Introduction

The use of nanomaterials had penetrated every possible field, and its influence is being observed in concrete technology as well. The potential use of carbon nanotubes (CNTs) in concrete is attributed to its inherent excellent mechanical properties [1-3]. The Multi-Walled Carbon Nanotubes (MWCNTs) is a type of carbon nanotube which has multiple concentric tubes and it exhibits tensile strength of 10 to 50 GPa [4, 5]. It has been already reported that the addition of CNTs can improve the mechanical performance of cement composites [6], and the MWCNTs in cement matrix can improve the strength through the effect of bridging in microstructural cracks [7, 8]. The addition of MWCNTs influences the durability and life-span of concrete through its reinforcement effect in the cement matrix [7, 9, 10]. Along with the mechanical behavior, the thermal, creep...
and shrinkage properties of concrete is also enhanced by CNTs [11-13]. Achieving uniform dispersion of CNTs/MWCNTs are challenging due to its hydrophobic nature, Van der Waals forces and weak interfacial interaction between nanotubes and composite matrix [14]. The main limitation of usage of CNTs are its high cost in relation to other nanomaterials available and the challenges faced through the dispersion of CNTs [15, 16]. The challenges in dispersion of CNTs overcame through two methods: i) Ultrasonication process, and ii) chemical dispersion (Use of surfactants for dispersion) and many researches were carried out aligning these methodologies. Even though surfactants/chemical dispersion prove to be a more effective way of dispersing the CNTs [17-19], the ultrasonication process which uses ultrasound energy to disperse particles in solution, proved to be a simple and cost effective way, which also gives considerable results to concrete when immediately used without any time delay into the concrete manufacturing process [20, 21]. Most of the early works concentrated on the strength enhancement of concrete when CNTs are added to the cement or concrete matrix, considering durability aspects such as creep and shrinkage [22]. This paper mainly concentrates on the influence of addition of MWCNTs on the compressive strength and weight density, and also the evaluation is made when this concrete is exposed to erosive environment such as chloride and acidic nature. The work is scrupulously designed and made to understand how an addition of MWCNTs in varying percentages ranging from 0 to 0.25% by weight of cement, influences the strength and resistance when the concrete is in normal condition and then exposed to severe conditions. Further, this work will also provide an insight on effective enhancement of the performance of normal concrete through MWCNTs addition.

**Aim and Objective of this Research**

The main objective of this research is to study the conventional concrete with and without multiwalled carbon nano tubes and its behavior is examined for its strength and weight density in normal and aggressive environment. The understanding of the strength and density in aggressive environment, gives an overall idea about the concrete’s durability property. Also, the microstructural differences between exposed and unexposed samples is studied and how the MWCNT’s influences the microstructure is presented and discussed.

**Material Properties, Sample Preparation and Testing**

**Materials**

The materials used for preparation of concrete are Ordinary Pozzolana Cement (OPC) of 53 grade and well grade coarse aggregate of size less than 20 mm and fine aggregate of Zone II as stipulated by Bureau of Indian Standards (BIS). The MWCNTs used in this study are commercially available in the form of black powder, and the properties of MWCNTs are listed in Table 1.

**Mix Design and Sample Preparation**

The mix is designed as per the guidelines stipulated by Indian standard (IS10262:2019). The concrete constitutes of 425.6 kg /m³ of cement, 149.8 kg/m³ of water, 817.10 kg/m³ of fine aggregate and 1258.8 kg/m³ of coarse aggregate. The MWCNTs are dispersed in water through the technique of mixing MWCNT with surfactant and applying ultrasonic energy for agitating the nano particles and this method is standardized as ultrasonication process which is used in this study for dispersion. MWCNTs are mixed with 50 ml of neutral water along with superplasticizer with additional 50 ml of neutral the solution is added to the dissolution and an ultrasonication bath was used for 30 min. The water dispersed with MWCNTs is used in concrete for mixing immediately after the ultrasonication process. The control specimens are prepared with potable water without any dispersed MWCNTs (MWCN-0). There are six mixes designated with identification (ID) codes such as MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25 which are based on the percentage addition of MWCNT in 0%, 0.05%, 0.1%, 0.15%, 0.2% and 0.25% by weight of cement respectively. The mixed concrete is cast in cubes of size 150 mm x 150 mm x 150 mm, and after 24 hours of casting the moulds are removed and placed in curing tank with water of temperature 25°C for the testing ages of normal compressive strength (unexposed condition).

