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Microstructural Analysis for Cement Mortar with Different Nano Materials

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Abstract. To study the effects of nanomaterials on the microscopic structure of the mortar interconnection zone that is prepared by a compound bond comprising nanomaterials. And to clarify its impact on compressive strength improvement. In this study, the compressive strength, SEM analysis and XRD analysis were estimated for mortar containing different amounts of ZrO_2, SiO_2, Al_2O_3 and $CaCO_3$ nanoparticles. Four different contents of each nanoparticles' types were used as a partial replacement of cement with 1%, 1.5%, 3% and 5% by the weight of cement. Results manifested that the mortar compressive strength enhancement can be ascribed to the microstructure amelioration of the interfacial transition region. Besides, XRD analysis and SEM micrographs elucidated the formation of hydration compounds and the improvement in bonding due to the existence of nanoparticles.

Introduction

One of the main topics in the industry of construction in the latest years has been the request for the cement materials that can decrease the emissions of carbon, and the majority of studies have concentrated on reducing the usage of cement or utilizing the cement alternatives. Therefore, the nanomaterials that are used to improve the properties can enhance the durability, strength and structural efficiency of the cementitious substances. Accordingly, they can help in improving the lifetime and quality of structures. The nanomaterials utilization with cement can decrease the emissions of (CO_2) that are associated with the manufacturing of concrete [1]. The nanoparticles possess a significant ratio of surface-area-to-volume. By such manner, the nanoparticles having 4 nm diameter possess higher than (50%) of their atoms at surface and are therefore too reactive. The behaviour of these materials is chiefly affected via the chemical reactions at the interface, and via the truth that they simply develop agglomerates. If a larger surface area has to be wetted, it reduces the free dispersant water in the aqueous systems existing in the blend. Thus, the nanoparticles utilization in concretes and mortars considerably adjusts their behaviour not only in the current state but also in the hardened states, in addition to the microstructural and physical/mechanical development [2]. *S. P. Kanniyappan et el.* obtained that the nanoparticles enhance the aggregates contact region structure, causing a proper bond between the cement paste and the aggregates which are fine demonstrated from the (SEM) and (TEM) images and the pattern of (XRD) of nano-silica powder (1%) level, and various percentages of (CNT) in the (OPC) cement provide excellent outcomes. *Hui Li et al.* found that the flexural and compressive strengths that measured at the (7th) day and (28th) day of the cement mortars blended with the nanoparticles are higher than those for the plain cement mortar. And, the microstructures between the plain cement mortar and the cement mortar mixed with the nanoparticles and the plain cement mortar depicted that the nano-SiO_2 and the nano-Fe_2O_3 occupied the pores and decreased the ($CaOH_2$) compound among the hydrates [4]. *Danna L. et al.* studied the influence of the zirconium oxide-synthesized nanoparticles addition upon the microstructural improvement and the physical-mechanical characteristics of cement mortars with the aggregates of limestone. It was proposed that the ZrO_2 reinforcing influence upon the mortars resulted via the nucleation locations influence in the principal phase (C–S–H) and the growth inhibition of big (CH) crystals, and the importance of filler created via the particles nanometric size [5]. *Liguo Wang et al.* investigated the modification of cement-based materials by nano-SiO_2 particles to find the influence of the nano-SiO_2 particle upon the hydration, mechanical properties, and the cement-based materials pore structure. The results depicted that the reaction of the nano-SiO_2 particles with the $Ca(OH)_2$ (crystal powder) initiated within one hour and developed (C–S–H gel). The speed of reaction increased with age, and the mechanical characteristics of the cement-based materials were enhanced via the (3%) nano-SiO_2 addition [6]. *M. R. Arefi* studied the influence of the (Al_2O_3) nanoparticles addition upon microstructure and mechanical characteristics of cement mortar, the SEM analysis revealed that the (Al_2O_3) nanoparticles decreased the crystals of ($CaOH_2$), occupied the pores and raised the cement mortar density [7].

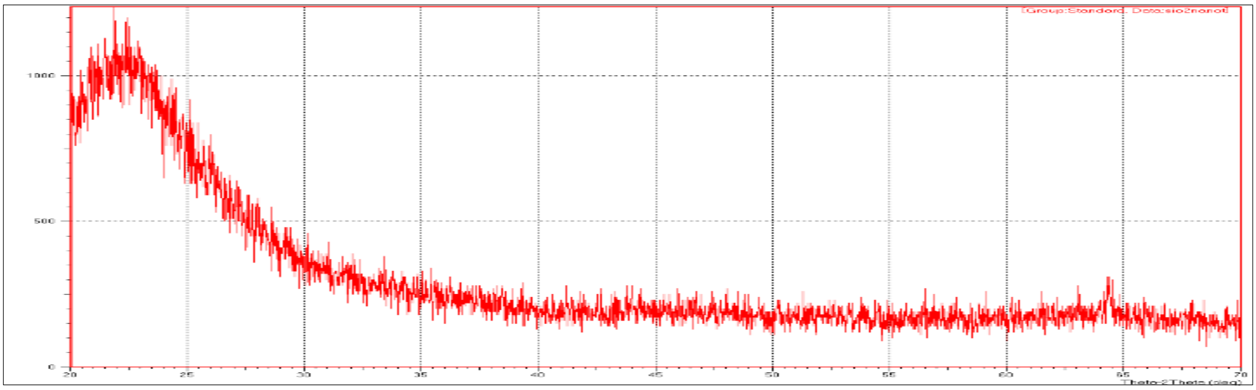
The literature manifested that the utilization of nanomaterial in a cementitious regime is chiefly owing to the truth that the mortar keeps the most intricate material, and its mechanism of hydration is yet not thoroughly recognized. Therefore, researchers and investigators have been concentrating upon the substantial scientific background of such essential element at a nano level. The present research was conducted to study the effect of using nanomaterials, which would be introduced into the cement mortar technologies with different contents. So, the research themes will focus on the befits and determinants of implementation theses replacements in the cement and concrete technology. Also, the optimum material for each type would be recognized.

