Effect of Nano- and Micro silica on compressive and bond strength in saline environments: An experimental and microstructural study

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***Abstract*- Simultaneous using of nanosilica (NS) and microsilica (MS) can improve the chemical and microstructural reactions of concrete. Hence, this improvement can increase the bearing capacity of reinforced concrete structures by increasing the compressive strength of concrete and the bond strength between rebar and concrete, especially in saline environments. Therefore, in this study, 14 mixes including different percentages of NS and MS based on two types of cement strength class have been designed to evaluate the compressive and bond strength in salt solution with two concentrations of 15% for cement 42.5 MPa (C42.5) and the concentration of 20% for cement 52.5 MPa (C52.5) cement. Scanning electron microscope (SEM) was also used to study the microstructural part of the rebar-to-concrete bonding surface. Experimental results showed that replacement of cement with 7% MS + 3% NS, increased compressive strength by 90% and the bond strength by 66% for C42.5. Also for C52.5, 5% MS + 5% NS improved 88% compressive strength and 59% bond strength. In addition to dependency of optimum mix design to cement type, it is seen that the increasing of CSC can control the degradation caused by increasing salt concentration.**

***Keywords* –** Nanosilica, Microsilica, Compressive strength, Bond strength, Microstructure.

1. Introduction

Today, the use of cement replacement materials such as nanosilica (NS) or microsilica (MS) for the manufacture of high-performance concrete is very common in marine reinforced concrete structures that caused increasing of durability and lifetime of structures. The lifetime of reinforced concrete structures is highly dependent on the microstructure and the porosity at the contact surface of rebar and concrete These silica particles which are finer than cement particles, due to pozzolanic reaction, improved the hydration process and production of calcium silicate hydrated (CSH), which in addition to reducing porosity and permeability, leads to increasing of adhesion in the rebar-to-concrete contact surface [1]. Presence of calcium hydroxide crystals at this surface not only improves electrical and corrosion resistance of steel rebars [2, 3]. The effect of MS and NS on the bond strength has been studied separately in the previous literature. Some research findings show that the addition of MS improves adhesion between concrete and rebar and improves bond strength. Gjorv et al. [4] improved the bond strength by 25% by replacing 8% MS with cement. They found that the presence of MS reduced the porosity and thickness of the concrete and rebar transition area due to Pozzolanic activities and reduced the accumulation of free water. Similarly, Sfikas [5], using 5% MS, increased the bond strength up to 12%. However, some previous literature has also shown that the addition of MS makes the concrete more brittleness and this weakness has resulted in the abrupt failure of the concrete. This means that the cover role of concrete for the rebar is negligible and consequently caused a decrease in bond strength [6]. In addition to MS, Carmo et al. [7] reported that the replacement of cement with 2% NS improved the bond strength by 27%. They have also suggested that NS with different percentages and even other structures must be evaluated because they can affect the results. In another study [8], by using 6% NS, bond strength between geopolymer concrete and rebar was improved by 43% which indicating higher NS percentages can provide even more bond strength.

In addition to pozzolanic role of MS and NS, these particles by placing between the aggregate and the cement paste, play a filler role that caused a reduction of porosity and increasing of concrete-mortar mix integrity. Since cement strength class (CSC) in cementitious base materials is affected by fineness of cement particles, the replacement of NS and MS can influence on the fineness of binder materials and consequently influence on their hydration process and their hardened mechanical properties [9]. Researches have shown that increasing of CSC caused a reduction of porosity and permeability and consequently properties such as durability, compressive and flexural strength improved [10-13].

The purpose of this study is evaluation of the compressive and bond strength of specimens containing variable percentages of NS + MS for two types of cement strength classes with 42.5 and 52.5 MPa while placed in salt water with concentration of 15% and 20%, respectively. Hence, compressive strength and rebar pull-out tests have been performed. Scanning electron microscope (SEM) has also employed to study the microstructural part of the interface between rebar and concrete.

