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Effects of Nano-Materials on Key Properties of Cementitious Composites: A Review

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ABSTRACT: Cement production industry is one of the largest industries, which is becoming one of the biggest environmental concerns of the world. About 6% of the global CO_2 emission comes from this industry. An improvement in cement quality and application process can result in a lot of savings in terms of resources and environmental pollution without hindering developmental needs. A detailed knowledge of the crystal structure of cement hydration products and advanced instrumentations to observe its nano-structure enables researchers and practitioners to undertake nano-modification of cementitious composites. To enhance binder characteristics, improving the nano-level fault is the new trend among the cement and concrete researchers. In this quest, many studies have been conducted by incorporating nano-scaled materials with cement, and observing their effects on the hydration products. To conduct meaningful research in cement and concrete technology, the researchers first need to know the existing knowledge gap and the current developments in this field. This study is an effort to bring the major recent findings together, identifying the gaps and providing the directions for future studies on the application of nano-materials in cementitious composites. This will help the experts to get an outline of this field and also set their goals according to their requirements.

KEYWORDS: Cementitious composites; Concrete; Mortar; Nano-particles; Nano-tubes.

1 INTRODUCTION

Cementitious composites such as cement paste, mortar, and concrete are the most versatile and widely used structural construction materials in most parts of the globe. This scenario is envisaged to continue in the decades to come due to the versatility and robustness of the above materials. However, on contrary to being the most eminent material in development and urbanism of the modern world, cement and concrete production industries are also widely regarded as one of the major contributors to global warming, due to high emission of carbon dioxide (CO_2) during their production processes.

When cementitious composites are driven to attain higher strength, it is achieved through modification of the microstructure and densification of their matrix by incorporating ultrafine and reactive powders as well as suitable chemical admixtures. The advancement in materials science and engineering with the evolution of nano-particles has also significantly influenced the research trends in cementitious composites. Research and field applications of nano-scaled particles in cementitious composites have accumulated considerable interests in recent years due to the deemed positive influences of these materials in cementitious composites.

The term "nano-materials" usually refers to the nano-scale matters with a surrounding interfacial layer of 1-100 nanometers (nm). The interfacial layer fundamentally influences all the properties of nano-scale matters (Batista et al. 2015). In concrete technology, "nano-engineering" refers to the techniques of manipulation of the cementitious composites at nanometre scale to develop some desirable properties in it (Sanchez & Sobolev 2010). Figure 1 shows the particle size comparison of common ingredients of concrete, common supplementary cementitious materials (SCMs) and nano-materials. Owing to the heterogeneous nature of cementitious composites, the addition of nano-materials (nano-particles and nano-reinforcement) has created a lot of research interests in recent years (Kawashima et al. 2013).

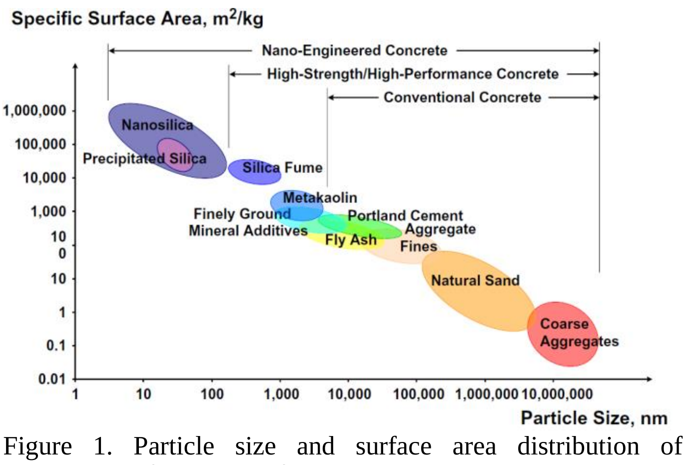


Figure 1. Particle size and surface area distribution of ingredients of concrete [from Sanchez & Sobolev (2010), as adapted from Sobolev & Gutiérrez (2005)].

Effects of Al_2O_3, TiO_2, Fe_2O_3, CuO, Cr_2O_3, ZnO, ZnO_2, SnO_2, ZrO_2, $CaCO_3$, and nano-clay particles were investigated as cementitious additives although nano-SiO_2 was the focus in most studies. In addition to simple cement replacement with nano-particles, alkali-activation of nano-particles also showed promising outcomes. An organic thermoset polymer like matrix structure has been found after the activation process, which is why the structure is referred as "geopolymer" or "inorganic polymer" (Juenger et al. 2011).

Alkali-activated nano-particles create different mechanical characteristics and lower environmental impacts (Behfarnia & Rostami 2017). Cement paste or mortar containing these types of nano-particles show lower carbon footprint than the ordinary Portland cement (OPC) based composites (Ouellet-Plamondon & Habert 2015). Moreover, with the modulus of elasticity in the order of TPa and the tensile strength in the scale of GPa, carbon nano-tubes (CNT) and carbon nano-fibres (CNF) have proven themselves as excellent reinforcing candidates for cementitious composites. In addition to arresting the crack propagation, they can impart the electromagnetic field shielding and self-sensing properties to cementitious composites (Gdoutos et al. 2016; Sanchez & Sobolev 2010; Stynoski et al. 2015).

The unitary cost of nano-materials is 100-1000 times higher than that of OPC (Mendes et al. 2015). Therefore, for effective industrial and commercial applications, it is crucial to completely understand the influences of nano-particles on the properties of cementitious composites prior to recommending their applications. This article summarises the major recent findings on the applications of nano-materials in cementitious composites. The main objective of this article is to provide an avenue for researchers and designers to get an outline of this field and to enable them to set a foundation in terms of optimising the mix design of cementitious composites incorporating nano-materials.

