Use of nano-silica in cement based materials—A review

Paratibha Aggarwal, Rahul Pratap Singh and Yogesh Aggarwal

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Paratibha Aggarwal\textsuperscript{1,*}, Rahul Pratap Singh\textsuperscript{1} and Yogesh Aggarwal\textsuperscript{1}

Abstract: The research nowadays is mainly focusing on the basic science of cementitious material at nano/atomic level. Further, researchers are continuing to improve the durability and sustainability of concrete and have realized significant increment in mechanical properties of cementitious materials by incorporating nano-silica. The review paper summarizes the effect of nano-silica addition on mechanical, durability and microstructure characteristics of paste, mortar and concrete. It provides the current development of application of nano-silica in paste, mortar and concrete. Finally, the future trend/potential and implication of nano-silica in cement-based materials is discussed.

Subjects: Concrete & Cement; Engineering & Technology; Nanoscience & Nanotechnology; Technology

Keywords: nanoparticles; concrete; durability; mechanical properties; microstructure; SEM; XRD

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Their areas of interest include use of nano-silica in concrete, its study of mechanical and durability properties. High-performance concrete, self-compacting concrete, their performance and durability aspects incorporating industrial by-products. Cement is one of the most energy-consuming materials widely used globally. Efforts are being made mainly to use supplementary cementitious materials in mortars and concrete directed towards the reduction of carbon footprint. The present research work is one such effort towards attaining the above goal.

PUBLIC INTEREST STATEMENT
Concrete is one of most commonly used material on earth after water. Use of nano-materials, particularly nano-silica as supplementary cementitious material, in manufacturing of paste, mortar, and concrete offer the potential of producing materials with new and interesting properties, such as enhanced strength and durability properties. In this article, a review of use of nano-silica in paste, mortar and concrete is presented which provides an insight in the use of nano-silica in recent past. It also provides the current development of application of nano-silica with future trend/potential and implication of nano-silica in cement-based materials.
1. Introduction

The importance of the cementitious materials in the construction industry is very significant; however, their variety of applications must not hide their complexity. They are indeed composite materials with multi-scale internal structures which have evolved over centuries. More specifically, the cement paste matrix is basically a porous material composed of calcium hydroxide (portlandite), aluminates and unhydrated cement (clinker) embedded into an amorphous nanostructured hydration product, the so-called C–S–H (calcium silicate hydrate) gel (Gaitero, Campillo, & Guerrero, 2008). This gel is the dominant hydration product of the cement paste, not only because it is the most abundant component (50–70% by volume), but also because of its exceptionally good mechanical properties.

Nanoparticles have a high surface-area-to-volume ratio. In this way, nanoparticles with 4-nm diameter have more than 50% of its atoms at the surface and are thus very reactive (Wiesner & Bottero, 2007). The behaviour of such materials is mainly influenced by chemical reactions at the interface, and by the fact that they easily form agglomerates. When higher surface area is to be wetted, it decreases free dispersant water in aqueous systems available in the mixture. Therefore, the use of nanoparticles in mortars and concretes significantly modify their behaviour not only in the fresh, but also in the hardened conditions, as well as the physical/mechanical and microstructure development (Senff, Labrincha, Ferreira, Hotza, & Repette, 2009).

