



SULFATE AND CHLORIDE RESISTANCE OF NANOSILICA AND MICROSILICA CONTAINED SELF-CONSOLIDATING CONCRETES

Ikbal N. Gorgis¹, Ali A. Jaber² and Maan S. Hassan³

¹ Civil Engineering Department, University of Technology (10066), Baghdad, Iraq.
Email: 40020@uotechnology.edu.iq

² Civil Engineering Department, University of Technology (10066), Baghdad, Iraq.
Email:

³ Civil Engineering Department, University of Technology (10066), Baghdad, Iraq.
Email: maan_s_h@yahoo.co.uk

<http://dx.doi.org/10.30572/2018/kje/090403>

ABSTRACT

This comparison study focuses on the impacts of using nano-silica (nS) on chemical attack resistance of self-consolidating concrete (SCC) and its effectiveness in comparison to similar replacement levels of the more widely employed micro-silica (mS). Two types of cement were used to produce concrete mixes and three different percentages (3, 4.5, and 6 %) of nanosilica and microsilica were added as a replacement of cement by weight. Concrete specimens were cast and exposed to four harmful conditions including: sulfate solution, chloride solution and both of them for a period of up to 400 days.

Based on the obtained results, replacement with colloidal nS proved to be significantly more effective in the chemical resistance than equivalent replacement of dry powder mS. The noticed improvements in chloride resistance and chloride penetration performance for concretes contained nS was correlated with the compressive strength results, which indicates for better pore structure characteristics. As expected, the improvement in the chemical resistance was more pronounced in concretes with cement type V.

KEYWORDS: Durability, Nanosilica, Microsilica, SCC, Cement type, Chloride attack, Sulfate attack

1. INTRODUCTION

Self-consolidating concrete (SCC) was developed to obtain durable concrete structures due to increased homogeneity. The flow behavior is obtained by using superplasticizers and high amount of fine particles then the pore structure of SCC differs from the pore structure of traditional concrete. SCC is characterized by the ability to compact itself by means of its own weight and without any need for vibration. SCC is being used increasingly in all elements of construction and civil engineering structures, such as substructures, infrastructure, and industrial floors that are regularly subjected to aggressive environmental conditions (Uysal et al., 2012; Leemann et al., 2010; Bassuoni and Nehdi, 2009).

Nano technology in the recent years has drawn many attentions of researchers and scientists, and that is because it uses nanoparticles and because of its unique physical and chemical characteristics (Ali et al., 2017). There has been a surge of interest in nanomaterials and their potential applications in producing high performance, sustainable, and durable concrete. The high pozzolanic reactivity is due to its high surface area. Nanosilica (nS) is commercially available in various nano-scale sizes depending on the method of synthesis and may be offered in a dry powder form or in a dispersant stabilized suspension (Batilov, 2016; Maan et al., 2006; Abdulkareem et al., 2016).

Concrete can be deteriorated for several reasons, and sulfate attack is reported to be a major contributor to concrete premature failure (Maes and De Belie, 2014). Sulfates can come from inner and a variety of outer sources, such as soils, groundwater, seawater, sewer pipes, organic materials in marshes, and mining pits. Sulfates are found in different forms including magnesium, sodium, calcium, potassium, and ammonium sulfate (Mathis, 1996). Due to its large presence of sodium sulfate attack (Na_2SO_4) in the soils and ground waters, it may be classified as one of the aggressive natural threats to concrete structures (Persson, 2003; Girardi et al., 2010; Geso\u015fl\u00fcglu et al., 2009). ACI Building Code 318-14 classified sodium sulfate as a very severe attack (A C I, 2015).

Calcium aluminates (C3A) and Portlandite are considered one of the most oversensitive hydration products that are attacked by from sodium sulfate. Sodium sulfate reacts with calcium hydroxide to form gypsum. Anhydrous or residual of calcium aluminates are rapid participates to formation of secondary ettringite which leads to the formation of very fine crystals with volume about (3–8) times the initial volume of the solid (Bonen, 1993).

Sulfate attack is a slow acting deteriorative phenomenon that can result in formation of ettringite, which can cause expansion, cracking, spalling, increased permeability, paste- to-

aggregate bond loss, paste softening, strength loss, and ultimately progressive failure of concrete (Marchand et al., 2003).

Concrete structures can also be exposed to chloride ions in addition to sulfate, particularly in structures near the sea, in arid areas or where sodium chloride is used as a de-icing salt during wintertime. Pore structure of concrete is the most effect of the electrical resistivity and chloride penetration in concrete mixes. A denser microstructure could provide higher electrical and chloride resistances for concrete. Enhancement to the electrical resistivity and resistance against chloride penetration can be achieved with pozzolanic admixtures like silica fume, which could provide a denser, more discontinuous, and tortuous microstructure (Neville, 1995).

Sulfate and chloride ions can be very harmful for the durability of concrete structures. Chlorides affect durability by initiating corrosion, it is important to notice that corrosion will only be initiated by the free chlorides and not by the fraction that is chemically bound to the cement hydrates or physically adsorbed at the pore walls. So chemical binding can also occur between chlorides and tetra calcium aluminoferrite (C4AF). Besides, the physical binding occurs due to interaction with calcium silicate hydrate (C-S-H) (Glasser et al., 2008).

Protection against chloride diffusion and sulfate attack requires improving the concrete microstructure and permeability reduction. Therefore, the addition of nanosilica to concrete can consume the crystals of calcium hydroxide, reduce the crystals size at the interfacial transition zone (ITZ), transmute the calcium hydroxide feeble crystals to C-S-H crystals, and improve the ITZ and cement paste structures (Nasution, 2015).

This research work is trying to provide valuable data concerning nanosilica and microsilica effects on the chemical resistance of SCC against sulfate, chloride, or both ions exposure conditions. The findings of this research work can provide an insight into an alternative mineral admixture for improving durability characteristics of SCC. This recognition may then improve its industrial application and being cost effective. Two cement types having normal and low tricalcium aluminate (C3A) content were used for producing SCC mixes.

2. EXPERIMENTAL PROGRAM

2.1. Materials

Two cement types were used, ordinary Portland cement (Type I) with moderate C₃A content (7.95%) and sulfate resisting Portland cement (Type V) with a low C₃A content (2.09%). Both types are commercial Iraqi cement and were conformed to the Iraqi Specification No.

5/1984 (COSQC Iraq, 1984) and ASTM C150/C150M-15 (ASTM C150/C150M, 2015). The chemical composition and physical properties of the two cement types are presented in Table 1.

Table 1. Chemical and physical properties of cement and admixtures.

Oxides	Chemical composition (%)				
	Cement (Type I)	Cement (Type V)	Limestone powder	Microsilica (mS)	Nanosilica (nS)
Chemical composition					
SiO ₂	21.93	21.95	1.02	95.14	30.1
Al ₂ O ₃	4.98	3.76	0.61	0.71	---
CaO	66.11	63.32	65.32	0.92	---
Fe ₂ O ₃	3.10	4.66	0.32	0.46	---
MgO	2.00	2.15	0.31	---	---
SO ₃	2.25	1.10	0.12	0.95	---
Loss on ignition (L.O.I)	2.39	1.93	31.5	1.41	---
Lime saturation factor (L.S.F)	0.93	0.85		---	---
Insoluble material	1.29	0.49		---	---
Physical properties					
Surface area (cm ² /g)	3760	3400	3900	20750	50000
Specific gravity	3.12	3.08	2.7	2.2	1.204
Bogue equations					
Dicalcium silicate (C ₂ S), %	19.14	20.90			
Tricalcium silicate (C ₃ S), %	58.10	55.83			
Tricalcium aluminate (C ₃ A), %	7.95	2.09			
Tetracalcium aluminoferrite (C ₄ AF), %	9.42	14.20			

Two types of silica were considered, microsilica (mS) MEYCO MS 610 supplied by BASF and meets ASTM C 1240-15 (ASTM C1240, 2015), with SiO₂ content > 90% and density of 2.2 g/cm³. Colloidal nanosilica (nS) produced by Jinan Yinfeng Silicon Products Company, with SiO₂ content > 90%, density 1.204 g/cm³, slight blue and transparency and pH value of 9.55 (see Table 1).