2 APPLICATIONS OF NANO-PARTICLES

In recent years, nanotechnology has been implemented in cement and concrete technology in various ways. The application of nano-particles in this area can be observed through three different approaches, as follows:

a. Supplementary cementitious material (SCM),
b. Alkali-activated additive,
c. Nano-reinforcement.

3 NANO-PARTICLES AS SUPPLEMENTARY CEMENTITIOUS MATERIAL

3.1 *Working mechanism of nano-SCM*

Nano-particles are of smaller size and lighter weight compared to OPC. The replacement of OPC with nano-particles improves the workability of cementitious composites, such as mortar, to a certain extent, as these particles are easier to stay suspended

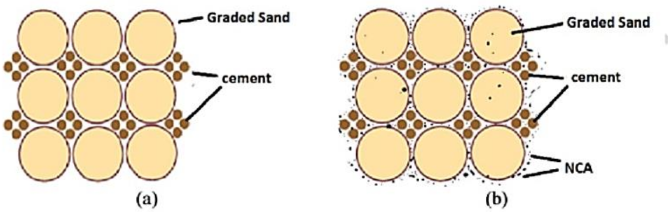


Figure 2. Packing of particles in mortar: (a) without nano-particles; and (b) with nano-particles (Lim et al. 2018).

in the fresh mixture. A drop of unit weight of the mixture and a higher packing of the particles also happen with the inclusion of nano-particles. The loss of unit weight, however, may cause a reduced flowability in mortar. In addition, a better packing of the particles causes a higher internal friction due to a reduction of free water. This also hinders the fluidity of mortar (Khotbehsara et al. 2015, 2018).

Nano-particles exhibit both filler and pozzolanic effects, because of which they can improve the microstructure and strength of cementitious composites, such as mortar. These particles fill the void between cement particles and behave as nuclei. After the initiation of the hydration, the hydrated products encapsulate the nano-particles, restricting the growth of $Ca(OH)_2$ crystals. Thus, nano-particles facilitate cement hydration by accelerating the formation of C–S–H gel and fill up large pores, resulting in a higher density and compact microstructure. On the other hand, at higher contents they cause a reduction of C_3S and β-C_2S phases in blended cement paste and agglomerate around the OPC grains, hindering the hydration (Mohseni et al. 2015, 2016; Morsy et al. 2012; Yang et al. 2015a). Figure 2 shows how nano-particles fill up the spaces in cementitious composites, such as mortar.

3.2 *Effect of nano-SCM on workability*

In recent years, nano-particles of SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CuO, Cr_2O_3, ZnO_2, SnO_2, ZrO_2, and $CaCO_3$ have been utilised in cementitious composites, such as mortar, partially replacing cement and their effect on workability have been studied. Nano-particles typically possess a specific surface area around 200 m^2/g and a diameter of 12-20 nm. In exception to the other types of nano-particles, nano-Fe_2O_3 has 60 m^2/g specific surface area and 60 nm diameter, and nano-ZnO_2 possesses of 50 m^2/g surface area and 50 nm diameter (Khotbehsara et al. 2015, 2018; Madandoust et al. 2015; Mohseni et al. 2015; Oltulu & Şahin 2014; Yang et al. 2015b). SiO_2, Fe_2O_3 and CuO nano-particles have been reported to improve the viscosity of freshly mixed cementitious composites, for example self-compacting mortar, thus reducing the segregation tendency (Madandoust et al. 2015).

Most of the above-mentioned nano-particles improved workability when used up to 5% cement replacement level. Nano-TiO_2 performed the best at 5% replacement level, in the presence of 25% fly ash (FA). A slump flow diameter of 258 mm and a V-funnel flow time of 7.6 s were achieved compared to 245 mm and 11 s for the control mix (Mohseni et al. 2015). Nano-particles of SnO_2, ZrO_2, and $CaCO_3$ showed positive effects on the mortar fluidity at 1% replacement level. Any further addition caused a drop in fluidity, though it was in the self-compacting range up to 5% (Khotbehsara et al. 2018).

In another study, the inclusion of 1-4% nano-CuO in the presence of 20-30% FA slightly reduced the flowability of mortar, though the effect of FA was more prominent (Khotbehsara et al. 2015). Larger particles (20 nm diameter) of SiO_2 and TiO_2 adversely affected the mortar fluidity. Only 1% of amorphous nano-TiO_2 (specific surface area 50 m^2/g) caused a drop in mini-slump flow diameter from 310 mm to 260 mm and a rise in mini V-funnel flow time from 7.4 s to 9.4 s (Rao et al. 2015). In combination with 10-30% palm-oil fuel ash (POFA), 0.5% amorphous nano-SiO_2 (particle size of 15 nm and specific surface area of 640 m^2/g) resulted in slight increase in workability. Any further addition caused a fall in the flow table test result (Farzadnia et al. 2015; Noorvand et al. 2013).

3.3 *Effect of nano-SCM on strength*

In many studies, SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CuO, Cr_2O_3, ZnO, ZnO_2, SnO_2, ZrO_2, and $CaCO_3$ nano-particles were incorporated to improve the strength properties of cementitious composites (for instance, mortar and concrete). Nano-particles were used with a content up to 5%, often in association with 20-30% FA, 5% silica fume (SF), 5-15% rice husk ash (RHA) or 10-30% POFA. (Farzadnia et al. 2013, 2015, Khotbehsara et al. 2015, 2018; Liu et al. 2015; Madandoust et al. 2015; Mohseni et al. 2015, 2016; Noorvand et al. 2013; Oltulu & Şahin 2014; Rao et al. 2015; Yang et al. 2015b). Table 1 shows a summary of these studies.

