

# Effect of Nano Materials on the Cement and Concrete Properties

R. Goyal<sup>1\*</sup>, V. K. Verma<sup>1,2</sup> and N. B. Singh<sup>1,2\*</sup>

<sup>1</sup>Department of Chemistry & Biochemistry, Sharda University, Greater Noida, Uttar Pradesh, India

<sup>2</sup>Research Development Cell, Sharda University, Greater Noida, Uttar Pradesh, India

\*Corresponding Authors: [goyalemba@gmail.com](mailto:goyalemba@gmail.com); [n.b.singh@sharda.ac.in](mailto:n.b.singh@sharda.ac.in)

**Abstract:** The importance of nanomaterials has been known for many years, but their usage in cement and concrete production is not accelerated and emphasized extensively. Cement and concrete are the base input material for the construction industry, and the industry is facing tremendous pressure to reduce its greenhouse gas emission (GHG); in 2021, the cement industry emitted about 7% GHG, equal to 2.5 Giga Ton gases of global GHG emission. It is estimated that by enhancing various supplementary cementitious materials (SCM), approximately 9% of the GHG emission of the cement industry can be reduced globally. It is also known that the cement hydration process is very sensitive and altered by many factors such as temperatures, amount of water, surface area, chemical properties, mineral phases, and type of SCM used. The alteration of hydration has adverse influences on cement and concrete performance. Nanomaterials can play an essential role by offsetting the adverse effects of high usage of SCMs in the cement, helping in increasing sustainability by reducing the intensity of CO<sub>2</sub>, and offering value-added features like self-sensing self-cleaning, antibacterial, anti-fungal, anti-algae, and anti-stain in the cement other than cement strength, which may promote the use of blended cement and replace ordinary Portland cement in the construction industry.

This comparative review aims to understand nanomaterials' advantages and challenges and compare their role and their influence on the cement hydration process based on the types of nanomaterials and their nature as Pozzolanic Nanomaterial (nano SiO<sub>2</sub>, nano MgO, Nano CaCO<sub>3</sub>, Nano Metakaolin), Metal oxide Nanomaterial (nano TiO<sub>2</sub>, nano CuO, nano ZnO, nano Al<sub>2</sub>O<sub>3</sub>, nano Fe<sub>2</sub>O<sub>3</sub>) and Carbon Based Nanomaterial (Carbon Nanotubes CNTs, Carbon Nano Fibers CNFs, Graphene Oxides).

**Keywords:** Carbon dioxide, Cement, Cementitious, Heat evolution, Hydration, Nanoparticles, Strength.

**Abbreviations:** CH - Calcium Hydroxide, C-S-H - Calcium Silicate Hydrate, NPs - Nanoparticles, OPC - Ordinary Portland Cement

## I. INTRODUCTION

After water, concrete is the material that is used the second most, and as cities and industries grow, so will concrete's consumption. Cement is a crucial component of concrete and is manufactured by heating large quantities of limestone at extremely high temperatures with fuels like coal, fuel oil, natural gas, tires, hazardous waste, petroleum coke, and virtually anything else that burns [1] and in this process, about 0.75-0.80 t CO<sub>2</sub> per ton of product emits and creates server threats to the environment [2-3].

While the cement industry is exploring various options such as using green power, hydrogen, switching to alternative energy sources, including carbon capturing storage and utilization, to get Net Zero emission targets, using the SCMs is the most effective and immediate solution to reduce the emission by 9% equal to 0.22 Giga Ton globally.

The use of various waste materials and SCMs offers many advantages in the cement and concrete performance, such as enhanced resistance to aggressive environments, lower heat of hydration, minimizing the risk of alkali-silica reaction, better ultimate strength of cement and concrete, and improved rheological properties of fresh mortar and concrete [4]. However, a few significant disadvantages are associated with using SCMs in the cement, such as prolonged initial and final setting time, delayed early strength development, and prolonged later strength. It could be a significant hesitation to use cement with SCMs as it will impact cost, higher labour cost, completion time, and delay in project delivery.

