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A Comparison of the Microstructure of self compacting concretes containing nano and microsilica

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Abstract

Self compacting concrete (SCC) is a new construction material in the world. The aim of this research is to construct self compacting concrete with high compressive strength using combination of nano silica and micro silica. For this purpose, nano silica, micro silica, Portland cement type 2, superplasticizer (SP), and gravel and sand have been used. Three different groups of samples with different compositions were made.In thefirst group samples had 11% microsilica ($MS_{11\%}$), second group of samples contain 11%microsilica+ nanosilica ($MS_{1-10\%}+NS_{1-10\%}$) and third group had 11% nanosilica ($NS_{11\%}$). Microstructure of samples was studied 7 and 21 days after setting. The XRD results and SEM Studies have shown that simultaneous use of 7 weight percent (wt%) nanosilica and 4 wt% microsilica instead of cement in concrete mix leads to the formation of a microstructure with the lowest portlandite content.

Key words: Self compacting concrete, Nano silica, Micro silica, Microstructure.

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1. Introduction

Following extensive financial and life losses caused by structures break down during natural disasters like earthquake, it has been essential to increase accuracy and security in construction of engineering structures. To increase structures safety and confidence, new compositions should be developed.

Nowadays, concrete is one of the widely used construction materials [1], and different materials have been added to concrete to obtain better properties[2-6]. Self compacting concrete (SCC) and hybrid cement are new innovations, and currently using in the construction industry [7,8]. Similar to other types of concrete, self compacting concrete is made of water, cement and natural aggregates[8,9]. The difference between self compacting concrete and normally vibrated concrete (NVC) is existence of nano silica, micro silica and superplasticizer in composition of SCC [3,9-12]. In self compacting concrete water is used in lower fractions [13,15-19], as weight fraction of water to cement is about %25 [20-23]. Impurities of water may affect the concrete, and decreases the setting of concrete, and then it is better to use purified water[20,24,25]. Higher specific surface of nano silica compared to micro silica causes higher pozzolanic activity of former material ?therefore nano silica has more use in concrete than micro silica [4,15, 18,26-28], also addition of nano silica increases durability and compressive strength of concrete [3-5,10,16,23,26-29]. Properties and operation of concrete depend on the nano structure of concrete and cement matrix, which creates integrity and continuity of the concrete [7,30-33]. Nano silica also decreases the time of hydration, then cement paste can reach the maximum temperature of hydration in smaller time [3, 4, 21,29,30]. Therefore, studying cement paste and concrete structure in nano scale is very important to develop new constructing materials [8,10, 27].In addition, using nano materials may lead to construct new structures without dependency to natural resources[8]. Considering that nano silica causes high specific surface in the base material and absorbs and maintains water, thus it decreases flow properties of mortar [30]. By increasing nano silica which has high specific surface, more water absorbed, then concrete mixture is encountered to water deficit. Therefore a superplasticizer is used to overcome water deficit and obtain better concrete with lower volume [12,14,19,29,32-34]. The properties of selfcompacting concrete with superplasticizers largely depend on the water to cement ratio (vol%) [17,18,22, 23], and mixing techniques [34,35]. This mixture should be able to fill the mold, passing through barriers [12,35,36], and resisting against shearing [11,33-36]. In order to determine whether the concrete is self compacting or not and to prove its self compacting, its desirable filling and deformability should be determined using L shaped box, V funnel, J ring and slump flow tests [9,23,33].

XRD can be used to study phase analysis and pozzolanic effect of nano and micro silica in self compacting concrete [36,37]. To determine the pozzolanic effect of nano and micro silica it should be noted the effects of portlandite ($Ca(OH)_2$, and calcium-silicate-hydrate (C-S-H). Portlandite is a needle like phase with low hardness which can increase crack formation and decrease compressive strength [10, 31].

On the other hand Alite (C_3S) and Bilite (C_2S) phases lead to the formation of calcium- silicate-hydrate (C-S-H) gel and portlandite. C-S-H is the main factor which increases the compressibility and compressive strength of concrete [8,31].

2. Experimental

2.1. Materials and Instruments

As the other type of concrete, water, cement and other concrete materials are used for making self-compacting concrete. Sand and gravel, portland cement type 2 , urban water, nanosilica made in Mingry nano material Chinese Company , microsilica made in Sina Powder Company, carboxyl ate-based Glenium super plasticizer[25] (with the density of 1070 g/lit and PH=7) made in Fan AvaranBeton Iranian Company were used as the concrete materials in this research. The specification of the fine-grained consumables is presented in Table 1.

