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Preference of Using Nano Silica\Magnetite Core-Shell on Enhancement Mechanical and Morphological Properties of Cement Mortar

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Abstract

This work aims to produce a cheap nano-sized admixture using silica oxide from rice husk and magnetite in the shape of the core-shell nanostructure, and investigate the effect of using different replacement ratios of cement by silica\magnetite core-shell nanostructure (SMCS) on the mechanical and morphological properties of cement mortars. Also, the present work compares this effect by the effect of using the same hybrid dosages of a nano-composite of silica and magnetite nanoparticles. SMCS consists of silica nanoparticles (NS) as the inner core, which green synthesized from rice husk after treatment by sol-gel method. While the outer shell was from magnetite nanoparticles (NM) synthesized by precipitation assistant by (ultra-sonication). Two scenarios were performed to analyze the effectiveness of using SMCS. In first scenario, Different replacement ratios of cement with SMCS (0% as a control, 2.5%, 5% and 7.5%) by weight of cement were tested. In the other scenario nano-composite of NS and NM were used to replace SMCS. Results show that using SMCS as a replacement material of cement enhancing the mechanical and morphological properties of cement mortars more overusing the same replacement ratios of nano-composite of NS and NM. Even though, enhancement of mortars properties occurred in both scenarios

Keywords: Core-shell nanostructure, Nano Silica, Nano Magnetite, Consistency, Compressive strength, Flexural strength, Microstructure.

1. INTRODUCTION

Nowadays numerous studies and works concerning the concept of sustainable and environmental issues, also fabrication of concretes using agriculture and industrial waste was enlarged [1–5]. In agriculture urban rice husk is a very big problem in the case of disposal, many farmers burning rice husk which caused air pollution problems. Therefore, governments, industry, and researchers tightened their attention to develop a cheap and sustainable material used as an addition to cement mortar to contribute a more sustainable construction. Numerous studies have been focused on the effect of silica oxide (SiO_2) as a pozzolanic material to improve mechanical properties and microstructure of cement mortar[6–8], and fresh and hardened properties of mid, high and ultra-high-strength concrete [9–12].

Suthatip Sinyoung et al, [13], used nano silica from rice husk ash calcinations and ash from rice husk industrial waste, as a new sustainable method of cement manufacturing by firing cement belite with calcium carbonate and calcium nitrate at 800 - 1100 ºC. Results show that nano silica from wastes of rice husk industries suitable as a material to produce low-temperature belite cement, especially in conjunction with calcium nitrate as the calcium source.

Nanotechnology gives a new concept of material science by using nanoscale and nanoparticles to develop materials structure, nanoparticles featured with large surface area, and high chemical reactivity. Many researches investigate the effect of different types of nanoparticles like as nano-silica, ferrite, titanium and metakaolin on improvement concrete and cement mortar properties [14–21].

Due to the scientific development of the nanotechnology field, nanoparticles in the shape of core-shell structure is a new approach used as a chemical motivation or photo-catalytic in cement mortar and concrete [18,20,22]. Core-shell nanostructure consists of two nanomaterials one of them forms the core of the particle and the other is the shell coating over the core, Core-shell nanostructure can be prepared by many simple and easy ways, using heat and sonic waves, [23]. It constitutes operability, stability and self-assembly moreover that the chemical action of core-shell nanostructure differed completely if using a blend consists of the two nano-particles which form NCS, as reported by *Zhao et al* [24].

Pawel Sikora et al, [18], Benefited the formation of nano core-shell structure to improve the mechanical properties of cement mortar exposed to elevated temperature. The used core-shell consists of magnetite (Fe_2O_3) as a core and coated by silica (SiO_2) as a shell coat. The cement specimens were fabricated with the replacement ratio of cement by 3 % and 5 % nano core-shell magnetite/silica or nano-magnetite, as well as a plain cement mortar fabricated as a control one to compare results. Specimens were exposed to elevated temperatures of 200, 300, 450, 600 and 800 ºC. The loss of mass after cooling and flexural and compressive strengths of the specimens were determined. They concluded that the presence of a core-shell is much more useful to improve the thermal resistance of cement mortars than pure nano-magnetite. Hence, this comparison was inaccurate, moreover that this conclusion doesn't express the truth. Where authors compare mortars contains silica and magnetite in one core-shell structure by mortars contain magnetite only, and they ignore the effect of silica in the mortars. While silica shell in the nano-particles improves compressive strength and prevents crack extension in cement mortars in general. Subsequently, improve the properties of mortars exposed to elevated temperatures.

In the study by *Jinfeng Sun at al*, [20], the nano core/shell of TiO_2/SiO_2 was used as a replacement material of cement by 1 % by weight to investigate cement hydration and compare with the same replacement ration of nano-TiO_2 through isothermal calorimetry. Results showed that the nano core/shell TiO_2/SiO_2 exhibited better hydration properties in terms of accelerated cement hydration, higher the degree of hydration and lower porosity, even though both types of nano-particles modified cement hydration. Also, the authors ignore the effect of silica in the mortars, so this comparison was inaccurate.

2. RESEARCH SIGNIFICANCE:

The scope of this study is to produce a cheap sustainable nano-sized admixture in the shape of the core-shell nanostructure, and rectification previous studies and do a correct and accurate comparison in studying and investigating mechanical and morphological properties of cement mortar contains replacement ratios of SMCS by the same dosages of a nanocomposite of NS and NM with the same dosages of core-shell formation. Whereas, authors cannot ignore one of the main components of the core-shell structure. Also, this work will answer a lot of scientific questions spin in the mind of nanotechnology researcher about the great effect of a small quantity of nonmaterial on improving the mechanical properties of cement mortar such as what mechanism of enhancement the mechanical properties of cement mortar by adding a certain amount (very small) of nonmaterial? Why there is a critical amount of nonmaterial to give perfect enhancement? And in our work what is the preferred form of nanomaterial used to enhance the mechanical and microstructural properties of cement mortar SMCS or magnetite-silica nano-composite? To answer these questions must be evaluated what is called "nano-power" which can illustrate the enhancement mechanism of cement mortar.

3. EXPERIMENTAL WORK:

In order to determine and compare the mechanical properties of cement mortar, seven different cement mortars containing deferent replacement ratios of cement by SMCS or nanocomposite of NS and NM were designed and prepared according to BS EN 196-1 [25]. These mortars divided into three series (control, group I with SMCS replacement ratios and group II with a replacement ratio of silica and magnetite nano-composite). Consistency of the fresh mortars has been identified by performing a twenty-one test with the flow table method. Eighty-four cube specimens having a dimension of 50 X 50 X 50 mm were prepared and cured to conduce the compression test after 7 and 28 days, while flexural strength test conducted using forty-two prismatic specimen of 40 X 40 X 160 mm using a three-point testing device, and tested at curing age of 28 days. Six specimens were utilized for each test and the average result was reported, all testes conducted according to BS EN standard, [25].

3.1. Materials:

Ordinary Portland Cement CEM I 42.5N in accordance with BS EN 197-1, [26] was used, the chemical composition of the cement presented in table 1, also quartz sand < 2.00 mm, having specific gravity equal to 2.5 used as a fine aggregate and tab water was used, the specification of sand and water was in accordance with British standard, BS EN 196-1 [25], BS EN 1008 [27], respectively. Three types of nanomaterial, silica/magnetite nano-core shell structure, nano-silica and nano-magnetite were prepared and characterized by the Egyptian Nanotechnology Center, Cairo University, Egypt.

Table 1. Chemical and Physical Properties of Cement CEM I 42.5N.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Cl^-	Loss on Ignition	Density g/cm^3	Fineness cm^2/g
22	4.8	3.2	63.2	1.6	2.5	0.05	2.2	3.18	3300

3.2. Synthesis and Characterization of Nano-Materials:

2.2.1 Materials:

$FeCl_3$ and $FeCl_2$ manufacture by Sigma Company, India. The ammonia of 34 % concentration, H_2SO_4 and HCl manufacture by Al Nasr Company, Egypt. and Rica husk form mill in El Mansoura area, North Egypt.

2.2.2 Synthesis of Magnetite nanoparticles:

13 grams of $FeC1_2.4H_2O$ and 26 grams of $FeCl_3.6H_20$ were dissolved in 60 ml of water under 40 °C using a mechanical

stirrer. Ammonia 34% concentration added drop by drop (about 60 ml) until the rubicund magnetite precipitate formed. Magnetite nanoparticles were washed to access the desired chemical, by placed on to a permanent magnet to accelerate settling. After standing on the magnet for 10 minutes, the clear magnetite nanoparticles were decanted, [28].