Materials

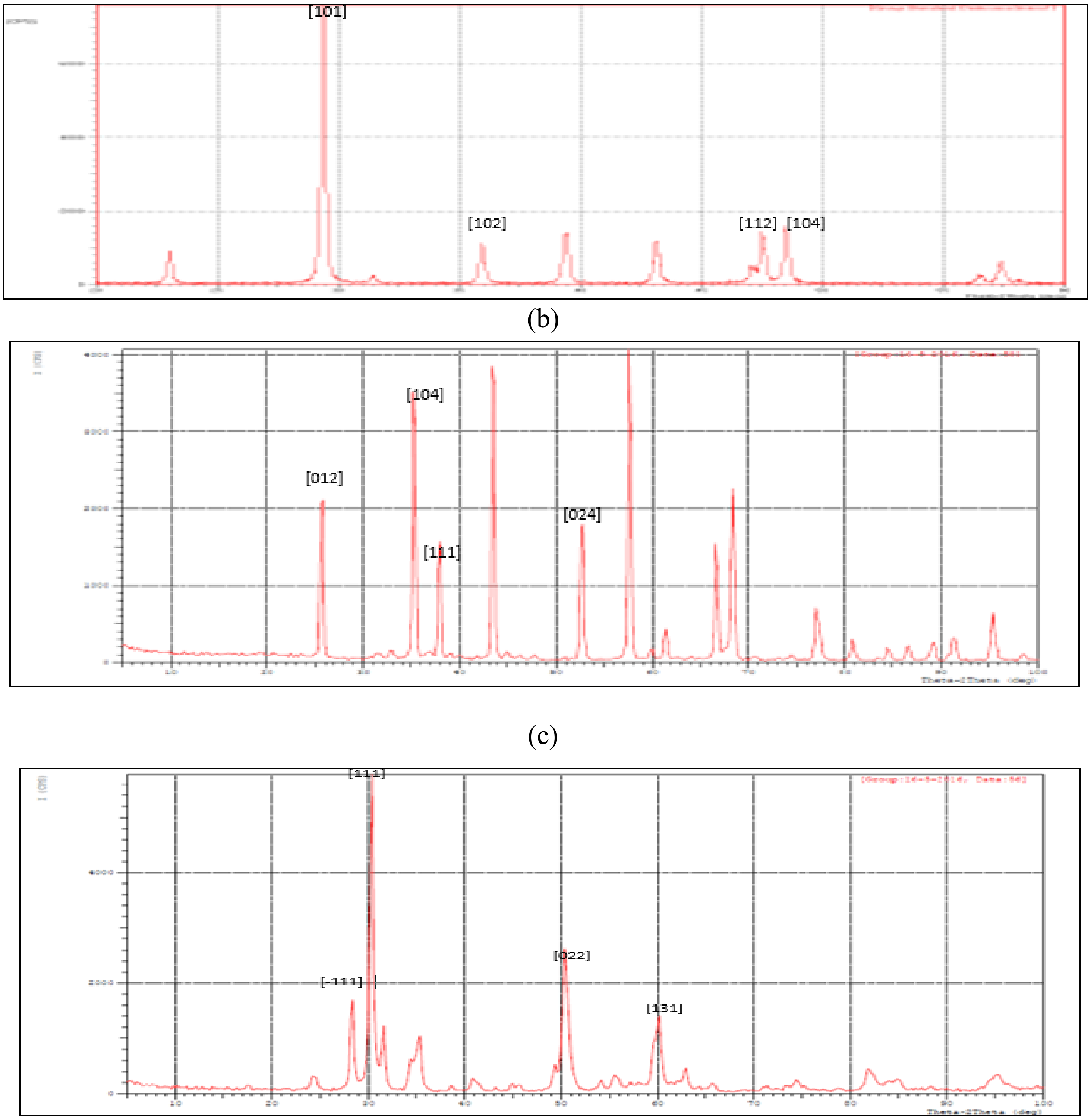
In the current research, the ordinary Portland cement (type I) confirmed to Iraqi Standard Specifications No. 5 [8] was used, and the cement chemical analysis is listed in Table 1. Nano ZrO_2 and nano Al_2O_3 nano $CaCO_3$, Nano SiO_2, and nano $CaCO_3$ were used as cement replacements in this study. Fig.1 showed the XRD spectra for each admixture while Fig. 2 displays the particle size analysis of nanoparticles. Glenium 54 (G54) high range water reducing admixture type F was introduced into the whole blends. Natural sand of river was utilized with the portion of sand that passes through 850 µm sieve according to the Iraqi standard specification No. 2080 [9].

