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Investigating the effect of the cement paste and transition zone on strength development of concrete containing nanosilica and silica fume

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ABSTRACT

Concrete performance is affected by aggregates, the bulk cement paste and particularly the interfacial transition zone (ITZ). In this regard, the ITZ is generally weaker than either of two main components of concrete, namely the aggregate and the bulk hydrated cement paste. On the other hand, the strength properties are highly influenced by the ITZs complex microstructure (which has a dynamic nature) and its gradual variations as a result of environmental conditions. Many attempts have been made to overcome the heterogonous deficiencies of concrete through the utilization of different pozzolanic materials such as nanosilica (nS) and silica fume (SF). In the present work, nS at 0%, 1.5%, 3%, 5% and 7.5% and SF at 0%, 5% and 7.5% by weight of cement were utilized to investigate their effect on the strength properties of concrete and corresponding cement paste at early and older ages. A microstructure study was also performed by SEM, XRD and EDS to realize the reasons for the obtained results. The results demonstrated that adding 3% or 5% nS to specimens free of SF would increase both cement paste and concrete compression strength. The microstructure analysis revealed that modification of the ITZ was responsible for this strength enhancement.

1. Introduction

Concrete is known as a porous, highly heterogeneous and multiphase composite material with aggregate, bulk cement paste and an interfacial transition zone (ITZ) between them. It is well-known that the ITZ is the weakest part in concrete, as well as an essential factor determining the concrete's performance. It is usually characterized by the following microscopic features: (a) the presence of higher porosity in comparison with the bulk cement paste and relatively large pores; (b) precipitation and deposition of larger size portlandite crystals and highly porous hydration products such as ettringite. Considerable attention has been paid to the influence of various factors regarding the ITZs microstructure on the overall response macro-properties of concrete, such as mechanical strength, elastic moduli and crack propagation mechanisms for justifying the significance of researching ITZ [1–9].

In order to develop high performance concrete, an essential strategy is to enhance the stiffness and strength of the ITZ to a level comparable to that of bulk paste aggregate. This might be achieved by involving supplementary cementing materials (SCM) such as silica fume to the concrete mixture. It has been stated that silica fume will significantly reduce both the interfacial region's porosity and the deposition of a portlandite rim, in addition to modifying the ITZ, resulting in improvements in mechanical strength and concrete durability properties [2,4–6,9–12].

Recently, new techniques have been effectively used to control cement-based materials' properties and performance, and for providing materials with new functions by adding nanosized particles to cement-based composites. Among these, nanosilica (Nano-SiO_2, nS) has attracted special attention because of its noticeable performance compared to other additives. [13,14]. nS particles have been found to enhance cement paste compression strength and improve its microstructure [15,16]. The addition of nS into mortar and concrete mixtures accelerates the hydration process, improving their strength and microstructure characteristics [17–23]. This leads to better bond strength of the aggregate–cement paste interface [15]. Higher strengths of mixtures with nS compared to those with silica fume have also been reported for mortars and concrete [17,18,23]. However, no distinct reports are available regarding whether these improvements are due to the capability of nS in the modification of the ITZ or the bulk paste.

Although there has recently been some efforts to characterize the local mechanical properties of the ITZ by microindentation or microhardness testing and the nanoindentation [24] method, it remains difficult to determine the local properties of the ITZ due

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to the complexity of the structure and the constraints imposed by existing analysis techniques [25]. In case of the lack of such specific techniques to directly measure the mechanical properties of the transition zone, a number of indirect approaches have been employed [26]. An indirect route for the evaluation of the physical and mechanical properties of the ITZ is to increase the volume fraction of the aggregate, while aggregate gradation remains constant [27,28]. Another [29] is to keep volume fraction constant, but crash the aggregate into a finer size, leading to an increase in the volume fraction of transition zones related to the specific surface area of aggregate and a decrease in the volume of bulk paste. However, despite many research studies on the effectiveness of different supplementary cementitious materials on the properties of the ITZ or bulk cement paste [4,6,7,30,31], a lack of information still exists that prohibits a full understanding of this complex phenomenon.

The present work aimed to evaluate how the performance of the ITZ and bulk cement paste in the concrete may be affected as a result of the utilization of nano- and microsilica admixtures. Compressive strength developments of both concrete and corresponding cement paste mixtures were compared and the results were evaluated by microstructure analyses.

2. Experimental procedures

A schematic procedure of the present study is illustrated in Fig. 1. As shown, nS and SF were used in predetermined mixtures and the compressive strength of both cement paste and concrete mixtures were determined at different ages. Subsequently, the results were verified by microstructural analysis.

2.1. Characteristics of materials

The Portland cement used was Type 1-425, equivalent to CEM I 42.5 N, as classified by the BS EN 197-1 standard [32], from the Hekmatan factory (Hamedan, Iran). SF (manufactured by Iran Ferrosilice Company) was used as a partial replacement for cement in this work. The chemical composition and selected physical characteristics of the cement and SF are summarized in Table 1. Hydrophilic amorphous SiO_2 nanoparticles supplied from Evonik Industries AG, AEROSIL® 200 as commercial pyrogenic nanosilica powder was used and labeled nS. The nS properties, according to the product data sheet, are presented in Table 2.

Coarse aggregate with a maximum size (MSA) of 19 mm and fine aggregate with a 3.4 fineness modulus were used. The specific gravity and water absorption of the coarse and fine aggregates were 2.56%, 2.20% and 2.61%, 3.09%, respectively. A commercial superplasticizer (SP) admixture as a polycarboxylic acid-based agent, (Gelenium 110P, BASF, Germany) with a density of 1.08 g/cm^3 was used to adjust the consistency of both the paste and concrete mixtures, and to efficiently disperse the nanosilica particles.

2.2. Characteristics of mixtures

Water–cement ratio 0.45 is usually used for producing normal concrete mixture. This selection may be helpful to gather a fundamental data regarding to the ITZ evaluation. Of course in the future study the lower and higher water–cement ratios compare to 0.45 are needed to examine how the grade of concrete may affect the results.