Among the nano-particles listed in Table 1, nano-SiO_2 produced the highest strength. Five per cent (5%) nano-SiO_2 of 15 nm diameter and 160 m^2/g surface area produced 99 MPa at 28 days, which is 25% higher than the strength of OPC paste samples (Qing et al. 2007). Nano-TiO_2, in association with 30% FA, produced 92 MPa at 28 days, though it was 3% lower than the strength of the samples without nano-particles (Rao et al. 2015). A compressive strength of 77 MPa was recorded for a combination of 5% SF and 1.25% nano-Al_2O_3, with an improvement of 18.5% (Oltulu & Şahin 2014). In the presence of 25% FA, nano-particles of SnO_2, ZrO_2, ZnO_2, $CaCO_3$, CuO, and Cr_2O_3, having a diameter of 15-20 nm and a surface area of 200 m^2/g, gained 40-47 MPa at 28 days (Khotbehsara et al. 2018; Madandoust et al. 2015; Yang et al. 2015b).

In terms of strength enhancement, nano-ZrO_2 exhibited the best performance. Four per cent (4%) nano-ZrO_2 enhanced the compressive strength by 31% at 28 days (Khotbehsara et al. 2018). Twenty-nine per cent (29%) increase was reported for 5% nano-TiO_2 when used with 10% RHA. This combination produced 58 MPa at 28 days (Mohseni et al. 2016). Nano-particles of SnO_2, ZnO_2, $CaCO_3$, and CuO showed 19-24% higher compressive strength when used in combination with 25% FA (Khotbehsara et al. 2018; Madandoust et al. 2015; Yang et al. 2015b). It seems these nano-particles do not have much chemical effect on cement hydration.

Cementitious mixtures with 5% SF gained higher strength than with 20-30% FA (Farzadnia et al. 2013; Madandoust et al. 2015; Mohseni et al. 2015; Oltulu & Şahin 2014). The highest level of performance was achieved for nano-Al_2O_3, followed by nano-SiO_2 and nano-Fe_2O_3. The respective optimum contents of these nano-particles were 1.5%, 0.5-1% and 1-1.5%, at which the compressive strengths above 77, 72 and 69 MPa, respectively, were achieved. The improved performance of nano-Al_2O_3 is credited to the interlocking of nano-Al_2O_3 particles that increases the friction between slipping planes; the chemical composition of the hydration products also changes in the presence of nano-Al_2O_3 (Oltulu & Şahin 2014).

Twenty-five per cent (25%) FA combined with nano-particles of SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CuO, Cr_2O_3, ZnO_2, SnO_2, ZrO_2, and $CaCO_3$ gained the compressive strengths of 40-47 MPa by 28 days (Khotbehsara et al. 2015, 2018; Madandoust et al. 2015; Mohseni et al. 2015; Yang et al. 2015b). In combination with nano-SiO_2 possessing a specific surface area of 640 m^2/g, 10% POFA produced a compressive strength of 75 MPa (Noorvand et al. 2013).

Calcium hydroxide (CH) liberated during cement hydration leaves pores in the matrix of cementitious composites at elevated temperatures. The lesser amount of CH and the better distribution of C–S–H contribute to retain a significant amount of strength under elevated temperatures. One per cent (1%) nano-Al_2O_3 maintained a higher residual strength than the reference mortar up to 800°C. Until 400°C, the mortar samples containing nano-Al_2O_3 (1-3%) had a better residual strength than that of the control specimens (Farzadnia et al. 2013).

Table 1. Physical properties of different nano-particles and their effects on the strength of cementitious composites

Nano-particle type	Particle size, nm	Specific surface area, m^2/g	Companion SCM	Best compressive strength (28 days), MPa	% increase in strength	Reference
Al_2O_3	13	100	5% SF	77	18.5	(Oltulu & Şahin 2014)
	15	180-250	–	75	0.0	(Liu et al. 2015)
	13	85-115	5% SF	63	16.0	(Farzadnia et al. 2013)
	15	200	25% FA	43	13.0	(Mohseni et al. 2015)
$CaCO_3$	20	200	25% FA	44	22.0	(Khotbehsara et al. 2018)
Cr_2O_3	15	200	25% FA	42	13.0	(Yang et al. 2015b)
CuO	15	200	25% FA	44	18.9	(Madandoust et al. 2015)
	15	200	20-25% FA	42	5.0	(Khotbehsara et al. 2015)
Fe_2O_3	20-60	60	5% SF	69	7.7	(Oltulu & Şahin 2014)
	60	60	25% FA	42	13.5	(Madandoust et al. 2015)
SiO_2	15	160	–	99	25.0	(Qing et al. 2007)
	20	260	30% FA	90	-5.0	(Rao et al. 2015)
	30	220	–	81	7.5	(Liu et al. 2015)
	15	640	10% POFA	75	11.0	(Noorvand et al. 2013)
	12	200	5% SF	72	10.8	(Oltulu & Şahin 2014)
	15	200	25% FA	43	15.0	(Madandoust et al. 2015)
	15	640	–	41	3.5	(Farzadnia et al. 2015)
	15	200	25% FA	40	5.0	(Mohseni et al. 2015)
SnO_2	20	200	25% FA	45	24.0	(Khotbehsara et al. 2018)