**Experimental Investigation**

The compressive strength is carried out in 2000 kN Compression Testing Machine (CTM) as per Indian standard (IS516(1959)). The cubes were cured in curing tank for a period of 7, 14, 28, 56, 90 and 180 days. The water is maintained at a temperature of 25°C, and the curing water is changed once in every 7 days.

**Table 1. Properties of MWCNTs.**

| Properties                | Value       |
|---------------------------|-------------|
| Diameter                  | 25 nm (Outer diameter) |
| Length                    | 10 micron (Average)   |
| Metal particles            | <1%          |
| Purity                    | >98%         |
| Bulk density              | 0.14 g/cm³    |
| Specific surface area     | 220 m²/g     |
| Amorphous carbon          | <1%          |
To create the exposure condition 5% concentration of sodium chloride solution and 5% concentration of diluted sulphuric acid is used, the acid solutions was prepared by mixing concentrated acid to water slowly, every 1 litre of potable water is added with 5% of concentrated sulphuric acid. Similarly, chloride solution was prepared by mixing sodium chloride salts in potable water, the salts were dissolved in the proportion of 5 kg salt for every 100 kg of water. The samples prepared are exposed to chloride and sulphuric acid after 28 days of normal curing. The Scanning Electron Microscopy (SEM) is done through Zeiss Scanning Electron Microscope at a magnification of 1000x with energy 20 keV and high resolution of 3.5 nm. For this analysis, from the 28 days cured sample (without exposure to aggressive environment), 8 weeks chloride and 8 weeks sulphuric acid exposed samples were taken and pieces of size 10 mm square cube were cut with a saw cutter. The samples were used for SEM images.

**Results and Discussions**

The results of compression strength of specimens in various ages of curing and the specimens’ weight density and strength after exposing to sodium chloride and sulphuric acid is observed and discussed in this section.

**Compression Strength**

The results of compressive strength of concrete on 7 days, 14 days, 28 days, 56 days, 90 days and 180 days is presented in Table 2 and Fig. 1. On 7th day, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25 attains the strength gain of 10%, 20%, 29%, 26% and 15% respectively in comparison to MWCN-0 i.e., the control specimen. On 14th day the strength gain of MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25 is 13%, 22%, 28%, 15% and 5% respectively in comparison to MWCN-0. On 28th day the strength gain of MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25 is 13%, 22%, 28%, 15% and 5% respectively in comparison to MWCN-0.

Table 2. Compressive strength of concrete specimens.

| Mix ID    | Compressive Strength in MPa |
|-----------|-----------------------------|
|           | 7 Days | 14 Days | 28 Days | 56 Days | 90 Days | 180 Days |
| MWCN-0    | 35.83  | 46.2    | 51.88   | 52.52   | 52.87   | 52.98    |
| MWCN-0.05 | 39.54  | 52.05   | 57.34   | 58.05   | 58.44   | 58.56    |
| MWCN-0.1  | 43.12  | 56.21   | 64.23   | 65.02   | 65.46   | 65.60    |
| MWCN-0.15 | 46.16  | 59.12   | 65.83   | 66.64   | 67.09   | 67.23    |
| MWCN-0.2  | 45.23  | 53.18   | 59.83   | 60.57   | 60.97   | 61.10    |
| MWCN-0.25 | 41.34  | 48.34   | 54.27   | 54.94   | 55.31   | 55.42    |

