Incorporation of nano-materials in cement composite and geopolymer based paste and mortar – A review

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HIGHLIGHTS

• Effect of nano-materials on fresh, hardened, durability and bond properties.
• Effective particle size of nano-materials improved the strength and durability.
• Significant optimum content of nano-materials for cement composite and geopolymer.
• Health and safety preventive measures on using nano-materials.

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ABSTRACT

The summary of developments in partially replaced cement composite and geopolymers by industrial by-products are presented along with different nano-materials. Many significant correlations have been studied on association with the better understanding of the interfacial transition zone, microstructural performance, mix design characteristics, setting behavior, mechanical properties, durability and bond strength. The effects of various particle size and different types of nano-materials and their optimal level of replacement have been reviewed on cement composite and geopolymer products. Application of nano-materials in both partially replaced cement composite and geopolymers has significant benefits towards the performance of mortar and paste. The health related issues on using nano-materials and methods can be used to overcome the risks of exposure have been discussed.

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1. Introduction

It is estimated that about a ton of cement is being produced for every human being per year and thus cement had become the second largest producer of greenhouse gas. In the construction sector, the use of high cement content is not generally acceptable practice due to both economic and environmental points of view. Approximately, 7% of the global carbon dioxide \((CO_2)\) emissions reported due to the cement production and the manufacture of each ton of cement produces about 650–920 kg of \(CO_2\). Therefore, the main concern of minimizing \(CO_2\) emission can be encouraged by reducing the cement usage in current construction practices [1].

At present, the main focus is on \(CO_2\) reduction by minimizing the use of Portland cement. The industrial by-product materials such as fly ash (FA), ground granulated blast furnace slag (GGBS), silica fume (SF), and metakaolin are considered as cementitious materials and have been used as partial replacements to decrease the consumption of cement. Besides, a large quantity of agro-industrial by-products such as palm oil fuel ash (POFA) and rice husk ash (RHA) are produced in the South-East Asian countries—Thailand, Indonesia, Vietnam, Philippines and Malaysia. Recently, several researchers have been investigating on utilizing the above-said industrial by-products as cement replacement material. The waste from palm oil industry such as POFA and oil palm clinker have great potential as cement replacement [2].

Generally, the industrial by-products are added to cement based materials in the form of powders. The recent interests on the high performance mortar and paste have led to utilize these new waste materials as cement replacement materials [3]. So far, there has been extensive research carried concerning the use of other forms of cementitious materials that have high silicon and aluminium contents [4–6]. However, there is some limitation on cement replacement. Even though the partial replacement of cement by industrial by-product improves the strength, a significant reduction in strength was observed when the replacement level goes more than 50% for preparing the mortar. This is mainly due to a low pozzolanic reaction active index. So, there is a limitation in the cement replacement [7]. Similar findings were observed by Lin et al. [8].

In such cases, the nano-materials were found more effective additives together with by-products in cement replacement. A better strength improvement was noticed for 25% FA and 3% nano-copper oxide (CuO) based mortar sample. Even if the content of FA beyond the limitation, it affects the strength [9].

On the other hand, research work on the development of cement free mortar and paste is gathering momentum and it is one of the emerging research areas, known as alkali activated binders and geopolymers. It leads to the development of cementless alternative material based on industrial by-products activated by alkaline solution. The geopolymer provides cement-less material having competent performance with the conventional cement based material [10]. In the 1970s, Joseph Davidovits developed geopolymer technology and illustrated alkali activated materials involved in the geopolymerization [1]. In fact, the geopolymer technology has the advantage on capitalizing on re-using industrial by-products as full cement replacement as binding material.

1.1. Overview of geopolymer material

Geopolymer is generally called as third generation cement following lime and ordinary Portland cement. In geopolymerization technology, many kinds of aluminosilicate materials such as kaolinite, feldspar and industrial wastes such as FA, GGBS, POFA, RHA, mining wastes etc. have been used as base materials. The chemical composition, mineralogical structure, fineness morphology and glassy phase content of these materials affect the activity of aluminosilicate sources. So, the source materials are vital in developing a stable geopolymer. The source materials must have a highly amorphous structure and possess sufficient reactive glassy content, low water demand and ability to release aluminium easily. The aluminosilicate materials are generally activated by alkaline activators such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (\(Na_2SiO_3\)) and potassium silicate (\(K_2SiO_3\)). The following reactions occur during the geopolymerisation process.

\[
(Si_2O_5Al_2O_3)_n + H_2O + OH^- \rightarrow Si(OH)_4 + Al(OH)^4-. \quad (1)
\]

In dissolution stage, the water liberation takes place. The expulsion of water during the reaction at geopolymerization stage is very important and provides workability to the mixes [11].

In geopolymerization, the heat curing process is one of the main roles in the development of strength. As the temperature increases, it increases the geopolymerization [12,13]. The authors [14] reported that the heat curing process in FA based geopolymer mortar improved the strength of geopolymer samples with 115 °C for 24 h. Dung et al. [15] investigated the effect of geopolymerization in slag and FA based mortar and reported a denser microstructure with better resistance against sulfate attack due to the better reactivity of slag and FA. Sata et al. [16] found that the strength of RHA and POFA based mortar was enhanced mainly due to the rapid formation of pozzolanic reaction because of the high reactivity of RHA and POFA particles.

Further, the enhancement of physical structure and strength of geopolymer matrices would be possible by incorporating nanoparticles. Presently, nanotechnology has several applications especially in producing nano composites that exhibit superior material properties [17].

\[
\text{Si(OH)}_4 + \text{Al(OH)}^4- \xrightarrow{\text{yield}} (-\text{Si}-0--\text{Al}-0-)_n + 4\text{H}_2\text{O} \quad (2)
\]
1.2. Overview of Nano-materials

Nano-materials are generally referred to materials with nanoscale size or bulk materials containing nanosized particles. The particles of less than 100 nm in diameter are called as nano-particles. The nano-materials exhibit an extraordinary strength with good physical and chemical properties. The inclusion of nanoparticle into the cementitious materials with spherical materials such as nano-SiO$_2$ (NS), nano-Al$_2$O$_3$ (NA), nano-TiO$_2$ (NT), nano-Fe$_2$O$_3$ (NF), nano-ZnO$_2$, nano-clay (NC), carbon nano-tubes (CNT) and carbon nano-fibers (CNF) [18]. The production of nano-materials based mortar and concrete using various methods have been developed by several researchers [19-24].

Immobilization of free water occurs when the nano-particles are added to cement grains. This is due to filling of voids between cement grains by nanoparticle and this is called filler effect. Also, the nano-particles take part in pozzolanic reactions and leads to the additional formation of calcium–silicate–hydrates (C–S–H) gel. The bond between aggregates and cement paste is enhanced at the interfacial transition zone (ITZ) by incorporating nanoparticles. Eventually, it improves the bond strength characteristics of the mix. The stiffness, shear, tensile and flexural strength of cement-based materials could be improved by nano-particles and it provides crack arrest and interlocking effects between the slip planes [25].

The incorporation of ultra-fine particles into Portland-cement paste and mortar results in different characteristics from conventional materials. The nano-sized solid particles of C–S–H or nano-sized porosity at the ITZ between cement and aggregate particles usually influence the performance of these cementitious based materials. The strength, workability, stability, shrinkage and bond strength characteristics are highly influenced by the nano-sized particles. Nano-materials can act as a nano-filler by filling the spaces between particles in C–S–H gel and also acts as a pozzolan since it has high surface area to volume ratio. The filler effect and pozzolanic reaction are the potential characteristics which significantly improve the chemical reactivity. Thus, it improves the pore structure of material by the formation of a dense microstructure of cement paste [26]. The high surface area of nano-particles is very important for hydration. The nano-material promotes the early hydration as well as accelerates the development of hydration products [27]. The additional formation of C–S–H gel fills the micro pores in the matrix. Thus it provides more effective hydration which leads to higher strength [28].

Nano technology is one of the emerging fields to develop novel materials with superior properties and high performance. The conventional construction materials properties could be improved by nanotechnology. Few research works have been performed on utilizing of nano-particles to improve the strength, workability and durability of cement mortar [29].

On the other hand, there are limited literatures are available on the incorporation of nano-materials in the geopolymer mortars and pastes. The influence of nano-materials on mortar/paste by the partial replacement of cement and geopolymer is discussed in the subsequent sections.