TiO_2	20	50	30% FA	92	-3.0	(Rao et al. 2015)
	25	50-80	–	76	0.8	(Liu et al. 2015)
	20	200	10% RHA	58	29.0	(Mohseni et al. 2016)
	15	200	25% FA	42	11.0	(Mohseni et al. 2015)
ZnO	50	50	–	74	-1.6	(Liu et al. 2015)
ZnO_2	15	200	25% FA	45	19.0	(Yang et al. 2015b)
ZrO_2	20	200	25% FA	47	31.0	(Khotbehsara et al. 2018)

Many agricultural and industrial by-products and natural minerals can also be used as nano-particles. Metakaolin (MK) nano-particles (with a Blaine surface area of 48 m^2/g and average dimensions of 100 × 50 × 10 nm) had a positive effect on strength for a replacement level up to 5%, and then the strength decreased with any further addition. Twenty-three per cent (23%) higher compressive strength was attained with 5% replacement of cement (Morsy et al. 2012). At high temperature exposure (up to 800°C), the higher (5-15%) the nano-MK content, the better is the strength gain. An exposure of 2 hours to 250°C resulted in a strength gain of 37% for the blended cement mortar samples containing 15% nano-MK, while the corresponding OPC mortar samples gained 28%. After an exposure to 800°C for 2 hours, the mortar samples containing 15% nano-MK lost about 47% of strength, compared to 57% of the control samples (Morsy et al. 2012).

Nano-FA (mean size of 40 nm) was not successful in producing higher strength in mortar at 7 days. As a pozzolanic material, FA needs lime to react. At early ages, the generation of lime from hydration of cement may not be quite sufficient for pozzolanic reaction. Accompanied by 1.2% nano-lime, the mortar samples containing 11.9% nano-FA achieved the compressive strength above 30 MPa, which was 151% more than the strength of the reference mortar within 7 days (Tudjono et al. 2014). Nano-RHA (mean size of 36 nm) up to 7.5% contents also enhanced the strength properties of mortar. Seven and a half per cent (7.5%) nano-RHA achieved the compressive strengths of 45 and 52 MPa at 28 and 90 days, respectively, which were 32% and 26% higher than that of the OPC mortar samples. It should be noted that nano-RHA could achieve a similar strength at lower contents compared to micro-RHA (Balapour et al. 2017).

3.4 *Effect of nano-SCM on durability*

Nano-SCM also contributes to enhance the durability performance of cementitious composites. It was observed that the water absorption of mortar dropped as the content of the nano-particles of TiO_2, Cr_2O_3 and ZnO_2 rose up to 5%. Among them, nano-Cr_2O_3 indicated the best performance. Three to five per cent (3-5%) of nano-Cr_2O_3 kept the water absorption at 6.7-6.8%, which was 21-22.7% less than that of the reference mortar samples. Although nano-ZnO_2 showed significant improvement at 3%, for both nano-TiO_2 and ZnO_2, the water absorption was 7.7-7.8% at 5% content (Mohseni et al. 2015; Yang et al. 2015b). Also, SnO_2, ZrO_2, and $CaCO_3$ nano-particles reduced the water absorption up to 3%, 4% and 3%, respectively. They were lower than that of the OPC mortar samples. These three nano-particles could reduce the water absorption by 9-12% (Khotbehsara et al. 2018).

Nano-SiO_2 and nano-Al_2O_3 did not perform as well as the other nano-particles. With a content of 0.5-1%, nano-SiO_2 reduces the water absorption and permeable void ratio of cementitious composites, such as mortar. The negative effect of 20% POFA can be eliminated by 0.5% content of nano-SiO_2 (Noorvand et al. 2013). It also decreases the permeability of cementitious composites. One per cent (1%) of nano-SiO_2 could overcome the adverse effect of POFA (up to 30%) on the permeability and keeps it same as that of the control mortar (Farzadnia et al. 2015). The optimum content for nano-SiO_2 and nano-Al_2O_3 was 3% and 1%, respectively, for water absorption. The specimens with three percent (3%) nano-SiO_2 and nano-Al_2O_3 had 8.4% water absorption. However, the mortar samples with five per cent (5%) nano-SiO_2 absorbed more water than that of the mortar mixture without nano-particles (Mohseni et al. 2015).

The above findings on water absorption were consistent with the Mercury Intrusion Porosimetry (MIP) test findings. For nano-SiO_2 and nano-Al_2O_3, 1.25% was the optimum level of replacement to reduce porosity. The incorporation of 1.25% nano-SiO_2 reduced 48% of the mercury intruded into the mortar samples without nano-particles. Two and a half per cent (2.5%) nano-SiO_2 increased the mercury volume by 43% in MIP test. In the case of 1.25% nano-Al_2O_3, it was 87% lower. The porosity became lower as compared to the control samples even for

2.5% nano-Al_2O_3. Nano-Fe_2O_3 had the best performance at 0.5% content, which reduced the porosity by 41%. The inclusion of nano-Fe_2O_3 showed an improvement even at 2.5% content (Oltulu & Şahin 2014). Nano-RHA also improves the water absorption of mortar. The water absorption of mortar was reduced by 30.8% at the age of 28 days when 7.5% nano-RHA was used in the mixture (Balapour et al. 2017).

