# Studying the Effect of Nano Additives and Coating on Some Properties of Cement Mortar Mixes

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## ABSTRACT

The experimental work is divided in two parts, in the first part was prepared the mortar samples and mixing proportions cement\sand (1:3)they were mixing these samples with nano scale ceramic powders ($ZrO_2$ and $TiO_2$) respectively the percentages by weight are taken from cement ratio (0.1, 1, 2.5, 5, and 10%) at particle size (50nm) and curing time (28day). The second part has included the preparation of mortar samples and then coated with a mixture of methanol alcohol, cement and ceramic nano-powders by cold spray technique by using compressed air at room temperature with pressure (8bar) and the spray distance (20Cm) and heating of the samples at (75C°), and then study mechanical thermal physical and structural properties for prepared samples.

The results of mechanical and physical tests showed large and significant improvement for all mixed and coated samples with nanoparticles, and that the highest value of the mechanical and physical properties obtained from cement coated samples with (%5$ZrO_2$), reaching the rate of increase in values of Vickers hardness by (%54), and wear resistance increased by (%66), while reaching the rate of decrease in values of total water absorption by (%79), The porosity has decreased at a rate of (%65), With regard to the dry density has increased at a rate of (%2.3). The higher values for the mixed samples reaching the rate of increase in values of Vickers hardness by (%38), and wear resistance increased by (%58), while reaching the rate of decrease in values of total water absorption by (%67), The porosity has decreased at a rate of (%51.68), With regard to the dry density has increased at a rate of (%1.9).

The thermal conductivity test results have shown that there is a marked decrease in values conductivity for all mixed and coated samples with nanoparticles and that the minimum value of conductivity obtained from coated and mixed samples with (%5$TiO_2$) as the value decreases conductivity for coated samples by (%64), while the lowest value for conductivity to the mixed samples by (%49). Results of Characterizations tests showed images of all of (SEM and AFM) Mortar reference sample that a high roughness as well as having to structure $Ca(OH)_2$ a needle shaped structures with the presence of large pores, while after adding and coating by nanoparticles shows the disappearance of structures needle and produce a homogeneous structure of compounds (C-S-H) and the disappearance of the pores and gaps further decrease in surface roughness this explains the clear improvement in the properties.

**Keywords:** Nano Particles, Mortar, Pozzolanic Reaction.



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# دراسة تأثير الطلاءات والمضافات النانوية على بعض الخواص لخلطات مونة الاسمنت


## الخلاصة

ينقسم الجانب العملي الى جزئين، في الجزء الاول تم تحضير نماذج المونة وبنسبة خلط اسمنت/رمل (3:1) حيث تم خلط هذه النماذج مع مساحيق سيراميكية نانوية ($ZrO_2$,$TiO_2$) على التعاقب وبنسب وزنية مأخوذة من نسبة الاسمنت (10,5,2.5,1,0.1%) وبحجم حبيبي (50) نانومتر ووقت معالجة لمدة (28) يوم، اما الجزء الثاني فقد تضمن تحضير نماذج المونة ومن ثم طلاؤها بخليط من كحول الميثانول والاسمنت والمساحيق النانوية وبتقنية الرش البارد بأستخدام الهواء الجوي المضغوط بدرجة حرارة الغرفة عند ضغط (8) بار ومسافة رش بمقدار (20) سم، وتسخين اولي للقواعد لدرجة (75) درجة مئوية، ومن ثم دراسة الخصائص الميكانيكية والحرارية والفيزيائية والتركيبية للنماذج المحضرة.

نتائج الفحوصات الميكانيكية والفيزيائية اظهرت تحسن كبير وملحوظ لجميع النماذج المخلوطة والمطلية مع الدقائق النانوية، وان القيمة الاعلى للخواص الميكانيكية والفيزيائية تم الحصول عليها من النماذج المطلية والمخلوطة مع (5$ZrO_2$%)، حيث بلغت معدل الزيادة في قيم صلادة فيكرز بنسبة (54%)، ومقاومة البلى ازدادت بمعدل (66%)،بينما بلغ معدل النقصان بالامتصاص الكلي للماء بنسبة (79%)، اما المسامية فقد تناقصت بمعدل (65%)، وفيما يخص الكثافة فقد تزايدت بمعدل (2.3%). أما القيم الاعلى بالنسبة للنماذج المخلوطة ، حيث بلغت معدل الزيادة في قيم صلادة فيكرز المايكروية بنسبة (38%)، ومقاومة البلى ازدادت بمعدل (58%)، بينما بلغ معدل النقصان بالامتصاص الكلي للماء بنسبة (67%)، اما المسامية فقد تناقصت بمعدل (52%)، وفيما يخص الكثافة فقد تزايدت بمعدل (1.9%).

أما نتائج فحص التوصيلية الحرارية فقد اظهرت ان هنالك نقصان ملحوظ في قيم التوصيلية ولجميع النماذج المخلوطة والمطلية مع الدقائق النانوية، وان القيمة الادنى للتوصيلية الحرارية تم الحصول عليها من النماذج المطلية والمخلوطة مع (5% $TiO_2$)، حيث بلغت قيمة النقصان بالتوصيلية للنماذج المطلية بنسبة (64%). اما بالنسبة للنماذج المخلوطة فقد بلغ مقدار النقصان (49%). نتائج الفحوصات التركيبية اظهرت صور كل من المجهر الالكتروني الماسح، ومجهر القوة الذرية لنموذج المونة المرجع انه ذا خشونة عالية وكذلك وجود لتركيب هيدروكسيد الكالسيوم $Ca(OH)_2$ بشكل تراكيب ابرية الشكل مع وجود مسامات كبيرة، بينما اظهرت الصور بعد الاضافة والطلاء بالدقائق النانوية اختفاء التراكيب الابرية وانتاج تركيب متجانس من مركبات (C-S-H) واختفاء المسامات والفجوات علاوة على نقصان في خشونة السطح وهذا ما يفسر التحسن الواضح في الخواص.


