Durability enhancement of concrete by incorporating titanium dioxide nanopowder into binder

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Abstract: In this paper, durability-related properties such as chloride penetration, water absorption and electrical resistivity of high strength self compacting concrete (SCC) containing titanium dioxide nanopowder have been investigated. For this purpose, different mixtures were designed with different amounts of nanopowder and Portland cement was replaced by 1 up to 5 wt% of nanopowder. Durability properties were evaluated by water absorption, capillary absorption and chloride penetration tests. The results showed that water absorption, capillary absorption and chloride penetration decreased rather significantly in the mixtures containing nanopowder in the binder which can lead to increased durability and lifetime of the concrete. It may be due to filler effect of the nanoparticles and more packed microstructure of the concrete binder which inhibits the ingress of water and chloride ions.

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1. Introduction

Self consolidating concrete (SCC) is a concrete which has little resistance to flow so that it can be placed and compacted under its own weight with no vibration effort, yet possesses enough viscosity to be handled without segregation or bleeding. The most important advantage of SCC over conventional concrete is its flowability. Other advantages of using SCC include shorter construction periods, reduction in the labor cost, and better compaction in the structure especially in confined zones where compaction is difficult. It has gained significant importance in recent years because of the advantages it offers [1–3]. Many researchers have used SCC containing admixtures to satisfy the great demand for fines needed for this type of concrete, thereby improving its mechanical, rheological and durability properties [4–6].

Several works can also be mentioned on incorporating nanoparticles into concrete specimens to achieve improved physical and mechanical properties such as using SiO_2 nanoparticles in mortars and cement-based materials [7–9], normal concrete [10,11] and high performance self compacting concrete [12].

Effects of TiO_2 nanoparticles on properties of concrete have been investigated in some works such as flexural fatigue performance of concrete for pavement [13], abrasion resistance of concrete [14], and hydration kinetics of titania-bearing tricalcium silicate phase [15].

Strength assessment of concrete is a main and probably the most important mechanical property, which is usually measured after a standard curing time. Concrete strength is influenced by lots of factors like concrete ingredients, age, ratio of water to cementitious materials, etc. The pore structure determines the transport properties of cement paste, such as permeability and ion migration. In the hydrated paste, the capillary and gel pores can be distinguished. The gel pores are very small. Although they constitute a network of open pores, the permeability of this network is very low. Conversely, the capillary pores are relatively large spaces existing between the cement grains. It is the capillary porosity that greatly affects the permeability of concrete [16]. Permeability of cement paste is a fundamental property in view of the durability of concrete: it represents the ease with which water or other fluids can move through concrete, thereby transporting aggressive agents. It is therefore of utmost importance to investigate the quantitative relationships between the pore structure and the permeability. Through experimental studies of the pore structure and the permeability of cement-based materials, a better understanding of transport phenomena and associated degradation mechanisms will hopefully be reached [17].

In the present study, durability-related properties in terms of water absorption, capillary absorption and chloride penetration of high strength self compacting concrete (SCC) containing titanium dioxide nanopowder have been investigated.

2. Materials

An ASTM Type II Portland cement (PC) was used to produce the various SCC mixtures. Table 1 summarizes physical properties and chemical composition of the cement used.

The nanopowder properties are presented in table 2. The coarse aggregate used was limestone gravel with a nominal maximum size of 12.5 mm. As fine aggregate, a mixture of silica aggregate sand and crushed limestone (as filler) was used with a maximum size of 4.75 mm. physical properties of the filler, fine and coarse aggregates are presented in table 3. All aggregates in this research were used in dry form and the aggregates are a mixture of eight particle sizes of fine and coarse aggregates. A polycarboxylic-ether type superplasticizer (SP) with a specific gravity of between 1.06 and 1.08 was employed to achieve the desired workability in all concrete mixtures. Furthermore viscosity modifying agent (VMA) for better stability was used.

