, for which many suggestions have been reported in the published literature. Reinforcement using nanomaterials proved to be an effective way to overcome this problem as it leads to a comparatively denser and compact microstructure [11–13]. Nanomaterials like Nanosilica (NS), Carbon nanotubes (CNTs), Metakaolin (MK), micro silica (MS), fly ash (FA), etc., are promising materials in enhancing the concrete and mortars mechanical and durability properties. NS has improved the mechanical strength of concrete and provides a sustainable solution in the construction field [6]. Similarly, excellent properties of CNTs like high strength and young's modulus makes these materials become a perfect choice as fiber reinforcement for cementitious composites[14]. NS particles possess a greater surface to volume proportion, leading to an improved specific surface area (SSA). Hence, the larger SSA of nanosilica particles added to the cement may be responsible for higher chemical activity [15]. Fine NS particles are capable of filling the pores and voids within the hydration products. This process improves the pozzolanic reaction which causes denser and compact microstructure leading to improved mechanical and durability properties[16,17]. Few researchers have investigated the change in mechanical properties by

incorporating CNTs and concluded that these CNTs give a better structure by improving composites' flexural and compressive strength [18–20]. Multi-walled carbon nanotubes (MWCNTs) are widely used in cementitious composites as the cost of production of MWCNTs is comparatively less than single-walled carbon nanotubes (SWCNTs) [21]. A flexural strength improvement of 25% has been observed by using a minimal quantity (0.08%) of MWCNTs [22]. One of the researchers investigated the influence of untreated CNTs and carbon nanofibers (CNFs) on the flexural strength, ductility, and toughness of mortar at 7, 14, and 28 days. It was found that the inclusion of a less amount of CNTs and CNFs improves the mechanical and durability properties [23]. Carriço et al. [24] investigated the impact of the addition of 0.05-0.1% CNTs on mechanical properties of cement mortar and found an increment of 21% and 25%, on the compressive strength. Addition of nanoparticles also effects the fresh state property (such as workability) of the composites. Workability is essential for the ease of placement, consolidation, durability, and strength of the mortar sample. Nanoadmixed mortar exhibit low workability if superplasticizer is not used. CNTs and NS are nanosized particle which has a high specific surface area due to which more water adheres to the surface of nanoparticles thus causing reduction in the freely available water for lubrication. This problem can be mitigated by adding superplasticizer in appropriate quantity.

The durability properties of cementitious composites incorporating nanomaterials have also been investigated by different researchers. An experimental study of mortar added with MS and NS was performed for strength and durability properties. Results revealed that the addition of both MS and NS would enhance the compressive strength, and resistance against sulphate and carbonation. It was also found that addition of 1% NS gave comparable results to that of 10% MS [25]. The present knowledge of microstructure, strength, and durability of cementitious materials by incorporating various types of nanomaterials was presented in a review article by Paul et al. [15]. Arel and Thomas [26] worked on the effect of nano and microparticle additives on the durability properties of mortar exposed to external and internal sulphate attacks. They found that NS and MS particles were more effective against these sulphate attacks compared to other minerals like MK and FA. The durability properties of mortar treated with microbacteria were investigated against solutions of sodium and magnesium sulphate both chemically and physically. Results showed that efflorescence and expansion were decreased in microbial-treated mortar samples [27]. Further, investigation of NS added concrete and mortar on the compressive strength and behaviour in sulphate solution was checked by replacing cement with NS (10%). Results showed the enhanced performance of concrete and mortar incorporated with NS than plain samples [28]. Due to denser microstructure, mortar admixed with MWCNTs showed improved water absorption characteristics [29]. In a recent study, Lee et al. [30] examined mortar performance with combined NS and CNT, and reported that 1% NS and 0.03% CNT gave best results for water absorption characteristics.

To the authors' knowledge, investigations on the strength and durability properties of mortar added with nanosilica (NS) and carbon nanotubes (CNTs) in sulphate environment are still limited, as past studies were mainly focused on dispersion issues and its influence on individual basis. Therefore, there is a need of exploring the combined effect of NS and CNTs for their effective utilization in the composites used for construction. Accordingly in the current study, an attempt has been done to assess various aspects of mortar behaviour by the inclusion of various types of MWCNTs and NS. In addition to this, SEM and EDS investigation was performed to correlate the obtained results by experimental investigations.

The prime objectives of this study are as follows:

- 1) To compare mortar specimens' mechanical and durability properties under sulphate attack containing various types of CNTs and NS at a specific w/c ratio under different curing ages.
- 2) The reaction of different types of CNTs with nanosilica and cementitious matrix was examined by SEM and EDS analysis.
- 3) To examine the impact of NS and CNTs on the abrasion resistance of mortar sample due to sulphate attack.

2. Materials and experimentation

2.1 Cement

Ordinary Portland Cement from Ultra Tech Company following the standards of IS: 8112-1989 (Reaffirmed 2005, Bureau of Indian Standard, New Delhi) of 43 grade with a relative density of 3.15 was used. The soundness test results were well within the requirements of IS: 8112-1989 with a value of 1.2 mm [31].

2.2 Indian standard sand

Sand conforming to IS: 650–1991 [32] of three sizes 2 to 1 mm, 1 to 0.5 mm, 0.5 to 0.09 mm by Pinal corporation, Ahmedabad, were taken. Its properties are mentioned in Table 1.

2.3 Nanosilica

Nanosilica, purchased from Fiber zone India, Ahmedabad, Gujarat, was taken. The specifications for nanosilica are listed in Table 2.

Table 1. Physical properties of standard sand

S. No.	Properties	Readings obtained	Recommendations as per IS: 2386 (part 1)-1963
1.	Modulus of fineness	2.58	2.2 – 2.6
2.	Specific Gravity	2.62	2.6 – 2.8

Table 2. Properties of nanosilica

S. No.	Properties	Values	Standard requirement
1.	Specific Surface Area (m ² /g)	202	200 + 20
2.	pH value	4.12	3.7 – 4.5
3.	Loss on Drying @ 105°C	0.47	< 1.5
4.	Loss on Ignition @ 1000°C (%)	0.66	< 2.0
5.	Sieve Residue	0.02	< 0.04
6.	Tamped Density	44	40 - 60

2.4 Multi-walled carbon nanotubes

MWCNTs (Un-treated and treated by carboxylic group) of two distinct outside diameters (10-20 nm and 30-50 nm) were brought by Adano Technology. Specifications of MWCNTs are listed in Table 3.

Table 3. Physical Parameters of MWCNTs

S. No.	Specifications	MWCNTs			
		Type I	Type II	Type III	Type IV
1.	Surface treatment	Untreated	Treated	Untreated	Treated
2.	Colour	Black powder	Black powder	Black powder	Black powder
3.	Purity (%)	> 99	> 99	> 99	> 99
4.	Average diameter (nm)	10 – 20	10 – 20	30 – 50	30 – 50
5.	Average length (µm)	1 – 5	1 – 5	10 – 20	10 – 20
6.	Amorphous carbon (%)	< 1	< 1	< 1	< 1
7.	Surface area (m ² /g)	370	370	400	400

2.5 Magnesium sulphate

Magnesium sulphate powder (97% purity) was ordered from Triveni Interchem, Pvt. Ltd. Valsad, Gujrat, for preparing sulphate solution.

2.6 Mixing, dispersion and sample preparation

Hand mixing of these nanomaterials can't give assurance of uniform mixing in water. In this study, sonication was done, which is the most commonly used method. MWCNTs (0.3% by weight of cement) and NS (1%) were taken and mixed in the calculated quantity of water with superplasticizer (0.4% by weight of cement). Solution thus formed, was then placed in Sonica Bath Sonicator for 20 minutes to get an adequately dispersed solution. Stages of sonication and samples with glued demic points used for length expansion measurements are shown in Fig. 1.



Fig. 1. (a) NS and CNTs mixed with water and superplasticizer; (b) Sonication for proper mixing of NS and MWCNTs; (c) Casted flexural specimens before testing.