Local natural fine aggregate (FA) and crushed coarse aggregate (CA) with a maximum size 12.5 mm were used; they were within the requirements of the Iraqi Specification No. 45/1984 (COSQC Iraq, 1984) and also conform to ASTM C33/C33M-13 (ASTM C33/C33M, 2013). The bulk density and specific gravity were 1670 kg/m³ and 2.65 for FA, 1685 kg/m³ and 2.63 for CA, respectively.

A limestone powder (LP) was applied as filler for all mixes of SCC with constant amount of 100 kg/m³ as shown in Table 1. Superplasticizer (SP) a unique polycarboxylic ether was added to adjust the mixes workability of the SCC, with specific gravity of 1.07, and long lateral chains. It conforms to the requirements of ASTM C494/C494-15 Type F (ASTM C494/C494M, 2015).

2.2. Mixture Characteristics

The ACI 237R-07 procedure (S.-C. Concrete, 2007) was followed to design the mixes of SCC. It provides a guideline for proportioning mixtures and the batches were prepared as trials mixes, then adjust the optimum proportions to conform the fresh and hardened properties of the standard specifications. The proportions mixes used in this study are kept constant, and the mS or nS contents were changed only as a replacement by cement weight.

A control concrete without incorporating any pozzolanic material was cast for comparison purposes; details of mixtures are presented in Table 2. It should be noted that the water content of the nanosilica hydrosols, the silica fume slurry, and the superplasticizer were considered as part of mix water. The workability of all concrete mixtures was kept constant in the slump range 695-740 mm. The difference in water demand of various mixes was accounted by the use of required amounts of the superplasticizer. SCC mixes were prepared accordingly and mixed for 5 min in total by using a pan mixer of 90 L capacity, following the mixing procedure recommended by (S.-C. Concrete, 2007) and explained in (Daczko, 2012).

The concrete mixtures were prepared at a water/powder ratio of 0.38 and cementitious materials content of 400 kg/m³. The replacement levels of cement by the solid content of nS and mS were 3, 4.5, and 6%. Higher replacement levels were not considered because of the significant increase in superplasticizer demand to achieve similar workability levels for the mixtures. After casting, the specimens (cubes and cylinder) were covered to minimize water evaporation, then demolded after 48h and cured in a water tank following ASTM C 192M-15 standard (ASTM C494/C494M, 2015) for 28 days. After that the specimens were divided into

four parts to be cured with water; sulfate solution tank; chloride solution tank; and combined solution sulfate and chloride until the age of testing (75, 150, 225, 300 and 400 days).

Table 2. Mixture proportions of the SCCs mix.

Mix design	Cement kg/m ³	mS kg/m ³	nS kg/m ³	FA kg/m ³	CA kg/m ³	LP kg/m ³	Water L/m ³	SP L/m ³	W/C em	W/P
SCC Ref. I	400	0	0	850	850	100	152	○	0.38	0.3
SCC 3% mSI	388	12	0	850	850	100	152	5.4	0.38	0.3
SCC 4.5 % mSI	382	18	0	850	850	100	152	5.8	0.38	0.3
SCC 6% mSI	376	24	0	850	850	100	152	6.4	0.38	0.3
SCC 3% nSI	388	0	12	850	850	100	152	11.82	0.38	0.3
SCC 4.5 % nSI	382	0	18	850	850	100	152	15.21	0.38	0.3
SCC 6% nSI	376	0	24	850	850	100	152	18.74	0.38	0.3
SCC Ref. V	400	0	0	850	850	100	152	○	0.38	0.3
SCC 3% mSV	388	12	0	850	850	100	152	5.4	0.38	0.3
SCC 4.5% mSV	382	18	0	850	850	100	152	5.8	0.38	0.3
SCC 6% mSV	376	24	0	850	850	100	152	6.4	0.38	0.3
SCC 3% nSV	388	0	12	850	850	100	152	11.82	0.38	0.3
SCC 4.5% nSV	382	0	18	850	850	100	152	15.21	0.38	0.3
SCC 6% nSV	376	0	24	850	850	100	152	18.74	0.38	0.3

2.3. Exposure conditions

The specimens were divided into four groups after 28 days' water curing; the first one was immersed in tap water tank until the age of testing. The second group was immersed in 5 % of sodium sulfate (Na_2SO_4) solution which is prepared according to ASTM C1012-13 ([Mortar et al., 2013](#)); each liter of the solution contains 50 gm of Na_2SO_4 dissolved in 900 mL of water, and then it was diluted with additional distilled or deionized water to obtain 1.0 L of solution. The solution mixed on the day before using, covering, and storing at 23.0 ± 2.0 °C. The pH value of the Na_2SO_4 solution ranges between (6 –8) and must be checked each week where it needs large amounts of Na_2SO_4 . Mehta ([Mehta et al., 1974](#)) recommended adding a suitable amount of sulfuric acid (0.1N H_2SO_4) to control the pH value of the solution. The correction by sulfuric acid solution was done daily during the first weeks of immersion, after that it became weekly in the rest of the test. The Na_2SO_4 solutions were totally renewed for every 8 weeks.

The third group was immersed in combined solution of 0.6 % Na_2SO_4 and 0.5 % sodium chloride (NaCl). According to [Abdalkader et al., 2015](#), specimens immersed in combined solutions which showed higher deterioration in concrete. And the last group was immersed in

a severe case of 6 % NaCl that was prepared according to ASTM C1202-12 (ASTM C1202 et al., 2012).

3. EXPERIMENTAL WORKS AND TEST RESULTS

3.1. Fresh properties

Fresh state of concrete, such as filling ability, viscosity, and passing ability were conducted by using slump flow and T50 cm, V-Funnel and V-Funnel at T5 minutes, J-Ring, and L-Box tests according to relevant ASTM standard and European Federation of National Associations (EFNARC) for SCC specifications (Daczko , 2012; EFNARC, 2005).

Using the provided materials, fourteen SCC mixes were casted according to the mix proportions listed in Table 2, and the results of fresh properties are presented in Table 3.

3.2. Hardened properties

3.2.1. Compressive strength

The test was conducted according to British specification 1881: Part 116, 1989 (BS Institutions, 1989) as well as ASTM C192/C192M-11 (ASTM C496/C496M-1, 2011) for standard cubes samples of (100) mm side length, were used. An electrical testing machine with 2000 kN capacity was used for testing cubes, and the average of three samples were used for each mix.

3.2.2. Splitting tensile strength

The test was conducted on the samples according to ASTM C 496M/496M -11 (ASTM C496/C496M, 2011). Samples of (100 mm diameter × 200 mm height) mm cylinders were used, and the average of two samples were used for each mix.

Table 3. Fresh properties of SCCs mix.

Mix design	Properties				
	Slump flow (mm)	Flow time (s)	V-funnel (s)	J-ring (mm)	L-box (H ₂ /H ₁)
SCC Ref. I	740	3.5	8.0	695	0.95
SCC 3% mSI	717	3.6	8.5	703	0.94
SCC 4.5 % mSI	710	3.2	9.0	696	0.93
SCC 6% mSI	705	2.9	9.4	702	0.91
SCC 3% nSI	705	3.2	8.7	710	0.93
SCC 4.5 % nSI	700	2.9	9.3	698	0.92

SCC 6% nSI	695	3.5	9.8	716	0.90
SCC Ref. V	735	3.4	8.2	704	0.94
SCC 3% mSV	720	3.2	8.8	720	0.93
SCC 4.5% mSV	710	2.9	9.0	713	0.92
SCC 6% mSV	706	3.0	9.2	699	0.90
SCC 3% nSV	710	3.3	9.0	717	0.92
SCC 4.5% nSV	705	3.5	9.3	722	0.91
SCC 6% nSV	700	2.8	9.7	690	0.89

3.2.3. Mass loss

Three cubic specimens (100 mm) from each SCCs were weighed after the 28 days moist curing and recorded as reference of zero reading (M_o). Then the specimens were exposed to three types of curing to water; sulfate solution; and combined sulfate and chloride solution until the age of testing.

