

Surface Treatment of Cement based Composites: Nano Coating Technique

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ABSTRACT

Geometry, size, and shape of the surface pores, as well as, capillarity, and exposure environment are directly influence strength and durability of cementitious composites. The current research aimed to improve the resistance to abrasion and decrease the surface porosity of cement-based composites by nano surface coating technique. All samples were coated with a mixture of methanol alcohol, ordinary Portland cement and nano powder of (TiO₂, MgO, ZnO and ZrO₂) separately in percentages of (1, 1.5, and 2 %) by weight of cement. The hardness, abrasion, water absorption, density, porosity, and microstructural analysis: Scanning Electron Microscopy and X-Ray Diffraction (SEM & XRD) were studied for all coated and control specimens. Results showed an improvement in mechanical properties for all coated specimens as compared to control. The highest Vickers micro hardness value had reached 29%, while the largest value of abrasion resistance had increased by 39% for coated samples with 2% ZrO₂. Also, the results showed a reduction in the porosity and water absorption of all coated samples, having highest scores obtained from the coated samples with 2% MgO. While the total water absorption rate decreased by 45% and the density had increased by 1% and the porosity had decreased by 46%. Additionally, the results of microstructural tests revealed pattern and images for each of SEM and XRD. Also,

results indicated that the nano coating leads to significant consumption of Portlandite (CH) associated with production of a stable structure of CSH and reduction of voids, and this is evident from the enhancement in the physical properties.

ARTICLE INFO

Article history:

Received: 19 September 2020

Accepted: 25 September 2020

Published: 22 January 2021

DOI: <https://doi.org/10.47836/pjst.29.1.20>

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Keywords: Abrasion resistance, cement composites, hardness, microstructure, nano coating, porosity

INTRODUCTION

Harmful agents present in the medium that concrete is subjected to, were the main reasons for degradation and low service life of concrete. Sulfates, carbon dioxide and chlorides from industrial and marine environments penetrate into pores and react chemically, causing expansive reactions and corrosion of steel bars (Quraishi et al., 2017). However, the porosity of the cement- based composites is influenced by many factors that may be due to its raw materials, the production procedure, and water / cement ratio, type of curing, compaction, and degree of hydration (de la Cruz Barroso et al., 2015). According to what was mentioned by Mehta and Monteiro (2006), “the empty pores present in the concrete could be classified according to their size to: gel pores: of 1 to 5 μm diameter; capillary pores: of 5 to 30 μm diameter; small air bubbles; of 30 μm to 1 mm diameter; and large air bubbles: of greater than or equal to 1 mm diameter”. The absorption rate investigated on concrete is governed by the capillary pressure of its pores, which is determined by the diameter, shape and connection of the pores present in the surface (Pellegrini-Cervantes et al., 2013). In the case of ion penetration, the capillary absorption of concrete is a very fast process, being considered a hundred times faster than its permeability (Aperador et al., 2016). The dispersion method impact for CaCO_3 nanoparticles on hydration rate, setting, and compressive strength of concrete. Nanoparticles can be used to increase the mechanical features of cement composites (Camilletti et al., 2013). Another study was made to assess the capability of concrete containing nano TiO_2 to degrade organic molecules. The extent of nano TiO_2 in the concrete mixes was 3, 6, 9, 12, and 15% by cement weight. The resulting concrete samples were subjected to sunlight for 24, 48, 72, and 96 hrs. The nano TiO_2 extinguish the organic molecules, by reducing the surface permeability and, as a result, resists certain kinds of air pollution (Elia et al., 2018). The compositions of nano coatings are nano powders dissolved in a fluid to reach an excessive surface area to volume ratio (Birgisson et al., 2012). Due to nanoparticles coatings, corrosion resistance, antivirus features are improved due to enhanced properties of hardness, adhesion, and wear (Mendes et al., 2015). In India, this coating technique was extensively utilized in the strengthening of New Delhi wealth Games building (Glenn, 2013). Thus, the use of organic coatings on concrete is the most common withstand method of concrete and reinforcements versus weathering and corrosion (Vera et al., 2013). Further, the inclusion of nano SiO_2 as thin film on aggregate surfaces enhances the efficiency of concrete. Mortar formed accompanying to nano SiO_2 of 0.32 by wt. % of cement, as a coating on aggregate surfaces exhibited an average 35% enhancement in compressive, flexural, and tensile strengths with a decline in chloride permeability (Zhuang & Chen, 2020). The previous and most nanotechnology researchers’ studies were focused on characterizing of concrete when nano particles were added in the concrete during mixing to increase strength (Ltifi et al., 2011; Zhang et al., 2019a; Zhang et al., 2019b; Rezania et al., 2019; Ali et al., 2020). Meanwhile, it is the

surface pores, which control the rate of entry and movement of detrimental agents that can alter concrete properties and causing a deterioration of its microstructure. Thus, the surface porosity of cement-based composites is vital in the durability of concrete, which is the main characteristic that determines the life for which they were designed. Further, the reason behind using nanomaterials was to enhance mortar performance is that the properties of the particles at the nanoscale are extremely better than the conventional particle size for the same chemical component. This means that novel building materials with superior properties could be produced by using nanoparticles.

