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## Use of nano-silica in cement-based materials – a comprehensive review

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Recently, nano silica (NS) has gained the attraction of academic researchers and the construction industry because of enhancing the properties of cementitious composites. Although there have been some related reviews, the comprehensiveness and advancedness need to be further improved. This paper is a detailed review of previously conducted studies to explore the influence of NS in cementitious composites for evaluating mechanical properties and durability. The impact of NS on the fresh state, i.e. setting time and workability, and in the hardened state, i.e. compressive, flexural, and split tensile strengths is considered. Besides, the long-term durability is discussed that include permeability, resistance against acid and base attack, abrasion resistance, and carbonation resistance. Furthermore, volume stability and microstructure of concrete with NS are presented. A huge number of studies showed the positive effect of NS with optimized content for improving the concrete properties, while a negative effect was observed with the use of excess NS content. The inclusion of NS in cementitious composites substantially enhances the mechanical properties, durability and microstructure. Meanwhile, better dispersibility is the key to ensure the strengthening effect of NS, which can be improved by changing the morphology/size of NS, optimizing the stirring method, and adding surfactants. Further investigation of the application of NS in special concrete is its development direction, and the effect of NS on the microstructure of main hydration products needs to be further explored.

**Abbreviations:** CR: crumb rubber; FA: fly ash; HPC: high-performance concrete; HSLWAC: high-strength lightweight aggregate concrete; HVFA: high-volume fly ash; ITZ: interfacial transition zone; NS: nano SiO<sub>2</sub>; OPC: ordinary Portland cement; RHA: rice husk ash; SCM: supplementary cementitious materials; SCLWAC: self-compacting lightweight aggregate concrete; SF: silica fume; SCC: self-compacting concrete; SAP: superabsorbent polymers; SEM: scanning electron microscopy; TGA: thermo gravimetric analysis; UHPC: ultra-high-performance concrete; W/B: water to binder; SSA: specific surface area

**Keywords:** Nano-SiO<sub>2</sub>; high-performance concrete; mechanical performance; durability; microstructure

### 1. Introduction

Concrete is the world's most commonly used material in the construction industry because of its high strength, better workability and local availability [1]. Substantial projects such as high-rise buildings, airports, tunnels and bridges require high-strength material and long-term serviceability [2]. However, these requirements are difficult to achieve by using ordinary concrete. Therefore, many studies have been conducted to produce high-performance concrete (HPC) for projects that require high durability and mechanical properties. Numerous methods can be used to prepare HPC, such as the incorporation of supplementary cementitious materials and admixtures. Admixtures are usually added in cement-based material to obtain HPC, and comprised of chemical and mineral admixtures, as shown in Figure 1 [3]. Nano mineral materials used in concrete contain nanoparticles that include metal and non-metal as well as organic and inorganic nanoparticles [2]. The crystal and surface structures of nanomaterials are substantially improved because of their ultrafine particle size [2]. The development came from fine particle size, high surface

area and quantum effect. Therefore, nanoparticle size material has many excellent chemical and physical properties, as compared with traditional material. Khooshechin and Tanzadeh [4] investigated the application of nano silicon dioxide (SiO<sub>2</sub>, NS) in cement and concrete mixtures. Their results indicated a 20.6% and 52% increase in compressive and flexure strengths of concrete with the use of NS, respectively with optimum content. The properties of cement mortar by adding NS were explored by Guefrech et al. [5]. The results indicated the different effects of NS on setting time and consistency. Adding NS improved the compressive strength by adjusting the microstructure of the cement paste [6]. Moreover, the inclusion of NS in the concrete resulted in a considerable improvement at an early age of compressive strength [7]. The inclusion of NS consumed the available portlandite and considerably improved the development of C-S-H gel, lead to substantial growth in the compressive strength of concrete [8].

Nanomaterials have already been applied in wide-ranging scientific fields, such as material science and civil engineering applications, especially during the last decade

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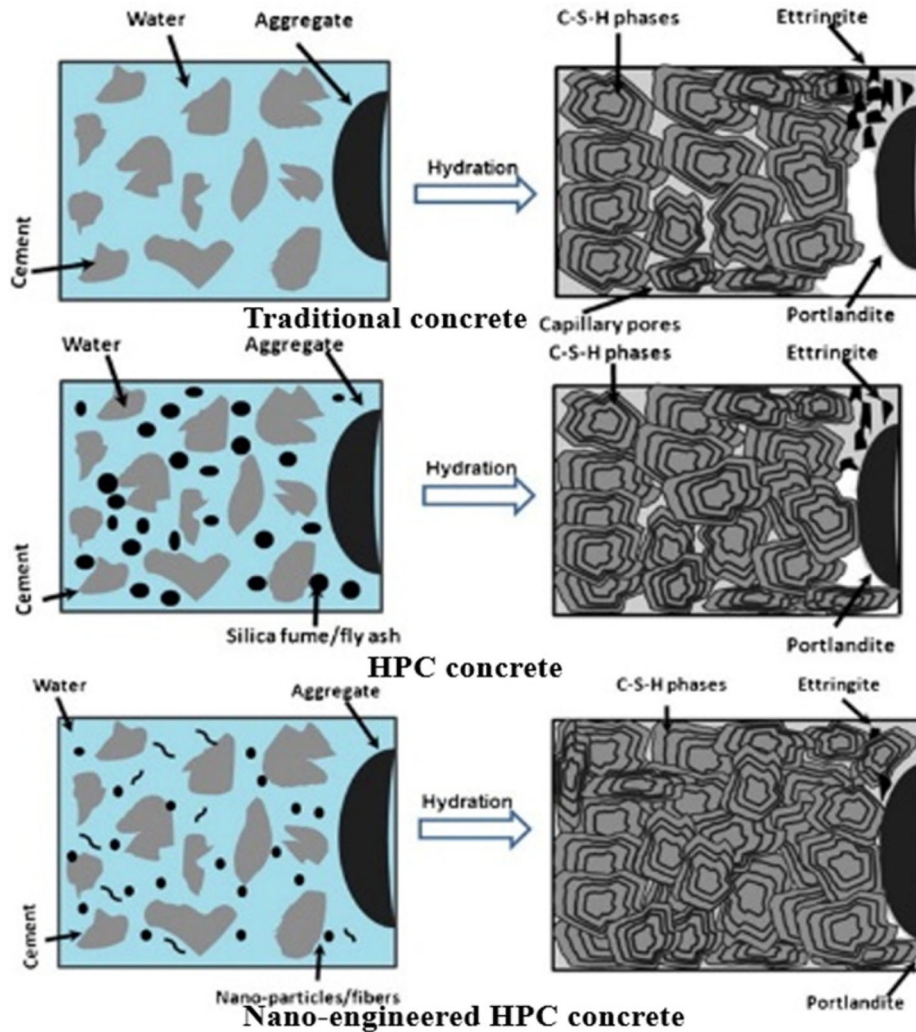


Figure 1. Nano-engineered cementitious composites, reproduced under license number 5503570203195 from [3].

[3]. Figure 2(a) shows that the maximum number of articles are published in the field of engineering (42.4%) and material science (30.4%). The incorporation of NS in concrete composites is increasing recently as evident from yearly-published 169 articles in 2020 as shown in Figure 2(b). The information is obtained from the Scopus database by searching the term ‘Nano silica in concrete.’ Nanomaterials with particle sizes less than 4 nm are very reactive because of their high specific surface area (SSA) [9]. Adding NS and fly ash (FA) decreases the free dispersed water in the concrete owing to the high SSA of NS. In addition to the fresh characteristics of concrete, physical, mechanical and durability were improved substantially [10, 11]. Many types of nanomaterials, such as NS, nano-TiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, nano-limestone, nano-CaCO<sub>3</sub>, nano-Fe<sub>3</sub>O<sub>4</sub>, nano-ZnO<sub>2</sub>, nano-metakaolin and nano-FA, have been used to improve concrete properties [12]. Among all these types, NS is extensively utilized in HPC because of a high specific area, high reactivity and high pozzolanic reaction in concrete. Additionally, NS can generate C-S-H gels and accelerate the dissolution of C<sub>3</sub>S because of its high reactivity [13]. In recent years, NS has been widely used in concrete production to reduce manufacturing costs and apply HPC in substantial

structures. Many studies have shown the impact of nanomaterials on concrete properties. The effect of NS on the performance of HPC is determined by testing fresh mix, durability and mechanical properties as well as characterizing the microstructure of HPC [14]. Mohammed and Adamu [15] investigated the influence of crumb rubber (CR) as the sand on the compacted concrete pavement with the incorporation of NS with various content (i.e. 0, 1%, 2% and 3%) to decrease the compressive strength owing to replacing normal fine aggregate by CR. The results show that the incorporation of NS enhanced the mechanical performance of concrete.

The concrete industry is one of the key elements for CO<sub>2</sub> production and is committed to reducing CO<sub>2</sub> emissions by 2030 [16, 17]. In concrete production, the OPC has high energy consumption and studies showed that CO<sub>2</sub> is released between 0.66–0.82 kg per kilogram of cement produced [18, 19]. This motivated the researcher to explore an alternative material in replacement with ordinary Portland cement (OPC) for sustainable construction. Cemented concrete is certainly one of the most commonly used building materials. Global production of Portland cement has been reported at approximately 4.1 Gt per annum [20]. The cement industry accounts for 8%