The cumulative mass change (Mct) for each specimen was calculated as follows:

$$Mct\% = \left[\frac{M_o - M_i}{M_o} \right] \times 100 \quad 1$$

where M_o is the initial mass at 28 days (zero reading) before exposure to sulfate or combined solution (kg), and M_i ($i = 75, 150, 225, 300$ and 400) is the mass after i days of exposure to sulfate or combined solution (kg).

3.2.4. Expansion of the specimens (Dimensional variation)

The length changes of the samples carried out according to ASTM C490/C490M-11 ([S. Practice, 2014](#)) by using prism samples with (285×75×75) mm size to measure the expansion of the specimens immersed in sodium sulfate solution (5%) and in fresh water. The average of two prisms was adopted at age of tests.

3.2.5. Electrical resistivity

The electrical resistivity of SCC was measured by using AC current according to the Swedish national testing and research institute procedure ([Tang et al., 2005](#)), and the average of three standard cubic specimens (100 mm) from each SCCs were used.

3.2.6. Chloride resistance and chloride concentration test

This test method covers the determination of the electrical conductance of concrete to provide a rapid indication of its resistance to the penetration of chloride ions. In this study, the

procedure carried out by ASTM C1202-12 ([ASTM Standard, 2012](#)) was followed to measure the chloride resistance of concrete at 56 days. According to [Quercia et al, 2014](#), chloride diffusion test became more reliable for SCC with nano-silica addition compared with other chloride migration tests. Two concrete discs of 50 mm thick were cut from the middle of one cylinder of 200 mm height and 100 mm diameter, by using diamond saw. The surface of the discs was first dried (left for two hours in air), then the surround surface for each disc (but not the ends) was painted with acrylic coating and left for one day in air to dry. After that discs were vacuumed into desiccator for 3-hrs, and then water was allowed to drain until full immersion is achieved and left for 24-hrs. The specimens were then moved to the testing cell, which is filled with (0.3 M NaOH) solution for the positive side and (3% NaCl) solution for the negative side of the equipment power supply. The test was started by applying 60 V DC between the cells and continued for a period of 6-hrs, during that measuring the total charge passed in coulombs which represent the concrete resistance to chloride ion penetration. The average of three specimens for chloride diffusion test was used (concrete cubes with 150 mm size are made and immersed in chloride solution). Powder collected from concrete specimens at age of 400 days is used to measure chloride ions concentration (acid chlorides) according to BS 1881- Part 124 ([BS 1881- Part 124, 1988](#)). Concrete powder is obtained by drilling 20 mm diameter holes using drilling hammer machine after removing the first 5 mm depth. Concrete powder for each mix is collected from three depths of cube surface as: 5-15 mm (10 mm average), 15-25 mm (20 mm average), and 30-40 mm (35 mm average). Then the powder is mixed together to prepare one sample to measure the chloride content at Kufa University Labs.

4. RESULTS AND DISCUSSION

4.1. Expansion of SCCs due to sulfate

Expansion of the control SCC mixtures made without addition of any nano- or micro- silica is shown in [Fig. 1](#). The observed expansion behavior of the control mixtures SCC-Ref I and SCC-Ref V made with type I and type V Portland cements, respectively, revealed that concrete contained low (C3A) performed better than concrete with higher (C3A) contents. Overtime, the observed difference in the expansion between the two control concrete was widened. This indicates that, with progressively longer exposure time to sulfate solution, the beneficial effects of type V cement with low (C3A) content became more significant. At earlier ages, however, both of the control concrete exhibit similar (during the first month) or convergent (during the latter two months) behavior. Because of the similar constituents of the

two control concretes, a reasonable suggestion that surface absorption and permeability of the concrete were the key properties to control the rate of expansion during the early period. At this stage no sulfate ion has penetrated through enough of the cement paste to react with the C3A reserved. With a progressively longer exposure period to the sulfate ion, the aggressive solution ingress deeper into the concretes and started to react progressively with the abundant mono-sulfate, calcium, and sulfate ions, and the difference between the two concrete become more apparent. The percentages of expansion of SCC-Ref I was 40% and 77.1% more than that of SCC-Ref V at age of 75 and 400 days of sulfate solution exposure, respectively.

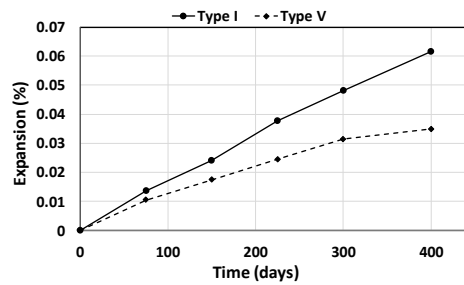


Fig. 1. Control mixture expansion.

4.2. Effect of nanosilica versus microsilica

Fig. 2 presents the development of expansion of the SCCs made with type I (Fig. 2a) or type V cements (Fig. 2b) and contained different nS and mS replacement levels. As shown, the increases in the concentration of nS and mS led to clear expansion behavior improvements of the tested concretes. Overtime, the improvement increased. In the case of nS, the 225-day expansion of the concretes having 3, 4.5, and 6% nS replacement levels were 5.2, 13.15, and 23.6% less than that of the control concretes SCC-Ref I, respectively. At 13.3 months (400-day), the expansion of the concretes having similar nS replacement levels were 9.6, 19.3, and 29.03 less than the control SCC-Ref I, respectively. For SCCs made with type V cement, similar trends were observed. This implies that there were continuous improvements associated with increasing the replacement levels.

Furthermore, up to the 300 days' period, higher concentration of nS replacement concrete made with type I exhibited less expansion than their lower replacement counterparts of nS concrete and also less than their counterparts of mS concretes. Following the 300 days, this behavior reversed, and concrete with mS started to outperform their counterparts of concrete with nS, as evident in Fig. 6a. In the case of SCCs made with type V, the expansion behavior remained in the same order for the whole 400 days. This behavior suggests that the long term

beneficial effects of using nS with SCCs are more pronounced in concretes made with Type V cement.

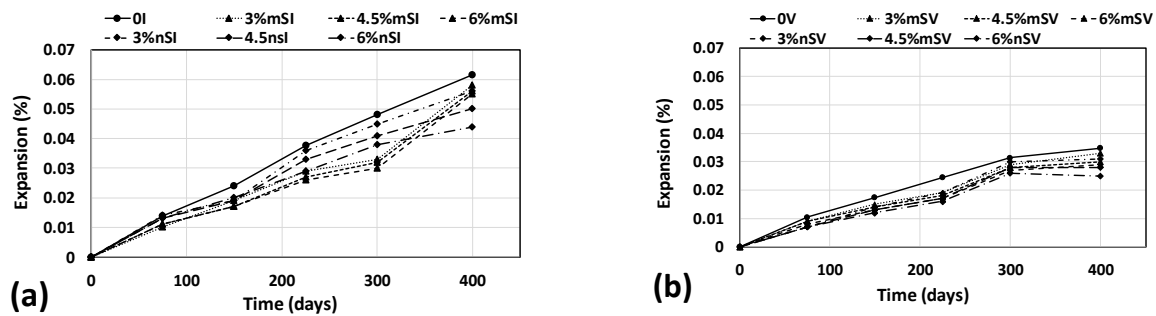


Fig. 2. Mixture series expansion with mS and nS replacement, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

4.3. Electrical resistivity results

The electrical resistivity results with a duration up to 400 days of exposure to sulfate solution, chloride solution, or both of them are presented in Figs. 3 to 5. In general, cement type is seemed to have no impact on the electrical resistance of the tested SCCs. The electrical resistivity behavior of the SCCs made with type I cements, Figs. 3a, 4a, and 5a, convergent with their counterpart's concretes made with type V, as presented in Figs. 3b, 4b, and 5b, respectively. This behavior is consistent for all of the three exposure conditions used.