The objectives of this research were to study the impact of nano coating on the performance of cement-based composite and to improve the resistance to the chemical as well as biological agent ingress using different types and doses of nanoparticles as coating layer and as a protective shield.

MATERIALS AND METHOD

Materials Characteristics

The raw materials used were type I cement, micro silica, fine aggregate, water, and super plasticizer. Ordinary Portland cement, conforming to I.Q.S 5/1984, was used to produce the specimens. Micro silica was used as pozzolanic admixture associated with 124% pozzolanic strength activity index. Results revealed that micro silica used in this study conformed to the requirements of ASTM C-1240-05 standard. A high range water reducer superplasticizer (Sika ViscoCrete 5930) with a density of 1.095 g/cm³ was used to increase dispersing of mixes, which had been classified as type G according to ASTM C494-14. The sand conforming to the Iraqi Specification No.45/1984 zone 2, was of 4.75 mm maximum size. The nano powders in addition to methanol alcohol used in this study were provided by Nanoshel Company (USA), and Table 1 presents their properties according to manufacturing origin.

Experimental Analysis

In this study, cement based composite boards with a density of 2200 kg/m³ were made and tested for 28 days following the ASTM C1185-12. In light of past research, the experimental factors were: three different percentages of nanoparticles (1, 1.5, and 2 %) by cement weight, and nano particle type (TiO₂, MgO, ZnO and ZrO₂). All the cement mixes used in this investigation had a constant water-to-cement ratio of 35%, superplasticizer-to-cement ratio of 1%, the replacement of microsilica by cement weight of 10%, and a cement-to-sand ratio of 1:2.75. All samples with dimension (305*152*12 mm), were preserved in the molds covered with wet burlap secured with a plastic sheet for one day to prevent moisture loss. After 28 days of moist curing, coating suspensions were prepared following

the procedure described by Ibrahim (2016). Using airbrush spray gun technique at 10 bar compressed air at laboratory temperature, sprayed distance 25 cm, feeding rate 300 ml/min and primary heating of the specimens to 100 °C before coating for 30 minutes to improve the bond between the coating layer and the substrate surface. After that, density, water absorption and porosity were determined in accordance to ASTM C642-06 using the water displacement method.

Table 1
The properties of used materials according to Nanoshel Company (USA)

Properties	Titanium dioxide nano powder	Zirconium oxide nano powder	Zinc oxide nano powder	Magnesium oxide nano powder	Methanol Alcohol
Chemical composition	TiO ₂	ZrO ₂	ZnO	MgO	CH ₃ OH
Purity (%)	99.9	99.9	99.9	99.9	99.8
particle size (nm)	50	50	50	50	/
Specific surface area (m ² /gm)	35	45	65	40	/
Color	White	White	White	White	colorless
Phase	Rutile	Tetragonal	Hexagonal	Cubic	liquid
Density (g/cm ³)	4.3	5.9	5.6	3.6	0.79

The abrasion test machine consists of rotating disc made of tool steel carried out by four parameters (load, time, sliding speed, and sliding distance). Applied load was 5 N, applied time was 1 min, and the constant sliding speed was 1000 rpm with constant sliding distance of 5 cm following ASTM C779-03. Vickers micro hardness tester was used to measure the hardness at indentation load of 0.1N for 15 second. Four values for the hardness were taken on each specimen surface and the average diagonal dimensions of this indent were measured to find the Vickers hardness according to ASTM E 384-99. In addition, the microstructural properties were investigated in terms of X-ray diffraction (XRD), and scanning electron microscope (SEM), for all coated and control specimens.

RESULTS AND DISCUSSION

Effect of Nano Coating on Vickers Hardness

The trends observed during the testing were similar to those seen by other researchers using the same nano particles. The increase observed was almost linear in nature for TiO₂, ZnO and ZrO₂ and nonlinear for MgO nano particles. Figure 1 demonstrates the correlation between Vickers hardness and nano particle type for both coated and control specimens. Higher hardness for coated cement composite specimens were directly related to their higher dosage in the coating film. When comparing between nano particles types, ZrO₂ specimens yielded 29 % higher hardness with the higher dosage in the coating film, despite

of convergence of results. Whilst ZnO specimens yielded only 13 % higher hardness as compared to control specimens. Zirconium oxide nano powder yielded the highest values of hardness due to both the accelerated pozzolanic activity between nano oxides and calcium hydroxide from cement hydration, which led to harder products and to the filling effect by the very tiny particles, thus reducing the number and size of surface pores. This trend is similar to that found by Ibrahim (2016).

