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EFFECT OF MICRO TiO_2 ON CEMENT MORTAR

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Abstract

TiO2 is a primary photocatalytic ingredient. If incorporated into building materials, it can keep surfaces clean and significantly reduce smog-forming air pollutants. Many researchers have focused on the ability of Nano TiO2 to reduce NOx emissions or other pollutants. However, developing countries are unable to widely utilize Nano materials due to cost and technology barriers, in spite of their great need to find means for protecting structures from pollution and improve air quality. Some studies proved that micro TiO2 (commercial grade) also has photocatalytic properties. However, the effect of this inclusion on key mechanical and durability properties needs to be verified before being recommended for wide use. In this research the effect of commercial grade TiO2 powder on fresh state flow, compressive strength, shrinkage, sulfate resistance and carbonation. The results indicated that TiO2 decreased the workability as mortars became more sticky and dry with increased TiO2 content. The compressive strength was also reduced in TiO2 containing samples compared to the control samples especially at early ages .However, TiO2 powder as an additive in mortar was useful in reducing carbonation due to the filler effect. No samples in the current investigation showed signs of cracking or expansive mass loss due to sulfate exposure. It is recommended that TiO2 powder should be used as an additive to the mortar plaster to help in controlling the air pollution problem. However, some mix adjustment may be needed to counteract the loss in flow and strength due to the inclusion of TiO2 powder.

Keywords: *TiO_2Powder; Air pollution; Carbonation; Compressive Strength; Shrinkage; Sulfate Resistance.*

Introduction

TiO_2 is a primary photocatalytic ingredient that can significantly reduce smog-forming air pollutants in urban and metropolitan areas (pollution abatement) [1-3].The number of TiO_2 patents is continually growing and currently include materials in concrete tiles, concrete paving, white cement (architectural concrete), applications on building surfaces, as well as environment-friendly cement (TioCem) [4-6].

Heterogeneous photo catalysis was first discovered by Fujishima and Honda in the 1970’s. It is a process involving a catalyst that absorbs UV energy from the sun and oxidizes or decomposes organic matters in either the atmosphere or aquatic environments [7]. In addition to photocatalytic properties, TiO_2 is chemically and biologically inert, non-toxic, which makes it an accessible material for general applications. The study of the usage of TiO_2 in construction materials as a photocatalytic material initiated in the early 1990s [8].

Previous investigations concentrated on the photocatalytic properties of Nano TiO_2 [9-10], as well as TiO_2 containing cement-based materials [8, 11]. The majority of this effort has been on characterizing and enhancing the photocatalytic efficiency.

Some time ago it was suggested [12] that there is potential for using commercial TiO_2 as a in the surface layer of exterior slabs to reduce air pollution. More recently a number of investigations have confirmed that commercial grade TiO_2powder has photocatalytic properties. Hanson [13] studied different TiO_2 types from different manufactures to help identify which crystalline type, particle size, purity, and quantity of TiO_2 would be the most appropriate product to add to the concrete matrix to create a photocatalytic, NO_x reducing concrete surface. TiO_2 powders used in that study were either commercially available as photocatalytic grade or

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other samples not manufactured for photocatalytic properties. It was concluded that only some TiO_2 powder types in the anatase phase had the ability to significantly decrease NO_x pollutant concentrations. The effective anatase phases were approximately 1.0 µm in average size and had purities between 83 and 97%. The less effective anatase phase had a smaller particle size and greater than 98% purity. It was noted that the efficiency was greater if $TiO_2$was available near the surface of the material's cross section, so that it can be activated by solar radiation. Hanson's [13] work showed that coarser and less pure anatase TiO_2 is an effective photocatalyst, and the optimum dose in the mix was below 9% by weight of cement. Gatto [14] used micro-sized TiO_2 powders for the photo-degradation of NO_x and toluene pollutants. It was found that all micrometric TiO_2 powders, even though they are sold as not photocatalytic materials, showed good results. It was recommended that micro TiO_2 powders should be used rather than Nano TiO_2 in order to reduce health problems associated with difficult recovery and consequently health hazards due to inhalation of Nano particles.

Research Significance

Although the effects of Nano TiO_2 on various mortar and concrete properties have been thoroughly investigated [e.g. 15-18], the authors could not cite any studies on the effect of commercial grade TiO_2 on the engineering properties of mortars.

