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Influence of pozzolans on properties of cementitious materials: A review

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Abstract. Use of additives/supplementary materials in partial substitution of cement is gaining widespread attention across the world due to the sustainability issue with production of cement. With their pozzolanic activity & filler effect, use of nano-pozzolans such as nano-silica has been proved as quite promising & cost-effective for use as supplementary cementitious materials. This study is aimed at highlighting the effect of partial substitution of cement/addition of various nano-pozzolans on the hydration, strength and microstructure of the cementitious materials. Further, the effect of incorporation of other pozzolans has also been discussed. Comparative account of pozzolanic activity of different pozzolans has also been critically analyzed. It has been found that the cement matrix gets improved in terms of its microstructure by partial substitution of cement/addition of pozzolan in appropriate amount resulting in enhancement of the bulk properties by consumption of portlandite. The improved compressive strength of cementitious materials not only results in enhancement of the durability but also the service life of the construction structures and results in reduction of the cost incurred in maintenance and repair. Thus, the cement demand can be decreased by the partial substitution of cement/addition of such materials. It will result in an ultimate reduction of the green-house effect and lead to sustainable development.

Keywords: cementitious materials; durability; nano-pozzolans; microstructure; strength

1. Introduction

Cement production is associated with increase in emission of global carbon dioxide responsible for the global warming and climate change, a threat to our environment. Further, performance of cementitious materials in terms of cost of production and maintenance, strength and durability are the other important issues in terms of sustainability. Hence, it is a major concern of practicing engineers, researchers and environmentalists to control and reduce the use of cement along with substitution of cement/addition of supplementary cementitious materials (SCMs) for sustainable construction practices (Heikal *et al*. 2013, Shaikh *et al*. 2014, Wongkeo *et al*. 2013, Younis and Mustafa 2018). Nano-pozzolans have attracted the widespread attention with their use as SCMs due to their unique cementitious properties. Pozzolans are the siliceous and aluminous materials that react chemically in fine powdery form with calcium hydroxide and water, the action termed as pozzolanic activity (Imam *et al*. 2018). Pozzolans are primarily used to enhance the performance of cementitious materials in terms of high strength, enhanced durability and sustainability. Both, natural pozzolans and artificial pozzolans are used as SCMs nowadays (Supit and Shaikh 2014). Table 1 lists important types of pozzolans. Out of these, nano-silica (NS) and micro- silica (MS) have gained the utmost attention in recent years due to their technical advantage and sustainability action. The technical advantage lies in the enhanced mechanical properties such as early and late age strength, split tensile strength, impact resistance and ductility and reduction in permeability and shrinkage (Jena and Panda 2018, Wang *et al*. 2016).

The sustainability action lies in the reduction in the amount of cement and increased durability of the cementitious materials leading to overall decrease in emission of carbon dioxide. Many researchers have obtained enhanced strength, durability and workability of cementitious materials with partial substitution of cement/addition of NS and MS (Mohsen *et al.* 2019, Seifan *et al*. 2020). Their application to develop the sustainable and environment friendly cementitious composites with high strength and durability is widely accepted (Feng *et al*. 2013, Wongkeo *et al*. 2013). NS and MS not only modify the physical and chemical properties, microstructure and hydration but also improve the behavior of the cementitious materials in the fresh and hardened states. The filler effect of MS and NS particles contributes to the microstructure development of the cement matrix due to the reduction in the porosity (Ehsani *et al*. 2017). Further, their participation in the pozzolanic reaction with the portlandite generated during hydration reaction leads to the consumption of the harmful portlandite and generates the useful calcium-silicate-hydrate gel (Horszczaruk *et al*. 2014, Qing *et al*. 2007, Zapata *et al*. 2013). The ultrafine nanoparticles of NS have a higher filler effect and better pozzolanic behavior as compared to the micro particles of MS that provide better performance to the cement matrix.

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Table 1 Classification of pozzolans

Pozzolans	References
Natural Pozzolans	
Volcanic ash	Khurram *et al.* (2018)
Diatomaceous earth	Senff *et al.* (2011)
Artificial Pozzolans	
Fly ash (FA)	Shaikh *et al.* (2014)
Silica fume (SF)	(Haruehansapong *et al.* (2014)
Nano-Al_2O_3	Oltulu and Şahin (2013)
Nano-SiO_2	Shaikh *et al.* (2014)
Nano-metakaolin	Morsy *et al.* (2014)
Nano-TiO_2	Feng *et al.* (2013)
Nano-$CaCO_3$	Supit and Shaikh (2014)
Nano-Fe_2O_3	Horszczaruk *et al.* (2020)

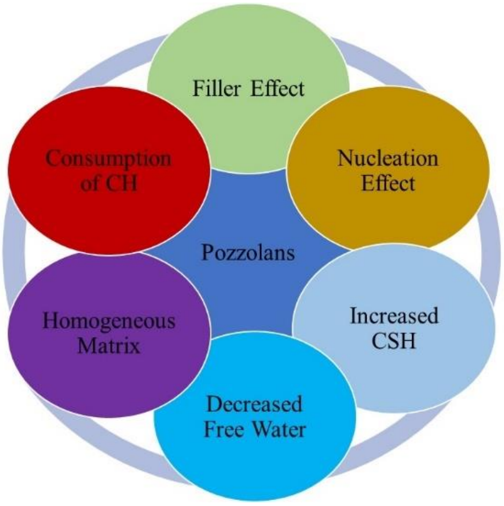

Fig. 1 Effect of participation of pozzolans in hydration reaction

2. Hydration and pozzolanic reaction

The hydration of cement results in formation of a sulphate rich solution by dissolution of the sulphates and gypsum that reacts with C_3A to form ettringite or calcium trisulphoaluminate hydrate (AF_t or $CaO.3Al_2O_3.3CaSO_4.32 H_2O$) that is responsible for the initial setting (Ghafoori *et al.* 2018 Gunasekara *et al.* 2020). The hydration of C_3S and C_2S produces hydrated phases known as tobermorite gel or calcium silicate hydrates or CSH gel and portlandite or calcium hydroxide [CH or $Ca(OH)_2$] (Sharma *et al.* 2019). Earlier studies have identified crystalline phases of alumina (Bescher *et al.* 2016), calcite (Mohammed *et al.* 2018), calcium silicate (Ylmén *et al.* 2009), ettringite (Maes and De Belie 2014) & portlandite (Kim *et al.* 2016, Lothenbach *et al.* 2012) in plain cement pastes. Researchers have also observed portlandite, ettringite, unreacted clinker phases and poorly crystallized CSH gel in the plain cement mortars after one day of hydration. After hydration age of twenty eight days, large amount of the crystalline calcium hydroxide and slight amount of C_2S & C_3S were observed (Kontoleontos *et al.* 2012). Lothenbach *et al.* (2012) obtained a moderate amount of gypsum & clinker in the XRD of the unhydrated low alkali cement blended with 10% of NS. The hydrated products were identified as ettringite & tobermorite due to reaction of alite in the first hour. The phase assemblage was characterized into hydrocalcite, ettringite & calcite after 305 years of hydration (Lothenbach *et al.* 2012).