The mix proportion was designed as per the codal recommendation of IS: 2250-1981 [33] having water to cement ratio of 0.55 and cement to sand ratio of 1:3 as shown in Table 4. Sonicated solution was added in a dry

mixture of cement and sand, thus forming a uniform paste which then filled in moulds of 160 mm × 40 mm × 40 mm conforming to IS: 10078-1982 [34]. Before filling the paste, oil was introduced in moulds to prevent sticking of paste in the mould. Compaction was done in 3 layers and 100% relative humidity is maintained for 24 hrs and then shifted to tank for curing till 28 days and later in sulphate water (formed by mixing 10% MgSO₄ in water as per ASTM C 1012) [35]. The concentration of sulphate ions was maintained by keeping the pH in the range of 6-7 with the addition of 0.5N H₂SO₄ weekly for the entire duration of curing.

Table 4. Composition of cement sand mortar

Mixes	Superplasticizer (% by cement weight)	Nanosilica (% by cement weight)	MWCNTs (% by cement weight)	Sonication time (min.)
CS	0.4	-	-	-
NS	0.4	1.0	-	20
U1	0.4	1.0	0.3	20
T1	0.4	1.0	0.3	20
U2	0.4	1.0	0.3	20
T2	0.4	1.0	0.3	20

CS: Control specimen with OPC; NS: Specimen with NS + OPC; U1: Specimen with OPC+ NS+ MWCNT (Type I); T1: Specimen with OPC+ NS+ MWCNT treated with COOH (Type II); U2: Specimen with OPC+ NS+ MWCNT (Type III); T2: Specimen with OPC+ NS+ MWCNT treated with COOH (Type IV).

2.7 Testing procedure

2.7.1 Flexural testing

A flexural testing machine was used for the flexural strength test, consists of 10mm diameter two roller supports, spanning 100 mm. The third roller with the same diameter and at the same distance from the first two supports was used to transmit the load 'P' on the opposite side of the sample, as shown in Fig. 2. The loading rate was maintained as 50 ± 10 N/s. Equipment with the sample is shown in Fig. 2. (b). Flexural strength is obtained as per (IS: 4031 (Part 8)-1988) [36].

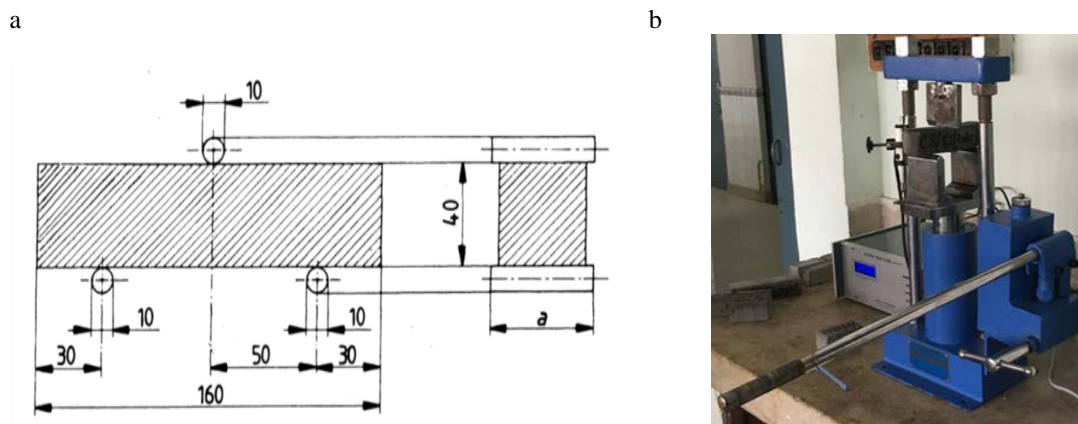


Fig. 2. (a) Schematic diagram for flexure testing; (b) Flexure testing machine.

2.7.2 Compression testing

Cubes of size 40 mm were obtained from the end portion of the sample after the flexure strength test, as shown in Fig. 3(a). The cut cubical specimens are shown in Fig. 3(b). The test was performed by putting the cube between two hard metal plates in a compression testing machine. The rate of loading was 200 kg/cm²/min. Compressive strength was determined as per (IS: 4031 (Part 8)-1988) [36].

2.7.3 Density, porosity and water absorption tests

A saw cut cubical mortar samples of size 40 mm × 40 mm × 40 mm was used for density, porosity and water absorption testing as per the specifications given in IS: 1528 (Part 15)-2007 [37] at various ages. For each sample type, the average values of density, porosity and water absorption of mortar were evaluated from three samples. These parameters were determined followed by Eqs. Complete details of evaluating the density, porosity and water absorption were given in [38].

$$\text{Density (g/cm}^3\text{)} = \frac{W_d}{W_w - W_{ssd}} \quad (1)$$

$$\text{Porosity (\%)} = \frac{W_{ssd} - W_d}{W_{ssd} - W_w} \times 100 \quad (2)$$

$$\text{Water absorption (\%)} = \frac{W_{ssd} - W_d}{W_d} \times 100 \quad (3)$$

where the weight of oven-dried specimen W_d is measured in the air. W_w is the water immersed weight and W_{ssd} is the saturated surface dry weight. These weights are measured as shown in Figs. 4 and 5. Past studies have successfully employed this method of porosity determination for cementitious composites [39,40].



Fig. 3. (a) Cutting of flexure specimens; (b) Cubical specimens (40 mm³) for compression testing.



Fig. 4. Determining dry and saturated weight



Fig. 5. Determining submerged weight

2.7.4 Expansion in length due to sulphate exposure

In this, flexural samples were cured in magnesium sulphate solution (10% litre of water), the pH of the solution is kept at 6.5 ± 0.5 . The concentration of sulphate ions was maintained by keeping the pH in the range of 6-7 with the addition of 0.5N H₂SO₄ weekly for total duration of 120 days. The sulphate water was changed every month as per the recommendations of ASTM C 1012 [36]. Sulphate attack was clearly visible in terms of scaling and edge softening of the specimens (See Fig. 6a,b). Samples exposed to 10% magnesium sulphate were tested at 56, 90, and 120 days for expansion by taking the distance between the demic points glued to mortar specimen by using an extensometer having least count of 0.002 mm, as shown in Fig. 6(c) and (d). Length change in percentage is given by the following expression

$$\text{Change in length} = \frac{L_2 - L_1}{L_1} \times 100 \quad (4)$$

where, L_1 = Original sample Length, and L_2 = sample length after time t

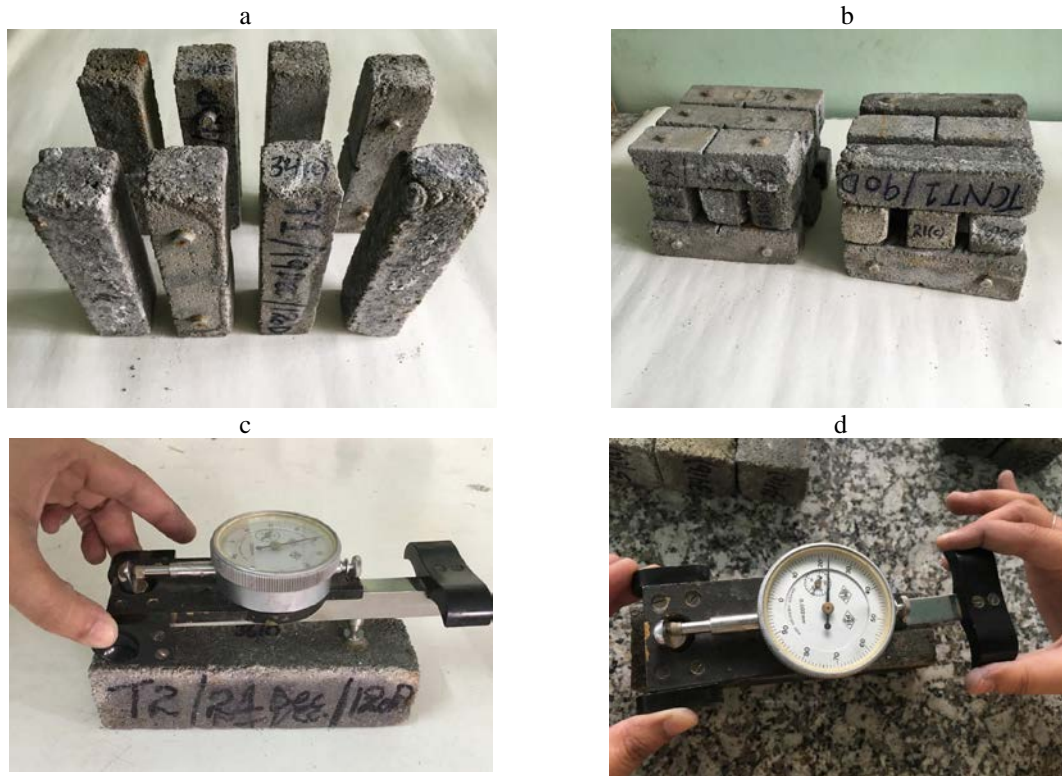


Fig. 6. (a,b) Flexural specimens showing signs of sulphate attack (c) Measurement of Length between demic points by Extensiometer; (d) Reading on Instrument.