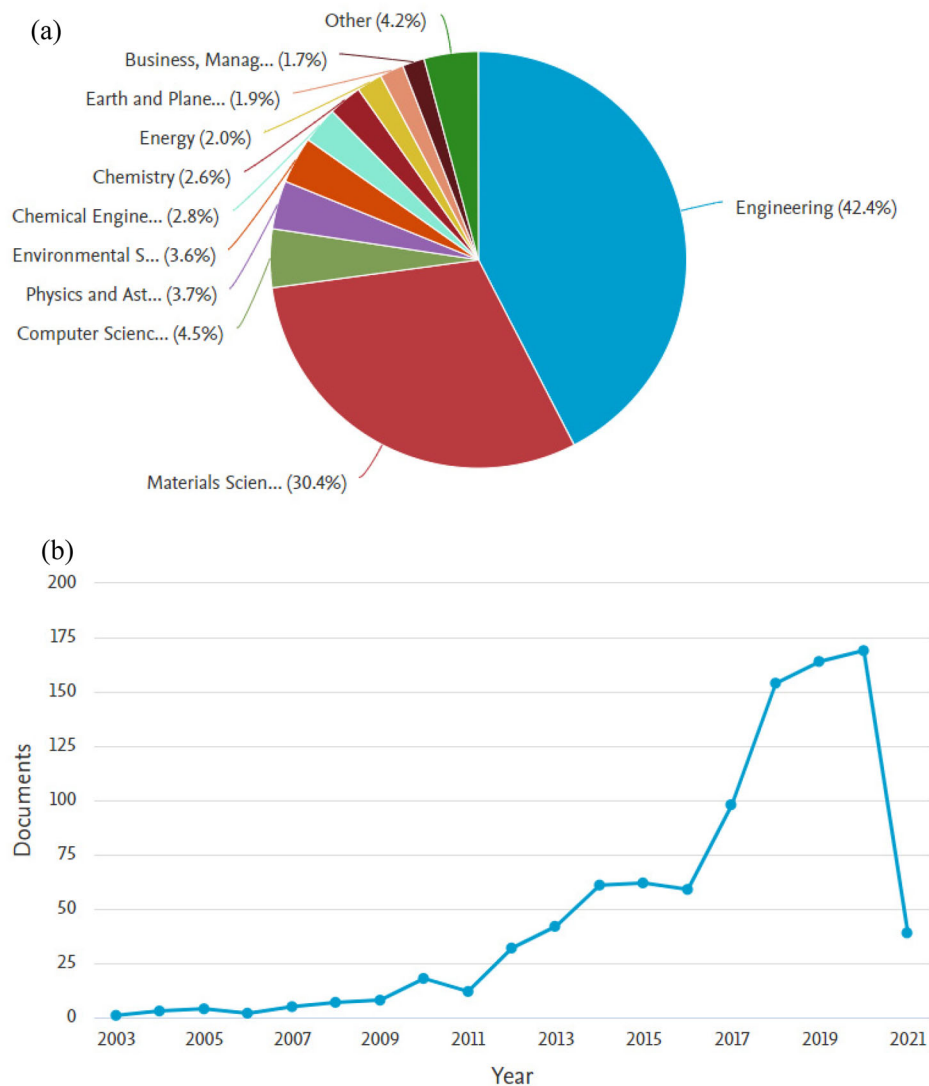


Figure 2. Information from Scopus database: (a) Documents by subject area; (b) Number of yearly published articles.

of the total greenhouse gas (CO<sub>2</sub>) emissions and is rising at an unprecedented pace as rapid industrialization increase. [19]. Massive amounts of concrete production also require the consumption of large quantities of fresh water (about 1 trillion liters per year) and raise severe concerns about water shortages issues. The use of NS in concrete is also recommended nowadays because of its efficient physical and chemical properties, and NS is widely used in cement-based materials (See Table 1). It reacts easily with calcium hydroxide due to the existence of high silica content and creates a high volume of C-S-H gel, which enhances the properties of concrete. The NS particle size loss the fluidity and raises the need for water when replaced with cement, while the strength at the early age of concrete increases [21]. NS has become an important material in recent years to enhance the strengths and durability of concrete (See Figure 3). These developments lead to a better service life for concrete construction and, consequently, a decrease in the maintenance cost of these structures. The high level of greenhouse gas emissions emitted during the cement clinker manufacturing is one of the major problems with Portland cement. Adding NS to cement-based products not only decreases the amount of

cement used in cement production considerably but can also avoid raw materials consumption in this process because of its specific characteristics. Therefore, it is necessary to conduct a critical review of the research on NS in cement-based materials to guide its engineering application.

Although there have been some research reviews on NS in cement-based materials in recent years, their comprehensiveness needs to be further improved. Barbhuiya et al. focused on the impact of NS on the fresh and mechanical properties of cement-based materials, while the durability and microstructure only involved permeability and SEM tests, respectively [1]. Abhilash et al. conducted a review on the mechanical properties and durability of NS-enhanced cement-based materials, but lacked the analysis and review of the microscopic mechanism [2]. On this basis, the fresh and hardened properties of NS-reinforced cement components were reviewed in more detail by Yang et al. but the microstructural evolution was not reviewed [6]. Therefore, it is necessary to conduct a more comprehensive review of the fresh and hardened properties of NA-reinforced cement-based materials, and to explain the influence mechanism from the microstructure.

Table 1. Summarize the application of NS in various cement-based materials.

Ref.	Binder	Type	NS	Average particle size (nm)	Specific surface area (m <sup>2</sup> /g)	Additive or replacement	Properties
[115]	PC + FA + slag	Paste	3%	40	300,000	Replacement	Compressive strength, hydration heat, TG, and pore structure
[116]	PC + SF	Recycled aggregate concrete	1%, 2%, and 3%	7–40	230	Replacement	Mechanical properties and microstructure
[63]	FA	Geopolymer	1%, 2%, and 3%	12	200 ± 25	Additive	Setting time, compressive strength, bond strength, XRD, SEM
[117]	Steel slag and slag	Alkali-activated material	0.5%–6%	15 and 30	300 and 200	Replacement	Compressive strength, efflorescence characteristics, microstructure
[30]	Volcanic ash	Alkali-activated material	1%–7.5%	35	80	Replacement	Setting times, workability, Compressive strength, XRD and SEM
[118]	FA	Micro-steel fibers reinforced geopolymer	1%, 2%, and 3%	12	210 ± 25	Additive	Mechanical properties and SEM
[99]	PC + FA	Engineered cementitious composites	0.5%, 1%, and 2%	15		Replacement	Mechanical properties, shrinkage, capillary water absorption, and microstructure
[119]	PC + FA	Engineered cementitious composites	1%–2.5%	30	200	Additive	High temperature resistance and SEM
[120]	PC + SF + slag	Lightweight engineered cementitious composites	1%–4%	12.1		Replacement	Workability, uniaxial tension, compressive test, and microstructure
[121]	PC + FA	High toughness fiber reinforced cementitious composites	1%–5%	20 ± 5 nm	600 ± 60	Replacement	Flowability, Flexural strength, microstructure
[122]	PC + SF	UHPC	1%, 2%, and 3%	20	230–300	Additive	Mechanical properties
[123]	PC + FA + LP	UHPC	2%	163.4, 182.3, 17300	300–400, 50, 300–400	Additive	Rheology, Calorimeter, and microstructure

\*PC: Portland cement, SF: silica fume, LP: limestone powder, and UHPC: ultra-high-performance concrete.

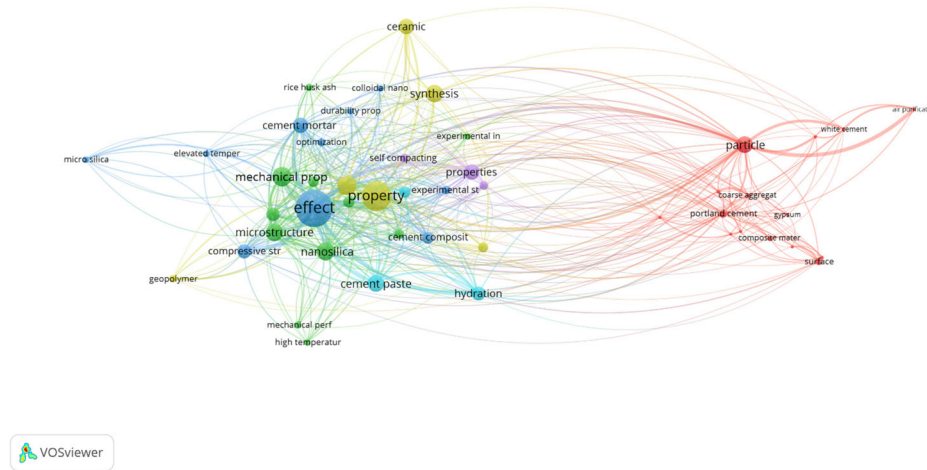


Figure 3. Text pattern analysis on the studied literature to visualise occurring scientific trends. The bigger the label, the higher the occurrence.

Table 2. Chemical and physical properties of NS.

Ref.	SiO <sub>2</sub> (%)	Loss of ignition	Specific gravity	Blaine fineness (m <sup>2</sup> /kg)	Surface-volume ratio (m <sup>2</sup> /g)	Particle size (nm)
[22]	99.8	≤ 1	2.2	–	150 ± 15	14
[23]	99.17		1.4	80000		35
[24]	99.9				160 ± 20	15 ± 5
[25]	99.8		2.2	150000		
[26]	≥ 99.8	≤ 1		150000		
[27]	99.9	0.1	2.33		60	40
[28]	99.89	0.11			60	45
[15]	99.8	≤ 6			100 ± 25	10–25
[29]	≥ 98.5		2.5		320–400	8–15
[30]			1.4		80	35
[31]	99.8	≤ 1.0	2.2		150 ± 15	14
[32]	≥ 98		2.65		193	20–30
[33]	99.8	≤ 1.0	2.2	0	150 ± 15	14
[34]	99.8	2.8			200	40.0
[35]	98.8	–		193000		20–30
[36]	>99.8	–	2.20	–	200 ± 25	12
[7]	98 %	≤ 1.0	2.1		200 ± 25	12

More importantly, this review focuses more on the long-term durability of NS-enhanced components. Furthermore, recent applications of NS in novel cementitious materials are also considered in this review, which are lacking in previous reviews, such as geopolymers, alkali-activated materials, engineered cementitious composite, ultra-high-performance concrete (UHPC). Concerning the basic analysis of the NS, the main objective of this review is to address the most important recent developments. This review investigates the effects of NS on the properties of concrete materials in the fresh and hardened state. The main parameters contribute most significantly to the fresh properties, mechanical parameters, durability aspects and microstructure of NS-modified concrete. The main determination of this review was therefore to point out, one by one, the positive and negative effects of these variables and to describe how future research should be based. In addition, this review included several ideas for potential study and contained a variety of suggestions for future research.

## 2. Chemical and physical properties of NS

The chemical compositions and physical characteristics of NS play a vital role in improving the performance of concrete (See Table 2). The specific gravity of NS between 1.4 and 2.65, and the particle size of NS ranges from 8 to 45 nm. For NS, the high purity and fine particle size is beneficial for its chemical and filling role in concrete.

