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Properties of Nano-Silica Modified Self-Compacting High-Volume Fly Ash Mortar

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Abstract: The effects of adding Nano-Silica (NS) into self-compacting high volume fly ash mortar have been investigated. Five self-compacting mixtures with different NS percentage (0, 1, 2, 3 and 4%) were prepared, cast and tested for fresh properties and as well as for compressive strength, accessible porosity, Interfacial Transition Zone (ITZ) and drying shrinkage. NS addition up to 2% has been found to improve hardened paste properties. However, more then 2% of NS will lead to adverse effects.

Key words: Nano-silica, compressive strength, access porosity, drying shrinkage, interfacial transition, zone

INTRODUCTION

With the advent of nanotechnology in the construction industry, NS particles have been incorporated into Portland cement mortar and concrete to improve its hardened properties. Strength, durability, shrinkage and reinforcing steel-concrete bonding are known to be improved by the integration of NS to concrete (Hou *et al*., 2013). Taking advantage of the particle size in the range of 10-25 nm, NS has the tendency to fill up the nano voids in the hardened paste matrix of the mortar and the concrete. Also, densifying the Interfacial Transition Zone (ITZ) located between aggregate and hardened paste matrix. In addition, the pozzolanic property enables NS to utilise the calcium hydroxide produced during hydration process of cement to release more Calcium Silicate Hydrates (C-S-H) gel. These lead to modifying the micro-structure of the hardened cement paste which consequently improving the hardened properties of mortar and concrete (Hou *et al*., 2013; Mohammed *et al*., 2016a, b; Bjornstrom *et al*., 2004; Singh *et al*., 2013; Taengua *et al*., 2015; Jala *et al*., 2015; Mohammed *et al*., 2012; Zhang *et al*., 2015; Rong *et al*., 2015). Owing to the fine size and nucleation capability, NS have been employed to decrease setting time and increase early age strength in cement-fly ash concrete (Zhang and Islam, 2012). Fly Ash (FA) is a by-product, waste material from thermal electricity generating power plant. Due to its pozzolanic property and availability in large quantities as waste, FA has gained lots of patronage for use as a cement replacement materials (Mohammed and Fang, 2011). Fly ash particles, generally have a spherical shape, therefore, concrete containing fly ash exhibits improving workability and cohesive which in turn results in improving fresh and hardened properties of concrete (Kocak and Nas, 2014). The quest for sustainability and to minimise the cost of construction led to the development of Self-Compacting Concrete (SCC). Conversely to obtain appropriate self compactability, SCC requires suitable deformability and viscosity of the mortar and paste phases (Puthipad *et al*., 2016). Usually, attaining self-compactability of fresh concrete demands among other factors, limiting aggregates content and incorporating superplasticizer. Consequently, SCC requires higher cement content and superplasticizer in comparison to conventional concrete. This leads to higher cost and reduction in the sustainability of the SCC. Furthermore, utilising higher cement amount in the manufacture of SCC has a drawback in respect to shrinkage (Kristiawan and Aditya, 2015). Shrinkage is the contraction in the volume of concrete due to the withdrawal of water by evaporation or cement hydration. When in harden state, loss of capillary water from cement paste as a result of evaporation will lead to shrinkage. However, if evaporation is controlled, concrete can still be able to lose its capillary water owing to progressing of hydration. Both processes of shrinkage lead to volume changes which take place in the cement paste while aggregates restrain the volumetric changes. The ratio of aggregates and cement in SCC is low and high, respectively. This ratio will encourage a relatively greater shrinkage in SCC when likened to conventional concrete (Kristiawan and Aditya, 2015). Partial replacement of cement amount in SCC with FA will minimise shrinkage. This is due to the slow pozzolanic reactivity rate of FA at an early age. FA tend to slow down early strength development of the mortar and concrete which in turn, minimise shrinkage. Many studies have been conducted, suggesting ways to cater for this shortcoming of late

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strength development of the fly ash-cement system. Some of the ways are mechanical grinding, chemical activator and hydrothermal treatment (Paya *et al*., 2000; Criado *et al*., 2010; Goni *et al*., 2003). However, limited studies are available on the integration of NS in self-compacting high-volume FA mortar, especially, drying shrinkage behaviour. Hence, the key goal of the experimental work described in this study aims to examine shrinkage response of NS modified self-compacting high volume fly ash mortar.