2.7.5 Abrasion resistance

To determine the abrasion resistance of cubical mortar specimens Los Angeles abrasion test was performed as per specifications of ASTM C 131 [41]. A hollow steel cylinder, with both ends closed, with an inside diameter of 70 cm and an inside length of 50 cm, fixed on stub shafts about which it rotates on a horizontal axis. Six cast iron spheres as abrasive charges each with an approximate diameter and weight as 4.8 cm and 5 kg respectively, were charged into the drum and rotated it for 16 min. The mass loss in percentage was determined as

$$\text{Percentage wear} = \frac{W_1 - W_2}{W_1} \times 100 \quad (5)$$

where, W_1 = Initial weight of the cubical specimen (5kg), W_2 = weight of specimens after testing (kg).

2.7.6 Observable deterioration

Normally, there was some apparent edge softening and scaling were seen on the specimen surfaces after various curing periods in sulphate solution. For the study of sulphate attack, each of the six flexural specimens for the mixtures tested, were individually designated after demolding. The first three samples of each mixture were transferred to the potable water curing tank, and the latter three to the 10% magnesium sulphate solution at constant room temperature and humidity environment. After respective curing periods, specimens were taken out from curing tank and allowed to dry at room temperature before visual inspection.

2.7.7 Ultrasonic pulse velocity test

Quality of the mortar specimen is observed by a non-destructive test. The time travel of pulse for a known path length was observed for calculation of pulse velocity, as shown in Fig. 7. Based on velocity observations, its quality can be categorised as Poor, Medium, Good and Excellent according to IS: 13311(part1) – 1992 [42].

2.7.8 Microstructural images

Microstructural images reflect the real picture of the matrix that was formed due to NS and MWCNTs addition in the mortar mix compared to the control one. After all tests at 28 and 120 days, a crushed sample was send to University Sophisticated Instruments Facility (USIF) Centre, AMU, Aligarh. The Scanning Electron Microscope (SEM) from JOEL, Japan, was used to see the samples at the microstructural level. EDS was also performed to

get the information about the elements available in the matrix. These images serve as strong evidence for correlating the results obtained from experiments.

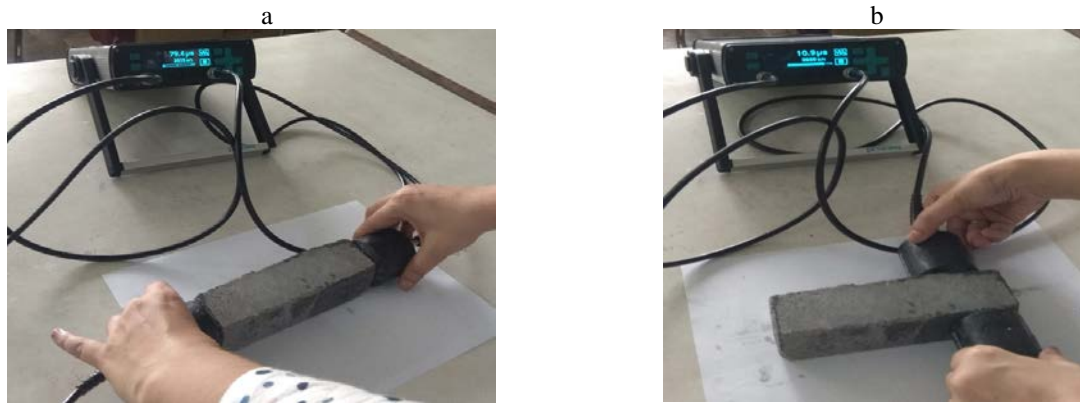


Fig. 7. (a) Ultrasonic pulse velocity test along the specimen length; (b) along the width.

3. Results and discussion

For studying various mechanical and durability properties viz. flexural and compressive strength, density, porosity, absorption of water, expansion in length, resistance against abrasion, resistivity, ultrasonic pulse velocity test at 28, 56, 90, and 120 days six types of mortar samples were taken.

3.1 Mechanical properties

3.1.1 Flexural strength

The addition of NS and CNTs have improved the average flexural strength of each type of flexural specimen at various ages. The trend of readings was first increased till 56 days and later decreased, as presented in Fig. 8. This improvement of strength was seen in the order of: CS < NS < U1 < T1 < U2 < T2. T2 has highest strength i. e. 9.08 MPa, which was 38.63% above than the CS at 56 days. Also, at 120 days, 31.43% increase was seen for T2 than CS even after exposure to sulphate solution. From all the samples, T2 shows better results in enhancing the flexural strength at all curing ages. The enhancement in the strength is because of the improved hydration due to these nano particles. NS and CNTs not only fill the pores but also act as a catalyst in increasing hydration reaction, thus enhancing the strength of the sample. Further, the decrement in strength after 56 days was because of two reasons. Firstly, a compound named ettringite which has expansive nature, might be formed due to the reaction of calcium aluminate and calcium sulphate. Formation of ettringite is increased in the presence of sulphates. Secondly, magnesium sulphate causes significant damage and debonding of C-S-H gel resulting into decreased flexural strength at 90 and 120 days. Although, even after sulphate attack, T2 outperformed other mortar samples.

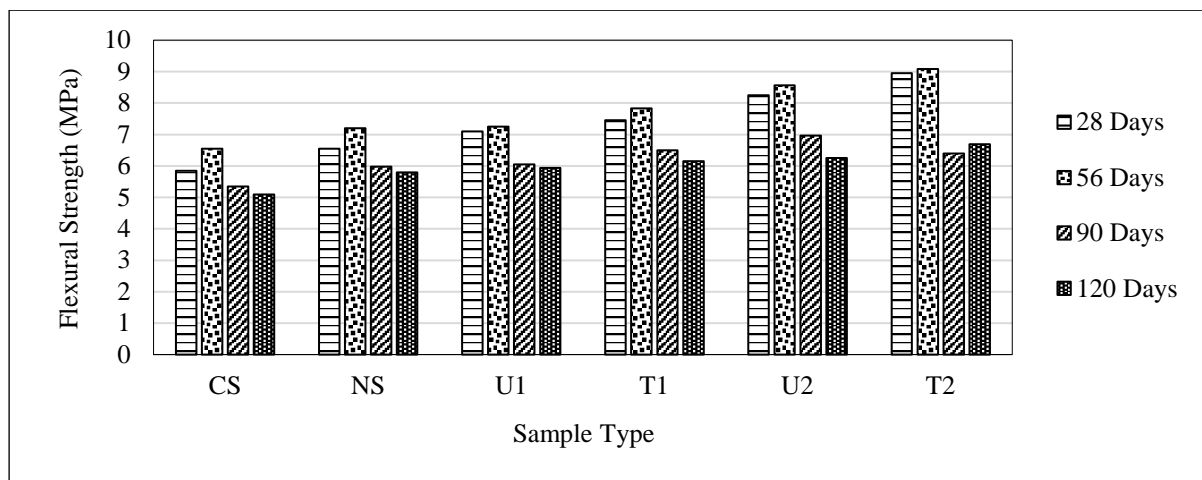


Fig. 8. Flexural Strength of mortar samples at different ages

3.1.2 Compressive strength

The readings of average compressive strength of each type of cubical samples is shown in Fig. 9. The same trend, as seen for flexural strength, was observed here also. The compressive strength of T2 was more than that of CS and other mixes at each age. The percentage increase in compressive strength was about 16.4% for T2 than CS at 56 days. Also, at 120 days, 15.35% increment was seen for T2 than CS. The addition of NS and CNTs confined the matrix and improve the capacity of taking load efficiently and in turn, enhance the strength. The reason for decreased strength from 56 to 120 days is the same as discussed in the above section. The results showed that T2 out performs all other other mix types at all curing ages.