In recent years, the use of nanoparticles has received particular attention in many fields of applications to fabricate materials with new functionalities. When ultrafine particles are incorporated into Portland cement paste, mortar or concrete, materials with different characteristics from conventional materials were obtained (Lee, 1998; Li, Xiao, Yuan, & Ou, 2004; Neville, 1996). The performance of these cementitious-based materials is strongly dependent on nano-sized solid particles, such as particles of calcium–silicate–hydrates (C–S–H), or nano-sized porosity at the interfacial transition zone between cement and aggregate particles. Typical properties affected by nano-sized particles or voids are strength, durability, shrinkage and steel-bond (Collepardi et al., 2005). Nanoparticles of SiO₂ (nano-silica) can fill the spaces between particles of gel of C–S–H, acting as a nano-filler. Furthermore, by the pozzolanic reaction with calcium hydroxide, the amount of C–S–H increases, resulting in higher densification of the matrix, thus improving the strength and durability of the material (Choolaei, Rashidi, Ardjmand, Yadegari, & Soltanian, 2012; Hou et al., 2013; Zapata, Portela, Sudrez, & Carraquillo, 2013). Previous researches (Björnström, Martinelli, Matic, Börjesson, & Panas, 2004; Lea, 1998; Qing, Zenan, Deyu, & Rongshen, 2007) indicate that the inclusion of nanoparticles modifies fresh and hardened state properties, even when compared with conventional mineral additions. Colloidal particles of amorphous silica appear to considerably impact the process of C₃S hydration (Björnström et al., 2004). Nano-silica decreased the setting time of mortar when compared with silica fume (SF) (Qing et al., 2007) and reduced bleeding water and segregation, while improved the cohesiveness of the mixtures in the fresh state (Collepardi, Olagot, Skarp, & Trol, 2002). Nano-silica-added cement paste showed reduction in setting time (Lin, Lin, Chang, Luo, & Cai, 2008; Singh, Agorwal, Bhattacharyya, Sharma, & Ahalawat, 2011; Singh, Bhattacharyya, & Singh, 2012), shortened duration of dormant and induction period of hydration, shortening of time to reach peak heat of hydration and increased production of calcium hydroxide at early ages (Ltifi, Guefrech, Mounanga, & Khelidj, 2011; Senff et al., 2009). When combined with ultrafine fly ash, better performance is assured than that achieved by use of SF (Lea, 1998; Li, Xiao, & Ou, 2004; Li et al., 2004). Besides, the compressive strength of mortar or concrete with SF was improved when compared with formulations without addition (Jo, Kim, Tae, & Park, 2007; Li et al., 2004; Li, Zhang, & Ou, 2006). Nano-silica addition increased the quantity of C–S–H and C–A–H in the paste (Tobón, Payá, Borrachero, & Restrepo, 2012). Addition of nano-silica into cement paste and mortar demand more water to retain its workability (Quercia, Hüsken, & Brouwers, 2012). To avoid adverse effects on workability, Berra, Carassiti, Mangialardi, Paolini, and Sebastiani (2012) suggested delayed addition of water, stating that instead of adding all the mixing water at a time, certain amount of water should be added later on. Nano-silica samples showed lesser strength loss after being exposed to elevated temperatures (Lim, Mondal, & Cohn, 2012). Mortar containing high volume of fly ash showed higher residual strength after being exposed to 700°C, and dehydration
of C–S–H produced calcium silicate, which acts as new binding material to retain residual strength (Rahel, Hamid, & Taha, 2012). The addition of nano-silica modified the porosity of the cement paste and increased the average chain length of silicate chains (Gaitero et al., 2008; Porro et al., 2005).

In particular, the developments in nano-science have had a great impact on concrete industry. Nano-materials have been used in concrete industry over the past decade. Few studies till date are reported with nanoparticles such as nano-silica (nano-SiO$_2$) and nano-titanium oxide (nano-TiO$_2$), nano-iron (nano-Fe$_2$O$_3$), nano-alumina (nano-Al$_2$O$_3$) (Li, 2004; Shekari & Razzaghi, 2011). Additionally, a limited number of investigations are dealing with the manufacture of nano-sized cement particles and the development of nano binders. Thus, limiting the review of literature work to use of nano-silica in cementitious compositions, research has shown that incorporation of nanoparticles in cement matrix could improve durability and mechanical properties of cement-based materials. Nano-silica (nS) in particular has found wide usage in this field because of its high reactivity and very large specific surface area, which results in a high degree of pozzolanic activity. Nano-silica further accelerates the dissolution of C$_3$S and formation of C–S–H with its activity being inversely proportional to the size, and also provides nucleation sites for C–S–H (Jo, Kim, & Lim, 2007). Even small additions (0.6 wt. % binder) of nS are very efficient and compare to much larger amounts of SF in terms of improvement in mechanical properties of cement-based materials. This is especially pronounced at early ages and for concretes with regular strength grade (Pourjavadi, Fakoorpoor, Khaloo, & Hosseini, 2012). From the nano-indentation studies, it was observed that the nano-silica addition significantly alters the proportions of low stiffness and high stiffness C–S–H (Hou et al., 2013; Mondal, Shah, Marks, & Gaitero, 2010).