MATERIALS AND METHODS

Experiment work

Raw materials: The chemical composition of Type 1 Portland cement and fly ash utilised in this study is presented in Table 1 (Mohammed *et al*., 2016a, b). The fly ash is Class F with calcium content <15% compliant to the specifications of ASTM C618. The locally available washed fine river sand having a specific gravity of 2.67 and sizes in the range of 250 μm and 1.18 mm. The NS properties are shown in Table 2. Portable tap water and a High Range Water Reducer (HRWR), polycarboxylate-based super plasticizer were used for mixing the ingredients.

Method of mixing: The fresh mortar was prepared as self-compacting with FA to Cement (C) ratio of 1.2. The FA to cement ratio of 1.2 is a typical ratio that has been used for cementitious composites in the literature to meet the requirement for high-volume fly ash consumption (Mohammed *et al*., 2016a, b) .The mixes proportions are presented in Table 3. The water-cement ratio of 0.32 was maintained for all mixes and HRWR used for adjusting flow spread to meet the requirement of self-compacting specified in.

Sample preparation and testing: Samples for compressive strength, Field Emission Scanning Electron Microscope (FESEM), shrinkage and Mercury Intrusion Porosimetry (MIP). Test standard the size of samples and number of samples are shown in Table 4. All mixtures were prepared as self-compacting mortars and are presented in Table 5 based on the specification of Efnarc.

Table 1: Components of cement and fly ash

Items	Cement (%)	Fly ash (%)
SiO_2	25.21	64.69
Al_2O_3	4.590	18.89
Fe_2O_3	2.990	4.900
CaO	62.85	5.980
MgO	1.700	1.990
Na_2O	0.980	2.410
K_2O	1.680	1.140
SO_3	0.230	0.310
Loss on ignition (%)	2.020	1.870
S.G	3.150	2.300
Blaine fineness (m^2/kg)	325	290

Table 2: Properties of nano-silica

Items	Quality
Appearance	High-dispersive white
Heat reduction (%) (105°C 2h)≤	3
Loss on ignition (%) (950°C 2h)≤	2
SiO_2 (%) dry base ≥	92
SiO_2 (%) 950°C 2h ≥	99.8
Carbon content (%)≥	0.3
Surface density (g/mL)≤	0.15
Specific surface (m^2/g) BET	100±25
Average particle size (nm)	10-25

Table 3: Mixture proportions

Mix ID	NS (wt. % of CM)	W/C	Water (kg/m^3)	Cement (kg/m^3)	Sand (kg/m^3)	Fly ash (kg/m^3)	HRWR (kg/m^3)
M1	0	0.32	187	583	467	700	8.2
M2	1	0.32	187	583	467	700	9.1
M3	2	0.32	187	583	467	700	9.8
M4	3	0.32	187	583	467	700	12.7
M5	4	0.32	187	583	467	700	14.5

Table 4: Test standard, size of samples and number of samples for hardened properties tests

Test	Standard	Size of sample (mm)	Number of samples
Compressive strength	ASTM C109/C109M	50×50×50	3
FESEM	-	15×15×5	1
MIP	-	10×10×5	1
Shrinkage	ASTM C157-08	25×25×285	3

Table 5: Testing requirements for SCC NS modified mortar

	Slump flow				V-funnel	L-box			
Mix ID	d_1 (mm)	d_2 (mm)	S (mm)	T_{50}	t_v (s)	H1 (mm)	H2 (mm)	H2/H1	VSI
M1	275	270	273	2	6	71	71	1.00	0
M2	273	272	273	2	7	71	70	0.99	0
M3	276	274	275	2	6	71	70	0.99	0
M4	269	267	268	3	6	72	69	0.96	0
M5	270	271	271	3	7	72	69	0.96	0

