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Effect of Nanosilica on the Sulfate Attack Resistivity of Cement Mortar

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ABSTRACT

The effect of nanosilica on the sulfate attack resistivity of cement mortar was investigated through study on the mechanical property evolution and the length change of the cement mortar under 5 wt.% sodium sulfate for 6 months. Meanwhile, the effects were compared with those of fly ash-replacement mortar. Results showed that by taking the advantages of nanosilica and fly ash in improving the property of cement mortar at early and later ages, the sulfate attack resistance of cement mortar can be enhanced in mechanical property increase and expansion reduction. Further, it implies that a combination of both pozzolans could enhance the sulfate attack resistivity of cement-based materials.

Keywords: nanosilica, sulfate attack, fly ash, mortar.

1.0 INTRODUCTION

Sulfate attack (ST) is one of the most-widely concerned issues of cement-based materials under service (Liu and Zhang, 2017. Piasta, 2017). It is normally accepted that concrete in harsh environment, such as salt-soil (Benavente and Cura, 2001), marine environment (Kwon and Lee, 2017), can potentially get corroded from external sulfates through its attack on the calcium hydroxide (Najjar and Soliman, 2017), the C-S-H gel (Santhanam and Cohen, 2002 and 2003), forming expansive ettringite (Song and Jiang, 2016), gypsum (Tian and Cohen, 2016), thaumasite (Rahman and Bassuoni, 2014), silica gel (Santhanam and Cohen, 2002 and 2003), and finally leading to the failure of the microstructure and cracking of the macrostructure.

To improve the ST resistivity, application of supplementary cementitious materials (SCMs, such as fly ash, blast furnace steel slag, silica fume, pozzolans) has been widely used (Benli and Karatas, 2017. Zhutovsky and Hooton, 2017. Zeli and Krstulovi, 1999. Sokkary and Assal, 2004. Sharma and Arora, 2018). It is normally accepted that SCMs not only replace/reduce the content of tricalcium aluminate, the most ST-prone component in concrete, but more importantly change the most easily attacked CH into additional C-S-H gel through its pozzolanic reactivity, leading to a densified microstructure and reduced sulfate ion penetration capability (Weerdt and Haha, 2011. Chen and Gao, 2017). It is the standard practice of using SCM of preparing concrete for harsh environment use.

More recently, application of nanomaterials into cement-based materials has aroused great interests to make a stronger, a less permeable, and more durable concrete (18-21 Jalal and Pouladkhan, 2015. Sanchez and Sobolev, 2010. Bastos and Barbeito, 2016. Rupasinghe and Nicolas, 2017). It is quite acceptable that a small amount of Nano particle would make a big difference (19, 21-23 Sanchez and Sobolev, 2010. Rupasinghe and Nicolas, 2017. Zhang and Cheng, 2015. Hou and Cheng, 2015). Among all the nanoparticles that can be potentially used in concrete in a big scale, nanosilica is the most promising one due to its fine particle size, high pozzolanic reactivity and relatively easier manufacturing processes. It is reported that nanosilica can beneficially consume 50% of calcium hydroxide at a dosage of 3 wt% of cement, and it can densify the porous structure of hardened cement concrete (Hou and Cheng, 2015), the generation of C-S-H through its reaction with calcium hydroxide [Hou and Qian, 2015], and modification of the C-S-H gel to a more sulfate-attack resistive one.

In this work, the performance of ST resistivity of nanosilica-modified cement mortar was studied through investigations on the strength development and expansion characteristics of the sample cured under 5 wt.% sodium solution to a period as long as 180 days. During this study, a comparison study was conducted between fly ash-modified mortars.

2.0 MATERIALS AND METHODS

2.1 Materials

In this study, Nanosilica, fly ash (type F) and OPC 42.5 (PI, Chinese standard GB 8076-2008) were used. Table 1 reports the chemical compositions of these materials. The particle size distribution and SEM image of these materials were presented in Figs. 1 and 2.

It shows that OPC and fly ash disperse in a broad size range from 0.1 micron to about 100 microns, while nanosilica is in a narrow size range with a mean size of 85 nanometers. SEM images show the same characteristics of the size distribution.