## INTRODUCTION

Nanotechnology is the term used to cover the design, construction and utilization of functional structures with at least one characteristic dimension measured in nanometers. Such materials and systems can be designed to exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes as a result of the limited size of their constituent particles or molecules. The reason for such interesting and very useful behavior is that when characteristic structural features are intermediate in extent between isolated atoms and bulk macroscopic materials, i.e. in the range of about $10^{-9}$ m to $10^{-7}$m (1 to 100 nm), the objects may display physical attributes substantially different from those displayed by either atoms or bulk materials. Ultimately this can lead to new technological opportunities as well as new challenges **[1].**Regarding literature survey about addition of nano particles for concrete, In **2013**, K. Behfarnia et al., [2] have studied compressive strength of normal concrete together with gas permeability of concrete containing various percentages from (1,2,3,4,and 5%) of $TiO_2$ and ZnO nanoparticles with average particle size (20nm) were investigated and the results were compared with each other and with that of the normal concrete. More types of tests were carried out on the specimens including X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The results indicated that $TiO_2$ nanoparticles decreased the compressive strength after 28 days of curing however; the permeability of concrete was lowered. Moreover, it seems that by adding $TiO_2$ nanoparticles up to 4wt% of the cement the mechanical and physical properties of concrete may improve. The ZnO nanoparticles strongly retard the setting time and increasing the amount of ZnO nanoparticles in the mixture, thoroughly stops the hydration process within the concrete. With increase in percentage of the ZnO up to 5wt % nanoparticles in concrete mixture, the lower compressive strength was obtained.

In **2013**, Masoud *et al.*, [3] have investigated synthesis of zirconia nanoparticles (Nps) and their ameliorative roles as additives concrete structures. Synthesized Zirconia Nps were studied with X-ray diffraction (XRD), UV-visible spectrophotometer, and transmission electron microscope (TEM). We used standard Portland cement in related experiment Concrete Structures. The experimental mixtures were prepared with different amounts of ZrO2 Nps with an average particle size of 20 nm. The experimental mixtures were prepared 0.125, 0.25, 0.5 and 2.0% $ZrO_2$ Nps/cement by weight. The modified cement with ZrO2 nanoparticles was studied with split tensile strength, flexural strength and setting time methods. Final results showed that Zirconia Nps could be used for their Ameliorative roles as Additives Concrete Structures.

In **2014**, Amr A. Essawy and S. Abd El.Aleem, [4] have studied Blends contain sulfate resisting cement (SRC), micro silica (MS) and nano-sized $TiO_2$ (nT) were prepared. The phase of nT is a pure. Incorporating 5wt. % of nT into cement blends gave more desirable physico-mechanical properties than others. The obtained results implied the following:

1. The values of compressive strength as well as bulk density have increased and that of total porosity has decreased with MS content up to 15% mass.
2. (5%) mass of nT into cement mixes increases the density and strength, because the nano-sized particles seem to act as effective fillers of voids.
3. Increasing the dosage of nT above 5% wt does not lead to significantly higher density and strength. Because, the production of hydrates is so greatly stimulated, even by a small quantity of inert nano-particles, as most of the capillary pores are filled up and the growth was confined by limited space.

Concerning literature survey about coating by nano particles for concrete, in **2013**, M.Guo, and C.Poon. [5] have studied a spraying method was employed to coat nano-$TiO_2$ particles on the surface of concrete surface layers. For comparison reasons, an intermixing method was also used to embed 5% nano-$TiO_2$ particles in the testing samples. Photocatalytic degradation of NO was evaluated to compare their air purifying efficiencies. A harsh abrasion was imposed on the testing samples to evaluate the resistance of the surface $TiO_2$-particles to weathering the results showed that after 7 days curing, all the $TiO_2$ sprayed samples displayed higher photocatalytic NO removal activities than the $TiO_2$ intermixed samples. After 28 days curing, a slight reduction in NO removal was observed. Although abrasion exerted a significant photocatalytic reduction on the $TiO_2$ sprayed samples, they still retained a NO removal ability that was higher than that of the $TiO_2$ intermixed samples.

In **2014**, Jian *et al.*, [6] have studied Environmental pollution has an evidently adverse impact on the buildings that are constructed by the glass fiber reinforced cement (GRC) materials. In the present work, the stable, neutral $TiO_2/SiO_2$ nano particles were prepared by using the Ti $(SO_4)_2$ as titanium source, HNO3 as peptizing agent, and $SiO_2$ as stabilizer through a simple and low cost process. The morphologies and structures of $TiO_2/SiO_2$ hydrosol were further characterized by the TEM, SEM, and FTIR measurement. In the synthetic hydrosol, lots of nanoparticles with the diameters in the range of 10–20 nm can be observed. Ti-O-Si band were formed, as observed from the FTIR spectrum. The $Na_2O{\cdot}SiO_2$ was detected from the SEM.The $TiO_2/SiO_2$ hydrosol can be compactly coated on the GRC surface due to the existence of Na2O·$SiO_2$ binder and exhibited high photocatalytic activity and stability in the degradation.

In **2014**, Lorenzo *et al.*, [7] have studied the Environmental pollution which is constantly increasing and it causes aesthetical concerns to urban buildings exposed to the atmosphere. Nano metric titanium dioxide ($TiO_2$) has become a promising photocatalytic material owing to its ability to accelerate degradation of many organic contaminants. Application of $TiO_2$ is rising and it found application on building industry. However, photocatalytic properties of this nanotechnology strongly depend on substrate morphology and on its nature. Thus, it is not correct to extrapolate photocatalytic activity on different types of substrate. Moreover, very few information is available about effectiveness of $TiO_2$ coatings after aging phenomena when applied on different substrate. This paper aims to investigate photocatalytic properties of $TiO_2$ (40-50nm) at percentage (0.5, 1%) applied on clay brick surfaces both after deposition and after aging process. $TiO_2$ characterization was carried out by assessing nano-film morphology, wettability and self-cleaning efficiency before durability test. Self-cleaning ability was also evaluated during aging test in order to evaluate its variation in long term applications. Results show that photocatalytic efficiency of $TiO_2$ remain stable after aging, thus $TiO_2$ shows a good photocatalytic efficiency when it is applied to clay brick substrate. In the long run, photocatalytic efficiency of clay brick specimens treated with $TiO_2$ is seven times higher than untreated specimens.

## Experiment Part

Experimental work consists of two sections, the first section is incorporating nano materials with particle size for nano materials of (50) nm. and five different percentages (0.1%, 1%, 2.5%, 5% and 10%) per weight of cement are used in order to study the impact of nano materials on performance of concrete.

The second section is coating nano materials with particle size for nano materials of (50) nm. and five different percentages of (0.1%, 1%, 2.5%, 5% and 10%) per weight of cement are used in order to study the effect of nano materials on performance of concrete.

## Preparation of Mixed Cement Mortar

Numbers of mortar mixtures was made for every test according to experimental design, All the mortars had a water-to-cementitious materials ratio (w/c) of 0.5 and a sand-to-cementitious materials ratio of 1:3 according to ASTM Specifications(C109).[8], Percentage of the nano materials varied from (0 , 0.1, 1, 2.5, 5, and 10%) by mass of the cementations materials. Mortars with ($ZrO_2$ and $TiO_2$) nano particles were compared with that the control mixture to evaluate the effect of dosage of nano materials at particle size (50nm).