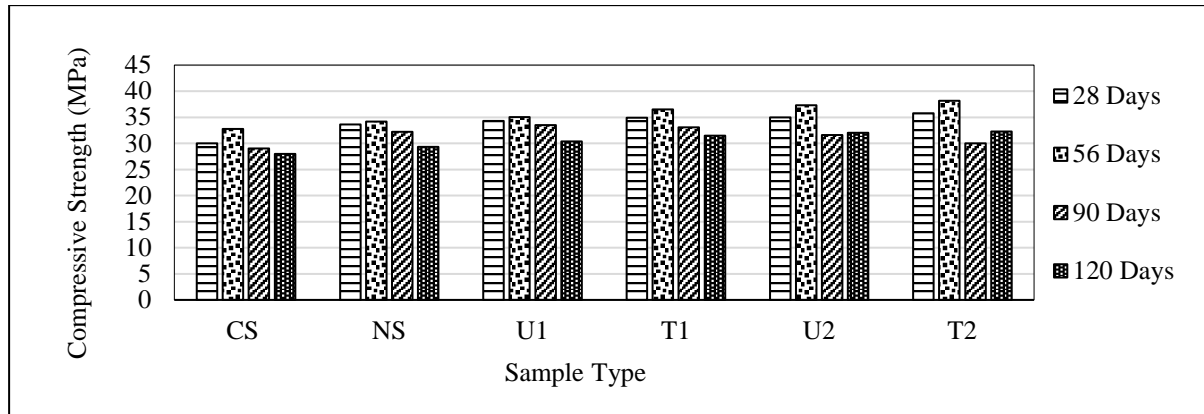


Fig. 9. Compressive strength of mortar samples at different ages

3.2 Durability properties

3.2.1 Hardened density

The addition of nanomaterials brings changes in cementitious composites at the microstructural level due to the filling of smaller voids. NS and CNTs act not only as a filler, but also as a catalyst for hydration reaction. Due to this, pores started to fill by these nanomaterials, and the hydration process resulted in C-S-H gel formation. Therefore, attaining a reasonable strength value which is because of the densification of the matrix. The maximum value of density at 28 days is 2.75g/cm^3 which is 28% greater than CS, and 2.86g/cm^3 at 56 days which is 30% more than CS for T2. The increase in density after 28 days may be attributed to the fact that active silica in NS can react with $\text{Ca}(\text{OH})_2$ to form secondary C-S-H gel making the matrix chemically stable and structurally dense. But after 56 days, density starts decreasing due to the ingress of sulphate ions leading to the formation of expansive products, causing a reduction in the strength. The trend followed by density values is the same as that of strength, i.e., first increased till 56 days and then decreased after 56 days, as shown in Fig. 8. Thus, showing a direct relationship between the density and strength values. Out of all the mortar specimens, T2 exhibited a maximum value of density at each age. The density of T2 was obtained as 27% more than the CS at 120 days, as presented in Fig. 10.

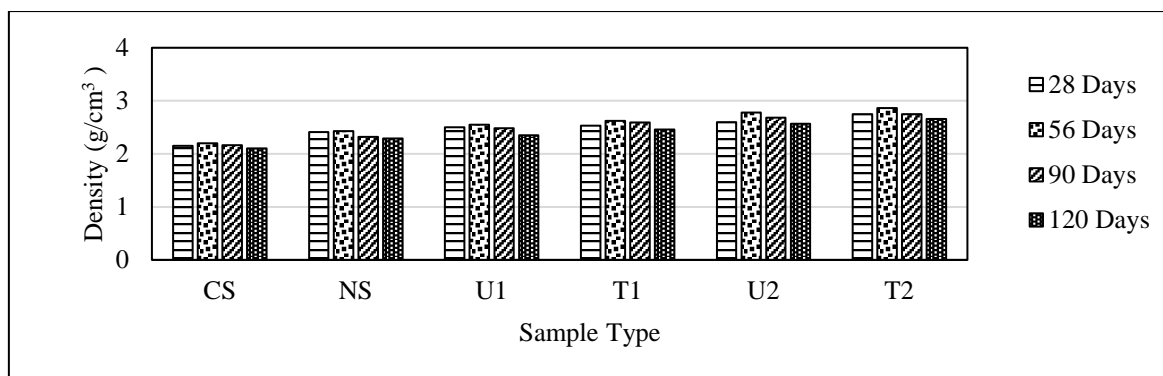


Fig. 10. Hardened density of mortar samples at different ages.

3.2.2 Porosity

The trend of porosity values due to sulphate attack are shown in Fig. 11. The reduction in the porosity is due to continuously filled pores by NS and CNT particles. With time more and more pores are filled by NS and CNTs

resulting in reduced porosity values. The reduction in the porosity value of T2 is 37%, 39%, 36%, and 37.3% than the CS at 28, 56, 90, and 120 days respectively. In the initial period, the rate of reduction in the porosity is a bit faster as nanoparticles more rapidly fill the pores on its inclusion, but in later stages, the rate of decrement of porosity gets a little bit slower, as seen from Fig. 11, which may be attributed to the fact that sulphate ions also ingresses in the remaining pores thus reducing the porosity of the matrix. Overall, 43% reduction in porosity is observed from 28 to 120 days.

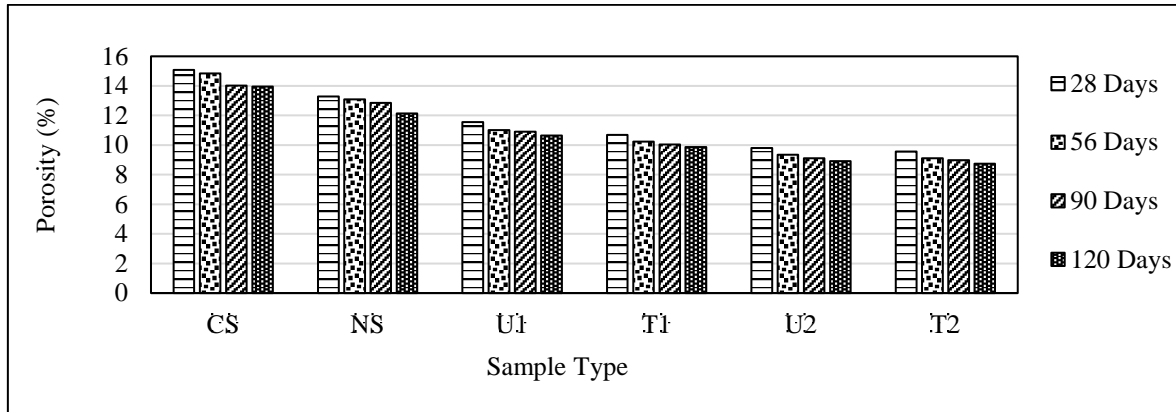


Fig. 11. Porosity of mortar samples at different ages

3.2.3 Water absorption

As observed from Fig. 12, the same trend is followed by water absorption values as in Fig. 11, i.e., the values decrease with time due to NS and CNTs. The addition of these nanomaterials leads to the filling of pores resulting in the denser matrix with no or fewer pores available to water, thus reducing water absorption value. The maximum and minimum values reported for water absorption are 7.01 % for CS at 28 days and 3.10% at 120 days for T2, respectively, as seen from Fig. 12. Overall decrement in water absorption values is found as 56%.