Silica fume and nanosilica were used at different levels in fifteen normal concrete and corresponding cement paste mixtures (0.45 w/cm ratio). Try had been done to gather a fundamental data regarding to the ITZ evaluation. The nS and SF dosages were 0%, 1.5%, 3%, 5% and 7.5%, and 0%, 5% and 7.5% by mass of the cementitious materials as a partial replacement for cement, respectively. Water to cementitious materials ratio (w/cm) of both the cement paste and concrete mixtures was constant and equal to 0.45. For the cement paste and concrete mixtures, water, superplasticizer and nanosilica powder were mixed using a rotational mixer and

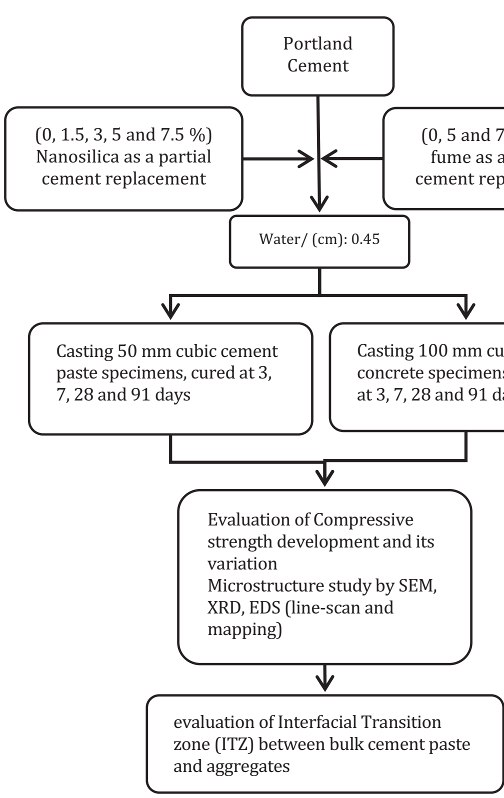

Fig. 1. Schema of the study procedure.

Table 1
Characteristics of the cement and silica fume.

Composition (%)	Cement	Silica fume
Chemical compositions		
SiO_2	21.6	85–95
Al_2O_3	4.91	0.5–1.7
Fe_2O_3	3.69	0.4–2
CaO	63.82	–
MgO	1.45	0.1–0.9
SO_3	2.14	–
Na_2O	0.52	0.15–0.2
K_2O	0.64	0.15–1.02
C_3S C2S	51.03	–
C_2S	23.45	–
C_3A	6.46	–
C_4AF	11.78	–
LOI (%)	–	1.5–2.5
Physical properties		
Specific gravity (g/cm^3)	3.12	2.21
Specific surface (cm^2/g)	3570	15,000

Table 2
Properties of nanosilica powder.

Properties	Results
Specific surface area (BET) (m^2/g)	25 ± 200
Average primary particle size (nm)	12
Tapped density (g/l)	50
Bulk density (g/l)	30
LOI (%)	⩽1

Table 3
Mix proportions of the cement paste and mini slump results.

Mix No.	Mix Design	nS (wt.%)	SF (wt.%)	(g)				SP (wt.%)	Mini-slump (mm)
				Cement	Nanosilica	Silica fume	Water		
1	NS0-Ref	0	0	2500.0	0	0	1125	0	72
2	NS0-SF5	0	5	2375.0	0	125.0	1125	0.16	73
3	NS0-SF7.5	0	7.5	2312.5	0	187.5	1125	0.23	75
4	NS1.5-Ref	1.5	0	2462.5	37.5	0	1125	0.52	78.5
5	NS1.5-SF5	1.5	5	2337.5	37.5	125.0	1125	0.56	69.5
6	NS1.5-SF7.5	1.5	7.5	2275.0	37.5	187.5	1125	0.63	77.5
7	NS3-Ref	3	0	2425.0	75.0	0	1125	1.03	81
8	NS3-SF5	3	5	2300.0	75.0	125.0	1125	1.12	73
9	NS3-SF7.5	3	7.5	2237.5	75.0	187.5	1125	1.20	76.5
10	NS5-Ref	5	0	2375.0	125.0	0	1125	1.68	78
11	NS5-SF5	5	5	2250.0	125.0	125.0	1125	1.83	78.5
12	NS5-SF7.5	5	7.5	2187.5	125.0	187.5	1125	1.89	79
13	NS7.5-Ref	7.5	0	2312.5	187.5	0	1125	3.01	79.5
14	NS7.5-SF5	7.5	5	2187.5	187.5	125.0	1125	3.46	74.5
15	NS7.5-SF7.5	7.5	7.5	2125.0	187.5	187.5	1125	3.61	79

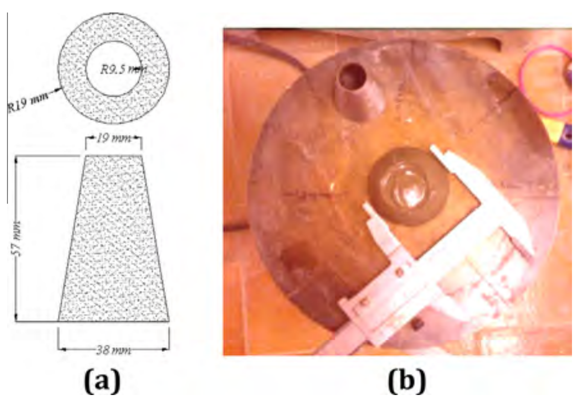

Fig. 2. Mini-slump cone (a) schematic shape and dimensions (b) measurement of spread.

homogenized by Ultrasonic probe for nearly 2 min. in order to effectively disperse and facilitate the deagglomeration of nanoparticles throughout the sonicated mixture.