The main purpose of this research was to investigate the properties of mortars containing commercial grade TiO_2. This is essential before the use this powder is recommended on a regular basis. The powder was utilized as an additive in small quantities not exceeding 9% by weight of cement. The experimental program has been developed to investigate the following:

1. The effect of TiO_2 content on flow of mortars in the fresh state.
2. The effect of TiO_2 content on compressive strength of mortars.
3. The carbonation potential of TiO_2 containing samples compared to samples without it.
4. The length change of mortars with and without TiO_2 as an indication of shrinkage.
5. The behavior of mortars with and without TiO_2 exposed to Sodium Sulfate Solution.

Experimental Program Materials

Ordinary Portland Cement (OPC) used throughout the test program was Suez Cement (CEM I 42.5 N). OPC surface area and specific gravity were 3500 cm^2/g and 3150 kg/m^3 respectively as specified by cement testing laboratory in Housing and Building Research Center and conforming to the requirements of ESS 4756-1/2013 [19]. The chemical composition of the cement is shown in Table1. Titanium Dioxide (TiO_2) was supplied from El Naser Pharmaceuticals Chemicals. TiO_2 was in solid state (powder), having slight odor and white color as shown in Fig. 1. TiO_2 purity was 98%. The physical properties of TiO_2 as obtained from the material manufacturer data sheet are illustrated in Table 2. Fig. 2 for X-Ray Diffraction analysis of TiO_2 reveals that it is mainly anatase phase. The particle size distribution of TiO_2 powder was measured by HORIBA Laser Scattering Particle Size Distribution Analyzer Partica LA-950. Fig. 3 and Table 3 show the particle size distribution and values for TiO_2 powder. Natural sand locally sourced from Giza desert was used as fine aggregate with average size (600µm-1.18 mm). The water used was the potable tap water.

Table 1. Chemical composition of portland cement

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	L.O.I
Content (%)	20.39	5.6	3.43	63.07	2.91	0.7	0.38	0.35	2.06

Fig. 1. Titanium dioxide powder physical appearance

Table 2. Physical properties of TiO_2

Name	TiO_2 powder
Appearance	white
Particle size	0.2912 - 0.6746 µm
Purity	98 %
L.O.I	0.13 %

