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Effect of the Nano Particles in the New Generation of Concretes, SCC

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Abstract:

Nanotechnology is a favorite research area that revolutionized mechanical and chemical properties of materials. Recently, focusing on concrete as a porous material with micro-scale and nano-scale pores enthusiastic researchers developed their investigations to find out microstructure and mechanical properties of concrete. The aim of this paper is to investigate the effect of nano-silica as an addition on new concrete generation called as "Self Consolidating Concrete", SCC, containing type V Portland cement. For designed mixes, the fresh properties (Slump Flow, L-box, V-funnel, J-ring) as well as the hardened concrete properties such as compressive strength, elasticity modulus, swelling and shrinkage values were measured. Results were compared with SCC specimens without nano-silica addition at short and long terms of ages until one year. In order to investigate the development on the microstructure of SCC, after reviewing on the study procedure on the micro structure of SCC, the scanning electron microscopy (SEM) imaging on specimens were also performed. Results showed that the use of nano-silica with micro-silica can improve the engineering properties of hardened SCC.

Keywords: *SCC, Nano-silica, Fresh properties, Engineering properties, SEM.*

1. INTRODUCTION

SCC is a new generation of concrete that can exhibit high deformability and can flow into place under its own weight without any external or internal consolidation and with limited signs of segregation. The design concept of SCC is mainly based on the combination of high deformability and segregation resistance to achieve self consolidating, facilitate casting, and improve in-situ performance. Recently, applicable discussion in concrete technology is one of the nanotechnology applications in concrete design. Visual examination, optical microscopy, and scanning electron microscopy (SEM) have been extensively used in microstructure research of hardened cement paste and concrete, providing additional understanding of macroscopically properties. Electron microprobe analysis studies of hardened cement pastes have contributed to the compositional characterization of hydration products and spatial information. Some of the materials such as silica fume, with a grain size distribution in the 0.02 to 0.3μm range, are too small to be observed in detail by SEM. Techniques with stronger magnification capabilities would be very useful in these cases, as well in better conceptions of the pure cement paste microstructure [1]. Conventional microscopy techniques, such as SEM, cannot provide such detailed images and surface texture characteristics of the fine materials (especially silica fume) and of the product microstructure [1].

It has been found that nano-silica additions improve the mechanical properties of SCC with respect to micro-silica [2]. Furthermore, it has been seen that this effect cannot stem from a pozzolanic reaction. In fact XRD studies has confirmed that, contrary to the case of micro-silica, in the case of nano-silica, the consumption of $Ca(OH)_2$ is completely negligible [3].

2. MATERIALS AND MIXTURE PROPORTIONS

The SCC mixtures investigated in this study were prepared with Portland cement type V consisting of micro-silica powder and nano-silica solution. Micro-silica activity is mainly due to the reaction of its active constituent with $Ca(OH)_2$ produced from cement hydration and the formation of hydrated products with binding properties. The additional of nano-silica to cement paste has been carried out, either in powder form or as a colloidal suspension. The specific gravity of micro-silica and nano-silica is 2.17 and 1.03. They are silica particles with a maximum size of 0.2µm and 50nm, respectively. In addition, nano-silica is a water emulsion with 50% dry solid. The chemical properties based on XRD of cement and micro-silica is presented in Table 1.

Table 1: *The chemical properties based on XRD of cement and micro-silica*

%	Cement type V	Micro-silica
CaO	63.91	0.49
SiO_2	21.67	93.86
Al_2O_3	3.51	1.32
Fe_2O_3	4.72	0.87
MgO	1.8	0.97
SM	2.63	-
AM	0.74	-
LSF	92	-
Cl^-	-	0.04
C_3S	59.3	-
C_2S	17.5	-
C_3A	1.3	-
C_4AF	14.4	-
Na_2O	-	0.31
K_2O	-	1.01
SiC	-	0.53
C	-	0.34
P_2O_3	-	0.16

A limestone powder with a specific gravity of 2.65 was used in order to enhance the viscosity. The super plasticizer was a "poly carboxylic ether" based admixture (PCE). Properties of the selected mixtures are presented in Table 2. The properties of fresh and hardened concrete of two mixes are studied; i) SCC included only micro-silica (SCCM), ii) SCC with both micro-silica and nano-silica (SCCMN). The obtained results of fresh properties of mixes are compared with the recommended values and it was concluded that the proposed design mixes can be considered as SCC (Table 3).