2.2.1. Cement paste mixtures and specimen preparation

Table 3 provides the mix proportions of 15 proposed cement paste mixtures. The cement paste mixtures were mixed using a paddle mixer and following the ASTM C305-14 procedure. In order to assess the proper dosage of superplasticizer the consistency and the flow behavior of the cement paste mixtures were evaluated utilizing a miniature slump cone (Fig. 2(a) and (b)), developed by Kantro [33] and also used by other researchers [34–36]. The 50 mm cement paste cube specimens were cast according to the specification of cube molds in ASTM C109-13 for determining compressive strength development via a three-, seven, 28 and 91-day curing-age and microstructure study.

2.2.2. Concrete mixtures and specimen preparation

Mix proportions of the concrete mixtures and the results of fresh concrete slump tests are shown in Table 4. A pan mixer was used and the mixing procedure was as follows. At the outset, fine aggregate and cement (or cement and SF) were initially mixed; then, half a solution of superplasticizer with mixing water, including nS (sonicated mixture), was added and mixed for nearly 2 min. In the final step, coarse aggregate and the rest of the sonicated suspension were added and mixed for 3 min. Following the mixture preparation, the slump test was conducted in accordance with ASTM C143-12. The proper dosages of superplasticizer were selected to adjust the consistency of the mixtures, avoid bleeding and promote the dispersion of nano-, microsilica and cement-particles. Eight 100 mm cube specimens were cast for each concrete mixture to be used for the determination of compressive strength development and microstructure study. As with the cement paste samples, the concrete specimens were de-molded after 24 h and immersed in water at 20 ± 1 °C until testing ages.

Table 4
Mix proportions of the concrete and slump results.

Mix No.	Mix Design	nS (wt.%)	SF (wt.%)	(kg/m^3)						SP (wt.%)	Slump cm
				Cement	Nanosilica	Silica fume	Fine Agg.	Coarse Agg.	Water		
1	NS0-Ref	0	0	400	0	0	948	776	180	0.48	10
2	NS0-SF5	0	5	380	0	20	948	776	180	0.49	9
3	NS0-SF7.5	0	7.5	370	0	30	948	776	180	0.64	9.5
4	NS1.5-Ref	1.5	0	394	6	0	948	776	180	1.38	10
5	NS1.5-SF5	1.5	5	374	6	20	948	776	180	1.42	12
6	NS1.5-SF7.5	1.5	7.5	364	6	30	948	776	180	1.23	11
7	NS3-Ref	3	0	388	12	0	948	776	180	1.67	12
8	NS3-SF5	3	5	368	12	20	948	776	180	1.70	11.5
9	NS3-SF7.5	3	7.5	358	12	30	948	776	180	1.65	12
10	NS5-Ref	5	0	380	20	0	948	776	180	2.28	11
11	NS5-SF5	5	5	360	20	20	948	776	180	2.58	10
12	NS5-SF7.5	5	7.5	350	20	30	948	776	180	2.46	12
13	NS7.5-Ref	7.5	0	370	30	0	948	776	180	3.09	9
14	NS7.5-SF5	7.5	5	350	30	20	948	776	180	4.54	9
15	NS7.5-SF7.5	7.5	7.5	340	30	30	948	776	180	4.50	8.5