The fine crystalline CSH gel occupies the voids in the cement matrix and is primarily responsible for hardening in the early and late ages of the cementitious material (Djelloul *et al.* 2018, Byung Wan Jo *et al.* 2019). Large CH crystals penetrate into some voids, but their characteristic weak, brittle, hexagonal prismatic crystalline and non-cementitious form prohibits the contribution towards strength because of small van der Waals forces. Further, the dissolution of CH in acidic and sulphate waters reduces the durability of the cementitious material (Biricik and Sarier 2014, Qing *et al.* 2007). The action of pozzolans as SCMs can be characterized in terms of filler effect, pozzolanic action and nucleation effect. The fine particles of pozzolans have a filler effect as these particles occupy the interstitial spaces in the cement matrix and the interfacial zone (ITZ) preoccupied by water molecules (Garg *et al.* 2020). This effect increases the packing and forms a uniform structure with less permeability. The amorphous silica present in pozzolans reacts with the CH and forms additional homogeneous clusters of CSH gel that further fills the voids in the matrix (Seifan *et al.* 2020). The fine particles of pozzolans with high surface area act as nucleation sites for the crystallization of CSH gel as now the crystallization takes place at both the grain surface and the pore space (Mohamed 2016). The nucleation effect accelerates the hydration and the reaction of C_3S that increases the availability of CH for reaction with pozzolanic particles (Garg *et al.* 2020). The disappearance of calcium hydroxide peak has been observed in the XRD profile of the cement pastes containing silica nanoparticles indicating the reaction of silica nanoparticles with the generated calcium hydroxide in the hydration reaction (Garg and Garg 2020). The utilization of harmful CH results in the production of additional CSH gel improves complex microstructure of the cement matrix in terms of density and homogeneity that contributes towards enhanced strength (Fig.1).

The finer particles of nano-pozzolans such as NS (Garg *et al.* 2020), nano-metakaolin (MK) (Machner *et al.* 2018), nano-TiO_2 (NT) (Qudoos *et al.* 2019), nano-Al_2O_3 (NA) (Niewiadomski *et al.* 2017), nano-Fe_2O_3 (NF) (Horszczaruk *et al.* 2020) and carbon nanotubes (CNT) (Stynoski *et al.* 2015) have pronounced pozzolanic activity that provides substantial improvement in the performance of the cementitious materials. However, the literature reveals significant effect of NS and MS as compared to other pozzolans in terms of enhanced strength, durability and sustainability (Li *et al.* 2017a, Ramesh Kumar *et al.* 2018). The cement mortars containing nano silica showed the presence of high amount of portlandite after 1 day of hydration. But, after 28 days of curing, the amount of portlandite decreased and CSH gel increased significantly contributing to the strength enhancement of the cement

Table 2 Use of pozzolans in performance enhancement of cement paste

Reference	Type of pozzolan	Particle size	Dosage of pozzolan (%)	Water binder ratio	Nature of Superplasticizer	Dosage of Superplasticizer (%)	Days of study
Heikal *et al.* (2013)	NS	15 nm	0-6.0	-	Polycarboxylate	1	3, 7, 28 and 90
	GGBS	-	0-45				
Wongkeo *et al.* (2013)	FA	5.22 µm	30-50	0.485	Naphthalene sulphonate	0.4-1.1	1 and 28
	Bottom Ash	7.81 µm	10-20				
	SF	0.1 µm	5.0-10				
Feng *et al.* (2013)	NT	20-50 nm	0.1-1.5	0.4	-	-	28
Qing *et al.* (2007)	NS	15 nm	1.0-5.0	0.22	Sulphonated melamine formaldehyde	2.5	1, 3, 28, 60
	SF	180 nm	2.0-5.0				
Horszczaruk *et al.* (2014)	NS	50 nm	3.0	0.57	-	-	28
Hosseinpourpia *et al.* (2012)	Asbestos	2-3 cm	5.0-15	1	-	-	3, 7 and 28
	Sulfite	1.2-1.5 mm	5.0-15				
	NS	34 nm	0.5-3.0				
Horszczaruk *et al.* (2020)	Nano Fe_2O_3/SiO_2	50-100 nm	1.0-5.0	0.5	-	-	28
Aleem *et al.* (2014)	NS	15 nm	1.0-6.0	0.25	Polycarboxylate	1	3, 7, 14, 28 and 90
Nochaiya *et al.* (2015)	NZ	100 nm	1.0-5.0	0.5	-	-	3, 7 and 28
Senff *et al.* (2009)	NS	9 nm	0-2.0	0.35-0.47	Polycarboxylate	0.7-3.6	28
	SF	-	0-20				
Kong *et al.* (2012)	Precipitated Silica	105.326 µm	0.25- 1.0	0.3	Naphthalene based	0.75	3, 28, 56 and 208

pastes (Kontoleontos *et al.* 2012).

Further, the CSH peaks get intensified with increase in nano silica due to the more formation of CSH gel (Liu *et al.* 2020). Table 2 summarizes the studies carried out by various researchers using various pozzolans in cement pastes.

