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THE EFFECTS OF T_iO_2 AND ZnO NANOPARTICLES ON PHYSICAL AND MECHANICAL PROPERTIES OF NORMAL CONCRETE

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ABSTRACT

In the present study, compressive strength of normal concrete together with gas permeability of concrete containing various percentages of T_iO_2 and ZnO nanoparticles 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 T_iO_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 and prohibits the formation of mortar. As concluded from XRD diagrams, it seems that an amorphous layer of $Zn(OH)_2$ is the main reason that prohibits C_3S phase to participate in hydration process. Besides, with increase in percentage of the ZnO nanoparticles in concrete mixture, the lower compressive strength was obtained.

Keywords: Concrete, nano particles, XRD, SEM

1. INTRODUCTION

Nano particles have been attracted increasing attention in recent years and their different types has been used in concrete mixtures in order to improve both the mechanical properties and pore structure of the concrete. The effect of these particles, mostly SiO_2 nanoparticles, has been studied by many researchers. Tao [1] investigated the water permeability and microstructure of concrete containing nano-SiO_2 and reported that presence of nano-SiO_2 can improve the resistance to water penetration in concrete specimens. Besides, an ESEM test in

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their study showed that the microstructure of the concrete containing nano-SiO_2 was more compact and these particles improved the pore structure of the concrete. Several studies demonstrated the more pozzolanic activity of nano-SiO_2 than that of silica fume and noticed its positive effects on the mechanical properties of hardened cement [2, 3]. More researchers assert that the amount of crystallization in hydrated cement increases as a result of an increase in the amount of nanomaterials [4, 5].

However, there are still few works done about incorporating other nanoparticles in concrete. For instance, H. LI and H. Xiao reported that mortars containing nano-SiO_2 or nano-$Fe2O_3$ have higher compressive and flexural strength than that of plain cement mortar [6]. In another study Li et al. [7] investigated the abrasion resistance of concrete incorporating nano-SiO_2 and nano-TiO_2 and concluded that the abrasion resistance of concrete containing TiO_2 nanoparticles is higher than that of concrete containing SiO_2 nanoparticles. Flores-Velez et al. [8] studied the effect of zinc-iron oxide nanoparticles on characterization and properties of Portland cement composites and reported a small retardation of the setting process as a result of these particles. The effect of zinc has been investigated by different researchers. Arliguie and Grandet [9, 10] reported the retardation of hydration of C_3S phase due to an amorphous layer of $Zn(OH)_2$ which is formed during the hydration of this phase. Fernandez Olmo et al. [11] demonstrated that ZnO has huge impact on setting time (ST) and retards the ST with respect to that of the cement. They also measured unconfined compressive strength (UCS) and showed that the UCS of the final product decreases at short ages in presence of ZnO. Similar results have been observed by Tashiro et al. [12, 13] who reported that a very small amount of hydrate is formed even after 28 days of curing in the presence of ZnO. Using X-ray diffraction (XRD) Hamilton et al. [14] announced that calcium zinc hydrate ($Ca[Zn(OH)H_2O]_2$) formed a protective layer which inhibited the hydration process which was detected after 28 days of curing.

In contrast, some researchers investigated the effects of ZnO_2 nanoparticles on flexural strength of self-compacting concrete [15] and reported that incorporating ZnO_2 nanoparticles up to 4wt.% as a partial replacement of cement leads to accelerate the formation of C-S-H gel by means of increasing the amount of crystalline $Ca(OH)_2$ at early ages of hydration. Moreover, they concluded that these particles could improve the pore structure of concrete and shift the distributed pores to harmless ones. Nazari and Riahi [16-20] studied different types of nanoparticles including nano-TiO_2 and announced that increasing TiO_2 nanoparticles up to 4wt.% can improve the physical and mechanical properties of concrete and the strength and resistance to water permeability can be improved as well.

However, some researchers do not agree that other nanoparticles except for SiO_2 nanoparticles can be classified as pozzolan and this disagreement is still seen among different researchers. It seems that more studies and experiments are necessary to accurately evaluate the effects of these new materials as cement replacement. In the present study, the influences of TiO_2 and ZnO nanoparticles on compressive strength and gas permeability of normal concrete were investigated. Several types of experimental tests were performed to examine these influences and obtained results were compared.

2. MATERIALS AND METHODS

2.1. Materials

Ordinary Portland cement (OPC) conforming to ASTM C150 [21] standard was used and its composition is shown in Table 1.

TiO_2 and ZnO nanoparticles with average particle size of 20 nm, produced by Nano Pars Lima co., Ltd were used. The properties of TiO_2 and ZnO nanoparticles are shown in Tables 2 and 3. X-ray diffraction diagrams of TiO_2 and ZnO nanoparticles are shown in Figures. 1 and 2.

Locally crushed natural gravel with maximum size of 12 mm and specific gravity of 2.67 g/cm^3 was used as coarse aggregate and locally natural sand with maximum size of 0.6 mm and specific gravity of 2.65 g/cm^3 and fineness modulus of 2.7 was used as fine aggregate.