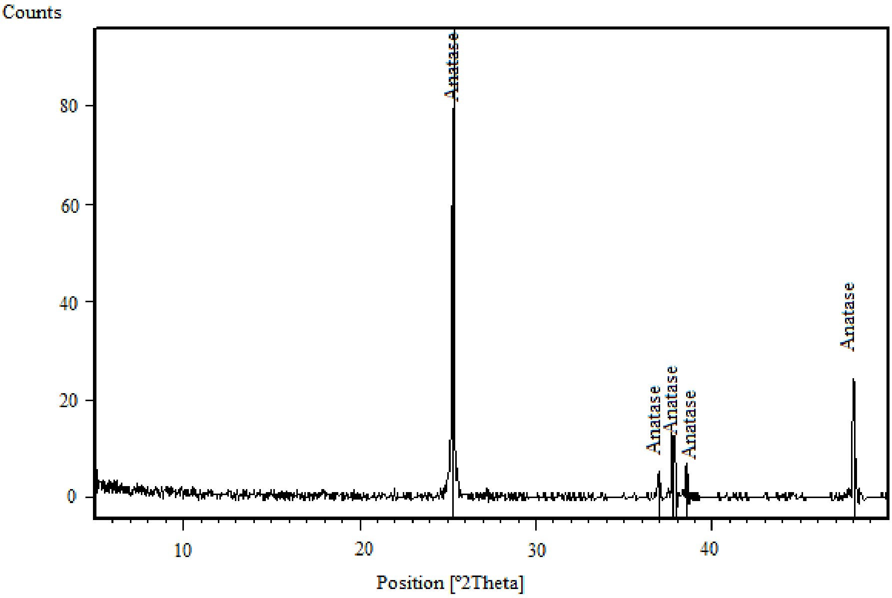

Fig. 2. X-Ray diffraction analysis of TiO_2

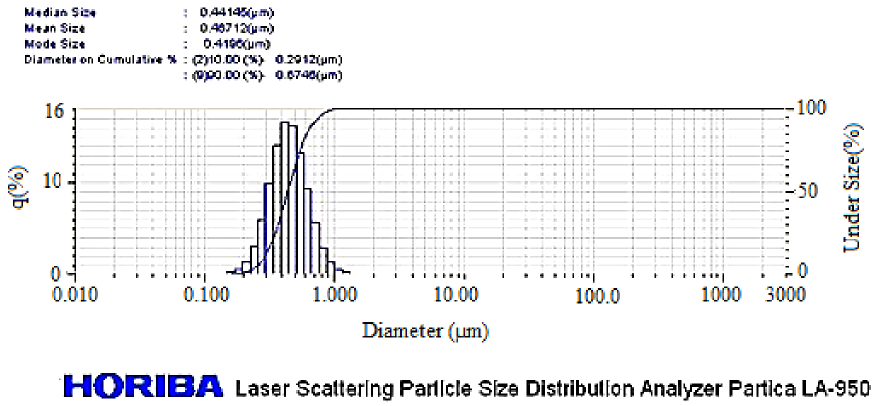

Fig. 3. Particle size distribution of TiO_2 powder

Table 3. Particle size distribution values of TiO_2 powder

No.	Diameter [µm]	q[%]	Under Size[%]
20	0.160	0.000	0.000
21	0.172	0.167	0.167
22	0.197	0.510	0.677
23	0.226	1.302	1.979
24	0.269	2.936	4.916
25	0.296	6.816	10.731
26	0.339	9.841	20.672
27	0.389	13.959	34.631
28	0.445	16.457	50.988

No.	Diameter [µm]	q[%]	Under Size[%]
29	0.510	16.138	67.126
30	0.584	13.267	80.393
31	0.669	9.263	89.646
32	0.766	6,538	95.184
33	0.877	2.867	98.051
34	1.005	1.286	99.337
35	1.151	0.498	99.835
36	1.318	0.165	100.000

Mixes and Sample Preparation Procedure

A total of four mixes were prepared in the laboratory. The control mix was prepared from natural sand, cement and water. The water to binder ratio for all mortars mixes was set at 0.50. The cement content of all mixes was 350 kg/m^3. The cement to sand ratio for all mixes was set at 1:3. Other mixes were prepared with different contents of TiO_2 particles as an additive at 3%, 6% and 9% by weight of cement. A small electrical mixer was used for mixing mortars. The samples were cubes 50mm × 50mm × 50mm and prisms 25mm × 25mm × 285 mm. The specimens were cast and compacted in two layers using a plastic compacting bar, where each layer was compacted 25 times. Then the molds were placed on compacting table and vibrated for about 15 seconds. The molds were immediately covered with plastic sheet to avoid moisture loss, and were kept at room temperature (23 ± 2°C) for 24 hours. The specimens were then de-moulded and were kept in water for seven days for moist curing.

Testing Procedures

The tests performed were Flow table, Compressive strength, change in length, and sulfate attack in accordance with ASTM C 1437 – 07 [20]; ASTM C109 / C109M - 16a [21]; ASTM C157 / C157M – 17 [22]; ASTM C1012 / C1012M – 15 [23], respectively. The details of the prepared cubes, prisms and tests performed are presented in Table 4.

Table 4. Details of experimental program

	Fresh State							
Tio$_2$ % added	Control	3%	6%	9%	Control	3%	6%	9%
Flow Test	Repeat test 3 times for each mix, flow= average of 3 readings							
	Hardened State							
Compressive Strength test	Specimens in Air							
	Control	3%	6%	9%				
	Testing (3) cubes for each at 28, 56, 90 days							
Carbonation Resistance					Specimens in CO2 Chamber			
					Control	3%		9%
					Testing (3) cubes for each at 28, 56, 90 days			
Shrinkage Test	Testing (5) prisms for each at 28, 56, 90 days							
Sulfate Attack					Specimens in Sulfate Solution			
					Control	3%	6%	9%
					Testing (5) prisms for each at 28, 56, 90 days			

Results and Discussion

Flow Table Test

Fig. 4 shows the flow table test results. The mortar consistency decreased as TiO_2 percentage increased. The reason may be that TiO_2 is hydrophilic material (the capability of TiO_2 to absorb the mixing water). Therefore, the increase in TiO_2 content in the mortar lead to a reduction in observed flow diameter [24].The flow is defined as the percentage increase in the average diameter of the spread mortar (D in cm), over the original diameter of the base (10 cm). The percentage expresses the degree of mortar consistency.