3. HARDENED CONCRETE TEST

Three different curing conditions were assumed. After 24 hours, the specimens were remolded and placed in the water, which was saturated with the five percent of lime. After 7 days, a group of specimens were transferred to a room with the temperature of 24±4°C and a relative humidity of 30±5% called as dry (D) condition and the other group cured in

Table 2: *Selected mix properties for 1m^3*

Mix Labels Materials	SCCM	SCCMN
Cement (Kg)	360	360
Micro-silica (Kg)	40	40
Nano-silica (Liter)	-	2.4
Water (Kg)	210	210
L.S.P (Kg)	300	300
Coarse Aggregate (Kg)	750	750
Fine Aggregate (Kg)	850	850
PCE (Liter)	3.675	3.675
W/CM[1]	0.525	0.525
W/P[2]	0.3	0.3

[1] CM: Cement+ Micro-silica

[2] P: Cement+ Micro-silica +Lime Stone Powder

Table 3: *Test result on plastic phase of SCC compared with EFNARC[4]*

Fresh Properties of SCC			
Type of Test	SCCM	SCCMN	Recommended Values
Slump Flow Diameter (mm)	670	690	650 to 800
L-Box (h_2/h_1)	0.9	0.9	>0.8A
J-Ring (mm)	650	670	Same as slump flow
V-Funnel* 5 minute (s)	6.85	6.95	6 to 12

Table 4: *Growing up rate in compressive strength at the different ages and different curing conditions respect to 28 days age.*

Mixes label	**Curing conditions**	**$M_{3/7}$**	**$m_{7/14}$**	**$m_{3/28}$**	**$m_{7/28}$**	**$m_{14/28}$**	**$m_{90/28}$**
SCCM	D	0.36	0.083	0.51	0.23	0.17	0.019
	W	0.314	0.16	0.507	0.28	0.146	0.034
	S	0.274	0.156	0.415	0.19	0.045	-0.16
SCCMN	D	0.376	0.042	0.504	0.21	0.17	0.15
	W	0.325	0.054	0.48	0.23	0.19	0.15
	S	0.268	0.098	0.42	0.2	0.12	0.2

sulfuric acid basin with pH 1.5 called as sulfate (S) condition. The remained were kept in water, up to 28 days age called as wet (W) condition and then they were cured in the same condition of (D). For hardened concrete phase, the following tests were carried out at different ages.

4. COMPRESSIVE STRENGTH AND MODULUS OF ELASTICITY TESTS

For two SCC mixes, concrete cube specimens of 10*10*10 cm were tested at 3, 7, 14, 28, 90,180 and 365 days age and results are shown in Figure 1.

The results at the different ages show that for any storage condition, either short or long term, the compressive strength for specimens consist of nano-silica is higher than specimens without nano-silica. In other words, the nano-particles were more valuable in enhancing strength than silica fume. Furthermore, it can be concluded that, at 28 days age, the mixes had a better behavior for dry storage conditions. However results show the higher compressive strength for (W) condition at 90 days age.

The slope of the lines (m), which are presenting the growing up rate of compressive strength between different ages, presented in Table 4. It indicates that specimens consisting nano-silica at 28 days age, are higher by 17, 14.7 and 15.2 percents.

Also, mixture with nano-silica in acid sulfuric environmental condition has better resistance over that of the specimens without nano-silica. This is an indication of the reduction in pores for SCC with nano-materials.

It can be seen that the compressive strength rate of SCC mixtures containing nano-silica are all higher than the control mixes (i.e., SCCM specimen) with the same W/CM. Different strength development in concretes can be attributed to pozzolanic reactions. The same conclusion is reported by recent research connected by Byung-Wanjo et al. on characteristics of cement mortar with nano-SiO_2 particles. They also concluded that, nano particles are thought to be more effective in pozzolanic reaction than silica fume. Also, the nano-SiO_2 would fill pores to increase the mortar strength, as silica fume does [5]. Therefore, it is confirmed that the addition of nano-SiO_2 to cement mortars improves their strength characteristics.