2. Influence of nano-materials in industrial by-products based cement composite

Various mix proportioning of cement based paste and mortar partially replaced by industrial by-products and incorporated with nano-materials were reported with high strength. The typical properties of mixes used for cement composite system are summarized in Table 1.

The properties of various mixes were examined in terms of water-cementitious ratio (w/c), different types of superplasticizers, industrial by-products and nano-materials. It was reported [32] that the incorporation optimum content of 9% of NS improved the compressive strength and provided better performance. Due to high content of nano-material, a very high w/c ratio of 0.65 was considered. Leon et al. [33] observed that on the addition of NS the critical pore size decreased and thus resulted in low porosity.

The effect of different nano-materials on mortar/paste in partial cement replacement by various industrial by-products are explicated in the following subsections.

2.1. Microstructural behavior of nano incorporated cement mortar/ paste

Khotbehsara et al. [9] investigated on the microstructure characteristics of cement mortar with partial replacement of FA along with incorporation of nano-CuO. It was found that very denser microstructure with lower porosity was obtained from the scanning electron microscope (SEM) analysis (Fig. 1) and they attributed it to the pozzolanic activity of FA as well as nano-particles. Li et al. [22] investigated on the microstructural behavior of cement mortar with NF and NS. The mortar specimens were prepared with 3, 5 and 10% of nano-particles by weight of cement with w/c ratio of 0.5. The mean particle size of NS and NF was 15 ± 5 nm and 30 nm respectively. After the cube compression testing, the SEM test was conducted on the crushed specimens; it was noticed that the NS was contributed to the hydration process and thus produced C–S–H gel that resulted in strength enhancement even at the addition of small quantity of NS.

Based on the SEM images and analysis (Fig. 2), nano-particles performed as a filler material, and also it enhanced the hydration process and thus improved microstructure when the nano-particles evenly dispersed in the system [22].

The authors [32] investigated on the cement composite with silica fume and with 9% of nano-SiO$_2$. It was found that the microstructure of control cement paste and cement paste with silica fume was similar. The silica fume has lesser pozzolanic activity and filling ability compared to NS. Also, the silica fume has larger particles that reduce the packing ability as well as pozzolanic activity.

On the other hand, the nano-particles of extremely small size could fill up the pores in the paste and improves the strength. It was found that NS of 40 nm particle size was suitable for fill up the pores and also it has an even dispersion in the cement system. Hence, it provides more denser and compacted microstructure. This result of microstructural analysis was supported with the compressive strength test result (Fig. 3). The NS of particle size 40 nm produced a higher compressive strength compared with 12 and 20 nm particle sizes. This is mainly because of the poor dispersion of the smaller particles of 12 and 20 nm particles that result in agglomeration [32].

Authors [35] reported that nano-alumina acts as filler material to fill up the pores of inert materials, hence the compactness of samples improved compared to the control mixes. When NA is added to cement composites with RHA more compacted microstructure with less pores was noticed from SEM analysis. This is mainly because of the efficiency of filling ability of voids by nanoparticles in cement-based composites. Also, it was found that the optimum content of 2% of NA was required to meet the denser
<table>
<thead>
<tr>
<th>Authors</th>
<th>Type of Nano material</th>
<th>Replacement material</th>
<th>Super-plasticizer</th>
<th>W/B</th>
<th>S/B</th>
<th>Sand</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mohseni et al. (2016) [31]</td>
<td>Nano-TiO₂ (20 nm)</td>
<td>RHA, Binder – 700 kg/m³ for control mortar, 500 to 700 kg/m³ for replacement, 9 and 15% of binder</td>
<td>Polycarboxylic acid based SP</td>
<td>0.4</td>
<td>–</td>
<td>Natural river sand, Fineness modulus (FM) = 2.25, Specific gravity = 2.58 g/cm³</td>
<td>Improved the Compressive Strength, OPC 47 MPa (28 d), RHA 10% 50 MPa (28 d), RHA 10% &amp; NS 5% 27 MPa (28 d)</td>
</tr>
<tr>
<td>Haruehansapong et al. (2014) [32]</td>
<td>Nano-SiO₂ (12, 20 and 40 nm)</td>
<td>Silica fume, average particle size of 0.1 μm 3% 6% 9% and 12 wt%</td>
<td>Viscocrete, 5720 (SIKA) 1.2% used</td>
<td>0.65</td>
<td>2.75</td>
<td>–</td>
<td>Improved the Compressive Strength, 9% is the optimum, OPC 23.52 MPa (28 d), NS 9% (40 nm) addition 36.32 MPa (28 d)</td>
</tr>
<tr>
<td>Nestor Leon et al. (2014) [33]</td>
<td>Nano-Al₂O₃ (20 nm)</td>
<td>RHA 10% &amp; NS 5% 57 MPa (28 d)</td>
<td>Naphthalene sulfonate based, (Darex Super 20) 2% used</td>
<td>0.35</td>
<td>2.75</td>
<td>–</td>
<td>Improved the durability, Critical pore size decreased, Porosity decreased, Improved the durability and strength, 2% is the optimum content</td>
</tr>
<tr>
<td>Mohseni et al. (2016)</td>
<td>Nano-Al₂O₃ (20 nm)</td>
<td>RHA (0 and 30%) Binder -450 kg/m³</td>
<td>Polycarboxylate type, 0.2 and 1% by wt.</td>
<td>0.49</td>
<td>–</td>
<td>–</td>
<td>Improved the strength with nano-Al₂O₃ addition and RHA up to 10 wt%, 2% is the optimum content</td>
</tr>
<tr>
<td>Senff et al. (2009) [20]</td>
<td>Nano-SiO₂ (9 nm)</td>
<td>Polycarboxylic acid based (Gelenium 51), 2.0 wt% used</td>
<td>–</td>
<td>0.35</td>
<td>2</td>
<td>1.2, 0.6, 0.3 and 0.15 mm fractions related to 25 wt%</td>
<td>Reduced the setting time</td>
</tr>
<tr>
<td>Mukharjee &amp; Barai (2014) [36]</td>
<td>Nano-SiO₂ (8–20 nm)</td>
<td>Colloidal Nano-SiO₂, (5 nm) up to 3%</td>
<td>–</td>
<td>0.40, 0.45 and 0.50</td>
<td>3</td>
<td>–</td>
<td>Reduced the setting time, Improved the compressive Strength</td>
</tr>
<tr>
<td>Aly et al. (2012) [37]</td>
<td>Nano-SiO₂ (15 nm)</td>
<td>Colloidal Nano-SiO₂, (5 nm) up to 3%</td>
<td>–</td>
<td>For a flow of 110 ± 5 mm</td>
<td>1 up to 1.18 mm particle size and specific gravity = 2.65 g/cm³</td>
<td>Improved the compressive and flexural strength, The optimum content is 3%</td>
<td></td>
</tr>
<tr>
<td>Heikal et al. (2013) [38]</td>
<td>Nano-SiO₂ (15 nm) used 1 to 6 wt%</td>
<td>PC replaced by 0 to 45% GBFS.</td>
<td>Polycarboxylate based SP (Conplast SP 610) 1% used</td>
<td>–</td>
<td>2.75</td>
<td>–</td>
<td>The composite of 45 mass% of GBFS and 3–4 mass% of NS produced the optimum mechanical properties</td>
</tr>
<tr>
<td>Lim et al. (2015) [39]</td>
<td>Nano POFA (&lt;1 μm)</td>
<td>GPOFA, TPOFA (up to 80%) Binder – 525 kg/m³</td>
<td>–</td>
<td>0.4</td>
<td>3</td>
<td>2.35 mm sieved and retained at 300 μm, SSD condition</td>
<td>Improved the compressive and flexural strength, The strength activity index was achieved up to 105%</td>
</tr>
<tr>
<td>Mohs eni et al. (2015) [40]</td>
<td>Nano-SiO₂, Nano- Al₂O₃, Nano-TiO₂ (15 nm)</td>
<td>FA (used 25%) 700 kg/m³ of binder of (OPC + FA)</td>
<td>Polycarboxylate acid based superplasticizer, dosage of 3.3 and 4.5 kg/m³</td>
<td>0.4</td>
<td>–</td>
<td>–</td>
<td>Best performance achieved for NS, NA, and NT were 3%, 1% and 5% respectively in strength and chloride permeability resistance</td>
</tr>
<tr>
<td>Lutfi et al. (2011) [41]</td>
<td>Nano-SiO₂ (9 nm) 0, 3, and 10 wt%</td>
<td>Binder – 450 kg/m³</td>
<td>–</td>
<td>0.5</td>
<td>3</td>
<td>–</td>
<td>Improved the microstructure with nano addition, Reduced the setting time, Improved the compressive strength, Strength increased up to 10% addition</td>
</tr>
<tr>
<td>Farzadnia et al. (2013) [42]</td>
<td>Nano-TiO₂ (21 nm) 1, 2, and 3 wt%</td>
<td>5% of Silica fume</td>
<td>Naphthalene sulfonate based (Darex Super 20) 2% used</td>
<td>0.35</td>
<td>2.75</td>
<td>2.36 mm of maximum size</td>
<td>Enhanced the compressive strength, 2% is the optimum incorporation</td>
</tr>
<tr>
<td>Rong et al. (2015) [43]</td>
<td>Nano-SiO₂ (20 nm)</td>
<td>Ultra-fine FA 35% by weight</td>
<td>Superplasticizer 2% used</td>
<td>0.2</td>
<td>2</td>
<td>River sand maximum size of 2.5 mm, Specific gravity=2.6 and FM=2.26</td>
<td>Improved the compressive and flexural strength, Enhanced the microstructure</td>
</tr>
<tr>
<td>Farzadnia et al. (2015) [44]</td>
<td>Nano-SiO₂ (15 nm) 1% used for all the</td>
<td>Ground POFA (32.16 μm) 0, 10, and 30% replacement level</td>
<td>–</td>
<td>0.5</td>
<td>2</td>
<td>Mining Sand of 2.36 mm</td>
<td>Produced a denser matrix</td>
</tr>
</tbody>
</table>