Table 1: Specification of fine-grained consumables

component(**Wt**%)	Portland cement type 2	micr silica	nano silica
SiO_2	22	95	99/9
Al_2O_3	6/6	0/9	-
Fe_2O_3	2/8	0/6	-
CaO	60/1	0/3	-
MgO	3/3	0/9	-
SO_3	2/1	0/5	-
LOI	2/6	2/1	0/1
Physical properties			
Surface/ mass ratio(m^2/g)	0/38	21	160
Avg. particle size	13µm	0/2µm	40nm
Density(g/cm^3)	3/15	2/4	2/2

According to the specification presented by the producer companies of the consumables, aggregation of coarse-grained materials was based on ASTM C33. In accordance with received information from resources [6,31], since the use of microsilica materials in the range of 10% had suitable efficiency and the use of nanosilica in the range of 7% represented interesting results, therefore, samples under investigation were categorized into 3 groups. The first group contained 11% nanosilica($NS_{11\%}$), the second group contained 11% nanosilica+microsilica ($NS_{1-10}\%MS_{1-10\%}$), and the last group contained 11% microsilica ($MS_{11\%}$). After the primary and secondary setting (took 7 and 28 days respectively), samples were studied under phase analysis (XRD) and electronic microscope (SEM).

2.2. Mixing Design of Self Compacting Concrete (SCC)

The characteristics of self compacting concrete have direct relationship with the type of cement being used, morphology, the mineral's type of the gravel and sand, the size of sand's and gravel's grain[28], the size of micro's and nanosilica's grain, the ratio of water to cement, the type and amount of super plasticizer and also mixing techniques. Self compacting concrete needs high ductility which can be balanced by the use of super plasticizer that in turn leads to the decrease in the ratio of water to cement. Self compacting concrete mixture should be arranged in a way that meets all the properties and characteristics of new and hardened concrete. A mix design can be categorized in the self compacting concrete group when it can completely provide all the three factors of filling ability, passing capability through barriers, and being resistant in the face of shearing. Table 2 shows the amount of used consumables in a cube meter in this research. In table 3, weight percentage of the fine-grained materials used in each sample has been presented.

Table 2: the amount of applied materials in self-compressed concrete ($1m^3$)

Mixed sample	Water/cement material(1)	Water (Kg/m^3)	Cement (Kg/m^3)	Sand (Kg/m^3)	Gravel (Kg/m^3)	Micro silica (Kg/m^3	Nano silica (Kg/m^3)	Super plasticizer (Kg/m^3)
NC	0,4	180	400.5	630	1030	-	-	5
$MS_{\%11}$	0.4	180	400.5	630	1030	49,5	-	5
NS%1MS%10	0.4	180	400.5	630	1030	45	4,5	5
NS%2MS%9	0.4	180	400.5	630	1030	40,5	9	5
NS%3MS%8	0.4	180	400.5	630	1030	36	13,5	5
$NS_{\%4}MS_{\%7}$	0.4	180	400.5	630	1030	31,5	18	5
$NS_{\%5}MS_{\%6}$	0.4	180	400.5	630	1030	27	22,5	5
$NS_{\%6}MS_{\%5}$	0.4	180	400.5	630	1030	22,5	27	5
$NS_{\%7}MS_{\%4}$	0,4	180	400.5	630	1030	18	31,5	5
NS%8MS%3	0.4	180	400.5	630	1030	13,5	36	5
NS%9MS%2	0.4	180	400.5	630	1030	9	40,5	5
NS%10MS%1	0.4	180	400.5	630	1030	4,5	45	5
NS%11	0,4	180	400.5	630	1030	-	49,5	5

(1): cement material: cement + nano and micro silica, NC= normal concrete

Table 3: Mix proportions of SCC mixes (wt%)

Mixed sample	Water/cement	Nano silica	Micro silica	Portland cement
NC	-	-	-	100
$MS_{\%11}$	40	-	11	89
$NS_{\%1}MS_{\%10}$	40	1	10	89
$NS_{\%2}MS_{\%9}$	40	2	9	89
$NS_{\%3}MS_{\%8}$	40	3	8	89
$NS_{\%4}MS_{\%7}$	40	4	7	89
$NS_{\%5}MS_{\%6}$	40	5	6	89
$NS_{\%6}MS_{\%5}$	40	6	5	89
$NS_{\%7}MS_{\%4}$	40	7	4	89
$NS_{\%8}MS_{\%3}$	40	8	3	89
$NS_{\%9}MS_{\%2}$	40	9	2	89
$NS_{\%10}MS_{\%1}$	40	10	1	89
$NS_{\%11}$	40	11	-	89

3. Result and discussion

3.1. Phase and Microstructure Examination.

The purpose of phase analysis of samples is to determine available phases and study pozzolanic effect of nano and microsilica on the self-compacting concrete. In the phase analysis of concrete, the pozzolanic effect of nano and microsilica on the formation of two phases of portlandite and calcium-silicate-hydrate (C-S-H) should be noted.