3. Microstructure of cement matrix

3.1 Microstructure of plain cement mortars

The microstructure of cement mortars is quite complex and can be characterized into distinct phases (Xue *et al.* 2021). Researchers have characterized the microstructure of cement mortars into five phases as the darkest phase indicating the pores, the less dark phases as calcium hydroxide, the brightest phases as the unreacted anhydrous cement grains, the outer CSH filling the cement matrix and the inner CSH as rim around the anhydrous cement grains. Li *et al.* (2004) observed stand-alone clusters of CSH gel linked by needle hydrates & calcium hydroxide crystals in the microstructure of the plain cement pastes. Qing *et al.* (2007) observed that in absence of NS/silica fume, the size of the biggest hexagonal paste of CH crystal at the paste-aggregate interface of mortars was up to 10 µm. Jo *et al.* (2007) also observed the microstructure of the plain cement paste to be less compact & with greater numbers of CH crystals. Ylmén *et al.* (2009) observed the microstructure of cement grains with varying time of hydration. It was observed that lumps & platelets were formed at the surface of the cement particles after 120 minutes of hydration and needle like structures of CSH gel are formed after 480 minutes of hydration. Kontoleontos *et al.* (2012) characterized CSH as Ca_3SiO_5 at 1 day and as Ca_2SiO_4 at early curing age. The microstructures of fractured surface of plain cement mortars revealed the presence of hexagonal CH plates and thin needle like ettringite inside the pores (Kontoleontos *et al.* 2012).

The microstructure of cement mortars and concrete has been reported to be heterogeneous due to presence of large pores or voids. Hosseinpourpia *et al.* (2012) observed pores & micro cracks along with calcium hydroxide crystals, ettringite needles and fibrillated CSH gel in the cement pastes. Zapata *et al.* (2013) observed massive crystals of AFt and platy calcium hydroxide in the porous structures of the plain cement mortars. Aleem *et al.* (2014) observed porous & flocculent form of slight C-S-H gel with sheets of massive calcium hydroxide in microstructure of neat cement pastes till 28 days of curing age. Similarly, Huang *et al.* (2017) observed loose microstructure of cement mortars with large crystals. Numerous voids have also been reported for the microstructure of concrete (Dhanya *et al.* 2019).

3.2 Microstructure of matrix with nano-pozzolans

The various phases in the microstructure of the matrix with pozzolans can be characterized into hexagonal plates of calcium hydroxide, needles of ettringite, sheets & flakes of CSH gel (Wang *et al*. 2016).

Ng *et al*. (2020) observed absence of large crystals of CH in the microstructures that were obtained with substitution of cement/addition of nanoparticles. Also, the microstructures were more compact & uniform and contained different forms of the various hydrate products. However, the decrease in strength at increased concentration of nanoparticles has also been assigned to the non-uniform distribution of nanoparticles leading to aggregation (Hakamy 2020). The size of the biggest hexagonal paste of CH crystal was found to reduce to 7 µm in presence of silica fume and up to 4 µm in presence of NS by Qing *et al*. (2007). Better interaction of NS with CH leading to reduction in its size was inferred in terms of its better nucleation size and high specific surface.

NS increases the production of calcium hydroxide at early age as compared to cement. However, depending upon the nature of nanoparticles, the formation time period of hydration products may vary. Nochaiya *et al*. (2015) observed the presence of hydration products in mortars containing 2.0 wt.% nano-ZnO after 7 days. Further, the beneficial effect of NS has been observed at low content & early age. At later ages & high content of NS, the agglomeration effect of nanoparticles results in reduced particle arrangement (Senff *et al*. 2009). Kong *et al*. (2012) obtained improved microstructure of hardened cement paste with precipitated silica fume on curing at 28 and 180 days by occupation of voids by hydration products. Pore refinement from 200-500 nm to 50-100 nm was observed at 28 days and to 10-20 nm at 180 days indicating the topochemical pozzolanic reactions between calcium hydroxide and agglomerates to form pozzolanic CSH gel (Kong *et al*. 2012). However, the penetration of the precipitated CSH has not been observed into the reacted agglomerates. Further the interfacial transition zone has been observed between the bulk pastes & large agglomerates leading to beginning of the strength enhancing effect of NS (Kong *et al*. 2012). Zapata *et al*. (2013) found the microstructure of the cement paste containing 15% silica fume denser with presence of high amount of AF_t crystals. Further, denser microstructure was obtained in the systems with NS. However, aggregates of AF_m and vitreous phase were also observed that led to reduced compressive strength (Zapata *et al*. 2013).

The optimized dosage of NS in presence of MS results in more densified gel structure of the cement matrix due to generation of CSH gel at very early age. The better improvement of microstructure with synergistic effect of MS and NS was found at lower concentration of water (Kooshkaki and Eskandari-Naddaf 2019). The high compressive strength of the blended mortars has been related to the cross linking of nanoparticles and release of entrapped water in presence of MS that causes extra hydration. Filler effect of nanoparticles was observed by Huang *et al*. in the microstructure of mortar containing 10% MS (Huang *et al*. 2017).

The microstructures of cement pastes containing 3% NS exhibited higher amount of platelet like & longer rod like hydrates of CSH resulted by the pozzolanic response of nanoparticles with the CH produced during hydration reaction as reported by Aleem *et al*. (2014). The upgradation of microstructure due to pozzolanic materials is attributed to the spatial dissemination and nucleation effect of nanoparticles. It is considered that this tendency of nanoparticles prevents the growth of CH crystals during cement hydration reaction resulting in strength enhancement (Singh *et al*. 2015). The microstructure has been further found to improve with increase in content of nanoparticles. As the nanoparticles were introduced, the microstructure was improved due to pozzolanic reaction with portlandite and filler effect of NS. Wang *et al*. (2016) found the refinement of the pore arrangement by nanoparticles resulting in a compact and uniform matrix with the formation of hydrated CSH & reduction of portlandite phases.

The strength enhancement behavior of pozzolans is attributed to the filling of empty spaces, in the matrix by finer particles and CSH gel. The microstructural development of the composites was observed by Yang *et al*. (2018) in presence of 2% nano-$CaCO_3$ for fly ash based mortars, with reduction in the amount of calcium hydroxide and ettringite and formation of CSH gel. The microstructures of cement pastes containing silica fume was better developed as compared to plain cement pastes in terms of uniform distribution of calcium hydroxide around CSH gel. Further, no needles of calcium hydroxide have been observed in the microstructures of the cement paste containing silica nanoparticles (Karunarathne *et al*. 2019). Fig. 2 represents the contribution of pozzolans in the improvement of the microstructure and other properties of cementitious materials leading to sustainable development. There has been found variation in the density of the microstructure that further improves as the dosage of nanoparticles is increased. Sharma *et al* noticed variable fibre like hydrate crystals in the matrix of the cement paste with variation in concentration of nanoparticles (Sharma *et al*. 2019). Garg and Garg (2021) observed several crystalline phases in the micrographs of cement pastes incorporating SF & ZnO nanoparticles at 28 days.