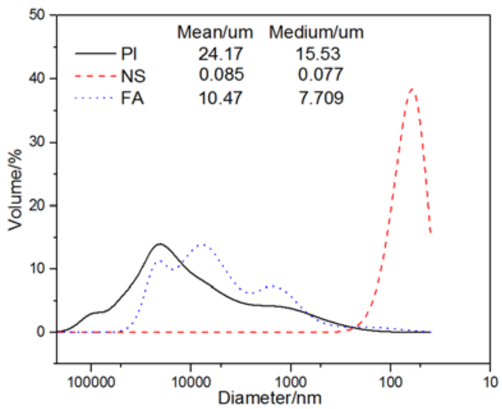
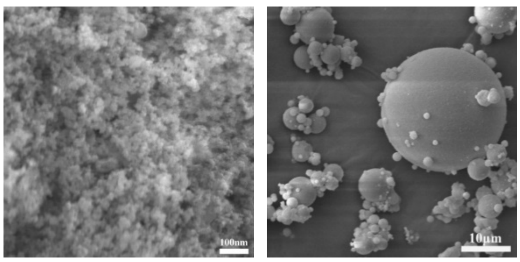


Fig.1. Particle size distributions of cement, nanosilica and fly ash

Table 1. Chemical compositions of cement, nanosilica and fly ash (wt. %)

composition	PI	Fly ash	Nanosilica
CaO	63.00	4.00	-
SiO_2	19.09	50.04	⩾98.00
Al_2O_3	4.09	35.21	-
SO_3	3.65	1.52	-
Fe_2O_3	3.20	5.38	-
MgO	2.27	0.54	-
LOI	4.70	3.31	-



(a) (b)

Fig. 2. SEM images of (a) nanosilica; (b) fly ash

2.2 Methods

<u>Sample Preparation</u>

The 7 days and 28 days old cement mortar samples (40×40×160mm for strength test and 25×25×285mm for the length change test) with w/c=0.35 and binder-to-sand ratio of 3 were used in this study, replacement of cement with 1, 3% of nanosilica, and 10, 30% of fly ash were conducted and the sample proportions are given in Table 2. Standard sand (GB/T 17671-1999) was used for preparing cement mortar. All samples were cured for 1 day at the ambient environment (ca. 25°C/50% RH) before demolding. After demolding, the samples were cured in standard curing chamber (22°C/95% RH) for 7 days and 28 days before moving into saturated lime solution (C Ref) and 5 wt.% Na_2SO_4 solution at 20ºC until the test (7, 28, 90, 180 days) (To simulate the circumstances of the young and old ages of samples when been attacked, in this work, mortar samples of 7 and 28 days were used for ST tests). During the experiments, the Na_2SO_4 solution was renewed after 1, 2, 3, 4, 8, 13, and 15 weeks and 4, 6 months.

Table 2. Mix proportions of mortars

Samples	Water-to-binder ratio	Cement (by mass %)	Nano silica (by mass %)	Fly ash (by mass %)
C	0.35	100	-	-
NS1	0.35	99	1	-
NS3	0.35	97	3	-
FA10	0.35	90	-	10
FA30	0.35	70	-	30

<u>Flexural and Compressive Strength</u>

Flexural and compressive strength of samples were tested and the strength ratio was calculated (Eq. 1) to show relationship of the sulfate attack resistance between different samples.

Strength ratio = (CRef/NS/SF sample strength)/(C sample strength)×100 (1)

The average value of three samples was used for the determination of flexural strength values, and six measurements were used for compressive strength values.

<u>Length Change</u>

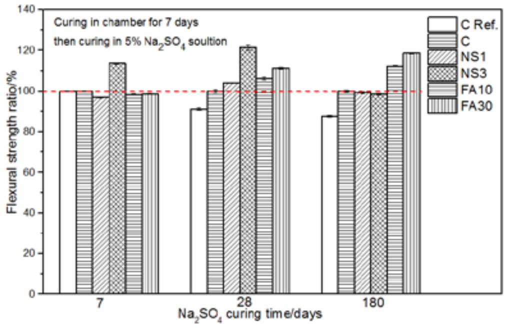
The length change of mortar was measured with 25×25×285mm cement samples. The test procedure was described in ASTM C1012/C1012M-15. All samples were immersed in 5 wt.% Na_2SO_4 and sulfate solution was also renewed by after 1, 2, 3, 4, 8, 13, and 15 weeks and 4 and 6 months.