(continued on next page)
<table>
<thead>
<tr>
<th>Authors</th>
<th>Type of Nano material</th>
<th>Replacement material</th>
<th>W/B</th>
<th>S/B Sand</th>
<th>Super-plasticizer</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ma et al. (2016) [27]</td>
<td>Nano-TiO$_2$ (21 nm)</td>
<td>FA 0, 1, 2 &amp; 3%</td>
<td>–</td>
<td>0.5</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>Shaikh et al. (2016) [45]</td>
<td>Nano-SiO$_2$ (25 nm)</td>
<td>FA 10, 20 &amp; 30%, 40, 50 &amp; 60%</td>
<td>–</td>
<td>–</td>
<td>0.4</td>
<td>–</td>
</tr>
</tbody>
</table>

- Increased the early age compressive strength by 3% and 20%, respectively
- The optimum contents of NT and FA are 3% and 20%, respectively
- Reduced the setting time with increase in NT and FA
- Improved the flow value with NT and FA
- Improved the compressive strength with NS and FA

Fig. 1. SEM images of mortar (a) without nano-CuO and (b) with nano-CuO at 28 days [9].

Fig. 2. SEM image of mixture [22].
microstructure and high strength criterions. Authors [41] also investigated the microstructure behavior of NS incorporated cement composite mortar. The denser microstructure revealed higher compressive strength up to 10% addition of nano-SiO₂.

Rong et al. [43] conducted a microstructural investigation on FA based specimens and suggested that up to 35% FA could be used as a partial cementitious replacement for cement. In order to enhance the strength, they utilized 3% NS and reported very dense microstructure in the specimen (NS3). Further, it could be noticed from Fig. 4 that a stronger bond between the paste and aggregate in NS3 specimens compared to control (N0) specimens.

Noorvand et al. [46] found that the ITZ improved with the addition of NS of 1% in the POFA replaced cement mortar. The permeable voids were decreased due to the filler effect of NS and also provide densification of matrix, known as nucleation effect.

2.2. Workability and mechanical behavior of nano incorporated mortar/paste

Farzadnia et al. [44] conducted an experimental investigation on ground POFA –NS based cement mortar. The NS of amorphous form with spherical morphology with a particle size of 15 nm was used. The replacement levels of cement by POFA were at 0%, 10%, and 30%. The SEM test revealed that an irregular particle shape was observed with lot of porous surfaces for unground POFA. However, the morphology was improved by grinding of POFA particles to a crushed form with rough texture.

The workability was measured through flow table and the control samples that contained no NS particles produced the highest flow of 115.5 mm. The workability was decreased when NS added to the mixture and hence the water demand was increased; this was attributed to a high specific surface area of NS. The workability

![Fig. 3. SEM image of nano silica incorporated cement paste [32].](image)

![Fig. 4. SEM images of N0 and NS3 [43].](image)

![Fig. 5. Compressive strength of cement composites with various curing periods [44].](image)
was decreased to 112 mm with the addition of POFA (30%) was due to porous texture of POFA. The effectiveness of NS was prominent after 3-days (Fig. 5) and as known it could be attributed to the more reactivity of NS [44].

Researchers [44] reported that the addition of POFA decreased the compressive strength at different ages. The reduction in the strength was mainly related to the lack of tricalcium silicate (C₃S) in the system as it leads to lesser development of hydrated products. Further, the porous structure and lesser amount of free water available in the system reduced the hydration and subsequently the strength in the mix P30.

Another study by the authors [30] investigated the influence of NS on the hydration and compressive strength of FA based mortars. The cement was partially replaced by FA (between 5% and 20% by weight of cement). The NS content between 0.5% and 3.0% of the cement weight having mean particle size of 60 nm was used in the preparation of mortar. Polycarboxylate based superplasticizer of 0.3% and 0.9% of total binder was used. The results showed that the compressive strength was enhanced with the increase in superplasticizer and slight reduction in strength was observed due to the high content of FA. It was concluded that the addition of NS improved the compressive strength and density of the mixes.

Mohseni et al. [31] examined the influence of nano-titanium (NT) in the cement composite partially replaced by RHA and found significant enhancement in the compressive strength compared to the control specimens. It is remarkably noted that the increased strength of mixtures with RHA of 10% with different curing periods was about 57 MPa with addition of PCE based superplasticizer, while there was a slight reduction in strength for RHA addition of 15% and beyond. The decrease in the strength was attributed to the high amount of RHA in the system which causes excess amount of silica to be leached out thereby resulting in decline of strength. With the incorporation of NT particles has a great influence on enhancement of strength. An increase in nano-particles up to 5% produced the compressive strength of 66 MPa in the mix with 10% RHA and this is considered as an optimal replacement level. The pozzolanic effect of RHA and nano-particles contributed to the compressive strength. In addition, the NT particles strengthened the gel that enabled stronger mixes.

They [31] also reported the ultrasonic pulse velocity (UPV) test results of the specimens; higher RHA and NT contents increased the UPV values. Even though, the specimens incorporated with RHA improved the UPV by about 8% compared to the control specimens, the addition of NT of 5% enhanced the pulse velocity significantly. The optimum content of RHA and NT was found significant at 15% and 5% respectively. In general, a high UPV indicates the good quality in cement-based materials. It was reported that the range of pulse velocity value of 3660–4575 m/s indicates good durability. All specimens achieved UPV values more than 3660 m/s. So, the mortar samples can be considered as durable with an incorporation of nano-materials as well as industrial by-products.

The authors [34] reported that the addition of POFA decreased the compressive strength with an optimum incorporation of 2%. Moreover, improved strength was found at elevated temperature of 1000 °C. They [27] also studied the addition of NT with FA based cement composite and reported reduced setting time.

Mukharjee and Barai [36] found that the setting time behavior was mostly associated with the fineness of cement for cement pastes specimens. When NS incorporated in the cement mixtures, the enhanced fineness improved the reactivity. In addition to that, NS particles perform as a nucleation sites and develop higher rate of hydration and consequently the setting time decreased significantly. Thus, NS addition to the cement paste was found more effective for improving the consistency and reduction of the setting time. The setting time of cement paste was considerably reduced since the NS has high water absorption characteristics.

The authors [20] studied on setting time characteristics of partially replaced silica fume based cement mortar and found that reduction in setting time for 1–2.5% incorporation of NS. It was mainly attributed to the more rapid development of hydration of cement in presence of NS. The NS incorporation leads to increase the production of CH even at early age when compared samples without nano addition. Therefore, a significant reduction in setting time was noticed in the mortar samples.