4. Effect on fresh and hardened properties of cement mortars and concrete

4.1 Effect of content

The performance of a cementitious material is analyzed in terms of its compressive strength. The strength enhancement has been linked to the densification of microstructure because of pozzolanic reaction with particles of nano silica by many researchers.

The introduction of nano clay resulted in enhanced brittle behavior due to the entrapment of water leading to increase in hydration, increase in densification & decrease in matrix voids. Strength of cement mortars blended with silica fume in presence of 1%, 2% & 3% halloysite nano clay improved significantly as studied by Farzadnia *et al*. (2013). Best results were obtained at 28 days of curing by

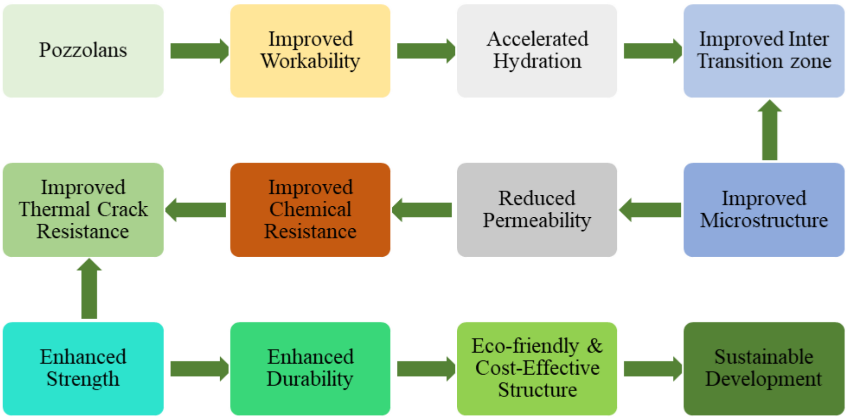

Fig. 2 Improvement in properties of cementitious materials with pozzolans

incorporation of 3.0% nano clay. The tabular shape of the nano clay particles was linked to strength hen the matrix due to cross linking effect (Farzadnia *et al*. 2013). However, no immediate enhancement in mechanical strength was observed by Kontoleontos *et al*. (2012) by addition of 2% & 4% colloidal nano silica in ultrafine cement. At early ages, the strength improved due to filler effect of the nanoparticles leading to densification. At later ages, the matrix densification, pore size refinement and reduction in calcium hydroxide content results in the production of secondary CSH gel that significantly improved the strength (Kontoleontos *et al*. 2012).

Researchers have linked strength enhancement in cement mortar containing pozzolans with the change in the cement matrix. The decline in strength of mortars with higher content of nano-$CaCO_3$ in comparison to control mix possibly due to agglomeration of nanoparticles was also observed by Supit & Shaikh. The highest strength was found for 1% nano-$CaCO_3$ at 7 and 28 days of curing on partially replacement of cement with 1-4% nano-$CaCO_3$ (Supit and Shaikh 2014). The nano-metakaolin particles are supposed to provide micro cracks resistance by cross linking with one hydration products. The addition of nano-metakaolin is found to improve the interfacial zone by linkage of alumina & silica elements in fly ash. Morsy *et al*. (2014) found the strength of 2.5, 5.0, 7.5 & 10.0% nano-metakaolin blended mortars at 60 days of curing was higher as compared to 20% fly ash blended cement mortars at the same age. However, the best results were obtained at the addition of 7.5% metakaolin. The decrease in strength at higher content of metakaolin was linked to the formation of agglomerates that hinder the hydration reaction (Morsy *et al*. 2014). Thus, an appropriate amount of the SCMs is required to obtain the best results.

Pozzolans improve the strength of the cementitious materials on partial substitution of cement/addition of their particles at a specified dosage (Wang *et al*. 2016). The filler effect of the nanoparticles leads to the enhancement in strength with facilitation of hydration reaction & formation of homogeneous & densified cement matrix. Singh *et al*. (2015) studied the compressive strength of mortar with variation of NS from 1 to 3% by weight of cement and a minimal water binder ratio (0.4). A maximum increase in strength was found for 1% nano silica at the ages of 3,7 & 28 days and was found almost 26% greater than that of control (Singh *et al*. 2015). Karunarathne *et al*. (2019) partially replaced cement with 2-6% NS & found maximum strength for 4% NS that acted as a filler and activator with nucleation effect for pozzolanic reaction leading to the increased density, homogeneity & compactness of the matrix. Shafiq *et al*. (2019) reported an experimental research for light weight & pozzolanic filler in mortars by substituting cement with 5-10% by weight of metakaolin in presence of 35 weight percentage of water. Significantly enhanced compressive strength was found at 28 days at optimized dosage of NS that overlapped the pozzolanic behavior of metakaolin (Shafiq *et al*. 2019). The increased strength of cement paste modified by 1.0-5.0% admixtures of nano-Fe_3O_4/SiO_2 nanoparticles at w/c ratio of 0.4 was studied by Horszczaruk *et al*. The maximum strength was observed at 3.0 mass percentage of the nano-Fe_3O_4/SiO_2 (Horszczaruk *et al*. 2020). The research suggested that water content of the mixtures also affects the behavior of pozzolans. The strength enhancement is considered due to refinement in interfacial zone and pore size along with matrix densification & reduction in $Ca(OH)_2$ content (Yue *et al*. 2020).