Fig. 1. Compressive strength of concrete specimens.
is 11%, 24%, 27%, 15% and 5% respectively in comparison to MWCN-0. On 56th day to 180 Days the strength gain of MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25 is 13%, 22%, 28%, 15% and 5% respectively in comparison to MWCN-0. It is observed that from 28th day to 180 day the strength gain in each specimen is minimum. This pattern shows that after 28 days the specimens neither attains additional strength nor loses the achieved strength on ages. After 28 days all the specimens’ strength was normalized and the strength increment is almost 1% to 2% after 28 days on all specimens. The MWCN-0.15 has the maximum strength and strength gain on all ages, all multi walled carbon nano tube added specimens shows strength gain in comparison to control specimen. The increase in mechanical behavior is attributed to the uniform dispersion of MWCNT present in the concrete matrix [23-25] and also due to the embedding nature of the MWCNT in hydration products which in turn increases the strength aspects [26]. The presence of carbon nano tube in cement matrix while manufacturing influences the strength attainment, and the strength increment is also attributed to the chemical nature of the dispersed MWCNTs.

Chloride Exposure

The concrete cubes were exposed to 5% concentrated chloride solution, for a period of 4 weeks and 8 weeks. The weight density and compression strength of exposed samples were observed in Table 3, Table 4, Fig. 2 and Fig. 3. Due to the exposure to chloride the cubes start losing its weight density and the loss of weight density after 4 weeks of exposure is 1%, 0.94%, 0.92%, 0.88%, 0.89% and 1.12% respectively for specimens MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25. After 8 weeks of exposure the loss in weight density is 1.05%, 1%, 0.99%, 0.95%, 0.97%, 1.34% respectively for the specimens MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25. From Fig. 2 it is observed that the loss of weight density during first 4 weeks is steep when compared to second 4 weeks period. It is also observed that samples such as MWCN-0.05, MWCN 0.1, MWCN-0.15 and MWCN-0.2 normalizes the weight density loss after 4 weeks, the specimen MWCN-0 which is control specimen too normalizes but the change in weight loss is higher when compared to other specimens, except MWCN-0.25. Only MWCN-0.25 has steeper weight density loss after 4 weeks period when compared to all other specimens. The observation from Table 3 and Fig. 2 shows that MWCN-0.15 and MWCN-0.2 has the best performance and has the least weight density loss when compared to all other samples, but there was a sudden increase in loss in weight density for the MWCN-0.25 sample. The compressive strength loss of 4 weeks exposed samples is 9.99%, 7.45%, 7.10%, 6.85%, 7.24% and 7.45% respectively for specimens MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25. The compressive strength loss
of 8 weeks exposed samples is 9.56%, 9.34%, 8.89%, 8.34%, 9.12% and 9.43% respectively for specimens MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25. the observation on compressive strength of exposed samples show that as the percentage of MWCN addition increases the strength loss decreases till 0.15% and after which the strength loss again increases. The best performing sample in strength and weight density is MWCN-0.15 under the chloride exposure. The pore filling effect uniform distribution of MWCNTs had led to increased resistance towards chloride exposure [27].

Acid Exposure

The concrete cubes were exposed to 5% concentrated sulphuric acid, and tested for its weight density and compressive strength, before exposure, 4 weeks of exposure and 8 weeks of exposure. The results of weight density before and after exposure is presented in Table 5 and Fig. 4, results of compressive strength of samples before and after exposure is presented in Table 6 and Fig. 5. The acid starts eroding the surface of the samples and thereby resulting in the loss of weight density. The loss of weight density after 4 weeks of exposure is 11.1%, 9.85%, 9.32%, 9.11%, 9.56% and 10.23% respectively for specimens MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25. The loss of weight density after 8 weeks is 15.8%, 13.23%, 12.87%, 12.34%, 12.96% and 13.89% respectively for specimens MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25. From Fig. 4, it is observed that as the days of exposure increases the loss in weigh density also increases. The maximum weight density loss is observed in MWCN-0.25% and least loss is observed in

![Fig. 2. Weight density before and after exposure to chloride solution.](image)

![Fig. 3. Compressive strength before and after exposure to chloride solution.](image)
observed that the control specimen MWCN-0 is the least performing sample. As the percentage of addition of MWCN increases the loss decreases, and all MWCN added samples perform well under compressive strength when compared to the control specimen. The best performing samples are MWCN-0.15, which has lesser loss in weight density loss and compressive strength when compared to all other samples. The distress in acid exposure is also reduced through same effect similar to chloride with uniform distribution and pore filling effect of MWCNTs along with proper dispersion [27, 28].