Similar findings were observed from the previous research works that showed an increase in NS particles reduced the setting time significantly [41,47] and this is one of the important characteristics for a repair material [48].

On flow behavior, significant improvement was reported in FA based cement composite with 2% of NS along with the enhancement in compressive strength; which was due to spherical shape of the fly ash particles as well as its high contents [45].

2.3. Durability behavior- nano incorporated cement replacement mortar/ paste

On the durability, the performance of cement mortar was enhanced with the incorporation of nano-materials. The chloride permeability on cement mortar incorporated with nano-materials such as NF, NA, NT, NS and NC had shown improvement to chloride penetration resistance. The apparent diffusion coefficients of chloride anion were reduced, DCI– were clearly interpreted and such improvement was found significant through the use of NS and NC [23]. The microstructural characterization analysis of NC incorporated mortar was analyzed and the total porosity and corresponding critical pore diameter were reduced compared to the control mortar. These significant differences were related to the change in distribution of pore size, also found that large pores capillary was decreased. Thus, the addition of NS influenced the critical pore size and significantly reduces the total porosity as well as pore size [33].

The authors [34] reported that the NA improved the durability of the silica fume based cement mortar. The naphthalene sulfonate based superplasticizer of 2% was used and found that the optimum content of NA is 2%. Mohseni et al. [40] reported that partially replaced FA-cement composite along with NS, NA and NT achieved a better performance with improved resistance against chloride
<table>
<thead>
<tr>
<th>Authors</th>
<th>Type of Nano material</th>
<th>Replacement material</th>
<th>Super-plasticizer</th>
<th>W/B ratio</th>
<th>Alkaline activator to Binder ratio</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yang et al. (2015) [58]</td>
<td>Nano-TiO₂</td>
<td>Slag, average particle size of 11.86 µm</td>
<td>–</td>
<td>0.4</td>
<td>0.4</td>
<td>Enhanced flexural and compressive strengths</td>
</tr>
<tr>
<td></td>
<td>20 nm to 100 nm</td>
<td>0 &amp; 0.5% used for all mixes</td>
<td></td>
<td></td>
<td></td>
<td>Compressive strength of 62.96 MPa (at 28 days)</td>
</tr>
<tr>
<td>Khater et al. (2015) [59]</td>
<td>Nano-clay (35–53 nm)</td>
<td>Granulate blast furnace slag (GGBFS)</td>
<td>0.27</td>
<td>0.27</td>
<td></td>
<td>The optimum nano-clay content was 1%</td>
</tr>
<tr>
<td>Gao et al. (2013) [60]</td>
<td>Nano-SiO₂</td>
<td>Metakaolin (MK)</td>
<td>–</td>
<td>–</td>
<td>0.97 &amp; 1.03</td>
<td>Improved compressive strength</td>
</tr>
<tr>
<td></td>
<td>(10 nm) SS = 670 m²/g</td>
<td>0, 1, 2, and 3 wt%</td>
<td></td>
<td></td>
<td></td>
<td>Compact microstructure</td>
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<td></td>
<td>0, 1, 1.5, 3, 5 and 7 wt%</td>
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<td>Improved compressive strength</td>
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<td>Reduced setting time</td>
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<tr>
<td>Adak et al. (2015) [63]</td>
<td>Nano Silver (20 to 50 nm)</td>
<td>FA (Class F)</td>
<td>–</td>
<td>–</td>
<td>0.57</td>
<td>Improved compressive strength</td>
</tr>
<tr>
<td>Nazari &amp; Riahi (2013) [64]</td>
<td>Nano-SiO₂ and Nano-Al₂O₃ (80 nm)</td>
<td>FA and RHA</td>
<td>–</td>
<td>–</td>
<td></td>
<td>Improved compressive strength</td>
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<tr>
<td></td>
<td>3 wt% used</td>
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<td>Prevention of early age cracking</td>
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<tr>
<td>Hassaan A et al. (2015) [66]</td>
<td>Nano Clay (&lt;13 µm)</td>
<td>FA</td>
<td>–</td>
<td>–</td>
<td>0.75</td>
<td>Improved compressive and flexural strengths</td>
</tr>
<tr>
<td></td>
<td>0, 1.0, 2.0, and 3.0 wt%</td>
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<td>Improved mechanical properties</td>
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<td>Denser microstructure</td>
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<td>Optimum content 2.0%</td>
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<td>High compressive strength</td>
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<td>Nano silica offers an extra nucleation sites for geopolymer formation</td>
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<td>The optimum content of 1%</td>
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<td>Improved mechanical properties</td>
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<td>Good workability with superplastician</td>
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<td>Compressive strength increased with nano clay up to 3%</td>
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<td>Homogeneous matrix developed</td>
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<td>Improved mechanical properties</td>
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<td>High strength observed at 2% NS (optimum dosage) 60 MPa at 28 days</td>
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<td>Good resistance against sulfuric acid attack</td>
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<td>More dense and less porous microstructure</td>
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<td>Optimum content is 0.5 wt%</td>
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<td>Increased compressive and flexural strengths</td>
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<td>Compressive Strength 55 MPa at 28 day</td>
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<td>Increased density and reduced porosity</td>
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<td>Flexural strength improved</td>
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<td>Produced a dense geopolymer paste</td>
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<td>Lower water absorption</td>
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<td>2.0% of nano-clay is the optimum</td>
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<td>Enhancement of compressive strength</td>
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<td>The optimum NaOH concentration of 8 M produced higher comp. strength</td>
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<tr>
<td>Abbasi et al. (2016) [70]</td>
<td>Carbon nanotubes</td>
<td>Metakaolinite</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>Increased compressive and flexural strengths</td>
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<tr>
<td></td>
<td>0, 0.5, and 1 wt%</td>
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<td>Compressive Strength 55 MPa at 28 day</td>
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<tr>
<td>Assaedi et al. (2016) [71]</td>
<td>Nano Clay (1.85 nm)</td>
<td>Low-calcium FA</td>
<td>–</td>
<td>–</td>
<td>0.75</td>
<td>Flexural strength improved</td>
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<td></td>
<td>0.1, 0.2, and 3.0 wt%</td>
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<td>Produced a dense geopolymer paste</td>
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<td>Surface area = 750 (m²/g)</td>
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<td>Lower water absorption</td>
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<td>2.0% of nano-clay is the optimum</td>
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<td>Enhancement of compressive strength</td>
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<tr>
<td>Nazari &amp; Riahi (2012) [72]</td>
<td>Nano-SiO₂ (80 nm)</td>
<td>FA and RHA</td>
<td>–</td>
<td>–</td>
<td>0.4</td>
<td>Reduced setting time</td>
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<tr>
<td></td>
<td>Nano-Al₂O₃ (80 nm)</td>
<td>Nano-SiO₂, Nano-Al₂O₃, and Nano-SiO₂</td>
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<td></td>
<td></td>
<td>Improved mechanical properties</td>
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<td></td>
<td>(NS) Surface area &gt; 800 (m²/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Good workability with superplastician</td>
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<tr>
<td></td>
<td>(NA) Surface area &gt; 10 (m²/g)</td>
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<td>Compressive strength increased with nano clay up to 3%</td>
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<td></td>
<td>Homogeneous matrix developed</td>
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<td>Improved microstructure</td>
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<td>Improved mechanical properties</td>
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<td>High strength observed at 2% NS (optimum dosage) 60 MPa at 28 days</td>
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<td>Good resistance against sulfuric acid attack</td>
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<td>More dense and less porous microstructure</td>
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<td>Optimum content is 0.5 wt%</td>
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<td>Increased compressive and flexural strengths</td>
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<td>Compressive Strength 55 MPa at 28 day</td>
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<td>Increased density and reduced porosity</td>
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<td>Flexural strength improved</td>
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<td>Produced a dense geopolymer paste</td>
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<td>2.0% of nano-clay is the optimum</td>
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<td>Enhancement of compressive strength</td>
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</table>
permeability. Madandoust et al. [49] investigated on mortar samples with partially replaced Portland cement by 25 wt% of FA. They used different nano-materials such as NS (15 nm), NF (60 nm) and nano-CuO (15 nm) up to 5 wt% of total binder; thus, the resulting mortar mixes showed denser microstructure with less pores. The chloride permeability decreased by 60%, 44% and 44%, correspondingly due to the addition of NS, NF and nano-CuO content of 3, 2 and 4 wt%, respectively.