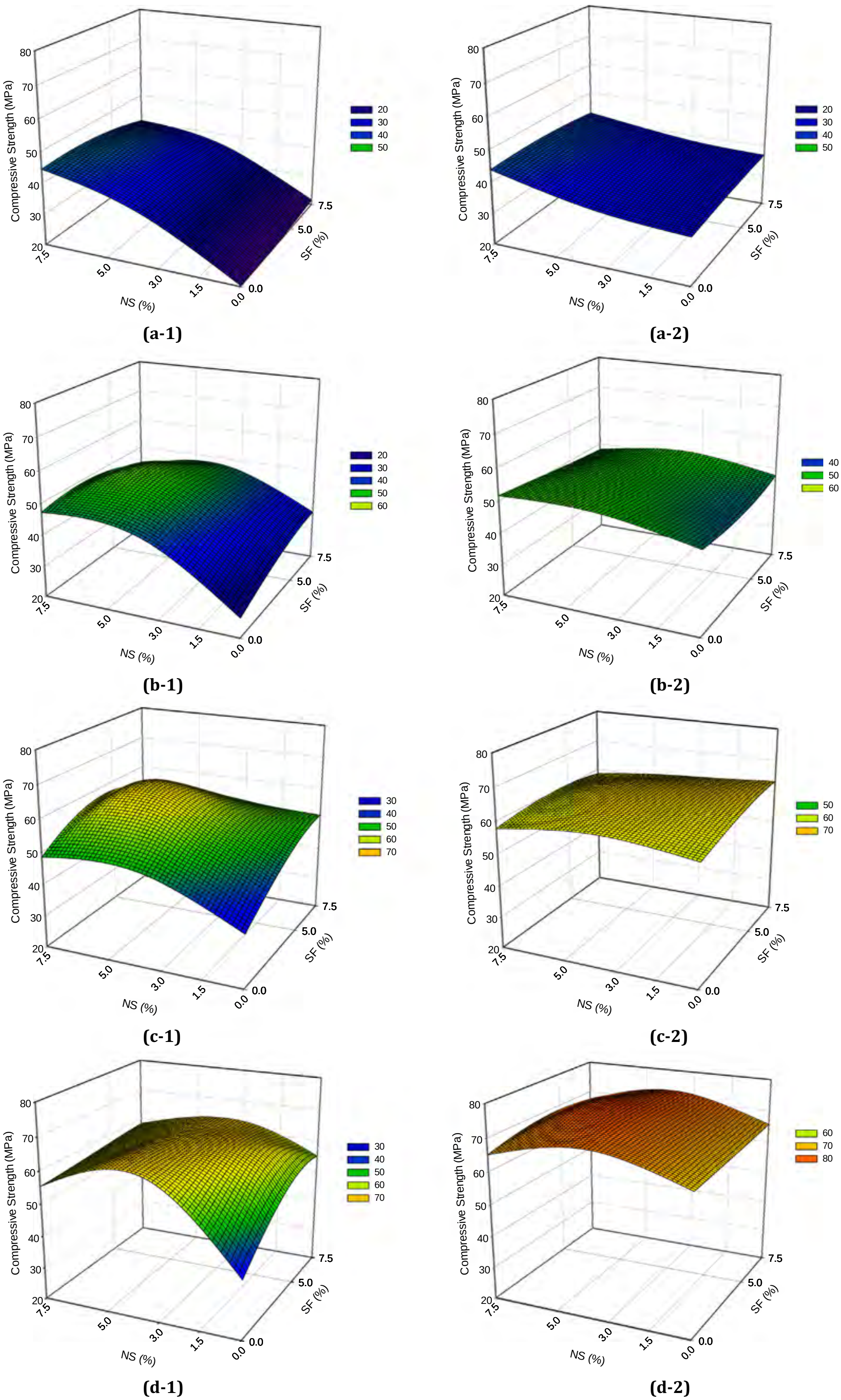

Fig. 3. Compressive strength of (1) cement paste and (2) concrete specimens as a function of nS and SF contents at (a) 3, (b) 7, (c) 28 and (d) 91 days.

Table 5
The rate of compressive strength development percentages for both cement paste and concrete mixtures.

Mix No.	Mix Design	nS (wt.%)	SF (wt.%)	3–7 days		3–28 days		3–91 days	
				Cement Paste	Concrete	Cement Paste	Concrete	Cement Paste	Concrete
1	NS0-Ref	0	0	28.6	32.2	79.3	64.7	87.6	81.6
2	NS0-SF5	0	5	46.3	37.5	104.6	72.3	109.5	87.3
3	NS0-SF7.5	0	7.5	65.0	28.4	136.8	71.1	153.8	77.9
4	NS1.5-Ref	1.5	0	23.0	24.2	53.6	46.3	79.7	65.4
5	NS1.5-SF5	1.5	5	53.5	24.8	96.0	68.0	132.6	83.6
6	NS1.5-SF7.5	1.5	7.5	56.5	31.8	85.8	77.1	109.6	89.6
7	NS3-Ref	3	0	25.5	38.3	39.6	64.4	79.9	91.1
8	NS3-SF5	3	5	44.7	38.8	75.1	82.8	100.3	101.9
9	NS3-SF7.5	3	7.5	37.1	34.4	56.5	62.0	87.8	91.0
10	NS5-Ref	5	0	13.7	26.5	28.2	49.8	52.3	74.5
11	NS5-SF5	5	5	26.5	22.2	51.1	52.8	52.8	79.5
12	NS5-SF7.5	5	7.5	21.9	23.1	39.5	57.4	60.7	71.9
13	NS7.5-Ref	7.5	0	6.1	17.8	8.9	31.8	24.4	48.5
14	NS7.5-SF5	7.5	5	15.4	6.9	34.5	36.1	45.8	51.8
15	NS7.5-SF7.5	7.5	7.5	7.4	12.6	28.9	37.3	43.3	58.2

Furthermore, in order to proceed conducting the microstructure studies, samples of the 28-day-cured-specimens were left in methanol solution to stop mortar hydration. The main aim of the studies were the evaluation of the matrix microstructure and to examine trends at the interfacial zone, as well as qualitative analyses of the abundance of elements with a distance along a line or two dimensional area analysis using SEM, XRD and EDS (qualitative analysis, including line-scan and elemental mapping).

3. Results and discussion

3.1. Consistency and workability

As shown in Tables 3 and 4, the required dosage of superplasticizer in the cement paste and concrete mixtures was more sensitive to nS content than to SF. This was due to the high fineness and large surface area of silica nanoparticles [15].

3.2. Compressive strength development

3.2.1. Cement paste specimens

The compressive strength of the cement paste versus the amount of silica fume and nanosilica are depicted in 3D graphs shown in Fig. 3(a-1)–(d-1) at the ages of 3, 7, 28 and 91 days, respectively. The results verified that increasing the nS content from 0% to 5% by weight of cement will lead to a significant increase of compressive strength by 118% and 80% at 3 and 7 days, respectively. Nevertheless, SF had a minor effect on strength development. These results show that nS is more efficient for enhancing the paste strength compared to SF [14,15,37,38]. On the other hand, utilizing 5% nS as a replacement for cement was revealed as a potent approach for physically filling the void space between larger particles, thereby promoting cement hydration and pozzolanic reaction with calcium hydroxide and forming more C–S–H gels, as well as acting as seeds to provide nucleation sites for cement hydration products [15,16,39–43]. However, when the nS content was increased to 7.5%, the strength of the cement paste decreased, regardless of SF content. This result may have been due to the large aggregation (firmly-held clusters) or agglomeration (loosely-held clusters) of nanoparticles, primarily because of their high specific surface area and van der Waals force; consequently, formation of weak spots throughout the microstructure of the cementitious composite led to sites of high-stress concentration [37,39].

As shown in Fig. 3(c-1), by adding 7.5% nS to the 5% SF specimen, the 28-days-strength decreased by about 20%. The conclusion can therefore be drawn that at an early age, both nS and SF will strongly act as filler, pozzolans and nucleation seeds to improve microstructure and decrease bulk porosity, leading to strong strength being gained. However, at longer curing ages, the influence of un-hydrated micro- and nanoparticles with relatively large aggregates or agglomerates will dominate. This is likely caused by self-desiccation and rapid depletion of the calcium ions inside the paste, due to nanoparticles' high specific surface area and wider nanopore structure [39].

3.2.2. Concrete specimens

Fig. 3(a-2)–(d-2) demonstrates the strength development of concrete specimens versus SF and nS contents at 3, 7, 28 and 91 days, respectively. The obtained results verified that similar to cement paste, adding nS will increase compressive strength, due to the physical and pozzolanic effect of amorphous silica nanoparticles [22,44–46]. It was confirmed that although both nS and SF contain highly reactive amorphous silica, the effect of the former – largely due to its much smaller size (about 10 times) – rather than the latter was obviously more substantial [15,47]. Although high activity of nS particles will increase early strength of concrete, when nS content was 7.5%, the strength of concrete was decreased, regardless of SF content. This was likely due to the agglomeration of nanoparticles in the concrete's microstructure.