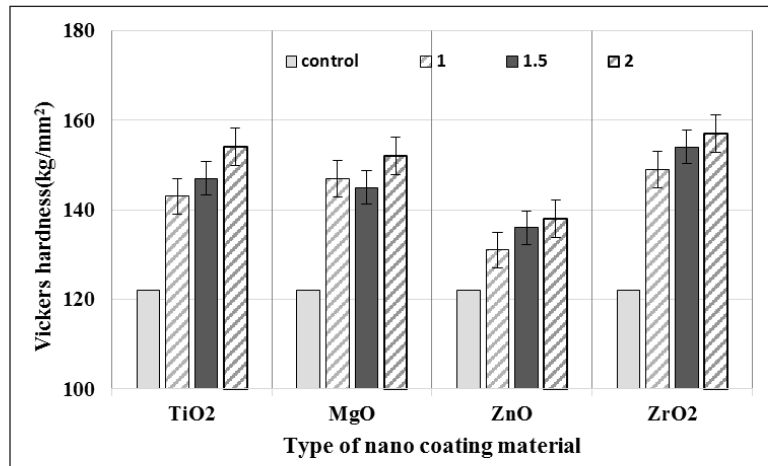


Figure 1. Effect of nanoparticles on the Vickers micro hardness for all cement specimens

Effect of Nano Coating on Abrasion

The word abrasion mainly points to dry wearing action, like in case of wear on pavements and concrete floors by vehicles. There is an essential inverse correlation between porosity and strength of all solid materials. Figure 2 shows histogram of the abrasion test results for all specimens after 28 days of curing. From Figure 2, it can be seen that the abrasion rate reached to the half of control specimen and often quarter that after coating by 2% ZrO₂, as compared with that of the control. It is also obvious that higher doses of 2% for all types were very beneficial to long term abrasion rate and, the lowered 1 % dose might be more desirable than high rate for economy consideration, hence decreasing the abrasion rate of the final composite. This could be due to the filling effect by the very tiny particles which reduced the volume and number of surface pores resulting in solidification of specimen surface. Moreover, as compared to control, an increase in the nano particles concentration in the coating film from (1 to 2%) decreased the abrasion rate by (21-28%), (14-26%), (9-23%) and (28-39%) for TiO₂, MgO, ZnO and ZrO₂, respectively. It was also noticed 1% ZnO showed the lower decrease in the abrasion of 39 g/min *10⁻⁸, while 1% ZrO₂ nano particles showed the higher decrease of 26 g/min *10⁻⁸. This trend is comparable to that found by Othman et al., (2016).

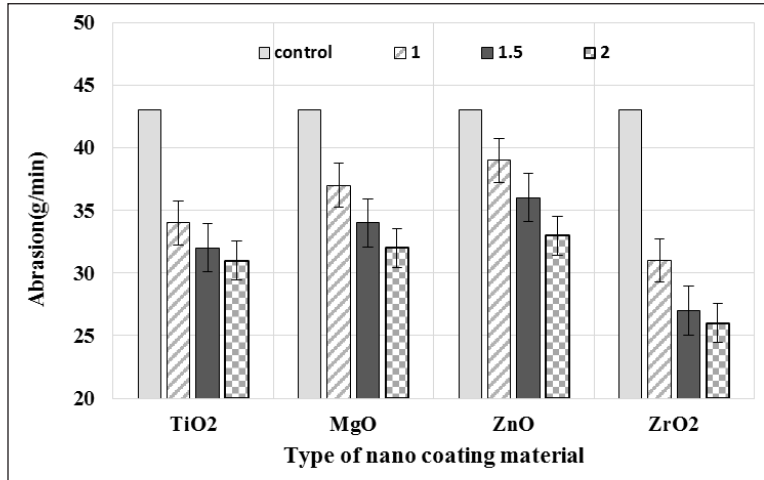


Figure 2. Effect of nanoparticles on the abrasion rate for all cement specimens

Effect of Nano Coating on Density

Figure 3 shows the average densities of all specimens after 28 days of curing. As discussed above, all of the mechanical properties calculated improved as the nano content increased in the coating film. The density for each nano particle type varied differently depending on the percentage of their mass addition in the coating film and to the density of each type. According to Figure 3, all coated specimens were heavier than the control, especially for 2% zirconium oxide nano particles which had the highest density of 2.262 g/cm³. This could be attributed to the high density of (ZrO₂) compared to other types. Else ways, 2% (MgO) showed the lower improvement in density in comparison to control due to the low density of nano MgO particles. However, all the nano coated films showed pozzolanic reactivity between nano oxides and calcium hydroxide from cement hydration leading to