## 3. Effect of NS on concrete in the fresh and hardened state

The high SSA of NS tends to increase the required amount of water to produce concrete, which directly affects the workability of concrete. Collepardi et al. [37] studied the properties of SCC incorporating NS and observed that the existence of NS decreased the segregation and bleeding as well as made the concrete more cohesive. Ghafari et al. [24] studied the performance of ultra-high-performance concrete (UHPC) mixed with NS, and they found that NS consumed Ca(OH)<sub>2</sub> higher than silica fume (SF). The

Table 3. Fresh and hardened properties of concrete at 28 d.

Ref.	Mix No.	NS	W/B ratio	Binder content (kg/m <sup>3</sup> )	Slump (mm)	Porosity (%)	Compressive strength (MPa)	Flexural strength (MPa)	S. tensile strength (MPa)	Young's modulus (GPa)	Water absorption (%)
[24]	M0	0	0.2	950	193	6.35	130				1.212
	M1	9.5	0.2	950	191	4.74	136				1.110
	M2	19	0.2	950	184	4.66	134				0.95
	M3	28.5	0.2	950	181	4.3	142				0.808
	M4	38	0.2	950	174	4.8	140				0.856
[38]	0-0	0.0	0.3	483	140		91.1			40.0	
	0-0.5	2.4	0.29	480	158		96.4			40.7	
	0-1	4.8	0.297	478	130		99.0			41.0	
	5-0	0.0	0.31	459	140		101.2			41.2	
	5-0.5	2.4	0.31	456	122		104.3			41.8	
	5-1	4.8	0.31	454	110		106.3			42.4	
[39]	C0	0%					30.5	3.4	2.2		
	CNS1	1%					31.7	3.5	2.4		
	CNS2	2%					32.7	3.6	2.5		
	CNS3	3%					35.2	3.7	2.6		
	CNS4	4%					34.5	3.6	2.4		
[40]	A1		0.47		70		30.9				1
	A2		0.47		68		35				1.18
	A3		0.47		65		34				1.05
	A4		0.47		60		27.5				1.19
	B1		0.45		65		37.9				0.9
	B2		0.45		61		41				1.16
	B3		0.45		70		40.5				0.95
	B4		0.45		67		36				1.195
[41]	SN0	0	0.48	414	110		56.3				2.39
	SN0.5	2.07	0.48	412	100		57.5				2.7
	SN1	4.14	0.48	410	80		60				3.02
	SN3	12.42	0.48	402	55		63				4.1
	SN5	20.7	0.48	393	20		52				4.82
	SM10	0	0.48	373			70				1.93
	SN1M10	4.14	0.48	369			71				2.63
[42]	A1	0%	0.45		117		26.07				
	A2	0.4%	0.45		101		24.55				
	A3	0.8%	0.45		79		22.20				
	A4	1.2%	0.45		52		27.21				
	B1	0%	0.5		129		25.83				
	B2	0.4%	0.5		114		23.89				
	B3	0.8%	0.5		102		21.89				
	B4	1.2%	0.5		81		24.12				
[43]	PC	0	0.48	350.0	120		42.11				6.17
	NSC3	10.5	0.48	350.0	90		49.13				4.94
	NSC5	17.5	0.48	350.0	60		54.80				4.81
	NSC7	24.5	0.48	350.0	20		52.04				4.75
[32]	NS1	5.2	0.31	520	170	7.18	62.8	46.4	6.42	41.9	2.98
	NS2	10.4	0.31	520	160	6.93	67.1	49.0	6.13	43.5	2.90
	NS3	15.6	0.31	520	140	6.83	63.9	46.5	6.60	42.8	2.85
[44]	NS0	0	0.45	400	100		64.7				1.9
	NS1.5	1.5	0.45	400	100		46.3				2.1
	NS3	3	0.45	400	120		64.4				1.9
	NS5	5	0.45	400	110		49.8				2.1
	NS7.5	7.5	0.45	400	90		31.8				1.8
[45]	LWC-C0	0	0.42	430	87		62				
	LWC-C1	4.3	0.42	430	95		65				
	LWC-C2	8.6	0.42	430	105		67				
[46]	CN0	0	0.31	516	43		56.5	7.6	3.9		
	CN0.5	2.58	0.31	516	39		60.1	8.87	4.3		
	CN1	5.16	0.31	516	32		63.6	9.5	4.45		
	CN1.5	7.74	0.31	516	38		65.7	10.2	4.56		
	CN2	10.32	0.31	516	42		68.3	10.6	5.1		
	CN2.5	12.9	0.31	516	45		66.6	9.4	4.87		
	CN3	15.48	0.31	516	47		64.7	8.3	4.62		
[47]	0NS	0	0.48	380	40	3.8	48				4.9
	0.3NS	0.3	0.48	380	40	3.9	50				4.8
	0.9NS	0.9	0.48	380	35	3.7	51				5.1

(Continued)

Table 3. (Continued).

Ref.	Mix No.	NS	W/B ratio	Binder content (kg/m <sup>3</sup> )	Slump (mm)	Porosity (%)	Compressive strength (MPa)	Flexural strength (MPa)	S. tensile strength (MPa)	Young's modulus (GPa)	Water absorption (%)
[33]	LWA-NS0	0	0.25	450			55				
	LWA-nS2.5	12	0.25	450			61				
	LWA-NS5	30	0.25	450			63				
[48]	A-0%	0	0.41	350	790		28		3		2.3
	A-0.25%	0.25%	0.41	350	775		32		3.2		1.8
	A-0.5%	0.5%	0.41	350	720		34		3.3		1.6
	A-0.75%	0.75%	0.41	350	670		37		3.6		1.3
[4]	A0S0G1	0	0.5	460	105		33.42	4.66	3.41		3.01
	A1S1G0.7	0.5	0.5	460	104		37.20	4.78	3.49		1.98
	A1S1.5G0.7	1.5	0.5	460	104		38.51	4.94	3.43		2.18
	A1.5S2G0.7	2	0.5	460	102		37.94	4.90	4.35		2.23
	A1S2.5G0.7	2.5	0.5	460	101		36.52	4.81	3.42		2.27
[49]	HPSCC500FA15%	0	0.38	500	910		36.1	4.5	2.7		3.3
	HPSCC400NS2%	8	0.38	500	740		71.3	4.6	4.8		2.8
	HPSCC500NS2%	10	0.38	500	820		82.1	6.1	4.7		2.9
[50]	NS1	0	0.48	400	640		43				
	NS2	1	0.48	400	670		48.7				
	NS3	3	0.48	400	690		43.5				
	NS4	5	0.48	400	760		68				
	NS5	7	0.48	400	810		69.8				
	NS6	10	0.48	400	840		68.4				
[34]	RA1-350	0	0.4	350	85		19.1				
	RA2-350	5.25	0.4	350	45		22.4				
	RA3-350	10.50	0.4	350	25		24.3				
[51]	HS	0	0.3	450	105		75.5	12.3			1.2
	HN-1.5	6.75	0.3	450	107		75.9	13.1			1.1
	HN-3	13.5	0.3	450	110		76.8	11.2			1.2
[35]	E1	5.2	0.32	520	80	10.06	62.21		9.03	47,867	4.11
	E2	10.4	0.32	520	75	8.47	66.18		9.97	47,162	3.45
	E3	15.6	0.32	520	70	6.67	67.43		9.06	48,666	2.69
[52]	NAC1	3.375	0.4	450	68		45	4.5	2.2		
	NAC2	6.750	0.4	450	60		46	4.65	2.43		
	NAC3	13.50	0.4	450	45		50	5.1	2.67		
[15]	R0-0	0%	0.36	268.69			40.4	5.73	3.36		2.01
	R0-1	2.69	0.36	268.69			44.0	6.13	4.05		1.85
	R0-2	5.37	0.36	268.69			54.9	6.33	4.7		1.61
	R0-3	8.06	0.36	268.69			67.0	7.33	5.87		1.61

incorporation of NS improved the strength and impermeability of UHPC. Also, the incorporation of NS in various proportions led to fewer capillary pores, and the optimum quantity of NS for enhancement in cement paste was 3%, by total weight. Table 3 shows the properties of concrete containing NS with different proportions by previous studies.

### 3.1. Fresh properties of concrete containing NS

#### 3.1.1. Workability

The workability of HPC can be determined by a slump or slump flow, especially with high-flow ability concrete. Bahadori and Hosseini [53] reported that the concrete containing NS had a lower slump value than that of normal concrete with a constant super-plasticizer ratio. Naji Givi et al. [54] investigated the slump of NS-modified concrete with constant water to binder (W/B) ratio, i.e. 0.4. The reduction in the slump value of concrete was due to the high SSA of NS, which required a high quantity of water to cover the surface of NS and the cement particles. Behfarnia and Rostami [41] studied the impact of nano and micro silica on properties of concrete. NS and micro-

SiO<sub>2</sub> were used as partial replacement of slag in alkali-activated slag concrete. It was concluded that using NS in concrete reduced the slump value owing to small particle size and high water demand. However, using NS of 5% by weight of slag resulted in a decreased slump by 82%. Another study concluded that using NS with optimum content did not affect the slump for all concrete mixtures [26]. Ghafari et al. [24] stated that adding 1% NS did not affect the slump values, but the use of 2% and 3% NS reduced the slump value by 9 mm and 12 mm, respectively. In order to overcome the negative effect of NS on concrete workability, the researchers also tried to adjust the content of super plasticizer to improve the fluidity of the mixture, as shown in Figure 4(a) [46].

Li et al. [38] concluded that incorporating micro and NS with a constant W/B ratio reduced the slump value. Also, increasing the NS content in the concrete improved its viscosity and yield stress [59]. Li et al. [60] conducted many tests to study the effect of NS and nano-CaCO<sub>3</sub> on the flowability of the UHPC and concluded that increased the content of NS and nano-CaCO<sub>3</sub> decreased flowability of concrete. Jalal et al. [49] observed that the mixed



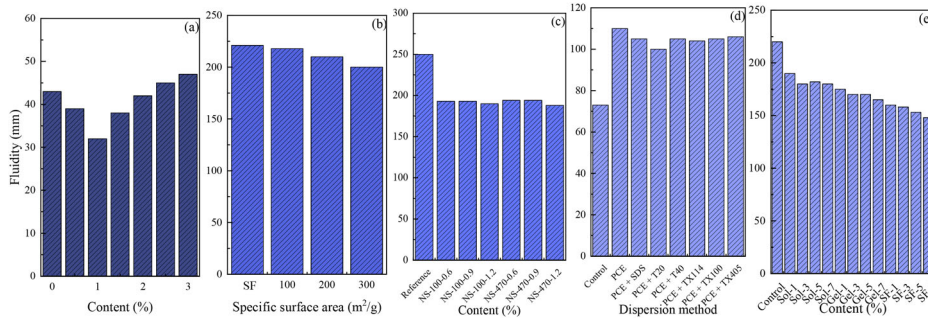


Figure 4. The fluidity of cement mixture with NS. (a) The effect of replacement ratio of NS, data from [46], (b) The effect of SSA (100, 200, and 300 m<sup>2</sup>/g) NS, data from [55], (c) The effect of SSA (100 and 470 m<sup>2</sup>/g) and content (0.6, 0.9, and 1.2), data from [56], (d) The effect of dispersion method (Sodium dodecyl sulfate (SDS), Polycarboxylate ether (PCE) based superplasticizer, Tweens (T20, T40) and Tritons (TX114, TX100, TX405)), reproduced under license number 5503600017242 from [57], (e) The influence of NS morphology, reproduced under license number 5503600115855 from [58].