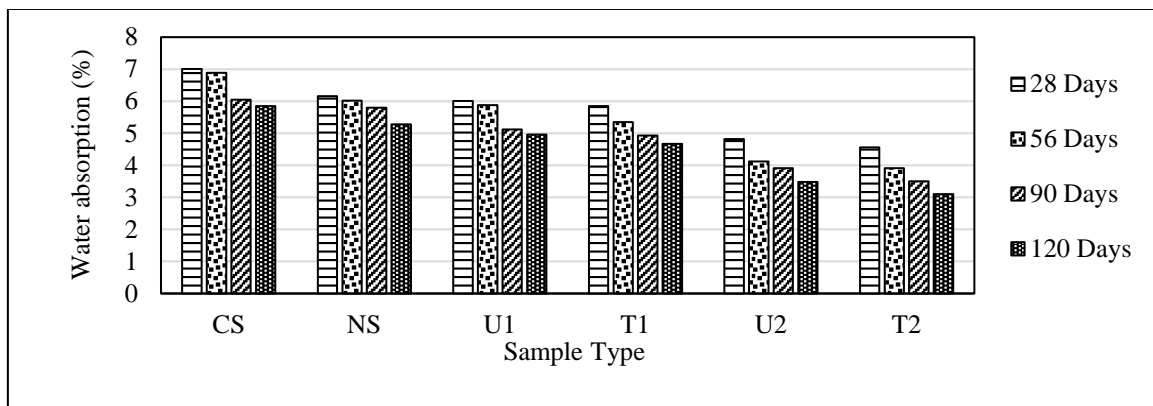


Fig. 12. Water absorption values (%) of mortar specimen at different ages.

3.2.4 Expansion of length due to sulphate attack

Table 5 shows the values of expansion in length due to attack of sulphate. It can be seen from Table 5 that the CS shows maximum expansion at each age than other samples with a maximum value of 0.091% at the age of 120 days which is about 63% more than the CS at the age of 56 days. Nanoadmixed cement mortar represents lesser values of expansion than CS at each age. All expansion values at each age are well within the limit, which is 0.1% for cement mortar as per specifications of ASTM C 1157 [43]. Table 5 also reflects that at increased immersion period, expansion gets increased for each type of sample. There may be two possible reasons for the above results. Firstly, resistance to sulphate attack is directly related to expansive hydrated compound formation in the hardened mortar mix. Till 28 days, there was no source of sulphate ions, so no formation of expansive products is seen; hence, no expansion is observed. But after 28 days, the presence of sulphate ions from the magnesium sulphate solution in which samples are immersed leads to reaction with $\text{Ca}(\text{OH})_2$, C-S-H gel, calcium-sulpho-aluminate hydrate forming gypsum, secondary ettringite, and in some cases thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$). These compounds cause internal stresses that may expand and, in some cases, may cause cracks in the cementitious composites.

Secondly, Magnesium sulphate causes very severe degradation despite the expansion. This is because magnesium itself takes part during the process of attack of sulphate to form $Mg(OH)_2$ (brucite), magnesium silicate hydrate, which leads to significant destruction and debonding of the paste or C-S-H gel from the base matrix results in increased loss of compressive strength and thus increasing expansion of the sample.

Table 5. Average Length Expansion values of NS and CNTs admixed cement mortar

Sample type	Length increment (%) at different age (days)		
	56	90	120
CS	0.056	0.076	0.091
NS	0.053	0.073	0.089
U1	0.049	0.070	0.085
T1	0.044	0.067	0.083
U2	0.043	0.065	0.082
T2	0.041	0.057	0.078

3.2.5 Abrasion resistance

Results of abrasion resistance are shown in Table 6 in terms of weight loss during the 16 min abrasion test. Each specimens showed increased abrasion resistance represented in terms of decreased weight loss of sample till 56 days. And after that resistance to abrasion reduces due to decreased strength from 56 to 120 days. High abrasion resistance is seen for T2 compared to CS and other nano admixed cement mortar at each age, as shown in Table 6.

Fig. 13 shows the mortar cubical specimens after abrasion testing carried out on the T2 samples at 28, 56, 90, and 120 days . The weight loss due to abrasion of the mortar samples ranged from 19.67% to 35.37% after 16 min of testing for different nano admixed samples. The lowest weight loss was detected for the T2 mortar mix at 56 days and the highest value was for the control specimen (CS) at 28 days. The weight loss seems to be proportional to the compressive strength of the mortar mix. Mortar with 1% NS and 0.3% treated CNTs (T2) showed a much higher resistance to weight loss (abrasion) when compared to the control (CS) and other sample types, i.e., NS, U1, T1, and U2. Mortar mix T2 on average show a 35% lower weight loss than CS mortar at 120 days. On the other hand, the weight loss for the mix U1 and U2 were reduced by 16% and 27%, respectively at 120 days. The lowest weight loss of the T2 mortar with 1% NS and 0.3% treated MWCNTs is believed to be the consequence of a denser and compact microstructure of the matrix.

Table 6. Abrasion resistance values of NS and CNTs admixed cement mortar

Sample Type	Weight loss (%) at different ages (days)			
	28	56	90	120
CS	35.37	30.21	31.55	32.37
NS	32.14	28.56	29.32	30.11
U1	30.56	26.31	28.89	29.56
T1	27.35	25.91	26.32	28.33
U2	24.48	21.85	23.92	25.62
T2	20.19	19.67	21.69	23.11



Fig. 13. Cubical specimens (T2) after Los Angeles abrasion testing

3.2.6 Physical appearance after sulphate attack

Typical pictures of the mortar flexural specimens that were stored in potable water are shown in Fig. 14(a), whereas in 10% magnesium sulphate solution for the mixes (CS, NS, U1, T1, U2, and T2) after 120 days are shown in Fig. 14(b-g). From Fig. 14(a), it can be seen that under potable water curing, all specimens showed yellowish surfaces. Furthermore, without NS and CNT addition (CS specimen), fairly excessive white scaling

were formed on the specimen surface along with some clearly disintegrated corners (Fig. 14b). With NS specimen, as shown in Fig. 14(c), some medium pores and efflorescence were formed on the surface of the specimen. With both NS and CNT added (U1 specimen), as shown in Fig. 14(d), only white scaling have been deposited on the specimen surface. In contrast, T1 specimen, as shown in Fig. 14(e), a fairly less whitish appearance were formed. Whereas, U2 and T2 showed lesser efflorescence and pores on the surfaces (Figs. 14f,g). These pictures clarify that the addition of NS and CNT is effective in mitigating disintegration under sulphate attack. The sulphate attack is particularly reduced for T2 specimens which uses treated CNTs compared to un-treated ones.

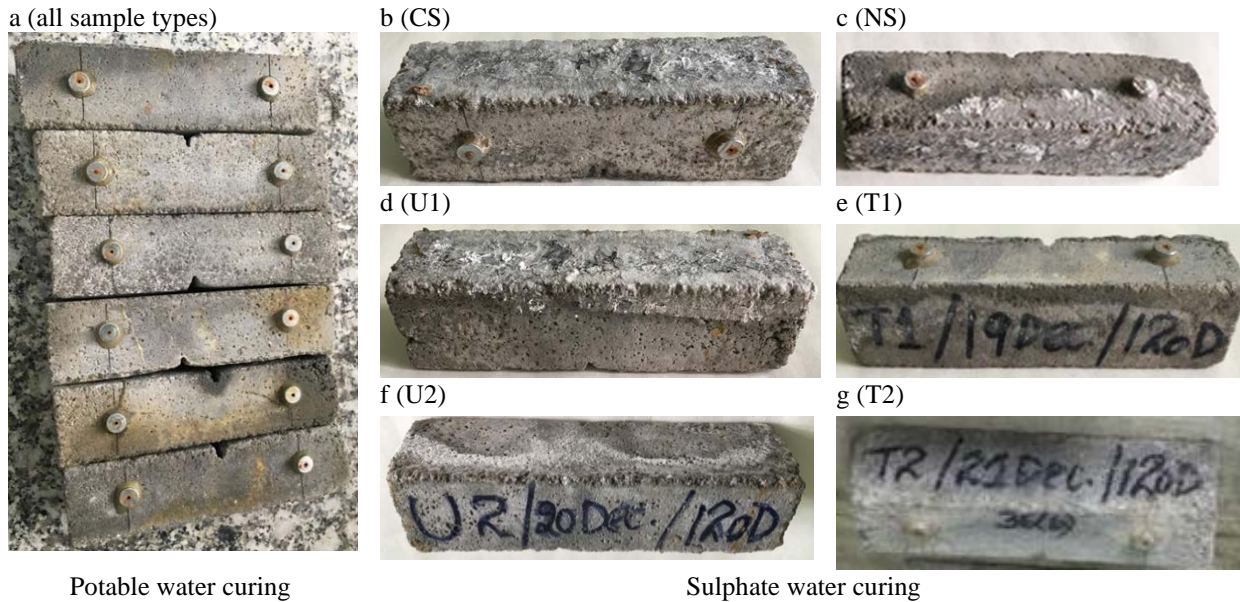


Fig. 14. Comparative photographs of flexural specimens after sulphate attack at 120 days