2.2.3 Synthesis of silica nanoparticles:

20 grams of rice husk ash obtain by burned pure clean rice husk in a muffle furnace at 750 °C at a rate of 10 °C per minute with soaking for 3 hours was stirred in 180 ml sodium hydroxide solution and heated for 1h at 90 °C. The obtained colorless, transparent, viscous and solution was allowed to cool down to room temperature. Then controlled PH at 2 by adding H_2SO_4 (5.00 mol/L) drop by drop with constant stirring then NH_4OH was added until pH become 8.5, and allowed to sit at room temperature for 1 h. silica nanoparticles were prepared by refluxing of extracted silica with HCl (6.00 mol/L) for 4 h and then washed repeatedly using deionized water to make it acid-free. It was then dissolved in a sodium hydroxide (2.5 mol/L) with stirring until PH become 8, [29].

2.2.4 Synthesis of silica/magnetite core-shell nanostructure:

24 grams of $FeC1_2.4H_2O$ and 48 grams of $FeC1_3.6H_2O$ were dissolved in a mixture of 100 ml deionized water and 25ml ethanol at 40 °C then add 8 grams silica nanoparticles with continues stir for 1h. 100 ml ammonia of 34% concentration adds to mixture drop by drop under subject sonication of 50 kHz with cycle 2, plus every 3 sec. and amplitude of 100 % for 1h. finally black precipitate obtains from centrifuge at 800 rpm was washing many times using ethanol and permanent magnet.

2.2.5 Characterization:

Characterization was carried out to confirm the formation of core-shell nanostructure with silica in core and magnetite nanoparticles in the shell without any undesired chemical from the synthesis method and give some information about its shape, size, surface area, roughness profile and pore size of SMCS. Conformed the composition of SMCS carried out by XRD (D8 Discovery–Bruker Company) at the condition of 40 KV and 40 AM (1600W) at speed scan 0.02 and 2theta (θ) range from 10 to 80 degrees, XRF (X-Met 8000 Oxford Instruments Co.) and Raman spectrometer (Lab. RAM-HR Evolution Horiba Co.) with acquisition time 50 sec, accumulations 1 without spike filter and delay time and objective was X100 with grating 1800 (450-850 nm) and ND filter 50%. The laser type was green of 532 nm. 2D and 3D shape, agglomeration, concentration and size carried out by transmission electronic microscope (TEM) model EM-2100 High-Resolution at magnification 25X and voltage 200 kV and Scanning electron microscope (SEM) was carried out by Jol 2000, Japan. Roughness profile carried out by an Atomic force microscope (AFM) using AFM 5600LS Agilent Technology Company. Surface area and pore size analysis carried out not only SMCS but also individual magnetite nanoparticles and silica nanoparticles to compare chemical activity between them by surface area and pore size analyzer model Nova Touch LX2 manufactured by Quanta chrome Co. Zeta potential and sizing were also determined in this sector by Nano Sight NS500 manufacture by Malven, UK.

3.3. Mixes Proportions:

The Control mix M1 was designed to achieve a reasonable cement mortar consistency with proportion 1:3:0.5 Cement to Sand to Water respectively. Whereas, three mixes of group I, M2, M3, and M4 were prepared with partial replacement ratios 2.5%, 5% and 7.5% of cement by SMCS. Another three mixes of group II, M5, M6 and M7 were prepared also to compare the effect of SMCS material by the molecular hybrid of nano-magnetite and nano-silica, the three mixes containing 2.5%, 5% and 7.5% of nano-silica and nano-magnetite as a replacement ratio of cement. The blending proportion of molecular hybrid of nano-magnetite and nano-silica was 70 % : 30 % respectively to satisfy the composition of core-shell. The composition of cement mortar presented in table 2.

Table 2. Composition of cement mortar, kg/m^3.

Sample		Cement	Sand	Water	SMCS	Nano-Silica	Nano-Magnetite
M1 (R)		496.4	1489.2	248.2	0.00	0.00	0.00
Group I	M2	483.99	1489.2	248.2	12.41	0.00	0.00
	M3	471.58	1489.2	248.2	24.82	0.00	0.00
	M4	459.17	1489.2	248.2	37.23	0.00	0.00
Group II	M5	483.99	1489.2	248.2	0.00	3.72	8.69
	M6	471.58	1489.2	248.2	0.00	7.45	17.37
	M7	459.17	1489.2	248.2	0.00	11.17	26.06

4. RESULTS AND DISCUSSION:

4.1. Characterization:

XRD chart and data fig. (1) of SMCS shows the best fit chart for silica and magnetite according to ICCD database, where magnetite nanoparticles match for COD 9005812 and silica nanoparticles COD 4124042. XRD pattern shown peaks identified to magnetite and silica nanoparticles without any contamination peaks confirming the formation of SMNC without any undesired chemical of synthesis method. Using Eva software from Burker D8 discovery software package elemental analysis and composition analysis carried out for SMCS XRD data, conforms formation of core-shell ratio was about 2.35:1, where the magnetite nanoparticles have 70.18 % and silica nanoparticles have 29.82 % also the percent of oxygen, iron and silicon was 35.5%, 52% and 14.4% respectively.

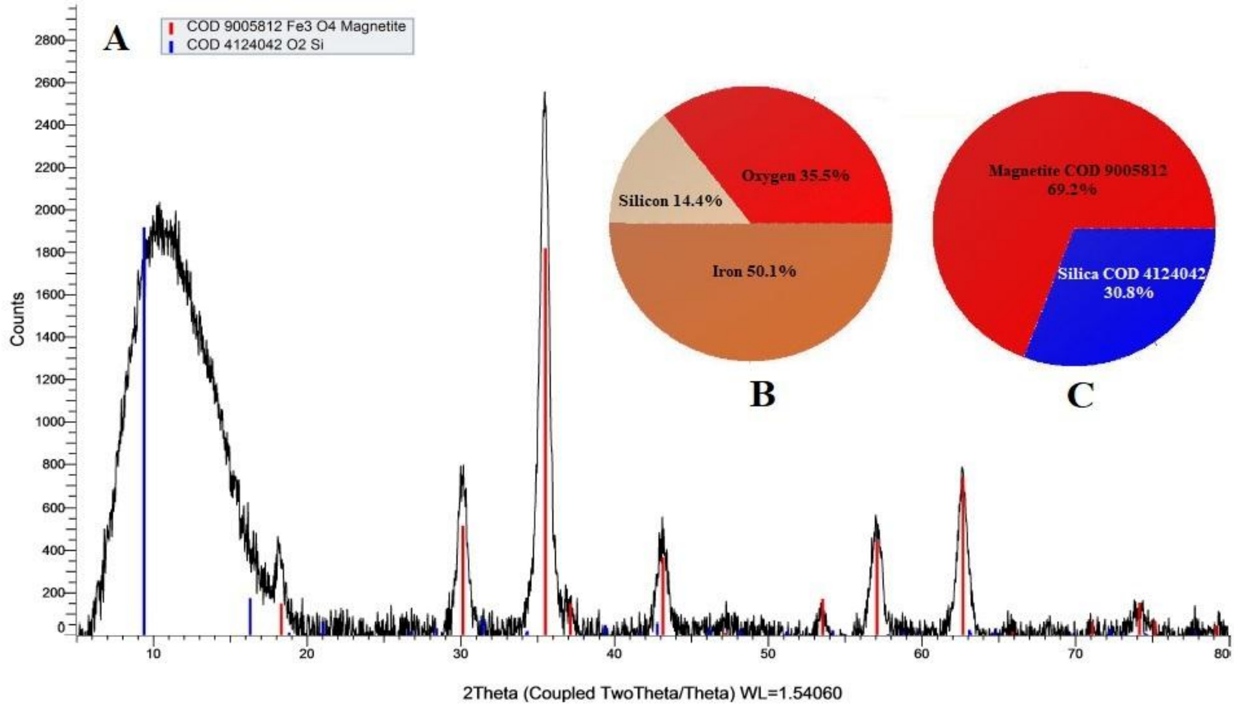

Figure (1): XRD pattern, elements and composition of SMCS

Also, XRF charts and data are shown in figure fig. (2), illustrate and ensure the formation of SMCS. Magnetite nanoparticles were about 70.22 %, while silica nanoparticles were about 29.78%.