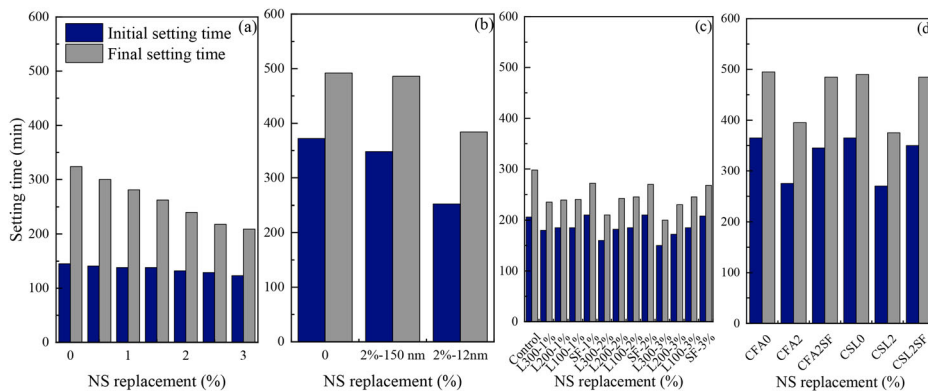


Figure 5. The setting time of cement paste with NS. (a) The effect of replacement ratio of NS on the plain paste, data from [46], (b) The effect of particle size (150 and 12 nm) NS on the pure cement paste, reproduced under license number 5503591180995 from [64], (c) The effect of SSA (L300: 300 m<sup>2</sup>/g, L200: 200 m<sup>2</sup>/g, L100: 200 m<sup>2</sup>/g) of NS on the pure cement paste, data from [65], (d) The effect of replacement ratio (0, and 2%) of NS on the high-volume FA cement paste (CFA) and high-volume slag cement paste (CSL), data from [55].

concrete with NS and SF reduced the flowability of the self-compacting HPC, but adding NS and SF enhanced its consistency. Güneş et al. [22] investigated the effect of NS on the workability of SCC. It was observed that the incorporation of NS increased the flow time and improved the consistency of self-compacting lightweight aggregate concrete (SCLWAC). It was recommended that the quantity of water should be adjusted when adding NS to the concrete for enhanced workability of HPC. In addition to the content of NS, its SSA and morphology are also key factors affecting the fluidity of cement components (See Figure 4). Generally speaking, as the SSA of NS increases, the fluidity of cement paste decreases, as presented in Figure 4(b).

In order to improve the fluidity of NS-modified cement components, researchers have made a number of attempts, including changing the dispersion of NS, the stirring method and the morphology of NS. Niu et al. used anionic surfactants and chloride salts to improve the dispersibility of NS, thereby improving the fluidity of NS-modified cement components [61]. This is mainly due to the formation of micelles that can encapsulate NS and the electrostatic repulsion among micelles, and the effect of CaCl<sub>2</sub> is more pronounced than that of NaCl. Sargam et al. systematically studied polycarboxylate ether based superplasticizers,

sodium dodecyl sulfate and anionic surfactants, as well as two groups of nonionic surfactants Tweens (T20, T40) and Tritons. The effect of (TX114, TX100, TX405) on the fluidity of NS-modified cement paste and effectively improved the fluidity of the mixture, as shown in Figure 4(d) [57]. In addition, Kooshafar et al. also found that NS sol had a lower negative impact on the flowability of the mixture than the addition of NS gel (See Figure 4(e)) [58].

### 3.1.2. Setting time

The setting time of cement paste can be affected substantially by adding NS. The setting time reduced significantly because of adding NS, while a gradual decrease was observed because of increased NS content, as compared with that of plain cement paste [62]. Similarly, increased NS content evidently reduced setting time despite an increase in yield stress and viscosity of concrete [59]. Zhang and Islam [55] reported that the two concrete samples containing slag and FA were modified by 2% NS, and the setting time was reduced. The setting time of concrete was decreased because of the high SSA of NS particles [62]. Chithra et al. [46] stated that an increase in the amount of NS in concrete up to 3%, resulting in decreased setting time but increased consistency owing to the acceleration of hydration (See Figure 5(a)). The same rule

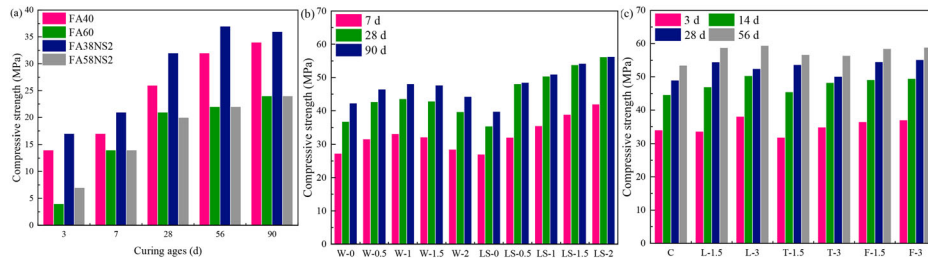


Figure 6. Compressive strength of NS-modified concrete. (a) Influence of NS on the strength of high-volume FA concrete, reproduced under Creative Commons license from [69], (b) Influence of curing system on NS-modified concrete (W: water curing, LS: lime solution curing), reproduced under Creative Commons license from [53], (c) Influence of active nano content of NS on NS-modified concrete, Active nano content of L is 14%–16%, T is 30%–32%, F is 40%–41.5%, data from [73].

applies to other types of cement compositions. Tanakorn et al. [63] explore the impact of NS on geopolymer concrete containing FA. Adding NS reduced the setting time and enhanced the properties of geopolymer. Due to the stronger pozzolanic effect of NS with small particle size, the setting time of the cement paste is shorter, as shown in Figure 5(b).

### 3.2. Mechanical properties

#### 3.2.1. Compressive strength

Many authors concluded that NS in multiple concentrations could enhance the compressive strength of concrete. Salemi and Behfarnia [66] reported that the incorporation of 5% NS increased the concrete strength up to 30%. Wang [67] noted the effect of 3% to 5% NS at an early ages on the compressive strength was more obvious than that of later age for UHPC. Said et al. [68] concluded that the concrete strength was improved owing to NS addition, particularly for concrete comprising FA and 30% NS. Supit et al. [11] similarly reported that the compressive strength of high volume fly ash (HVFA) concrete with 40% and 60% FA was increased at the early ages because of the incorporation of 2% NS. Li [33] stated that the inclusion of NS to HVFA concrete can enhance short- and long-term strengths [34]. The compressive strength of concrete containing HVFA up to 60% was increased at the early ages by 95% because of the incorporation of 2% NS, but the long-term strength showed no substantial improvement, as shown in Figure 6(a) [69]. Supit et al. [11] stated that the compressive strength value of concretes containing 2% and 4% NS was similar when the W/B ratio was constant at 0.4, which was used to assess NS efficiency in HVFA concrete.

The utilization of NS had increased the strength of the concrete containing FA at curing ages between 28 and 91 d, but NS did not improve the concrete strengths for the mixture prepared with slag [55]. The size and dosage of NS considerably affected the strength of concrete. The optimize percentage of NS in pozzolanic concrete was 0.5% to 1% of cement weight [70]. Adamu et al. [71] concluded that NS partial replacement decreased the strengths loss of HVFA pavement owing to the negative effect of CR by improving bonding between CR and cement matrix ultimately improved the pore structure. The pozzolanic behaviour of NS led to an increased in the development of compressive strength for cement mortar as compared with

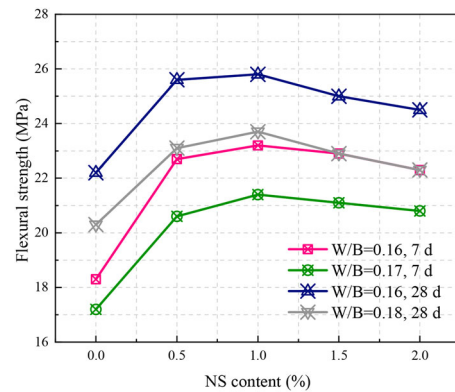


Figure 7. Impact of NS percentage on flexural strength of concrete, reproduced under license number 5503590445217 from [60].

that of control specimen without NS [27]. The compressive strength at early curing of the concrete includes NS with 15 nm as the mean particle size was larger than with 80 nm [72]. In contrast, Khaloo et al. [74] explore the effect on the compressive strength of concrete with low substitution level of NS having several particle sizes. Increase in strength of concrete was reported with a low content of the coarse NS (0.75 percent) than that with a fine particle size. Gopinath et al. [73] studied the effect of three categories of suspended NS gel comprising various quantities of active NS on the strength of the concrete. The concrete properties were improved by the incorporation of 3% NS gel with different active nano content, which had the maximum compressive strength gain at the active nano content of 40%–41.5% (See Figure 6(c)).