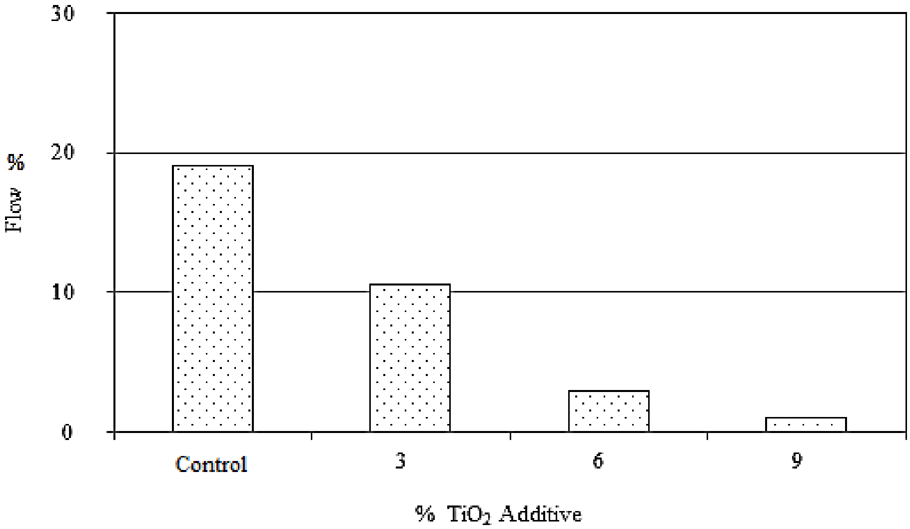

Fig. 4. Flow table test results of mortars

Compressive Srength Test

Fig. 5 shows the average compressive strength of all samples at the ages of 28, 56 and 90 days. The compressive strength decreased by increasing the amount of TiO_2 except for 6% TiO_2 mortars. In fact there is some improvement in compressive strength of 6% TiO_2 at the later age of 90 days. For mixes with 6% TiO_2, strength was better than 3% and 9% TiO_2. By increasing TiO_2 to 9%, the compressive strength was decreased by 39.9%, 30.5%, and 6.5% at ages 28, 56, and 90 days respectively compared to the control mix. This may be attributed to the possibility that the TiO_2 content in mixture was higher than the amount required to combine with the liberated lime during the process of hydration thus causing a deficiency in strength [24]. The increase in TiO_2 does not contribute to strength. Also, it may be due to the defects generated in dispersion of TiO_2 that causes weak zones [24]. Fig. 6 shows the ratio of strengths between TiO_2 mortar specimen and control specimen. It is clear that at later ages the difference in strength between samples with and without TiO_2 was small.

