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Transport properties of high-performance cementitious composites incorporating micro and nano SiO₂ into the binder

Abstract: In this paper, transport properties of high-performance self-compacting concrete (SCC), as one of the important cementitious composites incorporating micro and nano silica (NS) (SiO₂) into the binder, have been investigated. For this purpose, different mixtures were designed with different amounts of silica fume (SF) and NS admixtures. Different binder contents were also investigated to observe the binder content effect on the concrete properties. Corrosion behavior was evaluated by chloride penetration and resistivity tests. Water absorption and capillary absorption were also measured as other durability related properties. The results showed that water absorption, capillary absorption, and Cl ion percentage decreased rather significantly in the mixtures containing admixtures especially the blend of SF and NS. By addition of the admixtures, resistivity of the SCC mixtures increased, which can lead to reduction of corrosion probability.

Keywords: chloride penetration; corrosion; durability; high-performance cementitious composites, resistivity; transport properties.

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1 Introduction

High-strength concrete, according to the American Concrete Institute Committee ACI 363 R [1], is the concrete that has specific compressive strength of 41 MPa or more at 28 days. The high performance concrete (HPC) offers significant economic and architectural advantages over normal strength concrete (NSC) in similar situations and is suited well for constructions that require high durability.

Self-compacting concrete (SCC) is also considered as a concrete, which can be placed and compacted under its own weight with little or no vibration without segregation or bleeding. It is used to facilitate and ensure proper

filling and good structural performance of restricted areas and heavily reinforced structural members. It has gained significant importance in recent years because of the advantages it offers [2–5]. 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 in comparison with normal vibrated concrete (NVC). Siddique [6] investigated the properties of SCC made with different amounts of fly ash. El-Dieb [7] studied the mechanical and durability properties of ultrahigh-strength fiber-reinforced concrete with self-compacting characteristics. Kulakowski et al. [8] reviewed the silica fume (SF) influence on the reinforcement corrosion in concrete. There are some works on incorporating nanoparticles into concrete specimens to achieve improved physical and mechanical properties using nano SiO₂ and SF [9–13]. 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 [14]. The 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 the transport phenomena and associated degradation mechanisms will hopefully be reached [15].

In the previous part of the study, the effects of these admixtures on rheology and the strength of high-strength SCC were assessed. The aim of this study following the previous part of the research is to investigate the effects of

nano silica (NS) and SF on the durability-related properties of high-strength self-compacting concrete, along with the influence of different binder contents on the transport properties of high-strength SCC.

2 Materials and methods

2.1 Materials

An ASTM Type II Portland cement (PC) was used to produce the various SCC mixtures. In addition, SF and NS were used as admixtures. Table 1 summarizes the physical properties and chemical compositions of the cement and SF, and Table 2 shows the properties of the NS used. 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. 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, a viscosity-modifying agent (VMA) for better stability was used.

2.2 Mix proportions

A total number of 12 concrete mixtures were designed with a constant water/binder (w/b) ratio of 0.38 and a total binder content of 400, 450, and 500 kg/m³. Concrete samples were prepared with 10% and 2% (by weight) replacement of PC by SF and NS, respectively. The mixture

Chemical analysis (%)	Cement	SF
SiO ₂	20<	93.6
Al ₂ O ₃	6<	1.3
Fe ₂ O ₃	6<	0.9
CaO	<50	0.5
MgO	<5	1
SO ₃	<3	0.4
K ₂ O	<1	1.52
Na ₂ O	<1	0.45
Loss of ignition	<3	3.1
Specific gravity	3.15	2.2
Blaine fineness (cm ² /g)	3260	21,090

Table 1 Chemical composition and physical properties of cement and SF.

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

Table 2 Properties of NS.

proportions of concrete and binder paste are given in Table 3. The abbreviations used in the study for labeling the mixtures were adopted in such a way that they clearly show the main parameters and their amount. SCC is followed by the binder content. SF and NS are followed by their percentages.

2.3 Durability tests

2.3.1 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 45°C for a week, and after 14 days, the specimens reached a constant weight. The specimens were then immersed in water and scaled after 0.5, 1, 24, 72, and 168 h to check the weight increase and to calculate the water absorption percentage. In this test, water absorption can only take place in pores that are emptied during drying and filled with water during the immersion period.

2.3.2 Capillary test

When a non-saturated concrete element is in contact with water at one side and absorbed, water evaporation is possible from the other side, and a permanent flowing regime through capillary absorption is established [16]. The test carried out in this study for the 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±5°C. 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 the results of capillary depths were reported.