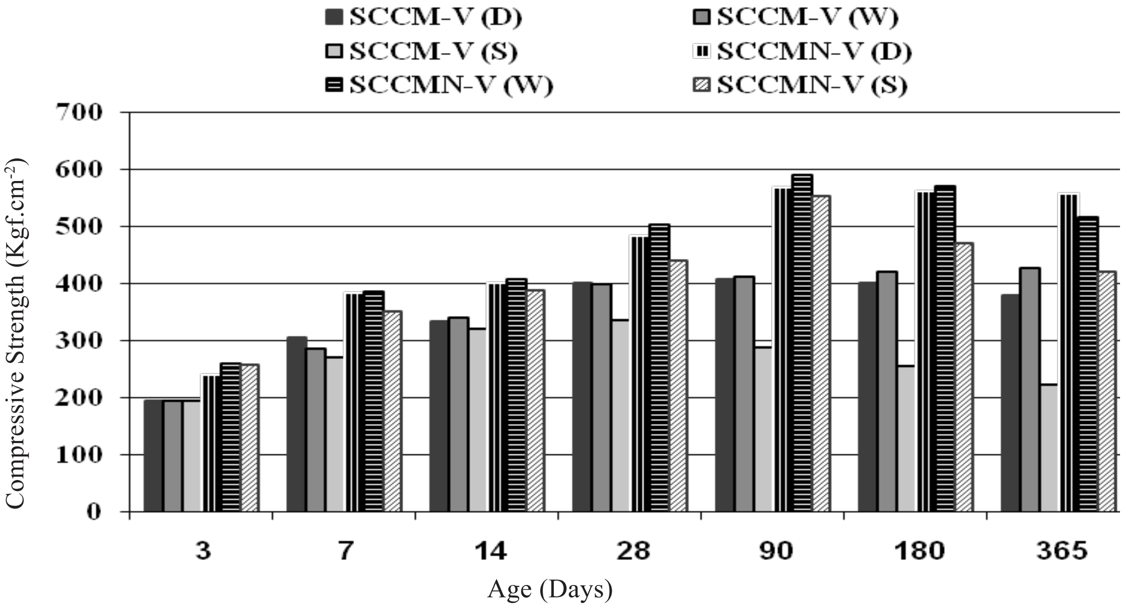

Figure 1: *Compression of strength tests for SCCM and SCCMN specimens*

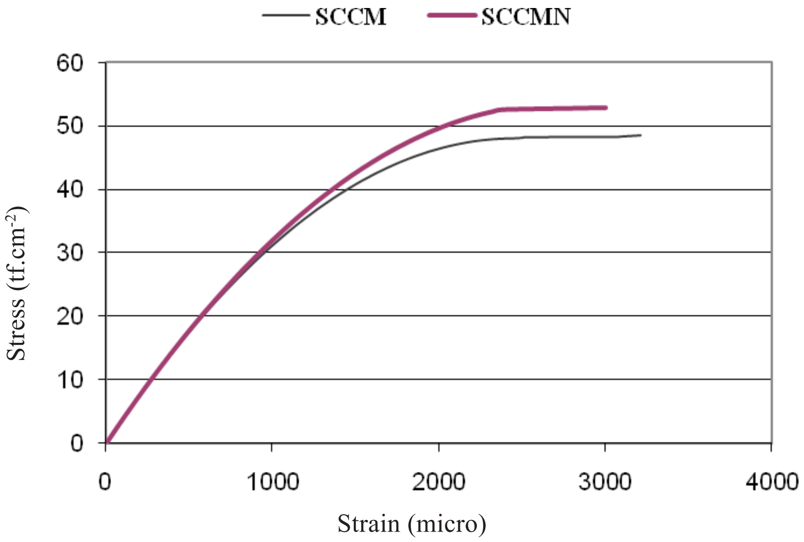

Figure 2: *Stress-Strain curve for SCCM and SCCMN for (D) condition*

For some specimens, the electrical strain gauges were fixed and the stress-strain diagrams are plotted and shown in Figure 2. There are several different definitions of the elasticity modulus. However, here the slope of a tangent to the curve at 33.3% of the ultimate strength of the SCC was considered as E_c. The obtained value of E_c for SCCM and SCCMN were 32000 and 34600 MPa, respectively and it can be concluded that a similar failure for both mixes.