We can state that Alite ($C_3S:3CaO.SiO_2$) and Bilite ($C_2S:2CaO.SiO_2$) are the basic

component of portlandite cement. At the beginning of water and cement mixture, Alite and Bilite are combined with water according to the following reaction and produce calcium-silicate-hydrate gel. During Alite and Bilite reaction with water, During portlandite $Ca(OH)_2$ will be produced as the reaction's by-product.

$$2(3CaO.SiO_2) + 6H_2O \longrightarrow 3CaO.2SiO_2.3H_2O+3Ca(OH)_2 \quad (1)$$

$$2(2CaO.SiO_2) + 4H_2O \longrightarrow 3CaO.2SiO_2.3H_2O+Ca(OH)_2 \quad (2)$$

Calcium–silicate-hydrate penetrates in a gel form through the surface of sand and gravel particles even capillary tubes, then settles there and becomes harden and finally leads to the formation of a uniform agglomerate. Also, portlandite is crystallized and exits the solution as a solid phase. Portlandite crystals as shown in Figure 1 part a, are needle like trigonal crystals and because of having low hardness (2.5-3 Mouse) leads to the decrease in concrete's resistance. Nano and microsilica because of the presence of additional $Ca(OH)_2$will react with portlandite and produce calcium-silicate-hydrate gel according to the following reaction:

$$3Ca(OH)_2+2SiO_2 \longrightarrow 3CaO.2SiO_2.3H_2On \quad (3)$$

The produced gel settles through Sand and gravel and becomes harden. In this way undesirable effect of portlandite will be neutralized. Along with above reactions aluminates-calcium ($C_3A:3CaO.Al_2O_3$) combines with water and plaster and produces sulfate-aluminates called Ettringit by the following formula: ($3CaAl_2O_3.3CaSO_4.3H_2O$).

Ettringit has a dihexagonal dipramidal (short and wide needle like) structure [38]. (Figure 1 picture b analysis). As the time passes ettringit combines with the remaining of aluminates-calcium in the concrete and by producing hardened monosulfate will settle in the concrete.Calcium–silicate-hydrate has a remarkable role in determining cement's resistance. Adding just nanosilica or just microsilica decreases portlandite phase to the calcium-silicate-hydrate but the effect of nanosilica is more than microsilica . SEM micrograph of sample (NS $_{11\%}$) microstructure is presented in Figure1. In part a of this figure,EDX analysis of thin and long needle like phases shows the formation of portlandite, in part b of the same figure , EDX analysis of wide and short needle like crystals shows the ettringit phase. In X-ray diffraction (XRD) analysis , mixed samples containing nano and microsilica are seen(Figure2) that by increasing nanosilica percentage in proportion to microsilica, portlandite couriers have been weaker in a way that portlandite couriers have been minimized in a sample containing 4% microsilica(MS $_{4\%}$) and 7% of nanosilica(NS $_{7\%}$). In microscopic picture of MS $_{11\%}$ (Figure3), needle like phases are clearly seen in 7-day self compacting concrete. With due attention to the microstructure form of mixed sample that contain 4% nano+7% microsilica(Figure4), 7-day self-compacting concrete is seen in which calcium hydroxide phase is remarkably lesser than both MS $_{11\%}$and NS $_{11\%}$ samples(they're shown in Figure 3 and figures1&5 respectively). By comparing and studying samples on 7th day and with due attention to the increase of nanosilica percentage to microsilica, it is seen that the amount of needle like phase of calcium-hydroxide is decreased and added to the amount of calcium-silicate-hydrate phase. Also, x-ray diffraction results of self-compressed mixed concrete sample have acknowledged this fact. It is important to note that the amount of portlandite phase in NS $_{11\%}$ sample (Figure5) is more than (NS $_{7\%}$MS $_{4\%}$) sample (Figure 4).

(The answer of question in page 7: The reason has been indiauted from line 12 to the same paragraph)

4. conclusions

Pozzolanic activity is subject to nano's and microsilica's amounts in the concrete composition.

In the mixed samples of the concrete containing nano and microsilica (NS $_{1-10\%}$MS $_{1-10\%}$), nanosilica shows its maximum pozzolanic effect aggressively during the first 7 days of setting while microsilica shows the same effect during longertime.

Mixed samples containing nano and microsilica (NS $_{1-10\%}$MS $_{1-10\%}$) and mixed sample of (NS $_{7\%}$MS $_{4\%}$) have the least amount of portlandite phase.

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