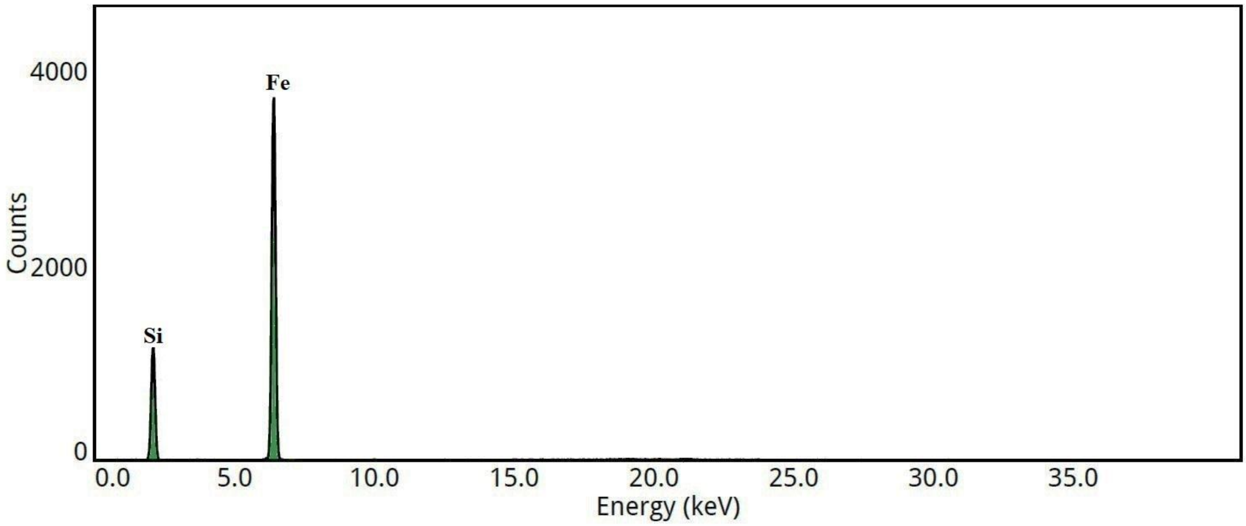

Figure (2): XRF chart of SMCS

Raman spectroscopy chart Fig. (3), illustrates the confirm formation of SMCS. Where three Raman peaks characteristic to magnetite nanoparticles at 293.55 cm-1, 548.76cm-1 and 696.14cm-1 and the characteristic peak of silica nanoparticles at 475.56 cm-1. A top view and 3D confocal images also can confirm the homogeneity of the SMCS.

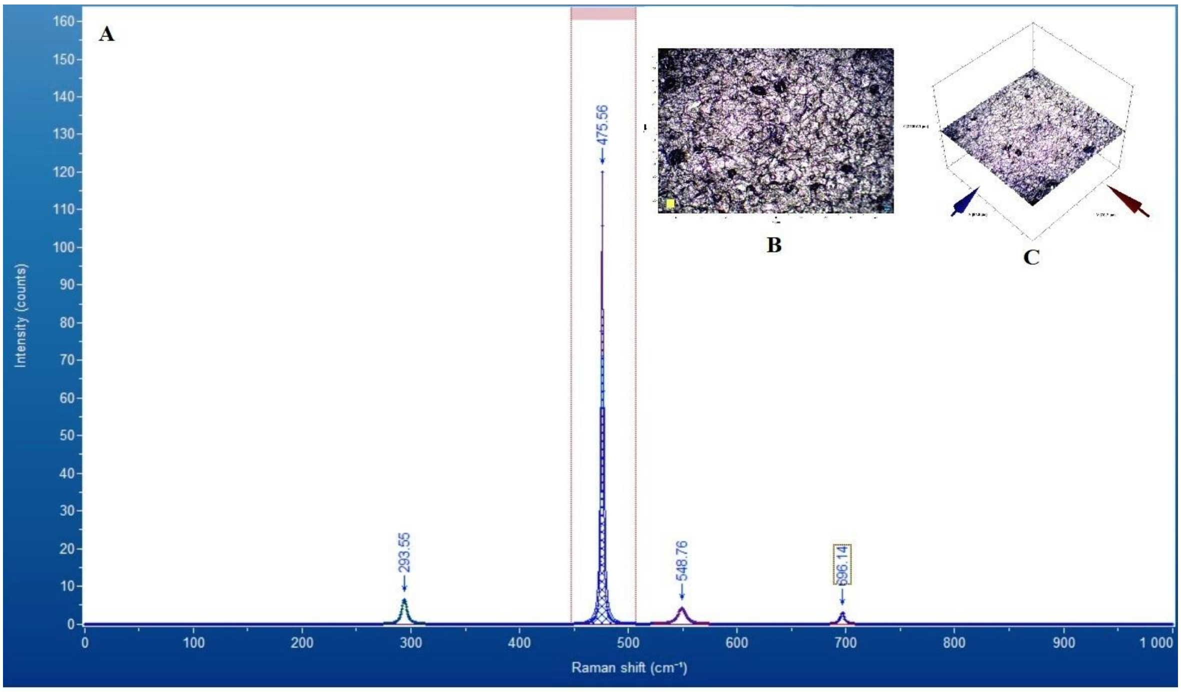

Figure (3): Raman chart, Top view image and 3D image of SMCS

TEM image Fig. (4), shows the spherical shape with porous silica nanoparticles (core) and magnetite nanoparticles (Shell) with clear edges between them. The agglomeration and concentration were well sorted. SEM image in Fig. (5) shows the 3D spherical porous silica nanoparticles (core). Also, TEM and SEM images show the size of SMCS range from 40 to 50 nm, with 25 nm for core and 15 nm for the shell.

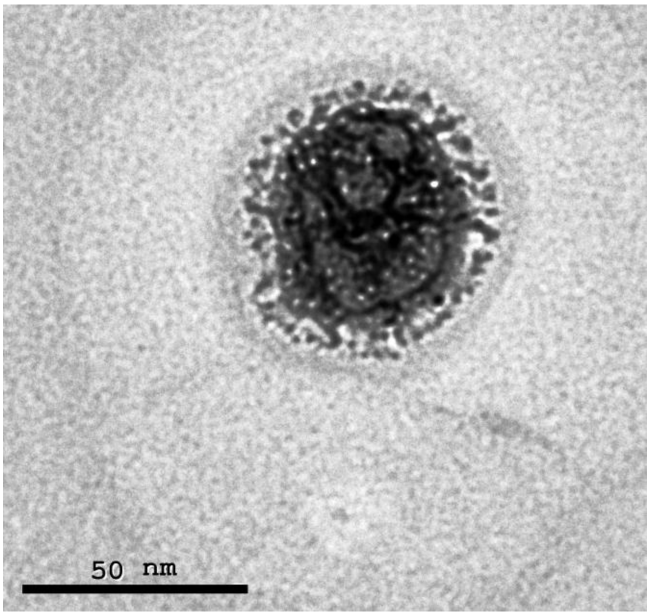

Figure (4): TEM image of SMCS

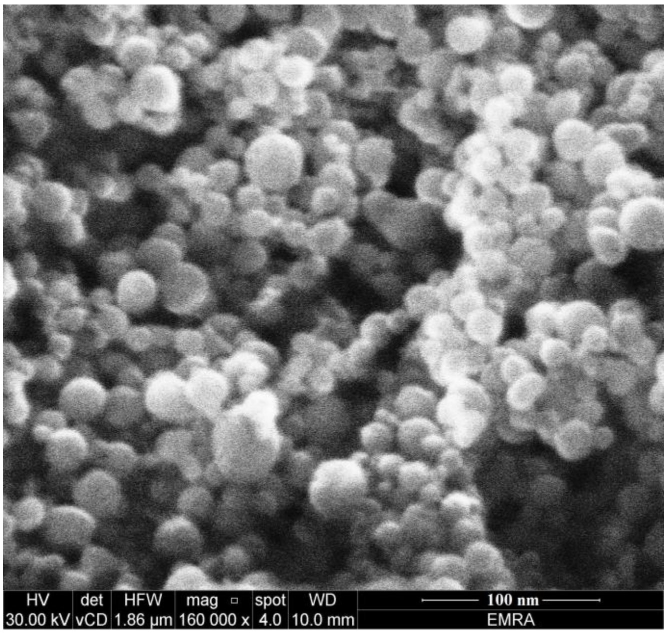

Figure (5): SEM image of SMCS

AFM top view and 3D images data showed the roughness profile of SMCS as shown in Fig. (6). AFM images were 500 nm x 500 nm and zoom in 100 nm x 100 nm, carried out to determine total roughness, spacing parameter and surface topography of SMCS. SMCS has homogenous surface topography with height parameter was 7.57 nm, 1.58, 4.62, 26.8 nm, 8.92 nm and 35.7 nm for root mean square height, skewness, kurtosis, maximum peak height and maximum peak peat for AFM image of 500 nm x 500 nm. But when zoomed in to one SMCS particle 100 nm x 100 nm roughness profile was 0.0784 nm, 0.0175 nm, 0.096 nm, 0.11 nm, 4.38, 26.4 and 48.8 nm for maximum peak height (RP), maximum valley depth (RV), total height (Rt), root mean square deviation (RMS), skewness, kurtosis and mean width of raw profile element of roughness profile (Rsm). Results of AFM images and data of particle size distribution showed in Fig (7) illustrate that SMCS has a nano-size (less than 100 nm). Also, show a high roughness profile of SMCS which makes it super-hydrophobic materials due to the presence of mesoporous silica nanoparticles in the core.