Zahedi et al. [50] conducted an experimental investigation on cement mortar with partial replacement of RHA by about 5–20 wt% along with NS of 2.5 and 5 wt%. Based on rapid chloride migration test (RCMT) results, the chloride resistance decreased for both 2.5 and 5 wt% addition of NS specimens compared to control mix. Also, it was observed that the electrical resistance improved with increase of NS content in the mortar. The authors [51] investigated on cement mortar with partial replacement of FA and GGBS, NS, micro silica (MS) and found that the durability of specimens against sulfate attack significantly enhanced by the incorporation of nano and micro silica.

Mohseni et al. [52] examined on NT incorporated RHA based cement composite mortars. The average particle size of NT was 20 nm. It was found that the water absorption decreased drastically with the addition of RHA and NT. The electrical resistivity and rapid chloride penetration test (RCPT) test results revealed that an optimum content of 15% RHA and 5% NT provided a significant improvement towards resistance of chloride penetration.

Oltulu and Sahin [53] investigated pore structure analysis of cement mortars along with SF and different nano-materials. The average particle size of NS, NA and NF are 12 nm, 13 nm and 20–60 nm, respectively. The Mercury Intrusion Porosimetry (MIP) test results indicated that the pore volume of the mortar specimens significantly reduced due to the addition of nano-materials. Moreover, the pore volume reduction in mortar samples improved the physico-mechanical behavior and it was attributed to the filler effect of nano-materials. Further, the hydration process of cement also enhanced and produces calcium silicate and/or calcium aluminates.

3. Influence of nano-materials in geopolymer

An intensive research work is being conducted to enhance the performance of various construction materials and improvement of strength and durability to develop a sustainable geopolymer paste and mortar by incorporating various nano-materials. The details of the investigations and the outcome are summarized in Table 2. The NS, NT, NA, NC and CNT are the mainly used nano-materials in the geopolymer products to enhance the performance. The nano-materials such as NS and NA incorporated geopolymer improved the mechanical strength of the specimens compared to the geopolymer reference specimens and cement composites [54–57]. In addition, a denser microstructure due to
the pore structure modification by the incorporation of nanomaterials (NS and NA) [54] along with reduction in the setting time was reported [56].

3.1. Microstructural behavior of geopolymer mortar/paste

The authors [59] conducted an experimental study on microstructural behavior of geopolymer mortar with NC. An enhancement in compressive strength was noticed with 1% of NC additive on GGBS based geopolymer at 28 days of curing when compared with other mixes and this was mainly attributed to high amorphous geopolymer content. Thus, it resulted in the formation of compact microstructure. The optimum content of NC addition was found 1%. Moreover, the addition of gelenium ACE based superplasticizer in this system enhanced the geopolymer microstructure and lead to the development of high performance based geopolymer composite. On the other hand, Assaedi et al. [65] found that the addition of 2% of nano-clay particle is more effective that reduced the porosity in geopolymer composites resulting in denser geopolymer matrices. The authors [68] observed a homogeneous matrix with improved microstructure. The alkali activator of 3% NaOH and 3% Na₂SiO₃ solution were used for geopolymer sample preparation.

The use of NS by the authors [62] with NaOH and Na₂SiO₃ solution as alkali activator with a molar ratio of 1.5 had enhanced the compactness and microstructure of the geopolymer. It exhibited relatively a smaller porosity and also very high flexural strength with an optimum incorporation of 1% NS.
The microstructural behavior of geopolymer paste samples were analyzed by X-ray diffraction (XRD) test. The XRD patterns of FA and geopolymer pastes containing NS have been investigated (Fig. 6). The XRD patterns of the geopolymer pastes containing NS (Control, S1, S2, and S3) are comparable to that of FA. It was found from the XRD analysis that a large quantity of quartz and a few magnesioferrite. The concentration of quartz was increased because of the presence of additional amount of SiO₂. The amorphous phases were identified at a broad hump about 25–38° 2theta due to change of the amorphous constituent in the geopolymer system. The trends of XRD patterns (Fig. 6b) were found similar for paste samples with NA, NS and control [48].

Another XRD investigation has been conducted on NS incorporated FA based geopolymer mortar. The analysis of XRD for the reference mortar, geopolymer without NS and with 6% NS was studied. A few specific extra peak positions were prominent in the XRD image for geopolymer mortar with an addition of 6% NS. The crystalline quartz was found in the region of 26–32° 2θ, which was because of the development of crystalline composite in geopolymer matrices (Fig. 7). It was concluded that the strength of geopolymer sample with 6% of NS performed better than the...
geopolymer without NS (12M0) due to more crystalline compound existence in the geopolymer matrix [54].

Infrared spectroscopy study on the degree of development and cross-linking of the binder gel in the low-calcium alkali-activated materials was conducted. These gels were assumed to form by means of chemically heterogeneous formation which depends on the relative rates and sites at which gel nucleation as well as growth processes occur [73]. Also, the outcomes achieved by application of synchrotron infrared microscopy (Fig. 8) to a geopolymer derived by the reaction of geothermal silica and sodium aluminate measured after 28 days of curing, with and without 0.5 wt% of Al₂O₃ nano-particles [73].

The nucleation process was enhanced and lead to the development of an additional silica-rich phase in the early periods of the reaction, which leaves more amount of Al available and advances the early strength development of geopolymer. This later releases of more silica subsequently improves the final strength [73].

The infrared spectroscopy data was very much useful to identify the effectiveness of the nano-particles. The band of infrared spectroscopy has the spectra to show the results. It was found that a greater degree of homogeneity in the geopolymer gel for nano-material seeded sample [74]. The nanostructural characterization is very much essential in the development and optimization of a new class of environmentally beneficial materials. The key engineering parameters, in particularly strength development and permeability were determined at a nanostructural level, and hence it is essential that gel structures can be examined and employed at this level.

FTIR and SEM test results demonstrated that the incorporation of NT into the geopolymer accelerates its hydration process, resulting in more hydration products as well as denser microstructure. The 28-day compressive strength of about 63 MPa was achieved [58]. In SEM analysis, the geopolymer reaction was more perfect with NS (Fig. 9a) and NA (Fig. 9b) and formed a denser microstruc-
ture. This confirmed the improvement of the nano-material to the structure of geopolymer [75].

The XRD technique was used to analyze the crystalline phase composition of 3% NT in geopolymer as well as reference geopolymer. The XRD results of geopolymer with incorporation of TiO₂ illustrated crystalline phases with anatase (A), quartz (Q), albite (AB) and mullite (M). The increment of the concentration of crystal structure was detected and indicating that more formation of hydrates (Fig. 10). This result is the evident of acceleration of hydration as well as rate of hydration of nano-TiO₂ [76].

The XRD patterns clearly exhibited the effect of α-Al₂O₃ nanoparticles incorporation on microstructure characteristics of FA-based geopolymer (Fig. 11). It was found that quartz and mullite were the main crystalline phases in all specimens at the geopolymerization condition [77].

The microstructure of TiO₂ group (5% NT) (Fig. 12b) was noticed very denser and compact microstructure than reference sample (Fig. 12a). So, the outcome of SEM test reveals that when nano-TiO₂ added to the geopolymer, it makes the specimen more compact and very dense microstructure with less cracks. Significantly, the porosity was decreased due to the denser microstructure with high amount of nano-TiO₂ [76].

The SEM analysis for sample F4 (5 wt% α-Al₂O₃ addition), F5 (10 wt% α-Al₂O₃ addition) and F6 (no α-Al₂O₃ addition) respectively and micrographs are presented in Fig. 13 (a–c). This supports that appropriate α-Al₂O₃ addition in the development of geopolymerization that increases the compressive strength of the mix F4 [78].

The specimens were analyzed by FTIR and it was found that a decline in the wave number of the major Si–O–T stretching band which is normally observed with the reduction of geopolymer Si/Al ratio which is essential for the development of high performance geopolymer [77]. A suitable amount of α-Al₂O₃ addition (for example 5 wt%) could decrease the ratio of Si/Al in activator solution. Thus, it supports the geopolymerization and promotes a greater level of structural reformation of geopolymer gel which could be explicated through the higher ability of the gel components present in the high-alumina system [77].