Unlike that, the increases in the concentration of nS and mS led to clear electrical resistivity improvements of the tested concretes. Overtime, the improvement increased. For instance, the 400-day resistivity of the concretes exposed to sulfate solution and having 6% nS or mS replacement levels were up to 27.6% or 16.4 % less than that of concretes contained 3% nS or mS, respectively. This implies that there was continuous electrical resistivity improvement associated with increasing the replacement levels.

In the case of concretes subjected to chloride environments (Fig. 9), the electrical resistivity behavior showed similar trend to that of sulfate solution with respect to the effect of different replacement level of both nS and mS. However, the rates of resistivity increase with time and were lower than that in concrete subjected to sulfate solutions. Furthermore, with time, the observed differences in the electrical resistivity between the two concrete made with type I and type V cement were maintained at the same amount. This indicates that, with progressively longer exposure time to chloride ions, the differences in C3A content effects have no impact on the resistivity of SCC.

The combined effect of chloride and sulfate ions presented in Fig. 8 indicate that the level of resistivity recorded with time were little higher than that recorded for concrete subjected to chloride ions only, but lower than sulfate solution specimens. Possible explanation of this result is that mixing the two chemical solutions led to reduce the deterioration effects of chloride solutions on the concrete resistivity.

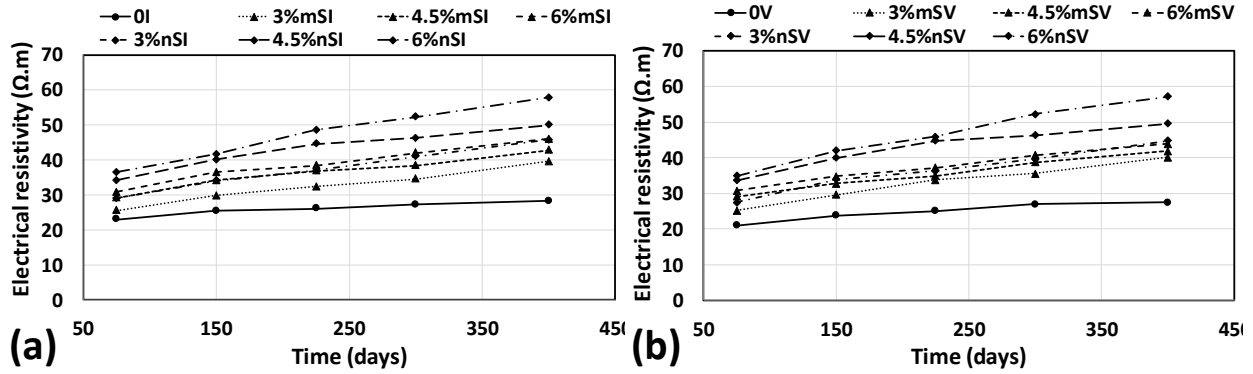


Fig. 3. Electrical resistivity values of SCCs containing mS and nS immersed in sulfate solution, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

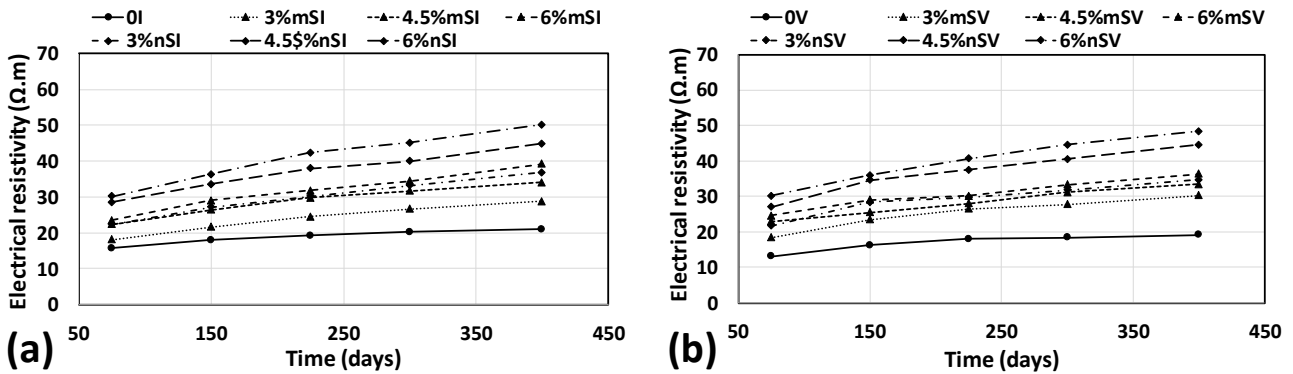


Fig. 4. Electrical resistivity values of SCCs containing mS and nS immersed in sulfate and chloride solution, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

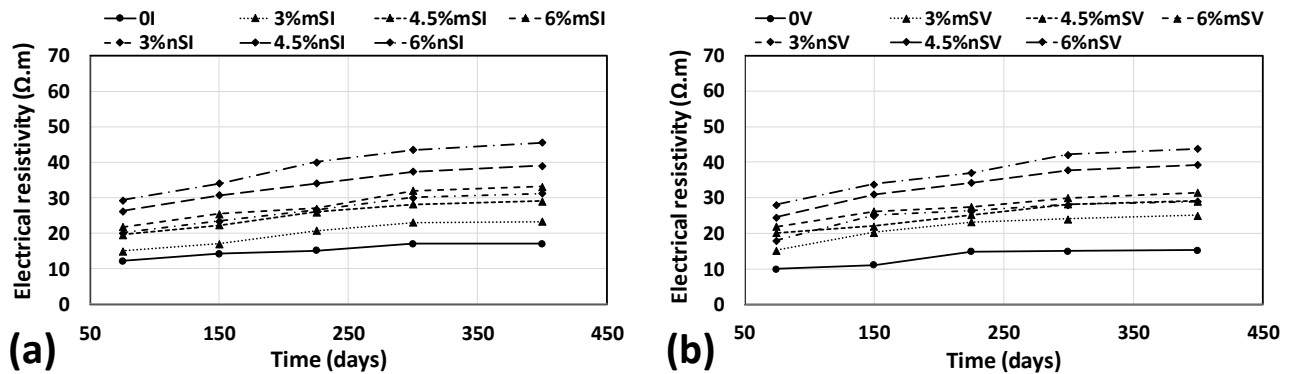


Fig. 5. Electrical resistivity values of SCCs containing mS and nS immersed in chloride solution, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

4.4. Compressive and tensile strengths loss

The compressive strength measurements at the 75-, 150-, 225-, 300- and 400-day ages involved testing three cubes of the sulfate exposed and three cubes of the water-cured SCCs for each type of cement. Results are potted in Figs. 6 to 10. Up to 400-day period of testing in this study; there was no definite evidence that strength loss attributed to sulfate attack occurred throughout this period. This is because almost all sulfate solution concrete showed a consistently higher increase in strength in comparison to the water-cured counterparts. Possible explanation to this trend is the effect of filling and compaction of the sulfate attack related expansive compound ettringite (Ghafoori et al., 2014). It is expected that with time and upon a longer time of continuous exposure to sulfate solution, losses in compressive strength could be developed and observed. Furthermore, the low w/c ratio and the high powder content (cement, silica, and limestone %) implemented in this study, resulted in generally less permeable SCCs where the sulfate solution could not successfully deteriorate the paste adequately enough to demonstrate strength loss effect in the 400-day period of test.

The splitting tensile strength measurements at the 75-, 150-, 225-, 300- and 400-day ages involved testing two cylinders of the sulfate exposed and two cylinders of the water-cured SCCs for each type of cement. Results are potted in Figs. 11 to 15. The results revealed that, in the case of SCCs modified with nS, there was no definite evidence that strength loss attributed to sulfate attack occurred throughout the 400-day period. This trend is similar to that of compressive strength loss behavior, which confirms the ability of nS in improving the effect of filling and compaction of the sulfate attack related expansive compound ettringite. In the case of mS, all sulfate solution concrete made with type I cement showed a comparable strength in comparison to the water-cured counterparts (Figs. 6a, 7a, 8a, 9a, and 10a).