2. Nano-material and cement composites
In the construction industry, extensive research is going on to improve the performance of various building materials and development of durable and sustainable concrete is one among them as is clear from Table 1. Among all the nano-materials, nano-silica is the most widely used material in the cement and concrete to improve the performance because of its pozzolanic reactivity besides the pore-filling effect.

2.1. Paste and mortar with nano-silica
Various researchers have investigated the effect of nano-silica on pastes and mortars. Nano-silica-incorporated cement pastes are studied to understand the hydration process and microstructure evolution. Basically, this approach is used for the study of fundamental science behind cement hydration. Mortar studies are used to explore the rheology and mechanical properties.

2.1.1. Fresh properties
Reduction in initial setting time (IST) and final setting time (FST) of pastes was observed on addition of nano-silica (Senff et al., 2009). Also, difference between the IST and FST decreased with increase in nano-silica content (Ltifi et al., 2011; Qing et al., 2007). With regard to the effect of nano-silica on the rheology behaviour of the cementitious mixes’ studies on cement paste and mortars, most of the researchers agree in indicating that the addition of nano-silica greatly increases the water demand of cementitious mixes as compared to the control ones. The plasticity loss of mortar with increased torque and yield stress in mixtures with nano-silica was more evident due to higher surface area (Senff, Hotza, Repette, Ferreira, & Labrincha, 2010; Senff et al., 2009). Berra et al. (2012) and Kawashima, Hou, Corr, and Shah (2012) worked on the rheology of cement pastes with various w/b ratios and suggested delayed addition of water by keeping certain amount of water to be added at a later stage. Also, addition of nano-silica into cement paste and mortar resulted in higher demand of water to retain its workability. Direct influence on water amount required in the mixture was observed when nano-silica was incorporated into the mortars in fresh state. This behaviour confirms the fact that additions of high surface area mineral particles to cement mixtures cause the need for higher amounts of water or chemical admixtures in order to keep the workability of the mixture. If the water content is kept constant, as in the actual conditions, an increase of nano-SiO$_2$ content will promote the packing of particles, decreasing the volume between them and decreasing the free water. Therefore, there is a higher internal friction between solid particles (Ltifi et al., 2011).
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Author</th>
<th>Concrete/ mortar</th>
<th>Materials used for comparison</th>
<th>Nano material used</th>
<th>Size of particle (nm)</th>
<th>Fineness (m²/g)</th>
<th>Water cement ratio</th>
<th>Additive or replacement</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Senff et al. (2009)</td>
<td>Paste</td>
<td>-</td>
<td>nS 1.5%, 2%, 2.5%</td>
<td>9</td>
<td>300</td>
<td>0.35</td>
<td>Replacement</td>
<td>Flow table, rheological behaviour, XRD</td>
</tr>
<tr>
<td>2</td>
<td>Qing et al. (2007)</td>
<td>Paste</td>
<td>1:0.22:0.025 SF 2%, 3%, 5% nS 1%, 2%, 3%, 5%</td>
<td>15</td>
<td>160</td>
<td>0.22</td>
<td>Additive</td>
<td>Compressive strength, bond strength, Setting time</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Liti et al. (2011)</td>
<td>Paste, mortar</td>
<td>-</td>
<td>nS 3%, 10%</td>
<td>9</td>
<td>300</td>
<td>0.35 - 0.59</td>
<td>Replacement</td>
<td>Rheological, compressive strength, water absorption</td>
</tr>
<tr>
<td>4</td>
<td>Senff et al. (2010)</td>
<td>Mortar</td>
<td>SF 0–20% nS 0–7%</td>
<td>9</td>
<td>300</td>
<td>0.35 - 0.59</td>
<td>Additive</td>
<td>Compressive strength, rheological behaviour, XRD</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Berra et al. (2012)</td>
<td>Paste</td>
<td>-</td>
<td>nS 0.8%, 3.8%</td>
<td>10</td>
<td>345</td>
<td>0.5</td>
<td>Additive</td>
<td>Physical mechanical stability test</td>
</tr>
<tr>
<td>6</td>
<td>Kawashima et al. (2012)</td>