Table 1 The cement chemical analysis

Oxide	Content, %
CaO	66.11
SiO_2	21.93
Al_2O_3	4.98
Fe_2O_3	3.10
MgO	2.0
K_2O	0.75
Na_2O	0.35
SO_3	2.25



(a)

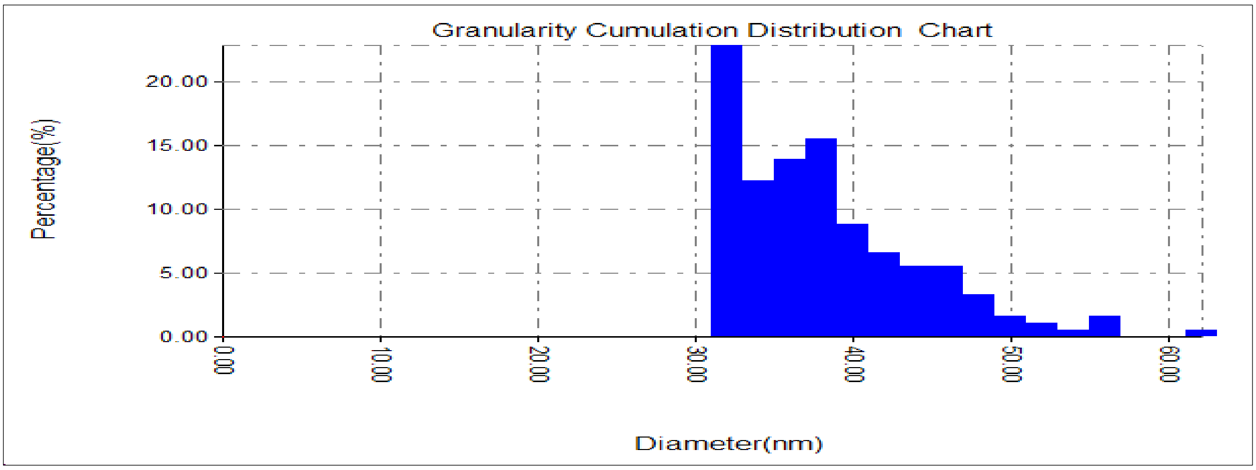


(b)

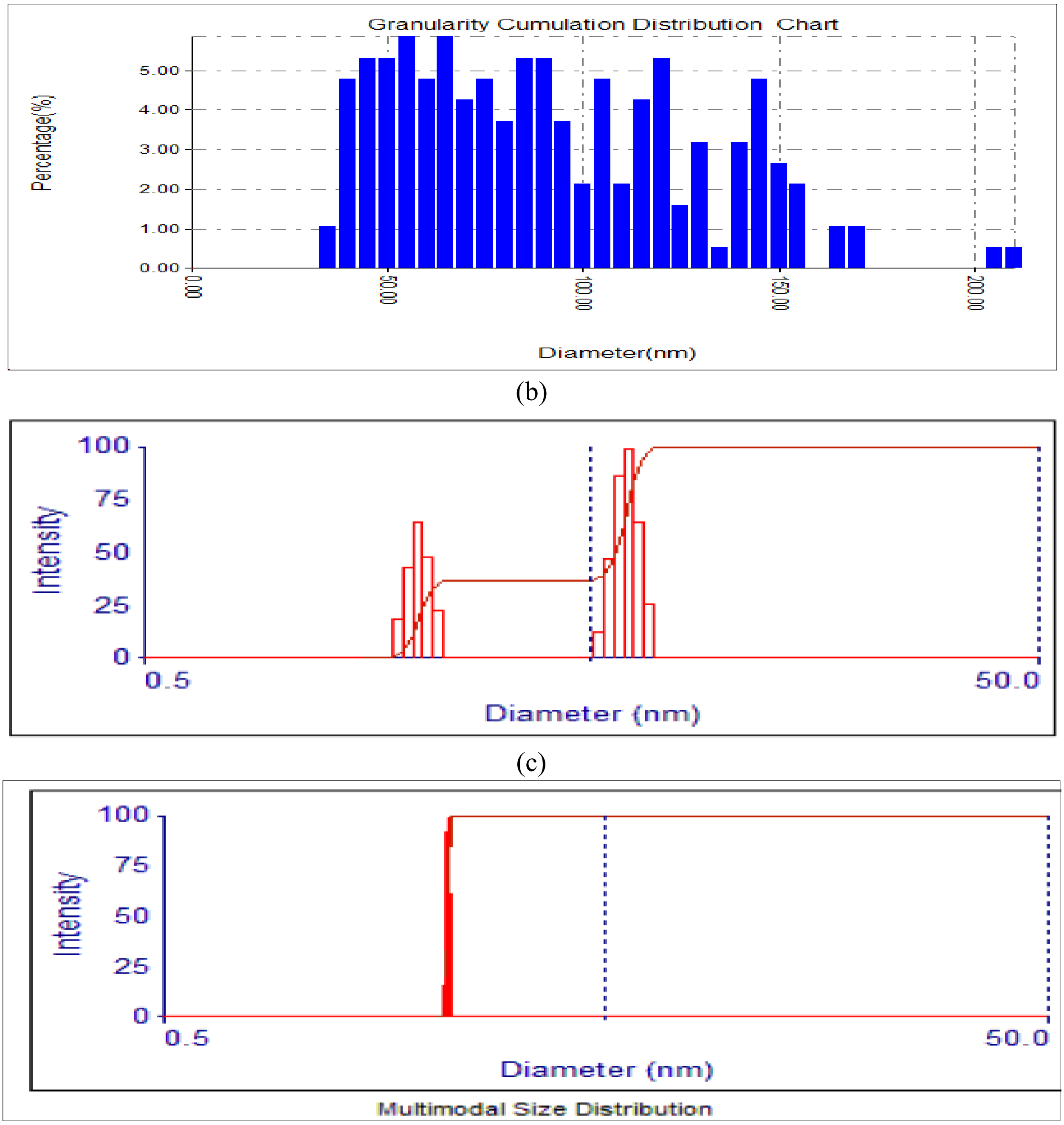
(c)

(d)

Figure 1 XRD spectrum for (a) nano SiO_2 (b) nano $CaCO_3$ (c) nano ZrO_2 (d) nano Al_2O_3



(a)



(b)

(c)

(d)

Figure 2 Particle size analysis of (a) nano SiO_2 (b) nano $CaCO_3$ (c) nano ZrO_2 (d) nano Al_2O_3

Mix proportion

Mortar mixes details for nano SiO_2, nano ZrO_2, nano $CaCO_3$, nano ZrO_2 and nano Al_2O_3, are shown in Table 2. Constant w/c ratio 0.45 was used for all mixes. The amount of superplasticizer type G54 was added and specified to the flow range (153-161 mm) according to ASTM C1240 [10]. The ASTM C 1437 [11] procedure was used for measuring the mortars flow. Sixteen mixes with nanoparticles were prepared in addition to the reference mix in this work.