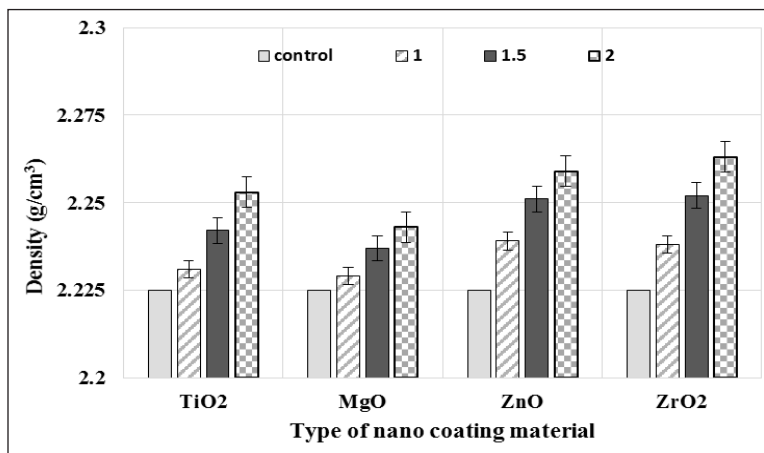


Figure 3. Effect of nanoparticles on the density for all cement specimens

further hydration products that altered the final density. Hence, increasing the nano particle dosage in the coating film (1 to 1.5 to 2 %) increased the density of specimen 0.3, 0.8 & 1.3 % for TiO₂; 0.2, 0.5 & 0.8 % for MgO; 0.6, 1.2 & 1.5 % for ZnO; 0.6, 1.2 & 1.7 % for ZrO₂. These results are in line with the values obtained by Khitab and Arshad (2014).

Effect of Nano Coating on Porosity

From Figure 4, it is observed that all coated specimens would show lower porosity especially MgO at 2% by weight of cement. A stronger adhesion between the coating film and the substrate surface besides the low density of nano MgO particles was assumed to be responsible for this. At higher doses, there would be a chemical interaction between the coating film and the specimen surface that filled the empty pores on the surface and beyond. However, the ability of mineral nano oxides to react at normal temperatures with CH (present in the hydrated Portland cement) and to form additional calcium silicate hydrate were responsible for the decrement in porosity of the final composite. As shown in Figure 4, all coated specimens had porosities in the range of 8-45 %, which was smaller than that of control without coating film. It was interesting to find that there existed a reverse linear relationship between the nano particle dosage in the coating film and the void ratio. The lowest porosity was achieved in 2% MgO (1.92%), and the highest was gained for ZrO₂ (3.26%) at 1% dose of addition.

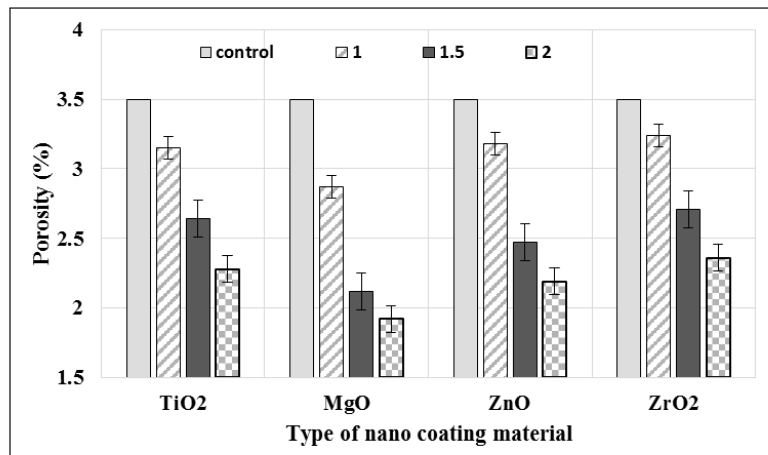


Figure 4. Effect of nanoparticles on the porosity for all cement specimens

Effect of Nano Coating on Water Absorption

Figure 5 represents the water absorption of all cement coated and the control specimens after 28 days of curing. It is obvious that the water absorption for all coated specimens was lower than the control, particularly for nano MgO coating of 2% has the lowest water absorption (45%) as compared to control. This could be attributed to the low density of nano

MgO particles leading to higher volume fraction in the coating film which decreased the surface porosity of specimens. Meanwhile, the lowest water absorption for 2% TiO₂, ZnO and ZrO₂ were 34, 37 and 31% respectively. Test results indicated that the water absorption of all specimens decreased continuously with increasing the nano particles dosage in the coating film. This could be due to the filling effect by the very tiny particles which reduced the volume and number of surface pores. Nevertheless, additional hydration products were gained during the pozzolanic activity between nano oxides and calcium hydroxide from cement hydration as indicated in SEM and XRD images.