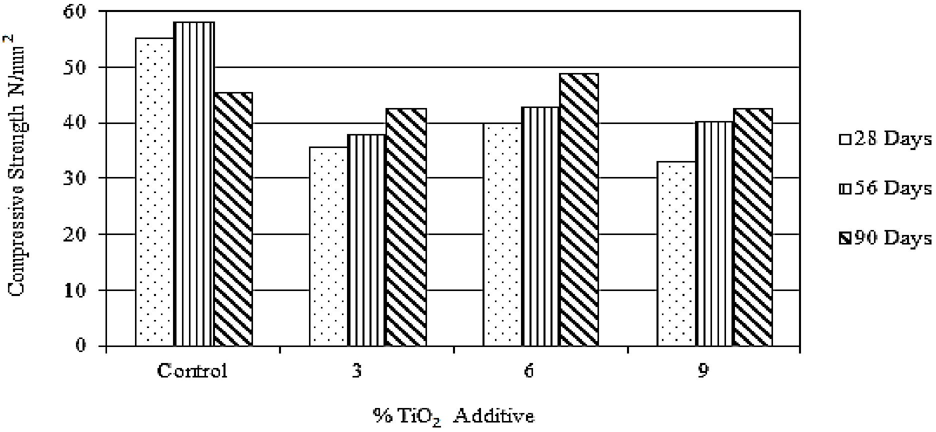

Fig. 5. Compressive strength results of cubes

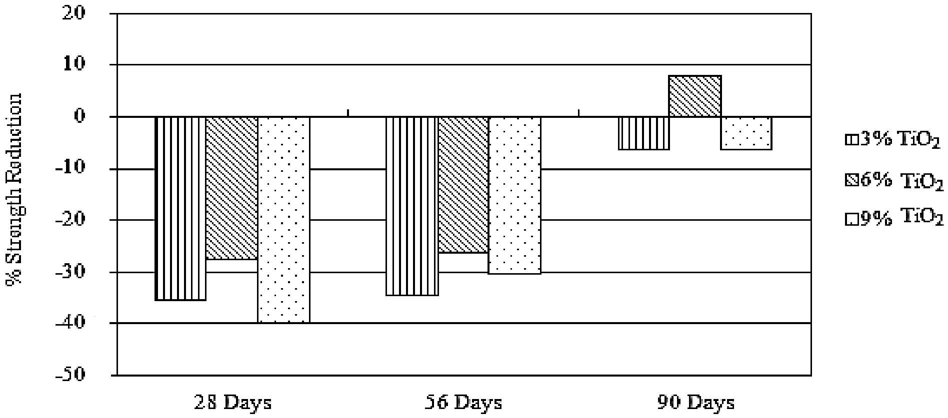

Fig. 6. Ratio of strengths between TiO_2 and control mortar at various ages

In a research that utilized Nano TiO_2 as a partial cement replacement it was reported that the compressive strength increased with higher TiO_2 Nanoparticle replacement at lower water-to-solids ratio (w/s = 0·40) and strength is not compromised by up to 10% TiO_2 replacement at higher w/s = 0·60 [25]. Similarly, mortar samples with 1, 3 or 5% nano-TiO_2 exhibited improved strength up to 28 days of curing compared to ordinary samples [26]. However, the Nano particles were dispersed a water reducer before mixing and naturally the Nano particles affect the microstructure in a more profound way compared to micro particles and this perhaps caused the observed enhanced strength.

Carbonation Depth

Fig. 7 illustrates the observations upon the application of Phenolphthalein Indicator to determine the effect of TiO_2 powder on the carbonation of mortar cubes exposed to CO_2 gas for 28, 56, and 90 days. It can be seen that the carbonation depth decreased as TiO_2 percentage increased. The carbonation depth of control samples was increased with long exposure to CO_2 gas. However, the presence of TiO_2 significantly reduced CO_2 depth especially at later ages.

The improvement in carbonation resistance with the inclusion of TiO_2 can be observed clearly after 28 days of curing. Similarly SEM test results had previously concluded that the incorporation of nano-TiO_2 particles refines the microstructure and improves the carbonation resistance [27].

In another investigation, TiO_2 partially replaced either fine aggregate or cement, it was reported that samples with TiO_2 exhibited slightly higher carbonation depths after 13 weeks of CO_2 exposure [28]. The depths were higher with high W/B ratios and increased replacement levels leading to lower alkalinity to start with.

Shrinkage Test

Fig. 8 and Fig. 9 show the average of change of length for test prisms kept in laboratory air for 90 days. Five samples were tested for each mix. The change in length was determined as follows:

$$\% \text{ Change in Length} = (L_0 - L_1) / L_0 \% \qquad (1)$$

Where:

L_0=Length of specimen after water curing.