<td>Mortar</td>
<td>Fly ash</td>
<td>nS 2%, 5%</td>
<td>20–10</td>
<td>0.43–0.45</td>
<td>Additive</td>
<td>Compressive strength, rate of heat of hydration</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Hau et al. (2013)</td>
<td>Mortar</td>
<td>-</td>
<td>nS 5%</td>
<td>10 nm</td>
<td>0.4</td>
<td>Additive</td>
<td>Hydration heat, morphology, CH content</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Stefanidou (2012)</td>
<td>Paste</td>
<td>-</td>
<td>nS 0.5%, 1%, 2%, 5%</td>
<td>14</td>
<td>200</td>
<td>0.34–0.51</td>
<td>Additive</td>
<td>Flexural and compressive strength, microstructure</td>
</tr>
<tr>
<td>9</td>
<td>Li et al. (2004)</td>
<td>Mortar</td>
<td>Nano-Fe₂O₃ (3–10%) Silica fume (3–15%)</td>
<td>nS 3%, 5%, 10%</td>
<td>15 ± 5</td>
<td>15 ± 5</td>
<td>0.5</td>
<td>Replacement</td>
<td>Compressive and flexural strength, microstructure</td>
</tr>
<tr>
<td>10</td>
<td>Jo et al. (2007)</td>
<td>Mortar</td>
<td>1:2:45 SF 5%, 10%, 15% nS 3%, 6%, 10%, 12%</td>
<td>40</td>
<td>60</td>
<td>0.5</td>
<td>Additive</td>
<td>Compressive strength, SEM, rate of heat of evolution</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Zapata et al. (2013)</td>
<td>Mortar</td>
<td>SF</td>
<td>nS 1.5–6%</td>
<td>25</td>
<td>109</td>
<td>0.35, 0.4</td>
<td>Replacement</td>
<td>Compressive strength, SEM, XRD</td>
</tr>
<tr>
<td>12</td>
<td>Oltulu and Şahin (2013)</td>
<td>Mortar</td>
<td>Fly ash</td>
<td>nS 0.5%, 1.25%, 2.5%</td>
<td>12</td>
<td>200</td>
<td>0.4</td>
<td>Replacement</td>
<td>Compressive strength</td>
</tr>
<tr>
<td>13</td>
<td>Aly et al. (2012)</td>
<td>Mortar</td>
<td>Waste glass 20%, 40%</td>
<td>nS 3%</td>
<td>5</td>
<td>500</td>
<td>–</td>
<td>Replacement</td>
<td>Compressive, fracture, flexural and impact strength, DTA/TGA, SEM</td>
</tr>
<tr>
<td>14</td>
<td>Gaitero et al. (2008)</td>
<td>Paste</td>
<td>-</td>
<td>nS 20%, 40%, 45%, 90%</td>
<td>20, 30, 120, 1,400</td>
<td>0.4</td>
<td>Additive</td>
<td>Compressive strength, flexure strength</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Zhang et al. (2012)</td>
<td>Concrete</td>
<td>SF</td>
<td>nS 0.5%, 1%, 2%</td>
<td>12 and 7</td>
<td>200.1 and 321.6</td>
<td>0.45</td>
<td>Replacement</td>
<td>Compressive strength, rate of heat of hydration, porosity</td>
</tr>
<tr>
<td>16</td>
<td>Zhang and Islam (2012)</td>
<td>Concrete</td>
<td>Fly ash, slag and SF</td>
<td>nS 1%, 2%</td>
<td>12</td>
<td>200.1</td>
<td>0.45</td>
<td>Replacement</td>
<td>Compressive strength, rate of heat of hydration, Setting time</td>
</tr>
<tr>
<td>17</td>
<td>Pourjavadi et al. (2012)</td>
<td>Concrete</td>
<td>SAP 0.1%, 0.3% nS 0.5%, 1%</td>
<td>19</td>
<td>172</td>
<td>0.45</td>
<td>Replacement</td>
<td>Compressive strength, flexure strength</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Li (2004)</td>
<td>Concrete</td>
<td>Fly Ash 50% nS 4%</td>
<td>10 ± 5</td>
<td>640 ± 50</td>
<td>0.28</td>
<td>Replacement</td>
<td>Hydration heat, pore size</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Naji Givi et al. (2010)</td>
<td>Concrete</td>
<td>-</td>
<td>nS 0.5%, 1%, 1.5%, 2%</td>
<td>15 and 80</td>
<td>160 ± 12 560 ± 32</td>
<td>0.4</td>
<td>Replacement</td>
<td>Compressive, flexure, and split tensile strength</td>
</tr>
<tr>
<td>20</td>
<td>Heidari and Tavakoli (2013)</td>
<td>Concrete</td>
<td>Ground ceramic powder 10–40% nS 0.5%, 1%</td>
<td>200 ± 30</td>
<td>0.5</td>
<td>Replacement</td>
<td>XRD, compressive strength, water absorption</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
Presence of nano-silica made cement paste thicker and accelerated the hydration process (Qing et al., 2007). Spherical morphology of fly ash helps increase the flowability of cementitious materials, whereas nanoparticles increase stiffness due to their higher specific surface area, thereby reducing fluidity of fly ash cement-blended nano-silica mortar with increase in the amount of nano-silica (Kawashima et al., 2012). The pozzolanic activity of nano-silica and CH adsorption of colloidal nano-silica (CNS) was investigated. It was observed that pozzolanic reaction of nano-silica was complete within 7 days of hydration (Hou et al., 2013).