4.2 Effect of superplasticizer

The efficiency of superplasticizer is attributed to the large surface area of these molecules that accelerates the hydration reaction and helps in attainment of an early strength. The presence of super plasticizer leads to the reduction in water demand and provides better results. Effect of addition of 0.5%, 1%, 2% & 5% of nano silica as admixtures on the Portland cement pastes has been studied by Stefanidou & Papayianni, in absence & in presence of super plasticizer. Without super plasticizer, the maximum strength was recorded for 0.5% NS. However, the mixes with 5% NS resulted in lower strength. The addition of super plasticizer resulted in increased strength with maximum value corresponding to 1% NS (Stefanidou and Papayianni, 2012). The super plasticizer not only decreases the initial total porosity & water requirement but also facilitates the formation of homogeneous composites. It also leads to increased degree of compaction & efficient hydration. Heikal *et al.* (2013) studied the enhanced strength of composite cement pastes of granulated blast furnace slag (GGBS) (30, 40 & 60%) and NS (1, 2, 4 & 6%) in presence of super plasticizer. The strength improvement with increase in NS content up to 4% was linked to the filler effect and better pozzolanic behaviour of NS that further enhanced in the presence of super plasticizer (Heikal, *et al.* 2013). Literature also reports the adsorption of superplasticizer molecules on the particles of cement and nano-additives in a competitive manner. Ghafari *et al.* (2016) have reported the higher extent of adsorption by nano-ZnO as compared to cement particles due to their fine particle size and enhanced surface area leading to retention of workability and increase of strength.

The dosage of superplasticizer has been illustrated to be dependent upon the type of nanoparticles. In general, the addition of higher content of nanoparticles requires higher dosage of superplasticizer that further increases as the water-binder ratio decreases. Li *et al.* (2017) reported lower demand of superplasticizer in presence of NS as compared to MS for the same value of compressive strength. Hospodarova *et al.* (2018) characterized the strength of cement mortar blended with cellulosic fibres in absence & presence of superplasticizer. Mortars with cellulosic fibres and superplasticizer possessed enhanced compressive strength, prolonged setting time, better workability due to enhanced bonding and filling of pores in the matrix resulting in improved microstructure. The effect was more pronounced for the early ages (Hospodarova *et al.* 2018). Superplasticizer is generally added in varied amount to control workability of cement paste and mortars. Yu *et al.* used superplasticizer to the mixes containing silica nanoparticles in presence of fly ash and poly vinyl alcohol fibres with varying composition to attain desired flow (Yu *et al.* 2020).

4.3 Effect of particle size

The nature and size of additive particles along with the incorporation route affects the behaviour of the cement composites. Singh *et al.* carried out granulometric synthesis of silica nanoparticles using non-ionic surfactants and studied their effect on cement pastes with varying composition as 0.25, 0.5, 1.0, 2.5 & 5.0%. The best results were obtained for cement paste with 5% NS (Singh *et al.* 2012). The effect of NS particle size was analyzed by Haruehansapong *et al.* on the mortar strength. Best results were obtained for mortars containing NS with particle size 40 nm, termed as most effective with uniform dispersion of particles, packing ability & pozzolanic behaviour. Further, the optimized replacement content of NS & silica fume was found to be 9%. The low replacement content was considered as less effective for pozzolanic reactivity while the higher content was considered to reduce the hydration reactivity leading to agglomeration of the particles (Haruehansapong *et al.* 2014). Saleh *et al.* (2015) used local sand to prepare NS particles of varying particle size ranging from 30-100 nm using ball milling method and incorporated in cement mortar to study the effect on mechanical strength. Best results were obtained for NS with particle size of 50 nm with a dosage of 6-8% resulting in significant improved mechanical strength (Saleh *et al.* 2015)

Hosseini *et al.* (2018) studied the effect of incorporating NS hydrosols with varying specific surface area in cement mortar in presence of blast furnace slag. The dispersion of nanoparticles with finer particle size proved more effective at early age than using coarser particles and strengthened the composites better and provided improved mechanical properties due to better binding at the inter transition zone. However, coarser NS was more effective at the later ages for continuation of pozzolanic reaction (Hosseini *et al.* 2018). Use of colloidal NS with particle size in the range of 8-15 nm was found to be more effective as compared to MS having particle size in the range of 100-300 nm in accelerating the hydration reaction and modifying the CSH gel. The system was found to attain an early age strength especially at lower dosage of NS (Sharma *et al.* 2019).

5. Comparison of pozzolans

Table 3 shows the work done by various researchers on cement mortars with incorporation of pozzolans. The pozzolanic activity of NS and MS differs remarkably due to difference in their particle size and chemical structure. The finer particles of NS have significantly high filler effect and nucleation effect. Further, the unsaturated Si-O bonds on the surface of nanoparticles increase the pozzolanic activity of NS. On the other hand, the pozzolanic activity of MS depends upon the cleavage of the saturated Si-O bonds at on the surface of micro particles. The better pozzolanic activity of nano silica has also been confirmed by Jo *et al.* at a w/c ratio of 0.5 with variation in NS content from 3% to 12% & silica fume from 5% to 15% by weight of cement. The researchers found a regular increase in strength of cement mortars containing 3%, 6%, 10% & 12% NS and 5%, 10% & 15% silica fume at w/c ratio of 0.5 at early curing. However, the strength containing NS was much higher as compared to the mortars containing silica fume with adjustment of water and super plasticizer doses to avoid cracking & self-densification of mortars. The study proved the better pozzolanic activity of NS as compared to silica fume (Jo *et al.* 2007).

The addition of super plasticizer was suggested at a higher content of NS to avoid self-desiccation & cracking. Senff *et al.* used a w/b ratio between 0.35 & 0.47 and partially replaced the cement with 1.75% & 3.5% NS in presence of polycarboxylic acid with the content varying from 3.0 to 3.6%. The analysis was carried out by replacing cement with silica fume at a weight percentage of 10% & 20% in presence of 0.7, 0.95 & 1.2 weight percentage of polycarboxylic acid.