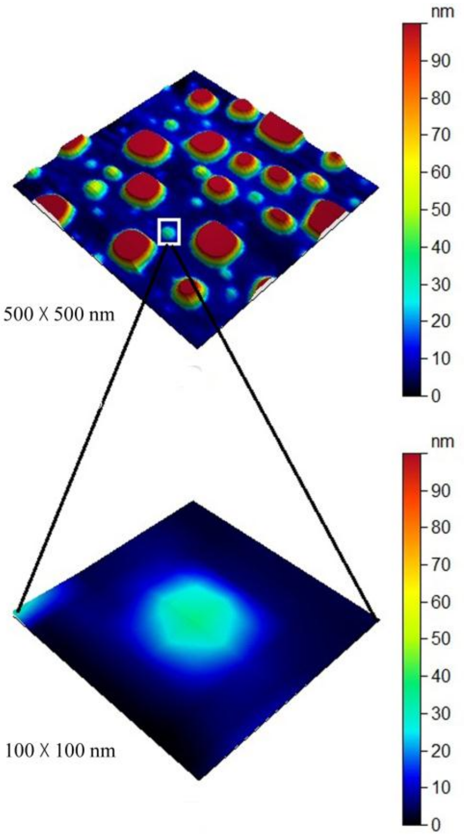

Figure (6):: AFM 3D Image

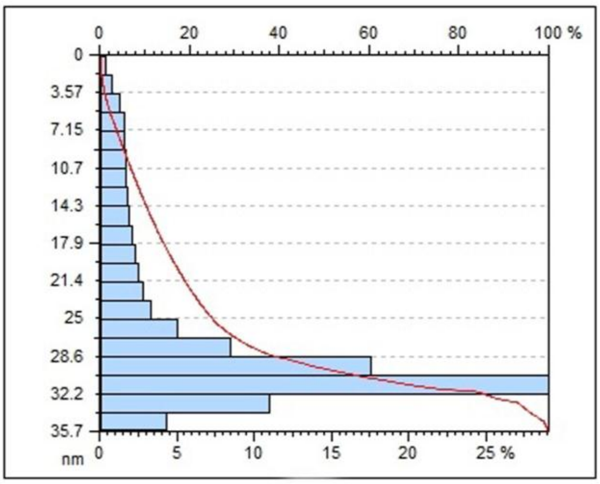

Figure (7): AFM particle size distribution graph

The surface area and pore volume of SMCS have been measure after degassing, by heating under vacuum condition at 50˚C for 4 hours, as shown in figure (8). Isotherm curve indicates the IV type of SMCS with mesoporous pores type which has capillary condensation of mesopores. BET surface area method using to determine the surface area of silica, magnetite nano-particles, and SMCS using N_2 adsorption-desorption properties on its surface. BET multi-points surface area was 264, 66 and 414.6 m^2/g for silica, magnetite nano-particles and SMCS respectively. The huge surface area of SMCS than silica and magnetite nanoparticles enhancement the mortar properties where chemical and physical activity should be increased. Pore volume is measured according to the BJH method. The pore volume was 0.49 and 0.42 cm/g for silica nanoparticles and SMCS respectively. The small pore volume of SMCS relative to silica nanoparticles due to the fill of magnetite nano-particles inside the mesoporous of silica core, which indicates that collide properties of SMCS enhancing mortar properties. Zeta sizing data illustrated the size of SMCS range from 35 to 40 nm with zeta potential -43, while it was about 35 and 15 nm for silica and magnetite nanoparticles respectively.

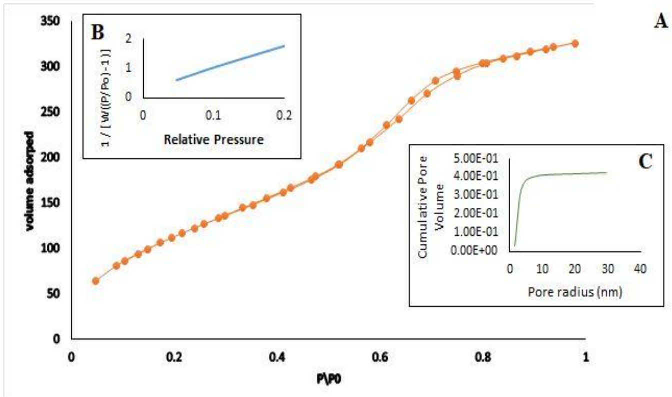

Figure (8): isotherm, BET surface area and pore volume

4.2. Experimental Results:

In this section results of all experimental tests were reported and presented in table 3.

Table 3. Experimental test results

Sample		Consistency mm	Compressive Strength 7 days N/mm²	Compressive Strength 28 days N/mm²	Flexural Strength N/mm²
M1 (R)		148	36.50	48.15	8.53
Group I	M2	144	428	55.61	8.92
	M3	138	42.20	58.25	9.12
	M4	134	41.32	56.40	9.06
Group II	M5	146	40.25	54.02	8.85
	M6	141	41.86	55.53	9.00
	M7	137	426	54.66	8.92

4.3. Consistency:

According to table 3, small replacement ratios of cement by nanoparticles has a slight effect on mortar consistency. Consistency decreases in group I which cement replaced by SMCS more over the second group. In group I consistency decreases by 2.7 %, 6.8 % and 9.5 % for mixes M2, M3 and M4 respectively, compared by the control mix M1, while in group II it was 1.4 %, 4.7 % and 7.4 % for mixes M5, M6 and M7 respectively, compared by the reference Mix M1, as shown in figure (9). Consistency decrement which occurs in group II is in agreement with many previous studies,[33–35]. These studies refer to shape, surface area and agglomeration of the nanoparticles may cause the decrement on consistency.

SMCS which used on the First group, has an evidential effect on consistency moreover than the nanocomposite of nanoparticles, this result agrees with *P. Sikora et al*, [18]. In the recent study the noticeable reduction in consistency between group I and group II may be caused by the amalgamation of magnetite and silica nanoparticles in one core-shell, the resultant core-shell has a large specific surface area compared by the same weight of nano-composite by about two times over as presented in characterization. Furthermore, the roughness profile of SMCS as shown by AFM top view, illustrate the high roughness profile of SMCS which makes it super-hydrophobic materials, which leads to reduce water demand and causes a reduction in consistency compared by the same weight of nano-composite. Moreover that, microscopic scanning indicated that using SMCS leads to form a dense mortar compared by the mixes containing nano-composite of, so it's another reason for the substantial increase in viscosity of fresh cement mortar which leads to decrement in consistency. Consequently, superplasticizer dosages are required to maintain consistency by increasing replacement ratios and specific surface areas of nanoparticles.

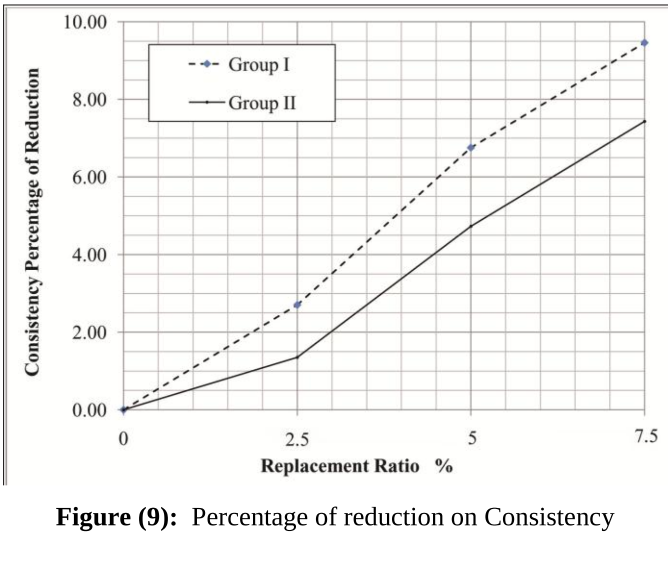

Figure (9): Percentage of reduction on Consistency

4.4. Mechanical Properties of cement mortars:

4.4.1. Compressive Strength:

According to the results of compressive strength after 7 and 28 days curing, which presented in table 3. Using nanoparticles leads to an improvement of compressive strength after 7 days compared by the control sample, the increments range from 11.1 % to 15.6 % for mortars contains SMCS, while it ranges from 10.2 % to 14.6 % for mortars group II containing nano-composite, as shown in figure (10). There is no significant effect between using SMCS or nanocomposite of nano-silica and nano magnetite on compressive strength after 7 days, these may be a reason for the same pozzolanic effect of the nanoparticle in the shape of core-shell with the individual nanoparticles.