S = d_1+d_2/2 where, s is the slump spread measured to the nearest 5 mm

RESULTS AND DISCUSSION

Fresh properties: The fresh properties of mortar mixes are shown in Table 4. The slump flow, L-box and V-funnel were used to evaluate the filling ability, passing ability and segregation resistance, respectively, of the self-compacting mortars. All the mortar mixes after adjusting with the HRWR fulfilled the requirements for SCC as prescribed in. The slump spread and T_{50} time measured for all the mixes was in the range of 265- 275 mm and 2-5 sec, respectively in accordance with requirements for SCC. The L-box measures ratios of H_2 H_1 for all mixes between 0.8 and 1.0. Also, evaluated is the Visual Stability Index (VSI) for all mortar mixes based on ASTM C1611. The VSI of zero has been assigned to all mortar mixes.

Compressive strength: The compressive strength of hardened samples at age of 28 days are shown in Fig. 1. It can be observed that the compressive strength increases as NS percentage increase up to 2%. However, the compressive strength decreases as NS percentage >2% is used.

The increase in the compressive strength is ascribed to the filling capability of NS particles which can fill up the nano voids within the hardened cement paste resulting in the more compacted microstructure. In addition, the NS utilises the $Ca(OH)_2$ released during cement hydration to generate more C-S-H gel which is responsible for strength increase. However, the reduction in compressive strength of mortar at the dosage of 3 and 4% of NS content could be ascribed to the coagulation of NS particles. This causes difficulty in the uniform dispersion resulting from excess NS particles. The excess is generated probably due to non-availability of $Ca(OH)_2$ to promote further hydration for utilisation of NS particles. This probably resulted in non-dispersive and results in decreased strength of mortar. Furthermore, the excess HRWR employed to maintain self-compacting requirements creates air pore in the matrix which contributes to decreased strength as well.

Field Electron Scanning Microscopy (FESEM): Generally, there are three phases of material in a normal concrete, they are the aggregate, hardened cement paste matrix and

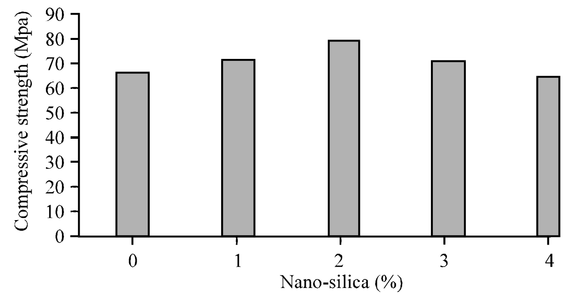

Fig. 1: Compressive strength of modified NS mortar

the Interfacial Transitional Zone (ITZ). Between the cement paste and the aggregate is a thin layer that bonds them which is referred the ITZ. This layer is usually porous due to the wall effect where water is restrained by cement particles from freely flowing and stagnate after hydration. This phenomenon encourages increased porosity of the ITZ and results in reduced strength. Though, the ITZ is influenced by other issues such as water-cement ratio, the texture of aggregate and size distribution of the aggregate. The target of this investigation was to explore the results of incorporation of NS in the high-volume fly ash mortar, therefore, other factors were maintained constant. In contrast to the normal concrete where the ITZ is considered and measured between coarse aggregate and cement matrix in the mortar which has fine aggregate, the ITZ between fine aggregate and cement matrix will be considered. For better understanding, the thickness of the ITZ measured between the fine aggregate and the cement matrix are supported with the results of the Mercury Intrusion Porosimetry (MIP). The images obtained by field electron scanning microscopy (FESEM) for the mortar mixes is presented in Fig. 2a-e. The measured average ITZ is as well shown in Fig. 3. Figure 2a-e, shows the thickness of the ITZ decreasing with increasing NS incorporation. This is as a result of the physical and chemical effects in which the ITZ is densified by the filling ability and the pozzolanic products of NS particles. The NS particles, due to their nano size fill up the nano-sized pores of the porous ITZ while the NS as well utilises the Calcium Hydroxide ($Ca(OH)_2$) released during cement hydration to