The best results were obtained for silica fume at w/b ratio less than 0.43 while for NS, best results were obtained at a w/b ratio higher than 0.43. The result was discussed in terms of low particle packing at the lower w/b ratio leading to higher friction between the ultra-fine particles. A regression model was also estimated to determine optimum content of NS & silica fume (Senff *et al.* 2009). These

Table 3 Use of pozzolans in performance enhancement of cement mortar

References	Type of pozzolan	Particle size	Dosage of pozzolan (%)	Water binder ratio	Nature of super-plasticizer	Dosage of superplasticizer (%)	Days of study
Wang *et al.* (2016)	NS	20 nm	1.0-5.0	0.5	Polycarboxylate	0.13-0.26	1, 3, 7 and 28
Seifan *et al.* (2020)	NS	20 nm	5.0-15	0.5	-	-	7, 14 and 28
	MS	2–10 µm	5.0-15				
	FA	2–100 µm	10-30				
Zapata *et al.* (2013)	NS	25 nm	2.0-3.0	0.35-0.40	Polycarboxylate	1.2-3.0	90
	MS	200 nm	1.0-10				
Oltulu and Şahin, (2013)	NS	12 nm	0.5-1.25	0.4	Polycarboxylate	0.75	3, 28, 56 and 180
	NA	13 nm	0.5-1.25				
	NF	60 nm	0.5-1.25				
	FA	1-20 µm	15				
Senff *et al.* (2011)	Diatomite	6 µm	0-10	0.33-0.38	Polycarboxylate	0.25	28
Rodríguez *et al.* (2013)	FA	15 µm	-	0.13-0.27	-	-	2, 28 and 60
	NS	20–30 nm	2.0-6.0	0.7			
Haruehansapong *et al.* (2014)	SF	100 nm	3.0-12	0.65	Polycarboxylate	-	1, 7 and 28
	NS	12-40 nm	3.0-12				
Senff *et al.* (2010)	NS	9 nm	2.0-3.5	0.35	Polycarboxylate	1.2-3.0	7, 28 and 90
	MS	0.15 µm	10-20				
Kontoleontos *et al.* (2012)	NS	50-100 nm	2.0-4.0	0.5	Polycarboxylate	2.0	1, 2, 7, 28
Morsy *et al.* (2014)	MK	-	2.5-10	0.5	-	-	3, 7, 28 and 60
	FA	10 µm	20				
Ghafoori *et al.* (2018)	NS	15-20 nm	3.0-6.0	0.485	Polycarboxylate	0.08-0.42	3, 182, 364
	MS	0.1-1.0 µm	3.0-6.0				
Sharma *et al.* (2019)	NS	8-15 nm	0.7-2.0	0.492	-	-	1
	MS	100-300 nm	0.7-2.0				
Biricik and Sarier, (2014)	NS	15 nm	5.0-10	0.5	Polycarboxylate	0.22-2.2	7 and 28
	SF	444.2 nm	5.0-10				
	FA	1513 nm	5.0-10				
Garg *et al.* (2020)	NS	40 nm	0.5-1.25	0.5	-	-	3, 7 and 28
	MS	0.20 µm	5.0-20				
Qudoos *et al.* (2019)	NT	10-60 nm	3.0	0.45	Superplasticizer	0.4-0.7	14, 28, 56, 84, 112, and 140 days
	NS	20-40 nm	0.5-2.0				
Stynoski *et al.* (2015)	CNT	20-40 nm	0.125	0.485	Polycarboxylate	0.428-6.44	28
	SF	45 µm	5.0				
	Carbon fibres	-	0.855				
Li *et al.* (2017a)	NS	5-20 nm	1.0-2.0	0.25-0.4	Polycarboxylate	0.3-4.8	1 and 7
	MS	1µm	10				
H. Li *et al.* (2004)	NS	15 nm	3.0-10	0.5	-	-	7 and 28
	NF	30 nm					
Byung W. Jo *et al.* (2007)	NS	40 nm	3.0-12	0.5	Polycarboxylate	1.2-3.3	7 and 28
	NS	15 nm	3.0-10				
Siang Ng *et al.* (2020)	NS	20-30 nm	1.0-5.0	0.485	-	-	7, 14 and 28
	NT	15 nm	1.0-5.0				
	NF	20-40 nm	1.0-5.0				

Table 3 Continued

References	Type of pozzolan	Particle size	Dosage of pozzolan (%)	Water binder ratio	Nature of super-plasticizer	Dosage of superplasticizer (%)	Days of study
Siang Ng *et al.* (2020)	FA	-	30	0.485	-	-	7, 14 and 28
Hakamy (2020)	NC	40-48 nm	1.0-3.0	0.48	-	-	28
Kooshkaki and Eskandari-Naddaf (2019)	NS	-	1.4-4.2	0.40-0.50	Polycarboxylate	-	3, 7, 14 and 28
	MS	-	4.0-13				
Singh *et al.* (2015)	NS	40 nm	1.0-3.0	0.4	-	-	1, 3, 7 and 28
	CNS	15-20					
	SF	0.1-10 µm					
Yang *et al.* (2018)	NC	2.13-3.03	2.0-8.0	0.4	Polycarboxylate	0.4-0.8	3, 7, 28, 60, 90, 180 and 360
	FA	36.8-40	-				
Karunarathne *et al.* (2019)	NS	10	2.0-6.0	0.4	-	-	7, 14, 28 and 56
	FA	-	30				
	Bentonite	1–5 µm	2.0-6.0				
Garg and Garg, (2021)	NZ	35 nm	0.3-1.2	0.4	-	-	3, 7, and 28
	SF	0.20 µm	5.0-15				
Farzadnia *et al.* (2013)	Nano-clay	15 nm	1.0-3.0	0.45	Naphthalene sulphonate	2	7 and 28
	SF	-	5.0				
Yu *et al.* (2020)	NS	-	0.5-1.5	0.4	-	-	28
	FA		50				
	PVA fibres		0.2-1.0				
Li *et al.* (2017b)	NS	5-20 nm	1.0-2.0	0.25-0.40	Polycarboxylate	1.0-6.4	28 and 90

researchers further extended their research at w/b ratio of 0.35 with 3.5% NS, 12.2% & 20% silica fume and 10.2% silica fume in presence of 2% NS. They observed better results for samples containing 10.2% silica fume in presence of 2% NS as compared to individual addition of NS or silica fume at 28 days & 90 days. The results were attributed to the higher surface areas available at early ages. However, silica fume showed better results at later stages due to the formation of agglomerates of nanoparticles leading to decreased packing of the matrix particles. Further substitution of cement with 20% silica fume showed reverse results at 7 days indicating the better pozzolanic behaviour of NS as compared to silica fume at early ages. The authors applied factorial design experiments (at a w/b ratio of 0.35 to 0.59 for cement mortar with partial substitution of cement by 3.5 & 7% weight percentage of NS and 10 & 20% weight percentage of silica fume in presence of 3% by weight of polycarboxylic acid as super plasticizer. A reduced compressive strength was observed for 20% silica fume & 7% NS. As per the factorial design, the compressive strength corresponded to 12.2% silica fume & 3.3% NS (Senff *et al*. 2009).