2.3.3 Cl ion percentage

After a curing period of 90 days, 150×150×150-mm cubic specimens were immersed in 3% NaCl solution for 90

No.	Concrete ID	w/b	Cement	SF	NS	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	SCC400SF10NS2%	0.38	352	40	8	177	1003	578	2.5	2
11	SCC450SF10NS2%	0.38	396	45	9	177	1003	578	2.81	2.25
12	SCC500SF10NS2%	0.38	440	50	10	177	1003	578	3.12	2.5

Table 3 Mix proportions of the concrete specimens.

days. Then, the specimens were dried in the oven for 24 h. After that, in order to prepare some pulverized concrete samples (powder samples) for the test, all six 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 six 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, the total chloride content of the 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 the 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).

$$\text{Cl}(\%) = \frac{3.5453(V \cdot N)}{W} \quad (1)$$

W : weight of pulverized (powder) concrete prepared from the sample

N : normality of AgNO_3 solution

V : volume of AgNO_3 solution

2.3.4 Resistivity test

The resistivity test setup includes an electrical resistance measurement device and two electrodes, which can be both attached to the concrete sample surfaces, or one

may be attached to a steel rebar embedded in the concrete sample and the other attached to the concrete sample surface [17–19]. For this test, 100×100×100-mm cubes were used, and measurements were made at 7, 28, and 90 days. The resistivity values were calculated by using Eq. (2).

$$r = \frac{RA}{L} \quad (2)$$

where R , A , L , and r are the resistance (Ω), the area of the sample (m^2), the length of sample (m), and the resistivity ($\Omega \cdot \text{m}$), respectively.

The test procedure can be summarized in this way: after curing the sample in the water for specific ages (7, 28, and 90 days), the surfaces of the sample were dried. Two copper plates were attached to the upper and lower surfaces of the concrete sample by cement paste, and two wooden non-conductive blocks were placed under and on the concrete sample. A schematic of the test setup is illustrated in Figure 1.

3 Results and discussion

3.1 Water sorption

The water absorption results of the concrete samples at different time intervals are presented in Table 4. As can be seen, an increase in the binder content from 400 to 450 and 500 kg/m^3 resulted in a water absorption decrease by 11.5% and 15.3%, respectively, at the first time step of water absorption (0.5 h) in the samples without any admixtures. Water absorption decrease in the samples containing 2% NS in the first time step appeared to be

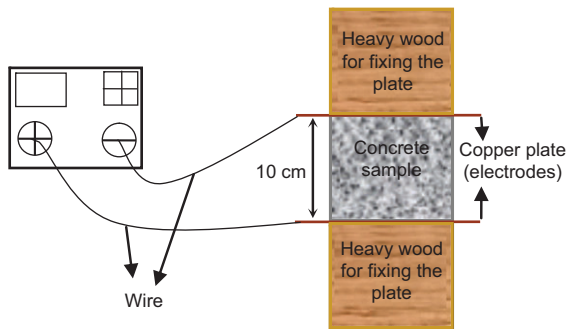


Figure 1 Schematic of resistivity test setup.

35%, 28%, and 32% for the binder contents of 400, 450, and 500, respectively. The addition of 10% SF resulted in water absorption decreases in the same duration by 31%, 26%, and 34% for the binder contents of 400, 450, and 500, respectively, which is similar to the values obtained in the mixtures containing 2% NS. The reductions in water absorption in the mixtures containing 2% NS and 10% SF were obtained as 46%, 43%, and 50% for the binder contents of 400, 450, and 500, respectively, which is noticeable and reveals the good performance of SF and NS blends in the SCC mixtures.

From the results, the influence of the different binder contents, and the addition of SF and NS that varies on the water absorption properties of SCC can be seen and compared. The trends generally show a desirable effect of admixtures especially micro and NS blends on the water absorption properties of the SCC samples. With this respect, more desirable performances were observed in the mixtures containing 10% SF and 2% NS with a binder content of 500 kg/m³.

The electrical resistance values (R) read from the electrical device are substituted in Eq. (2), and then, the resistivity values are calculated, and then, the resistivity values were calculated. Using Table 5, the probability of corrosion can be determined.

3.2 Capillary water sorption

The capillary water absorption results of the SCC samples at different time intervals are presented in Table 6. The results show that the height of the absorbed water in the concrete samples has decreased by increasing the binder content from 400 to 500 and the addition of SF and NS admixtures. An increase in the binder content from 400 to 450 and 500 leads to capillary water absorption from 2.8 to 2.64 and 2.5 mm in 3 h and from 8.6 to 6.9 and 6.6 mm in 72 h, respectively, in which the capillary water height decreases seem more significant at longer times. It may be due to the fact that the samples that were fully dried in the oven have more tendency to absorb water at earlier times; however, at longer times, the effect of the binder contents and SF and NS admixtures comes to be revealed more and the results considered to be more realistic and reliable. The addition of 2% NS resulted in capillary water absorption of 3.6, 3.3, and 3 mm for the binder contents of 400, 450, and 500, respectively, in 72 h for which the reductions of 58%, 52%, and 54% compared to the mixtures without any admixture can be considered. The addition of 10% SF with the binder contents of 400, 450, and 500 resulted in capillary water absorption decrease by 60%, 52% and 53%, respectively, in 72 h compared to the mixtures without any admixture. The same reductions observed for the mixtures