3.0 RESULTS AND DISCUSSIONS

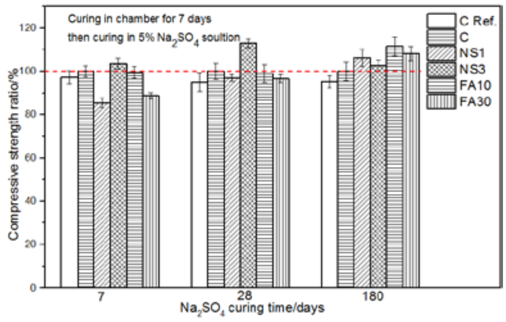
The flexural and compressive strength of the 7-day cured sample in standard curing chamber and then in sodium solution for different ages are shown in Fig. 3 and those of the 28-day curing samples are shown in Fig. 4.

From Fig. 3 it can be seen that the immersion of the 7-day old sample in Na_2SO_4 shows a comparable or even higher flexural/compressive strength than those cured in lime solution (C ref.), and this could be due to the activation effect of the sodium sulfate on cement hydration.

For the NS and FA replacement mortar, it can be seen that different effects are seen. It is obvious to see in Fig 3 (a) that NS3 samples shows 18% and 22% increase of flexural strength after curing in 5 wt.% Na_2SO_4 for 7 and 28 days, the same trend is seen in the compressive strength plot. It also shows that NS1 has no significant effect on flexural strength at 7 and 28 days. For fly ash replacement cement mortar, comparable flexural strength is seen after 7 days curing, but higher values (8% and 12% at 28 days) are seen after 28 days curing, showing he beneficial effect on sulfate attack resistivity. When comparing the effects of NS and fly ash, it can be sees that 3% of NS shows better effect than 30% of fly ash.



(a)



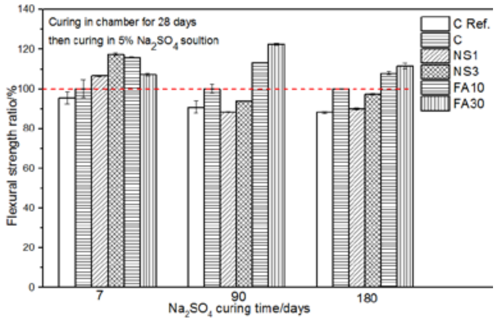
(b)

Fig.3. Flexural and compressive strength of cement mortar samples cured for 7 days and then cured in 5 wt.% Na_2SO_4 solution for certain days (a) Flexural strength; (b) compressive strength

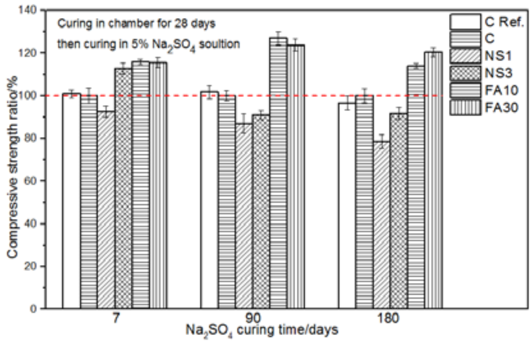
After 180 days curing, it can be seen that a comparable flexural strength is seen in NS-added mortar to those of control, but increases are seen in the FA-replacement mortar (12% and 19% at 180 days). When comparing the compressive strength at 180 days, it shows that both nanosilica and fly ash improve the compressive strength ratio, showing their benefits in enhancing the ST resistivity of cement mortar.

The flexural and compressive strength of samples cured for 28 days before curing in 5% Na_2SO_4 solution were showed in Fig 4. It can be seen that at 7 days, NS sample exhibits higher flexural strength (19%) than the control and the FA sample and the compressive strength of NS sample was similar with FA sample.

With the increase of the immerse time, NS sample revealed lower flexural and compressive strength compared with the control and the FA-added samples at 90 and 180 days, which shows that NS could only beneficially increase the mechanical property of cement mortar of old age at the early ST period. The reasons are unknown yet and obviously needs more work.