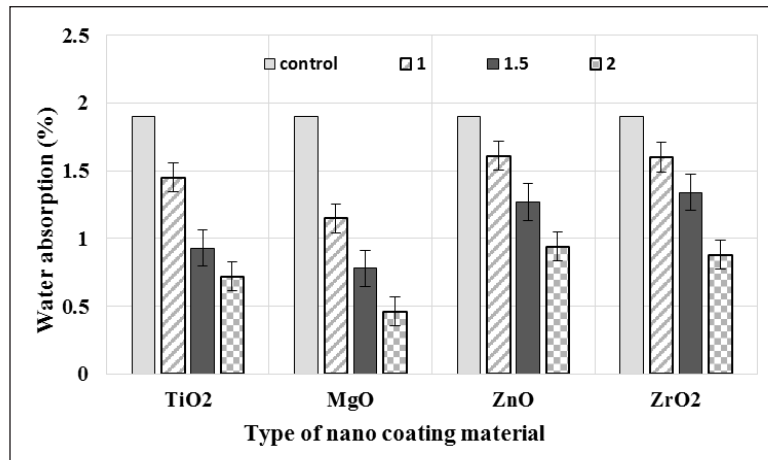


Figure 5. Effect of nanoparticles on the water absorption for all cement specimens

XRD Patterns

After 28 days of curing, XRD analyses were conducted to investigate the activity of incorporating nanoparticles for control and coated cement composite specimens. According to “Joint Committee on Powder Diffraction Standards (JCPDS)”, the components shown in the Figure 1 to 6 were: Portlandite: Ca(OH)₂, hexagonal crystallized, Tobermorite: Ca₅Si₆(O, OH, F)₁₈.5H₂O, orthorhombic crystallized, Ettringite: Ca₆A₁₂(SO₄)₃(OH)₁₂. 26H₂O, hexagonal crystallized, CSH: CaO.SiO₂.H₂O, poor crystallized, CS: CaSiO₃, monoclinic crystallized, Zirconium Oxide: ZrO₂, tetragonal crystallized, Titanium Dioxide: TiO₂, rutile, Magnesium Oxide: MgO, cubic crystallized, and Zinc Oxide: ZnO, hexagonal crystallized. The results of the X-ray diffraction spectra presented in Figure 6 to 10 include data from representative mixtures from the testing matrix control and coated with four types of nano powders. According to Figure 6, major peak humps of Ca(OH)₂ was observed in the diffraction pattern 2θ values of 21.5°, 29.5° and 37° for control mixes. Meanwhile, a minor peak of (CSH, CS and ettringite) were noticed in the diffraction pattern between 2θ values of 22°, 25° and 52°. It is also evident from XRD patterns in Figures 7 to 10 that the CH intensity decreased with the ZrO₂, TiO₂, MgO, and ZnO coated nanoparticles.

However, the results are agreeable with those of obtained by Ahmed et al. (2017). It is therefore concluded from Figure 7 to 10 that the nanoparticles chemically reacted with CH produced during the hydration of cement. The pozzolanic reactivity of nanoparticles can significantly improve the microstructure, so enhancing the mechanical performance of the cement composites (Othman et al., 2016).

