The Mn-Ferrite nanoparticles were prepared using citrate nitrate auto combustion method. The Multiwalled Carbon Nanotubes (MWCNTs) and MnFe$_2$O$_4$ nanoparticles were characterized by BET to measure the surface area. XRD data of MnFe$_2$O$_4$ nanoparticles clarified that the sample was formed in single phase spinel structure without any extra peaks indicating any secondary phase. The High-Resolution Transmission Electron Microscopy (HRTEM) micrograph of MnFe$_2$O$_4$ nanoparticles indicated that the particles are in an agglomerated state due to the absence of surfactant and high magnetic properties of Mn-Ferrite nanoparticles. Also, HRTEM micrograph showed that the walls of MWCNTs are straight having high crystallinity without any kinks. The mechanical properties were measured at different ratios of MWCNTs and nano-ferrite to cement. The obtained values indicated that the addition of MWCNTs and nano-ferrite increase the compressive and flexural strength of cement mortar and decrease the total intrusion volume.

Keywords: MWCNTs, MnFe$_2$O$_4$ nanoparticles, HRTEM, Compressive strength, Flexural strength

INTRODUCTION

Concrete is one of the most prevalent materials on the ground and holds promises to be a cornerstone for our expansion in construction industry. More than 10 billion tons of it are produced every year for everything from major infrastructure projects like bridges, tunnels, dams, to homes, stadiums, and skyscrapers. However, cementitious materials in general, are very brittle and characterized by a very low tensile strength and strain capacity (Tyson, 2011; AlSalaami, 2007). The mechanical property of concrete arises from a phenomenon that occurs at the micro and nano scale, i.e., interlinking of dendrites of calcium silicate hydrates during the hardening process. Nanoscale binders can modify the structure of concrete material and enhance its properties including bulk density, mechanical performance, volume stability, durability and...
sustainability of concrete (Grebler, 2012).

Within the last few years, an increasing interest is in the application of nanoparticles in concrete, because nanoparticles due to its high specific surface area and high activity offers the opportunity to improve the mechanical properties of concrete and enhance the understanding of concrete behavior (Nazari, 2010). CNTs and ferrite nanoparticles are quickly becoming one of the most promising nanomaterials because of their unique mechanical properties.

The superior mechanical properties of the CNTs and ferrite nanoparticles alone don’t ensure the improvement of mechanical properties of cement. The properties of the concrete composite are strongly influenced by two major factors. The first is the dispersion of these nanomaterials within the cementitious matrix. The other is the bond strength and energy between the matrix and surface of the CNTs or ferrite nanoparticles (Tyson, 2011).

Several researches have been done on the partial replacement of cement with supplementary nanomaterials to improve their mechanical properties. The most of these researches are focusing on using SiO\(_2\) (Zhang, 2012) nanoparticles and CNTs (Tyson, 2011). There are a few studies on incorporating of different nanoparticles such as Fe\(_2\)O\(_3\) (Yazdi, 2011), Al\(_2\)O\(_3\) (Ali Nazari, 2011), CaCO\(_3\) (Liu, 2012), TiO\(_2\) (Meng, 2012), ZnO\(_2\) (Ali, 2011), ZrO\(_2\) (Mohammed, 2011) and CuO (Ali, 2011).

The effects of nano-silica (NS) on setting time and early strengths of high volume slag mortar and concrete was discussed (Zhang, 2012). He used a constant water-to-cementitious materials ratio (w/cm) 0.45 for all mixtures. He found that compressive strength of the slag mortars increased with the increase in NS dosages from 0.5% to 2.0% by mass of cementitious materials at various ages up to 91 days.

Nano-ZrO\(_2\) (NZ), Nano-Fe\(_3\)O\(_4\) (NF), Nano TiO\(_2\) (NT) and Nano-Al\(_2\)O\(_3\) (NA) were added to concrete mixtures to investigate its mechanical properties and durability (Sjhekaria, 2011). Results of this study showed that nanoparticles can be very effective in improvement of both mechanical properties and durability of concrete. The results indicated that the Nano-Al\(_2\)O\(_3\) is most effective nanoparticle of examined nanomaterials in improvement of mechanical properties of high performance concrete.