The obtained results are in a good agreement with other results [15,16]. They also concluded that nS particles enhanced cement paste strength and improve its microstructure. Furthermore, the addition of nS into mortar and concrete mixtures accelerates the hydration process, improving their strength and microstructure characteristics [17–23,48]. This leads to better bond strength of the aggregate–cement paste interface [15]. Higher strengths of mixtures with nS compared to those with silica fume have also been reported for mortars and concrete [17,18,23].

3.2.3. Strength gain of both the paste and concrete

The mechanisms by which silica fume can enhance the performance of cementitious systems, including cement paste, mortar and concrete, have been described in the ACI Committee 234 report [49]. In the report, it is stated that the mechanism of physical and chemical interactions may be responsible for enhancing the strength characteristics of silica fume specimens. These mechanisms are mostly applicable to nanosilica as high reactive silica, with a higher specific surface area.

3.2.3.1. Physical influence. The result of incorporating extremely fine particles of nS will significantly reduce bleeding and increase

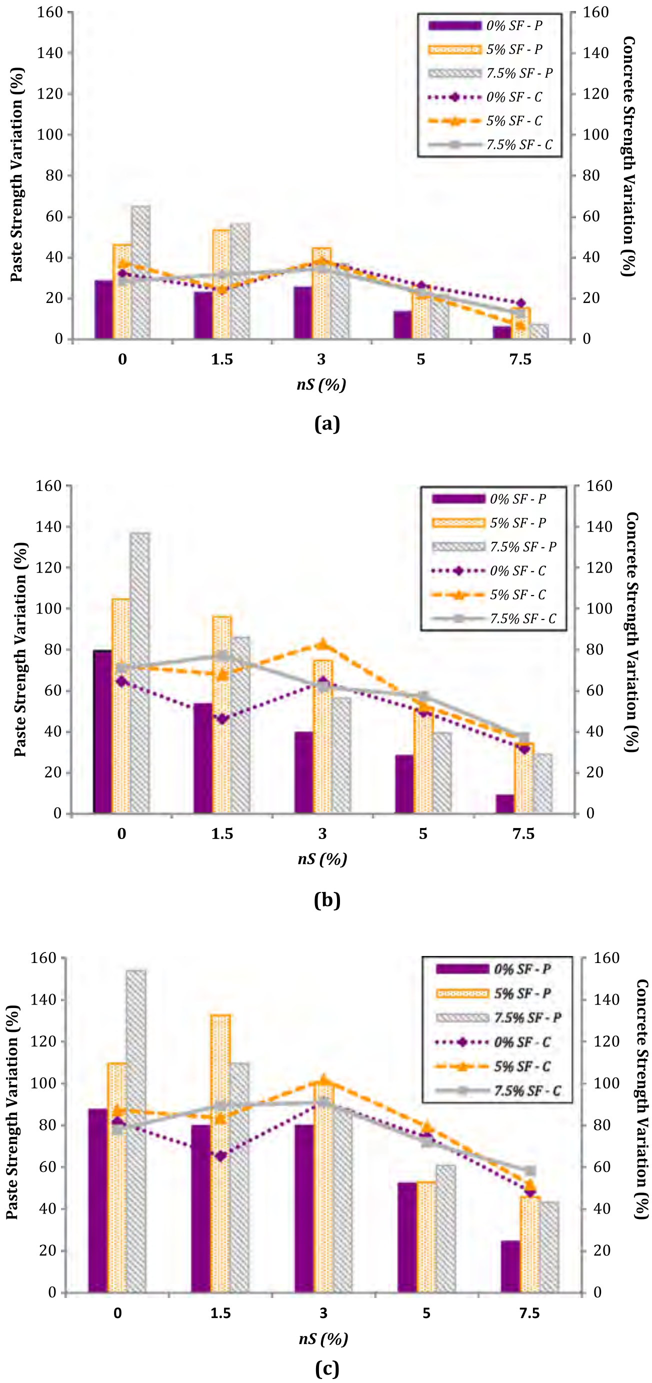

Fig. 4. Cement paste and concrete compressive strength variation percentage at (a) early age (3–7 days), (b) middle curing age (3–28 days) and (c) long-term (3–91 days) for mixtures incorporating 0%, 5% and 7.5% SF.

the packing density of solid materials, acting as nanoreinforcement and also as a filler, filling any remaining voids in the partially hydrated cement paste. It will also promote the acceleration of cement hydration by providing high numbers of nucleation sites for the precipitation of cementitious hydration products leading to cement-hydration phases-formation.

3.2.3.2. Chemical influence. Similar to SF, nS – as a highly reactive pozzolan – reacts with calcium hydroxide (CH) during cement hydration to form calcium silicate hydrates (CSH), which form in the voids of CSH gels (xCaO·ySiO$_2$·zH$_2$O) produced by cement hydration in its final stages, thus producing a compact microstructure. Due to the smaller particle size of nanosilica, the pozzolanic reaction of nS may have started sooner and could therefore have been more effective. [14,41,50].

3.2.3.3. Microstructure modification. The nS may reduce porosity of not only the bulk cement paste, but also the transition zone between the bulk paste and aggregates, and could have done so more effectively than silica fume according to the physical and chemical effects of nS [51]. These effects led to an increase in density of the bulk cement paste and improved bonding strength between the cement paste and aggregates, as is discussed in Section 3.3.

3.3. Assessing the interfacial transition zone using the strength gain variation approach

In order to evaluate the influence of nS and SF on the ITZs performance, the values of compressive strength development rate at 7, 28 and 91 days were determined according to the strength at 3 days for different cement pastes and concrete mixtures. These values are summarized in Table 5 and graphically shown in Fig. 4(a)–(c).

The results showed that silica fume had a considerable influence on cement paste strength; the maximum rates of strength development were 65%, 137% and 154% for 7-, 28 and 91-days specimens, respectively; these results belong to the cement paste specimen labeled NS0-SF7.5.