3.2.7 Ultrasonic pulse velocity

This is done to assess the quality of cementitious composites. Higher the value of pulse velocity, better will be the quality of composites. Table 7 represents the UPV values of different types of the sample at different ages. These values are in accordance with the values mentioned in IS 13311(Part 1): 1992 [42]. There is a decrement in UPV values with the passage of time, as reflected by Table 7, indicating that the quality degrades with the increased curing age in sulphate medium. UPV values and compressive strength also have a direct relationship that can be seen clearly from compressive strength graph in Fig. 9 and UPV values in Table 7. The range of variation in the values is from 4.8 Km/s to 3.2 Km/s, i.e., excellent (> 4.5 Km/s) to medium quality (3-3.5 Km/s) of the matrix is observed. The percentage decrease in the values from the sample at 28 days to sample at 120 days is 21%, 20%, 19%, 17%, 16% 15% showing that the quality of CS is affected significantly than other samples. This is because CS will have an adverse effect than nano admixed mortar (with NS and CNTs) in sulphate solution. That's why UPV values of CS are comparatively lesser than other samples. Even after sulphate attack, the value of UPV for T2 is more at each age, leading to fairly good results, thus showing a proper densified mortar sample.

Table 7. Average UPV values of NS and CNTs admixed cement mortar

Sample type	UPV (km/s) at different Age (days)			
	28	56	90	120
CS	3.8	4.0	3.7	3.2
NS	4.0	4.1	3.5	3.3
U1	4.2	4.5	3.8	3.4
T1	4.4	4.6	4.0	3.5
U2	4.5	4.7	4.2	3.6
T2	4.7	4.8	4.5	3.9

3.3 Microstructural images

3.3.1 SEM analysis

Fig. 15 (a) to (f) represented the SEM images of the mortar specimen at 28 days. Fig. 15 (a) showed the development of significant compounds viz. C-S-H gel and CH (Portlandite) having cylindrical rod shaped with

larger diameter which are responsible for attaining the strength of mortar. Fig. 15 (b) revealed that the addition of NS results in the filling of voids leading to slightly enhanced strength of the matrix. Fig. 15 (c) to (f) represented CNTs along with the NS particle in the mortar matrix. CNT particles are properly distributed among the matrix showing the good dispersion of these nanoparticles. Nanoparticles reduce the size of portlandite by filling the spaces between the hydration products hence, enhancing the strength of the composites incorporating CNTs.

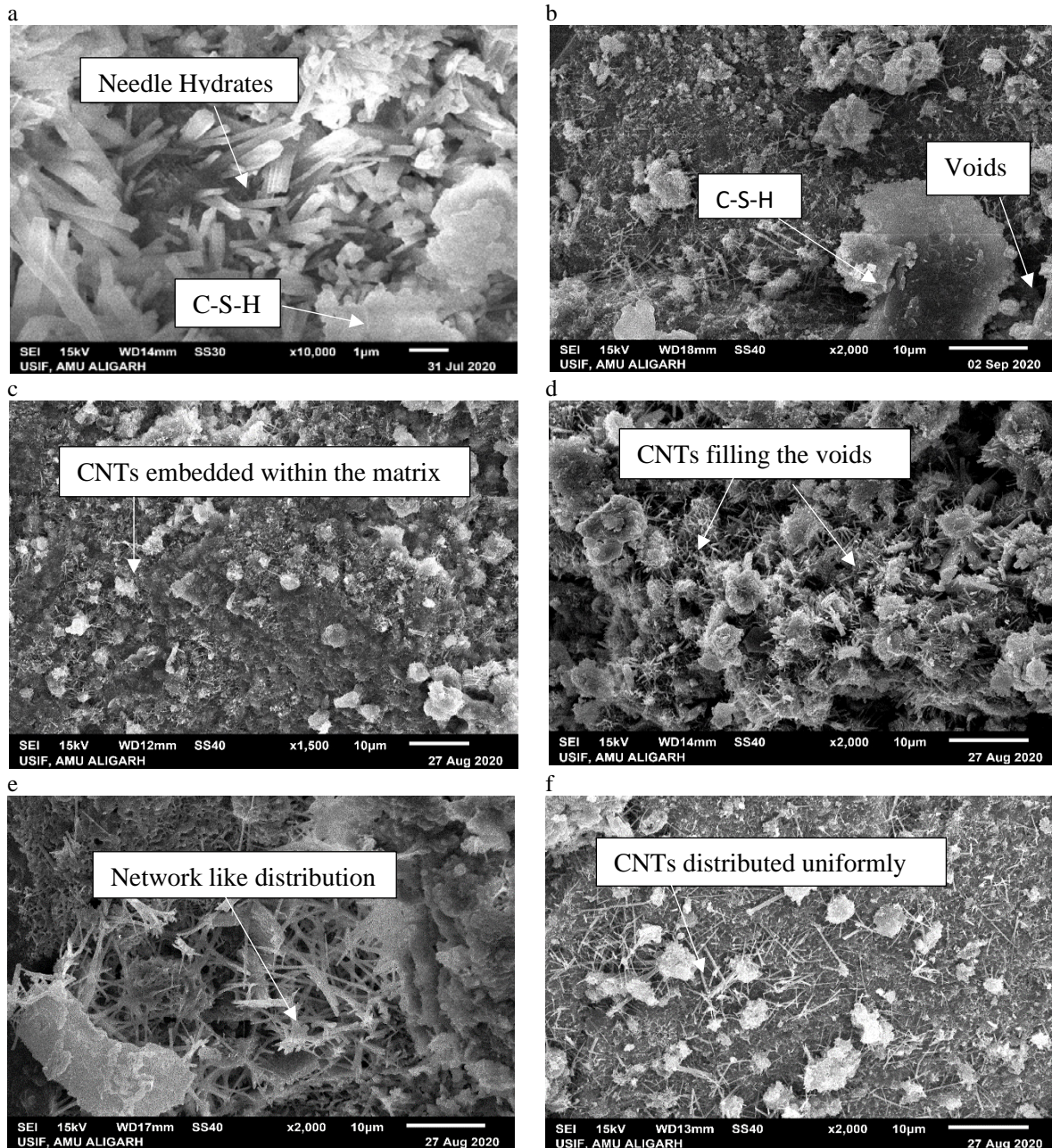


Fig. 15. SEM images of mortar sample at 28 Days (a) Control sample; (b) Nano-Silica; (c) Untreated 1; (d) Treated 1; (e) Untreated 2; (f) Treated 2

The changes in the microstructure of all mortar specimens at 120 days are given in Fig. 16 (a) to (f). Fig. 16 (a) revealed the presence of pores along with the hydration product. These pores caused a reduction in the strength of CS than the strength at 28 and 56 days. Since NS can fill the voids and densify the matrix even then, some pores are present, which was due to the degrading effect of sulphate ingressed in the matrix because of curing in sulphate solution Fig. 16 (b). In Fig. 16 (c), CNTs were distributed along with the matrix with some needle-like structures (expansive product named ettringite) responsible for the decrement in the strength. Fig. 16 (d) represented the clustering of some CNT particles due to Vander Waal forces and the uniform C-S-H gel, resulting in increased strength than CS and NS admixed cement mortar. The formation of ettringite, an expansive product, can also be

seen from Fig. 16 (e), and the CNT particles dispersed properly within the cement matrix filling the gaps. Fig. 16 (f) showed a more densified matrix due to covering cracks by CNT particles. This became the proof for enhanced strength of T2 than other mortar samples at 120 days even after sulphate attack.