Different curing methods can affect the compressive strength of concrete. Givi et al. [54] noted that different curing methods for concrete samples have different effects on the strength of NS-modified concrete. The strengths of samples that were cured in lime solution were lower than those cured in water for the curing ages of 7–90 d (See Figure 6(b)). This was because of the higher amount of crystalline formation in the lime solution. Behfarnia and Salemi [43] concluded that the compressive strength of concrete incorporating NS was considerably greater than that of concrete containing the same content of nano- $\text{Al}_2\text{O}_3$ . Du et al. [45] concluded that the effect of NS on the strength of LWAC at an early ages was remarkable, whereas the benefits of NS might disappear with prolonged curing time. The strength of recycled aggregate

concrete was improved by adding low content of NS, i.e. less than 3% [52]. Another study by Behfarnia and Rostami [41] indicated that the use of NS in the concrete mixture containing slag increased the strength of concrete. The increasing ratio of strengths at 28 and 90 d in concrete specimens containing 3% NS was 12% and 11%, respectively. Güneyisi et al. [22] used NS with treated FA aggregates to increase compressive strength. The inclusion of NS in the FA concrete enhanced the compressive strength values up to 78.5, 65.0 and 49.0 MPa for different W/B ratios of 0.25, 0.37 and 0.50, respectively. Güneyisi et al. [33] stated that the combined effect of 5% NS and treated aggregate considerably improved the strength of concrete. Another study concluded that the use of 4% NS increased the strength, while an increase in the content of NS up to 6% resulted in reduced strength [26].

### 3.2.2. Flexural and splitting tensile strengths

The improvement in the flexural strength can be achieved by using NS and other nanomaterials together. Li et al. [75] observed that the use of NS in concrete substantially improved the flexural strength of concrete. Givi et al. [54, 76] reported that the flexural strength of NS-blended concrete was improved with 1.0% NS, than that of the control concrete and the specimens that have been cured in water. Li et al. [60] studied the effect of nano-CaCO<sub>3</sub> and NS on the flexural strength of the UHPC. The findings exhibited that the low content of NS and nano-CaCO<sub>3</sub> less than 1% increased flexural strength of UHPC at 7 and 28 d, whereas increasing NS dosage more than 1% reduced the flexural strength, as shown in Figure 7.

Gopinath et al. [73] stated that the flexural strength began to decrease because of the increased NS dosage to >3% and became lower than that of the control sample. Amin et al. [77] concluded that the addition of nano-Fe<sub>2</sub>O<sub>4</sub> and NS increased the flexural strength of HPC by 23% than the control sample. Moreover, the combination of NS and the hybrid fibers (steel and polypropylene fibers) in the concrete can increase the strength of concrete [78]. Amin and Abu El-Hassan [77] used different nanomaterials to investigate the mechanical properties of concrete. The results showed that the flexural strength was increased when NS was increased up to 3%, but the strength was decreased when the replacement level exceeded 3%, even though it was still more than the control sample. However, increased addition of NS more than 3%, by cement weight had a negative effect on the flexural and splitting tensile strengths of concrete [77]. Gesoglu et al. [25] studied the flexural strength of concrete with 2% of NS and found that the control concrete has lower strength than that of other mixtures containing NS. Similar conclusions were also found in the previous studies [77, 79]. Gesoglu et al. [25] studied the effect of using binary and ternary blends of Nano and micro SiO<sub>2</sub> on the properties of UHPC. The results displayed that NS in the UHPC increased the splitting tensile strength, especially at 90 d. Hasan-Nattaj and Nematzadeh [35] conducted many tests to determine the concrete tensile strength. The splitting tensile strength of concrete was

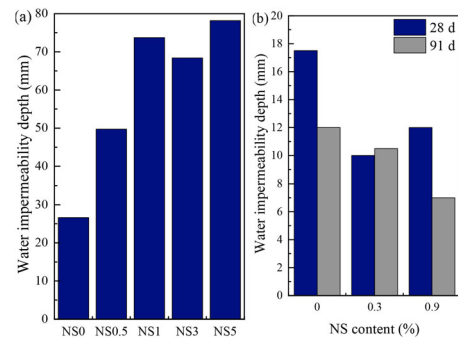


Figure 8. Effect of NS on the water permeability, reproduced under license number 5503590254909 and 5503590126943 from [41, 47].

increased with an increase in NS, especially with a 10.4 kg/m<sup>3</sup> proportion.

## 4. Durability

Adding NS to the concrete can enhance its durability by refining pore structure and changing product type and content. Li et al. [38] stated that the use of micro-silicon and NS resulted in enhanced durability of concrete. Massana et al. [80] investigated the durability of high-performance SCC containing the NS with different percentages. The addition of NS produced the concrete with high compactness and amended the durability. Recently, Fu et al. [2] investigated the effect of NS on the durability of concrete. They examined the freeze–thaw resistance, carbonation resistance, sulfate corrosion resistance, chloride ion, and corrosion resistance. They concluded that the addition of an appropriate amount of NS improved the compaction of the microstructure of cement-based materials and reduced the permeability through pozzolanic reaction and filling effect.

### 4.1. Water permeability

Higher water permeability always means low durability of concrete materials. The underwater concrete structures, especially in deep water, need high requirements of water impermeability. In order to research the impact of NS on impermeability of concrete, Ji [81] carried out multiple tests with a concrete for water permeability. The results indicated that the water impermeability of NS-modified specimen was better than that of plain specimen. Du et al. [47] reported that the low content of NS ranging between 0.3% and 0.9% and could improve the water impermeability of concrete, as shown in Figure 8(b). However, Behfarnia et al. also found that NS performed poorly on the water penetration resistance of alkali-activated materials, as shown in Figure 8(a) [41].

Givi et al. [62] determined the water absorption coefficient that assesses the effect of NS on the water permeability of HPC. The NS content in concrete was 0.5%, 1%, 1.5% and 2%, by cement weight. It was concluded that the NS enhanced the water impermeability of HPC, especially with using 2% NS. The uniform particle size of NS had a considerable effect on the permeability of

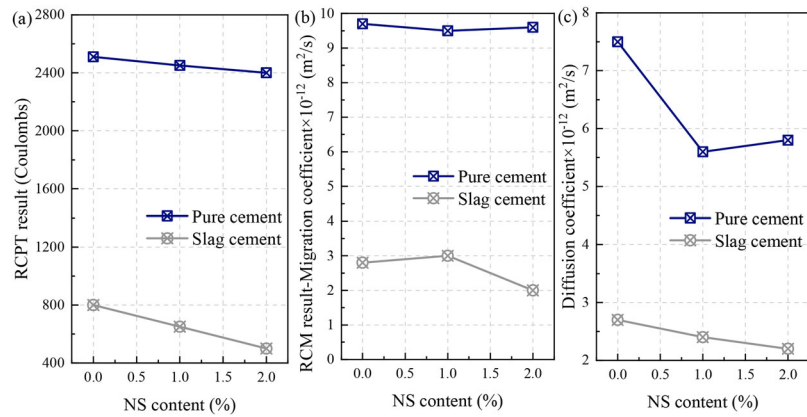


Figure 9. Effect of NS content on the chloride permeability of LWAC. (a) Rapid chloride permeability test by ASTM C 1202, (b) Rapid chloride migration by NT Build 492, and (c) Chloride diffusion test by NT Build 443 & BS 1881-124, reproduced under license number 5503581452938 from [45].

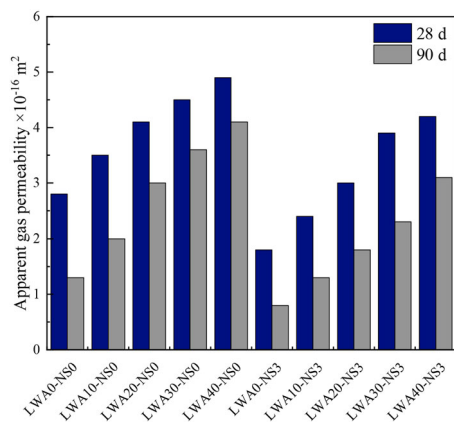


Figure 10. Gas permeability test of HSLWCs at 28 and 90 d, LWA: Lightweight coarse aggregate, reproduced under license number 5503581317948 from [31].

concrete containing NS. Givi et al. [82] stated that NS with particle size over 80 nm in concrete had better water impermeability than those of particle size less than 15 nm at 28 d. The use of NS improved pore structure and microstructure, and decreasing the water permeability of SCC [83]. Esmaeili and Andalibi [84] observed that adding up to 9% NS decreased the water permeability of the concrete up to 53%. The addition of 5% NS reduced the water permeability to that of 2.5% NS [33]. An increase in NS percentages decreased the permeability of concrete samples [85].

#### 4.2. Chloride permeability

Chloride permeability is one of the important test to evaluate durability of concrete. Zhang and Li [86] examined the effect of NS on the chloride impermeability of pavement HPC. It was reported that the concrete containing NS enhanced the chloride impermeability of HPC, and the low content of NS improved the chloride impermeability. Gopinath et al. [73] stated that the chloride impermeability of specimen containing NS was considerably better than that of without NS. Du et al. [47] concluded that the chloride impermeability of the specimen containing low content (0.3%) of NS was enhanced, and the diffusion

coefficient and chloride migration coefficient of the concrete sample was decreased by 31% and 28.7%, respectively. Based on the rapid chloride permeability results by Said et al. [87], the concrete incorporating lower content of NS had a substantial influence on decreasing the conductivity and refining the pore structure of concrete as well as reducing the physical penetration depth of the concrete sample. In addition, Zhang and Islam [55] reported that the SF or 2% NS could reduce the charges passed through the concrete samples including slag or FA, as compared with that of the control sample. The same results were obtained by Supit and Shaikh [11] for concrete incorporating a high quantity of FA (40% and 60%). Based on the accelerated and non-accelerated chloride diffusion tests conducted by Du et al. [45], the addition of NS in lightweight aggregate concrete (LWAC) led to higher resistance against chloride penetration, as shown in Figure 9.

#### 4.3. Gas permeability

The gas permeability test is one of the most significant tests to examine the pore structure of concrete. Atmaca et al. [31] determined the effect of NS on gas permeability of high-strength lightweight aggregate concrete (HSLWAC). It was observed that the addition of 3% NS in HSLWAC decreased gas permeability up to 40% and increased the mechanical properties of HSLWAC. Figure 10 shows that the gas permeability coefficients of HSLWAC were increased with an increase in replacement content of traditional aggregate by LWA at 28 and 90 d. The higher value of gas permeability coefficients was  $4.896 \times 10^{-16}$  and  $4.141 \times 10^{-16}$  m<sup>2</sup> at 28 and 90 d, respectively. The inclusion of 3% NS to the HSLWAC mixtures decreased gas permeability up to 30.95% at 28 d and 40.65% at 90 d, as shown in Figure 10. Gas permeability was reduced because of the improved compactness and pore structure of concrete as well as accelerated cement hydration and decreased porosity of concrete.