Moreover, a high mechanical strength as well as low permeability of geopolymer was produced by means of alternative activators derived from modified NS. Also, the results of microstructural anal-

Fig. 15. SEM image with EDS spectra shows agglomerated nano silica particles [80].

Fig. 16. Interaction between NS and Ca(OH)₂ at the interface between paste and aggregate at age of 28 days determined by XRD [82].
ysis was proved that the geopolymer gel was more firmly connected with partially reacted FA particles in NS derived specimens and reduced porosity was also noticed [79].

The NS used of average particle diameter of 18–25 nm on FA-based geopolymer matrices containing NS up to 3.0% by weight enhanced the geopolymeric reaction and acted as voids-fillers, producing matrices with higher densities [80].

The XRD spectra of NS and FA indicate the diffraction pattern. The NS displays a complete amorphous (glass) phase. The physical structure and mechanical performance of geopolymer matrix were

Fig. 17. X-ray diffraction patterns of fly ash, GP and GPNC-3 [83].

Fig. 18. FTIR spectra of all samples [83].
influenced by the amorphous phase (Fig. 14) and the strength of geopolymer increased [80]. Similar research findings were reported by previous researcher [81]. The SEM images with energy dispersive spectroscopy (EDS) spectra of the matrix of geopolymer paste containing 3.0 wt% NS in dry mixing is shown in Fig. 15 and it indicates that the peak of agglomerated NS particles embedded in the matrix which can be clearly observed in the spectra of the particles. This is more evident for the strength development of the product [80].

The influence of NS on conventional cementitious materials as well as alkali-activated FA shows the interaction between NS and Ca(OH)$_2$ at the interface between paste and aggregate at age of 28 days as determined by XRD (Fig. 16). The improvement of ITZ in mortars with the addition of NS was evident [82].

In addition, during the hydration process, the Ca(OH)$_2$ crystals can group at ITZ between aggregates along with cement paste matrix that was found harmful and reduces the compressive strength. The development of Ca(OH)$_2$ crystals was reduced by NS incorporation in the mixtures due to high reactivity and specific surface area of nano-particles. Thus, nano-materials can reduce the amount of Ca(OH)$_2$ crystals accumulation and generate more CSH gel to fill the voids and improves the compactness of interfacial transition zone along with binding matrix [82].

The effect of NC on geopolymer products was investigated and it has two important phases: quartz and mullite. These crystalline phases generally are the resultant product of fly-ash based geopolymer paste. In geopolymeric reaction, these phases are not reactive and exist as unreactive and filler particles in the resultant geopolymer paste (Fig. 17). The mechanical properties of geopolymer matrix considerably get affected by this amorphous phase. It was clearly noticed that when the amorphous phase increases in geopolymer, it leads to enhancement of strength of the resultant products [83].

The FTIR spectra of all samples (Fig. 18) produced a strong peak at $\sim$1000 cm$^{-1}$ which relates to Si–O–Si asymmetric stretching vibrations at the geopolymerization reaction. The maximum level of geopolymerization among all samples was identified with the addition of 2 wt% of NC. The XRD and FTIR analyses found that a high amorphous phase in the geopolymeric system and geopolymerization reaction was improved after the incorporation of nano-clay to the paste. The SEM results confirmed that a very denser matrix with less unreacted FA particles subsequently adding up the nano-clay [83].

NS was incorporated to slag based geopolymer with 0, 0.5, 1 and 1.5 wt% to the binder. The superplasticizer of Gelenium ACE was used at 4% of dry weight to confirm the highest dispersion of the NS [57].

A clear crystalline quartz peak was noticed with the addition of 1.5% NS and also a broader amorphous glassy phases in the band was observed with 1 and 1.5% of NS. While the change of amorphous component takes place into crystalline one in the geopolymer products which indicates the glassy band turned to be intense. So there is a positive reflection on their microstructural and mechanical properties with increase of NS content (Fig. 19).
It was noticed from the Fig. 20 that when adding 1 & 1.5% of NS, the amorphous geopolymer structure develops a massive layer of geopolymer materials [57].

3.2. Mechanical/ workability behavior of geopolymer mortar/paste

A significant improvement in compressive strength was found in geopolymer with and without the addition of NS. The compressive strength of geopolymer mortars without NS produced higher strength than the reference cement mortar specimen at all curing periods. In geopolymer products, due to the alkali activation of the binder, all the mixtures exhibited higher compressive strength for both with or without NS. The incorporation of NS was found more significant up to 6% in geopolymer [54].

The denser matrix of the specimens enhanced higher compressive strength values since it depends on the physical structure of the samples. The compressive strength was improved with nano-materials in geopolymer matrix (Fig. 21). In a comparable study, it was examined that the incorporation of 1.0–2.0 wt% of NA and NS particles increased the geopolymeric reaction as well as geopolymer gel in the resultant geopolymer matrices. Hence, it increased the density and consequently improved the compressive strength of the resulting material [80].

On the other hand, Gao et al. [60] observed that a rapid development in early age strength and steady progress in later strength with a geopolymer incorporated NS. When the amounts of 0%, 1%, 2%, and 3% NS were added in the metakaolin based geopolymers, it improved the compressive strength at higher rate with an optimal amount of NS is 1%. From another study, it was found that NS incorporation up to 2% showed a positive effect on compressive strength at various curing periods of 3, 7 and 28 days, but further addition confirmed negative effects [84]. The authors [61] reported that the incorporation of NS improved the compressive strength with 1% of optimum amount on FA-silica fume based geopolymer.

The alkali activation of metakaolin (MK) based geopolymer with Na$_2$SiO$_3$ and NaOH alkaline solutions offered a high improvement in mechanical strength, increased bulk density and with less porosity for the addition of 1% of NS with solid-to-liquid ratio of about 1.03. The flexural strength also increased with the addition of NS into the geopolymer. It was found significant with an optimum addition of 1% for NS in line with strength and porosity [85]. Therefore, the identification of optimum content of nano-materials is
very important to achieve the respective high performance in strength as well as workability.

Another research on the use of RHA and FA as binders with NS or NA based geopolymers was conducted. The highest compressive strength of RHA and FA incorporated NS based geopolymers was found with an optimum NaOH of 8 M along with 3 wt% of NS. But, the effect of NA was comparatively lower on the strength compared to NS [55]. The authors [63] investigated on compressive strength characteristics of nano-silver incorporated FA based geopolymer. The alkali activator was the combination of Na$_2$SiO$_3$ solution and NaOH with a proportion of 1:1.75. A significant enhancement in the compressive strength was noticed with the use of nano-silver.

The microstructural and compressive strength characteristics on municipal solid waste incinerated FA (CFA–MSWIFA) based composite geopolymers were investigated. The results indicate that both NS and NA represented a good modification effect on geopolymer. The optimum contents of NS and NA were 1.5% and 2.0%, respectively. When the NS increased from 0.5%, the compressive strength was found to increase up to 1.5%. A poor dispersion of the nano-materials occur when the dosage is higher, which causes weak zone in the geopolymer system. The results showed that 1.5% of nano-SiO$_2$ was the optimum content to the composite geopolymer. The 28-day compressive strength of sample with 1.5% NS reached a maximum value of 57.4 MPa. Similarly, it was noticed in Fig. 22(b) that NA also has no obvious improvement in the early strength at the age of 3 days. Under the experimental conditions, the compressive strength of sample with an addition of 2.0% NA reached a maximum value of 56.8 MPa at the age of 28 days. This may be due to that the nano modifier that has large surface area with an increased reaction speed, and with the small size effect, the nano-materials filled the gaps making the structure more compact, thus increased the strength [75].

For FA based geopolymer samples with 5 wt% of NA was investigated and found that the compressive strength increased with an increase in NaOH concentration. The higher concentration of NaOH dissolves the raw materials and results in improved geopolymer gel formation in the system. Also, it was observed that the compressive strength increased with a decrease in Si/Al ratio. So, the Si/Al ratio was found essential since it is related with the degree of geopolymerization [77].