2.1.2. Mechanical properties

With regard to the influence of nano-silica on the mechanical strength development of cementitious materials, the addition of nano-silica to Portland cement (PC) pastes was found to increase the compressive strength to an extent that was dependent on the nano-silica content, water-to-binder weight ratio (w/b), and curing time. Paste compressive strength was studied (Berra et al., 2012; Qing et al., 2007; Stefanidou, 2012) along with bond strength (Qing et al., 2007) and flexural strength (Stefanidou, 2012). As a general observation, increase in paste strength was observed, with increase in content of nano-silica at early ages along with increase in pozzolanic activity. An increase of approximately 17–41% and 20–25% in compressive strength was observed at the 3rd and 28th days (Qing et al., 2007), 7–11% at the 7th day (Berra et al., 2012) and an average increase of about 25% was observed on addition of 0.5–2% nano-silica (Stefanidou, 2012). The increase in gain of strength and optimum nano-silica content were observed to be 5% (Qing et al., 2007), 0.8% (Berra et al., 2012) and 0.5% (Stefanidou, 2012). The bond strength increase was observed between 16–43% at 7 days and 26–88% at 28 days (Qing et al., 2007). The flexural strength at the ages of 3 days was also observed to be maximum with 1–2% nano-silica content (Stefanidou, 2012).

Li et al. (2004) investigated cement mortars with nano-SiO$_2$ or nano-Fe$_2$O$_3$ to explore their super mechanical and smart potentials. Compressive strength increase in mortar mixes was observed 5.7–20.1% (7 days) and 13.8–26% (28 days). Jo et al. (2007) observed 53.67–63.9% (7 days) and 52.5–62.7% (28 days) increase in mortar mixes compressive strength and suggested the requirement of using higher content of nano-silica must be accompanied by adjustments to water and superplasticizer dosage in the mix in order to ensure that the specimens do not suffer excessive self-desiccation and cracking. Same results were observed by Litifi et al. (2011), and 6.9–16.9% increase in compressive strength at 90 days was reported (Zapata et al., 2013). On addition of nano-silica to fly-ash concretes (Hou et al., 2013; Kawashima et al., 2012; Öltulu & Şahin, 2013), almost same results were observed with early age strength gain as high as 60%, which became equal at later stage to that of various mixes (Kawashima et al., 2012) and 58–66% i.e. average of 63% increase on strength (Öltulu & Şahin, 2013). Also, flexural strength increase was reported as 28% at 7 days and 19.2–27% at 28 days (Li et al., 2004) and 42–55% at 28 days, along with fracture energy and impact strength increase at 28 days (Aly et al., 2012).