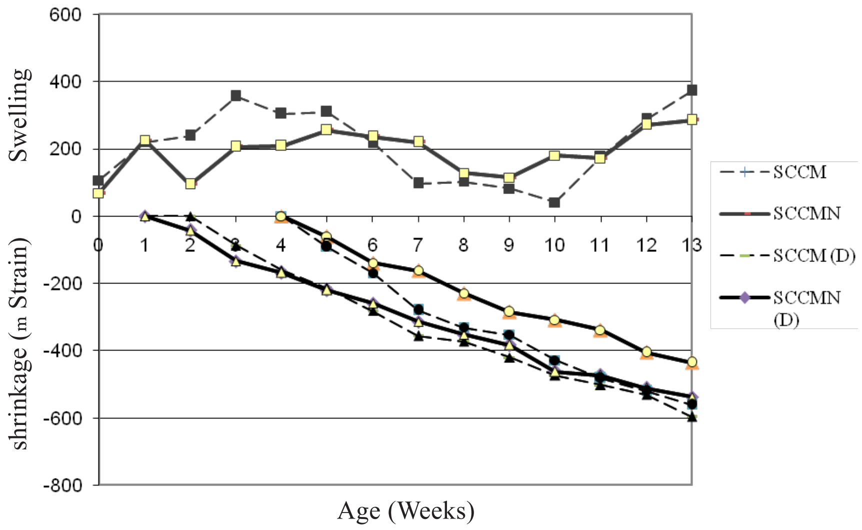

Figure 3: *Comparison of swelling and shrinkage test of SCCM, SCCMN*

Table 5: *Averaged atomic number and BE of clinker and cement phases, composition, cement chemist notation and, densities.*

Phase	*Z*	*H*
Ferrite	16.65	0.1860
Free Lime	16.58	0.1882
Belite	15.06	0.1716
Arcanite	14.56	0.1662
Aluminate-cub	14.34	0.1639
Aluminate-ort	13.87	0.1588
Aphthitalite	13.69	0.1577
Syngenite	13.60	0.1556
Anhydrite	13.41	0.1535
Bassanite	13.03	0.1489
Gypsum	12.12	0.1381
Thenardite	10.77	0.1249
Periclase	10.41	0.1213

5. SWELLING, SHRINKAGE TESTS AND DISCUSSIONS

For each case of table 2, two prism specimens of 10*10*45 cm were cast and then they were kept in (W) condition. At different ages the amount of swelling was measured by the mechanical strain gauge and the results are plotted in Figure 3. As shown, the amount of swelling for the specimens with nano-silica is reduced by an average of 31% for the first six weeks and then increased until 11 weeks by an average of 48%. It seems that it is because of the pore reduction at nano scale.

To study the shrinkage of SCC mixes, for two storage conditions (D) and (W) at different ages the amount of shrinkage was measured by the mechanical strain gauge and results are plotted in Figure 3. It was reported that the use of only micro silica in SCC mixes causes to reduce the amount of shrinkage, about 70% compared with SCC mixes having no micro-silica [6]. For two curing conditions, the shrinkage amount of mixes consists

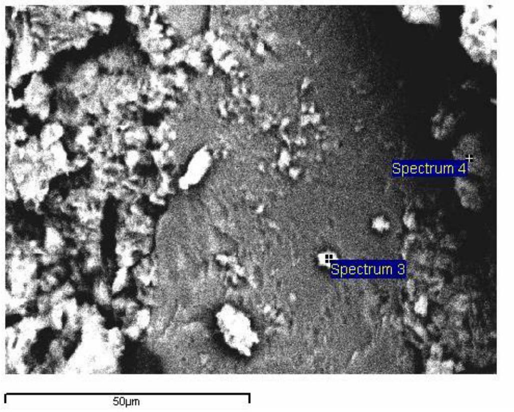

Figure 4: *SEM image of SCCMN*

of both micro silica and nano-silica had the lowest shrinkage values for (D) curing conditions, i.e. the value reduced by 5-25%.