Carbon nanotubes and carbon nanofibers were used for enhancing the mechanical properties of cementitious materials (Tyson, 2011). He added untreated CNTs and CNFs to cement matrix composites in concentrations of 0.1% and 0.2% by weight of cement. The flexural test was performed to record its mechanical properties at 7, 14, and 28 days. SEM images verified poor dispersion within the cement paste matrix, the bridging effects, which transferred the load across the nano and microcracks, and the fibers pull out because of their weak bond. For all cases, the addition of CNFs and CNTs improved flexural strength of the cement paste compared to the control sample.

The aim of this study is to find the optimized percentage of adding MWCNTs and MnFe\(_2\)O\(_4\) nanoparticles to achieve the highest values of compressive and flexural strength of cement mortar.
MATERIALS AND METHODS

Materials and Mixtures

Cement
Ordinary Portland Cement (OPC) grade (CEM I 52.5N) obtained from AL-Areash Cement Manufacturing Company of Egypt conforming to the British standard BS 12/1996 was used as received. The chemical properties of the cement are obtained from Analytical Axios Advanced X-ray fluorescence (XRF) and the results are reported in Table 1.

MWCNTs and MnFe$_2$O$_4$ Nanoparticles
MWCNTs was used as received from Yurui (Shanghai) chemical Co., Ltd. with diameter 20-55 nm and average surface area was 98.31 m$^2$/g. The properties of MWCNTs are shown in Table 2. High-Resolution Transmission Electron Microscopy (HRTEM) are shown in Figure 1.

MnFe$_2$O$_4$ nanoparticles with average diameter of 49 nm and average surface area of 27.28 m$^2$/g was prepared by citrate nitrate auto combustion method at materials science lab. (1) (Ahmed, 2008 and 2012). The properties of MnFe$_2$O$_4$ nanoparticles are also shown in Table 2. HRTEM and powder X-ray diffraction (XRD) diagrams of MnFe$_2$O$_4$ nanoparticles are shown in Figures 2 and 3, respectively.

Aggregates
Coarse sand (0.5-2 mm) was used to produce cement mortar.

Super Plasticizer
Sika ViscoCrete® -5930 is an aqueous

| Table 1: Chemical and Physical Properties of Portland Cement (wt%) |
|------------------|------------------|------------------|------------------|------------------|
| Al$_2$O$_3$      | SiO$_2$          | CaO              | TiO$_2$          | Na$_2$O          | MgO              | SO$_3$          | K$_2$O          | Fe$_2$O$_3$      | LOI              |
| 4.46             | 15.15            | 66.89            | 0.37             | 0.58             | 0.58             | 4.02            | 0.22            | 4.49             | 3.24             |

| Table 2: Properties of MWCNTs and MnFe$_2$O$_4$ Nanoparticles |
|-------------------|-------------------|-------------------|-------------------|-------------------|
|                   | Average Diameter/nm | Average Surface Area /(m$^2$/g) | Average Volume/ (cc/g) | Purity/ % |
| MWCNTs            | 20-55              | 98.31              | 0.0494             | 97               |
| MnFe$_2$O$_4$     | 49                 | 27.28              | 0.0134             | 98-99            |

Figure 1: HRTEM Micrograph of MWCNTs
solution of modified polycarboxylate was used. Table 3 reports some of the physical and chemical properties of polycarboxylate admixture used in this study.

**Mixture Proportioning**

Nine mixtures of cement mortar were prepared in the laboratory trials. These mixtures included a reference sample of plain cement mortar, three mixtures of cement mortar with MWCNTs at 0.3 wt%, 0.5 wt% and 0.7 wt% by weight of dry cement, three mixtures of cement mortar with MnFe$_2$O$_4$ nanoparticles at 0.3 wt%, 0.5 wt% and 0.7 wt% and two mixtures of cement mortar with both MWCNTs and MnFe$_2$O$_4$ nanoparticles at 0.15 wt%, 0.3 wt% for each of them. Table 4 summarizes the composition of the nine mixtures.

The superplasticizer was dissolved in water, and then MWCNTs and MnFe$_2$O$_4$ nanoparticles were added and good stirred at a high speed for 2 min. The binder content of all mixtures was 635 kg/m$^3$. The total mixing time including homogenizing was 5 minutes.
Cubic Specimens with 50 mm edge length were used for compressive tests and prism specimens with dimensions 40 x 40 x 160 mm were used for flexural tests. The moulds were covered with polyethylene sheets and moistened for 24 h. Then, the specimens were demoulded and cured in water at room temperature prior to test days (Yazdi, 2011). The strength tests of the samples were determined after 2 and 14 days of curing. The tests were carried out triplicately and average strength values were obtained.