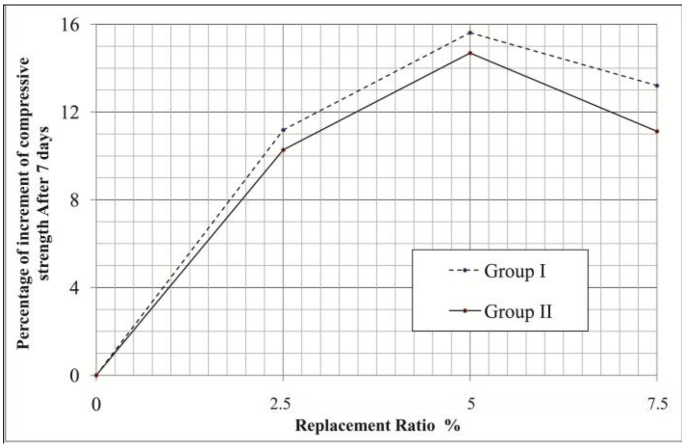

Figure (10): Increments of Compressive strength after 7 days

Samples containing SMCS showed a clear enhancement in compressive strength after 28 days moreover than nano-composite and control samples. The increments compared by the control sample M1 were 15.5%, 21 % and 17.1 % for group I samples M2, M3 and M4, respectively. While the increments were 12.2 %, 15.3 %, 13.5 % for group II samples M5, M6 and M7 respectively, as shown in figure (11). Enhancement in compressive strength was attributed to the pozzolanic effect of the nano-silica core and the filling effects of iron oxide shell, which leads to forming denser and more compacted microstructures. Also, it was noticeable that the optimal dose of using SMCS as a replacement ratio of cement was 5%. Increasing the replacement ratio moreover 5%, leads to an increase in the specific surface area of cementitious binder, which decreases the ratio between crystals and cement strengthening gel, and resulting decrease in strength and the mortar becomes more porous.

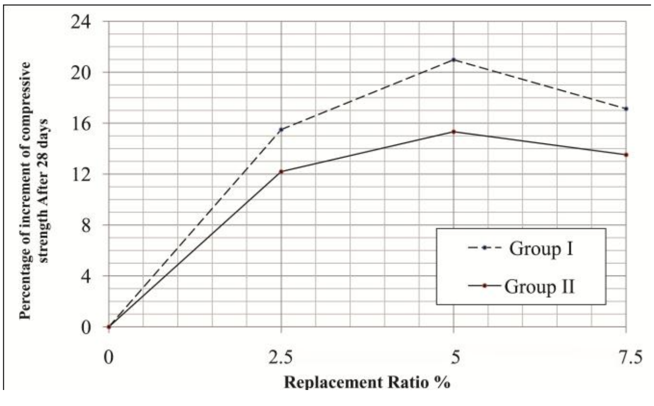

Figure (11): Increments of Compressive strength after 28 days

4.4.2. Flexural Strength:

Results of flexural strength presented in table 3 show that mortars having replacement ratios of cement (2.5%, 5% and 7.5%) by nanoparticles have a slight effect on flexural strength. However, flexural strength test results demonstrate similar trends to compressive strength test results. Increments of flexural strength of mortars containing SMCS compared by the control sample M1 were 4.9%, 7.2 % and 6.6 % for group I samples M2, M3 and M4, respectively. While the increments were 4.1 %, 5.9 %, 4.9 % for group II samples M5, M6 and M7 respectively, as shown in figure 12.

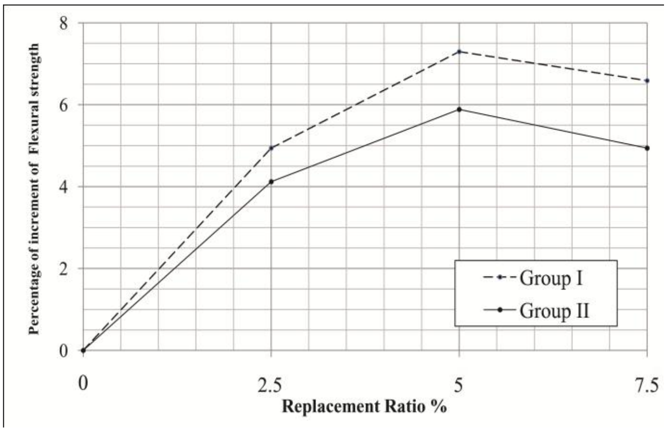

Figure (12): Increments of flexural strength.

G. Quercia et al, investigate that bonding between cement paste and fine aggregate is an important factor in increasing tensile strength, [33]. Also, *A. Khaloo et al*, show that the properties and formation of interfacing transaction zone (ITZ) have more effect on tensile strength than on compressive strength, [34]. According to recent study mortars containing replacement ratios of SMCS show better performance of flexural strength comparing by mortars containing a nanocomposite of nanoparticles and control samples. Enhancement of flexural strength related to the high surface area of SMCS compared by the nanocomposite of nano-silica and nano magnetite, SMCS improves the microstructure of cement mortar by forming a denser material which leads to strengthening ITZ.

4.5. Micro-Structural Morphology Investigation:

The enhancement mechanism which accord in cement mortars can be illustrated by the expression of *"nano-power"*. The evolution has been done on M1 (control sample), M3 and M6 by XRD, Specific surface area by the BET method, pore size by DH method, pore size distribution by DFT method, SEM and observation the surface by stereomicroscope. The huge chemical activity and the ultra nanofiller are the two reasons which resulting in *"nano-power"*, as presented in the graph shown in figure 13. The chemical activity of pozzolanic nano-materials can be evaluated by measure BET surface area and minerals composition by XRD and SEM. Also, pozzolanic nano-materials as nano-filler evaluated by measure DH Pore size, DFT pore size distributions and stereomicroscope.

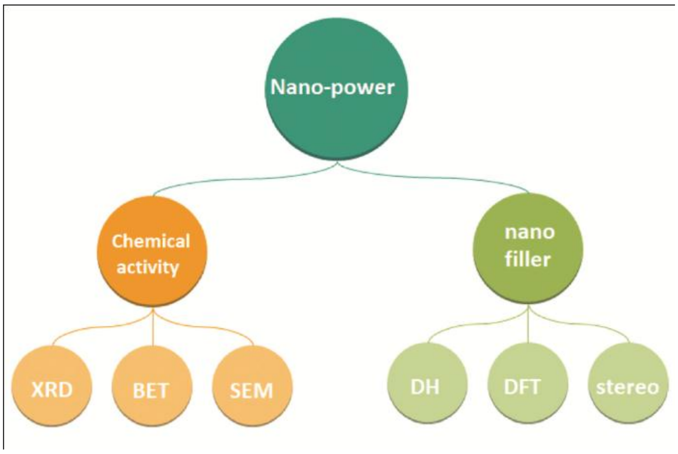

Figure (13): Methodology of nano-power effect

4.5.1. Chemical activity:

Chemical activity depends on the specific surface area, however, the specific surface areas by BET (Multi-points) method are 264, 66 and 414.6 m^2/g for magnetite-silica nano-composite and SMCS, respectively. So SMCS is a pozzolanic activator higher than magnetite-silica nano-composite, where SMCS act as nuclei for the cement phase result of rapid formation of C-S-H by the pozzolanic reaction, decrease the amount and volume of residual $Ca(OH)^2$ crystals and increase ITZ cohesion and coherence between aggregates and solid – semi-solid cement past more than magnetite-silica nano-composite.

XRD pattern of Control samples illustrates the presence of anhydrous cement compounds such as $Ca(OH)^2$ crystals and tricalcium silicate (Ca_3SiO_5) which indicated incomplete pozzolanic reaction. Otherwise, XRD pattern of SMCS sample refers to the best complete pozzolanic reaction and its high chemical activity, by forming of several minerals such as Ilvaite (I), C-S-F-H (at 2 theta = 32.85, 33.4, 36.78, 42.7, 47.87 and 60.5 □) which formed by the reaction of (CH) of cement with Fe in shell and Si in the core of MSCS, Jaffeite (J) C-S-H (at 2 theta = 17.66, 27.12 and 41.65 □) which formed by reacting of (CH) of cement with Si in the core of MSCS, Ettringite (E) C-S-A-H (at 2 theta = 15.8, 21.3, 22.2 and 23.1 □) which formed by reacting of Al and (CH) of cement with Si in the core of MSCS, and Prehnite (P) (at 2 theta = 19.08, 25.08, 38.8, 46.8 and 49.13□) which have a very sharp and strong peak (C-S-A-F-H) which formed by reacting of Al and (CH) of cement with Fe in shell and Si in the core of MSCS which have large percent more over all other minerals. XRD shows a high mineralization ability of the SMCS sample due to the huge chemical activity of SMCS than magnetite-silica nano-composite. Figure 14 shows the XRD high mineralization ability of the SMCS sample due to the huge chemical activity of SMCS than magnetite-silica nano-composite.