L_1=Length of specimen at a specified test age

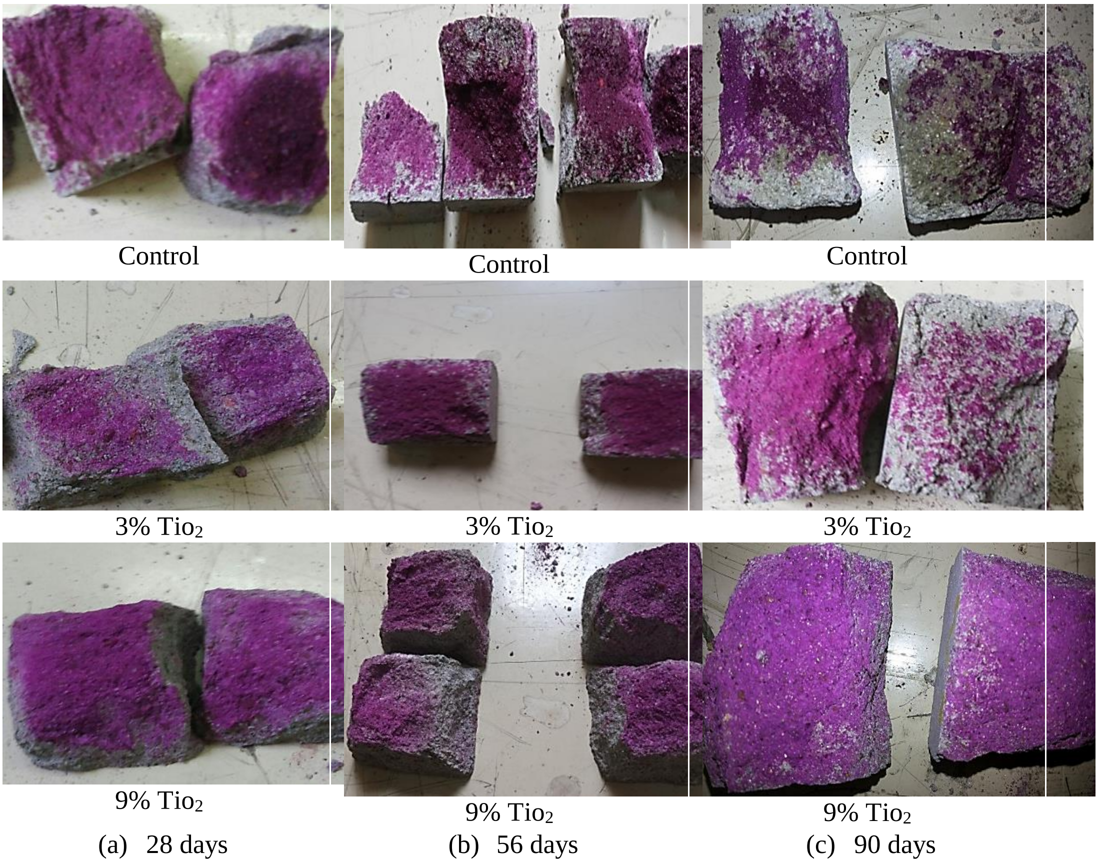

Fig. 7. Carbonation depth test at different ages
(a) 28 days (b) 56 days (c) 90 days

It can be seen that the percentage change in lengths lightly increased with increasing TiO_2content at all ages. Naturally, the shrinkage increased with time. Similarly, in an investigation using Nano TiO_2 in concrete it was reported that after 28 days, the dying shrinkage rate of the concrete with 1% nano-$TiO_2$was 1.6 times that of ordinary concrete [29]. However, mortar samples with 1, 3 or 5% nano-TiO_2exhibited less water loss during shrinkage measurements compared to those without nano-TiO_2 [26]. It should be noted that the Nano particles act in a different manner compared to the micro particles and this perhaps caused the reduction in shrinkage. Fig. 9 indicates that the TiO_2 percentage had a small effect on length change values as all samples with TiO_2 exhibited similar shrinkage at each testing age.