2. EXPERIMENTAL PLAN

2.1 Raw materials and Mix designs

Two ordinary Portland cement type 1 with CSC of 42.5 and 52.5 MPa according to EN 197-1 [14] were used for manufacturing of specimens. Microsilica (MS) and Nanosilica (NS) were also used as supplementary cementitious materials (SCM). MS which also known as silica fume is a byproduct of the production of ferrosilicium alloys in electric arc furnaces. The consumed nanosilica is a SiO2-based irregularly shaped nanoparticle which dispersed in water by concentration of 30%. Chemical compositions and physical properties of cementitious materials tabulated in Table 1.

Table 1. Chemical compositions and physical properties of cementitious materials.

	(%) Chemical compositions						Physical properties	
	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Particle size (μm)	Specific surface ($m^2.gr^{-1}$)
C42.5	20.2	64	4.6	3.5	1.64	2.4	1-100	3
C52.5	21	64.18	4.7	3.52	1.93	2.53	1-100	3.6
MS	98	-	-	-	-	-	0.1	20
NS	30	-	-	-	-	-	0.025	210

A Polycarboxylates -based super plasticizer (PCE) has been used to achieve a sufficient performance and better dispersion of silica particles in the mixture. Natural sand and gravel respectively with fineness modulus of 2.45 and 2.65 were used as aggregates in accordance with ASTM C33 [15]. Table 2 shows the specimens mix designs manufactured with C42.5 and C52.5 and containing different percentages of NS and MS.

Table 2. Mix designs.

Mix ID.	Agg. (gr)	w (gr)	c (gr)	MS (wt%)	NS (wt%)	PCE (gr)
CTRL-C42.5	3800	585	1330	0	0	4
CTRL-C52.5	3800	585	1330	0	0	6
MS10-C42.5	3800	585	1197	10	0	19
MS10-C52.5	3800	585	1197	10	0	21
MS8.5 NS1.5-C42.5	3800	585	1197	8.5	1.5	18
MS8.5 NS1.5-C52.5	3800	585	1197	8.5	1.5	20
MS7 NS3-C42.5	3800	585	1197	7	3	18
MS7 NS3-C52.5	3800	585	1197	7	3	20
MS5 NS5-C42.5	3800	585	1197	5	5	17
MS5 NS5-C52.5	3800	585	1197	5	5	19
MS3 NS7-C42.5	3800	585	1197	3	7	16
MS3 NS7-C52.5	3800	585	1197	3	7	18
NS10-C42.5	3800	585	1197	0	10	15
NS10-C52.5	3800	585	1197	0	10	17

2.2 Preparations and Curing of Specimens

The aggregates and cementitious materials were first mixed for 2 minutes. After that, water and super plasticizer were added and the mixing was continued for another 3 minutes. Finally, cubic molds with dimensions of 100 × 100 × 100 mm and cylindrical molds with dimensions 100 × 150 mm were used for compressive and pullout specimens respectively. pullout specimens were also reinforced by a steel rebar with a diameter of 16 mm and an embedded length of 120 mm (Fig. 1). After 24 hours and demolding, specimens made with C42.5 and C52.5 were exposed to 15% and 20% salt water for 90 days, respectively.

Fig. 1. Preparing of Pullout Specimens.

2.3 Experimental Tests

Compressive strength test was performed for cubic specimens with dimensions of 100 × 100 × 100 mm in accordance with BS 1881-116: 1983. A servo control universal machine with a maximum load capacity of 200 kN was used to measure the maximum compressive force applied up to failure. The compressive strength (f_c) calculated according to the following formula:

$$f_c = \frac{F}{a^2} \quad (1)$$

Where F is the maximum load and a is the dimension of the specimens.

To evaluate the bond behavior between rebar and concrete, an axial shear stress test called pullout test was performed by Zwick machine. The test is performed with a loading speed rate of 1 mm/min and the "force-slip" curves recorded from rebar pull-out up to bond failure mode (concrete splitting or rebar pull-out). Since the bond stress varies along the embedded length of the rebar, an average bond stress (f_b) is defined as Equation (2):