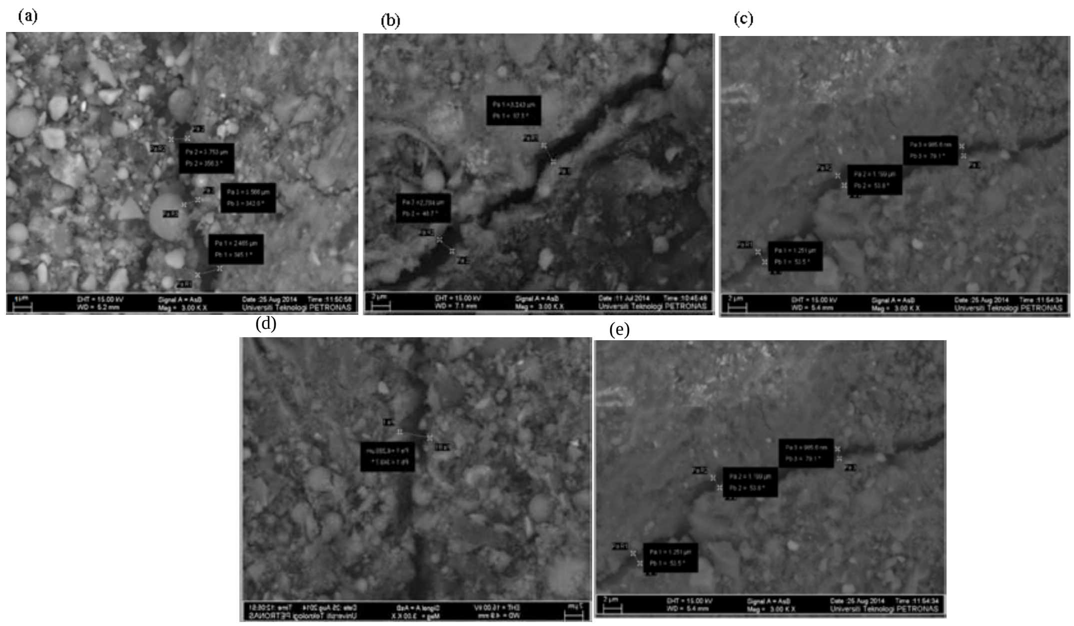

Fig. 2: FESEM of specimens with nano-silica percentages; a) 0%; b) 1%; c) 2%; d) 3%; e) 4%

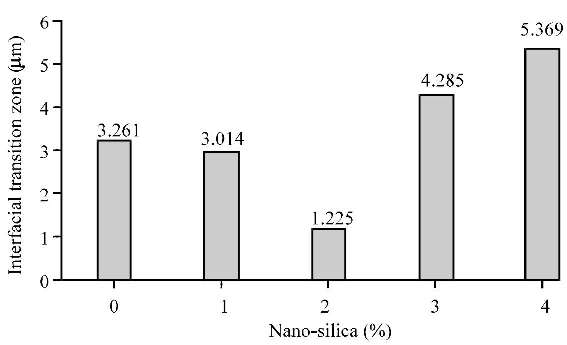

Fig. 3: ITZ versus NS incorporation

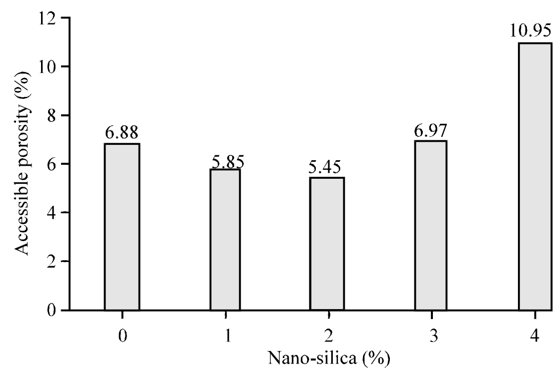

Fig. 4: Accessible porosity of NS modified mortar

further hydration. This leads to the reduced thickness of the ITZ. However, as shown in Fig. 2d and 2e as the quantity of NS increases, the thickness of the ITZ increases. This is due to the coagulation and non-dispersion of the NS particles. The excess NS particles exceeded the threshold for utilisation as filler and pozzolanic reaction. The excess NS coagulates and creates more porous pores which increase the thickness of ITZ.