The strength of the mortars through addition of precipitated silica with very large agglomerates and silica fume with small agglomerates with weight percentage 0.25%, 0.5%, 0.75% & 1.0% was studied by Kong *et al.* (2012). At 28 days, 6.8% enhancement in strength was observed for 1% silica and 12% enhancement was observed for 1% silica fume. The result was related to the better filler effect of silica fume with small agglomerate as compared to precipitated silica with large agglomerates (Kong *et al*. 2012). A fluctuation in the compressive strength values has been found at early & later ages. The lower powder ratios result in an increase in strength at early age, while the higher powder ratios exhibit the effect at later age. Better pozzolanic behaviour of silica nanoparticles as compared to micro particles was also observed by Zapata *et al*. (2013) under different doses of super plasticizer. Maximum strength was recorded at 1.0 weight percentage of nano silica & 15 weight percentage of MS. In case of MS, a regular gain of strength was observed. However, the higher content of NS dropped the strength due to poor dispersion of the nanoparticles leading to non-interaction with calcium hydroxide (Zapata *et al*. 2013).

The strength has been found to increase with thermal treatment due to enhancement of internal autoclaving reaction leading to improvement of pozzolanic reaction and formation of low Ca/Si ratio containing additional CSH gel. With further increase in temperature, the crystalline structure decomposes leading to increased porosity & decrease in strength. The effect of colloidal NS and silica fume on 40% fly ash substituted cement mortars was studied by Hou *et al*. (2013). At early ages, colloidal NS produced more strength as compared to the silica fume indicating the better pozzolanic behaviour of colloidal nanoparticles. However, the strength was comparable at the late ages (Hou *et al*. 2013). An increase in strength of cement mortars blended with undensified silica fume, fly ash & ground bottom ash was observed by Wongkeo *et al*. (2013). It was observed that the strength of mixes sealed with plastic sheeting was higher due to continued hydration in absence of loss of moisture. The strength also increased with increase in curing temperature and was attributed to the accelerated rate of pozzolanic reaction & hydration.

An increase in auto-claving time up to 9 hrs. increased the strength. The result was linked to the formation of crystalline tobermorite that declined the porosity of the matrix (Wongkeo *et al*. 2013). Reduced carbonation of hardened cement paste with NS in comparison to MS was reported by Lim and Mondal at early ages. The effect was attributed to the modification in CSH gel indicating the better pozzolanic activity of NS as compared to MS (Lim and Mondal 2015). Similar effect was observed by Sharkawi *et al*. with improved durability properties of mortar containing NS (Sharkawi *et al*. 2018). Comparatively lower dosage of NS was found to be more effective as compared to MS for partially substituting cement in support of sustainable construction practices. NS was found to impart higher mechanical strength to the systems (Garg *et al*. 2020).

6. Effect of binary/ternary blends

A significant effect of the amount and type of nano material has been noticed on the compressive strength of the mortars with rate of increase varying between 51% & 82%. Li *et al*. (2004) found a growth in compressive strength when cement was partially replaced with 3%, 5% & 10% of nano-Fe_2O_3 & nano-SiO_2 with a water cement ratio (w/c) of 0.5. In case of nano-Fe_2O_3, the compressive strength increased with the decrease in volume fraction but effect was reversed in case of nano-SiO_2. The authors suggested that due to different functions of two nanoparticles, the optimum mixing volume differ resulting in different behaviour of strength (Li *et al*. 2004). Compressive strength at early age, standard age & late age was studied by Oltulu and Sahin (2020) for single, binary & ternary substitution by nano silica, nano-Al_2O_3 & nano-Fe_2O_3. Similar effect was observed for the other nano powders and best results corresponded to 1.2% nano-alumina at 180 days. For binary substitution 0.5% nano silica & nano alumina corresponds to maximum compressive strength. In case of ternary substitution, a combined ratio of 0.5% of the nano powders corresponded to the best results. It was inferred that single substitution is better than binary & ternary substitution due to negative effect of the interaction between the nano powders in combination (Oltulu and Şahin 2011). Hosseinpourpia *et al*. (2012) have studied the strength of cementitious composites strengthened with natural based fibre & NS. The strength of the composites was found to improve more effectively in presence of nanoparticles mixed with higher fibre doses due to the improved pozzolanic behaviour of nanoparticles enhanced hybrid system of the matrix (Hosseinpourpia *et al*. 2012). Rodriguez *et al*. (2013) reported the enhanced strength of an alkali activated fly ash binder in presence of NS based activators. The strength of mortars containing activators based upon sodium was higher as compared to activators based upon potassium. The presence of Na+ was found to promote the dissolution of aluminosilicate solids by favoring the release of monomers of silicates & aluminates (Rodriguez *et al*. 2013).

It has been reported that optimized addition of NS strengthened the cement mortar containing SF/MS/FA due to their better interaction with calcium hydroxide crystals and also improved the capillary permeability of the mortar (Table 4). Shaikh *et al*. (2014) observed highest early strength of fly ash (40%) cement mortar containing 2% NS indicating the improvement in compactness of composite mortars in presence of nano silica. Mohamed (2016) found appreciable and increased compressive strength of samples containing hybrid nanoparticles of nano silica in presence of nano clay that was attributed to the filler effect of hybrid nanoparticles. Ehsani *et al*. (2017) found better strength development of mortar mixes containing nano silica in presence of fly ash as compared to samples containing no fly ash with improvement in microstructure and reduced capillary adsorption rate. The activity of pozzolans is found to increase in binary/ternary blends with appropriate combination (Garg *et al*. 2020, Li *et al*. 2017b). An increase in the strength of the mortars containing 2% NS & 10% MS was observed by Li *et al*. (2017a). The effect was attributed to the escalation of behaviour of pozzolans in combination leading to synergistic effect (Li *et al*. 2017a). Likewise, Sharkawi *et al*. (2018) recorded an enhancement in the strength by the incorporation of 2% NS & 8% MS. The effect was more conspicuous at later ages. The similar effect was observed by Li *et al*. (2019) by incorporation of an optimized dosage of 1% NS & 5% SF leading to enhanced resistance for sulphate and chloride attack. Garg *et al*. (2020) reported better results at an optimized dosage of 1% NS & 10% MS in cement mortar leading to improved mechanical strength.