The rate of strength development for the concrete specimens was highly affected by nS rather than SF. Incorporation of nS into the SF concrete specimens enhanced strength development more than in concrete without nanosilica. Although the strength development rate of 3% nS cement paste was not changed in comparison with the reference or the 1.5% nS pastes, the strength gain rate of corresponding concrete was increased to a much higher degree than the corresponding paste (Fig. 4(a)–(c)). The maximum rates of 39%, 83% and 102% were obtained for NS3-SF5 specimens at 7, 28 and 91 days, respectively. This result revealed that nanosilica, as a very fine nanoparticle, enhanced the ITZ layer of concrete more than did paste fractioning. This result interpreted the degree of ITZ enhancement. This result revealed effectiveness of the strength development evaluation. It is notable that higher amounts of either nS or SF in the specimens will not improve their strength, which may be due to the agglomeration of nanoparticles and SF in the ITZ and the body of concrete specimens.

From the results yielded by this study, it was concluded that the highest rates of compressive strength development were obtained in mixtures incorporating 3% or 5% nS and 5% SF. As production of the cement hydration is known as nano and micro scale particles; for this reason XRD and SEM analysis of the hydration products and also the surface between gel and aggregates of the nano and micro structure analysis is known as an effective and reliable method for assessment of the hydration products. In order to evaluate the performance of nS in changing the ITZ, microstructure analysis, including XRD and SEM, were performed.

3.4. Microstructural analysis

3.4.1. XRD analysis

Chemical components of cement paste and concrete specimens (NS0-Ref, NS3-Ref, NS5-Ref and NS0-SF5) were obtained by XRD analysis, as can be seen in Fig. 5(a) and (b), respectively. The analysis results indicated the following crystallization compositions in the cement paste: portlandite (Ca(OH)$_2$) and C–S–H, while the compositions in the concrete specimen were as follows: portlandite, C–S–H, CaO, CaCO$_3$ and SiO$_2$. The intensity of the

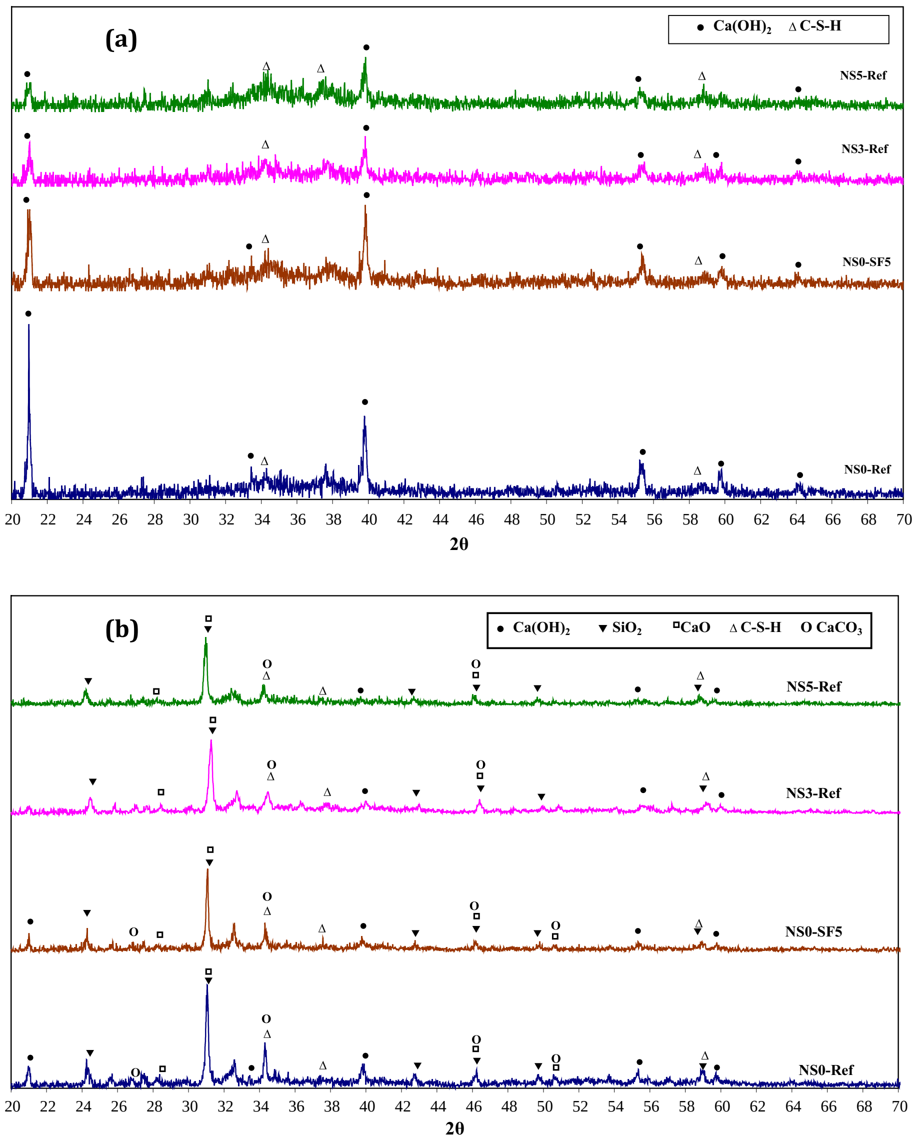

Fig. 5. XRD pattern of hardened (a) cement paste and (b) concrete, incorporating 0%, 3% and 5% nS (NS0-Ref, NS3-Ref and NS5-Ref) and 5% SF (NS0-SF5) at 28 days.

compositions marked in XRD patterns differed significantly throughout different mixtures. As demonstrated in the cement paste patterns (Fig. 5(a)), the intensity of CH decreased in the presence of 5% SF; this reduction was considerable, as nS was added by 3% or 5% according to the weight of cement. This result revealed that by consuming more CH, nS acted as a higher pozzolanic performance than SF; the compressive strength development results were in a good agreement with those for microstructure analysis. Similar to the paste results, XRD patterns in Fig. 5(b) show that the intensity of signals related to CH crystals mostly decreased and even disappeared in mixtures containing 3% and 5% nS. Thus, it is assumed that CaO and $CaCO_3$ signals were weak in nS-incorporated-mixtures, mainly due to the high intensity of pozzolanic activity, causing the elimination of un-hydrated phases of Portland cement, such as CaO. As discussed in Section 3.2, a significant decrease in CH content can be attributed to the high degree of the hydration process of cementitious materials, leading to a reduction of porosity throughout the bulk paste, as well as transition zone layer modification [52]. It was clear that the SiO_2 spectral feature could be attributed to siliceous aggregates in the mixtures.