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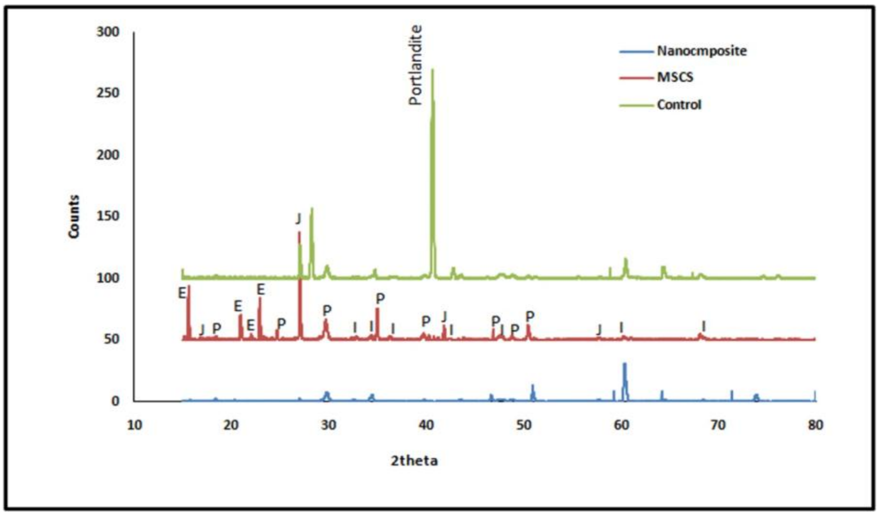

Figure (14): XRD pattern of control, nano-composite and SMCS Samples.

Interestingly, SEM images of SMCS as shown in Figure 15, illustrate the convert of mineral consist of cement mortar to nano one with size range from 4 nm for jaffeite (spider network) and 40 nm for ettringite (tubs) where the sheet structure such as prehnite and ilvaite have a thickness size range from 50 to 60 nm. This dramatic change from micro-minerals to nano-minerals may be the most important reason for the enhancement of the mechanical properties where the nano-minerals have higher mechanical properties than the micro-size one. Magnetite-silica nano-composite sample SEM image as shown in Figure 16, illustrates the presence of micro minerals consist of cement mortar such as ilvaite and ettringite.

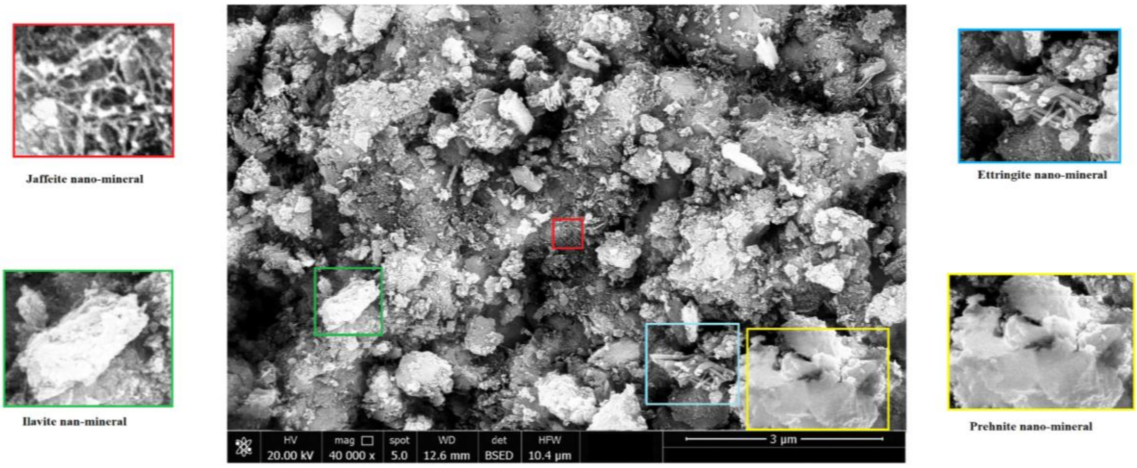

Figure (15): Nano-minerals on SMCS mortars

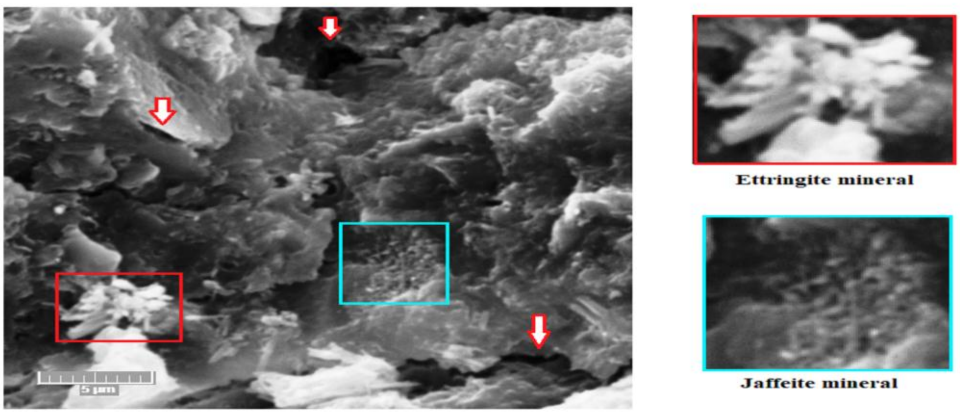

Figure (16): The minerals consist of cement mortar for SMCS

4.5.2. Ultra-nano-filler:

Nano-materials act as ultra-nano-filler, which reduces the amount and volume of cement mortar voids and pores which enhancement the mechanical properties. Also, ultra-nano-filler enhancement of the pore size distribution on mortar cement surface and reduce capillary pores (5-50nm) to gel pores (1-5nm). Moreover that, DFT analysis and by DH method in Figures 17 and 18, proof the homogeneity of pores distribution of SMCS sample moreover than magnetite-silica nano-composite and control samples, which indicate the better mechanical properties of SMCS sample, due to the presence of weak zones with different types and sizes of pores in control and magnetite-silica nano-composite samples, while in SMCS samples the pore size reduce to one size approximately ranged from 1 to 5 nm, with pore volume equal to 0.033cc\g.