$$f_b = \frac{P}{\pi d_b l_e} \quad (2)$$

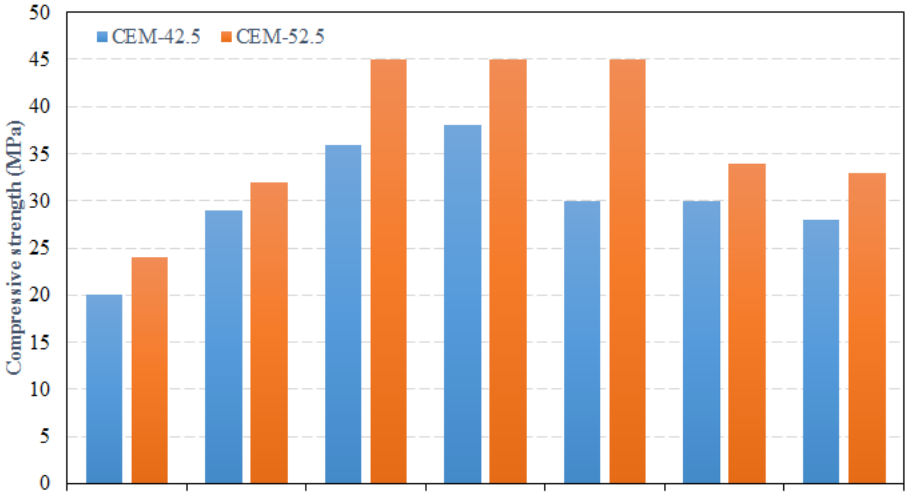
Where P is the peak point load, d_b is bar diameter and l_e is embedded length of bar.

3. RESULT AND DISCUSSION

3.1 Compressive Strength

The results of compressive strength test for the specimens containing NS and MS, manufactured with C42.5 or C52.5, which exposed in 15% and 20% salt water solution for 90 days, are shown in Fig. 2. It is seen that CSC has a direct and significant effect on the compressive strength. By increasing of CSC from C42.5 to C52.5, f_c increased up to 50% and averagely 22.1% improved (Fig.2 row ■→■). On the other hand, it can be seen that the addition of NS and MS significantly increased the compressive strength compared to the control specimen, so that for the C42.5, f_c is improved up to 90% and by an average of

59.2% (Fig.2 row ■) and for C52.5 increased up to 87.5% and 62.5% on average (Fig.2 row ■). As noted by other researchers [16-19], the addition of MS and NS with the pozzolanic behavior increases the hydration rate and production of CSH gels, which ultimately improves the mechanical properties of concrete such as compressive strength. It should be noted that the optimum percentages of NS and MS for C42.5 are 7% MS and 3% NS, while for C52.5, the optimum percentage of MS and NS are in the range of 5-8.5% and 1.5-5% respectively. Another notable point is the synergistic effect of NS and MS in increasing compressive strength, which has been evaluated and confirmed by other authors [20-23]. In general, it can be concluded that the replacement of cement with NS and MS significantly increases the compressive strength. Also CSC has a direct effect on compressive strength.