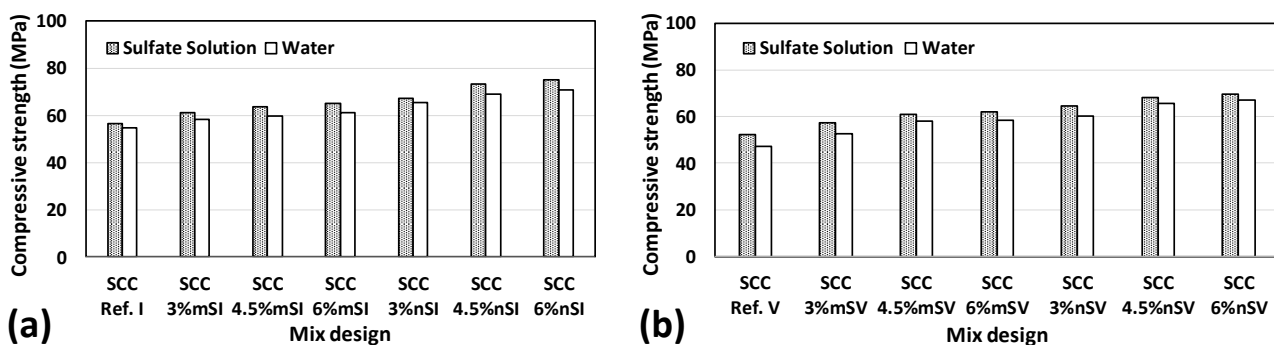


Fig. 6. Effect of sulfate on compressive strength at 75 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

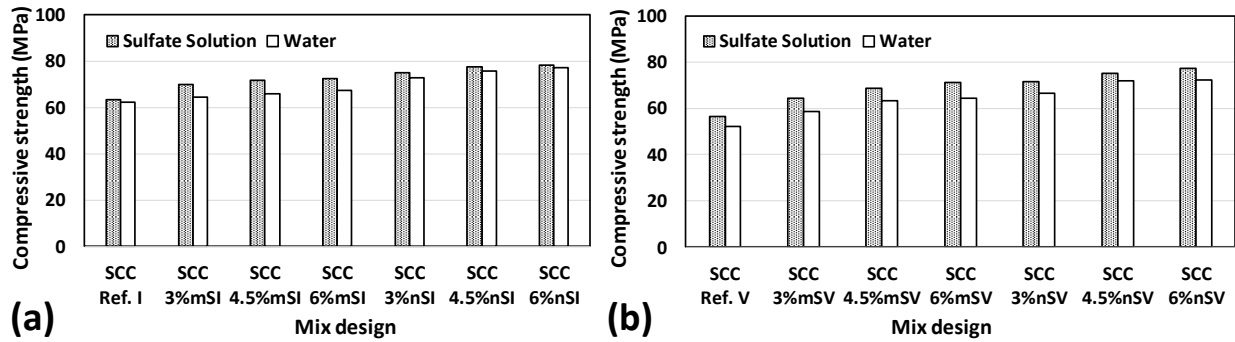


Fig. 7. Effect of sulfate on compressive strength at 150 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

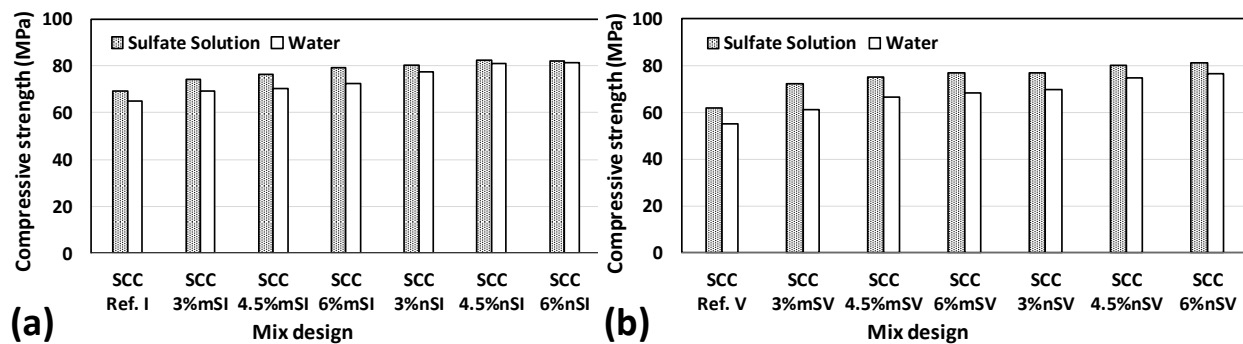


Fig. 8. Effect of sulfate on compressive strength at 225 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

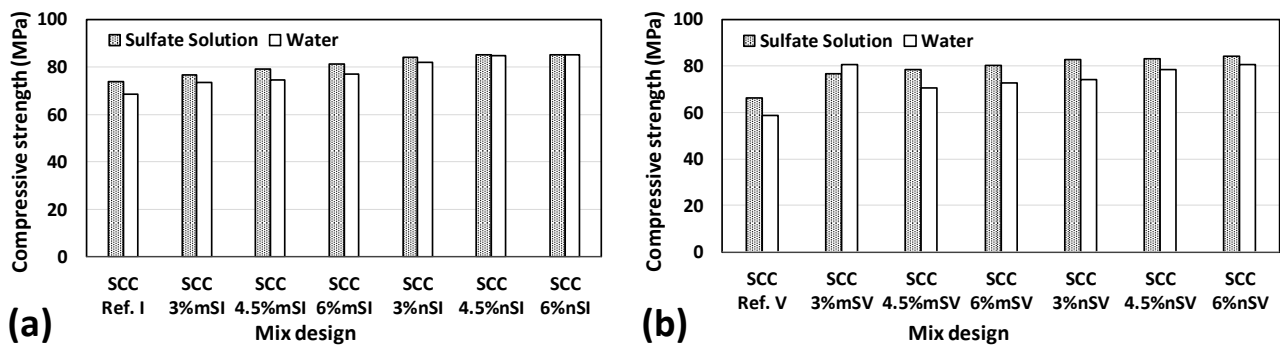


Fig. 9. Effect of sulfate on compressive strength at 300 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

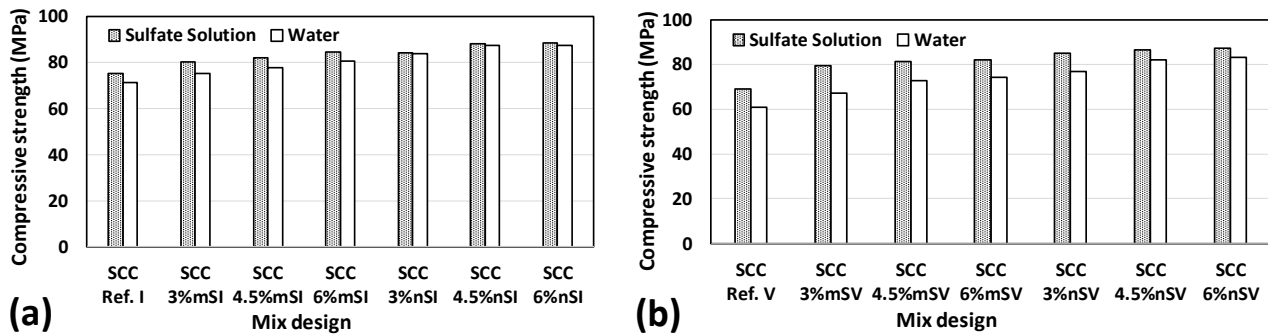


Fig. 10. Effect of sulfate on compressive strength at 400 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