Mortars were mixed at an ambient temperature of about 30℃. To prepare mortar mixtures, the solid materials were dry mixed first. Nano materials and water was mixed first using ultrasonic mixer with 750 Watts power input for 15 min. The sonicated mixture was then mixed with sand, and mixed for 4 min. From each mortar mixture, before placing the paste, the inside mold was oiled in order to cast the sample out easily. The mold was placed on a soft board in order to be the base of specimen free of defects. The molded specimens were covered with wet burlap for the first 24 hr to prevent moisture loss. After demolding, the specimens were cured in a fog room at a temperature of about 28–30 ℃ until the time of testing. The (mechanical, physical, and thermal) properties of the mortars were determined at (28 days).

## Preparation of Emulsion Solution

1- The two types were prepared by adding methanol alcohol ($CH_3OH$) as a medium to (0.1, 1, 2.5, 5, and 10% of $ZrO_2$ per weight of cement in 100ml), (0.1, 1, 2.5, 5, and 10% of $TiO_2$ per weight of cement in 100ml).

2- To homogenize the solutions, magnetic stirrer was used for 30 min.

3- The solutions were applied for coating the specimen by using airbrush spray gun coating technique.

4- Step (2) is repeated for the new solutions.

## Results and Discussion:

### Wear Test:

This test was conducted by the wear test machine (pin-on-disc), the tests were carried out by varying two of the following four parameters and keeping other two constant:

a-Applied load was 5N.b-Applied time was 5min. - Constant sliding speed was 950 rpm.

d- Constant sliding distance was 6 cm. and then calculate adhesive wear rate, according to the following relationship:

$$W.R = \Delta W \setminus S.D \quad \dots (1)$$

Where: W.R: Weight sliding wear rate (gm/min).
ΔW: Weight difference before and after the test. S.D: Sliding distance.
Figure (1) shows the wear rate of mixed samples including the as control sample, and Figure (2) shows the wear rate of cement coated samples including the as control sample, the comparative wear rate for the mixed samples shows that higher than the coated samples, so the coatings improve the wear resistance especially for zirconia coated which has the lowest wear rate that may be due to high mechanical properties between the others. So wear rate of control sample is higher than mixed samples and coated samples. The explanation may be that the sliding of abrasives on a solid surface results in volume removal, and wear mechanism depends on the hardness of the composite component which is a key parameter in governing the amount of material removal, so that hard coating increases the effective hardness of the composite which act to reduce the amount of material removal which means decreased in the wear rate [9]. The Figures (3) and (4) displayed comparisons between mixed samples and cement coated samples with nano material ($ZrO_2$ and $TiO_2$) respectively, with percentages (0.1, 1, 2.5, 5, and 10%) for nano material at particle size (50nm) and curing time (28 day).

**Hardness Test:**

Vickers micro hardness tester is used to measure hardness for the samples. The indentation load is(1N)for loading time of 15 sec.Four values for the hardness are taken on each specimen surface and the average diagonal dimensions of these indent has been measured to find the Vickers hardness according toASTM E384-99 eq. (2).

$$H.V = 1.8544*P \setminus (d_{av})^2 \qquad ...(2)$$

Where: P: is the applied load (kg). $d_{av}$: average of two diagonal lengths (mm).
The result hardness values are average values of three places performed on all samples. Figure (5) shows Vickers micro hardness value of mixed samples with nano material ($ZrO_2$ and $TiO_2$), with percentages (0.1, 1, 2.5, 5, and 10%) for nano material at particle size (50nm) and curing time (28 day). including the as control sample, and Figure (6) shows Vickers micro hardness value of cement coated samples with nano material ($ZrO_2$ and $TiO_2$) respectively, with percentages (0.1, 1, 2.5, 5, and 10%) for nano material at particle size (50nm) and curing time (28 day) including the as control sample, The comparative Vickers micro hardness for the mixed samples shows that less than the coated samples, so the coatings improve the Vickers micro hardness especially for zirconia coated which has the higher micro hardness that may be due to high mechanical properties between the others. So Vickers micro hardness of control sample is less than mixed samples and coated samples. From the two Figures (5) and (6)it is clear that the hardness of specimens increases with increasing nano materials content, apparently because of the improvement in density. The hardness values are highly correlated with relative density and porosity, so reducing the number of defects in a specimen is a common way of increasing its micro hardness [10]. The Figures (7) and (8) displayed comparisons between mixed samples and cement coated samples with nano material ($ZrO_2$ and $TiO_2$) respectively, with percentages (0.1, 1, 2.5, 5, and 10%) for nano material at particle size (50nm) and curing time (28 day). The Figures leading to a conclusion that hardness values of cement coated samples with different percentages of nano materials is higher than mixed samples with different percentages of nano materials.

**Thermal Conductivity Test:**

Hot Disk method was used for determining the thermal conductivity (K). The Hot Disk TPS 500 Thermal Constants Analyzer, Figure (9) shows the thermal conductivity of mixed samples including the as control sample, and Figure (10) shows the thermal conductivity of cement coated samples including the as control sample, The comparative thermal conductivity for the mixed samples shows that higher than the coated samples, so the coatings decreases the thermal conductivity especially for titania coated which has the lowest thermal conductivity that may be due to low thermal properties between the others. So, thermal conductivity of control sample is higher than mixed samples and coated samples. The two Figures(9)and(10)shows reduced of thermal conductivity and increased in thermal insulation with existing of nano powder and will agreement with(Z.Zhang et al.,2012)[11].The Figures (11) and (12) displayed comparisons between mixed samples and cement coated samples with nano material ($ZrO_2$ and $TiO_2$,) respectively, with percentages (0.1, 1, 2.5, 5, and 10%) for nano material at particle size (50nm) and curing time (28 day). The Figures leading to a conclusion that thermal conductivity of cement coated samples with different percentages of nano materials is less than mixed samples with different percentages of nanomaterials.

**Total Water Absorption Test:**

The specimen was used to calculate the total absorption for the reference and (mixed or coated) modified concrete (with nanoparticles). This test was carried out accordance to ASTM C642-1997[12]. The percentage of total absorption can be calculated from the following equation:

Total absorption (%) = (W2-W1)/W1 *100 . … (3)

W1: the average weight of dry specimen (gm). W2: the average weight of wet specimen (gm).