3.4.2. SEM and the EDS elemental analysis

Different series of SEM micrograph of the ITZ between the bulk cement paste and aggregate for reference concrete and the sample incorporating nS was carried out. Fig. 6 shows the result for the reference and 3% nS specimens. In order to detect the chemical compositions depicted in SEM images and their concentrations distributed around the ITZ, qualitative EDS elemental analysis, including line-scan and elemental mapping scan techniques (for Si, Ca, O, S, Al and Fe) corresponding to the same SEM images were performed; related graphs and images are provided in Figs. 7 and 8, respectively.

3.4.2.1. Microstructure of reference concrete (without nS and SF). Fig. 6(a) shows the SEM micrograph of the ITZ between the aggregate and the bulk paste in the reference concrete specimen. Directly next to the aggregate surface, which has been covered by a small amount of irregularly-structured C–S–H gels, a non-uniform area of porous matrix, the so-called interfacial transition zone, has been formed [6]. Line- and mapping EDS-spectra (Figs. 7(a) and 8(a)) show that the above-mentioned special

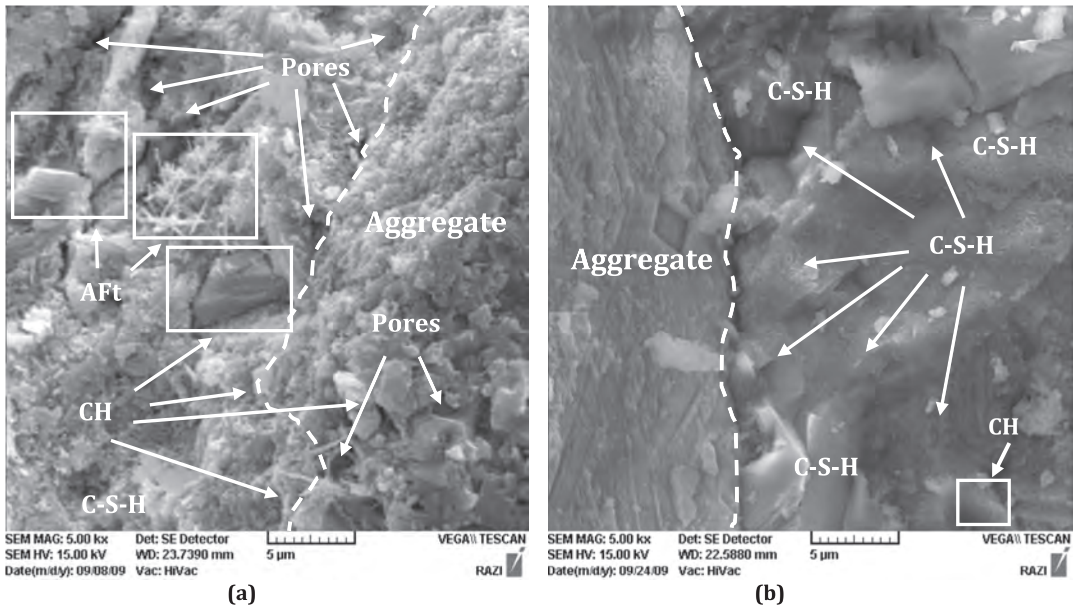

Fig. 6. The SEM micrographs of the ITZ between the aggregate and bulk cement paste for (a) the reference concrete (NS0-Ref) and (b) the sample incorporating 3% nS (NS3-Ref).

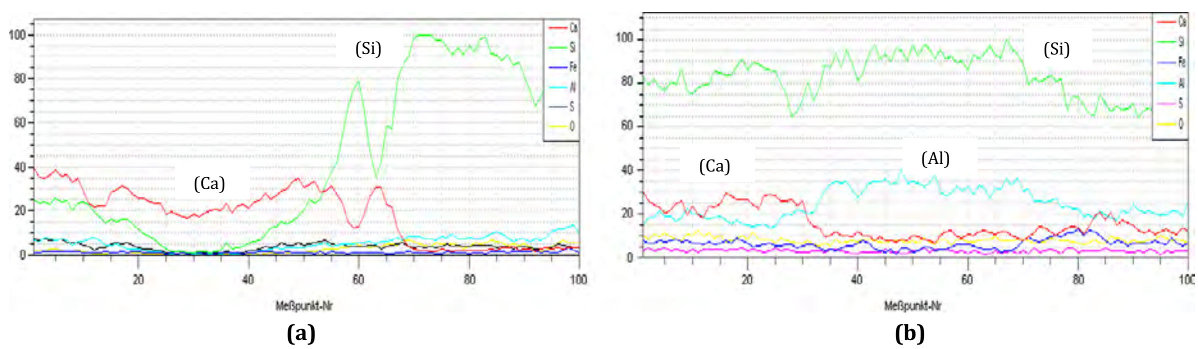

Fig. 7. The profiles of elemental analysis by EDS line-scan corresponding to the SEM images of the ITZ for (a) the reference concrete (NS0-Ref) and (b) the sample incorporating 3% nS (NS3-Ref).