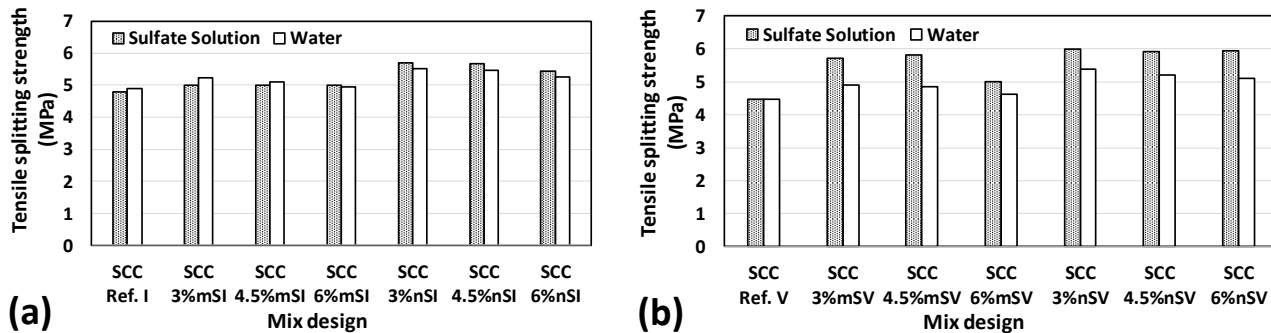


Fig. 11. Effect of sulfate on tensile splitting strength at 75 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

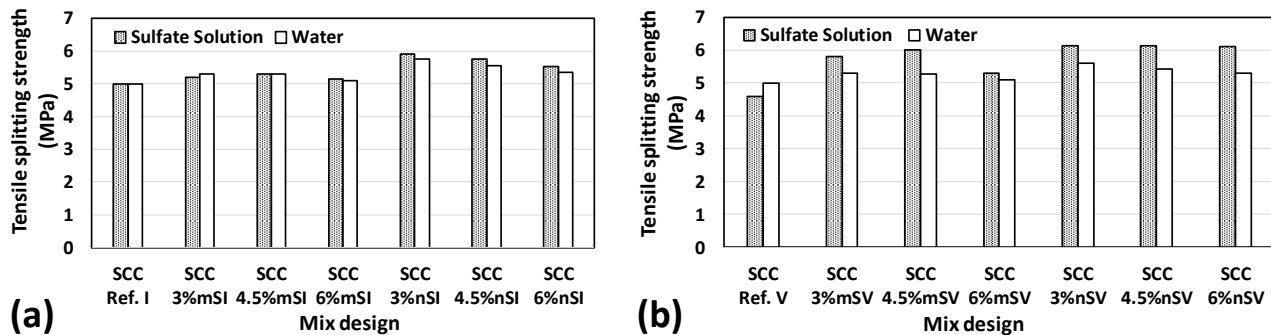


Fig. 12. Effect of sulfate on tensile splitting strength at 150 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

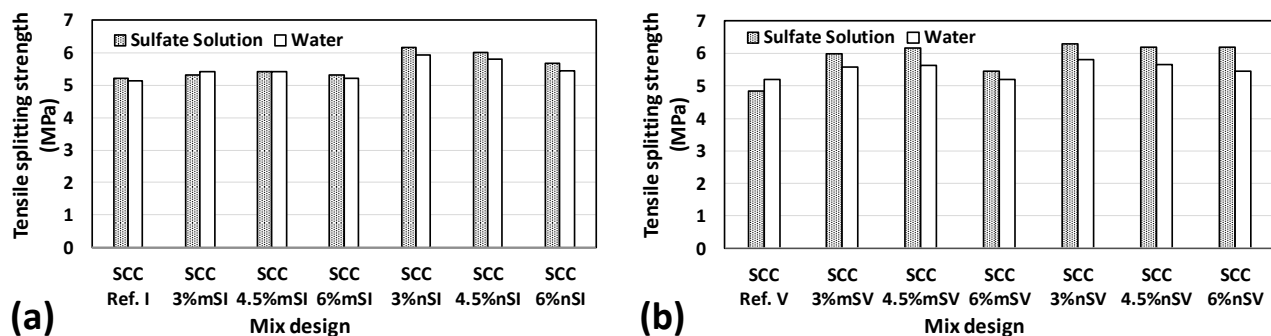


Fig. 13. Effect of sulfate on tensile splitting strength at 225 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

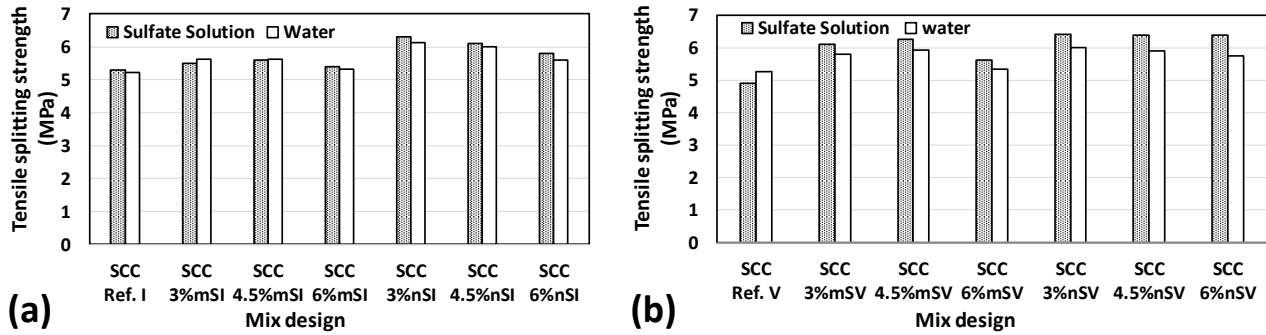


Fig. 14. Effect of sulfate on tensile splitting strength at 300 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

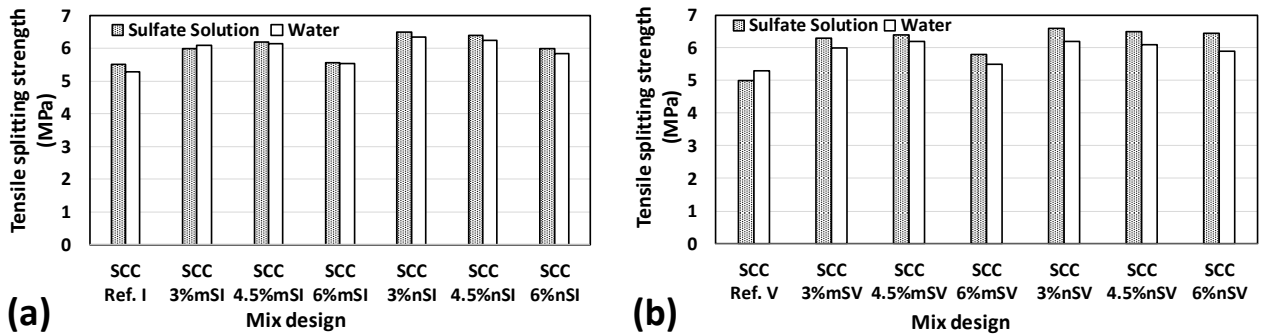


Fig. 15. Effect of sulfate on tensile splitting strength at 400 days for SCCs with, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

4.5. Mass loss

Two concrete cubes from each mixture were weighed at the 75-, 150-, 225-, 300- and 400-days ages of the sulfate exposed and water-cured SCCs for each type of cement. Results are potted in Figs. 16 and 17. Specimens were exposed to an isolated container of 5% sodium sulfate solution for the test period to observe and measure any mass loss that could occur due to chemical sulfate attack. At the end of the 400-day test, there was no significant mass loss for any of the SCCs made with type V cement. In contrast, there was some observable mass loss of the SCCs made with type I cement. However, no localized cracking or surface flaws in the control, mS-, and nS-contained cubes were appeared even after 400 days (as shown in Fig. 18). In general, the low C3A concrete and those with nS replacement exhibited less mass lose and had better appearance.