Table 5. Weight density in kg/m³ before and after exposure to sulphuric acid.

| Mix ID   | Before Exposure (28 days weight density) | 2 Weeks exposure | 4 Weeks Exposure |
|----------|------------------------------------------|------------------|------------------|
| MWCN-0   | 2423.24                                  | 2154.26          | 2040.36          |
| MWCN-0.05| 2423.72                                  | 2184.98          | 2103.06          |
| MWCN-0.1 | 2424.20                                  | 2198.27          | 2112.21          |
| MWCN-0.15| 2424.69                                  | 2203.80          | 2125.48          |
| MWCN-0.2 | 2424.17                                  | 2192.42          | 2110.00          |
| MWCN-0.25| 2423.66                                  | 2175.72          | 2087.01          |

Fig. 4. Weight density before and after exposure to sulphuric acid.

MWCN-0.15. The 0.15% addition of MWCN increases the resistance towards sulphuric acid in concrete. The compressive strength results were presented in Table 6 and Fig. 5. The loss in compressive strength after 4 weeks of exposure is 19.89%, 18.67%, 15.23%, 14.12%, 15.98% and 18.14% respectively for specimens MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25. After 8 weeks of exposure the specimens losses 29.75%, 27.83%, 24.32%, 21.32%, 24.87% and 27.24% respectively for specimens MWCN-0, MWCN-0.05, MWCN-0.1, MWCN-0.15, MWCN-0.2 and MWCN-0.25. From the results it is observed that the control specimen MWCN-0 is the least performing sample. As the percentage of addition of MWCN increases the loss decreases, and all MWCN added samples perform well under compressive strength when compared to the control specimen. The best performing samples are MWCN-0.15, which has lesser loss in weight density loss and compressive strength when compared to all other samples. The distress in acid exposure is also reduced through same effect similar to chloride with uniform distribution and pore filling effect of MWCNTs along with proper dispersion [27, 28].

Table 6. Compressive strength in MPa before and after exposure to sulphuric acid.

| Mix ID   | Before Exposure (28 days Strength) | 2 Weeks exposure | 4 Weeks Exposure |
|----------|------------------------------------|------------------|------------------|
| MWCN-0   | 51.88                              | 41.56            | 29.20            |
| MWCN-0.05| 57.34                              | 46.63            | 33.66            |
| MWCN-0.1 | 64.23                              | 54.45            | 41.21            |
| MWCN-0.15| 65.83                              | 56.53            | 44.48            |
| MWCN-0.2 | 59.83                              | 50.27            | 37.77            |
| MWCN-0.25| 54.27                              | 44.43            | 32.32            |
Scanning Electron Microscopy (SEM) Analysis

Figs 6 to 11 shows the Scanning Electron Microscopy (SEM) images of MWCN-0 to MWCN-0.25 respectively. Each figure is categorized to (a), (b) and (c), where (a) represents the SEM image of sample after 28 days of curing and without exposure to adverse conditions, (b) represents the SEM images of cured samples which is exposed to 8 weeks of chloride solutions, and (c) represents the SEM images of cured samples exposed to 8 weeks of sulphuric acid solution. Fig. 6a) to Fig. 11a) shows that as the percentage of MWCNT increases the visibility increases, Fig. 8a) and Fig. 9a) shows that the MWCNT are dispersed and embedded with the hydration products which is also the reason behind the strength gain, Fig. 10a)

![Fig. 6. SEM Images of MWCN-0 a) After 28 days b) after 8 weeks of chloride exposure c) after 8 weeks of sulphuric acid exposure.](image1)