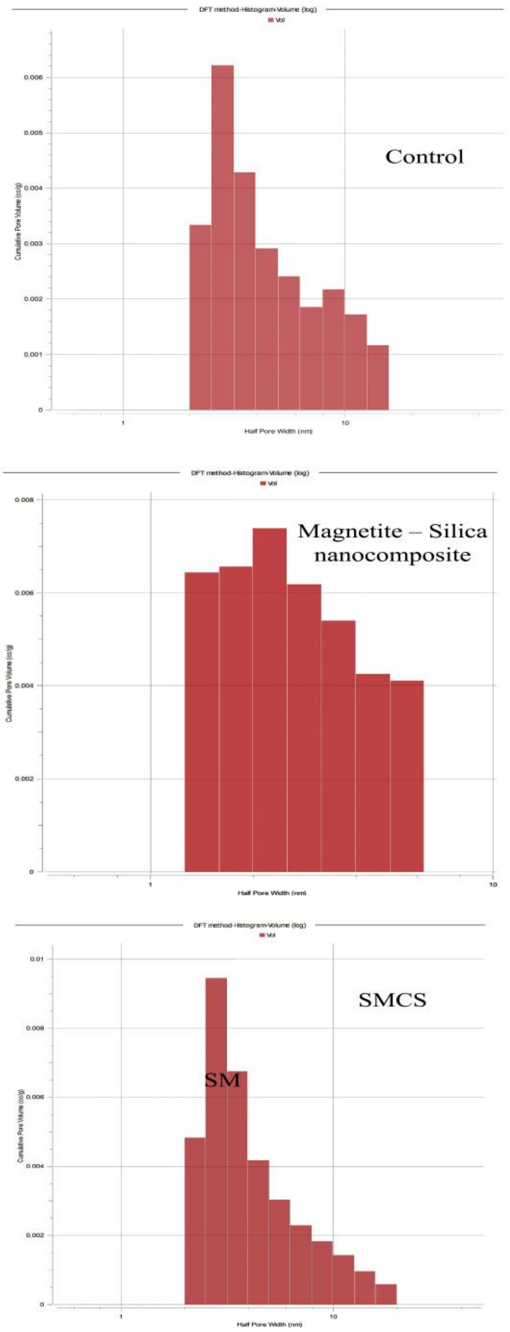

Figure (17): DFT histogram

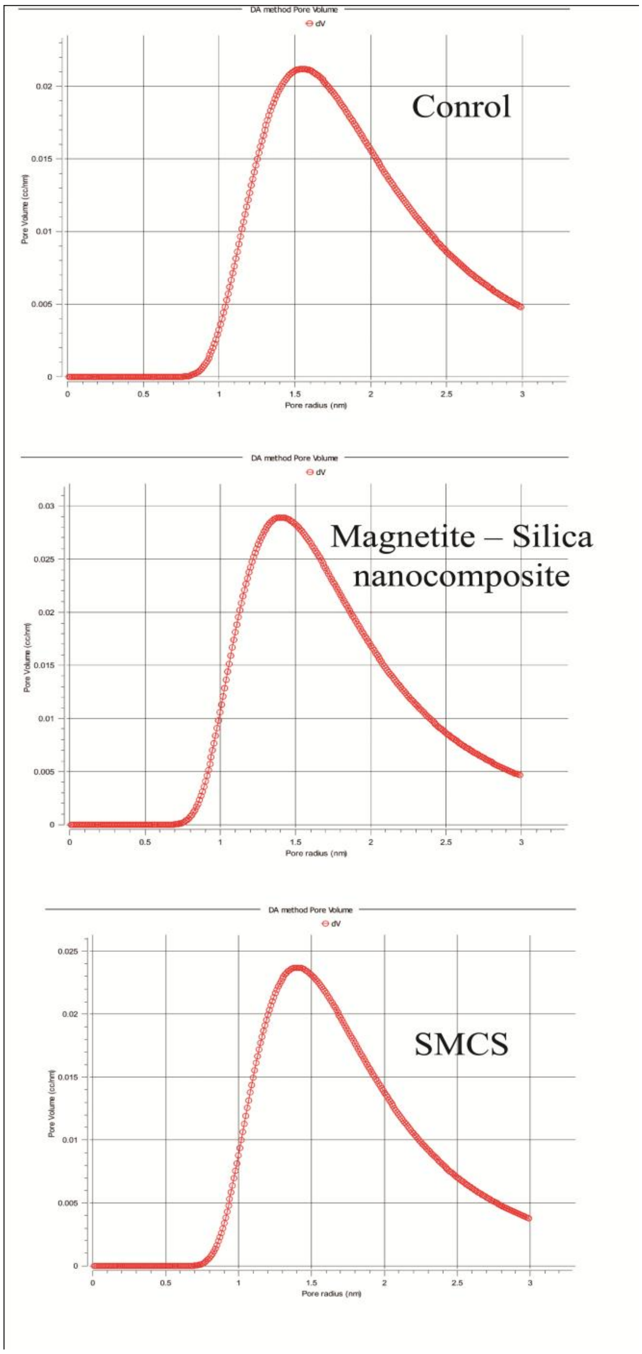

Figure (18): DH pore size

Magnetite-silica nano-composite sample SEM image, shown in Figure 19 illustrates the presence of large pores and small cracks. SEM image of the control sample shown in Figure 20 illustrates the presence of different types and sizes of the pore, weak zones and cracks. Also, stereomicroscope images, in Figures 21and 22, confirm the presences of different shape and size pores and cracks in the control sample, which decrease in magnetite – silica nano-composite sample. Otherwise, cracks and pore formation are greatly enhanced by using SMCS, as shown in the stereomicroscope image in figure 23.

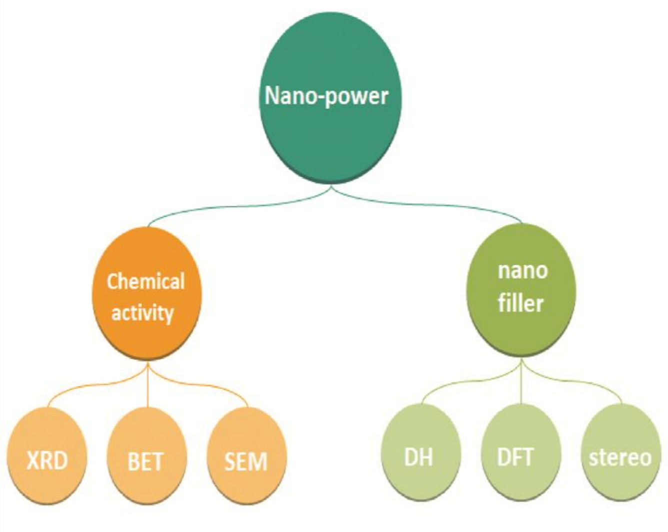

Figure (13): Methodology of nano-power effect

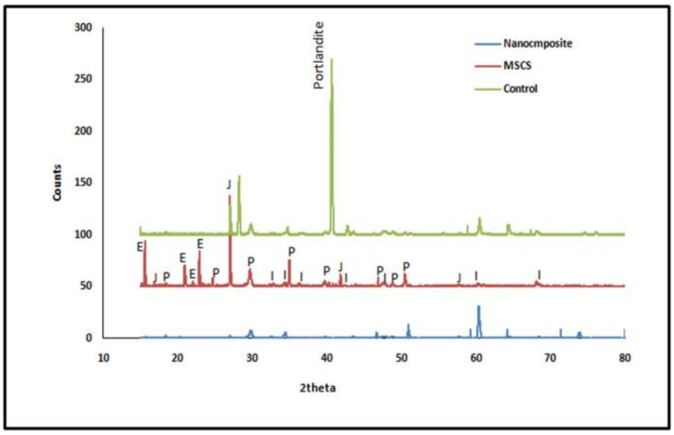

Figure (14): XRD pattern of control, nano-composite and SMCS Samples.