6. SCANNING ELECTRON MICROSCOPY (SEM) IMAGING

Two particularly useful imaging methods in SEM are backscattered electron (BE) and X-ray (XR) imaging. Combining the BE and accompanying XR images via image processing allows their segmentation into the constituent phases of the microstructure. Once the image is segmented, it may be analyzed to extract information such as bulk phase abundance, phase surface area, and feature size. Contrast is generated by the different phases relative to their average atomic number. This is observed by the differential brightness in the image. The backscatter coefficient η is a measure of the backscattered electron fraction and, for a pure element of atomic mass Z, may be estimated [7].

The back scattered electron coefficient of a multi element phase is estimated using the mass fractions (C_i) and η values for each constituent:

$$\eta = \sum C_i \eta_i \tag{1}$$

Contrast between constituents may be calculated as:

$$C = \frac{\eta_2 - \eta_1}{\eta_2} \tag{2}$$

Table 5 is a list of some phases from clinker and cement, in descending order of their gray level intensity. The 6.8% contrast between alite and belite is relatively strong that between belite and cubic tri-calcium aluminate, at 1.5%, is generally too weak to distinguish these constituents. If the contrast between phases is so weak that it precludes discrimination, they are chemically distinct, and therefore X-ray imaging can be used to distinguish them from each other.

X-ray microanalysis systems generally employ an energy-dispersive detector. The X-ray signal is used to determine which elements are present and in

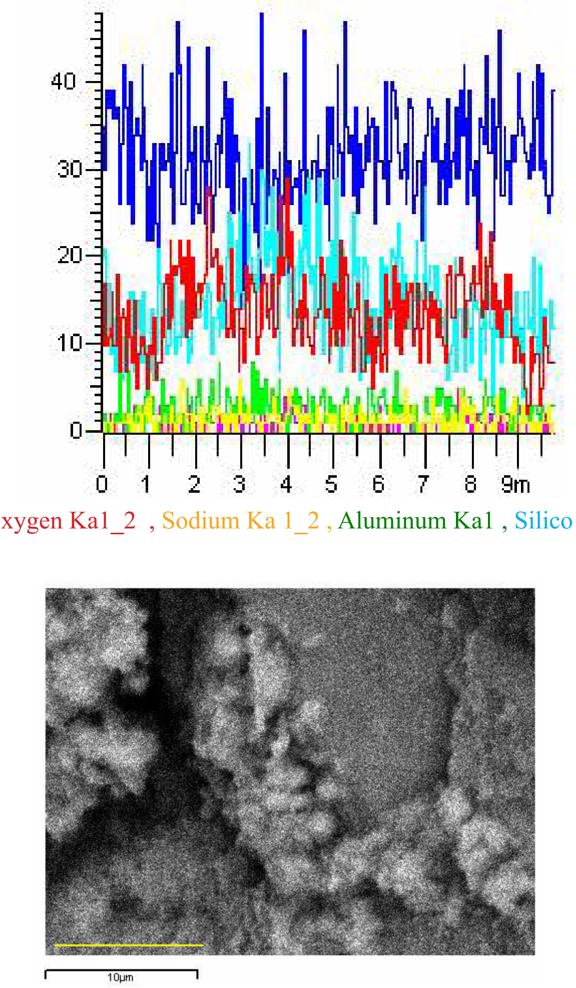

Figure 5: *X-Ray analysis of cement paste*

what concentration, and graphical display of relative concentrations through line scans and X-ray imaging of element spatial distribution and relative concentrations. Mass concentration to a few tenths of a percent can be detected for some elements. The relative accuracy of quantitative analysis (using certified standards, and solid, homogeneous specimens) is about ±20% for concentrations around 1%, and about ±2% for concentrations greater than 50% [8].

Figure 4 shows the cement paste, aggregate interface in SCCMN. So, compositions of elements were determined with image processing software of captured image. Figure 5 shows the line diffraction from yellow line.

7. CONCLUSIONS

The addition of nano-silica in SCCM mixes causes the decreasing of the swelling value and increasing the compressive strength. For all ages and curing conditions studied, a reasonably better serviceability conditions can be expected while used in structural concrete and also its durability is enhanced.

Comparing the micro-silica and nano-silica in SCC, showed that reducing the pore size causes the more dense and durable concrete structures.

SCC containing nano-silica and micro-silica reduces the swelling amount by 31 and 48% as concrete age is increased.

Also SEM test showed that, the progress of hydration in the case of using nano-silica developed from 28 days age respect to using just micro-silica.

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