Table 1. Chemical composition and physical properties of cement

Chemical analysis (%)	Sio2	Al2O3	Fe2O3	CaO	MgO	SO3	K2O	Na2O	Loss of ignition	Specific gravity	Blaine fineness (cm2/g)
Cement	20<	6<	6<	<50	<5	<3	<1	<1	<3	3.15	3260

Table 2. Properties of TiO2 nanopowder

Diameter (nm)	Surface volume ratio (m^2/g)	Density (g/cm^3)	Purity (%)
15±3	165±17	<0.15	>99.9

Table 3. Sieve analysis and physical properties of the filler, fine and coarse aggregates

Sieve size (mm)	Filler (%passing)	Fine aggregate (%passing)	Coarse aggregate (%passing)
12.5	100	100	97.9
9.5	100	100	79.3
4.75	100	98.38	13.2
2.36	100	76.45	0
1.18	100	46.65	0
0.6	100	39.32	0
0.3	100	15.26	0
0.15	90.9	3.62	0
0.075	33.7	0	0
Bulk density (kg/m^3)		1460	1450
Specific gravity (g/m^3)		2.619	2.6
Absorption (%)	8	2.72	0.4

3. Mix proportions and preparation of the specimens

A total number of 6 concrete mixtures were designed with a constant water/binder (w/b) ratio of 0.38 and total binder content of 450 kg/m^3. Concrete mixtures were prepared with 0, 1, 2, 3, 4 and 5 wt% of cement replacement by TiO_2 nanopowder. The mixture proportions of concrete and binder paste are given in table 4.

Since the SP plays a very important role in the flowability of SCC mixes, a modified mixing procedure was adopted to take the benefit of action of adsorption of molecules of poly-carboxylic ether based SP on the cement particles for all the mixes. SCC mixtures were prepared by mixing the coarse aggregates, fine aggregates and powder materials (cement and nanopowder) in a laboratory drum mixer. The powder material and aggregates were mixed in dry form for 2 minutes. Then half of the water containing the whole amount of Super plasticizer was poured and mixed for 3 minutes. After that, about 1 minute rest was allowed and finally rest of the water containing VMA was added into the mixture and mixed for 1 minute [12].

Cubic samples of 100×100×100 mm were also made for durability tests (water absorption, capillary absorption and chloride penetration tests). All specimens were cast in one layer without any compaction. The molds for SCC were covered with polyethylene sheets and moistened for 48 h. Then the specimens were demoulded and cured in water at a temperature of 20ºC until the test time. The code assigned to the mixtures was SCC-Nx which SCC-N denotes the self compacting concrete containing nanopowder and x is the wt% of the nanopowder.

Table 4. Mix proportions of the concrete specimens

No	Concrete ID	w/b	Cement	Silica fume	Nano TiO2	Filler	Fine aggregate	Coarse aggregate	Sp	VMA
			(kg/m^3)							
1	SCC400	0.38	400	-	-	177	1003	578	2.5	2
2	SCC450	0.38	450	-	-	177	1003	578	2.81	2.25
3	SCC500	0.38	500	-	-	177	1003	578	3.12	2.5
4	SCC400SF10%	0.38	360	40	-	177	1003	578	2.5	2
5	SCC450 SF 10%	0.38	405	45	-	177	1003	578	2.81	2.25
6	SCC500 SF 10%	0.38	450	50	-	177	1003	578	3.12	2.5
7	SCC400NS2%	0.38	392	-	8	177	1003	578	2.5	2
8	SCC450 NS 2%	0.38	441	-	9	177	1003	578	2.81	2.25
9	SCC500 NS 2%	0.38	490	-	10	177	1003	578	3.12	2.5
10	SCC400SF10NS 2%	0.38	352	40	8	177	1003	578	2.5	2
11	SCC450SF10NS 2%	0.38	396	45	9	177	1003	578	2.81	2.25
12	SCC500SF10NS 2%	0.38	440	50	10	177	1003	578	3.12	2.5

4. Durability tests

4. 1. Absorption test

This test is based on BS 1881-Part 122 for testing water absorption in hardened concrete. The 100×100×100 mm specimens were dried in an oven at 45ºC for a week and after 14 days specimens reached to constant weight. The specimens were then immersed in water and scaled after 0.5, 1, 24, 72 and 168 hours to check the weight increase and to calculate the water absorption percentage. In this test, water absorption can only take place in pores which are emptied during drying and filled with water during the immersion period.