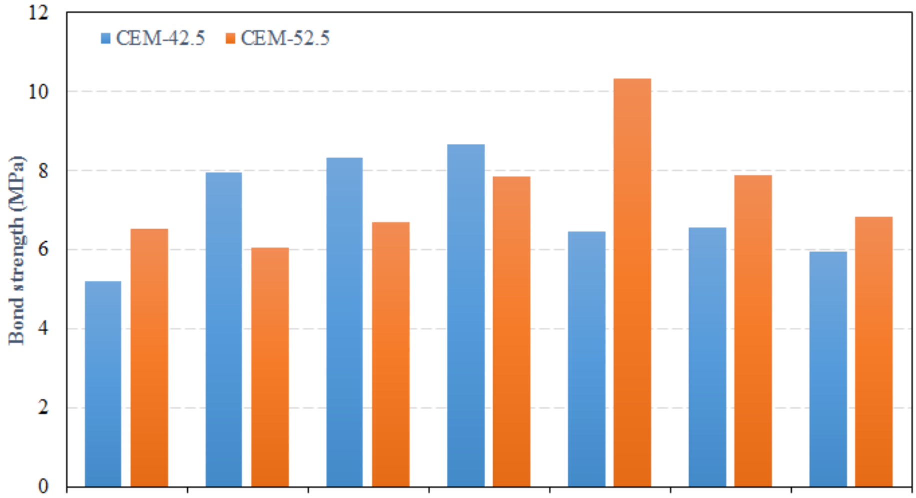


		CTRL	MS10	MS8.5 NS1.5	MS7 NS3	MS5 NS5	MS3 NS7	NS10	average (%)
Relative to CTRL-C42.5 (%)	■	0	45	80	90	50	50	40	59.2
Relative to CTRL-C52.5 (%)	■	0	33.3	87.5	87.5	87.5	41.7	37.5	62.5
Relative to CSC (%)	■→■	20	10.3	25	18.4	50	13.3	17.8	22.1

Fig.2. Compressive strength of specimens containing different percentages of MS and NS.

3.2 Bond Strength

The values of bond strength obtained from pullout test are shown in Figure 3. It is generally observed that the addition of NS and MS improved the bond strength of all specimens. It is seen that the specimens made with C42.5 improved bond strength up to 66.2% and on average by 40.3% compared to the control specimen (Figure 3 row ■), while for specimens made with C52.5, this incensement of bond strength was 58.8% and 16.8%, respectively (Figure 3 row ■). This relative reduction of bond strength can be due to the placement of specimens in different concentrations of salt water. In other words, as the salt concentration increased, the bond strength decreased. Also, the effect of CSC on the bond strength trend of specimens containing NS and MS can also be observed. However some specimens made up of C42.5 have higher strength than C52.5 specimens, but the overall results show that with increasing CSC, bond strength increased by an average of 9.6% (Figure 3 rows ■→■). Also, the maximum bond strength for C42.5 and C52.5 belong to the MS7 NS3 and MS5 NS5 mixes respectively. It can be concluded that the addition of NS and MS improved bond strength and this incensement has also a direct relation with CSC.



	CTRL	MS10	MS8.5 NS1.5	MS7 NS3	MS5 NS5	MS3 NS7	NS10	average (%)
Relative to CTRL-C42.5 (%) ■ (blue)	0	52.4	59.7	66.2	23.6	26.1	14	40.3
Relative to CTRL-C52.5 (%) ■ (orange)	0	-7.1	2.6	20.4	58.8	21.2	5.1	16.8
Relative to CSC (%) ■→■	24.9	-23.8	-19.7	-9.5	60.5	20.1	15.1	9.7

Fig.3. Bond strength of specimens containing different percentages of MS and NS.

3.3 Microstructure

Fig. 4 shows the SEM images of the control and optimum bond strength specimens (for C42.5 include CTRL and MS7NS3 and for C52.5 including CTRL and MS5NS5 specimens). As it can be seen in Figs. 4b and 4d, the hydrated cement particles decreased compared to the CTRL specimens which indicate an increase of cement particle activity due to addition of NS and MS. On the other hand, these changes are accompanied by an increase in the rate of production of hydration products, which caused more formation of CSH gels, porosity reduction and consequently creating a denser structure [24]. This decrease in porosity not only increases compressive strength but also by reducing permeability and emission of salt water caused an improvement of the coating layer of concrete and protects embedded rebar, which can also lead to an increase of bond strength. In Lee et al. study [25], it was also concluded that bond strength is directly related to the amount of hydration products. In other words, the addition of NS and MS increases the adhesion of rebar to concrete and increases its bond strength due to increasing the hydration products rate. In addition, the results of the study of Adak et al [8] show that the bond strength is directly correlated with the amount of CSH gel created, which can be a reason of bond strength improvement by the addition of NS and MS.

On the other hand, by comparing Figs. 4-a and 4-b with Figs. 4-c and 4-d, it is observed that increasing of CSC has improved the microstructural properties. The CSC based on the cement particles fineness has the same effect of NS and MS replacement which by increasing the cement particle size in a larger volume (up to 90% of cementitious material) it increases the hydration products and crystalline composition.

As a result, the use of higher CSC containing SCM such as the simultaneous use of NS and MS has a synergistic effect on microstructural properties such as hydration, porosity and permeability which lead to an improvement of the concrete mechanical properties such as compressive strength and bond strength.