Proportions of concrete, age improvement, presence of chemical additives such as NS or SF, aggregate type and type, and properties of pore structure are the main factors affecting gas permeability [88]. Güneysi et al. [33]

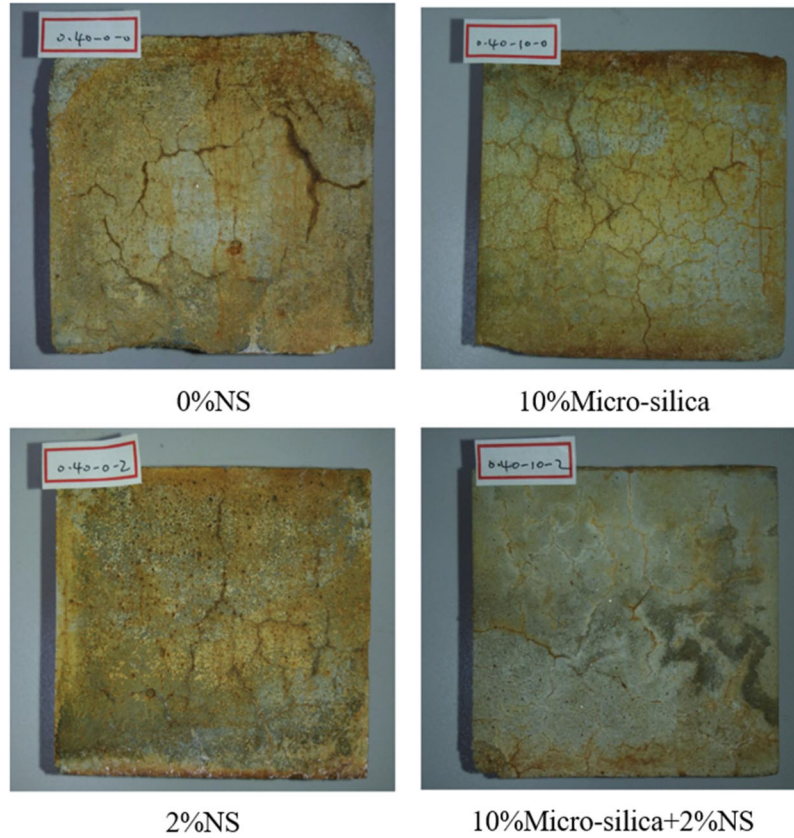


Figure 11. Influence of NS on the sulfate attack of concrete, reproduced under license number 5503580814187 from [90].

conducted a gas permeability test to determine the porous material of concrete. It was noted that an increase in NS up to 5% by using the same aggregate types resulted in decreased gas permeability coefficient of SCCs. The gas permeability test illustrated that NS refined microstructure and pore structure of SCCs. Another study by Ghafari et al. [24] exhibited that using NS reduced the gas permeability of concretes of NS1%, NS2%, NS3% and NS4% up to 7.5%, 24.2%, 31.9% and 25.7%, respectively.

#### 4.4. Resistance to acid and sulfate attacks

Bassuoni and Rahman [63] exhibited the effect of using NS and nano- $\text{Al}_2\text{O}_3$  on the physical salt attack in FA concrete. It was concluded that concrete containing 30% FA reduced the mass loss and surface scaling at the same W/B ratio, which depended primarily on the type and dosage of nanoparticles. Huang et al. [89] exhibited the effect of NS on the concrete properties exposed to the sulphate attacks especially ( $\text{MgSO}_4$ ) solution. They concluded that increasing the NS replacement from 1% to (5–8 wt.%) led to the deterioration of blended mortars exposed to  $\text{MgSO}_4$  solution. While the use of 1% NS in cement mortar led to reduce the strength losses compared to other cement mortars with high W/B ratio. Li et al. [90] concluded that the addition of nano and/or micro  $\text{SiO}_2$  would substantially improve the resistance of sulfate. The addition of 1% NS was nearly as good as the addition of 10% micro  $\text{SiO}_2$ , as presented in Figure 11. The compressive strength of all concrete mixtures containing NS under the sulphuric condition was higher than that of the reference sample owing

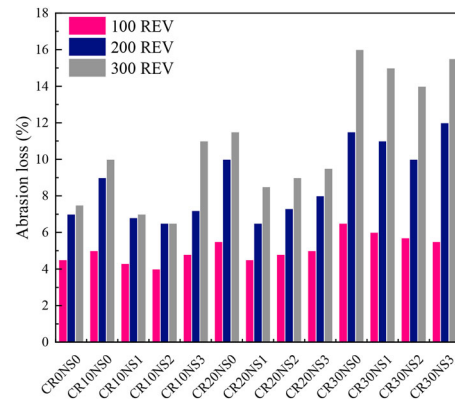


Figure 12. Abrasion loss for HVFA concrete, reproduced under license number 5503581189172 from [71].

to the enhanced bond between the hydrated cement paste and the aggregates [85].

#### 4.5. Abrasion resistance

Abrasion resistance is an important test to evaluate the concrete used for pavement structures. Nazari and Riahi [91], Riahi and Nazari [92], and Soleymani [93] studied the abrasion resistance of specimen containing NS for various curing ages. The HPC of the pavement required excellent abrasion resistance because of the dynamical loads on the pavement structures. Li et al. [94] studied the abrasion resistance for specimen containing NS in pavement structures using side and surface indices of abrasion resistance. Chithra et al. [46] presented the effect of

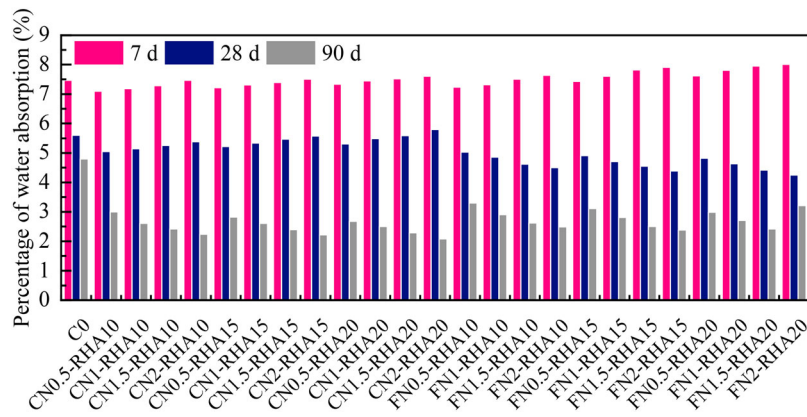


Figure 13. Percentage of water absorption of NS-modified concrete, data from [96]. The average particle sizes of CN and FN series NS is 80 and 15  $\mu\text{m}$ , respectively.

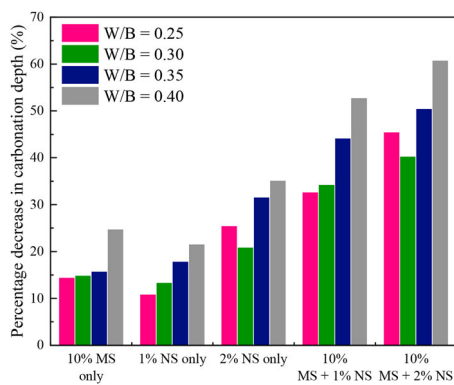


Figure 14. Effect of replacement level of NS on percentage decrease in carbonation depth of concrete, reproduced under license number 5503580814187 from [90]. MS: micro-silica.

colloidal NS on the properties of HPC with a constant replacement of 40% copper slag as sand. Concrete was produced by adding colloidal NS with cement replacement of 0.5%, 1%, 1.5%, 2%, 2.5% and 3%. The abrasion resistance of HPC containing NS in terms of wear depth at 28 and 90 d. It was noted that the wear depth decreased with an increase in concrete age for all mixtures. The increasing amount of NS in the concrete decreased depth of wear, showing that the increased quantities of NS improved the abrasion resistance. Haruehansapong et al. [95] conducted the influence of NS particle sizes on the durability of cement mortar. Three various particle sizes of NS, (i.e. 12, 20 and 40 nm) were used in the mortar with and without SF. Substantial trends were achieved in which the particle size of NS directly influenced abrasion resistance. NS with a particle size of 40 nm achieved the best result for abrasion resistance. Mohammed and Adamu [15] reported that with the addition of 3% NS, by total binder weight resulted in improved abrasion resistance of concrete with the substitution of 10% CR as sand. Adamu et al. [71] presented that the use of NS up to 3% improved the abrasion resistance of HVFA. Figure 12 shows that the incorporation of NS as 1% and 2%, by cement weight, which effectively reduced the loss in abrasion resistance of HVFA, especially when the CR was used as a fine aggregate replacement by 10% (See Figure 12). Similarly, 1% NS reduced the loss in abrasion

resistance of HVFA with the use of CR as a fine aggregate replacement by 20%.

#### 4.6. Water-absorption capacity

Supit and Shaikh [11] found that the water-absorption value of the reference sample at 28 and 90 d was reduced by the incorporation of NS into the concrete. Bahadori and Hosseini [53] reported a different reduction for water absorption of concrete at 2 d of curing with increased NS of 1% to 3% using cement reduction. Najigivi et al. [96, 97] conducted experimental studies to determine the effect of NS on the water absorption of the ternary blended concrete containing rice husk ash (RHA). It was found that the optimum content of NS and RHA for optimal resistance of water absorption was 2% and 20%, respectively, as shown in Figure 13. Increased content of NS decreased water absorption of LWC at the initial stage and secondary water-absorption stage [45]. Heidari and Tavakoli [70] reported that the combination of NS decreased the water absorption of the concrete substantially with the incorporation of ground ceramic powder. Ghafari et al. [37] presented that the water absorption of concrete containing NS was reduced with the further incorporation of NS content. The incorporation of NS by 1%, 2%, 3% and 4%, by total binder weight reduced the water absorption in specimens by 8.5%, 21%, 33% and 29%, respectively. Li et al. [29] concluded that colloidal NS reduced water absorption and micro-scale pores of NS-modified recycled aggregate concrete.