<table>
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<th>Additive or replacement</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Zhang and Li (2011)</td>
<td>Concrete</td>
<td>Polypropylene fibre</td>
<td>nS 1%, 3%</td>
<td>10 ± 5</td>
<td>640 ± 50</td>
<td>0.42</td>
<td>Replacement</td>
<td>Compressive and flexure strength, pore structure, chloride permeability</td>
</tr>
<tr>
<td>22</td>
<td>Jalal et al. (2012)</td>
<td>Concrete</td>
<td>SF 2%, 10%</td>
<td>nS 2%, 10%</td>
<td>15 ± 3</td>
<td>165 ± 17</td>
<td>0.38</td>
<td>Replacement</td>
<td>Chloride penetration, water absorption, electrical resistivity</td>
</tr>
<tr>
<td>23</td>
<td>Ji (2005)</td>
<td>Concrete</td>
<td>Fly ash</td>
<td>nS</td>
<td>15 ± 5</td>
<td>160 ± 20</td>
<td>0.49–0.5</td>
<td>Replacement</td>
<td>Water permeability, SEM</td>
</tr>
<tr>
<td>24</td>
<td>Kang et al. (2012)</td>
<td>Mortar</td>
<td>–</td>
<td>nS 0.75%, 1%</td>
<td>100–200 and 200–400</td>
<td>142.9 and 157.8</td>
<td>0.3</td>
<td>Additive</td>
<td>Microstructure, compressive strength</td>
</tr>
</tbody>
</table>

Table 1. (Continued)
2.1.3. Durability properties
Jo et al. (2007) observed by examining the rate of heat of evolution that nano-scale silica behaves not only as a filler to improve microstructure, but also as an activator to promote pozzolanic reaction. Gaitero et al. (2008) revealed reduced calcium leaching of nano-silica-added cement paste ascribing it to the densification of the paste, transforming of portlandite into C–S–H by means of pozzolanic reaction and modification of internal structure of C–S–H gel, all of which make the cement paste more stable and more strongly bonded. Higher values of water absorption and apparent porosity (Senff et al., 2010) were observed along with unrestrained shrinkage and weight loss of mortars with increase in nano-silica content (highest at 7% nano-silica wt. %). For fly ash replaced cement-based materials, CH generated by cement hydration is critical for later stage pozzolanic reaction. Nano-silica addition has great influence on the CH content of fly ash–cement paste. Also, depletion of Ca(OH)₂, was more severe when the nano-silica dosage and fly ash replacement ratio are high (Kawashima et al., 2012). Hou et al. (2013) observed acceleration of cement hydration and maturation of gel structure in CNS added paste, achieved through an acceleration of the dissolution of cement particles and a preferred hydration and hydrates precipitation on CNS particle surface. Although CNS can accelerate cement hydration to a great extent in the early age, the later hydration of cement is hindered.

2.2. Concrete with nano-silica
Nano-silica incorporation into cement concrete is the direct application approach of nanomaterials. Researchers have worked on the mechanical and durability properties and microstructure analysis of concrete with nano-silica as discussed below.

2.2.1. Fresh properties
Reduced setting times were observed by various researchers on incorporation of nano-silica in concrete which is same as observed for pastes and mortar (Zhang & Islam, 2012; Zhang, Islam, & Peethamparan, 2012). Also, decrease in initial and final setting time was observed on incorporation of nS in various quantities, with increase in viscosity and yield stress reported (Pourjavadi et al., 2012).