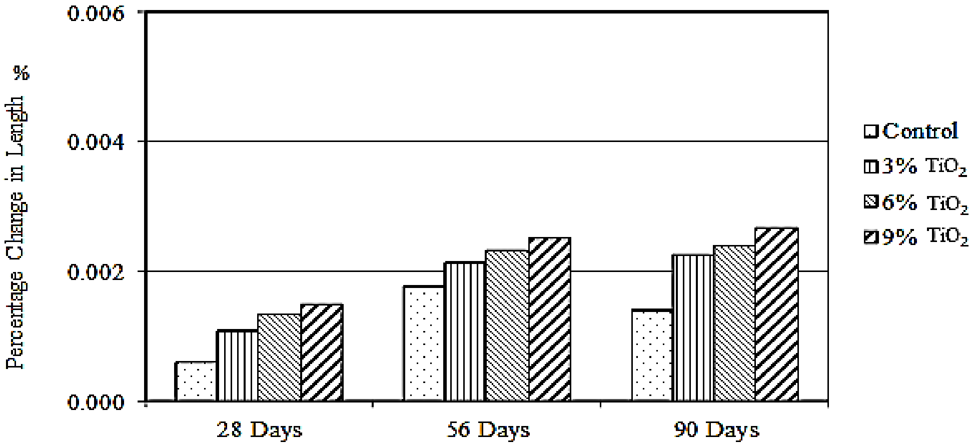

Fig. 8. Percentage change in length of prisms kept in air

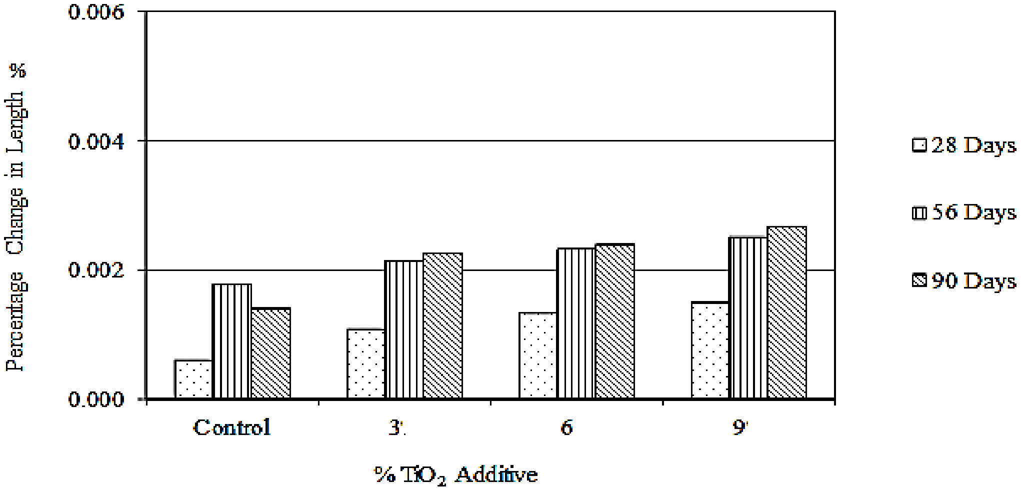

Fig. 9. Percentage Change in length of prisms kept in air at different ages

Sulfate Attack Test

Fig. 10 shows the prism samples immersed in sulfate solution in glass container. The top of the container was glass plate then sealed to prevent evaporation. Fig. 11 shows the average of change of length test prisms during 90 days sulfate solution exposure. Five samples were tested from each mix. It can be observed that the expansion of mortar prisms was decreased by increasing TiO_2 percentage at all ages except for 9% TiO_2. The 9% TiO_2 mortar prisms were shrinking in sulfate solution. Table 5 shows the percentage mass loss of prisms kept in sulfate solution. It can be seen that the shrinkage of 9% TiO_2 samples was not due to mass loss. In fact no samples exhibited cracking in the current investigation. Mass loss values were smaller with higher percentage of TiO_2.