The E.M POWERPLAST which is a HRWA polycarboxylate based admixture produced by Abadgaran co., Ltd was used. Some of the properties of polycarboxylate admixture, used in this study, are shown in Table 4.

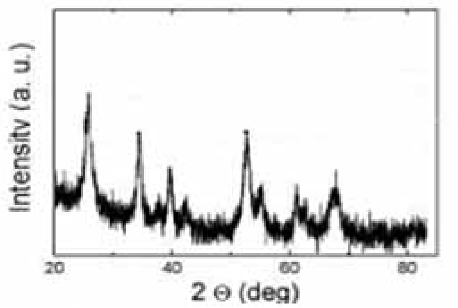


Figure 1- *XRD analysis of TiO_2 nanoparticles*

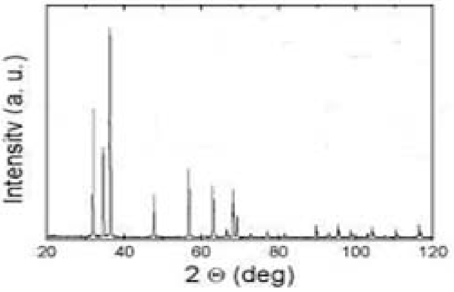


Figure 2- *XRD analysis of ZnO nanoparticles*

Table 1- *Chemical and physical properties of Portland cement (wt%).*

Material	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	SiO_2	LOSS	IR	Free CaO	Total Alkalis
cement	4.9	3.3	63.5	2.1	2.3	21.5	0.6	0.4	1	0.75

Specific gravity: 3.1 g/cm3.

Table 2 - *The Properties of nano-TiO_2.*

Type	Diameter (nm)	Surface volume ratio (m^2/g)	Bulk Density (g/m^3)	Purity (%)		Appearance
TiO_2 (rutile)	20	40	0.46	+99		White powder
Certificate analysis (content of elements)						
TiO_2	Al	Mg	Si	Ca	S	Nb
≥99%	≤17ppm	≤65ppm	≤120ppm	≤75ppm	≤130ppm	≤80ppm

Table 3- *The Properties of nano-ZnO.*

Type	Diameter (nm)	Surface/volume ratio (m^2/g)	Bulk Density (g/m^2)	Purity (%)	Appearance
ZnO	20	90	0.65	+99	White powder
Certificate analysis (content of element)					
ZnO	Cu		Mn	Pb	Cd
99%	3ppm		5ppm	9ppm	9ppm

Table 4 - *The Properties of polycarboxylate admixture.*

Appearance	Specific gravity (g/cm^3)	Solid content (%)	PH
Dark-brown liquid	1.15	40	6.5

2.2. Experimental Design

Totally, 3 series of mixtures were prepared in the laboratory trials. C series, control group, was consisted of cement, fine and coarse aggregates and 1.8wt% of cement highly reduced water admixture. The ratio of coarse aggregates to fine aggregates was 1.80 in mixtures. T and Z series were prepared with different contents of TiO_2 and ZnO nanoparticles, respectively. In the T series, mixtures were prepared with the cement replacement by TiO_2 nanoparticles from 1.0 to 5.0wt% and 1.8wt% HRW admixture. Z mixtures were prepared with the cement replacement by 0.5wt% and also from 1 to 5wt% of ZnO nanoparticles and 1.8wt% of cement HRW admixture. The water to binder (cement + nanoparticles) ratio for all mixtures was set at 0.55. The binder content of all mixtures was 300 kg/m^3. The proportions of the mixtures are presented in Tables 5 and 6.

Table 5**:** Mix Proportions Concrete Mixtures Containing TiO_2 Nanoparticles.

Code	TiO_2 nanoparticles (%)	HRW admixture (%)	CA/FA	Quantities (kg/m^3)	
				Cement	TiO_2 nanoparticles
C	0	1.8	1.8	300	0
T_1	1	1.8	1.8	297	3
T_2	2	1.8	1.8	294	6
T_3	3	1.8	1.8	291	9
T_4	4	1.8	1.8	288	2
T_5	5	1.8	1.8	285	15

Water to binder (cement + TiO_2 nanoparticles) ratio is 0.55. CA= Coarse Aggregate, FA= Fine Aggregate.