2.2.2. Mechanical properties
Concrete strength is influenced by lots of factors like concrete ingredients, age, ratio of water to cement materials, etc. Nano-silica incorporation into concrete resulted in higher compressive strength than that of normal concrete to a considerable level. Li et al. (2004) reported 3-day compressive strength increase by 81% and also at later stages, same trend was observed with 4% nano-silica in high volume fly ash concrete. Naji Givi, Abdul Rashid, Aziz, and Salleh (2010) also reported higher compressive strength at all ages, for nano-silica blended concretes up to maximum limit of 2% with average particle size of 15 and 80 nm. Same results were obtained for split tensile and flexural strength. Pourjavadi et al. (2012) reported that negative effect of super absorbent polymer reduced compressive strength by addition of nano silica, but same results were not observed for flexural strength. An increase of about 23–38% and 7–14% at 7 days and 28 days, respectively, in compressive strength of nano-silica concrete was reported, whereas low increase of 9.4% (average) was reported for flexural strength. Zhang and Islam (2012), Zhang et al. (2012) used GGBFS, fly ash and slag and increase in compressive strength was observed as 22% (3 days) and 18% (7 days) and 30% (3 days) and 25% (7 days) of concretes with GGBFS and fly ash and slag, respectively. Heidari and Tavakoli (2013) incorporated nano-silica in ground ceramic concrete and improvement in strength at early stage was observed.

2.2.3. Durability properties
Durability properties of concrete include aspects such as permeability, pore structure and particle size distribution, resistance to chloride penetration, etc. Investigations on nano-silica concrete for its permeability characteristics showed that the addition of nano-silica in concrete resulted in reduction in water absorption, capillary absorption, rate of water absorption, and coefficient of water absorption and water permeability than normal concrete. The pore structure determines the transport properties of cement paste, such as permeability and ion migration. Reduction in water absorption, capillary absorption, rate of water absorption and water permeability has been observed by various researchers (Li, 2004; Zhang & Li, 2011; Zhang et al., 2012). Pore size distribution in concrete was refined and
porosity lowered even at short time, curing on addition of 4% nano-silica (Li, 2004; Zhang & Li, 2011). Also, increasing nano-silica dosage decreased capillary porosity (Zhang et al., 2012). Water absorption capacity of nano-silica concretes decreased with incorporation of nano-silica (Jalal, Pouladkhan, Norouzi, & Choubdar, 2012; Zhang et al., 2012). Enhancement of resistance to chloride penetration of concretes with addition of nano-silica was reported (Jalal et al., 2012; Zhang & Li, 2011). Zhang and Islam (2012) studied the behaviour of high-volume fly ash and slag concretes with nano-silica addition and reported that the addition of nano-silica reduced the length of dormant period during hydration and also accelerated the hydration. Chloride ion penetration was also reduced with the addition of nano-silica into fly ash and slag concrete.

3. Microstructure analysis
XRD and SEM observations have been reported by a number of researchers (Aly et al., 2012; Hou et al., 2013; Ji, 2005; Jo et al., 2007; Kong et al., 2012; Li et al., 2004; Pourjavadi et al., 2012; Qing et al., 2007; Senff et al., 2009; Stefanidou, 2012). Li et al. (2004) observed from SEM images that the nanoparticles were not only acting as a filler, but also as an activator to promote hydration process and to improve the microstructure of the cement paste if the nanoparticles were uniformly dispersed. Ji (2005) also revealed through ESEM test that microstructure of concrete with nano-silica was more uniform and compact than that of the normal concrete. Qing et al. (2007) showed from XRD powder patterns of NS and SF that strong broad peaks of NS and SF were centred on 23° and 22° (2θ), respectively, which was in keeping with the strong broad peak that is characteristic of amorphous SiO$_2$. The results showed that both NS and SF were in an amorphous state. SEM examination was performed to verify the mechanism predicted by compressive strength test (Jo et al., 2007) and nano-silica particles were found to influence hydration behaviour and lead to the differences in the microstructure of the hardened paste. The microstructure of the mixture containing nano-SiO$_2$ revealed a dense, compact formation of hydration products and a reduced number of Ca(OH)$_2$ crystals. Qing et al. (2007) showed that NS can reduce the size of CH crystals at the interface more effectively than SF. Senff et al. (2009) also showed that nano-silica addition contributed to the increased production of CH at early stage compared to samples without nano-silica. Aly et al. (2012) showed through SEM micrographs show that the densest mortar structure was observed for the specimen with a hybrid combination of waste glass powder (WG) and colloidal nano-silica (CS). Stefanidou’s (2012) observation recorded a denser structure in nano-modified samples. Also, Kong et al. (2012), through SEM observation, recorded an obvious microstructure improvement of the hardened cement paste (HCP) and the ITZ in mortar by adding nano-silica, regardless of its agglomerate size. It was found that C–S–H gels from pozzolanic reaction of the agglomerates cannot function as binder. The gels from cement hydration did not penetrate into the pozzolanic gels. Pourjavadi et al. (2012) reported that the addition of 1% nano-silica reduced the porosity of hardened cement paste because of super pozzolanic performance and production of higher amounts of C–S–H gel. In addition, the microstructure was considerably improved due to the micro and nano-filling effects. Crystals of portlandite were reduced in size and quantity as a consequence of the pozzolanic reaction and crystal growth control by nano-silica.