Several nanomaterials can be used to improve or modify the performance of the cement in the presence of supplementary cementitious materials. Using nanomaterials in ordinary Portland and blended cement enhances the cement performance, neutralizes the adverse effect of various supplementary cementitious materials, and adds valuable features to the cement [5]. Nanomaterials affect cement hydration, influencing cement performance, such as setting

time, early strength development, water requirement, and other parameters [6]. The significant and widespread applications of nanomaterials are given in Fig. 1 [7].

In this comparative review paper, the focus is on developing an understanding of the impact of various nanoparticles on cementitious systems with different natures, i.e., Pozzolanic Nanomaterial (nano-SiO<sub>2</sub>, nano-MgO, Nano-CaCO<sub>3</sub>, Nano-Metakaolin), Metal oxide Nanomaterial (nano-TiO<sub>2</sub>, nano-CuO, nano-ZnO, nano-Al<sub>2</sub>O<sub>3</sub>, nano-Fe<sub>2</sub>O<sub>3</sub>) and Carbon Based Nanomaterial (Carbon Nanotubes - CNTs, Carbon Nano Fibers - CNFs, Graphene Oxides) and their impact on hydration including cement performance.

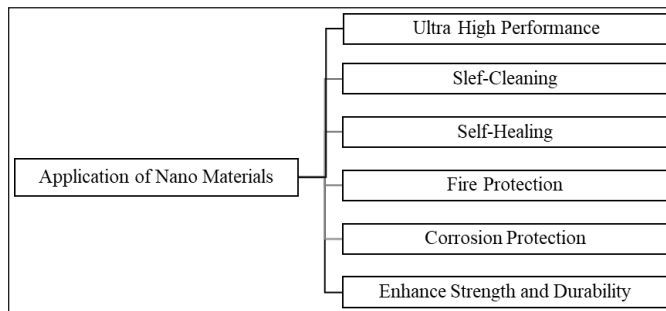


Fig. 1: Major Applications of Nanomaterials

## II. CEMENT HYDRATION MECHANISM

When cement comes in contact with the water hydration process starts immediately and generate heat, forming various hydrated product such as Calcium Silicate Hydrate CSH, Calcium Hydroxide Ca(OH)<sub>2</sub>, Calcium Sulfoaluminate ettringite (AFt), and Monosulphate (AFm) including a small portion of unreacted cement [8]. The hydrated products formation depends on the four major mineral phases Alite (C<sub>3</sub>S), Belite (C<sub>2</sub>S), tricalcium aluminate (C<sub>3</sub>A), and tricalcium aluminate (C<sub>4</sub>AF) available in the cement [9].

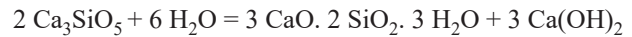
Hydration of cement is a highly complicated and sensitive process, and it depends on the types, characteristics, and concentration of materials used, their chemical and mineralogical composition, water, temperature, and environment, which effects the heat generation in the hydration process [10].

The hydration rate of cement, which is mainly responsible for cement performance, is greatly influenced by reactions at phase boundaries, nuclei development (nucleation), and mass movement from substrates to products, which happens mostly by diffusion and hydrate crystal development [11].

Adding nanomaterials influences the cement fineness and has a positive effect, such as increasing its responsiveness, enhancing strength at early ages, and decreasing bleeding. But same time has some negative effects such as higher water demand, high heat of hydration, high shrinkage, and higher reactivity with aggregates [5].

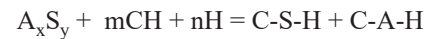
The water is required not only for the workability of cement but also to complete the cement's hydration reaction, which ultimately gives the properties of cement. It is observed that the water demand varies with varying the dose of nanomaterials in the cement [12].