Incorporation of 1-5% nano-particles of SiO_2, Al_2O_3, TiO_2, Cr_2O_3, SnO_2, ZrO_2, $CaCO_3$, and ZnO_2 decreases the rapid chloride permeability of cementitious composites. Amongst these nano-particles, only 1% nano-SiO_2, nano-ZrO_2, nano-$CaCO_3$ and nano-ZnO_2 had resulted in marginally "moderate" chloride permeability, according to ASTM C1202. All others indicated "low" permeability, while the control mix had a "moderate" chloride permeability (ASTM C1202-17 2017; Khotbehsara et al. 2018; Mohseni et al. 2015, 2016; Yang et al. 2015b). Nano-SiO_2 had the best resistance at 3% cement replacement. The mortar samples with nano-Al_2O_3 had almost the same chloride permeability for all contents used in the range of 1-5%.

Rapid chloride permeability test (RCPT) value declined with the increase of nano-TiO_2 content. Five per cent (5%) of nano-SnO_2 and nano-TiO_2 had the lowest RCPT value among various nano-particles. Five per cent (5%) nano-SnO_2 caused a drop of 58% in RCPT test result (Khotbehsara et al. 2018). The mortar samples with 5% nano-TiO_2 had the RCPT value of 1200 coulomb compared to 2800 coulomb of the OPC mortar (Mohseni et al. 2015). Three per cent (3%) nano-Cr_2O_3 and 5% nano-ZnO_2 both reduced the value of charge passed to 57% of the control mortar samples. These were the best results for these two nano-particles used with a content in the range of 1-5% (Yang et al. 2015b). Furthermore, the incorporation of nano-RHA improved the rapid chloride migration test results even at 7.5% content (Balapour et al. 2017). For 7.5% nano-RHA, the normalised migration coefficient was 123% at 28 days, when determined according to NT BUILD 492 measurement method (Balapour et al. 2017; NT BUILD 492 1999).

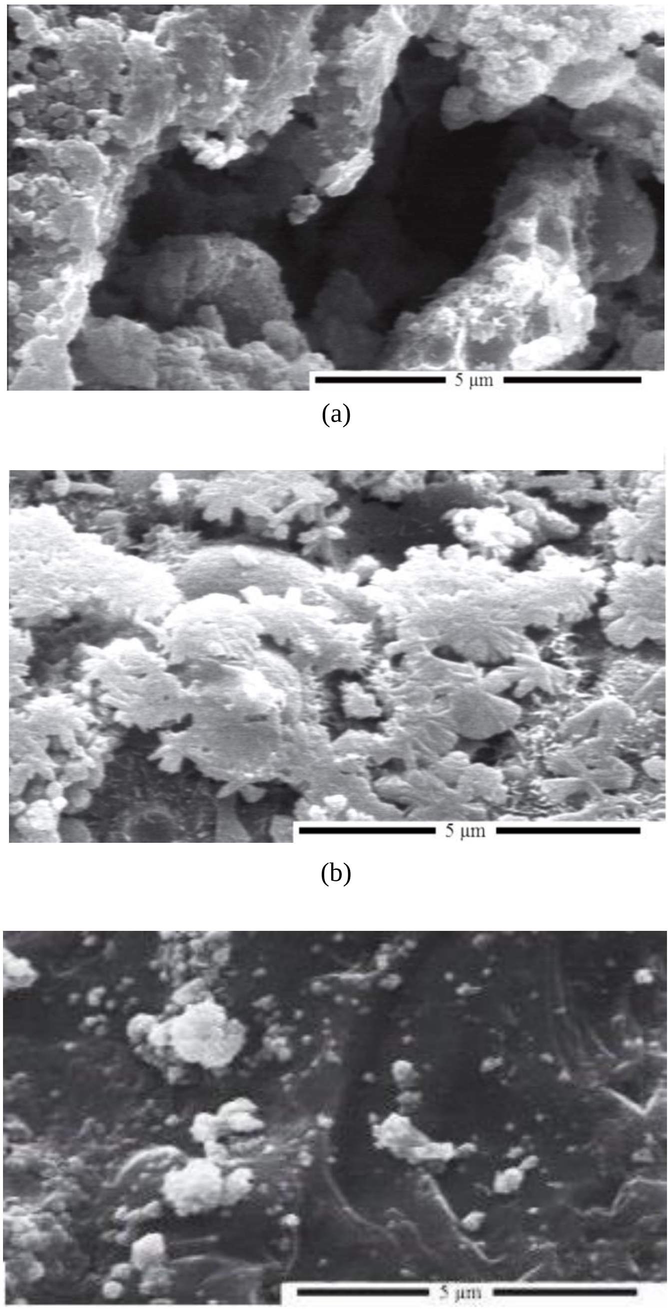
For electrical resistivity and corrosion resistance, nano-SiO_2 showed the best performance at 3% level. The resistivity of mortar declined with an increased nano-Al_2O_3 content and improved with an increase in nano-TiO_2 content. However, 5% nano-TiO_2 had the best performance. Only 3% nano-SiO_2 and 5% nano-TiO_2 produced a corrosion rate designated as "low", whereas it was in "high" range for the reference samples, when determined in accordance with ACI 222R-01 (ACI 222R-01 2001; Mohseni et al. 2015). A similar effect was also observed for Cr_2O_3 and ZnO_2 nano-particles. Although 3% content had the highest electrical resistance, 3-5% nano-Cr_2O_3 had the "low" level of corrosion rate. The electrical resistivity increased with the inclusion of nano-ZnO_2 for 1-5% cement replacements. At least 4% nano-ZnO_2 was required to achieve "low" corrosion rate (Yang et al. 2015b). Raising nano-RHA content from 0 to 7.5% resulted in a rise in the electrical resistivity of 116% at 28 days (Balapour et al. 2017).