4. Conclusions and summary
The present paper reviews the current state of the field of nanotechnology in concrete and recent key advances. Current status of nano-silica opens up widely for research in cementitious compositions. Applications of nanotechnology have the potential to make breakthrough in materials technology. Nano-silica application in paste, mortar and concrete is a good way of enhancing their properties. It has been observed that optimum quantity of nano-silica to be used is still contradictory and it is for the researcher to decide the optimum quantity for his/her own material. Using nanotechnology in future will make it possible to design materials for their specific purpose of application. New developments have taken place in the nano-engineering and nano modification of concrete; however, current challenges need to be solved before the full potential of nanotechnology can be realized in concrete applications, including proper dispersion, compatibility of the nanomaterials in cement.

Some of the outcomes from the literature reviewed can be summarized as:
Direct influence on water amount required in the mixture was observed when nano-silica was incorporated into the mortars in fresh state. This behaviour confirms the fact that additions of high-surface area mineral particles to cement mixtures cause the need for higher amounts of water or chemical admixtures in order to keep the workability of the mixture.

Compressive strengths increase with increase in nano-silica content, which acts as activator to promote hydration and also to improve the microstructure of cement paste if nanoparticles were uniformly dispersed. The compressive strength is enhanced with nano-SiO₂ addition, especially at early stages, and the pozzolanic activity of nano-silica is much greater than that of SF. It was observed that nano-silica-blended concretes have higher strength as compared to non-blended concretes. Compressive strength is higher at all stages for nano-silica-blended concretes.

Nano-Silica was observed to have no positive effect on the strength gain of fly ash-replaced cement-based material at later stages. Flexural and split tensile strengths also improved by increasing the silica nano-particle content. Fly ash-based cements have low initial pozzolanic activity, but the addition of a little nano-SiO₂ significantly increases pozzolanic activity. Thus, nano-SiO₂ activates fly ash.

Nano-SiO₂ adsorbs the Ca(OH)₂ crystals reducing the size and amount of the Ca(OH)₂, making the interfacial transition zone of aggregates and binding paste matrix denser. The nano-SiO₂ particles fill the voids of the C–S–H gel structure and act as nucleus to tightly bond with C–S–H gel particles, making binding paste matrix denser, resulting in an increase in long-term strength and durability of concrete. Nano-scale SiO₂ behaves not only as filler to improve mortar cement microstructure, but also as a promoter of pozzolanic reaction.

Future research should address the following issues.

1. Physical state and dispersion of nano-silica into the concrete is a major issue requiring thorough study.
2. The optimum quantity of nano-silica for concrete or cement paste needs to be determined for certain percentage, which depends on the type of nano-silica, i.e. colloidal, dry powder, etc., and also the average particle size of nano-silica. A relationship needs to be established between optimum quantity and characteristics of nano-silica.
3. Most of the research works are limited to cement pastes and mortars, with only a few researchers having worked extensively on mechanical properties and permeability of the concrete incorporating nano-silica as is clear from the review paper. Durability properties still need to be investigated further on carbonation, corrosion resistance, acid resistance, sulphate resistance.
4. Optimization, fresh, mechanical, microstructural and durability properties of concrete along with mathematical modelling of concrete behaviour requires extensive research.

Additionally, introduction of these novel materials into the public sphere through civil infrastructure will necessitate an evaluation and understanding of the impact they may have on the environment and human health.