(a)

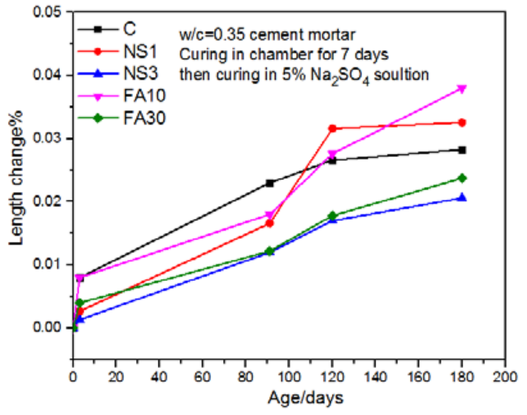


(b)

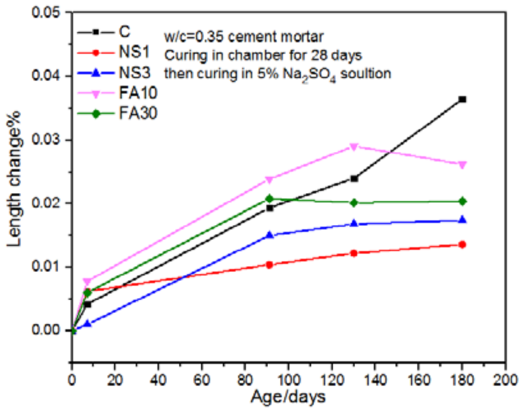
Fig.4. Flexural and compressive strength of cement mortar samples cured for 28 days and then cured in 5 wt.% Na_2SO_4 solution for certain days (a) Flexural strength; (b) compressive strength

FA samples showed 15%/25% and 10%/15% increase of flexural strength and 30%/25% and 15%/20% increase of compressive strength. It can be conclude from Fig 4 (a) and Fig 4 (b) that the Nano silica can effective improved the mechanical property and the sulfate attack resistance at early ages, but fly ash can be beneficial for later ages.

The length change of cement mortar samples cured in 5% Na_2SO_4 is shown in Fig.5. When samples immersed in Na_2SO_4 solution at 7 days age, the NS3 and FA30 sample revealed better effect to reduce the length change, but the reduction of NS1 and FA10 sample is inferior to NS3 and FA30, it is also inferior to control sample after 120 days soaking. Nanosilica and fly ash can significant reduce the expansion of cement mortar in sulfate attack at early age. The reduction of calcium hydroxide content in the fly ash/nanosilica-added mortars could lead to a lesser formation of expansive agents, thus a reduced expansion can be resulted. A greater reduction seen in the higher pozzolan replacement mixture shows the basic requirement for decreasing expansion.



(a)



(b)

Fig.5. Length change of cement mortar samples cured for 7/28 days and then cured in 5% Na_2SO_4 solution for certain days

After 28 days curing, NS samples exhibit great benefits in reducing expansion in Na_2SO_4 solution. Meanwhile, fly ash does not show beneficial effect in reducing expansion effect before 90 days ST. after about 4 months, all samples show beneficial effects in reducing expansion after ST, and 1% and 3% NS could reduce the expansion to as mu as 50% than that of the control sample.

4.0 CONCLUSIONS

In this study, the effect of nanosilica and fly ash on the strength and length change of cement mortar exposed to sulfate attack was investigated and compared. It can be concluded that:

- Nanosilica can significantly improves the sulfate attack resistance cement mortar at early age (7 days). Flexural and compressive strength of nanosilica-added sample increase 25% and 20% compared to the control samples and reduced the length change to 0.02% when control sample showed a 0.028% length change. However, Nano silica exhibited a negative effect for later age strength gain (28 days) when cured in sulfate solution, even though it is beneficial to decrease the expansion.

- Samples with fly ash showed an obviously increased flexural and compressive strengths (about 25% and 30% respectively) for later age samples. 30% replacement of cement by fly ash effectively reduced the expansion of cement mortar in 5% Na_2SO_4 environment, but the use of fly ash also decreased the early strength of cement mortar in sulfate solution.

Thanks to the different effects of nanosilica and fly ash on early and late ages of cement mortar in sulfate attack, it is possible to greatly improve the sulfate attack resistance of early or late age cement-based materials when both Nano silica and fly ash are used together. This research is currently in progress.

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