The dispersion of the nano-materials is very important criteria. The dispersion of nano-materials in uniform manner is the most significant issue for a successful preparation of a nano modified composite. Recent studies by researchers have explored many techniques to obtain a good dispersion system. To synthesize the nano-modified FA based geopolymer, Al$_2$O$_3$ nanoparticles were dispersed directly in the activating solution prior to mix with FA [86].

The authors [64,72] found that the incorporation of NS and NA improved the compressive strength of FA and RHA based geopolymer samples. The authors [66] examined on compressive strength characteristics of geopolymer samples with NS addition. It was found that the NS offered an extra nucleation sites to the formation of geopolymerization which lead to high compressive strength. Ridha et al. [67] reported that mechanical characteristics of FA and SF based geopolymer showed a better performance with 1% of NS.

The compressive strength was improved with slag based geopolymer specimens and the slag actively enhanced the geopolymeric structure. It was observed that the compressive

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**Fig. 23.** Setting time of geopolymer paste [48].

**Fig. 24.** Charge passed through fly ash based geopolymer mortar samples with 6% NS, without NS and cement mortar samples [54].
strength values increased significantly by adding the gelenium ACE based superplasticizer and also enhanced the workability in geopolymer specimens. The resultant product was obtained in a uniform composition that enhanced the strength [57].

The increase of NS content in high calcium FA based geopolymers decreased the setting time and increased the mechanical properties. The decrease in the setting time of geopolymer pastes with the incorporation of NS (Fig. 23), was attributed to the rapid activation by means of readily available free calcium ions from high calcium FA and lead to the formation of CSH. Also, the incorporation of NA seemed to have a similar behavior on setting time [48].

Gao et al. [60] investigated on the setting behavior of geopolymer paste. It was noticed that the initial and final setting times decreased significantly as the solid-to-liquid (S/L) ratio of geopolymer increased. The initial setting times of 0%, 1%, 2%, and 3% NS samples at the S/L ratio of 0.97 were 315, 295, 277, and 240 min, and their final setting times were 375, 360, 330, and 285 min, respectively. This result clearly state that adding nano-particles decrease the initial and final setting times, which could be due to the surface effect, small size, and high surface energy.

The authors [84] reported that flowability was reduced with the addition of NS and exhibited a major influence at even little amounts. A significant decrease in slump flow was noticed with the increase of NS. It was concluded that the slump flow was considerably reduced because of very finer particle size of NS. The authors [88] studied on strength and workability characteristics of geopolymer sample with nano-clay incorporation up to 3%. It was observed that a good workability and enhanced compressive strength when 4% of Gelenium ACE based superplasticizer addition to the geopolymer samples.

The usage of superplasticizer (polycrylic type) improved the mixture workability but the immediate addition of superplasticizer after the mixing water containing NS seemed to be inappropriate. This might be due to the direct interaction between superplasticizer and NS that reduces the reactivity of NS. In contrast, a delayed addition of the superplasticizer allowed the mixture ingredients to be dispersed uniformly without significantly affecting the NS reactivity [87].

At the same time, the workability behavior is very essential for a geopolymer mortar when incorporated with nano-materials. Besides, superplasticizer is also desirable for getting a high strength and flow in geopolymer based products. In contrast, the influence and benefits of polycarboxylate based superplasticizer on ordinary and blended cements are widely reported in the literature and found that good performance in workability as well as strength [88–90]. Based on the analysis on workability, a polycarboxylate-based superplasticizer was found more effective in FA based geopolymer. Thus, a better dispersion capability was achieved by the addition of superplasticizer that reduced the stiffness of the mix and improved the fluidity of the mixture [91].

The increase in NS and NA in the mix lead to a decrease in both initial and final setting times. Thus, an increase in the quantity of nano-particles tends to accelerate setting in high calcium FA systems [56].

The effect of NS and NA on setting time characteristics of geopolymers was investigated. The incorporation of NS as additive for FA based geopolymer showed reduction in the setting time and also NA slightly reduced the setting time of the geopolymer specimens [92].

Deb et al. [93] reported that the workability characteristic of geopolymer mixtures was good as the mixtures could be easily handled during casting of the samples. Large reduction in the setting times was achieved by incorporating NS. Similar effect was observed by another researchers [94].

Also, it was reported by SEM analysis that the addition of NS tends to form a dense microstructure. The NS contributed in pozzolanic reaction and also acted as filler materials for the development of compact microstructure with better interlocking morphology and produced a higher compressive strength [22,95,96].

Careful attention should be given while the mixing of nano-materials in the preparation of geopolymer because high specific surface of nano material that induces water demand in the mixture. Hence, the selection of appropriate superplasticizer is important to achieve the required workability. Nemotollahi and Sanjayan [97] investigated the effect of different superplasticizers such as naphthalene, melamine and modified Polycarboxylate based on the workability and strength of a class F fly ash geopolymer paste. The workability and strength of fly ash based geopolymer directly depends on the type of activator and the superplasticizer. It was reported that modified Polycarboxylate based SP was the most efficient type for the fly ash based geopolymer activated by NaOH and Na2SiO3. On the other hand, it was noticed that NS incorporated cement paste and mortar, the water demand was increased to retain its workability [98].

### 3.3. Durability behavior of geopolymer mortar/paste

Unlike cement mortar/paste, there are not many articles on the durability aspects of geopolymer mortar/paste. This review focused on those limited literatures and describes the durability behavior of geopolymer mortar/paste specimens such as water absorption, acid resistance, chloride penetration and carbonation resistance. The reduced amount of water absorption in geopolymer specimens due to the nano filler effect was reported; the optimum contents of NS and NA were 2% and 1%, respectively. Hence, the effect of nano-materials and geopolymeric reactions produce a dense matrix resulted in lower water absorption [92]. The authors [99] reported that noticeable decrease in water absorption value with increasing time of hydration mainly at later ages for all geopolymer mortars specimens with or without CNT and this is attributed to the formation of dense geopolymer structure and reduction in matrix porosity. The water absorption values decreased in the case of 0.1% CNT with geopolymer mortar when compared to the control specimens. The water absorption increased for geopolymer mortar specimens with further addition of CNT beyond 0.1%.

Deb et al. [69] examined the acid resistance of fly ash based geopolymer mortar with 2% NS. The geopolymer mortar specimens were immersed in 3% sulfuric acid solution for 90 days and then the changes in mass were recorded. It was reported that the mass loss after 90 days of acid exposure for fly ash only geopolymer specimen without NS was 5.41% as compared to 1.9% for the mix.
with 2% NS. Also, relatively more damages were observed at the corners of the specimens without NS and some minor erosion was noticed in case of NS incorporated specimens. Moreover, the strength loss of the specimens without NS ranged from 30% to 41% while that of the specimens with 2% NS ranged from 9% to 11% after 90 days of immersion. Therefore, the acid resistance of geopolymer mortars significantly enhanced with the addition of 2% NS.

In RCPT, a smaller amount of charge was passed in geopolymer mortar with 6% of NS. A high concentration of the charge was noticed in the case of geopolymer mortar without NS. The diffusion coefficient was less because of the existence of high content of crystalline compound in NS based geopolymer mortar. Thus it improved the durability of the resultant product (Fig. 24). The optimum content of 6% NS was found to achieve dense structure with high compressive strength [54].

The carbonation phenomenon is considered as critical in durability study of FA based geopolymer, since it is one of the most detrimental durability characteristics. These results exhibited as shown in Fig. 25 reveals the effect in carbonation resistance of geopolymer pastes with the addition of nano-TiO₂ particles. It was observed that the control specimens exhibited higher carbonation depth values than nano-TiO₂ incorporated samples and thus, nano-TiO₂ addition effectively improved the carbonation resistance. It was reported that the addition of nano-TiO₂ particles improved the microstructure and this in turn enhanced the carbonation resistance of geopolymer samples [76].

3.4. Bond/shear behavior of geopolymer mortar/paste

Based on the literature review conducted, there are not much structural behavior has been investigated on geopolymer mortar/-
Regarding the health effects of engineered nanoparticles [100]. Consumers, and government agencies have raised more concerns about occupational and environmental exposures during routine working but also possible accidental release of the nanomaterials. The risks occur not just due to inhalation and absorption; similarly, the effect of nano-particles could spread more easily and can be internalized in the body, making it difficult to remove. Consequently, researchers, manufacturers, workers, and government agencies have raised more concerns regarding the health effects of engineered nanomaterials. The evidence on health related issues through exposure to nanoparticles in human, particularly by respiration has been reported [101].