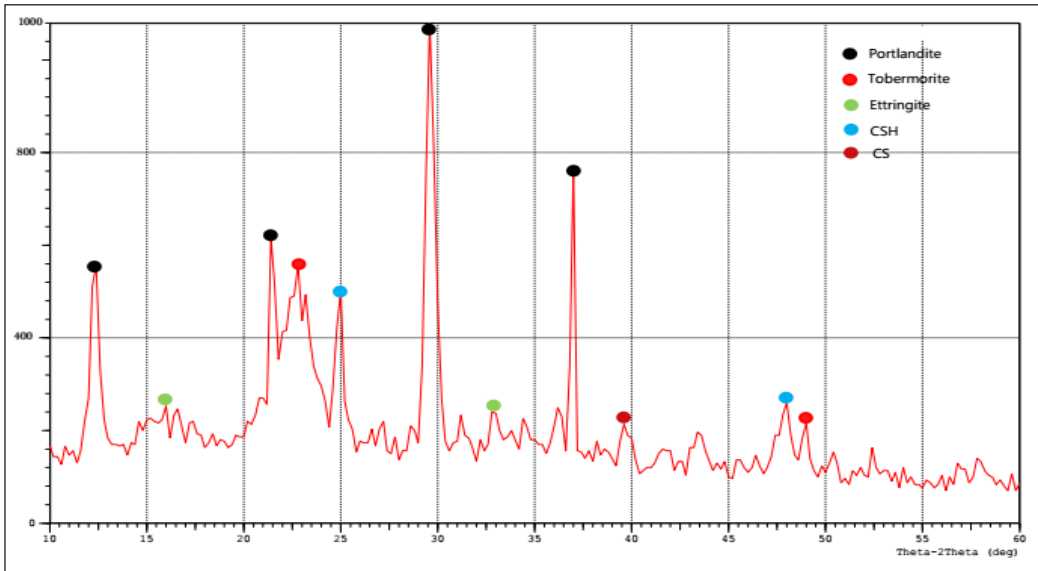


Figure 6. The XRD patterns for the control cement specimen

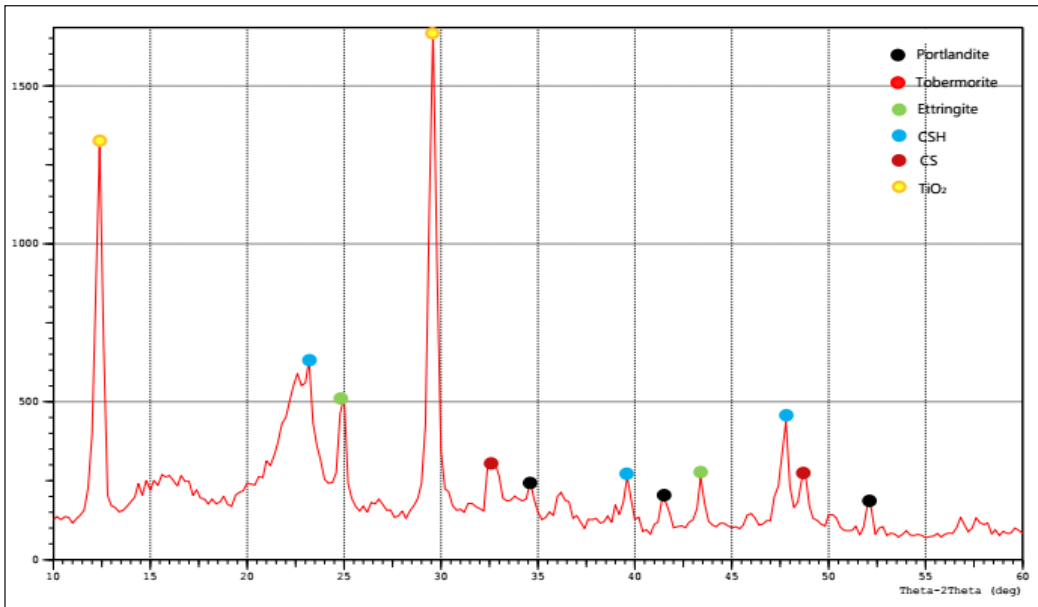


Figure 7. The XRD patterns for the cement coated specimen with 2% TiO₂ nanoparticles

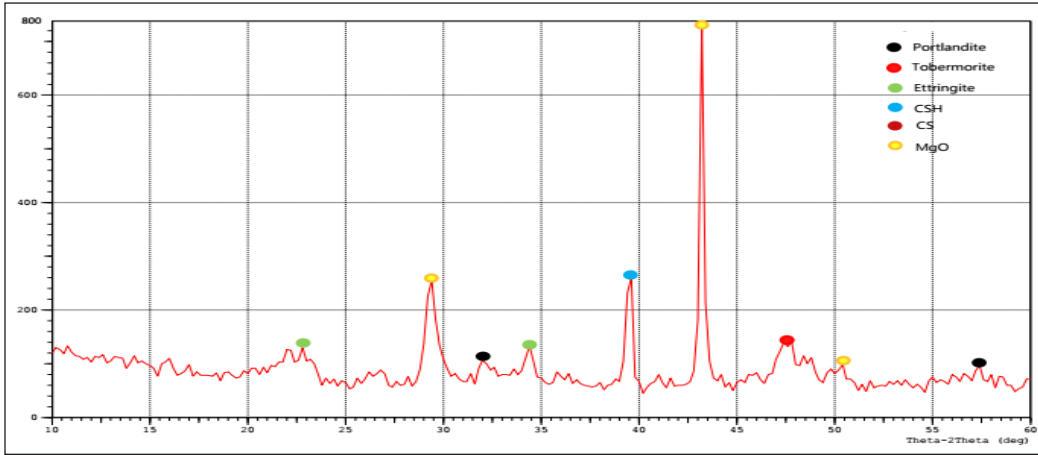


Figure 8. The XRD patterns for the cement coated specimen with 2% MgO nanoparticles