Table 2 Mortar Mixes

Mix symbol	Cement, g	Sand, g	Nano SiO_2 g	Nano ZrO_2 G	Nano Al_2O_3 G	Nano $CaCO_3$ g	G54/ cement%	Flow, mm
Control	500	1375	-	-	-	-	0.5	160
1NS	495	1375	5	-	-	-	0.75	153
1.5NS	492.5	1375	7.5	-	-	-	0.5	155
3NS	485	1375	15	-	-	-	0.6	160
5NS	475	1375	25	-	-	-	0.7	157
1NZ	495	1375	-	5	-	-	0.65	157
1.5NZ	492.5	1375	-	7.5	-	-	0.65	156
3NZ	485	1375	-	15	-	-	0.7	156
5NZ	475	1375	-	25	-	-	0.7	155
1NA	495	1375	-	-	5	-	0.55	160
1.5NA	492.5	1375	-	-	7.5	-	0.57	161
3NA	485	1375	-	-	15	-	0.6	158
5NA	475	1375	-	-	25	-	0.6	157
1NC	495	1375	-	-	-	5	0.54	159
1.5NC	492.5	1375	-	-	-	7.5	0.55	157
3NC	485	1375	-	-	-	15	0.57	156
5NC	475	1375	-	-	-	25	0.57	154

Where NS: blends with nano SiO_2
NZ: blends with nanoZrO_2
NA: blends with nano Al_2O_3
NC: blends with nano $CaCO_3$

Compressive strength test

According to ASTM C183M [12] (50 mm × 50 mm ×50 mm) mortar cubes were cast using the mixes proportion shown in Table 3, w/c ratio of 0.45. Specimens were cast, and throughout the moulding, and the cubes were mechanically shaken. Beyond (24) hours, these specimens were de-moulded and subjected to curing in distilled water with two groups the first group were cured for (7) and the second group were cured for (28) days. And, beyond curing, such specimens were examined for the compressive strength utilizing a compression testing machine. The tests were carried out according to ASTM C 109/109[13] on three samples, and the average values of compressive strength were determined.

Results and Discussion

Results of compressive strength

The compressive strength results for the mortar mixes with ZrO_2, SiO_2, Al_2O_3 and $CaCO_3$ nanoparticles are explained in Fig.3 and Fig.4, the compressive strength for the reference mix was 22 MPa and 26 MPa for 7 and 28 days' age, respectively. For combinations with nano SiO_2, a remarkable enhancement in the strength was recognized with the increment of nano SiO_2 content up to 3% replacement for both ages 7 and 28 days. Then, the compressive strength decreased at 5% replacement, but it was still higher than the reference mix. The nano SiO_2 exhibited a higher pozzolanic activity since it reacts with the (CH) that made during the hydration of cement and caused a higher strength-carrying (C-S-H) into the paste, and these results came to an agreement with A. Al Ghaban [14] and Khomich V. A. [15]. For the nano ZrO_2 replacement, they also showed that the compressive strength rises via the addition of nanoparticles of ZrO_2 up to (3.0%)

replacements by the weight of cement and after that, it reduces despite the addition of (5%) of nanoparticles of ZrO_2 made the specimens having compressive strength more significant than the reference mix. The decreased compressive strength via the addition of more than 3% of nanoparticles of ZrO_2 maybe because the (ZrO_2) nanoparticles amount that exists in the blend is higher than the amount needed to combine with the released lime during the process of hydration, hence resulting in more leaching out of silica and creating a lack in the strength when it takes the place of a part of cementitious substance but doesn't share in strength [16]. For nano $CaCO_3$ and nano Al_2O_3 replacements, respectively, both replacements revealed an excellent enhancement in the compressive strength with raising the nanoparticles content. Nano $CaCO_3$ can react with (C_3A) to make mono-carbonate that is a material with a particular framework having vigorous bonds of H_2 between the atoms of O_2 and the groups of the inter-layer water's carbonate [17], thus shared in the enhancement of properties of the betimes-age compressive durability and strength of the concrete. The increase in compressive strength for mixes with nano alumina is owing to fast consumption of $Ca(OH)_2$ that was developed during the Portland cement hydration, especially at the betimes ages that are associated with the nano Al_2O_3 particles' significant reactivity, this was demonstrated by *M. R. Arefi* [7] and *Mohan Kantharia* [18]. When comparing the effect of nanomaterials on the compressive strength value of the cement mortar, we find that the more significant increase found in mixes containing SiO_2 nanoparticles followed by ZrO_2, except for mixes with Al2O3 where a greater improvement appears after 3% of replacement, $CaCO_3$ nanoparticles also enhance the strength of mortar. This difference in the values of compressive strength can be attributed to the variation in chemical reactivity for each type of nanoparticles and the difference in particle size, which significantly affect the general properties of cement paste.