#### 4.7. Carbonation resistance

The use of NS to enhance the carbonation resistance of concrete is a common strategy. Behfarnia and Rostami [41] performed many tests to evaluate the carbonation depth by exposing the specimens under high concentrations of  $\text{CO}_2$  in controlled conditions. The results obtained in Figure 14 show that the carbonation depth for 14 and 28 d reduced with an increase in replacement ratio of NS. The replacement of 5% NS increased carbonation depth from 7.09–8.71 mm to 12.17–13.57 mm for 14 and 28 d, respectively. Li et al. [90] used three 100 mm cube samples to test carbonation depth and cured them in lime-saturated water at  $20 \pm 2^\circ\text{C}$  for 26 d. It was noted that the

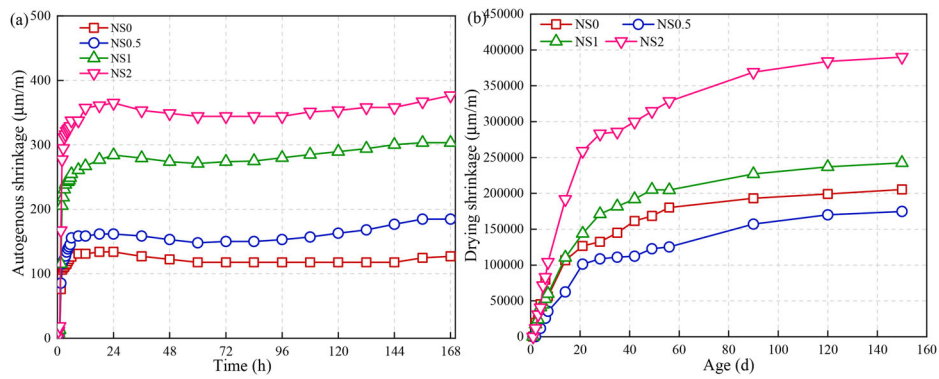


Figure 15. The effect of NS content on volume stability of engineered cementitious composites with SAP, autogenous shrinkage (a) and drying shrinkage (b), reproduced under license number 5503580452980 from [99].

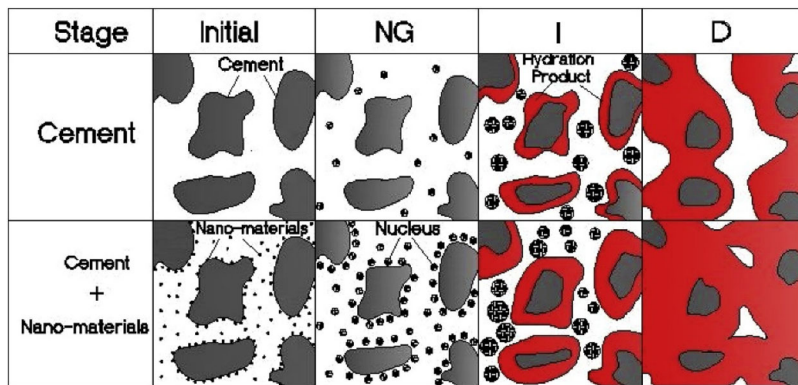


Figure 16. The hydration mechanism of cement composition with NS, reproduced under license number 5503580594796 from [100].

carbonation depth decreased as the W/B ratio decreased. Using NS had better effect on carbonization resistance compared to micro-silica, as shown in Figure 14. When the content of NS was 2%, its reduction effect on carbonization depth was already higher than that of adding 10% MS. When NS and MS were used in combination, the effect of improving the carbonation resistance of concrete was more obvious.

## 5. Volume stability

Shrinkage is the decrease in total volume at a constant temperature without any external loading. It substantially affects the durability and structural behavior of the concrete. Adding a large amount of NS may cause shrinkage, resulting in higher cracking risk. Güneyisi et al. [33] observed that using 2.5% and 5.0% NS with constant W/B ratio in the SCC samples reduced 61-d drying shrinkage by 10% and 14%, respectively. Güneyisi et al. [33] investigated the physico-mechanical properties of SCLWAC containing NS. The drying shrinkage of SCLWAC was tested for all concrete samples. The results illustrated that using 5.0% NS decreased drying shrinkage up to 23%. Haruehansapong et al. [95] observed that mortar containing 40 nm of NS achieved the lowest shrinkage, thus minimizing the cracks in concrete samples. The cement mortar samples with the particle sizes of NS (12 and 20 nm) had the highest drying shrinkage as compared with that of NS with a particle size of 40 nm. However,

Sadrmomtazi et al. [98] investigated the drying shrinkage of concrete samples containing NS at 42 d. The cement was partially replaced by NS at 0%, 3%, 5% and 7% by weight. The W/B ratio was fixed at 0.5. The results displayed that the drying shrinkage increased with increase in NS replacement. Zhang et al. [99] applied superabsorbent polymers (SAP) and NS to synergistically improve the shrinkage and mechanical properties of engineered cementitious composites. Their study found that the incorporation of NS to SAP-incorporated pastes increased the autogenous shrinkage of the mixture due to its acceleration of the reaction process, as shown in Figure 15(a). Meanwhile, an appropriate amount of NS could improve the pore structure of the cement mixture, thereby reducing its drying shrinkage (See Figure 15(b)).

## 6. Microstructural

The concrete containing appropriate amount of NS enhanced the compactness of the microstructure because of the improved interface effect, filling effect, small size effect, and surface effect of nanoparticles [67]. Meng et al. [100] compared the hydration behavior of cement pastes with and without NS, and found that NS adsorbed a large amount of hydration products to form crystal nuclei during the nucleation crystal growth stage as shown in Figure 16. Meanwhile, more nuclei in the nanomaterial could continue to grow during the diffusion reaction stage, and the growth of these nuclei refined the pore structure and improved the

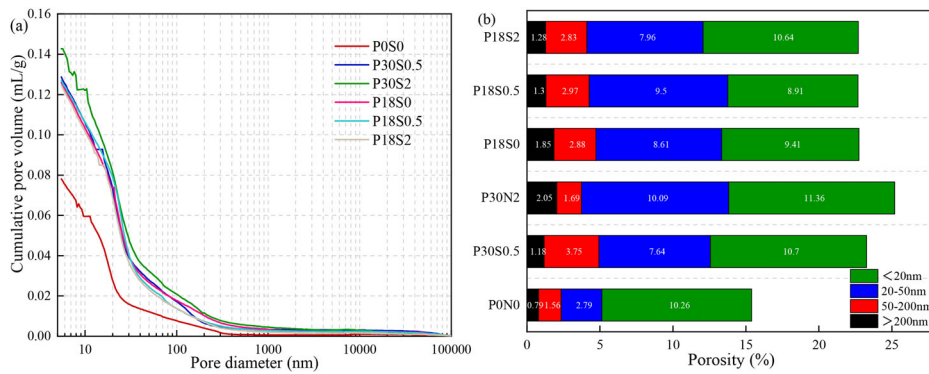


Figure 17. Pore structure of cement composition with NS, reproduced under license number 5503580452980 from [99].

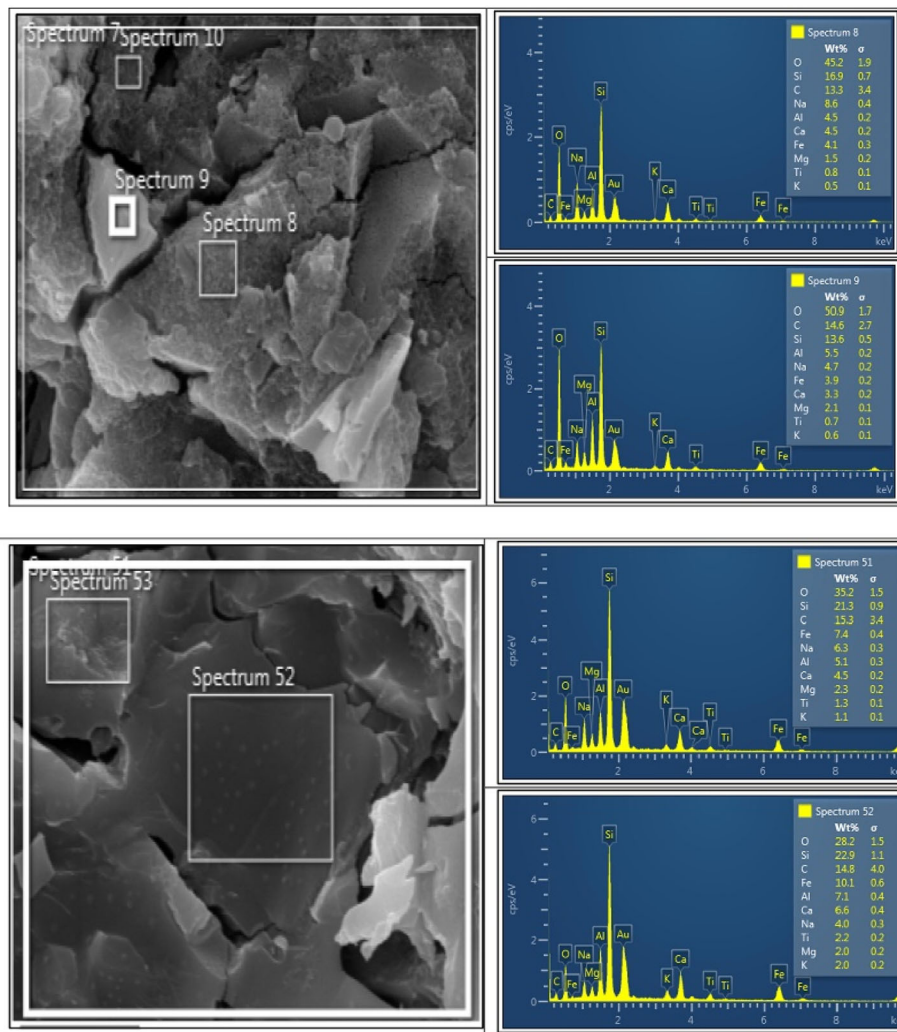


Figure 18. The SEM of alkali-activated paste containing NS, reproduced under license number 5503580280492 from [30].

compactness of the sample. Similarly, Wang et al. [101] also found that the incorporation of NS accelerated the hydration rate of  $C_3S$ , making the C-S-H gel denser, and thus reducing the porosity of the paste. Zhang et al. used NS to eliminate the adverse effect of SAP on engineered cementitious composites, and found that the incorporation of NS effectively improved the pore structure of the samples, as shown in Figure 17 [99]. Said et al. [87] conducted the microstructural and thermal analysis of the content containing NS to determine the pozzolanic and filler effect. It was

found that NS enhanced the pore structure of NS concrete. The nucleation effect of NS improved the cement hydration and produced huge quantities of C-S-H gel [102]. Ji [81] used the scanning electron microscopy (SEM) test and stated that the concrete improved by NS showed extra compacted structure as compared with that of without NS. Givi et al. [54] reported that the filler effect was enhanced by NS, and an additional C-S-H gel was produced because of the higher pozzolanic reactivity of NS in the lime solution-cured samples.