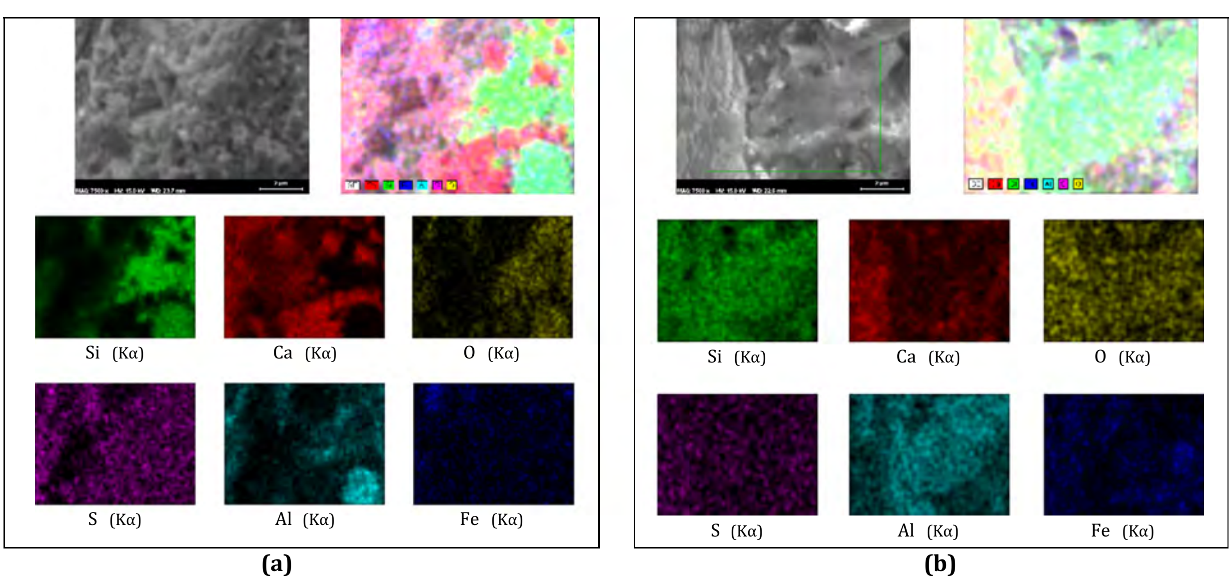

Fig. 8. The images of the elemental analysis by EDS color-mapping-scan corresponding to the SEM images of the ITZ for (a) the reference concrete (NS0-Ref) and (b) the sample incorporating 3% nS (NS3-Ref). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

microstructure included big portlandite (CH) crystals in contact with the aggregate surface, many pores and large pockets of porous materials such as Aft needle crystals. These microstructure analysis results fully validated the obtained macroscopic results of the compressive strength test.

3.4.2.2. Microstructure of concrete incorporating 3% nS. The SEM image in Fig. 6(b) demonstrates the ITZ between the bulk paste and aggregate for concrete containing 3% nS. The microstructure of the interfacial zone of mature concrete incorporating nS was clearly dense and uniform, and its structure was not very different from that of the bulk cement paste matrix. In contrast to the reference concrete, the EDS analyses (Figs. 7(b) and 8(b)) showed that no large CH crystal rim could be observed in the ITZ or near it. There was only a small CH rim farther away from the interface, nearly in the bulk paste area (Fig. 6(b)). Thus, no specific borderline could be measured between the bulk paste matrix and the ITZ, and it appeared that the bulk paste matrix extended right up to the aggregate edge. These characteristics could be attributed to the fact that most CH crystals had been consumed in the pozzolanic reaction with nanosilica in order to produce more C–S–H gels, thereby providing less porosity in both the ITZ and the bulk paste, leading to more uniform development of the ITZ.

One other relevant issue that may have contributed to the differences in microstructure discussed above was the lack of, or almost non-existent formation of water-filled spaces [6] surrounding the concrete aggregates in the fresh and hardened stages of the cementitious materials matrix containing nS or SF. Fig. 6(b) shows the space around the aggregate, which is surrounded by a dense and solid matrix, in contrast to the nS-free sample, where large pores and some gaps exist throughout the ITZ (Fig. 6(a)). The more efficient solid matrix within the ITZ matrix, modified by nS, may be the result of less bleeding due to the high specific surface area of amorphous silica nanoparticles. Subsequently, the microstructure results revealed that the wall effect [7] was expected to be less critical in nS- and even SF-containing-samples. The main reason for this might be that very tiny particles of nS and SF can approach and increase the packing density of the area around the aggregate surface, and do so much more efficiently than the larger cement particles, thereby causing the much denser and more uniform ITZ.

4. Conclusions

In this research, on the basis of obtained experimental results, the following concluding remarks can be made:

(1) Introducing nS into both cement paste and concrete mixtures will lead to a considerable increase in early age compressive strength. The highest compressive strength result of 44 MPa was obtained for the NS7.5-Ref sample. This result revealed that the early age compressive strength of the concrete specimens was influenced more by nS than SF.
(2) Utilization of nS (by 3%) had a more significant effect on the later age strength of concrete than for the cement paste.
(3) SF can enhance cement paste strength development rates more than concrete rates.
(4) The addition of SF increased the strength of nS-free paste samples only at 7, 28 and 91 days. This trend was also observed for corresponding concrete samples, except mixture No. 3.
(5) The simultaneous presence of nS and SF provided the greatest effect on the strength development enhancement of both cement paste and the concrete samples known as NS5-SF5. Generally, through the paste and concrete mixtures in which SF content was increased, the optimum strength values belonged to the mixtures incorporating smaller nS contents.
(6) Based on the results of the strength gain variations of all mixtures, at a 5% replacement, nS modified the ITZ layer.
(7) Lack of strength sensitivity in concrete mixtures including nS to change in SF contents, as well as levels of nS above 3%, were attributed to the excellent performance of nanosilica in terms of modifying and improving the cement paste aggregate interfaces and the ITZ paste.
(8) In the reference concrete sample, the microstructure of the ITZ was characterized by a large CH layer surrounding the aggregates and by some large pores. On the other hand, it was found that the ITZ microstructure was significantly changed when 3% nS was introduced.
(9) Both XRD and SEM analyses showed that ITZ promotion was generally responsible for enhancing the strength development properties of nanosilica specimens.

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