No.	Concrete ID	Water absorption (%)					
		Time (h)	Time (h)	Time (h)	Time (h)	Time (h)	Time (h)
		0.5 h	1 h	24 h	48 h	72 h	168 h
1	SCC400	2.6	3.2	5.3	5.5	5.6	5.8
2	SCC450	2.3	3.15	4.5	4.7	4.8	4.9
3	SCC500	2.2	3.1	4.3	4.4	4.6	4.9
4	SCC400NS2%	1.7	2.2	2.7	2.8	2.85	3
5	SCC450NS2%	1.65	2.1	2.4	2.6	2.6	2.8
6	SCC500NS2%	1.5	1.95	2.4	2.5	2.6	2.7
7	SCC400SF10%	1.8	2.25	2.65	2.7	2.74	3
8	SCC450SF10%	1.7	2.2	2.6	2.64	2.7	2.9
9	SCC500SF10%	1.44	1.7	2.2	2.3	2.4	2.5
10	SCC400SF10NS2%	1.4	1.8	2	2.2	2.3	2.4
11	SCC450SF10NS2%	1.3	1.65	1.9	1.8	2	2.1
12	SCC500SF10NS2%	1.1	1.4	1.6	1.7	1.9	2

Table 4 Results of water absorption by time.

Electrical resistivity ($\Omega\cdot\text{m}$)	Probability of corrosion
120<	Not probable
50–120	Probable
<50	Inevitable

Table 5 Relation between electrical resistivity and probability of corrosion [23].

containing blends of 2% NS and 10% SF were 66%, 65% and 66%, respectively. As can be seen, the water proofing effects of SF and NS on SCC tend to appear more obviously in the mixtures containing both SF and NS with a higher binder content. As can be inferred from the water absorption results, this performance may be attributed to the more packed and refined microstructure and pore structure of the concrete achieved by the addition of SF and NS.

As is clear from the results, the mixture containing the SF and NS blends with a binder content of 500 has the lowest capillary water absorption values. On the whole, the addition of silica micro and especially nano particles improves the pore structure of the concrete. On the one hand, nano particles can act as a filler to enhance the density of concrete, which leads to the porosity of the concrete that was reduced significantly. On the other hand, nano particles cannot only act as an activator to accelerate cement hydration due to their high activity, but also act as a kernel in cement paste, which makes the size of the $\text{Ca}(\text{OH})_2$ crystal smaller and the tropism more stochastic.

The high enhancement of the durability properties in the SF- and NS-blended SCC is due to the rapid consuming of $\text{Ca}(\text{OH})_2$, which was formed during the hydration of PC especially at the early ages related to the high reactivity of the NS particles. As a consequence, the hydration of

No.	Concrete ID	Capillary water sorption (%)			
		Time (h)	Time (h)	Time (h)	Time (h)
		3	6	24	72
1	SCC400	2.8	2.82	6.5	8.6
2	SCC450	2.64	3.5	5.8	6.9
3	SCC500	2.5	3.4	5.5	6.6
4	SCC400NS2%	2.2	2.7	3.4	3.6
5	SCC450NS2%	2	2.4	3.1	3.3
6	SCC500NS2%	1.8	2.3	2.9	3
7	SCC400SF10%	2.1	2.5	3.3	3.4
8	SCC450SF10%	1.9	2.2	3	3.3
9	SCC500SF10%	1.7	2.16	2.9	3.1
10	SCC400SF10NS2%	1.9	2	2.8	2.9
11	SCC450SF10NS2%	1.7	1.9	2.5	2.4
12	SCC500SF10NS2%	1.5	1.7	2.1	2.2

Table 6 Results of capillary absorption by time.

the cement is accelerated, and larger volumes of reaction products are formed. Also, NS particles recover the particle packing density of the blended cement, directing to a reduced volume of larger pores in the cement paste.