Table 6**:** Mix Proportions of Concrete Mixtures Containing ZnO Nanoparticles

Code	ZnO nanoparticles (%)	HRW admixture (%)	CA/FA	Quantities (kg/m^3)	
				Cement	ZnO nanoparticles
C	0	1.8	1.8	300	0
$Z_{0.5}$	0.5	1.8	1.8	298.5	1.5
Z_1	1	1.8	1.8	297	3
Z_2	2	1.8	1.8	294	6
Z3	3	1.8	1.8	291	9
Z4	4	1.8	1.8	288	12
Z5	5	1.8	1.8	285	15

Water to binder (cement + ZnO nanoparticles) ratio is 0.55. CA= Coarse Aggregate, FA= Fine Aggregate

2.3. Mixing Procedure

In the experiments, the HRW polycarboxylate admixture was dissolved in water, and then the nanoparticles in each mixture were added and stirred for 3 minutes at high speed. The mixing sequence was consisted of mixing of cement and aggregates for one minute in the mixer and then about two third of water containing the pre-dissolved nanoparticles was added and homogenized for 3 minutes. Then the remaining water was introduced and the materials were blended together for another two minutes. The whole mixing process took 6 minutes

2.4. Measurement of Properties

Several types of tests were carried out in order to measure the properties of the specimens. Results obtained from the tests are presented in the following sections.

a) *Compressive strength evaluation tests*:

In order to evaluate the compressive strength, cubic specimens with the edge length of 100 mm were made. For T and C series of mixtures moulds were kept in a moist room for 24 hours and then the specimens were demoulded and cured in water at a temperature of 20°C. Besides, an initial retardation which was about 12 h was seen in the first day of hydration period of the T mixture. This initial retardation has been reported by some other researchers [22, 23]. For the Z series, an extreme retardation was observed even for the mixtures containing 0.5wt% of ZnO nanoparticles. The retardation took about 9 to 13 days long dependent upon the different percentage of ZnO nanoparticles. After setting, specimens were demoulded and cured in water at a temperature of 20°C prior to test days. Compressive strength test of all specimens was carried out conforming to the ASTM C 39 [24] after 28 days of curing. For each mixture, shown in the Tables 1 and 2, the concrete cubes were subjected to test by using universal testing machine. The tests were carried out triplicately and average strength values were obtained.

b) *Permeability tests*:

In the present study, permeability tests were carried out by means of measuring the coefficient of Oxygen absorption according to ASTM D4525-90 [25]. This standard is used to measure the permeability of rocks against the permeation of gases but it is accepted to be also proper for concrete specimens. Besides, this method is also based on RILEM TC 116-PCD [26].

In this study, cylindrical specimens with the diameter of 150 mm and the height of 300 mm were made and cured in water for 28 days. Then each specimen was cut into three samples one from the top, one from the bottom and the last one from the middle part of the specimen. These three samples, needed for the permeability tests, were cut with the height of 50 mm and diameter of 150 mm. Then samples were dried in a hot oven for three days and kept in a cold oven for four days. Finally, the coefficient of permeability was obtained from the average coefficients of these three samples for each specimen. To measure the coefficient of permeability, the DARCY'S LAW can be applied as the flow is continuous.

$$V = K_V \times i \qquad (1)$$

where V is the linear velocity of the flow (m/s), i is the hydraulic head gradient and K_y is the coefficient of permeability (m/s). The test apparatus is shown in Figure 3.

c) *Scanning Electron Microscopy (SEM):*

The samples for this test were cured for 28 days and then dried in oven for another 2 days. The test was performed according to ASTM C1723-10 [27] and micrographs for the specimens were obtained.

d) *X-ray diffraction (XRD):*

The samples for this test were cured for 28 days and then ground into powder in order to achieve higher accuracy. Then XRD analysis was taken from 0° to 100°.

Figure 3. Apparatus used for evaluation of the permeability.

3. RESULTS AND DISCUSSION

3.1. Compressive Strength

The compressive strength of C, T and Z series at 28 days of curing are shown in Tables 7 and 8. As the results show in Table 7, all the specimens containing TiO_2 nanoparticles have lowered compressive strength in comparison to C mixture at 28 days of curing. This is probably as a result of the negative impacts of TiO_2 nanoparticles on C_2S hydration which contributes to long- term properties of hydrated concrete. Tao Meng et al.[28] reported that the strength of cement mortar which was substituted by TiO_2 nanoparticles increased at early ages and decreased remarkably after 28 days of curing. Moreover, it was concluded that "the main reason for the improvement of strength is the decrease and modification of orientation index for the nucleus function, not the increasing amount of hydration products". Consequently, the lower compressive strength at 28 days of curing contradicts the pozzolanic activity of these nanoparticles. On the other hand, it seems that by adding TiO_2 nanoparticles up to 4 wt% (T_4) the highest compressive strength in the T mixture is achieved.

Table 7: Compressive strength of C and T series

Code	f_{c1}(MPa)	f_{c2} (MPa)	f_{c3} (MPa)	$f_{c,average}$ (MPa)
C	35	38	34	35.7
T_1	28	27	30	28.3
T_2	27.5	25.5	25	26
T_3	31.5	30	30.5	30.7
T_4	27	31	32	30
T_5	24	27	28	26.3

It can be seen from Table 4 that ZnO nanoparticles also decrease the compressive strength with respect to C series. Besides, as it is shown in Table 4, by adding ZnO nanoparticles up to

5 wt%, the compressive strength of the specimens decreased extremely. This could be due to the fact that by adding ZnO nanoparticles, these particles completely stopped the hydration process and prevented the formation of cement paste within the concrete; and as a result, an extreme decline in the compressive strength was observed. In addition, separation of the aggregates in all specimens containing ZnO nanoparticles was clearly observed in the experiments. Figure 4 illustrates this separation and dissimilarities between specimens containing ZnO nanoparticles and the other specimens. The average compressive strength of C, T and Z series are shown in Figure 5.