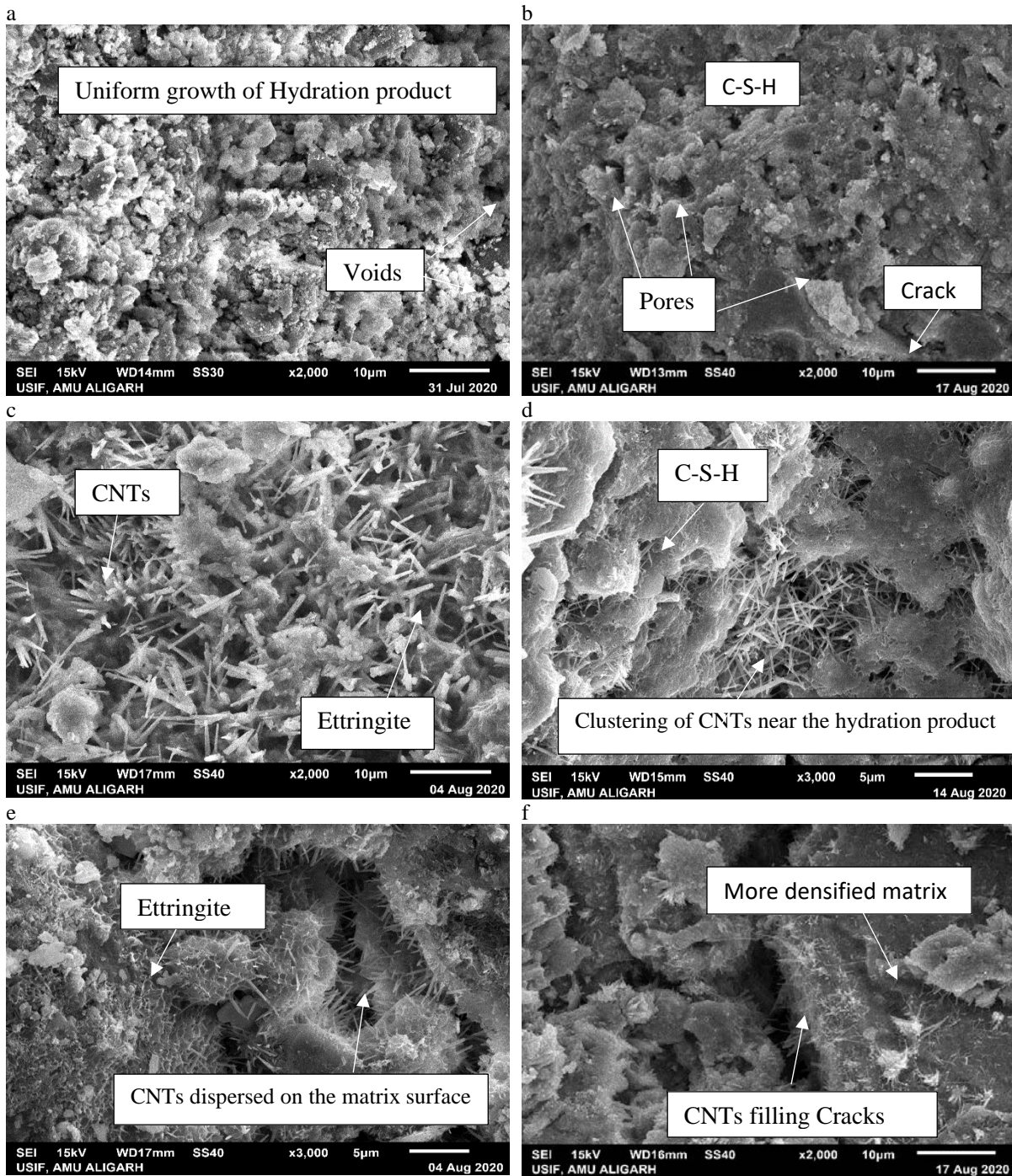


Fig. 16. SEM images of mortar sample at 120 Days (a) Control sample; (b) Nano-Silica; (c) Untreated 1; (d) Treated 1; (e) Untreated 2; (f) Treated 2

3.3.2 EDS Analysis

Energy Dispersive Spectroscopy was performed to locate nanoparticles' presence, determine nearby materials, and confirm the strength results. Fig. 17 and Fig. 18 illustrate the EDS analysis of all types of specimens at 28 and 120 days, respectively, near a CNTs location.

It was observed from Fig. 17 (a) and (b) that Calcium is the primary element. Silica was present as a result of the hydration of cement. The presence of gold is due to the coating of the sample before the test. Other elements

like oxygen, aluminum, etc., were also present because these are constituents of cement. In Fig. 17 (c) to (f), Carbon is also the main element in addition to calcium, indicating the presence of CNTs in the matrix.

Similarly, Fig. 18 (a) to (f) showed the EDS analysis of mortar samples at 120 days. Calcium was present in a high percentage due to the hydration reaction in Fig. 18 (a). In Fig. 18 (b), silica was also present in a high amount due to the hydration reaction. Fig. 18 (c) to (f) Carbon was present in a considerably high amount in addition to calcium and silica, indicating the presence of CNTs. Sulphur was also seen because of the curing of the sample in sulphate solution.

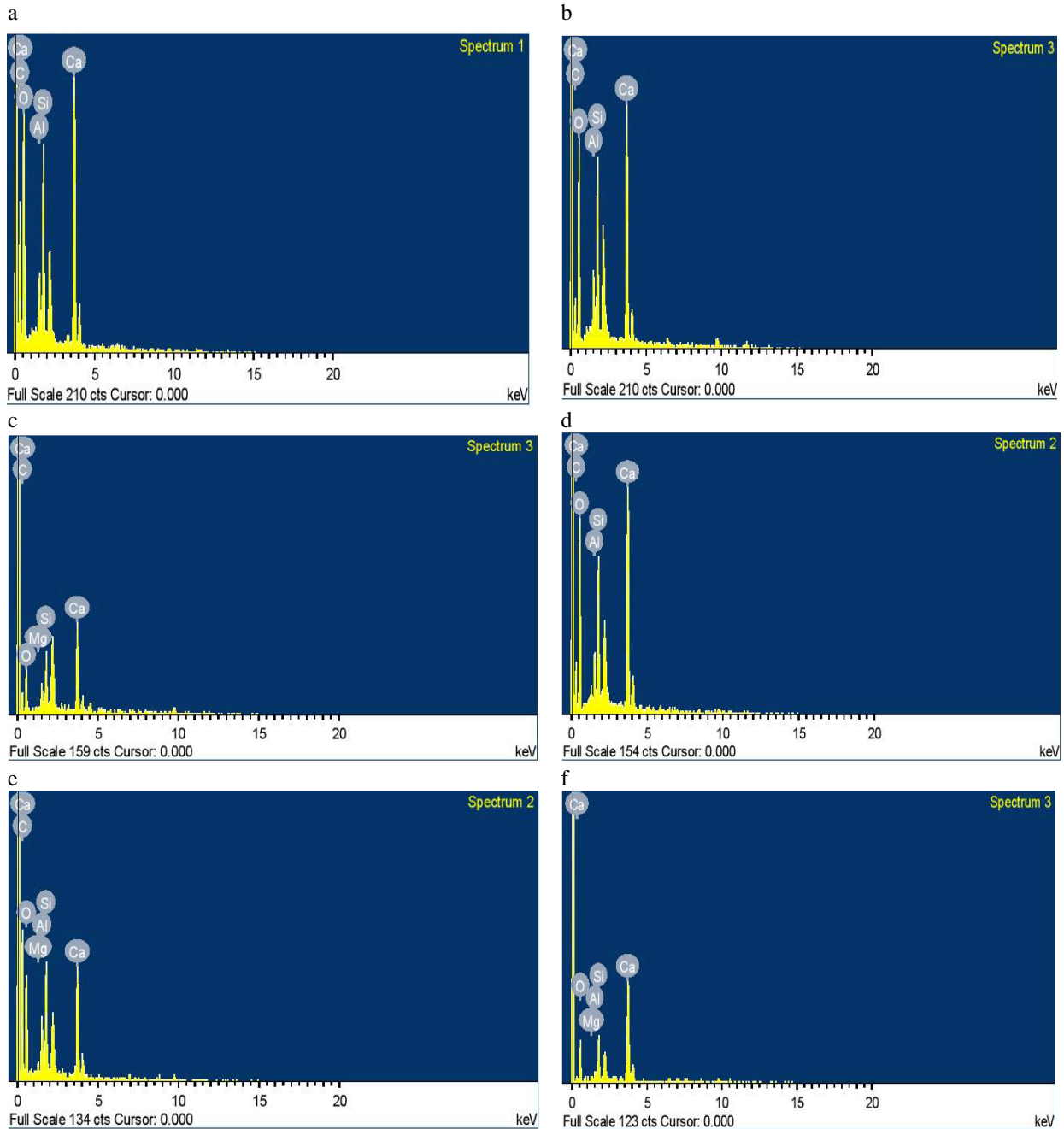


Fig. 17. EDS images of mortar sample at 28 Days (a) Control sample; (b) Nano-Silica; (c) Untreated 1; (d) Treated 1; (e) Untreated 2; (f) Treated 2