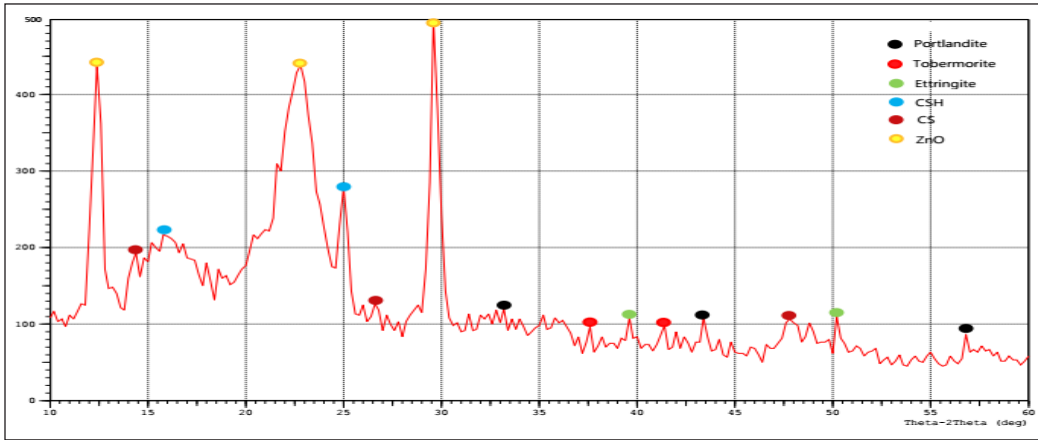


Figure 9. The XRD patterns for the cement coated specimen with 2% ZnO nanoparticles

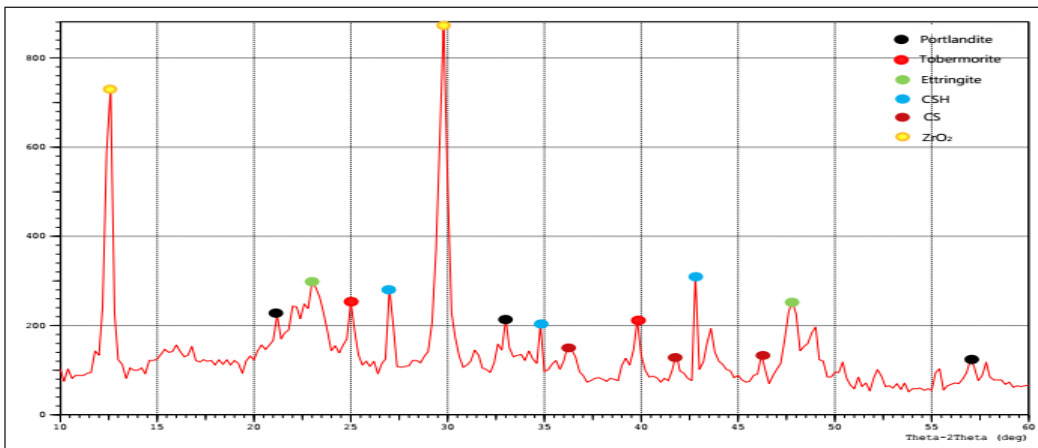


Figure 10. The XRD patterns for the cement coated specimen with 2% ZrO₂ nanoparticles

SEM Analysis

SEM analysis of the cementitious composites offered a good qualitative view of the mineralogy that lies inside the composite structure. Figure 11 views the SEM micrographs of control and coated with four types of nano powders fractured surface after 28 days of moist curing. Four representative images for each specimen were obtained and only one SEM micrograph was chosen from them. The existence of CH crystals connected to the CSH gel (arrow 1/a) indicates that the microstructure was weak and also explains the reduction of mechanical properties for the control mix. Whereas it seems clear that the surface pores were partially filled with 2% TiO₂ nano particles and/or additional hydration products from the pozzolanic activity (arrow 2/b). Also, it is obvious that after 2% MgO nano coating, there was a good adhesion force between CSH and CS, so no cracks appeared within ITZ (arrows 3/c). However, the cross section of 2% ZnO used here, was composed of large crystals of CH, so the fracture crack at failure initiated rapidly within ITZ so reducing the final composite strength (arrows 4/d). This is an indication of low pozzolanic activity for Zinc oxide nano powder. This is the opposite of what happened to the composite after ZrO₂ nano coating (arrows 5/e). The surface black holes were completely filled with extra CSH from the pozzolanic activity and there was no indication for CH crystals in