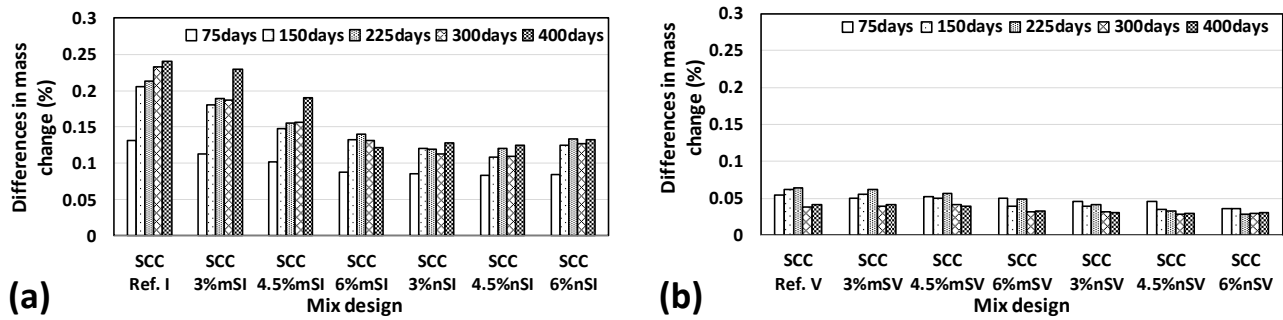


Fig. 16. Differences in mass change between results of sulfate solution with water, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

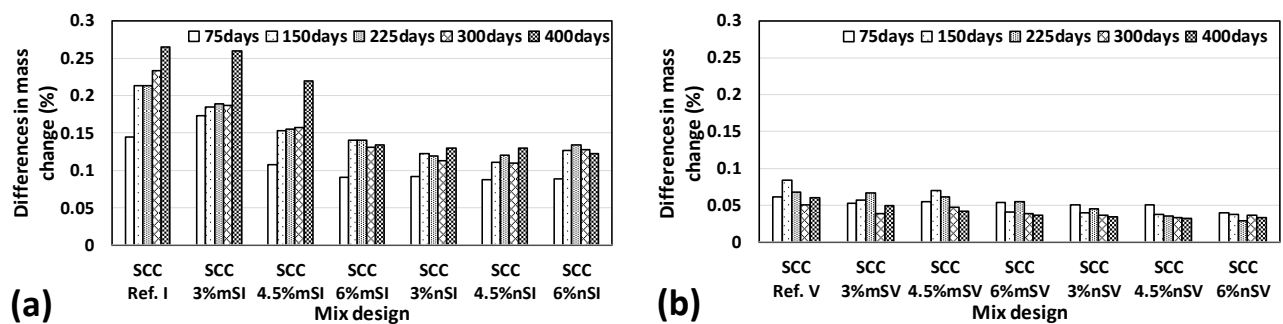


Fig. 17. Differences in mass change between results of sulfate and chloride solution with water, (a) ordinary Portland cement and (b) Sulfate Resistance cement.

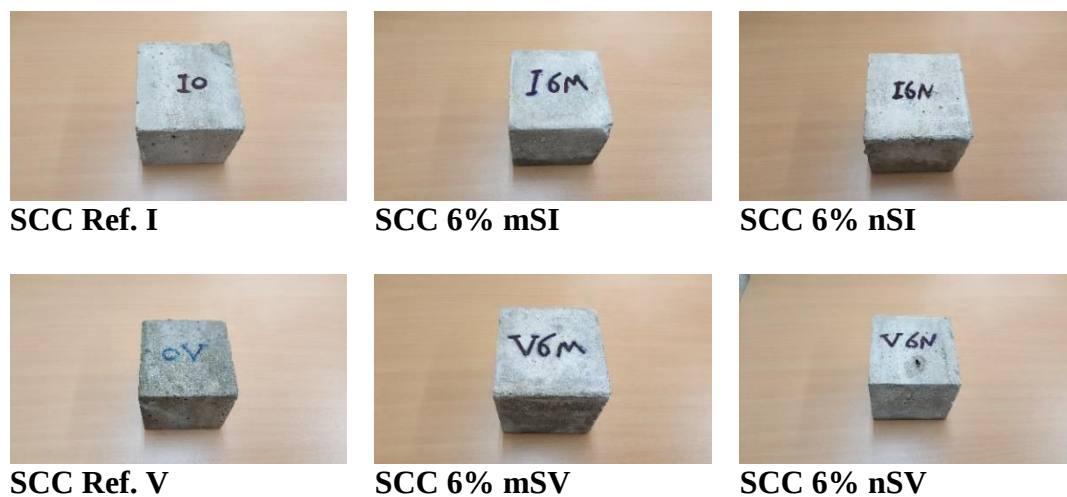


Fig. 18. Type V versus type I cement SCCs cubes after 400 days of exposure to Na_2SO_4 solution.

4.6. Chloride ions concentration

The chloride content (acid soluble) of SCCs containing mS and nS as a replacement of cement weight at 400 days are shown in Fig. 19. Chloride contents for all mixes were determined at

three levels drilled from 150 mm cubes specimens. The levels were 10, 20, and 30 mm depth, and the powder was collected and mixed together to prepare one sample, and then to measure the chloride content at Kufa University Labs. Fig. 19 indicates that nS has a clear enhancement in chloride penetration effect as compared with SCCs containing mS, and this is due to the improvement of the microstructure of the mix containing nS, which reduces the porosity of concrete and prevents the inner of the chloride solution. Besides, the cement type V has a good resistance to chloride penetration as shown in Fig. 19 b; this behavior could be due to the differences in the chemical compositions between the two types of cement used particularly with the same C_3A contents.

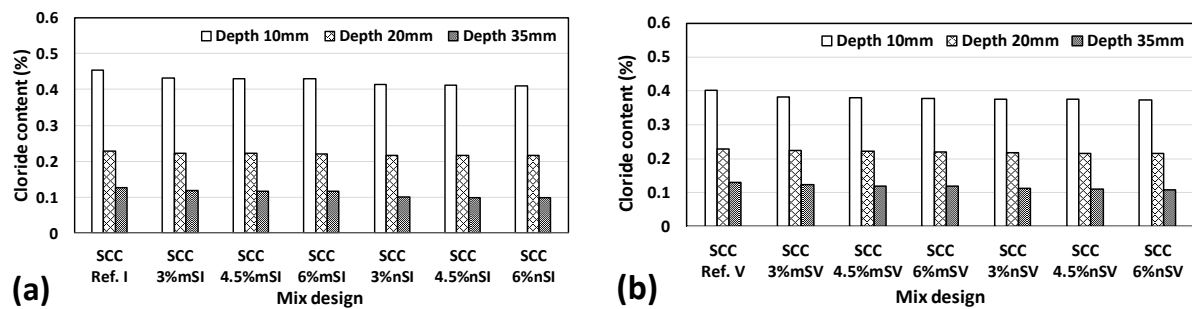


Fig. 19. Chloride ions concentration at difference depth in SCCs.

5. CONCLUSIONS

Based on the experimental results of SCCs containing nS and mS before and after exposure to chemical attack and regression analysis that were presented in this study, the following conclusions can be drawn.

1. Concrete with low (C_3A) content has a better sulfate resistance than concrete with higher (C_3A) contents. Overtime, the observed difference in the expansion between the two control concrete was widened. This indicates that with progressively longer exposure time to sulfate solution, the beneficial effects of type V cement with low (C_3A) content became more significant. Because of the similar constituents of the two control concrete, a reasonable suggestion that surface absorption and permeability of the concrete were the key properties to control the rate of expansion during the early period.
2. The Use of nS and mS reduced the expansion of SCCs made with both low- and moderate- C_3A cement. The spread in expansion for all nS and mS replacements for both cement is relatively increased, indicating that there was continuous improvements associated with increasing the replacement levels.