4.2. Capillary test

The test carried out in this study for determination of capillary water absorption is based on RILEM CPC 11.2, TC 14-CPC for testing capillary absorption in hardened concrete. The 100×100×100 mm specimens were dried in the oven at 40±5ºC. They were put on rods in a water bath in such a way that they were immersed in water for no more than 5 mm. In this test, unidirectional flow depths of the specimens were measured and results of capillary depths were reported.

4.3. Chloride ion penetration

After curing period of 90 days, 150×150×150 mm cubic specimens were immersed in 3% NaCl solution for 90 days. Then specimens were dried in the oven for 24 hours. After that, in order to prepare some pulverized concrete samples (powder samples) for the test, all 6 faces of the cubic specimens were drilled by depths of 0-5, 5-10, 10-15, 15-20 and 20-30 mm and the concrete powder samples obtained from all 6 faces for each depth were blended and in this way, the samples were prepared for the next step of the test [ASTM C1218].

In this test method, total chloride content of pulverized concrete sample is determined by the potentiometric titration of chloride with silver nitrate [ASTM C114]. The pulverized concrete sample prepared is solved in nitric acid solution and then if the solution is acidic, a little of $NaHCO_3$ is added to this solution until pH value reaches 6 or 7. Then the K_2CrO_4 indicator is added so that the color of the solution changes to light yellow. Eventually, 0.05 N $AgNO_3$ is added until the color of the solution turns to orange-yellow (weak brown) and the volume of the $AgNO_3$ solution is measured. In order to determine the Cl ion percentage, the volume of the $AgNO_3$ solution is substituted in Eq. (1).

$$Cl^{-}(\%) = \frac{3.5453(V.N)}{W} \tag{1}$$

W: weigh of pulverized (powder) concrete prepared from the sample
N: normality of $AgNO_3$ solution
V: volume of $AgNO_3$ solution

5. Results and discussion

5. 1. Water absorption

The percentage of water absorption results of the concrete samples after 90 days of curing at different time intervals are presented in table 5.

Table 5. Results of water absorption by time

No	Concrete ID	Time (hour)					
		0.5	1	24	48	72	168
		Water absorption (%)					
1	SCC-N0	2.35	3.12	4.54	4.72	4.85	5.12
2	SCC-N1	2.13	3.06	4.42	4.64	4.72	4.93
3	SCC-N2	1.97	2.73	4.25	4.45	4.39	4.68
4	SCC-N3	1.55	2.46	3.86	4.18	4.23	4.46
5	SCC-N4	1.15	2.17	3.55	3.91	4.06	4.22
6	SCC-N5	1.38	2.38	3.65	3.98	4.12	4.35

The results show that the percentage of water absorption is decreased by increasing the TiO_2 nanoparticles content up to 4.0 wt% and then it is increased. Once again, this may be due to unsuitable dispersion of the nanoparticles in the cement paste when the content of the nanoparticles goes beyond 4.0 wt%. Therefore, it can be suggested that prolonged curing, increasing the age and percentages of TiO_2 nanoparticles can lead to reduction in permeable voids. This is due to the high action and filler effects of TiO_2 nanoparticles. Another finding is that the interfacial transition zone in concrete is improved due to high reactivity as well as filler effect of the TiO_2 nanoparticles. This finding is partially in confirmation of the results of the study by Bui et al. [18]. It has also been shown that that by addition of TiO_2 nanoparticles, the total specific pore volumes of concretes are decreased, and the most probable pore diameters of concretes shift to smaller pores and fall in the range of few-harm pore [11], which indicates that the addition of nanoparticles refines the pore structure of concretes and hence the transport properties of the SCC is improved. With increasing the nanoparticles' content more than 4 wt%, some flocculation of the nanoparticles due to higher volume may be formed and the additional cement replacement by nanofillers may lead to weakening of the pore structure of the concrete.

5.2. Capillary absorption

The capillary water absorption results of the SCC-N samples at different time intervals are presented in table 6.

The results show that the height of absorbed water in the concrete samples again has decreased by increasing the TiO_2 nanoparticles up to 4 wt% and then increased.