Figure (13) shows the total water absorption of mixed samples including the as control sample, and Figure (14) shows the total water absorption of cement coated samples including the as control sample, The comparative total water absorption for the mixed samples shows that higher than the coated samples, so the coatings decreases the total water absorption especially for zirconia coated which has the lowest total water absorption that may be due to high density which is lead to decrease porosity and penetration. So, total water absorption of control sample is higher than mixed samples and coated samples. The decreasing in water absorption may be due to enhancement of the concrete porosity by both physical and chemical mechanisms of nano materials. It makes the pore structure of mortar more homogeneous by decreasing the number of large pores, without the additions of nano materials, the CH crystals grow large and tend to be strongly oriented parallel to the aggregate particle surface[13]. The Figures (15) and (16) displayed comparisons between mixed samples and cement coated samples with nano material ($ZrO_2$ and $TiO_2$) respectively, with percentages (0.1, 1, 2.5, 5, and 10%) for nano material at particle size (50nm) and curing time (28 day). The Figures leading to a conclusion that total water absorption of cement coated samples with different percentages of nano materials is less than mixed samples with different percentages of nanomaterials.

The dry density can be concluded by using the procedure specified accordance to ASTM C642-1997.[12], The specimen were dried in oven at (100-110 °C) for 24 hours then moved and weighted, after that the specimen was immersed in water for 24 hours, and moved, finally the submerged weight of the specimen was obtained. This test was conducted at ages of 28 day. The dry density can be calculated from the equation:

Dry density (gm/$Cm^3$) = W1/ (W1-W2) *ρw … (4)

W1: dry weight of specimen (gm). W2: submerge weight of the specimen (gm).

$\rho_w$: the density of water is equivalent to 1 (gm/$Cm^3$).

The density of hardened concrete is a function of the densities of the initial ingredients, mix proportions, initial and final water content, air content, degree of consolidation, degree of hydration, volume changes, and subsequent gain or loss of water, among other factors. Dependence on these factors makes density an effective indicator of the uniformity of raw materials, mixing, batching, placing, sampling, and testing. A significant change in density signals a change somewhere in the process. [14]

Figure (17) shows the densities of mixed samples including the as control sample, and Figure (18) shows the densities of cement coated samples including the as control sample, The comparative densities for the mixed samples shows that less than the coated samples, so the coatings increases the densities especially for zirconia coated which has the highest density that may be due to high density which is lead to decrease porosity and penetration. So density of control sample is less than mixed samples and coated samples, this behavior is associated with the extremely fine particles of nano materials that enter the spaces between cement grains, thus improving packing as filler and improves the interface zone with aggregate. The Figures (19) and (20) displayed comparisons between mixed samples and cement coated samples with nano material ($ZrO_2$ and $TiO_2$) respectively, with percentages (0.1, 1, 2.5, 5, and 10%) for nano material at particle size (50nm) and curing time (28 day). The Figures leading to a conclusion that dry density of cement coated samples with different percentages of nano materials is higher than mixed samples with different percentages of nano materials, This preference is because the coated mortar covers the surface and proofing water and reduce permeability leading to increase in dry density.

**Porosity Test:**

This test is performed accordance with ASTM C642-1997. [12], porosity test conducted at ages of 28 day. The test procedure was similar to that of total absorption test exception that the third weight of specimen was computed by using a sensitive balance. The third weight represented the submerge weight of the specimen. Porosity can be calculated by using the following equation:

$$\text{Porosity } (\%) = (W2-W1)/ (W2-W3) *100 \quad ... (5)$$

Where: W1: the average dry weight of specimen (gm).
W2: the average wet weight of specimen (gm). W3: the average submerges weight of specimen (gm).

Porosity consider one from the mechanisms that are directly related to the quality of concrete, it can provide useful information relating to the pore structure, permeation characteristics and durability of the concrete surface zone that is penetrated [15]. Figure (21) shows the porosity of mixed samples including the as control sample, and Figure (22) shows the porosity of cement coated samples including the as control sample, The comparative porosity for the mixed samples shows that higher than the coated samples, so the coatings decreases the porosity especially for zirconia coated which has the less porous that may be due to high density which is lead to decrease porosity and penetration. So porosity of control sample is higher than mixed samples and coated samples, This behavior is associated with the extremely fine particles of nano materials that enter the spaces between cement grains, thus improving packing as filler and improve the interface zone with aggregate. The Figures (23) and (24) displayed comparisons between mixed samples and cement coated samples with nano material ($ZrO_2$ and $TiO_2$) respectively, with percentages (0.1, 1, 2.5, 5, and 10%) for nano material at particle size (50nm) and curing time (28 day). The Figures leading to a conclusion that porosity of cement coated samples with different percentages of nano materials is less than mixed samples with different percentages of nano materials, This preference is because the coated mortar covers the surface and proofing water and reduce permeability leading to decrease in porosity.

**Scanning Electron Microscope:**

The scanning electron microscope is comparatively more useful in studies which investigate quantification of microstructural properties, such as micro cracks and voids. It has a greater depth of field and high spatial resolution which produces focused images of poor specimens. [16]

Figure (25) shows the SEM micrographs of the control mortar mixture at the age of 28 days demonstrate porous structure that is full of large size pores and presence of $Ca(OH)_2$. Also it can be seen from same Figures the existence of many CH crystals connected to the C-S-H gel which indicates that the hydration process is not completed and also explains the low records of mechanical properties for the control mixture. The Figures (26) and (27) displayed SEM of mixed samples with nano material ($ZrO_2$ and $TiO_2$) respectively, with percentages (5% $ZrO_2$), (5% $TiO_2$) which gave the best results at particle size (50nm) and curing time (28 day). The previous Figures shows that prepared samples are denser and more organized of the control sample with a small number of $Ca(OH)_2$ crystals and small sized pores while the control mixture the C-S-H gel existed in the form of clusters lapped and jointed together by many CH needles hydrates. It can also be noticed from the same photos that the CH needles are invisible and there is a compact structure with the absence of the un-hydrated crystals and voids and more uniform and homogeneous than that of the cement mortar sample which explains the best mechanical properties. This could be due to the high activity of many particles that promote the pozzolanic reaction to produce more C-S-H gel in order to record high mechanical properties at early age. While the Figures (28) and (29) displayed SEM of cement coated samples with nano material ($ZrO_2$ and $TiO_2$,) respectively, with percentages (5% $ZrO_2$) and (5% $TiO_2$) which gave the best results at particle size (50nm) and curing time (28 day). The previous Figures show that coated prepared samples are denser and more organized with absence of large pores compared to the mixed samples. It can also noticed from the same photos there is a compact structure with the absence of the large voids and more uniform and homogeneous than the mixed sample which explains the best mechanical properties, Also can be seen the presence of a soft structure for nano particles and there is arranging of area that appears. Clustered groupings in the pocket with alots of nano grain cover the surface fills pores to increase the strength.