3. The Use of nS and mS improved the electrical resistivity of the tested concrete. The 400-day resistivity of the concrete exposed to sulfate solution and having 6% nS or mS replacement levels was up to 27.6% or 16.4 % less than that of concretes contained 3% nS or mS, respectively. This behavior was consistence regardless the type of exposure condition used.
4. Up to 400-day period of testing in this study, there was no definite evidence that strength loss attributed to sulfate attack occurred throughout this period. This is because almost all sulfate solution concrete showed a consistently higher increase in strength in comparison to the water-cured counterparts. Possible explanation to this trend is the effect of filling and compaction of the sulfate attack related expansive compound ettringite.
5. There was no significant mass loss for any of the SCCs made with type V cement at the end of the 400 days and had better appearance. In contrast, there was some observable mass loss of the SCCs made with type I cement.
6. Nanosilica had a clear enhancement in chloride penetration effect as compared with SCCs containing mS, and cement type V had better resistance to chloride penetration than cement type I.

6. REFERENCES

- Uysal, M., Yilmaz, K., and Ipek, M., "The effect of mineral admixtures on mechanical properties, chloride ion permeability and impermeability of self-compacting concrete," *Constr. Build. Mater.*, vol. 27, no. 1, pp. 263–270, 2012.
- Leemann, A., Loser, R., and Münch, B., "Influence of cement type on ITZ porosity and chloride resistance of self-compacting concrete," *Cem. Concr. Compos.*, vol. 32, no. 2, pp. 116–120, 2010.
- Bassuoni, M. T. and Nehdi, M. L., "Durability of self-consolidating concrete to sulfate attack under combined cyclic environments and flexural loading," *Cem. Concr. Res.*, vol. 39, no. 3, pp. 206–226, 2009.
- Jaber, A. A., Gorgis, I. N. and Hassan, M. S., "Relationship between Splitting Tensile and Compressive Strengths for SCC Containing Nano- and Micro silica," *Int. Conf. Build. Constr. enviromental Eng.*, 2017.
- Batilov, I. B., "Sulfate Resistance of Nanosilica Contained Portland Cement Mortars" no. December, 2016.

- Hassan, M. S., Gorgis, I. N. and Jaber, A. A., 2006, "Fresh and hardened properties of nanosilica and microsilica contained self-consolidating concretes," *ARPJ. Eng. Appl. Sci.*, vol. Vol.12, No.
- Abdulkareem, R. T., Hassan, M. S., and Gorgis, I. N., "Effect of Steel Fibers, Polypropylene Fibers and/ or Nanosilica on Mechanical Properties of Self-Consolidating Concrete," *Eng. & Tech. Journal*, vol. 34, no. 3, pp. 527–538, 2016.
- Maes, M. and De Belie, N. "Cement & Concrete Composites Resistance of concrete and mortar against combined attack of chloride and sodium sulphate," *Cem. Concr. Compos.*, vol. 53, pp. 59–72, 2014.
- Mathis, R. P. "Freezing and thawing, deicing salt, and sulfate resistance of concrete pavers," Southern Illinois University at Carbondale, 1996.
- Persson, B. "Sulphate resistance of self-compacting concrete," *Cem. Concr. Res.*, vol. 33, no. 12, pp. 1933–1938, 2003.
- Girardi, F., Vaona, W. and Di Maggio, R. "Resistance of different types of concretes to cyclic sulfuric acid and sodium sulfate attack," *Cem. Concr. Compos.*, vol. 32, no. 8, pp. 595–602, 2010.
- Gesoglu, M., Güneyisi, E. and Özbay, E. "Properties of self-compacting concretes made with binary, ternary, and quaternary cementitious blends of fly ash, blast furnace slag, and silica fume," *Constr. Build. Mater.*, vol. 23, no. 5, pp. 1847–1854, 2009.
- ACI C. 318, "Building Code Requirements for Structural Concrete (ACI 318-14): An ACI Standard: Commentary on Building Code Requirements for Structural Concrete (ACI 318R-14), an ACI Report," 2015.
- Bonen, D. "A microstructural study of the effect produced by magnesium sulfate on plain and silica fume-bearing Portland cement mortars," *Cem. Concr. Res.*, vol. 23, no. 3, pp. 541–553, 1993.
- Marchand, J. Odler, I. and Skalny, J. P. *Sulfate attack on concrete*. CRC Press, 2003.
- Neville, A. "Chloride attack of reinforced concrete: an overview," *Mater. Struct.*, vol. 28, no. 2, p. 63, 1995.
- Glasser, F. Marchand, P. J. and Samson, E. "Durability of concrete degradation phenomena involving detrimental chemical reactions," *Cem. Concr. Res.*, vol. 38, no. 2, pp. 226–246, 2008.
- Nasution, A., Imran, I., and Abdullah, M., "Improvement of Concrete Durability by Nanomaterials," *Procedia Eng.*, vol. 125, pp. 608–612, 2015.
- COSQC Iraq, "Standard Specification for Portland Cement," Iraqi Specif. No. 5, 1984.

- ASTM C150/C150M-15, "Standard Specification for Portland Cement," ASTM Int. West Conshohocken, PA, vol. 04.01, p. 7, 2015.
- ASTM C1240-15, "Standard Specification for Silica Fume Used in Cementitious Mixtures," ASTM Int. West Conshohocken, PA, vol. 04.02, p. 9, 2015.
- COSQC Iraq, "Standard Specification for Concrete Aggregates," Iraqi Specif. No. 45, 1984.
- ASTM C33/C33M-13, "Standard Specification for Concrete Aggregates," ASTM Int. West Conshohocken, PA, vol. 04.02, p. 11, 2013.
- ASTM C494/C494M-15, "Standard Specification for Chemical Admixtures for Concrete," ASTM Int. West Conshohocken, PA, vol. 04.02, p. 10, 2015.
- S.-C. Concrete, "ACI 237R-07," Am. Concr. Inst. Farmingt. Hills, MI, USA, 2007.
- Daczko, J. A. "Self-consolidating concrete: applying what we know". CRC Press, 2012.
- Mortar, H., Specimens, C., Mortars, C., Cabinets, M., Rooms, M. and Curing, A. "Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a," pp. 1–8.
- Mehta, P. K. "Evaluation of Sulfate Resisting Cements by a New Test Method.," 1974.
- Abdalkader, A. H. M. C., Lynsdale, J. and Cripps, J. C. "The effect of chloride on cement mortar subjected to sulfate exposure at low temperature," Constr. Build. Mater., vol. 78, pp. 102–111, 2015.
- ASTM C1202 - 12, "Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration," ASTM Int., pp. 1–8, 2012.
- EFNARC, "The European Guidelines for Self Compacting Concrete, Specification, Production and Use," Eur. Proj. group, <http://www.efnarc.org>, May, 2005.
- B. S. Institutions, "Method for determination of compressive strength of concrete cubes," London BS, 1889.
- ASTM C496/C496M-11, "Standard Test Method for Splitting Tensile Strength for Cylindrical Concrete Specimens," ASTM Int. West Conshohocken, PA, vol. 04.02, p. 5, 2011.
- ASTM C496/C496M, "Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens," Am. Soc. Test. Mater., pp. 1–5, 2011.
- Practice, S. "Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste , Mortar , and Concrete 1," vol. i, pp. 1–5, 2014.
- Tang, L. and others, "Guideline for practical use of methods for testing the resistance of concrete to chloride ingress," Chlortest Rep., 2005.
- A. Standard and others, "Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration," West Conshohocken, PA ASTM Int., 2012.

Quercia, G., Spiesz, P., Hüsken, G. and Brouwers, H. J. H. “SCC modification by use of amorphous nano-silica,” *Cem. Concr. Compos.*, vol. 45, pp. 69–81, Jan. 2014.

BS 1881- Part 124, “Testing Concrete - Part 124: Methods for Analysis of Hardened Concrete,” *Br. Stand.*, 1988.

Ghafoori, N. I., Batilov, B. and Najimi, M. “Sulfate Resistance of Nanosilica and Microsilica Contained Mortars,” no. 113, 2016.