Table 8: Compressive strength of Z series

Code	fc_1(MPa)	fc_2 (MPa)	fc_3 (MPa)	fc,averge (MPa)
$Z_{0.5}$	34	28	30.5	30.8
Z_1	33.5	31	28	30.8
Z_2	24.5	30	29	27.8
Z3	21	18	20	19.7
Z4	1	1.5	2	1.5
Z5	0.5	0.5	0.4	0.47

(a) (b) (c) (d)

Figure 4. Samples of (a) Z_4 specimen, (b) C specimen, (c) Z_5 specimen and (d) T_4 specimen.

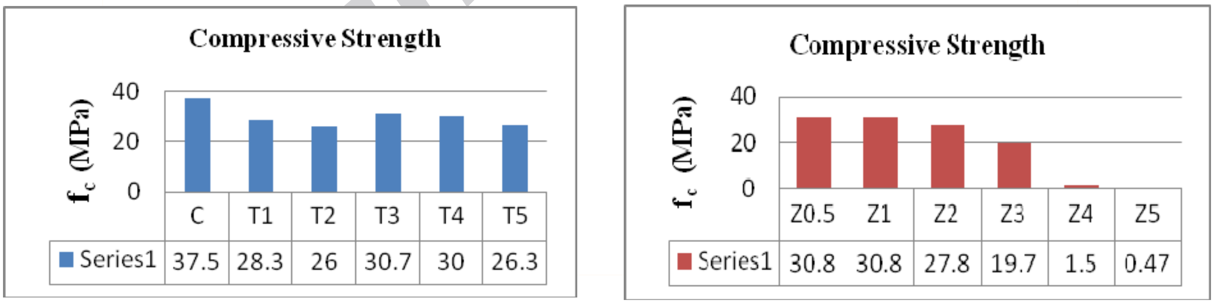


Figure 5. Compressive strength of C, T and Z series.

3.2. Scanning Electron Microscopy (SEM)

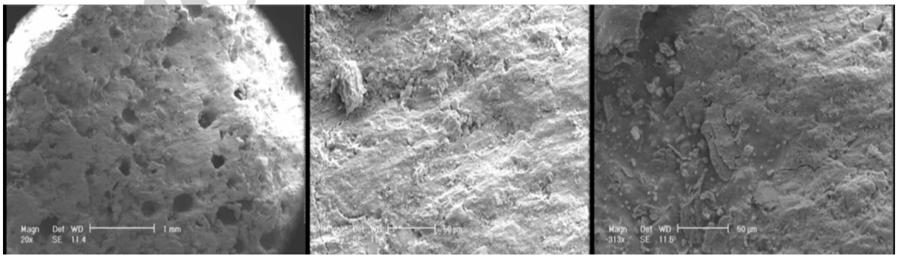
The SEM micrographs of C, T and Z series are shown in Figures 6 and 7. The morphological analysis evinced substantial differences in either the form or the texture of the different reaction products in pastes with nanoparticles. As the SEM results in Figure 6 (a) reveals, the pore structure of C series is more uniform and homogenous than that of T series after 28 days of curing. The micrographs corresponding to cement paste of T series show anhydrous cement that after 28 days of curing has not yet reacted. As the Figure shows the pores related to the T series are larger in size and therefore more harmful. Consequently, higher compressive strength was achieved in the C series in comparison to the T series after 28 days of curing. Having more porous microstructure with more harmful pores, the TiO_2 nanoparticles seem not to participate in pozzolanic reactions in order to improve the strength and pore structure.

The SEM micrographs of specimens containing nano-ZnO are shown in Figure 7. As it is illustrated in Figure 7, with increase in percentage of ZnO nanoparticles, the structure of corresponding cement paste has become more porous and less compact in the pastes containing nano-ZnO. In addition, remarkable differences can be recognized between the micrographs of Z series and other ones regarding the mortar microstructure in Figure 7. In this figure, cracks and pores of the specimens containing 0.5% and 3% of ZnO nanoparticles ($Z_{0.5}$ and Z_3) can be recognized clearly. In addition, the perfect bond between the particles in $Z_{0.5}$ and Z_3 series is seen in the micrographs. In contrast, in Z_5 series the segregation of the particles is the dominant phenomenon which leads to a severe decrease in physical and mechanical properties of the specimens including the compressive strength and the coefficient of permeability, presented in Tables 8 and 9, respectively. These differences in the properties of the specimens were considerably increased when the percentage of ZnO nanoparticles was increased from 3wt% to 4wt% and more.