**Atomic Force Microscope:**

AFM is instrument used to evaluate the surface topography and morphology of the prepared cement mortar samples. The shape and particles size distribution of the mixes and coatings can be found from the AFM images. The aim of this investigation is to obtain information about the surface morphology and geometry of structures[17], The Figure (30) show the topographic structures in 2D views for the cement mortar sample seem to give less homogeneous and high roughness surface was (32.2nm) with average diameter is (527.67nm), The Figures (31) and (32) displayed the topographic structures in 2D of mixed samples with nano material ($ZrO_2$ and $TiO_2$,) respectively, with percentages (5% $ZrO_2$) and (5% $TiO_2$) which gave the best results at particle size (50nm) and curing time (28 day). From this Figures, seem to give more homogeneous than cement mortar because of the addition of nano particles which is reduced surface roughness and average diameter, the surface roughness for this Figure was (8.77nm) and (9.09nm) respectively, while the average diameter was (233.45nm) and (388.98nm) respectively. The Figures (33) and (34) displayed the topographic structures in 2D of cement coated samples with nano material ($ZrO_2$ and $TiO_2$) respectively, with percentages (5% $ZrO_2$) and (5% $TiO_2$) which gave the best results at particle size (50nm) and curing time (28 day). From this Figures, seem to give more homogeneous than mixed samples because of the nano particles which is reduced surface roughness and average diameter, the surface roughness for this Figures was (5.57nm) and (7.13nm) respectively, while the average diameter was (218.08nm) and (211.98nm) respectively.

**CONCLUSIONS:**

In order to reach the ultimate goal of the cement coating application reinforced by nanoparticles and be equivalent was conducted (mechanical, physical ,thermal, and structural properties), on the coated samples to determine the efficiency and equivalent of the mixed samples has been the following conclusion, incorporating and coating by nano particles to cement mortar mixtures:-

1. Generally enhances their mechanical properties, by yielding higher wear resistance and Vickers micro hardness than cement mortar, where the highest value obtained from coated samples with (5% $ZrO_2$), reaching the rate of increase (%66) and (%54) respectively.

2. Generally enhances their thermal properties, by yielding higher thermal insulation than cement mortar, where the highest value obtained from coated samples with (5% $TiO_2$), reaching the rate of increase (%64).
3. Generally enhances their physical properties, by (increasing density and decreasing total water absorption and porosity) compared to cement mortar, where the highest value obtained from coated samples with (5% $ZrO_2$), reaching the rate of increase (%2.3), (%79), and (%65) respectively.
4.SEM,andAFMand(mechanical,themal insulation,and physical)properties results indicate that the addition of nanoparticles leads to significant consumption of Portlandite(CH)in the pozzolanic reaction, while the coating of nano particles leads to significant reduction of voids and gaps, increasing the dosage of nanoparticles up to(5%)of($ZrO_2$and$TiO_2$)enhancing the properties.
5. The (mechanical, thermal insulation, and physical) tests reveal that the cement coated samples with nano particles have higher properties than mixed samples.
6. The (mechanical and physical) tests reveal that the zirconium oxide has higher properties than titanium oxide.
7. The thermal insulation test reveals that the titanium oxide has higher properties than zirconium oxide.