**Mercury Intrusion Porosimetry (MIP)**

MIP Poresizer 9320 V2.08 was used to characterize the pore structure in porous material as a result of its simplicity, quickness and wide measuring range of pore diameter (Abell, 1999; Tanaka, 2002). MIP gives us details about the dimensions of pores (Abell, 1999). To prepare the samples for MIP measurement, the concrete specimens after 14 days of curing were first broken into smaller pieces, and then the cement paste fragments selected from the center of prisms were used to measure pore structure. The samples were immersed in acetone to stop hydration as fast as possible. Before mercury intrusion test, the samples were dried in an oven at about 110°C until constant weight is obtained by removing...
moisture in the pores. MIP is based on the assumption that the non wetting liquid mercury (the contact angle between mercury and solid is greater than 90°) will only intrude in the pores of porous material under pressure (Abell, 1999; Tanaka, 2002). Each pore size is quantitatively determined from the relationship between the volume of intruded mercury and the applied pressure (Tanaka, 2002). The test apparatus used for pore structure measurement is Auto Pore III mercury porosimeter. The surface tension of mercury is taken as 485*10^{-5} \text{N/cm} (485 \text{dyne/cm}), and the contact angle selected is 130 deg. The maximum head pressure applied is (4.68 \text{psi}).

**Field Emission Scanning Electron Microscope (FE-SEM)**

After the samples had been tested, the fracture surface was cut into an approximately 1 × 1 × 0.5 mm. Then, a Field Emission Scanning Electron Microscope (FE-SEM) (JSM-7500F, JEOL, Tokyo) was used to observe the fracture surface of the samples.

**RESULTS AND DISCUSSION**

Figures 4-7 show compressive and flexural strength of cement mortar specimens after 2 and 14 days of curing, respectively. The results show that the compressive and flexural strength increases by addition of MWCNTs content till 0.7 wt % replacements to cement mortar. This was due to the interfacial interactions between MWCNTs and cement hydrates to bridge nanocracks and pores to achieve good bonding with the cement hydration products.

On the other hand, by the addition of MnFe$_2$O$_4$ nanoparticles with 0.5 wt%, the compressive and flexural strength increase after which it decreases. The reasons that allow MnFe$_2$O$_4$ nanoparticles to increase the strength of concrete can be explained as follows. The addition of MnFe$_2$O$_4$ nanoparticles reduces the quantity and size of Ca(OH)$_2$ crystals and fills the voids of Calcium Silicate Hydrate (C-S-H) gel structure. This make the structure of hydrated products denser a (Ali, 2011) compact (Ali, 2011). Increasing MnFe$_2$O$_4$ nanoparticles more than 0.5 wt%, the compressive strength reduces. This matter is because nanoparticles due to their high surface energy have the tendency towards agglomeration. When MnFe$_2$O$_4$ nanoparticles are over added to the concrete, it is not uniformly distributed in cement paste and due to agglomeration, weak zone appears in the concrete specimen. The highest values of compressive and flexural strength achieved by the addition of both MWCNTs and MnFe$_2$O$_4$ nanoparticles by 0.3 wt% for each of them with enhancement by 19 % for compressive strength and by 21% for flexural strength compared to the control specimen. This is due to the ability of MnFe$_2$O$_4$ nanoparticles to fill the voids at the nanoscale and MWCNTs to act as bridges across voids and cracks that ensure more compact and durable cement mixture.

The mercury intrusion results of the C0 specimen and N$_3$-2 specimen are shown in Figures 8 and 9. Figure 8 represents the variation of incremental intrusion, reflecting pore volume against pore diameter, which indicates that most pore diameter of the specimen are distributed between 0.1 micrometer to 1 micrometer. Figure 9 represents the cumulative intrusion, reflecting the total connected pore volume of pore sizes.
Figure 4: Compressive Strength of Specimens After 2 Days of Curing

Figure 5: Compressive Strength of Specimens After 14 Days of Curing

Figure 6: Flexural Strength of Specimens After 2 days of Curing
Figure 7: Flexural Strength of Specimens After 14 days of Curing

Figure 8: Incremental Intrusion Versus Diameter for Specimens of Concrete (left: C0, right: N3-2)