3.4 Practical implication of the study

Cementitious composites with addition of NS gained early strength as compared to that of conventional composites and are more durable. It is also observed that the addition of NS improved workability of composites while the addition of water reducing admixtures is at a minimum quantity. About 20%–30% of cement content can be reduced by nano silica. The restoration of heritage buildings requires special mortar as a binding material. Thus, nano silica can be a suitable material in the preparation of cement mortar. As compared to other nano

materials, CNT is the best nano material in terms of improving flexibility and enhancing the mechanical strength. Offshore well heads can be plugged in a short time to prevent oil leakage into the ocean waters by the use of CNT admixed mortar. Furthermore, steel reinforcement section can be replaced by CNT which permits extra loads to be handled. By replacing steel, it was believed that more lightweight and less reinforcement sections can be created. Technical issues, cost, and toxicology have so far prevented the large scale use of nanomaterials in cementitious composites.

In general, utilizing nanotechnology in the traditional construction practices brings a very positive impact without hampering the original property of the construction materials. Nanotechnology improves strength, durability, resistance against aggressive environment without affecting the desired behaviour of the materials. In addition to this, nanotechnology can reduce production, maintenance and retrofitting costs of the structure by improving the durability of construction materials.

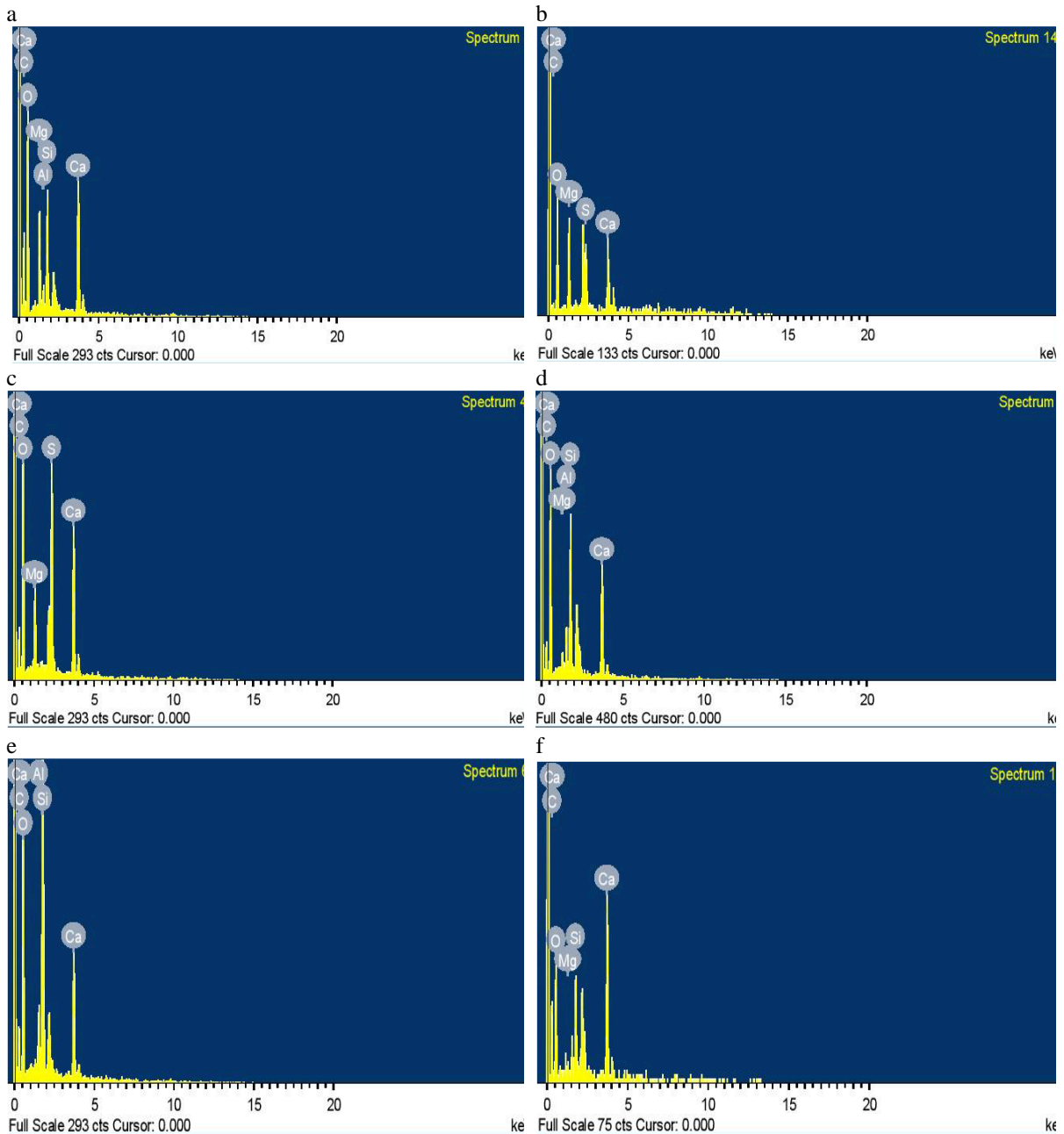


Fig. 18. EDS images of mortar sample at 120 Days (a) Control sample; (b) Nano -Silica; (c) Untreated 1; (d) Treated 1; (e) Untreated 2; (f) Treated 2

4. Conclusions

The various conclusions from the exhaustive experimental study can be summarized as follows:

- 1) Nano-reinforced cementitious composites hardened relatively faster compared to control samples at early ages. This is because of the quick hydration reaction in the presence of NS and CNTs.
- 2) In general, at all curing ages, the mechanical strengths of samples in sulphate environment containing NS and CNTs, were higher than the control samples. This may be attributed to the bond improvement between the sand and cement paste and filler effect of nanoparticles which leads to less pores in the blended matrix. The impact of sulphate attack on mechanical strengths is more pronounced after 56 days.
- 3) The porosity of the matrix is decreased due to the pore filling effect of NS and CNTs particles. Till 28 days, CNTs and NS fills the pore and densify the structure. But after 28 days, not only CNTs and NS participated in the pore filling process, but ingress of sulphate ions also causes some pores to fill thus, reducing the porosity of cement mortar. Overall, a 43% reduction in porosity is observed. Also, water absorption values also decreased by 56% as these nanomaterials could act as nano fillers.
- 4) Due to the transportation of sulphate ions in the cement mortar, length expansion took place. CNTs admixed cement mortar showed less expansion values compared to the control specimen. The maximum expansion value is well within the specified limits given in ASTM C 1157.
- 5) Abrasion resistance of samples also followed the same pattern as observed in the case of strength. T2 shows 29% reduction in weight loss compared to CS at 120 days.
- 6) Microstructural images strongly correlate the results from the experimental findings. The denser and improved microstructure is showing improved properties for nano admixed mortar. From the research, it could be suggested that NS and MWCNTs are good reinforcing materials for improving cement mortar's mechanical and durability properties. Also, treated MWCNTs performed relatively better than the untreated ones.
- 7) This study has paved the way for the future researches of nanotechnology in the construction industry. Lot of studies is still required to set up the guidelines of using these nanomaterials in the cementitious composites. Also, researchers can check the suitability of nanocomposite slurry as a coating on the reinforcement in the reinforced concrete structures.

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