4. Nanomaterials – health issues and safety measures

The extensive use of nanomaterials in construction industries increases the exposure to nanoparticles. Due to their larger surface area per mass unit compared to that of larger particles, nanoparticles are capable of harming human body through inhalation and absorption; similarly, the effect of nano-particles could spread more easily and can be more biologically active. Consequently, researchers, manufacturers, consumers, and government agencies have raised more concerns regarding the health effects of engineered nanomaterials [100]. The evidence on health related issues through exposure to nanoparticles in human, particularly by respiration has been reported [101].

4.1. Health related issues on using nano-materials

The potential routes of human exposure of nanomaterials are mainly inhalation and absorption. The risks occur not just due to exposures during routine working but also possible accidental release of the nano-particles. The exposure assessment should be carried out when nano-materials are used for each activity [102]. The toxicity of nanomaterials depends on a number of factors such as particle size, surface area, crystallinity, surface chemistry, and particle aggregation/agglomeration tendency [103]. Srikant and Asmatulu [100] investigated the effects on the nano-particles on biological system. The nanosized particles of Al2O3 & TiO2 have highest toxicity than their micro-sized particles. The toxicity of macro ZnO was similar to nano ZnO. The toxicological hazard was assessed and observed that the nano-particles of ZnO, TiO2, CeO2 and Al2O3 have the effect due to high toxicity, oxidative stress, membrane damage and least cytotoxic, respectively.

It was also reported that these nano-particles can impair cell function in human. The exposure to nano-particles decreases cell area, cell proliferation, mobility and the individual particles can penetrate easily through the cell membrane in the absence of endocytosis. Once the particles enter the cell membrane, the particles are sequestered in vesicles, which with increasing incubation time, continue to fill up until they rupture. They are also known to cause neural toxicity, a pulmonary inflammation [104].

4.2. Safety measures to overcome the risks of exposure to nano-materials

The interaction of nano-particles with human is still a matter of investigation by researchers. There are many preventive measures and safety measures that have been evaluated by researchers [105,106] and social agencies [102,107]. The use of nano-materials is enormous in research and continues to expand and the information about potential health effects and exposure limits for these nano-materials is still being developed; hence the employers and researchers should use a combination of some of the suggested measures and best practices to control potential exposures [102,107].

The protective measures and actions are categorized under four aspects as engineering control, administrative controls, personal protective equipment (PPE) and medical screening and surveillance. In engineering control, the use of ventilated enclosures (e.g., glove box, laboratory hood, process chamber) is the suggested safety precaution while working with nano-materials. The ventilated enclosures must be equipped with high-efficiency particulate air (HEPA) filters. Where operations cannot be enclosed, local exhaust ventilation can be provided that is equipped with HEPA filters as these filters are designed to capture the impurity at the point of generation or release. In administrative controls, appropriate information that encourages the use of good hygiene practices must be provided and handwashing facilities are recommended. A detailed procedure can be established to address cleanup of nanomaterial spills and decontamination of surfaces to minimize the exposure. The use wet wiping and vacuum cleaners equipped with HEPA filters is strongly recommended with the prohibition of dry sweeping or use of compressed air for cleanup of dusts containing nano-materials [102,107].

PPE aspect is considered as a supplemental option to help support advanced levels of exposure control. PPE may comprise respiratory protection devices, dermal protection and eye protection. The researchers and workers must have been provided with appropriate PPE such as respirators, gloves and protective clothing. In the aspect of medical screening and surveillance, it is essential to make sure that proper medical screening is available and surveillance measure of workers exposed to nano-materials is implemented [102,107,108].

5. Conclusions and future work

Based on the review, it is concluded that the incorporation of nanomaterials in partially replaced cement composite and geopolymer mortar/paste has significant potential to be used as an effective building material in civil engineering field applications. The mass utilization of various industrial by-products is possible only by utilizing these wastes to produce geopolymer material. A number of fundamental characteristics have been explored and high strengths attained by many researchers. By means of nanotechnology, the reactivity as well as physical and mechanical properties of basic construction materials improved to a greater extent. So far, NS, NA, NT and nano-clay have been widely used in cement composite and geopolymer products. Many researchers investigated the effect of these nano-materials incorporation in geopolymers.

This comprehensive overview of the literature review mainly focused to observe the effect of nano-materials incorporation on partially replaced cement composite by industrial by-products and geopolymer mortar and paste.
1. The nanoparticles are considered as an additional source material or additives to increase the further reactivity of the cement based as well as geopolymer based binders. The nano-materials incorporation in both cement composite and geopolymer has performed better compared to the samples without nano-materials which is mainly attributed to the combined effects of pozzolanic activity and filler effect of nano-materials which forms denser microstructure. Therefore, the porous nature of major industrial by-product materials can be overcome by the incorporation of nano-materials.

2. Many research works have been conducted on partially replaced cement pastes and mortars by industrial by-products such as POFA, FA, RHA and SF with various nano-materials. But, the overall performance of the cement based products in terms of strength, workability and durability is comparatively much lower than the nano-materials incorporated geopolymers. At the same time, the partially replaced cement based paste and mortars specimens produced high strength and good workability due to the addition of nano-materials. The nano-particles of small size could fill up the pores in the mortar and paste and progresses greater strength. But, extremely smaller particles of nano-material lead to agglomeration problem due to poor dispersion of the nano-particles. So far, the effect of NS, NA and NT has been extensively investigated by many researchers in the partially replaced cement based paste and mortar.

3. In partially replaced cement based mortar and paste, the optimum content of nano-materials is 2–3% by the weight of binder materials. The effective particle size of the nano-materials such as NS, NA and NT is less than 25 nm which improved the mechanical strength, workability and durability. The physico-mechanical behavior enhanced due to the reduction in pore volume in mortar/paste specimens and the nano-materials plays a vital role in filler effect. Further, the hydration process of cement also enhanced and produces calcium silicate and/or calcium aluminate gels to enhance strength.

4. In partially replaced cement based mortars, the optimum content of nano-materials is 2–3% by the weight of binder materials. But, extremely smaller particles of nano-material lead to agglomeration problem due to poor dispersion of the nano-particles. So far, the effect of NS, NA and NT has been extensively investigated by many researchers in the partially replaced cement based paste and mortar.

5. For geopolymer based paste and mortar, the particle size of the nano-materials of more than 10 nm is effective in geopolymerization. The particle size of nano-materials used in geopolymer is generally larger compared to that of cement based products. Moreover, nano-particles dispersion is influenced positively by the alkaline solutions. In geopolymer mortar and paste, the optimum content of nano-materials is 1–2% by the weight of binder materials in most of the cases reviewed.

6. The FTIR results evidently represent the reduction in stretching band for geopolymer specimens with nano-materials incorporation. Hence it indicates the reduction of geopolymers Si/Al ratio which is essential for the development of high performance geopolymer.

7. The nano-materials reduce the flowability of the mix, because of the very finer particle size as well as significantly higher surface area of the nano-materials. Hence, the selection of size of nano-materials as well as superplasticizer is very essential. The superplasticizer influences the workability and strength of geopolymer mortar/paste. The modified Polycarboxylate (PCE) based superplasticizer was found better among the different types on the workability and strength.

8. The setting behavior of geopolymer paste significantly decreased as the solid-to-liquid (S/L) ratio of geopolymer increased. The initial setting time of 0% and 2% NS samples at an optimum S/L ratio of 0.97 were 315 and 240 min, and their final setting time were 375 and 285 min, respectively. This result clearly state that adding nano-particles decrease the initial and final setting time, which could be due to the surface effect, small size, and high surface energy as well as the optimum S/L ratio of geopolymer.

9. The exposure to nano-sized particles can cause human health impacts, particularly by respiration problems. The inhalation and absorption are the possible ways of human exposure to nano-materials. The toxicity of nano-materials depends on a number of aspects such as particle size, surface area, crystallinity, surface chemistry, and particle aggregation/agglomeration tendency. Though implementation of using personal protective equipments (PPE) is considered as mandatory, the strict adherence to engineering and administrative control measures in addition to medical screening and surveillance would enable the workers to use nano-materials safely.

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