7. Future aspects

Nanotechnology can be used to modify the different properties of cement mortar and concrete in interest of sustainable construction practices. Exposure to alkali and silica in cement and aggregates leads to onset of alkali silicate reaction that can be prevented by the partially substituting cement with pozzolanic nanomaterials. The overall properties of concrete - such as longevity and coloration - can be altered by the presence of nano particles. Nano particles include nano silica, nano clays, nano titanium-dioxide, nano iron-oxide, nano alumina, copper oxide, zirconium oxide, and zirconium oxide. Nano-materials in concrete are supposed to speed up C-S-H gel formation and improve concrete's mechanics and durability. Fly ash increases the consistency and strength of the concrete as much as possible, although this can cause a decrease in early strength afterwards.

Table 4 Use of pozzolans in performance enhancement of concrete

References	Type of pozzolan	Particle size	Dosage of pozzolan (%)	Water binder ratio	Nature of superplasticizer	Dosage of superplasticizer (%)	Days of study
Shaikh *et al.* (2014)	NS	25 nm	1.0-6.0	0.4	Naphthalene sulphonate	1.1-1.8	3, 7, 28, 56 and 90
	FA	10 µm	40-70				
Younis and Mustafa (2018)	NS	20-30 nm	0.4-1.2	0.48	Polycarboxylate	0.5	28
Supit and Shaikh (2014)	NC	15-40 nm	1.0-4.0	0.4	-	-	3, 7 and 28
	FA	0.4 µm	40-60				
Mohsen *et al.* (2019)	CNT	5-10 nm	0.03-0.25	0.5	Polycarboxylate	1.25	28
Ehsani *et al.* (2017)	NS	12 nm	1.5-7.5	0.45	Polycarboxylate	0.04-3.08	3, 7, 28, 91
	FA	-	15-25				
Gunasekara *et al.* (2020)	Hydrated lime	-	13-18	0.3	Polycarboxylate	-	7 and 28
	NS	15 nm	3z				
	FA	20 µm	49-59				
Mohammed *et al.* (2018)	NS	10-25 nm	1.0-3.0	0.3	Superplasticizer	0.3-1.25	28
	FA	-	10-70				
Lothenbach *et al.* (2012)	NS	10-25 nm	10	1.1	Polycarboxylate	0.026	1-1310
	Slag	-	59				
Mohamed (2016)	NS	40 nm	0.25-3.75	0.36	Polycarboxylate	2.5	7, 28 and 90
	Nano-clay	0.20 µm	0.25-3.75				
	SF	40 nm	20				
Niewiadomski *et al.* (2017)	NS	10-20 nm	0.5-4.0	0.42	Polycarboxylate	4	360
	NA	50 nm	0.5-3.0				
	NT	25 nm	0.5-4.0				
Liu *et al.* (2020)	NS	15-20 nm	0.5-4.0	0.46	Polycarboxylate	0.1-0.37	7, 28 and 90
	FA	1µm	30				
Sharkawi *et al.* (2018)	NS	8-20 nm	1.0-3.0	0.43	Polycarboxylate	0.6-2.5	3, 7, 28 and 56
	MS	-	3.0-15				
Mustakim *et al.* (2020)	NS	8-20 nm	0.5-2.5	0.43	Polycarboxylate	0.8	3, 7, 14 and 28
	SF	-	0.5-2.5				
	FA	8-20 nm	39.5-41.5				
	GGBS	-	58				
Shafiq *et al.* (2019)	MK	-	1.0-2.0	0.35	Polycarboxylate	0.5-1.6	3, 7, 28 and 90
	NS	10-25 nm	1.0-2.0				
Yue *et al.* (2020)	NS	12.1 nm	2.0	0.4	-	-	3, 7, 14, 28 and 90
	SF	-	5.0				
	FA	-	10.0				
	Micro-$CaCO_3$	1250 nm	1.0				

The density and structure of the concrete is improved by adding Nano-Silica, which helps to increase the strength of the concrete. The addition of Nano-silica increases cement's resistance to segregation and also enhances cement's resistance to water absorption and prevents calcium leaching. Nano iron can self-sense its deformation and also increase hardness and tensile strength. Nano titanium makes a self-cleaning concrete. Studies have shown that nano-technology can significantly increase the lifetime of long bridges. The sulfate and chloride ions that penetrated concrete contributed to microcracking and resulting structural damage within the concrete. Researchers have also conducted experiments in order to find an efficient way to increase the life span of concrete by slowing the entry of chloride and sulfate ions into concrete. In reality, the issue of concrete cracking has contributed to the collapse of concrete structures. Fibre wrapping is widely used for increasing the strength and longevity of existing structures. The technology utilizes nano silica particles and resins along with hardeners. As the fibre sheet is wrapped with the concrete base, the aggregated nanomaterials are able to penetrate the concrete cracks and cover the cracks, on the surface of the concrete.

8. Conclusions

The review of the current investigations reveals the beneficial role of nano-pozzolans in cementitious materials. The partial substitution of cement/addition of MS and NS in appropriate amount can enhance the bulk properties due to improved microstructure. The partial substitution of cement and addition of pozzolans decreases the cement requirement and ultimately reduces the cement production demand with achievement of additional strength and durability. This is due to acceleration of the hydration reaction due to nucleation effect and better packing of cement matrix because of the consumption of portlandite in the pozzolanic reaction. The enhanced compressive strength and durability of cementitious materials ultimately results in enhancement of the service life of these materials and reduction in the incurring cost of maintenance and repair. The proper tailoring of these materials can surely help the global community in speedy, cost effective and sustainable construction practices. However, the complete benefits of these materials depend upon some critical points. Sufficient data is not available on the physical state and dispersion of pozzolanic materials. The performance of the modified microstructure depends upon the optimum amount of the pozzolanic material that further depends upon various parameters such as nature, physical state, particle size, water-binder ratio and super plasticizer. These parameters cannot be fixed arbitrarily for use in different cases and suitable mathematical models are required. However, not much data is available on the durability and shrinkage behaviour of cementitious materials with partial modification of cement. Thus, systematic experimental investigations are required to assess the optimization of fresh and hardened properties of such materials.

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