Zhang and Islam [55] stated that the inclusion of NS in concrete enhanced the microstructure. The porosity of cement paste was reduced and ITZ of the cement matrix and the aggregates was improved, which was attributed to the sequences of chemical and physical effects. Maida et al. [103] used the SEM test to show the effect of NS on concrete containing polypropylene macro synthetic fibers. The SEM results illustrated that the NS treatment supported the bonding of the concrete hydration products, and improved the ITZ. Ibrahim et al. [30] used NS as a partial replacement for natural pozzolan. SEM and XRD were utilized to determine the morphology and mineralogy of the concrete, respectively, as shown in Figures 18 and 19. The study indicated a remarkable enhancement in the properties of concrete owing to NS addition. Ibrahim

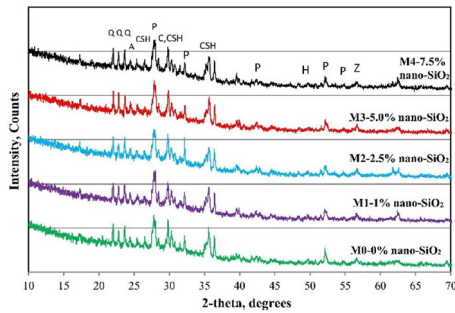


Figure 19. XRD of alkali-activated paste containing NS, reproduced under license number 5503580280492 from [30].

et al. [30] found that the incorporation of NS increased the Si/Al ratio in the alkali-activated matrix and allowed it to produce Si-O-Si bonds, which resulted in a significant improvement in the strength and microstructural of the samples.

Du et al. [47] concluded that the specimen comprising NS gained low porosity and additional homogeneous microstructure at ITZ owing to the filler effect and pozzolanic reaction of NS. Khaloo et al. [74] performed the microstructure studies of HPC comprising NS with different particle sizes. It was concluded that the coarser particle size NS showed less acceleration of cement hydration and lower pozzolanic reactivity than the finer NS. Furthermore, NS with coarser particle size showed a better effect on the HPC matrix because it was denser and could be easily compacted. Givi et al. [76] stated that NS with a particle size of 15 nm could generate more C-S-H gel at an early ages than in the case of NS with a particle size of 80 nm. Abundant NSs existed in ITZ under sidewall and filling effect, which provided nucleation sites to promote hydration and increase compactness of ITZ, as shown in Figure 20 [104]. The nucleation of NS promoted the formation of high-density C-S-H gels, reduced the content of Ca(OH)<sub>2</sub>. Meanwhile, it reduced the structural defects in loose Ca(OH)<sub>2</sub>, thereby optimizing the ITZ of the concrete (See the nanoindentation results are shown in Figure 21) [105].

Supivt et al. [11] stated that NS can react faster with free lime than FA and generate further C-S-H to fill the

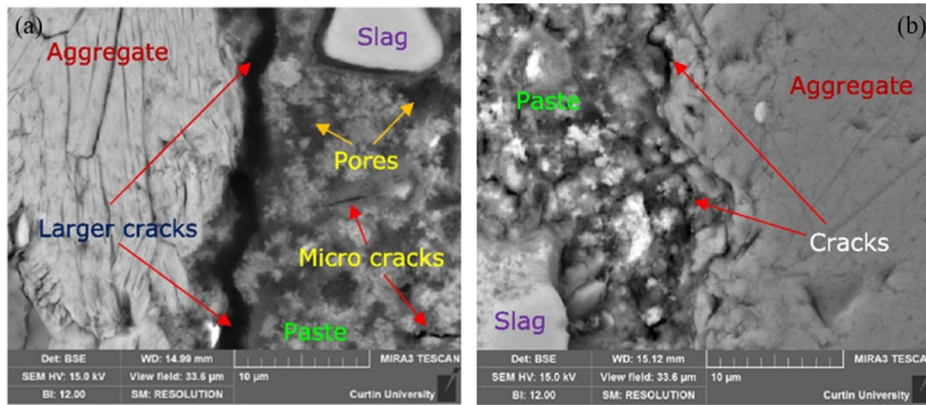


Figure 20. The ITZ of concrete without (a) and with NS (b), reproduced under license number 5320400745643 from [104].

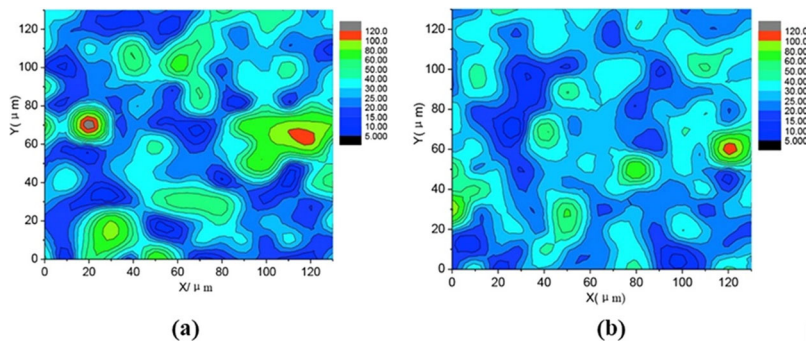


Figure 21. The nanoindentation results of matrix without (a) and with NS (b), reproduced under license number 5503580088260 from [105].

pores owing to the large SSA and fairly small particle size of NS in HVFA concrete. Mukharjee and Barai [106] indicated that the porosity of ITZ of recycled aggregate concrete was reduced by the addition of NS owing to the effect of the pores filling nanoparticles. Al-Bahar et al. [107] investigated the influence of the partial replacement of OPC with micro and NS on the properties of hydrated cement paste using SEM analysis. It was concluded that the compressive strength values for NS achieved better results than micro-SiO<sub>2</sub> owing to better pozzolanic action and particle size gradation. Microstructural analysis of concrete containing NS using TEM and SEM techniques showed that the obtained product was more compact and uniform than traditional concrete. The incorporation of NS reduced the calcium amount in cement paste and improved the concrete durability [10, 108–114]. Du et al. [47] investigated the microstructure of specimen incorporating NS with different contents (0.3% and 0.9%). The SEM results indicated that the ITZ morphology was homogeneous for NS concrete. The strength improvement was due to the presence of NS that enabled forming further C-S-H gels because of its high fineness and reactivity, and the ITZ was enhanced despite of the low replacement content.

## 7. Conclusions

The effect of Nano Silica (NS) on fresh, mechanical properties, durability and microstructure of concrete was reviewed in detail from the past until recent literature. Adding NS to cement mortar or concrete mixtures can effectively increase concrete strength because of pore filling that ultimately decreases the porosity. Future research should address the following issues to obtain the full benefits of NS in cementitious composites.

1. The incorporation of an appropriate amount of NS consumes the available portlandite and considerably rises the development of C-S-H gel, leading to substantial growth in the compressive strength of concrete. The initial and final setting times were reduced noticeably because of increased NS content as compared with that of plain concrete.
2. Numerous studies reported that the fluidity and workability of concrete decreased substantially due to the inclusion of NS. In addition, increasing the NS content in the concrete improved the viscosity and yield stress of concrete. The fluidity of NS-modified cement-based materials can be effectively improved by adding surfactant, changing the dispersion mode, adjusting the morphology of NS and grafting.
3. Incorporation of appropriate amount of NS improves the mechanics and durability of specimen due to its pozzolanic reactivity, filling and nucleation effects. Meanwhile, the performance of NS in mixtures is closely related to its particle size, purity, specific surface area and morphology. Generally speaking, the strengthening effect of fine particle size and high purity NS on the mechanical properties of concrete is more obvious under the premise of ensuring the concrete has better workability. In general, 2%–3% NS of cement mass is recommended for strengthening the properties of concrete.
4. NS has a significant effect on improving the performance of defective concrete. When recycled aggregates, polymer components (rubber particles, superabsorbent polymers) and fibers are used in concrete materials, the further incorporation of NS can effectively improve the interface between the weak components and the cement paste, thereby improving the performance of multi-component concrete.
5. Using multiple nanomaterials or admixtures to replace a single NS reinforcement system may be one of the effective ways to ensure the workability of concrete and improve its durability. When supplemental cementitious material or micro-silica is used in combination with NS, the performance of concrete samples is improved compared with the single NS reinforcement system.

However, the published literature establishes the probability of using NS into concrete, but still, subsequent recommendations and possibilities for future research are required. Determine the optimum volume fraction of NS for its use in cement paste or concrete in a particular amount. The optimum quantity of NS primarily depends on the medium particle size and the type of NS (dry powder, and colloidal). Many previous studies were conducted to address concrete characteristics such as setting time, compressive strength, and workability. Only a few studies were conducted extensively on permeability and water absorption of NS in concrete. However, limited concrete properties were investigated for such as shrinkage, acid resistance, and sulfate resistance and should be studied in the future. Mathematical and statistical modeling of cement paste and concrete mixed with NS need to be developed in the future for extensive research to obtain novel outcomes for a better understanding of concrete performance.

1. More deep study and methods on the dispersion of NS are still need in the regular concrete mixture to avoid the agglomeration effect. Meanwhile, the effect of NS on the fresh property of cement components should be tested and analyzed from the perspective of rheology. Although the properties of the concrete are improved by incorporating an optimized NS content, the detailed mechanism of concrete at the micro-level together with chemical analysis is still missing for NS with the combination of other materials like fibers.
2. Initial stable toughness is a vital factor during the analysis of fracture mechanics and needs to be

evaluated. Therefore, NS can be an effective material to improve fracture performance at an initial stage. To study the effect of various fiber addition on properties of concrete materials with the use of NS for improvement in bond strength and fiber-matrix interface.

3. Another important aspect is to study the long-term behavior of NS under various aggressive surroundings such as the effect of seawater corrosion. Analysis of concrete with NS after exposure to fire and thermal tests is also essential to consider because the small size and higher surface area of NS can be beneficial under high temperature.
4. Although the performance effect of NS on concrete has been extensively studied, its effect on the structural of main gel-like products of the cement/alkali-activated component needs to be further explored. Consequences of NS on durability features of the high-performance concrete component (e.g. engineered cementitious composites, geopolymer, fiber-reinforced concrete) is also a hot topic for future.

#### Disclosure statement

No potential conflict of interest was reported by the authors.

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