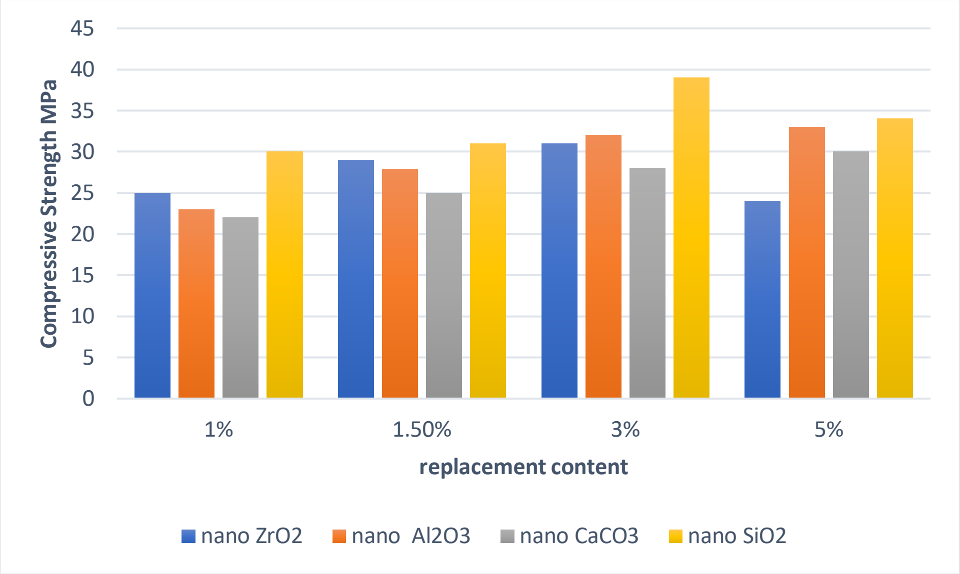


Figure 3 The results of compressive strength for the mortar mix with nano replacement (7 days' age)

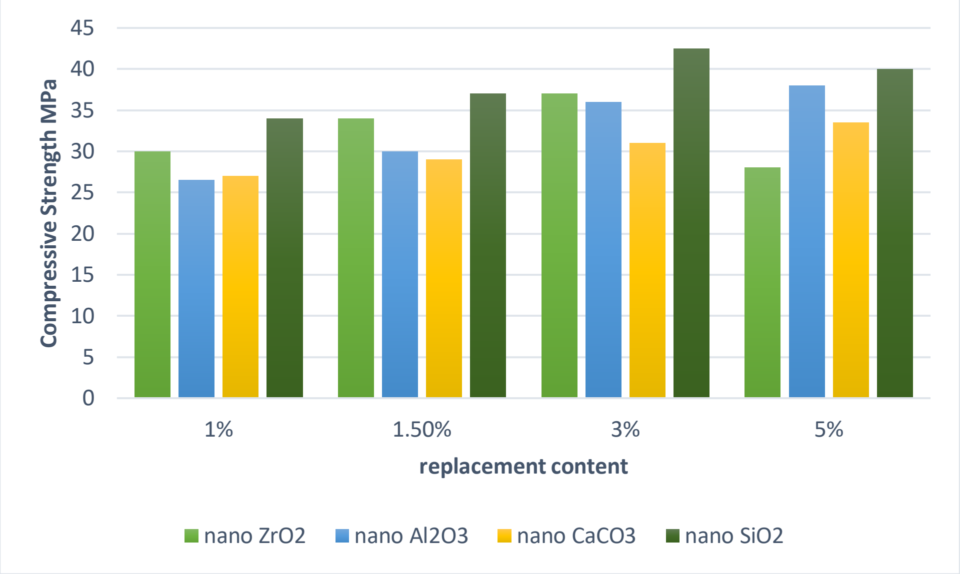


Figure 4 The results of compressive strength for the mortar mix with nano replacement (28 days' age)

XRD Analysis

Broken pieces from compressive cubes were used as a sample for the phases composition measurement of the material and the degree of crystallization. The Intel diffractometers scan range is (2 to 70) degree, the scan speed is 5 deg/min, and the XRD wavelength is (1.5405AO) used to obtain the pattern XRD pattern for each mortar mix. Figures (5-9) show the results of the XRD analysis for the control mix and the modified mortar mixes beyond the curing for (28) day. For the replacement by the control mix, the spectrum of (XRD) demonstrated that the calcium carbonate peak slowly raised and that the calcium hydroxide (CH) peak reduced. Such a phenomenon can be attributed to the consumption of calcium hydroxide (CH) by a pozzolanic reaction in which it combined with the silica to form the CSH gel [19]. This action was seen with a varying degree for each mix depending on the type of nanoparticles, the combination with nano SiO_2 depicted more significant effect compared to the rest of mixes because of the higher pozzolanic reactivity compared with other mixes which affect the intensity of CH peak. The mortar pastes diffraction spectra analysis of without and with the nano particles exhibit the predominance of (CH), (CSH), ($CaCO_3$) and Quartz (Q). These results were fully compatible with the work of research [20], which states that the XRD analysis of the ordinary Portland cement concrete samples evinced that the concrete is composed mainly of Calcite and Silica.