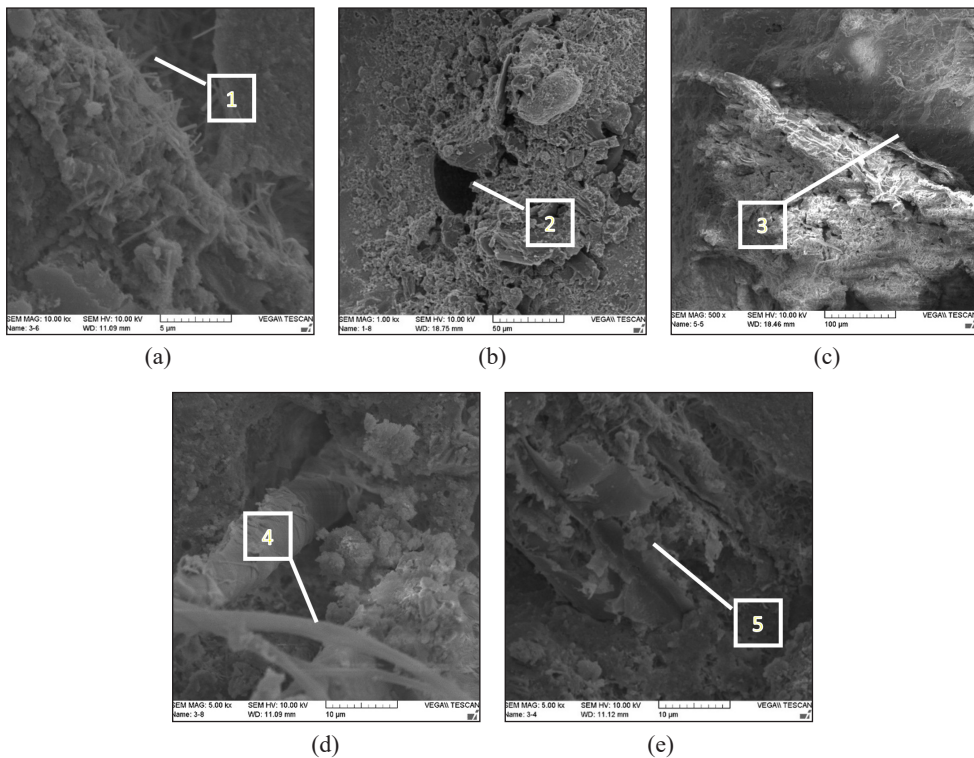


Figure 11. SEM images of fractured surface at 28-day for specimens: (a) control; (b) coated with 2% TiO₂; (c) coated with 2% MgO; (d) coated with 2% ZnO and (e) coated with 2% ZrO₂

the morphology. Therefore, the coated cement matrix is denser than control mix that can enhance the interfacial transition zone, and certainly promote the strength and density of the end composite. The results are in accordance with prior work done by Du et al. (2019).

CONCLUSION

Based on the analysis of data compiled throughout this study, these conclusions are summarized as follows:

1. Higher hardness was observed for coated specimens that directly related to their higher dosage in the coating film. 2% ZrO₂ yielded 29 % the superior hardness whilst, ZnO specimens yielded only 13 % higher hardness as compared to control.
2. The abrasion rate reduced after coating by nano particles, as compared to control. Higher doses of 2% for all types were very beneficial to long term abrasion rate, thereby decreasing the abrasion rate of the final composite.
3. All coated specimens were heavier than the control, especially for 2% ZrO₂ nano particles which had the highest density of 2.262 g/cm³.
4. All coated specimens showed lower porosity, especially MgO at 2% by weight of cement due to both the accelerated pozzolanic activity between nano oxides and calcium hydroxide and to the filling effect by the very tiny particles leading to the reduction in the number and size of pores.
5. 2% MgO coating had the highest water absorption (45%) as compared to control. Meanwhile, the water absorption for 2% TiO₂, ZnO and ZrO₂ were 34, 37 and 31% respectively.
6. It was evident from XRD patterns that the CH intensity decreased with the coated ZrO₂, TiO₂, MgO, and ZnO nanoparticles.
7. The surface black holes were completely filled with nano particles and/or extra CSH from the pozzolanic activity and there was no indication for CH crystals in the morphology except for ZnO.
8. ZrO₂ was the best nano material that improve the performance of cement-based composites. For economic consideration, 1.5 % was the preferable dose that maximize the performance of cement-based composites. Over this dose (2%) a low improvement was noticed.

ACKNOWLEDGEMENT

The authors thank the Kerbala Technical Institute, Al-Furat Al-Awsat Technical University for helping in the preliminary examination of raw materials.

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