Table 6. Results of capillary absorption by time

No	Concrete ID	Time (hour)			
		3	6	24	72
		Capillary water absorption (mm)			
1	SCC-N0	2.6	3.5	5.8	6.9
2	SCC-N1	2.5	3.4	5.6	6.3
3	SCC-N2	2.5	3.3	5.4	6.1
4	SCC-N3	2.4	3.1	5.1	5.6
5	SCC-N4	2.2	2.8	4.6	5.0
6	SCC-N5	2.2	2.9	4.8	5.2

Concrete permeability is an inherent property of concrete that chiefly depends upon the geometric arrangement and characteristics of the constituent materials. The permeability of concrete is mainly controlled by the solidity and porosity of the hydrated paste present in bulk paste matrix and interfacial transition zone. In the hydrated paste, the capillary and gel pores can be distinguished. The gel pores are very small. Although they constitute a network of open pores, the permeability of this network is very low. Conversely, the capillary pores are relatively large spaces existing between the cement grains. It is the capillary porosity that greatly affects the permeability of concrete [19]. The permeability of SCC is typically lower than that of ordinary concrete. Previous researches have shown that SCC results in very low water and gas permeability [20]. It has also observed that by adding nanoparticles, the amounts of is pores decreased, which shows that the density of concretes is increased and the pore structure is improved [11]. This is mostly attributed to the denser microstructure and refined pores. Good flow properties along with nanoparticles' filler effect of SCC-N mixtures result in superb packing condition due to better consolidation and smaller pore structure due to nanoparticles addition, and thus contribute to reduce the permeability of concrete.

5.3. Chloride penetration

In this work, the chloride penetration has been determined as a fraction of the concrete sample weight. Presented in table 7 are the results of chloride percentages at different depths of the concrete samples. The results show a general decrease in chloride percentage by depth of concrete sample which conveys the fact that the concrete ingredients especially aggregates are clear from chloride ions.

Table 7. Percentage of chloride penetration at different average depths of the concrete samples

No	Concrete ID	Average depth (mm)				
		2.5	7.5	12.5	17.5	25
		Chloride penetration (%)				
1	SCC-N0	3.55	1.54	0.74	0.45	0.23
2	SCC-N1	2.42	1.45	0.68	0.38	0.20
3	SCC-N2	2.28	1.28	0.62	0.37	0.17
4	SCC-N3	2.05	1.10	0.48	0.25	0.13
5	SCC-N4	1.85	0.92	0.41	0.21	0.09
6	SCC-N5	1.88	0.95	0.42	0.25	0.11

Based on the results obtained, a decrease in chloride penetration can be observed by increasing the TiO_2 nanoparticles up to 4 wt%. The results obtained in this study are in agreement with those of other researchers. For example Detwiler et al. [21] investigated the effectiveness of using supplementary cementing materials to increase the chloride resistance of accelerated cured concrete and they found that concretes containing supplementary cementing materials performed better than the Portland cement concretes. As well, use of supplementary cementing materials can also prevent deleterious expansions related to both delayed ettringite formation [22] and alkali–silica reaction [22]. Regarding the positive effect of TiO_2 nanoparticles as supplementary cementing materials on chloride penetration of SCC, it may be due to the fact that the nanoparticles located in cement paste as kernel can further promote cement hydration as a consequence of their high activity and it can lead to more homogeneous and compact cement paste. Consequently, the pore structure of concrete is improved evidently. With increasing the content of nanoparticles more than 4 wt%, the improvement on the pores structure of concrete is weakened. This can be attributed to that the distance between nanoparticles decreases with increasing content of nanoparticles, and $Ca(OH)_2$ crystal cannot grow up enough due to limited space and the crystal quantity is decreased, which leads to the ratio of crystal to strengthening gel small and the shrinkage and creep of cement matrix increased, thus the pore structure of cement matrix is looser relatively which could result in chloride penetration increase.

6. Conclusion

The results obtained in this study can be summarized as follows:

- Both water absorption and capillary absorption results showed rather significant decrease by addition of TiO_2 nanoparticles, since the nanoparticles act as nanofillers and improve the resistance to water permeability of concrete.
- Nanopowder addition could result in superb packing condition due to better consolidation and smaller pore structure, and thus contribute to reduced the permeability of concrete.
- Chloride penetration decreased by depth, by addition of nanoparticles which could be as a result of more packed microstructure achieved by addition of nano particles and paste volume increase.
- With increasing the content of nanoparticles more than 4 wt%, the improvement on the pores structure of concrete is weakened which could result in chloride penetration increase.

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