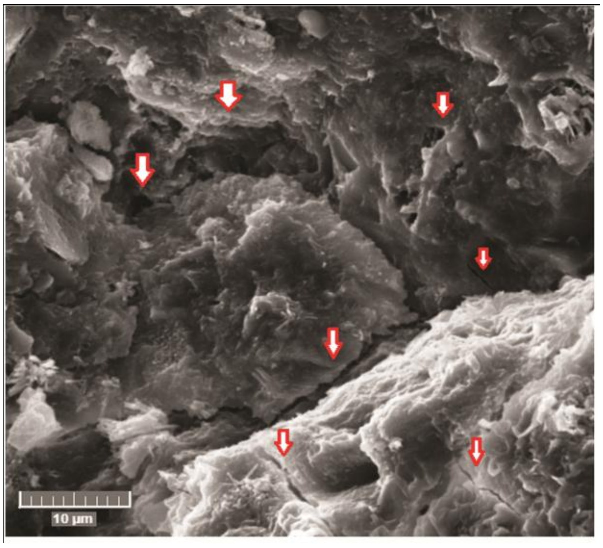

Figure (19): SEM image of nanocomposite

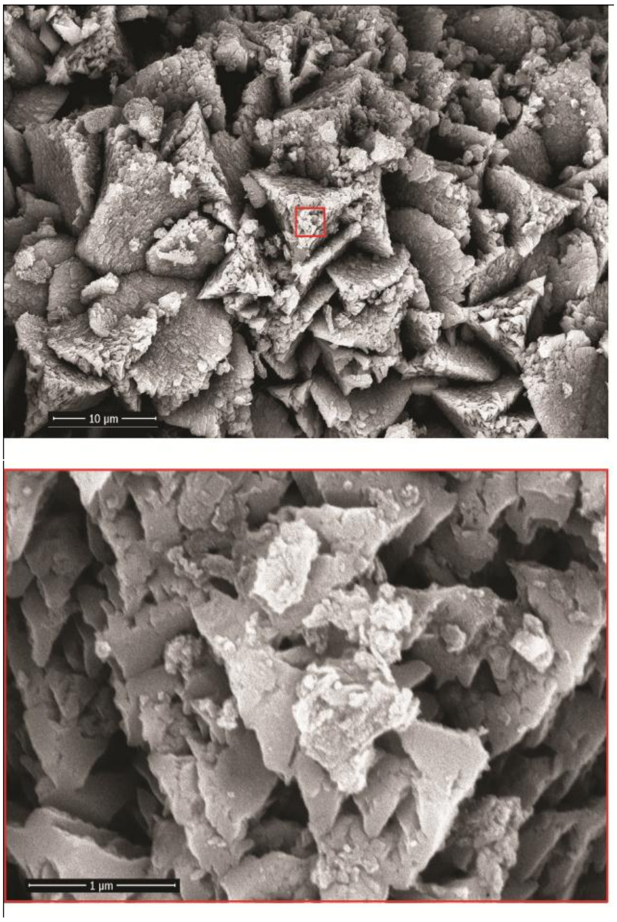

Figure (20): SEM images of control sample

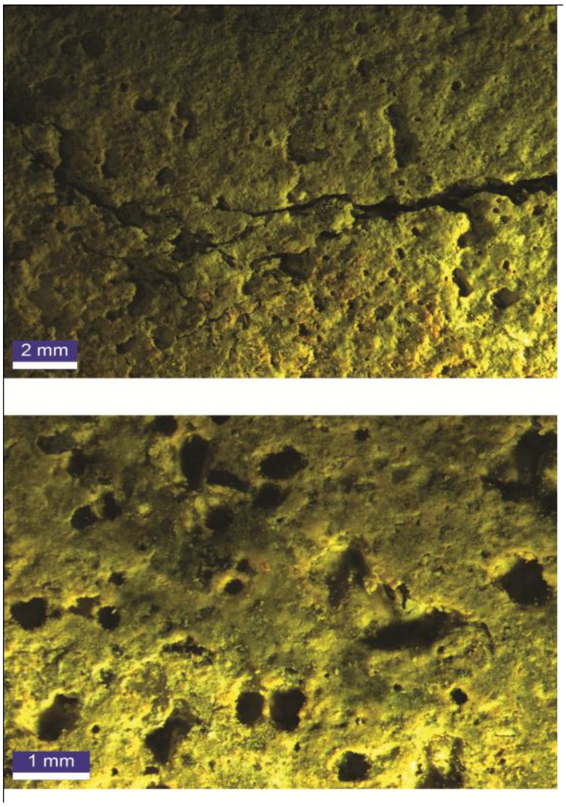

Figure (21): Stereomicroscope image of control sample

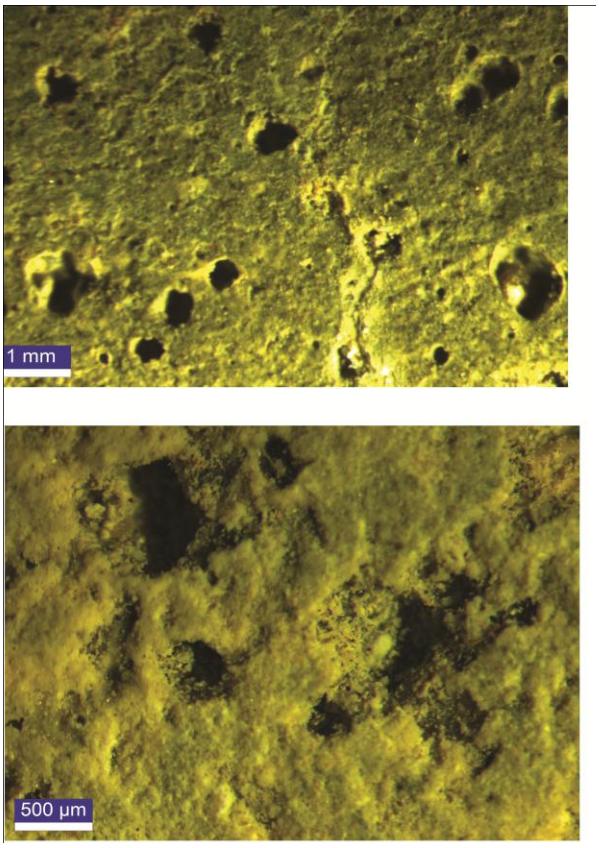

Figure (22): Stereomicroscope images of nano-composite sample.

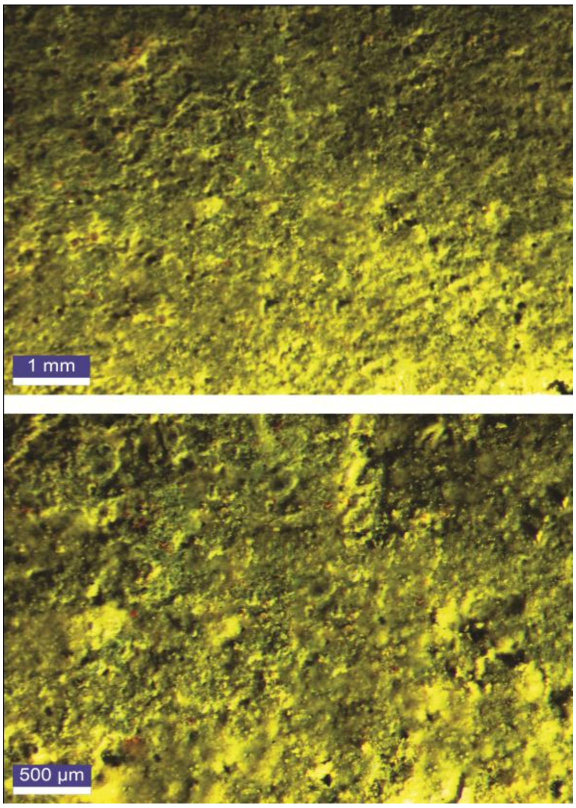

Figure (23): Stereomicroscope images of SMCS

In abbreviate, Nano-silica (core) acted not only as a filler material to modify the microstructure of the cement matrix but also silica core increase the pozzolanic reaction, hence increasing the mechanical properties and refining the microstructure of the cement matrix. Furthermore, magnetite which coat the silica core increases the specific surface area of the nano core-shell more over the molecular hybrid, which leads to increase chemical activity and oxidation of iron oxide nano-particles in the cement matrix which enhancing mechanical properties and microstructure of the cement matrixes which contains nano core-shell more over the molecular hybrid.

4.5.3. The critical amount of nano-materials:

According to our results, the mechanical properties and morphology of cement mortar increase by increasing the amount of SMCS and magnetite-silica nano-composite until reach to 5% the best enhancement has been done then the mechanical properties come down by increase replacement amount of SMCS and magnetite-silica nano-composite! This amount (5% in our work) can be called "the critical nano-power", which can define as the amount of nanoparticles give a perfect enhancement. The mechanical properties of samples contain replacement ratios less than critical nano-power amounts have an uncompleted pozzolanic reaction and a large amount of pores and cracks. While the other samples which have a large amount of replacement ratios moreover than critical nano-power have low mechanical properties value due to the agglomeration of nanoparticles and decreasing the roughness profile of cement mortar surface, which leads to uncompleted pozzolanic reaction and forming of weak zones.

5. CONCLUSION

Based on the results described in this research study herein, the following conclusion can be drawn:

1. Using replacement ratios of cement by SMCS nanostructure leads to a clear enhancement in mechanical and micro-structural properties of cement mortars, moreover than mortars contain the same replacement ratios of nano-composite of NS and NM.
2. A slight decrease in consistency was recorded by using replacement ratios of SMCS moreover using nano-composite of NS and NM compared by the control mix. This decrease is related to the high surface area of the core-shell nanostructure, which causes by covering the core nano silica by magnetite shell. So it is important to take this effect on the design of mixes.
3. The SMCS mortars have higher compressive strength compared with those with hybrid nano-composite, due to its chemical activity depends on the specific surface area, which produces a rapid formation of C-S-H by the pozzolanic reaction and decrease the amount and volume of residual $Ca(OH)^2$ crystals and increase ITZ cohesion and coherence between aggregates and solid – semi-solid cement past more than magnetite-silica nano-composite
4. Mixes containing replacement ratios equal to 5% SMCS

achieve the best performance of mechanical properties, by forming a denser and compacted mortar and improving micro-cracks and pores.

5. Using SMCS leads to an enhancement on flexural strengths, but with a lesser extent if it compared by compressive strength. Whereas, the efficiency SMCS on improving ITZ which exposed to a tension force was less if it compared to its efficiency on improving ITZ which exposed to a compression force, such as compressive strengths after 7 and 28 days.
6. SMCS mortars show strong interfacing zones hybrid nano-composite, as a result of forming minerals which consist of the cement mortar in a range of nanometers. This leads to control pore size and reduce it to one size approximately ranged from 1 to 5 nm, with pore volume equal to 0.033cc\g.
7. DH pore size and stereomicroscope images, show the homogeneity of pore size and very narrow cracks in mortars containing SMCS, compared by the control sample.
8. The critical amount of nano-materials or optimal dose, which can give the perfect enhancement on mechanical properties, was a 5 % replacement ratio of cement.

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