All the above-mentioned durability properties are directly connected with the microstructure of cementitious composites, for instance mortar and concrete. Figure 3 shows the change in the microstructure of mortar due to the inclusion of 2% nano-Cr_2O_3 and 4% nano-ZnO_2, in the study performed by Yang et al (2015b). The micrograph of the sample without any nano-particles shows large pores. Two per cent (2%) nano-particles filled up the pores and made a denser structure. Four percent (4%) nano-particles caused a significant reduction in the amount of $Ca(OH)_2$ crystals and produced a compact microstructure in the hardened mortar. It means that these nano-particles will be conducive to improve the strength, transport properties, and durability performance of cementitious composites.

3.5 *Special Attributes of nano-SCM*

Nano-particles can provide added features to the cementitious composites. Nano-TiO_2 imparts "self-cleaning" and "de-polluting" characteristics in cementitious composites through photocatalysis (Nahar et al. 2017; Sanchez & Sobolev 2010; Scrivener & Kirkpatrick 2008). In the presence of sunlight, its strong oxidizing power can prevent the build-up of dirt and organic growth, preserving the clean appearance for a longer time (Scrivener & Kirkpatrick 2008). This photocatalytic nature can also break down pollutants, such as NOx, CO, VOCs, chlorophenols, and aldehydes from the vehicle and industrial emissions, and thus contribute to reduce pollution (Sanchez & Sobolev 2010; Scrivener & Kirkpatrick 2008).

Nano-Fe_2O_3 provided "self-sensing" property in the mortar. This feature enables the structural health monitoring of structures, such as tunnels and bridges, without embedded or attached sensors (Sanchez & Sobolev 2010).



(a) (b) (c)

Figure 3. SEM micrographs of mortar: (a) without any nano-particles; (b) with 2% nano-Cr_2O_3; and (c) 4% nano-ZnO_2 (Yang et al. 2015b).

4 NANO-PARTICLES AS ALKALI-ACTIVATED ADDITIVES

4.1 *Working mechanism of alkali-activated additives*

Nano-particles, when activated by alkali, can lower the Ca/Si ratio, shorten the silicate chain, increase the structural disorder, and exhibit foil-like morphology in the hydrated product, making it more thermodynamically unstable. These effects enable the C–S–H to easily rearrange and reorganise under stress (Ye & Radlińska 2017). Besides, nano-particles form a layered and laminated structure of alkali metal-silicate phase in alkali-activated C–S–H system (Behfarnia & Rostami 2017). This is how alkali-activated nano-particles enhance the strength properties of cementitious composites.

4.2 *Effect of alkali-activated additives on strength*

Alkali-activated nano-particles, especially SiO_2, Al_2O_3, TiO_2, etc. have been utilised by replacing OPC, thus contributing to sustainable construction. Although alkali activation results in significant improvement in strength, this technique could result in a marginal reduction in strength without the use of any SCM. A summary of alkali-activated nano-particles and their effects on the strength of cementitious composites, particularly cement paste and mortar are provided in Table 2.

4.3 *Effect of alkali-activated additives on durability*

Activated nano-SiO_2 negatively affects the resistance of cementitious composites, particularly mortar, against CO_2 penetration. With the increased activated nano-SiO_2 content, the carbonation depth in mortar is increased. The substitution of cement by 5% nano-SiO_2 with the particle size of 20-30 nm increased the carbonation depth from 7.09 mm and 8.71 mm to 12.17 mm and 13.57 mm for 14-day and 28-day cycles, respectively. The water penetration depth of the mixture with micro-silica was 13.53 mm, but the addition of nano-silica increased the value by almost 280%. Also, five per cent (5%) nano-silica in cement paste increased the electric charge from 2,897 C and 1,923 C to 12,188 C and 4,765 C at the age of 28 and 90 days, respectively, which indicates a reduction in the chloride ions penetration resistance. Nano-silica particles filled the pores in the mortar matrix and formed a laminate structure, due to which the reduction in the resistance of mortars against the penetration of undesirable agents occurred. (Behfarnia & Rostami 2017).

Table 2. Impacts of alkali-activated nano-particles on the strength of cementitious composites

Activator	Nano-particle type	Nano-particle size/surface area	Major impacts on strength	Reference
12M NaOH	SiO_2	4-16 nm	Achieved a compressive strength of 42.88 MPa at 28 days, with an improvement of 77%.	(Adak et al. 2014)
10M NaOH	SiO_2	12 nm	Compressive strength reached 51.8 MPa at 90 days, compared to 39.4 MPa strength of the control paste.	(Phoo-ngernkham et al. 2014)
4M NaOH	SiO_2	20-30 nm	After 3% addition, the mortar achieved the compressive strength of 63 MPa at 28 days and 76.5 MPa at 90 days	(Behfarnia & Rostami 2017)
10M NaOH	Al_2O_3	13 nm	With 2% nano-Al_2O_3, the compressive strength became 56.4 MPa at 90 days while it was 39.4 MPa for the control mixture.	(Phoo-ngernkham et al. 2014)
NaOH with a Na_2O concentration of 4% (by mass of paste)	TiO_2	20-100 nm	With the addition of 0.5% nano-TiO_2, the compressive strengths increased to 25.76, 39.15 and 62.96 MPa, which were higher than 23.48, 33.91 and 57.56 MPa recorded in the reference cement paste at 3 days, 7 days and 28 days, respectively.	(Yang et al. 2015a)
2.5M NaOH	RHA & POFA	2345 m^2/kg and 1800 m^2/kg	Compressive strength was increased significantly by 15% and 5% at the ages of 1 day and 90 days with 1% nano-POFA. The increases in compressive strength at those two ages were 12% and 2%, respectively, for 1% nano-RHA.	(Lim et al. 2018)
12.5M NaOH	SiO_2, $NaAlO_2$ & $Ca(NO_3)_2$	167 nm	Compressive strength of 43 MPa was achieved after 14 days curing which was equivalent to the 28 days strength of the reference mortar.	(Jo et al. 2014)