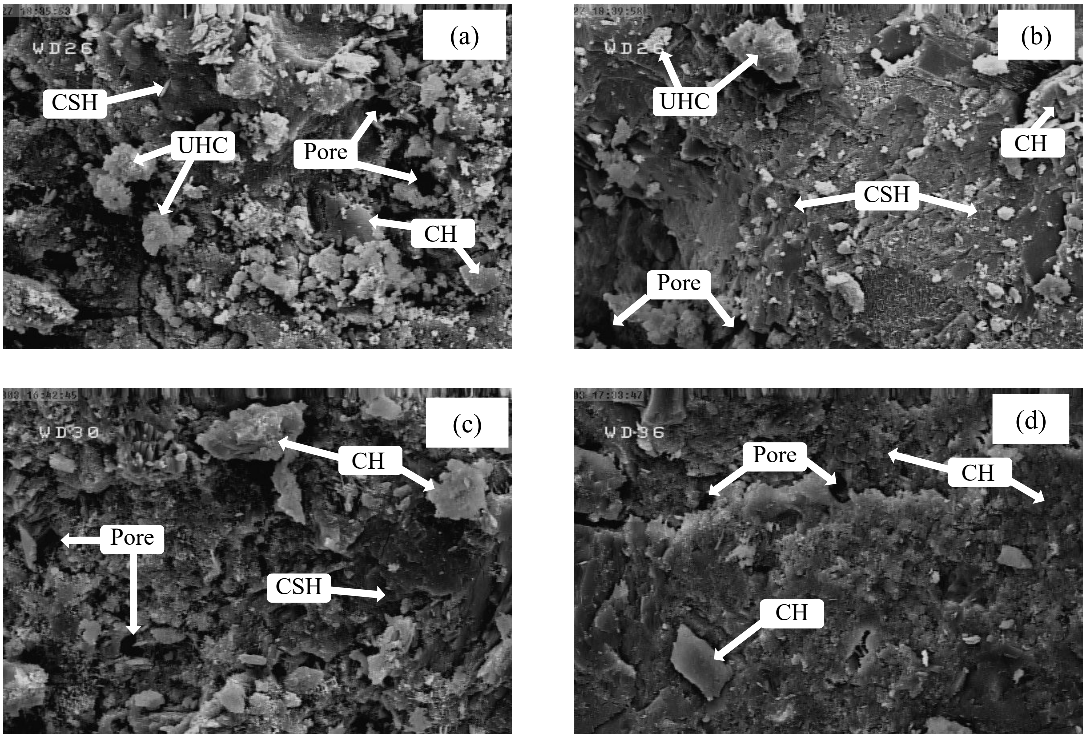


Fig.4. SEM images of specimens (a) CTRL-C42.5, (b) MS7NS3-C42.5, (c) CTRL-C52.5 and (d) MS5NS5-C52.5.

4. CONCLUSION

In present study, the effect of different replacement percentages of NS and MS for two CSC of 42.5 and 52.5 MPa on compressive and bond strength of 14 specimens exposed to saline environments was investigated. The results are as follow:

- Simultaneous use of NS and MS and its replacement with part of the cement improves the mechanical properties such as compressive and bond strength. Compressive and bond strength increased up to 90% and 60% respectively.
- Cements of higher CSC due to higher fineness increase the hydration rate and improve the concrete properties such as compressive and bond strength. Also, the difference between the fineness of these two types of cement resulted in different optimized mix designs; the optimal mix designs for maximizing compressive and bond strength for C42.5 is 7% MS + 3% NS and for C52.5 is 5% MS + 5% NS.
- The microstructural results from SEM images show that the additions of MS and NS, due to the pozzolanic role, increase the hydration products. This increase leads to reduce porosity of the specimens and thus not only increase the compressive strength but also increase the diffusion resistance of the destructive ions in the concrete. On the other hand, porosity reduction of the specimen at the contact surface of the rebar to the concrete and increasing of the hydration products such as CSH gel leads to increase of bond strength.
- The results show that CSC has a direct effect on compressive strength, bond strength and microstructure improvement and should be considered as an effective factor in the mix design. A higher CSC can also be used to control damages caused by increasing of salt water concentrations in the environment.

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