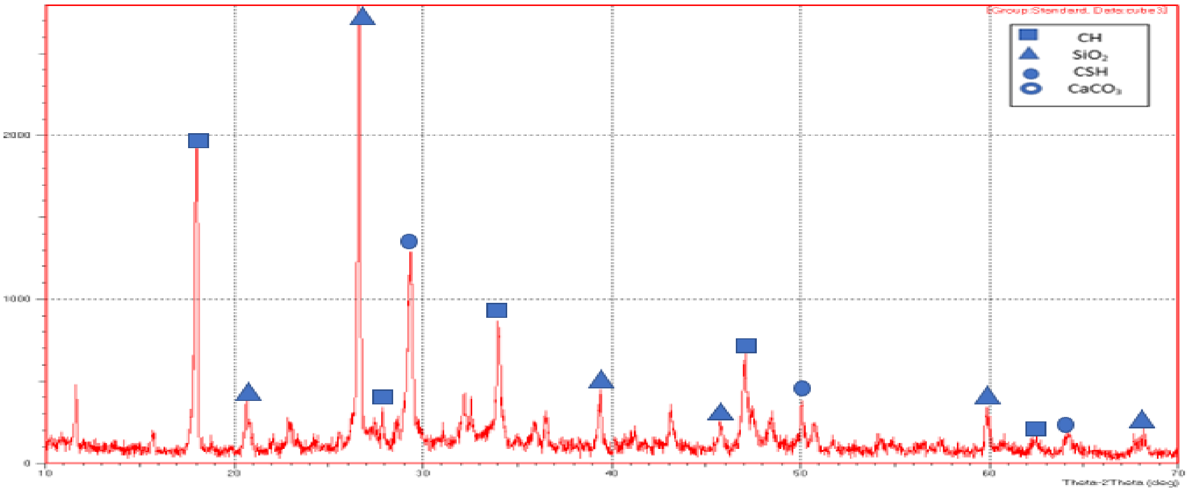


Figure 5 The characterization measurement (XRD) pattern of reference mortar mix

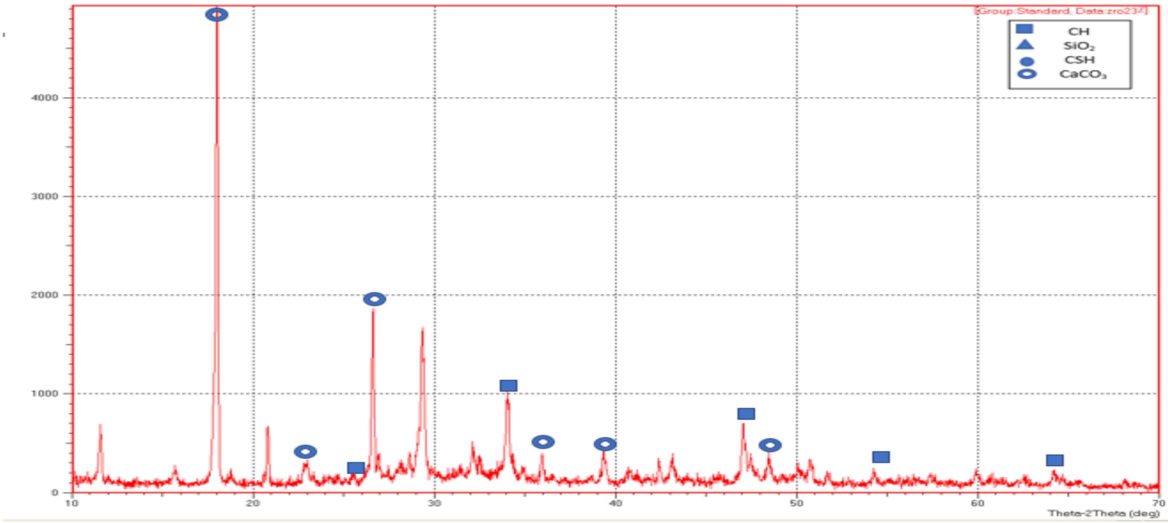


Figure 6 The characterization measurement (XRD) pattern of mortar mix with nano ZrO_2

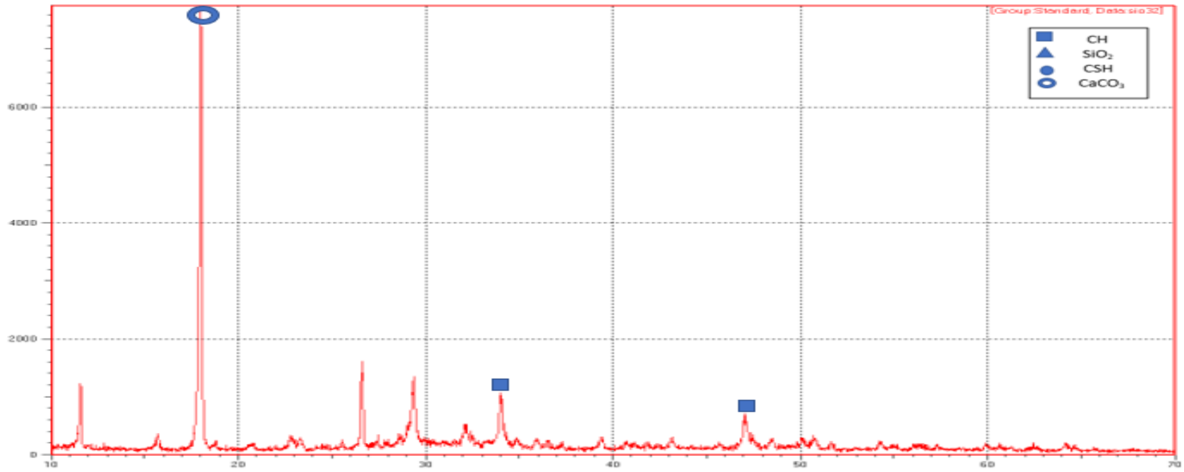


Figure 7 The characterization measurement (XRD) pattern of mortar mix with nano SiO_2