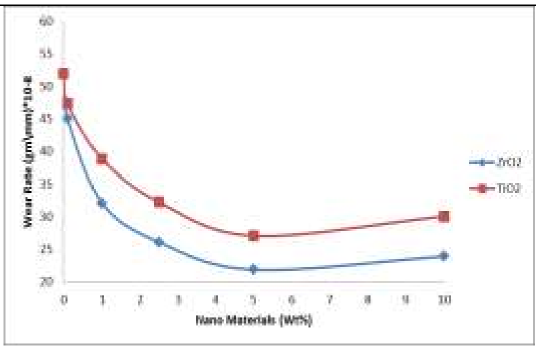



**Figure (1): Effect of nano particles on wear rate for mixed samples.**

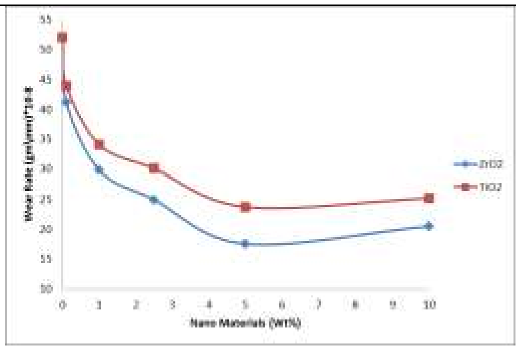



**Figure (2): Effect of nano particles on wear rate for cement coated samples.**

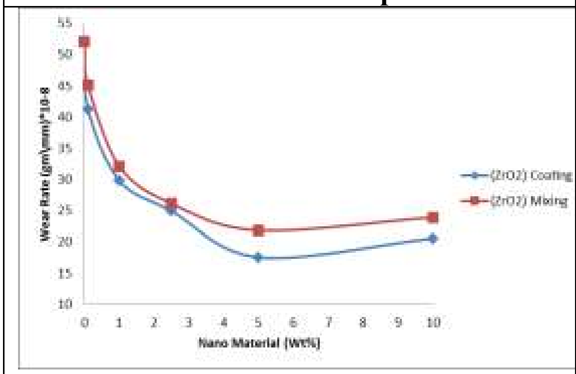



**Figure (3): Effect of ($ZrO_2$) nano particles on wear rate for mixed samples and cement coated samples.**

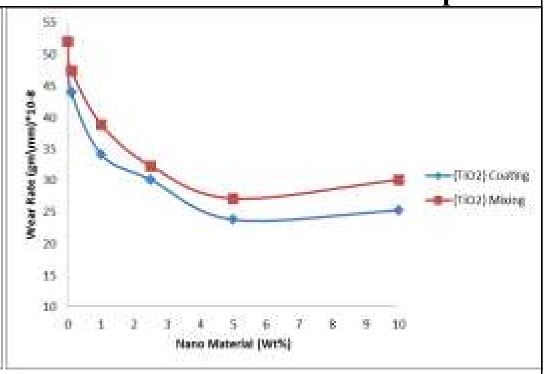



**Figure (4): Effect of ($TiO_2$) nano particles on wear rate for mixed samples and cement coated samples.**

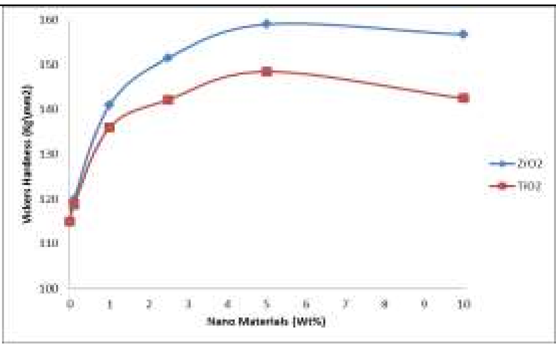



**Figure (5): Effect of nano particles on Vickers Micro Hardness for mixed samples.**

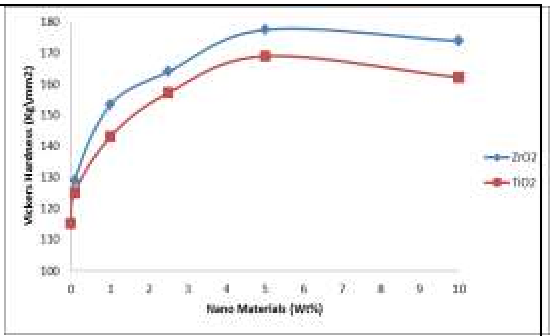



**Figure (6): Effect of nano particles on Vickers Micro Hardness for cement coated samples.**

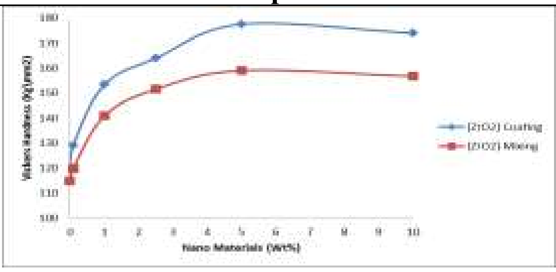



**Figure (7): Effect of ($ZrO_2$) nano particles on Vickers Micro Hardness for mixed samples and cement coated samples.**

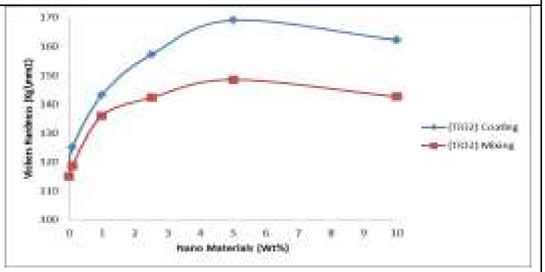



**Figure (8): Effect of ($TiO_2$) nano particles on Vickers Micro Hardness for mixed samples and cement coated samples.**