![Fig. 7. SEM Images of MWCN-0.05 a) After 28 days b) after 8 weeks of chloride exposure (c) after 8 weeks of sulphuric acid exposure.](image2)
shows the MWCNT embedded to hydration product along with few protruding fibres, also in this sample few patches of agglomeration is also noticed. Fig. 11a) shows larger occupation of MWCNT, hence the embedding action has not taken place completely and also there was agglomeration of MWCNT observed. From the images, it is observed that the MCNT are embedded with hydration products, also it is shown that the MWCNT are well dispersed in concrete until MCNT-0.2 sample and small amount of agglomeration is noticed in MWCNT-0.25 (a) samples, which reflects in reduced compressive strength. The MWCNT added is properly dispersed embedded to hydration products and anchored well in concrete bridging the cracks [29]. The strength gain is attributed to the dispersion of MWCNT in the concrete and its dispersed orientation [7]. Thus, the fully disbursed MWCNT with its multiple orientation provides highly effective stable system with good integration [30]. Figs 6b) to Fig. 11b) shows the samples of MWCNT-0 to MWCN-0.25
under chloride exposure. From Fig. 6b) it is observed that the crystallization of products was observed. From Figs 7b) to Fig. 9b) the crystallization is reduced as the percentage of MWCNT increases. Fig. 8b) shows that the embedded MWCNT with products reacts and crystallization is visible around the MWCNT. Fig. 11b) shows the sample with MWCNT-0.25 and larger micro cracks were observed in these samples as there is disintegrated microstructure. There is evidence of crack generation and expansion which can lead to the distress in concrete and influencing their binding behavior [31]. Fig. 6c) to Fig. 11 c) show the samples under acid exposure and there is larger efflorescence observed in the MWCNT-0 samples due to the erosion of hydration products. MWCN-0.05 on Fig. 7c) shows the eroded region with broken crystallization. Fig. 8c) and Fig. 9c) shows more confined and denser micro structure and also crystallization had reduced due to the protective layers formed through embedded MWCNT, this provides more resistance for acid to penetrate and react. Fig. 10c) shows again increased crystallization due to larger pores when compared to earlier samples, and Fig. 11c) shows heavier disintegration due to higher presence of MWCNT, also the crystallization is larger when compared to all the other samples. Also, it is noted that the embedded MWCNT are visible although the cracks, due to its disorientation. The behavior of this concrete shows that resistance is based on the crystalline hydration products and layers, instead of depending towards the micro crack [32].

Conclusions

This study shows that the addition of MWCNTs in the range of 0.05% to 0.25% increases the compressive strength of concrete, and in the range of 0.5% to 0.25% the resistance towards chloride and acid environment improves, thus enhancing the durability property of concrete. All the batches with MWCNTs have increased the compressive strength in comparison to control specimen; with 0.15% of addition has the maximum strength gain. Also, it is noted that after 28 days of curing the compressive strength get normalized on all mix, which shows that there is no later age strength development, and most of the strength attainment is completed within 28 days. The same pattern of behavior is observed on concrete under chloride and acid exposed condition, which also shows a considerable resistance on all MWCNTs added mixes in comparison to the control specimen. The effect due to chloride and acid is resisted maximum at 0.15% MWCNTs added specimens. The phenomenal performance increment is attributed to uniform distribution and pore filling effect of MWCNTs. The SEM analysis shows that until 0.20% of addition of MWCNTs in concrete, the MWCNTs gets well embedded with the hydration products resulting in higher performance of concrete in exposed and non-exposed condition. A little amount of protruding MWCNT is noted in 0.20% MWCNT added specimens which results in a little strength loss in comparison to 0.15% MWCNTs added specimen. It is also noted through the SEM images that 0.25% MWCNTs added specimens possess microcracks, which may lead to future distress in concrete. The addition of MWCNTs has influenced to the formation of protective coating through its embedding behavior, which in turn reduces the crystallization effect due to severe exposure conditions. Ultimately, this study concludes that the well uniformly dispersed MWCNTs in concrete can improve the performance of concrete both in severe exposure condition and unexposed condition. Consequently, the addition of 0.15% of MWCNTs has the best performance effect in comparison to the other mixes considered in this study.

Conflict of Interest

The authors declare that they have no conflict of interest.

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Data Availability Statement

All the data used in this article are available in the manuscript tables and figures.

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