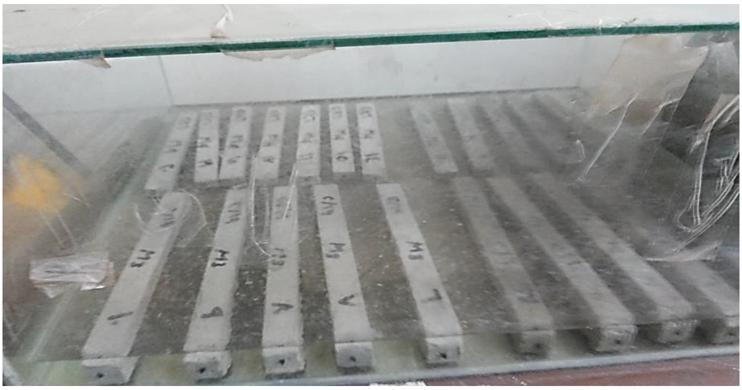

Fig. 10. Setup for sulfate attack test

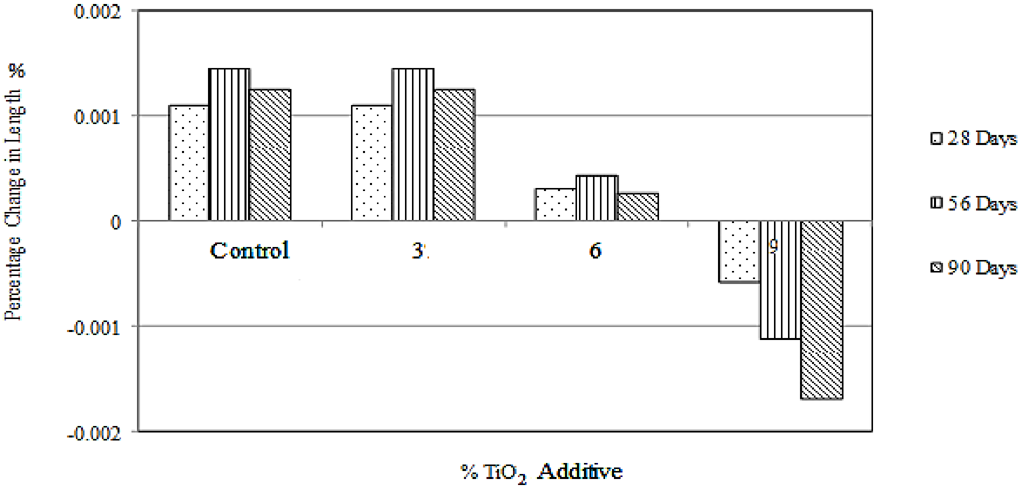

Fig. 11. Percentage Change in length of prism kept in sulfate solution

Table 5. Percentage mass loss of prisms kept in sulfate solution

Mix	28 Days	56 Days	90 Days
Average for Control	0.50%	0.86%	0.69%
Average for 3% TiO_2	0.50%	0.86%	0.69%
Average for 6% TiO_2	0.47%	0.25%	0.08%
Average for 9% TiO_2	0.40%	0.10%	0.06%

It has been reported that the use of TiO_2 Nano particles improves the resistance to water permeability of concrete when it is mixed in cement pastes [30, 31]. This improved water ingress resistance should contribute to better resistance to all chemical attack including sulfate attack.

In another publication, samples of 5%, 10%, and 15% Nano TiO_2 mortar prisms were immersed partially in 15% Na_2SO_4 solution developed heavy efflorescence within several days after the start of the experiment, with white deposits covering whole sample surfaces. However, no cracking was observed on the sample surfaces. Therefore, the aesthetics of the samples were negatively affected, but the soundness was not impaired [32].

The effect of TiO_2Nano particles on Fly Ash concrete properties was investigated. The results confirmed higher resistance to sulfate attack due to addition of Nano particles to Fly Ash concrete. In addition, Fly Ash-nano titanium dioxide specimens showed lesser weight loss compared to Fly Ash concrete without Nano TiO_2 [33].

Conclusions

The addition of TiO_2 reduces the flow of the mortar mixes measured in accordance with ASTM: C 1437– 07.

The compressive strength of mortars was tested in accordance with ASTM C109/C109M-16a and was reduced with inclusion of TiO_2; however, this decrease in strengths was less noticeable at later ages.

The samples kept in laboratory air all exhibited comparable shrinkage regardless of the TiO2 content. However, shrinkage of these mortars was slightly higher than the control mortar.

By storing the samples in the proposed built CO_2 chamber for up to 90 days, the samples containing TiO_2 showed small or no carbonation depth. However carbonation occurred in the control samples.

Samples with 3% TiO_2 exhibited similar behavior to the control samples when exposed to sulfate for up to 90 days. The test was conducted in accordance with ASTM C1012-04. Samples with higher TiO_2 exhibited better performance compared to the control samples without TiO_2. No samples in the current investigation showed signs of cracking or expansive mass loss due to sulfate exposure.

The properties of samples containing micro TiO_2 used in this investigation may show similar trends to the properties reported in the literature for Nano TiO_2. However, it should be remembered that the mechanism of action of each type of particle at the microstructure level is different and the comparison was quoted here to draw the attention to the expected behavior in service for both types of materials.

The current consensus in the literature [34] points towards the beneficial effect of TiO_2 additions to cement composites as the product has self-cleaning, self-disinfecting, and depolluting effects.

It is recommended that TiO_2 should be used as an additive to the mortar plaster. However, the mortar with TiO_2 would need to be optimized for consistency and compressive strength to be used effectively.

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