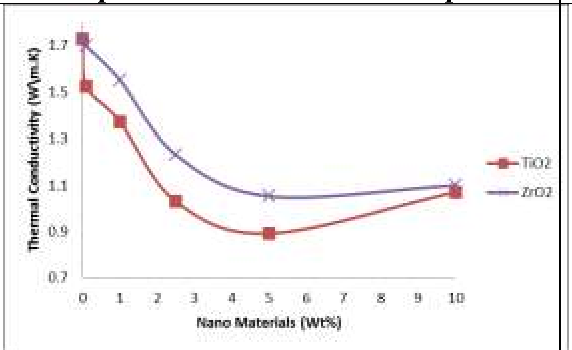



**Figure (9): Effect of nano particles on Thermal Conductivity for mixed samples.**

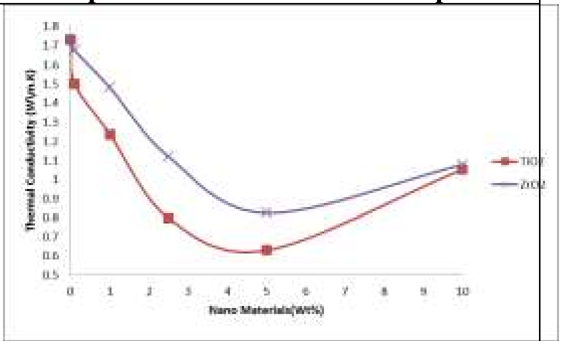



**Figure (10): Effect of nano particles on Thermal Conductivity for cement coated samples.**

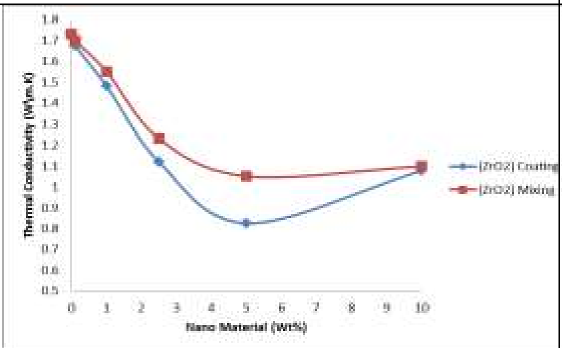



**Figure (11): Effect of (ZrO2) nano particles on Thermal Conductivity for mixed samples and cement coated samples.**

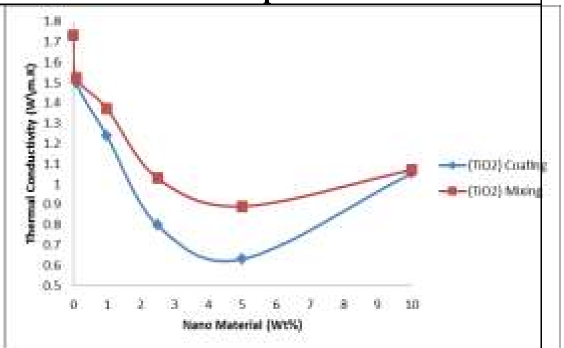



**Figure (12): Effect of (TiO2) nano particles on Thermal Conductivity for mixed samples and cement coated samples.**

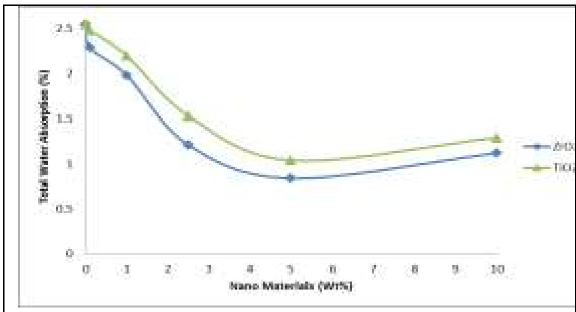



**Figure (13): Effect of nano particles on Water Absorption for mixed samples.**

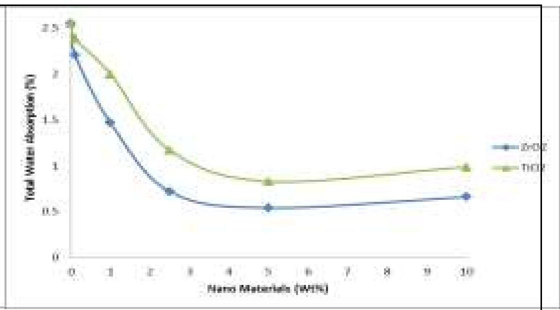



**Figure (14): Effect of nano particles on Water Absorption for cement coated samples.**

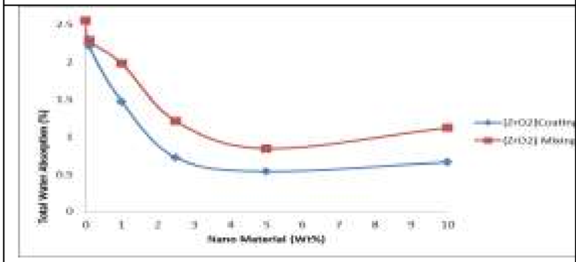



**Figure (15): Effect of (ZrO2) nano particles on Water Absorption for mixed samples and cement coated samples.**

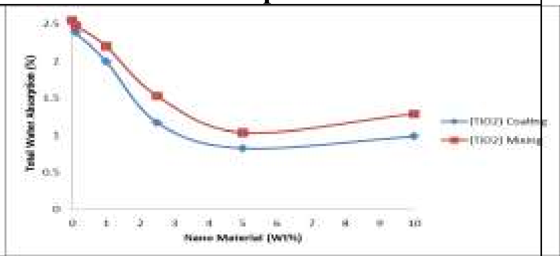



**Figure (16): Effect of (TiO2) nano particles on Water Absorption for mixed samples and cement coated samples.**

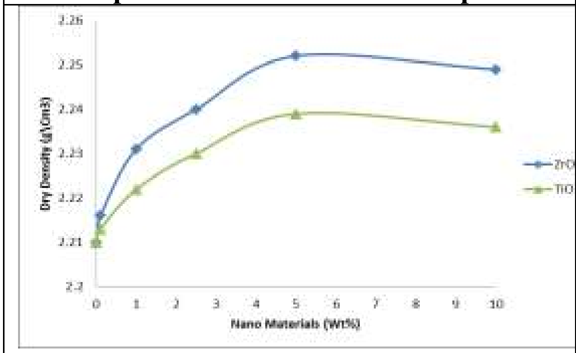



**Figure (17): Effect of nano particles on Dry Density for mixed samples.**

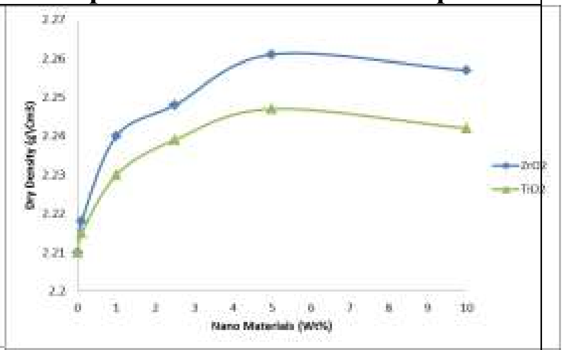



**Figure (18): Effect of nano particles on Dry Density for cement coated samples.**

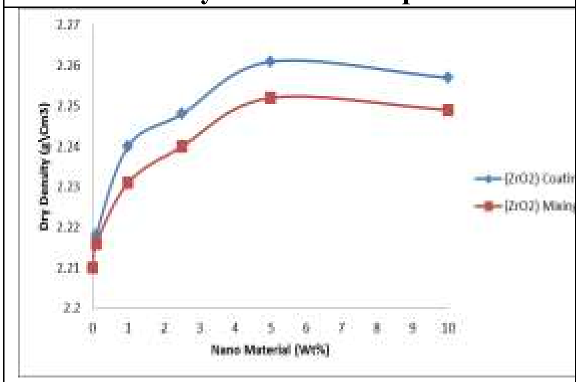



**Figure (19): Effect of (ZrO2) nano particles on Dry Density for mixed samples and cement coated samples.**

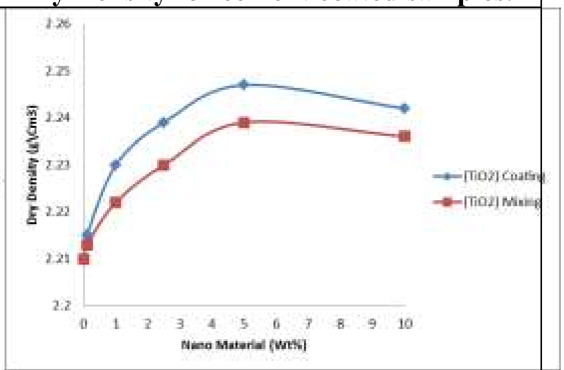



**Figure (20): Effect of (TiO2) nano particles on Dry Density for mixed samples and cement coated samples.**

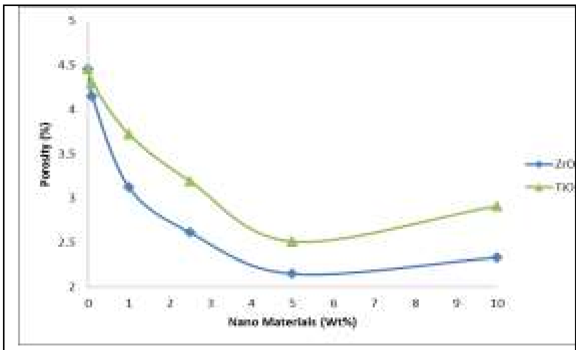