5 NANO-SCALED REINFORCEMENTS

5.1 *Working mechanism of nano-reinforcement*

Flaws exist at the nano-scale in hydrated cement products (Manzur & Yazdani 2015). Amorphous C–S–H is the “glue” within the cementious matrix. CNT and CNF decrease the porosity and increase the stiffness of C–S–H, and thus reinforce the cement matrix at nano-scale (Sanchez & Sobolev 2010). Due to their nano-scaled dimensions, CNT and CNF can be dispersed in the cement paste at very minute scale, which would not be possible with conventional fibres (Manzur & Yazdani 2015). Proper dispersion is a critical condition for the advantageous application of the strongly hydrophobic CNT and CNF (Stynoski et al. 2015). These nano-reinforcements tend to stick (agglomerate) together because of the Van der Waals’ force, generated from their large surface areas. Manual stirring will not provide sufficient energy to break down the agglomeration. Ultrasonic vibration is able to distribute the CNT bundles across the cement paste. In aqueous solution, sonication fails to produce a stable mixture. Polar impurities (i.e.: hydroxyl or carboxyl end groups) are successful in enhancing the dispersion of nano-tubes within the fresh cementitious matrix. Polycarboxylate based water reducing agents were effectively used as surfactant to disperse nano-tubes within the aqueous solution (Manzur & Yazdani 2015). Figure 4 shows the outcome of two types of dispersion techniques applied on two different sized CNT. Where CNT-A has a diameter of 42 nm and length of 400 nm and CNT-B has a diameter of 80-400 nm and length of 150 nm.

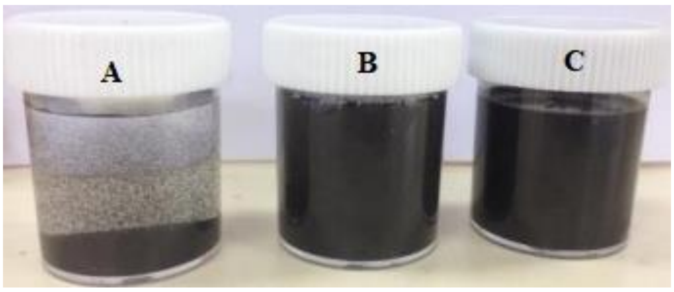


Figure 4. (a) CNT-A dispersed via ultrasonication (without surfactant); (b) CNT-A dispersed via ultrasonication (with surfactant); and; (c) CNT-B dispersed via ultrasonication (Lim et al. 2016)

5.2 *Effect of nano-reinforcement on workability*

The effect of nano-reinforcement on the rheology or workability of cement-based composite materials, particularly mortar, could not be found in any recent studies. Having large surface, nano-tubes and nano-fibres adhere more water compared to other particles. Besides, water may get entrapped within the agglomerated clumps of fibres if the dispersion is not sufficient (Manzur & Yazdani 2015). From these deductions, it can be concluded that the workability cementitious composites may drop significantly if nano-tubes and/or nano-fibres are introduced in the mixture.

5.3 *Effect of nano-reinforcement on strength*

Multi-walled CNT (MWCNT), with a content up to 0.5% (w/w) and an approximate surface area of 100 m^2/g was observed to enhance the compressive strength of mortar, a widely used cementitious composite. A compressive strength of 35.3 MPa was recorded at 28 days, which is 11% higher than that of the control mortar without any nano-reinforcement (Danoglidis et al. 2016). Nano-tubes of a lower content (0.3%), but a higher surface area (233 m^2/g) provided 16% higher strength over the reference mixture at 28 days. Any further addition resulted in a reduction in the compressive strength (Manzur & Yazdani 2015). In both cases, polycarboxylate based surfactant and ultrasonic energy were applied for the proper dispersion of nano-tubes (Danoglidis et al. 2016; Manzur & Yazdani 2015).

The flexural strength of cementitious composites was not affected by the CNT in the same way as the compressive strength (Danoglidis et al. 2016). The flexural behaviour of nano-fibres reinforced mortar mostly depends on the pull-out action of fibres and crack-bridging, which are affected by non-uniform fibre distribution. The probability of non-uniform fibre distribution is greater for a higher concentration of nano-reinforcement (Manzur & Yazdani 2015). In most of the recent studies, 0.1% (w/w) MWCNT was found to be the most advantageous (Danoglidis et al. 2016; Gdoutos et al. 2016; Manzur & Yazdani 2015).

When used with a content of 0.1% (w/w), MWCNT with a diameter of 20-45 nm and a length around 10 μm enhanced the flexural strength of mortar by 87%, providing a flexural strength of 10-11 MPa at 28 days (Danoglidis et al. 2016; Gdoutos et al. 2016). For the same content, MWCNT with 10-20 nm diameter and 10-30 μm length had a much lower flexural strength. At 28 days, the mortar samples with such MWCNT reached 5.6 MPa which was 19.5% higher than that of the control specimens' flexural strength (Manzur & Yazdani 2015).