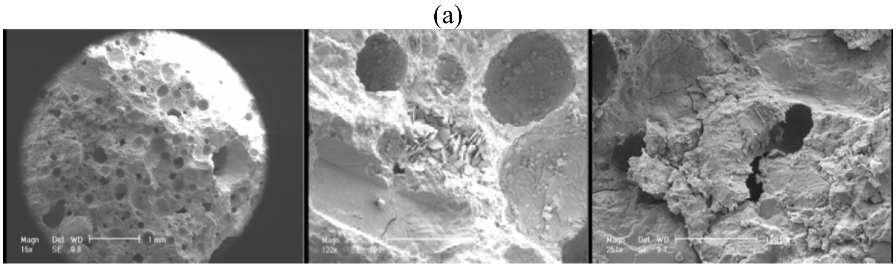
Table 9**:** Permeability test results of C, T and Z series.

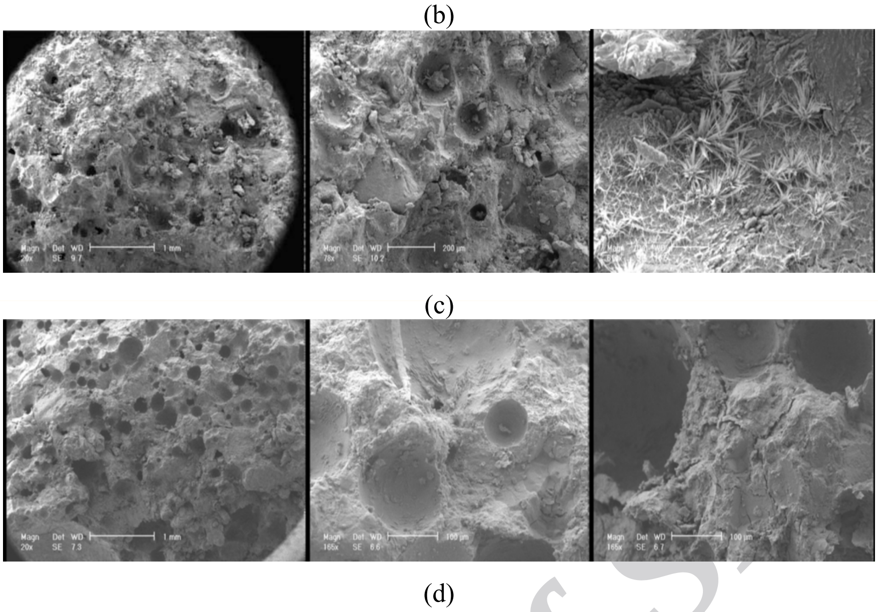
Code	Ktop ($m^2 \times 10^{-16}$)	Kmiddle ($m^2 \times 10^{-16}$)	Kbottom ($m^2 \times 10^{-16}$)	Kaverage ($m^2 \times 10^{-16}$)
C	17.2	16.6	16.8	16.9
T1	4.4	4.4	4.2	4.3
T3	4.6	6	5	5.2
T4	3.8	2.5	3.2	3.2
T5	4.1	4.6	3.7	4.1
Z0.5	3.3	2.5	N.A	2.9
Z1	67.3	71.9	70.5	69.9
Z4	-	221.7	-	221.7
Z5	-	-	-	-

Mark (-) shows that the sample was not testable due to its high permeability.



(a)