3.3 Cl ion percentage

In this test, the Cl ion percentage has been determined as a fraction of the concrete sample weight. Presented in Table 7 are the results of the Cl ion presence at different depths of the concrete samples. The results show a general decrease in Cl ion presence by a depth of the concrete sample that conveys the fact that the concrete ingredients especially aggregates are clear from Cl ions. In a depth of 0 to 5 mm, the increase in binder contents from 400 to 450 and 500 in the samples without any admixture resulted in the reductions of the Cl ion amounts by 16.6% and 29%, respectively. In depth of 0 to 5 mm of the samples containing 2% NS, the Cl ion penetration decreased by 43%, 40%, and 43% for the binder contents of 400, 450, and 500, respectively. The reductions in the samples containing 10% SF were obtained as 52%, 40%, and 43% for the same binder contents, respectively. The samples containing a blend of 10% SF and 2% NS showed significant Cl ion penetration decrease as 62%, 60%, and 56% for the same binder contents, respectively. As can be considered, SF and NS addition has resulted in a relatively significant decrease in Cl ion percentage, which may be in virtue of a more refined pore structure of the concrete obtained by the addition of the admixtures especially nano particles and pozzolanic effect of this material.

The results obviously show descending trends by increase in depth. Comparison is easier in lower depths; however, in higher depths, the curves get closer together, and the differences get smaller. According to the results, again, it is confirmed that the mixture with the binder content of 500 containing NS and SF has the most desirable durability performance.

3.4 Resistivity

Considering the results presented in Table 8, at the earlier ages (7 days), with different binder contents and admixtures amount, corrosion is probable. However, at the higher ages, by an increase in binder content and the addition of SF and NS admixtures, the probability of corrosion occurrence decreases and approaches to the improbable level. Only for the mixtures with a binder content of 400 without any admixture at the age of 90 days do the electrical resistivity results fall in the range where corrosion is

No.	Concrete ID	Cl ion percentage				
		Mean of depth (mm)				
		2.5 (mm)	7.5 (mm)	12.5 (mm)	17.5 (mm)	25 (mm)
1	SCC400	4.2	1.7	0.8	0.52	0.19
2	SCC450	3.5	1.5	0.74	0.43	0.17
3	SCC500	2.98	1.4	0.65	0.37	0.14
4	SCC400NS2%	2.4	1.1	0.62	0.42	0.15
5	SCC450NS2%	2.1	0.9	0.48	0.37	0.13
6	SCC500NS2%	2	0.85	0.43	0.32	0.12
7	SCC400SF10%	2.3	0.81	0.51	0.32	0.14
8	SCC450SF10%	2.1	0.78	0.49	0.3	0.12
9	SCC500SF10%	1.7	0.4	0.43	0.23	0.09
10	SCC400SF10NS2%	1.6	1	0.4	0.29	0.09
11	SCC450SF10NS2%	1.4	0.75	0.38	0.25	0.07
12	SCC500SF10NS2%	1.3	0.55	0.33	0.11	0.03

Table 7 Cl ion percentage at different average depths of the concrete samples.

probable. In the mixtures containing 2% NS, 10% SF, and a blend of SF and NS, the increase in the electrical resistivity values are considerable, and the corrosion tends to become impossible. As can be inferred from the results, the resistivity values for the mixture with a binder content of 500 and without admixture were obtained as 54, 95, and 144 at the ages of 7, 28, and 90 days, respectively. The resistivity values for the mixture with the same binder content containing 2% NS and 10% SF increased from 125 at the age of 7 days to 320 and 589 at the ages of 28 and 90 days, respectively, which are considered to be outstanding.

It is noted from the results that by the passing time, the resistivity values have increased. The resistivity curves also show incremental trends by increasing the binder content. It can be deduced from the resistivity results that although both binder content and admixture factors seem to be effective on the resistivity values of the SCC, the role

of the SF and NS admixtures appears to be much more influential. It is clear that the highest resistivity belongs to the SCC500SF10NS2% mixture.

4 Conclusion

- Both water absorption and capillary absorption results showed rather a significant improvement by the addition of admixtures especially the blend of micro and nano materials for the binder content of 500 kg/m³.
- The resistivity results showed increases at higher ages, especially for the mixtures containing higher percentages of admixtures. The binder content increase also had an increasing effect on the resistivity values.
- The Cl ion percentage decreased by depth, by the addition of micro and nano particles, and by the binder content increase, which could be as a result of a more packed microstructure achieved by the addition of nano particles and paste volume increase.
- From the microstructure point of view, more refined microstructure and smaller pores may be achieved by the addition of SF and NS, which can lead to enhanced durability and microstructural properties of the SCC mixtures.

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No.	Concrete ID	Resistivity ($\Omega \cdot m$)		
		7 (days)	28 (days)	90 (days)
1	SCC400	47	72	110
2	SCC450	49	89	120
3	SCC500	54	95	144
4	SCC400NS2%	47	128	402
5	SCC450NS2%	53	162	423
6	SCC500NS2%	77	223	478
7	SCC400SF10%	44	121	313
8	SCC450SF10%	49	151	388
9	SCC500SF10%	73	211	541
10	SCC400SF10NS2%	89	157	437
11	SCC450SF10NS2%	95	216	523
12	SCC500SF10NS2%	125	320	589

Table 8 Results of electrical resistivity for different mixtures.

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