Accessible porosity: The measured porosity decreases with the incorporation of NS particles. Nonetheless, the porosity increases as the percentage of NS increase >2% as shown in Fig. 8. This is in good agreement with the results of the compressive strength. This provides an evidence that excess amount of NS particles in the concrete mixes leads to produce more porous hardened paste due to the coagulation and non-uniform dispersion of NS particles. Non-uniform dispersion of NS has been assumed due to the observation during mixing procedure. Figure 4 (a-e), 9-11 shows the pore size distribution for high volume fly ash mortar control (0% nano-silica) and different percentage of NS incorporation (1 and 2%) (Fig. 5). With increasing NS amount, the total pore volume decreases. This is owing to the filling ability and pozzolanic involvement of NS particles. The average pore sizes range from 10-100000 nm. However, the pore size distribution with higher volume indicate mixes with higher porosity and permeability, since permeability is encouraged by greater capillaries (Li *et al*., 2016). While Fig. 4d and e show pore size distribution with increasing pore volume as NS percentage incorporation increases more then 2%. Also, the distribution of the pore

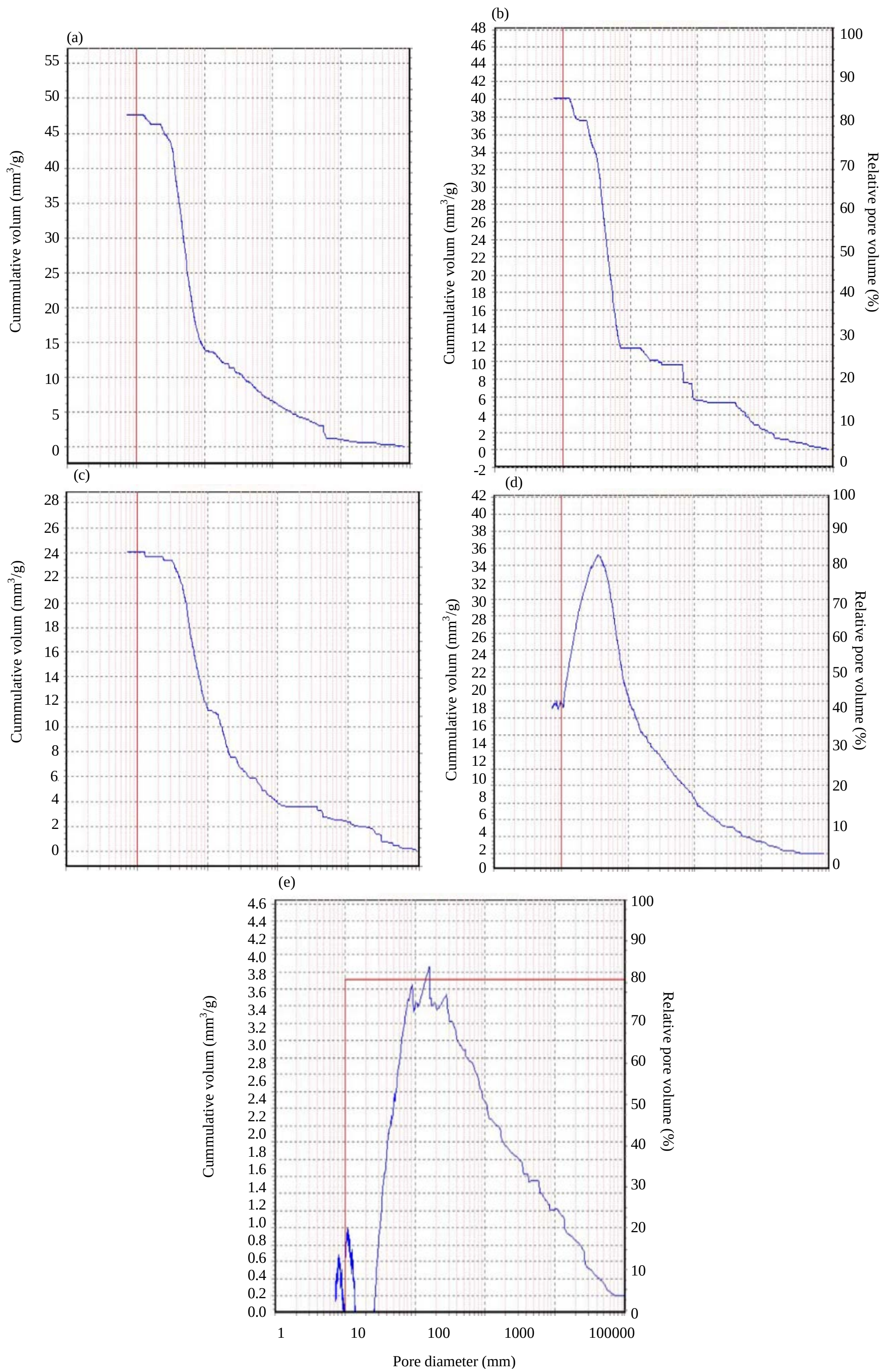

Fig. 4: Distribution of pore size in specimens with nano-silica at percentages; a) 0%; b) 1%; c) 2%; d) 3%; 4) 4%

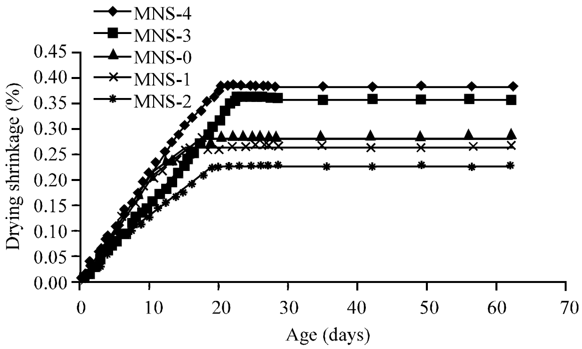

Fig. 5: Drying shrinkage of NS modified mortar

diameter is within the range of 10-100000 nm in size. This shows that the total pore volume increases as the incorporation of NS amount are more then 2%. This is because of the coagulating effect and non-uniform dispersion of excess NS amount. This leads to creating more pores, thus increasing the total pore volume (Li *et al*., 2016).