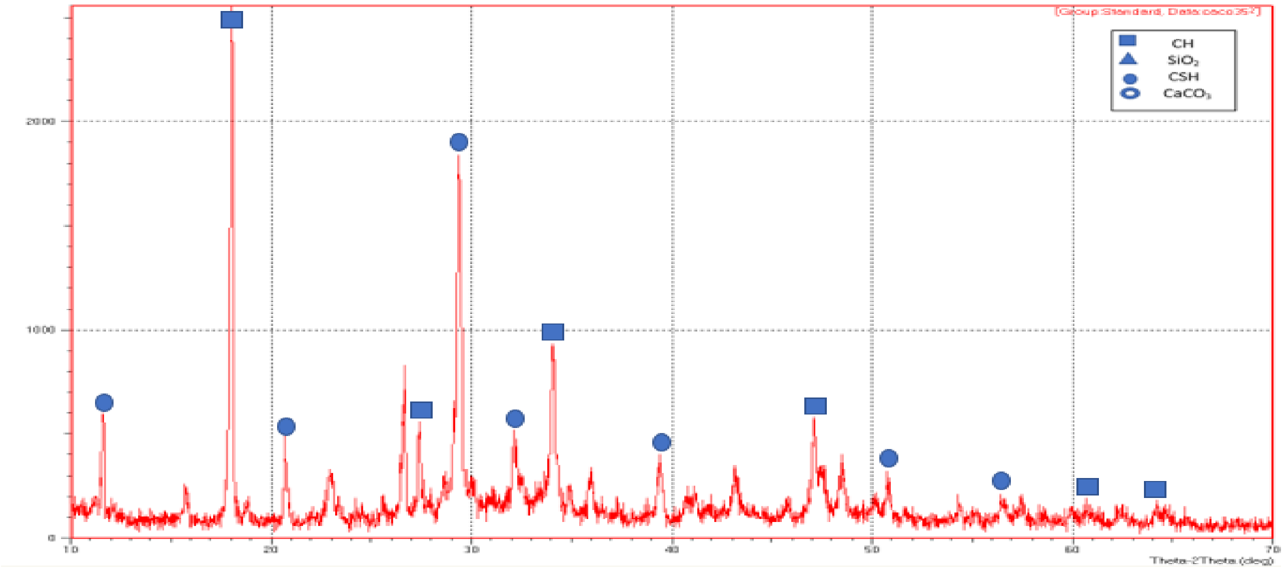


Figure 8 The characterization measurement (XRD) pattern of mortar mix with nano $CaCO_3$

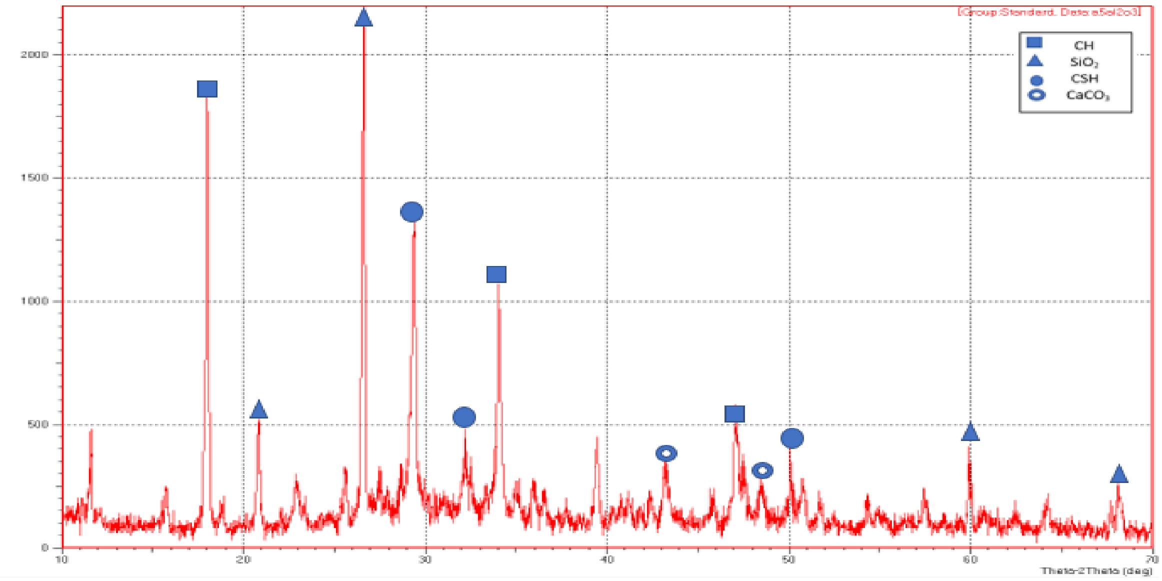
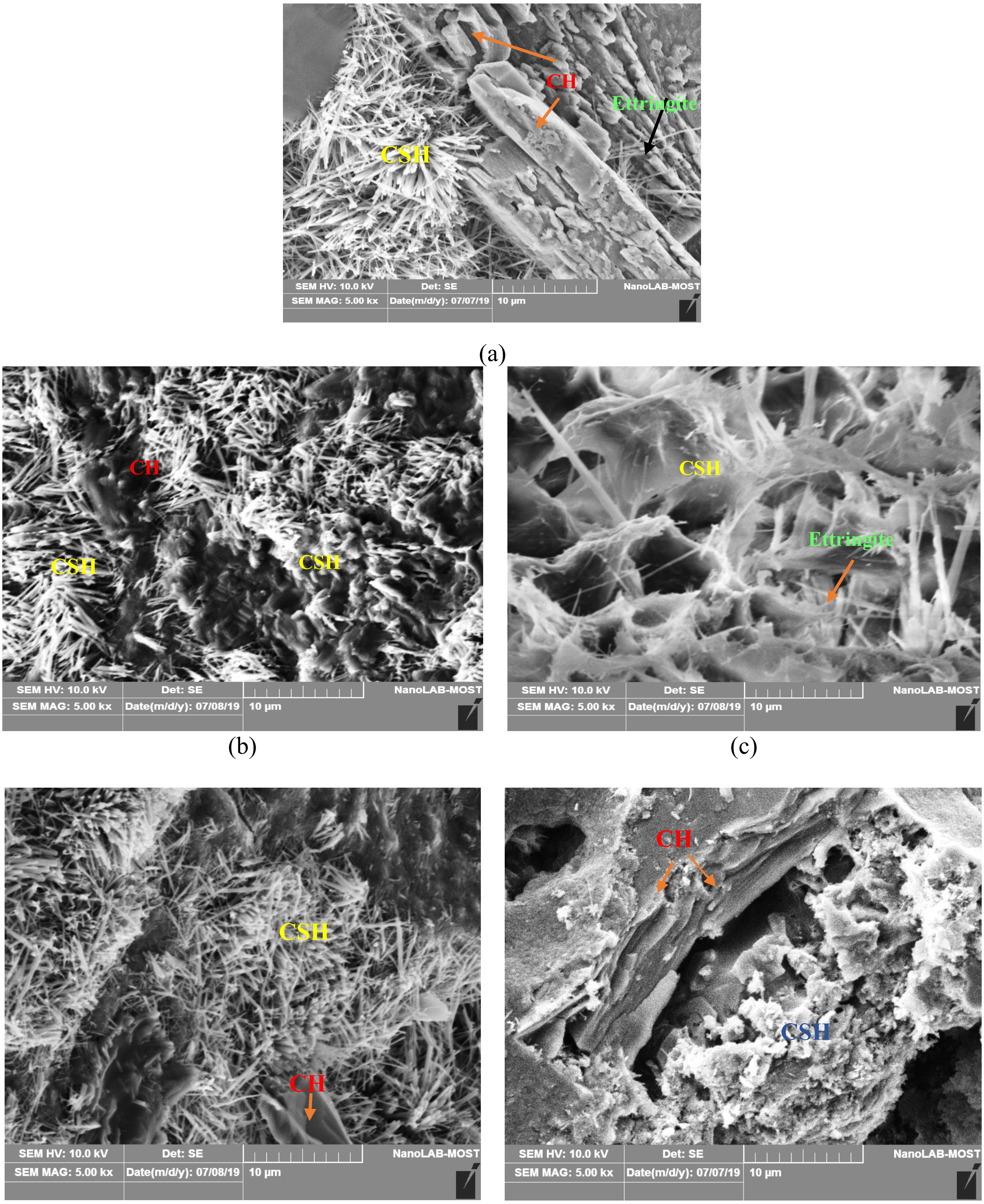