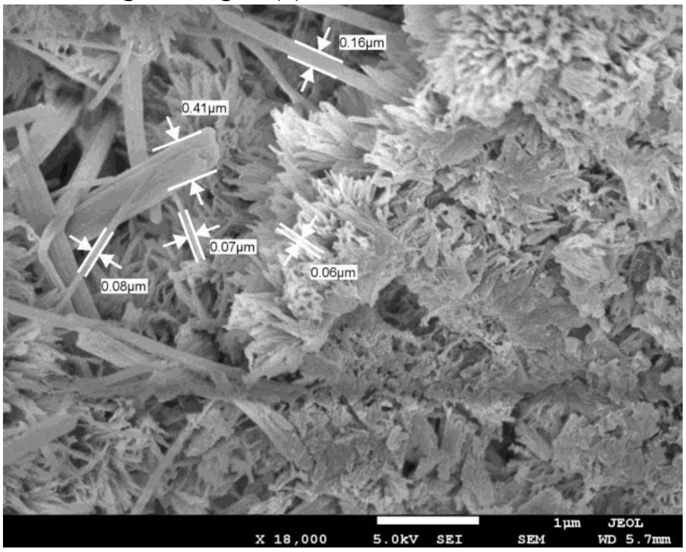


Figure 5. SEM micrograph of cement composite including CNT (Lim et al. 2016)

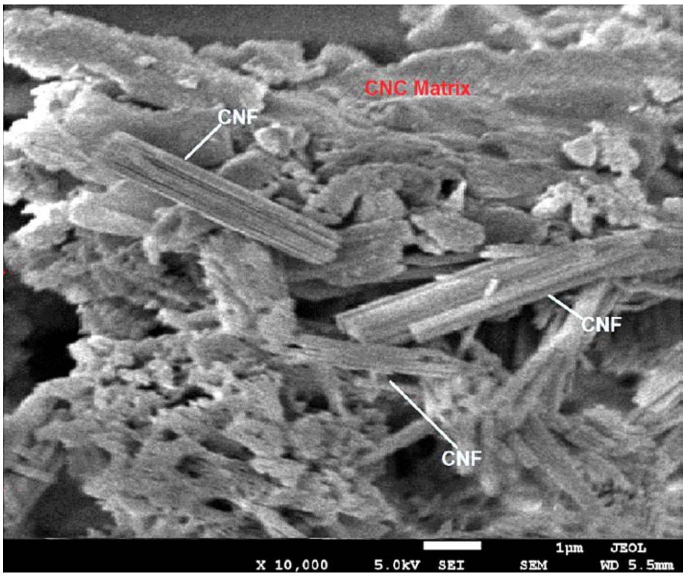


Figure 6. Distribution of CNF within the carbon-neutral cement composite matrix (Lim et al. 2018)

CNT with 20-40 nm diameter and 0.5-40 μm length provided only 4% higher flexural strength when used with a content of 0.125% (w/w). In cementitious composites, silica-functionalisation improves the interfacial transition zone between the products of cement hydration and nano-reinforcements that is more porous due to a high level of calcium hydroxide. Silica-functionalised CNT of the same type achieved 9% more flexural strength compared to the control samples. In association with 5% silica fume, the plain and silica-functionalised CNT enhanced the strength by 20% and 23%, respectively. It should be noted that 5% silica fume alone raised the strength by 15% (Stynoski et al. 2015). Even in carbon-neutral cement, 0.006 kg/m^3 CNF exhibited a 31% higher peak flexural strength at 28 days (Lim et al. 2018). Figure 5 shows the microstructure of cement matrix containing CNT from the study undertaken by Lim et al. (2016), while Figure 6 shows the distribution of CNF within the matrix of cementitious composite containing carbon-neutral cement studied by Lim et al. (2018). Both figures indicate that CNF and CNT were well-distributed within the cement matrix that contributed to improve the flexural strength of cementitious composites.

5.4 *Special attributes of nano-reinforcement*

MWCNT imparts “self-sensing” property to the cementitious composites. When this material was used with 0.1% content, the piezo-resistivity was raised by 10.6%, which is an indication of the amplified sensitivity (Danoglidis et al. 2016).

6 RESEARCH GAPS & RECOMMENDATIONS

This study reveals that the research on utilising nano-materials in cementitious composites has not achieved a matured stage at present. A literature survey identified substantial research gaps, which can be bridged by researchers to achieve more meaningful outcomes and directions for using nano-materials in construction. In this context, the following specific recommendations are given.

a. Comprehensive research is needed to determine the optimum content of different nano-materials in cementitious composites.
b. Studies on the effects of alkali-activated nano-particles and nano-reinforcement on the durability of cementitious composites are very limited. More investigations are required in this area.
c. Production and processing techniques of nano-materials should be improved to make them commercially viable.
d. Economic and efficient dispersion methods for CNT and CNF need to be established.
e. Life-cycle cost-benefit analysis should be performed to analyse the feasibility of using nano-materials in cementitious composites.

7 CONCLUDING REMARKS

Nano-materials have started a new chapter in cement and concrete technology for construction applications. The recent developments show the enormous potential of these materials. These “miniscule” materials have started to transform the traditional concepts of cement and concrete production. Most of the recent studies have shown remarkable improvements in the strength, durability, and microstructure characteristics of nano-engineered cementitious materials. Even a small amount of nano-material can make a huge impact on the overall performance of cementitious composites. In conjunction with improving the conventional properties, nano-materials have introduced many unique features to cement and concrete. However, it is still a long way to go to enable the practical utilisation of nano-materials successfully in different cementitious composites for real-world construction applications. Proper understanding and optimisation are crucial for the commercialisation of such special materials.

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