Shrinkage: Shrinkage in cement-based materials is largely due to loss of water in the hardened paste. The hardened paste is a conglomerate of C-S-H gel which upon loss of water generates tensile stresses responsible for shrinkage within the cement paste. The addition of NS particles encourages densification of the hardened paste through filling up the fine pores which lead to utilisation of the available water for further pozzolanic reaction to produce a more C-S-H gel. This process brings about reduced paste water and improved densification of the paste as well. The drying shrinkage was evaluated over a period of 62 days and is presented in Fig. 5. With up to 2% of NS particles addition, the results of drying shrinkage are even lower than the control mixture (0% of NS particles).

This is due to the highly compacted and densified microstructure of hardened paste. The minimised paste water also aided restriction of drying shrinkage. However, increasing the percentage of NS particle further than 2% leads to increasing drying shrinkage. This is due to the creation of pockets of pores that are filled up with a solution which could give an opportunity for increased drying shrinkage values.

CONCLUSION

For self-compacting high-performance mortar with fly ash to cement ratio of 1:2, the optimum amount of NS particles is 2%. At this percentage, hardened properties are improved due to the modification of the microstructure of the hardened paste. However, employing NS >2% will lead to adverse effects. The hardened properties are reduced and the self-compactibilty is as well jeopardised.

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