Figure 9: Cumulative Intrusion Versus Diameter for Specimens of Concrete (Left: C0, Right: N3-2)
Table 5 shows that by the addition of both MWCNTs and MnFe$_2$O$_4$ nanoparticles by 0.3 wt% for each of them, total intrusion volume of specimens are decreased. This leads to decreasing total pore area and median pore diameter of cement mortar (area), but median pore diameter (volume) of these specimens is increased. On the other hand, Table 6 shows that the addition of MWCNTs and MnFe$_2$O$_4$ nanoparticles leads to decreasing the porosity, increase the average pore diameter and decreasing the bulk density and the apparent (skeletal) density of these specimens of cement mortar. This means that the regularity of porosity is similar to that of total intrusion volume and the regularity of average pore diameter is similar to median diameter (volume). The increase of average pore diameter and median diameter (volume) are due to the ability of MWCNTs and MnFe$_2$O$_4$ nanoparticles to fill the small pores. The decrease of density is due to the replacement of cement by MWCNTs and MnFe$_2$O$_4$ nanoparticles which have a lower density leading to a decrease in the density of the composite.

Figures 10, 11 present FE-SEM photographs of the cement mortar of C0 specimen and N3-2 specimen after 14 days of curing. The results confirmed an improved microstructure in the cement mortar with MWCNTs and MnFe$_2$O$_4$ nanoparticles addition. In the control specimen showed in Figures 10a, 11a, the microstructures were non-compact, with extensive

<p>| Table 6: Average Pore Diameter, Bulk Density, Apparent (skeletal) Density and Porosity of C0 and N1 3-2 specimens |</p>
<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Average Pore Diameter/nm</th>
<th>Bulk Density/(g/mL)</th>
<th>Apparent (Skeletal) Density/(g/mL)</th>
<th>Porosity/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>20.3</td>
<td>2.48</td>
<td>3.89</td>
<td>36.32</td>
</tr>
<tr>
<td>N 3-2</td>
<td>28.4</td>
<td>2.17</td>
<td>2.53</td>
<td>16.00</td>
</tr>
</tbody>
</table>

**Figure 10: SEM Micrograph of Specimens of Concrete After 14 Days of Curing (Left: C0, Right: N3-2)**

a) 50 µm

b) 50 µm
presence of large crystals of calcium hydroxide. However the voids among cement particles have been occupied by the hydration products, many connected capillary pores were observed.

The cement mortar specimen with MWCNTs and MnFe$_2$O$_4$ nanoparticles addition showed denser formations of hydration products than the control specimen as showed in Figure 10b, 11b. It is obvious that, regardless of the presence of many pores, the density is significantly improved and the volume of pores reduced due to the ability of MnFe$_2$O$_4$ nanoparticles to fill the pores. This leads to improving impermeability thus the durability and the microstructure of the hardened cement-based materials (Deyu, 2012). The calcium hydroxide was appeared as ill-crystals (Morsy, 2011) as shown in Figures 10 and 11. the pozzolanic reaction between MnFe$_2$O$_4$ nanoparticles and calcium hydroxide liberated during hydration produced additional C-S-H gel resulting in significant improvement in mechanical properties of blended mortar.

In addition, the microscopic observation also reveals that the MWCNTs were covered by C-S-H. The MWCNTs were found embedded as individual fibers in the paste and acting as bridges between hydrates and across cracks (Morsy, 2011).

**CONCLUSION**

The obtained results can be summarized as follows.

1. The results showed that cement specimen reinforced with both MWCNTs and MnFe$_2$O$_4$ nanoparticles after 2 and 14 days of curing have higher compressive and flexural strength compared to the control specimen. MWCNTs and MnFe$_2$O$_4$ nanoparticles accelerate consumption of crystalline Ca(OH)$_2$ which quickly are formed into C-S-H during hydration of cement specially at early ages due to the high reactivity of these nanoparticles.

2. The pore structure of cement mortar containing both MWCNTs and MnFe$_2$O$_4$ nanoparticles with 0.3 wt.% was improved
and the volume of all mesopores and macropores was decreased.

3. FE-SEM images showed that specimen reinforced with both MWCNTs and MnFe$_2$O$_4$ nanoparticles with 0.3 wt. % is more compact and less porous in the paste with admixture than the control one.

REFERENCES