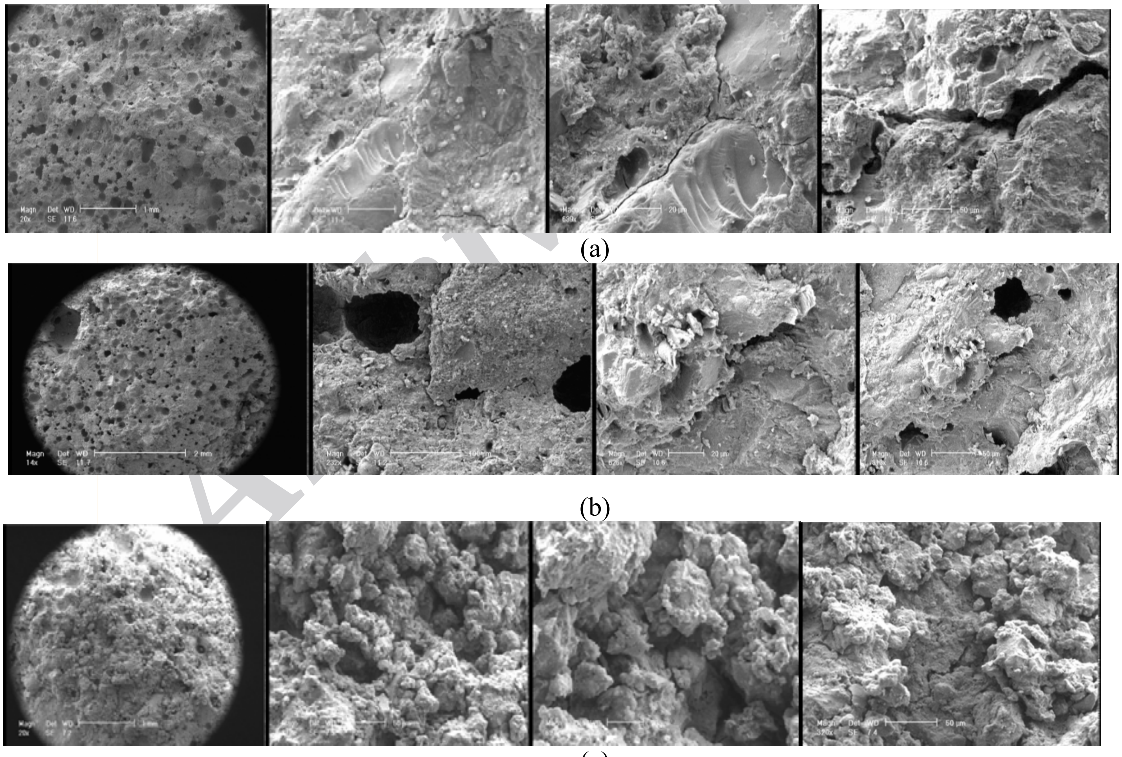


(b)

(c)

(d)

Figure 6. SEM micrographs of (a) C series, (b) T_2 series, (c) T_3 series and (d) T_5 series.



(a)

(b)

(c)

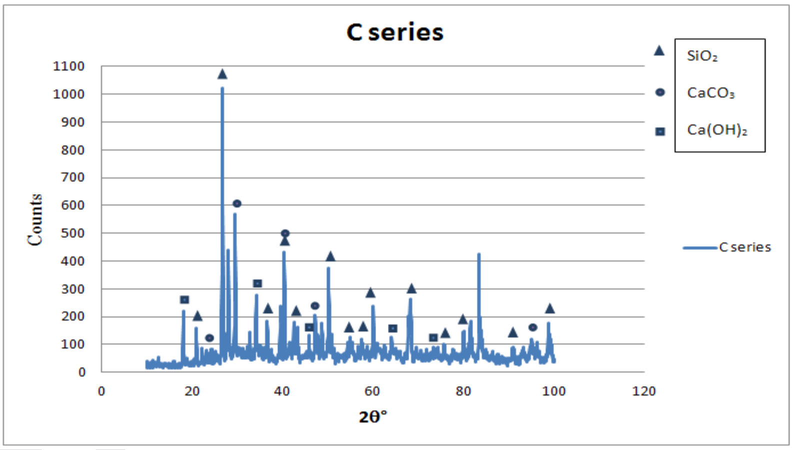
Figure 7. SEM micrographs of (a) $Z_{0.5}$ series, (b) Z_3 series and (c) Z_5 series

3.3. X-ray diffraction (XRD) diagrams

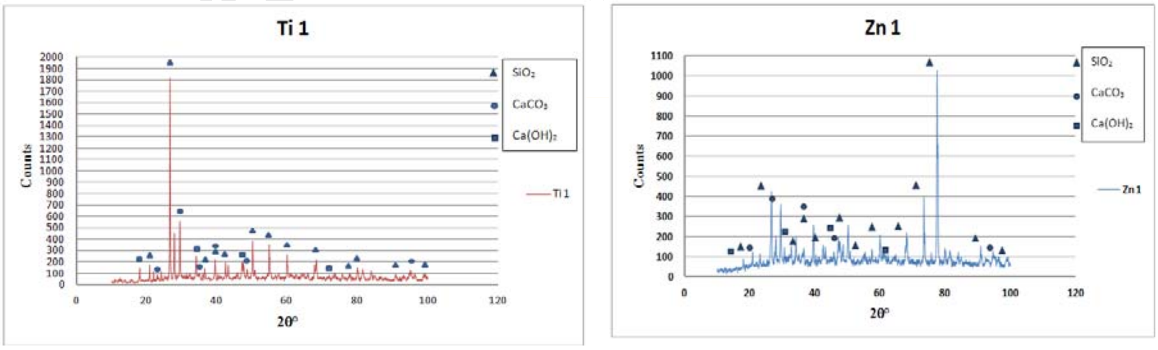
XRD diagrams of C, T and Z series are shown in Figure 8. As it is shown in the XRD diagrams for T series after 28 days of curing, the peaks related to $Ca(OH)_2$ formation can be observed in T_1 to T_5 series and the intensity of this formation in all of the T series is approximately the same as the C series; therefore, it can be concluded that TiO_2 nanoparticles did not react with $Ca(OH)_2$ formation in order to produce more hydrated products and this again contradicts the pozzolanic activity of these nanoparticles. Besides, as the XRD diagrams for Z_4 and Z_5 series illustrate, the peaks related to Ca_3SiO_5(C_3S, also known as Alite) formation were recognized in these series even after 28 days of curing. This formation is the main compositions of cement mortar and participates in cement hydration reactions as follows:

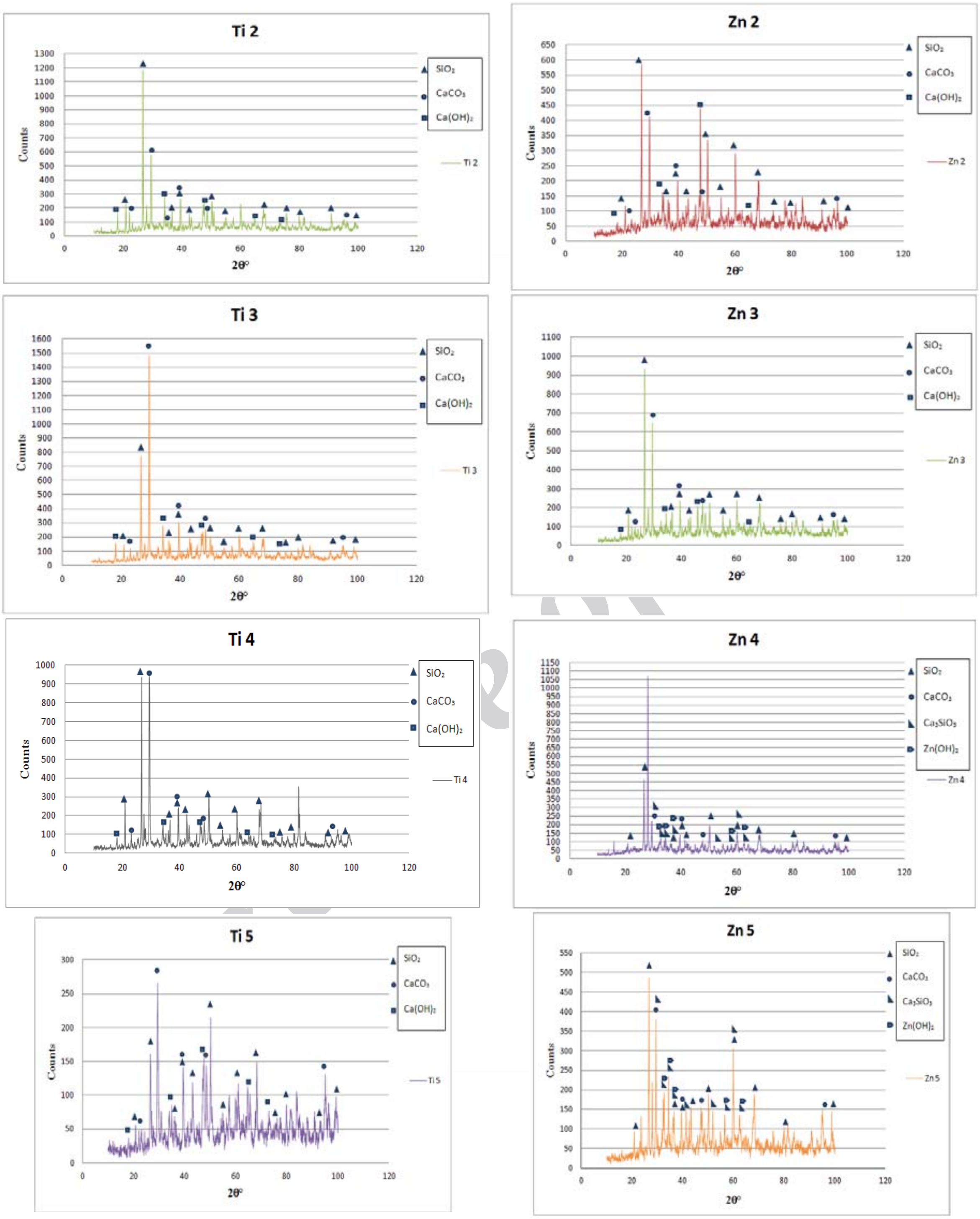
$$2Ca_3OSiO_4 + 6H_2O \rightarrow 3CaO2SiO_2 3H_2O + 3Ca(OH)_2 \qquad (2)$$

Hence, the existence of Ca_3SiO_5 in Z_4 and Z_5 series even after 28 days of curing proves that increasing the percentage of ZnO nanoparticles to 4wt% and more hinder the cement hydration reactions within the concrete. In addition, as it is shown in these two diagrams, the peaks related to $Zn(OH)_2$ were observed and it seems that this compound form a protective layer that inhibits the normal hydration of cement grains and specially C_3S phase. Furthermore, there is no sign of $Ca(OH)_2$ in Z_4 and Z_5 series and this is another reason that shows hydration process was not taken place even after 28 days of curing.



(a)





(b) (c)

Figure 8. XRD diagrams of (a) C series, (b) T series and (c) Z series.