Figure 9 The characterization measurement (XRD) pattern of mortar mix with nano Al_2O_3

Results of SEM Analysis

Broken pieces from the compressive cubes were used as a sample for the SEM test. Before using the broken samples' pieces in SEM, they must pass through a coater device, because the concrete nature does not conduct the electron ray, so it is coated with conducting materials such as gold**.** The SEM images of mortar pastes with and without nanoparticles are shown in Fig. 10. From the SEM analysis of the cement mortar paste samples, it is evident that no clear nanoparticles are seen; hence, it's proved that all the nanomaterials contribute in the hydration process with varying degree.

It can be seen by comparing Fig.10 (a) for reference mix with Fig. 9 (b-c-d-e) that the microstructure of paste containing nanoparticles is much denser than the paste of the reference mix. By comparing all figures, the development of the additional hydration outputs, like CSH and ettringite, can also be revealed but in different quantities depending on the replacement type. ZrO_2 nanoparticles enhance and densify the microstructure of mortar as a result of promotion of the hydration process, according to Ali Nazari et al. [16]. In Fig.9 (c), the nano-silica accelerated the rate of hydration, so it was sufficient to achieve the improvement in the strength of mortar due to the reacted grains present in the hydrated cement paste. Excessive CSH formation was found due to the nano-silica greater reactivity because of its higher surface area and pozzolanic activity [21]. Similar condensation of the microstructure can also be shown in the paste due to the addition of N2 Al2O3 in Fig.9 (e) that shows more evolution (CSH) earlier than the last. According to the mechanism proposed by Faiz Uddin Ahmed et al. that showed the most significant increase in hydration product formation and strength development when adding Al_2O_3 nanoparticles to cement mortar [22]. The same trend was evident in the mix with $CaCO_3$ nanoparticles due to the reacted nanoparticles; the (C-S-H) gel presence within the mix was appropriate, which illustrated a good strength improvement.



(a)

(b) (c)

(d) (e)

Figure 10 SEM photomicrograph for mortar mix with (a) reference mix (b) nano ZrO_2 mix (c) nano SiO_2 mix (d) nano Al_2O_3 mix (e) nano $CaCO_3$ mix

Summary

The following conclusions may be drawn from the obtained experimental data:

- In micrographs of (SEM), the predominant stages present in the microstructure were Portlandite (CH) and (CSH) and ettringite which generated due to the hydration process. With the microscopic structure differences observing the mature cement depending on the differences in the morphology of the main stage that arises during the moisture of cement paste which helps in predicting the properties of cement mortar.

- The XRD results elucidated that the addition of silica fume, fly ash and glass powder effects on the hydration product quantity and distribution. It was clear that the microstructural behaviour of mortar influences the strength characteristics of the mix.
- It was obtained that the cement could be beneficially substituted with the nano SiO_2 and nano ZrO_2 particles up to a maximum limit of 3.0% which enhanced the compressive strength of cement mortar remarkably.
- It was found that the compressive strength of mortar increased gradually with the increasing the content of nano Al_2O_3 and nano $CaCO_3$ particles up to 5% by the weight of cement.

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