**Figure (21): Effect of nano particles on Porosity for mixed samples.**

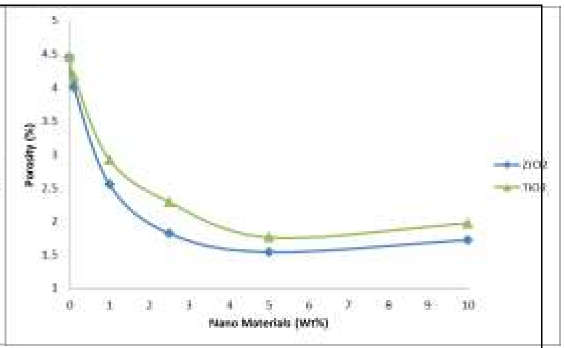



**Figure (22): Effect of nano particles on Porosity for coated samples.**

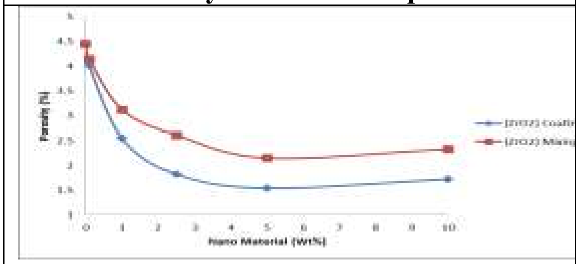



**Figure (23): Effect of (ZrO2) nano particles on Porosity for mixed and cement coated samples.**

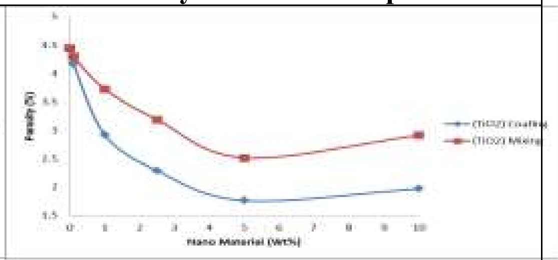



**Figure (24): Effect f (TiO2) nano particles on Porosity for mixed and cement coated samples.**

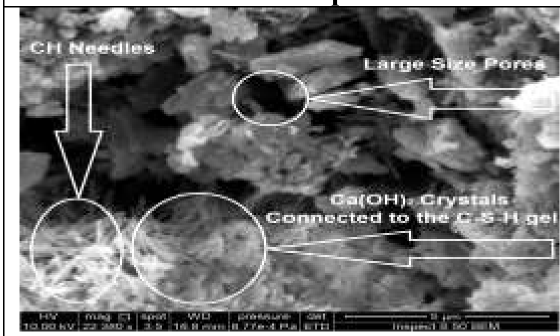



**Figure (25): SEM image of mortar before incorporating nano materials at 28 day.**

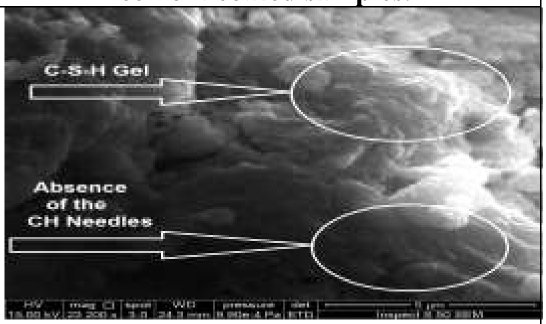



**Figure (26): SEM image of mixed sample with nano ($ZrO_2$) at 28 day.**

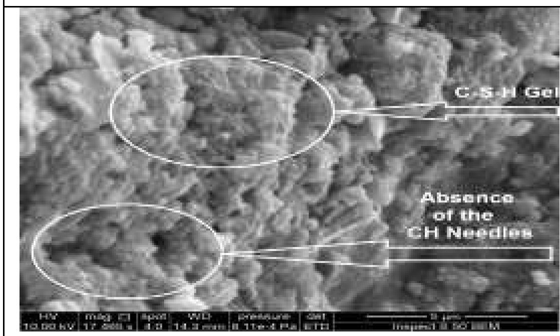
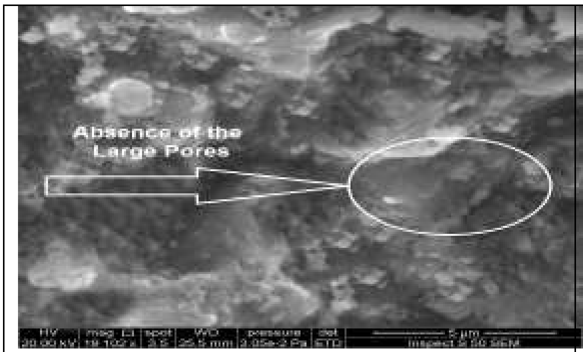



**Figure (27): SEM image of mixed sample with with nano ($TiO_2$) at 28 day.**


**Figure(28)SEM image of cement coated sample with with nano ($ZrO_2$) at 28 day.**




**Figure(29)SEM image of cement coated sample with with nano ($TiO_2$) at 28 day.**

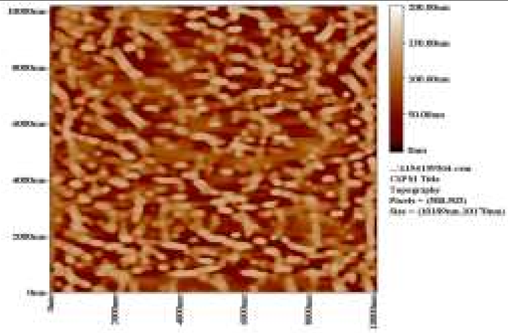


**Figure (30): AFM image of mortar before incorporating nano materials at 28 day.**

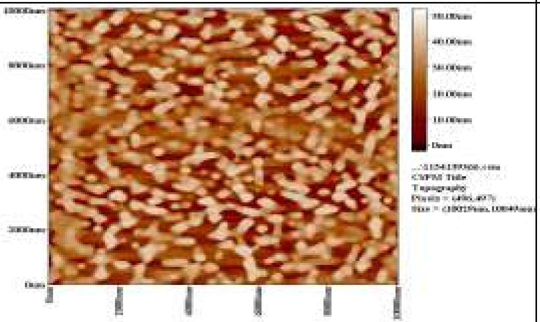


**Figure (31): AFM image of mixed sample with with nano ($ZrO_2$) at 28 day.**

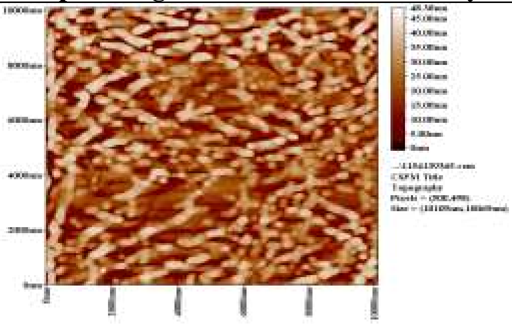
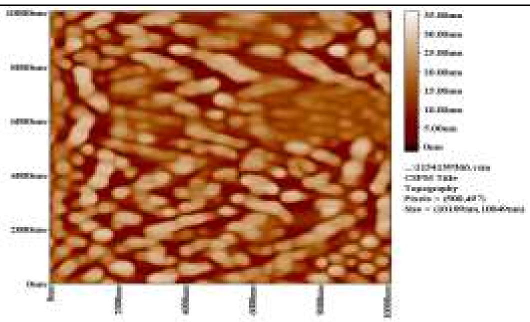
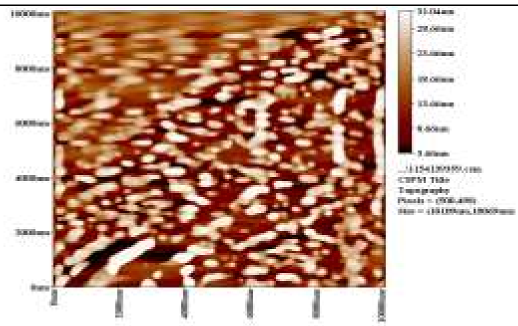


**Figure (32): AFM image of mixed sample with with nano ($TiO_2$) at 28 day.**



**Figure(33)AFM image of cement coated sample with with nano ($ZrO_2$) at 28 day.**



**Figure(34)AFM image of cement coated sample with with nano($TiO_2$)at28 day**

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