3.4. Coefficient of permeability

As it is mentioned before, specimens made for this test were cut into three samples with the height of 50 mm and the diameter of 150 mm. Figure 9 shows some of the samples used in this test. Table 5 shows the permeability test results of C, T and Z series. As it is stated in Table 5 all the T series specimens except for T_2 series have lower coefficient of gas permeability in comparison to C series; consequently, it seems that by increasing the percentage of TiO_2 nanoparticles in the mixture to 4wt% the pore structure of the concrete improves remarkably. This could be due to the fact that these nanoparticles acted as fillers and improve the resistance of concrete toward gas permeability, but as it is mentioned before this improvement is not as a result of more formation of hydrated products. Permeability test results of the Z series show that concrete samples containing ZnO nanoparticles have a highly permeable structure. In addition, for Z_4 and Z_5 series remarkable differences were observed. The coefficient of permeability could obtain only for the middle sample of the specimen of Z_4 series and was measured 221.7×10^{-16} (m^2), as it is stated in Table 5, this value is much higher in comparison to other series. Once again, this is due to the high permeability of Z_4 and Z_5 series as a result of ZnO nanoparticles inhibition of formation of mortar within the concrete. Besides, it seems that although incorporation of ZnO nanoparticles in the mixture retards the setting time, using 0.5wt% of ZnO nanoparticles recovers the pore structure of the concrete and lower coefficient of permeability is achieved in comparison to C series. This is again thought to be mainly because of functioning as nano fillers.

Figure 9. Samples used in permeability evaluation test

4. CONCLUSIONS

In recent years, different types of nano particles have been used in concrete in order to improve the pore structure of concrete. Most researches have studied the use of SiO_2 nanoparticles. Few studies have incorporated other nanoparticles in concrete. In the present study, the influence of TiO_2 and ZnO nanoparticles on compressive strength and gas permeability of normal concrete were investigated. The results obtained can be summarized as follows:

1. Both TiO_2 and ZnO nanoparticles decreasee the final compressive strength of concrete. This is probably as a result of the negative impacts of TiO_2 and ZnO nanoparticles on C_2S hydration which contributes to long-term properties of hydrated cement.
2. ZnO nanoparticles caused extreme retardation of 9 to 13 days regarding the setting time of the cement. Besides, increasing the percentage of ZnO nanoparticles in the cement mixture

completely stopped the hydration process.

3. XRD diagrams of concrete samples containing nano-TiO_2 (T series) shows the peaks related to $Ca(OH)_2$ with approximately the same intensity as the normal concrete specimens. This means that these particles do not react with $Ca(OH)_2$ in order to produce more hydrated products.

4. XRD diagrams of specimens containing 4wt% and 5wt% of ZnO nanoparticles, Z_4 and Z_5 series, illustrated the existence of Ca_3SiO_5 (C_3S, also known as Alite) and nonexistence of $Ca(OH)_2$ even after 28 days of curing. This means that increasing the percentage ZnO nanoparticles in concrete mixture to 4wt% and more thoroughly inhibited the hydration reactions within the concrete. Moreover, the compound $Zn(OH)_2$ which was observed in the XRD diagrams of these two series was thought to form a protective layer which inhibited the normal hydration of cement grain especially in C_3S phase.

5. Permeability test results of the T series showed that existence of less than 4wt% of TiO_2 nanoparticles in the concrete mixture improves the pore structure of the concrete and the lowest coefficient of permeability is achieved in this series. This is mainly because of performance of nano-TiO_2 as nano fillers and not the formation of more hydrated products. Permeability test results of the Z series showed that incorporation of ZnO nanoparticles in the concrete mixture lead to a highly permeable cement paste. Furthermore, the samples for Z_4 and Z_5 series were mostly not testable due to their high permeability since these particles inhibited the formation of mortar within the concrete.

6. The SEM micrographs showed that the pore structure of C series was more uniform and compact than that of T series after 28 days of curing and that was why the higher compressive strength was achieved in this series. Based on the SEM micrographs, concrete samples containing nano-TiO_2 had more porous microstructure and TiO_2 nanoparticles seem not to participate in pozzolanic reactions in order to improve the strength and pore structure. Regarding Z series, as micrographs showed, with increase in percentage of ZnO nanoparticles, the structure of corresponding cement paste became more porous and less compact. These effects were considerably increased when the percentage of ZnO nanoparticles was increased from 3wt% to 4wt% and more.

7. Considerable differences can be seen between the SEM micrographs of Z_5 series and the other series of $Z_{0.5}$ and Z_3. Severe segregation between the particles in Z_5 series highly affects the physical and mechanical properties of the specimens such as the compressive strength and the permeability.

Acknowledgments: This work has been developed as a project for evaluating the effects of nano TiO_2 and ZnO nanoparticles on the physical and mechanical properties of normal concrete. Participation of the following partners in the project is highly appreciated: Isfahan University of Technology, Tehran University and Nano Tar Pak Company.

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