In the presence of water and calcium hydroxide from cement hydration process, the nanomaterials, particularly those of pozzolanic character, react and produce extra calcium hydroxide to improve the performance of cementitious qualities. As seen below, the major hydration reaction [13].



(Where Ca<sub>3</sub>SiO<sub>5</sub> - Tricalcium silicate, H<sub>2</sub>O - Water, CaO · 2 SiO<sub>2</sub> · 3H<sub>2</sub>O - Calcium silicate hydrate, Ca(OH)<sub>2</sub> - Calcium hydroxide)

And the pozzolanic reaction is denoted as below,



(Where A<sub>x</sub>S<sub>y</sub> - Pozzolan, CH - calcium hydroxide, H - Water, C-S-H - calcium silicate hydrate, C-A-H - calcium aluminate hydrate)

Some nanoparticles act as efficient fillers for void filling and decrease the porosity, which can be assigned to accelerated hydration reaction rate and rapid accumulation of hydration products in the water-filled voids due to the nuclei effect [12]. Nanomaterials are categorized into two main groups (Table I) based on their activities during the hydration process [14].

TABLE I: CATEGORIES OF NANOMATERIALS BASED ON ACTIVITY

Activity	Type of Nanomaterials
Active	Nano-SiO <sub>2</sub> , Nano-CaCO <sub>3</sub> , Nano-Metakaolin, Nano-Al <sub>2</sub> O <sub>3</sub>
Inert	Graphite Nanoplatelet, Carbon Nanofiber, Carbon Nanotube, Graphene Oxide, Nano-TiO <sub>2</sub> , Nano-Fe <sub>2</sub> O <sub>3</sub>

## III. POZZOLANIC NANOMATERIALS

### A. Effect of Nano Silica (NS)

The Nano Silica (NS) is a silicon dioxides powder found in two varieties of nano-silica, P-type and S-type. It can also be manufactured by the concentration of silicon metals and ferrosilicon alloys in the cyclone through the vaporization of silica [15]. The primarily NS particles are characterized by their large surface areas, which promote the agglomeration of NS particles that cause poor dispersion [16] and may disrupt the hydration process.

The dispersion is a big challenge (Fig. 2), and to prevent agglomeration, it is crucial to know Nanoparticles' mixing chronological sequence. Mixing sequences could demonstrate

the impact on concrete strength according on the NS type, particle size, dosage level, mode of dispersion, kind of dispersant employed, and water-cement ratio chosen [16]. Additionally, improved dispersion accelerates the nucleation process by increasing the seeding effect [17].

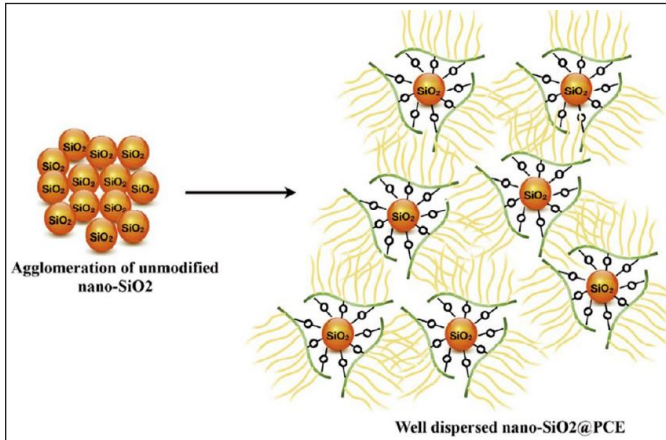


Fig. 2: Agglomeration and Dispersion of Nano SiO<sub>2</sub>

Due to the large fine particle size, the NS greatly impacts early hydration reactions. Using nano silica reduced free water and fluidity as both is closely related [18]. The hydration reaction process and induction time are sped up by early-age hydration heat evolution and kinetics of Portland cement with various doses of NS at various hydration temperatures. The nucleation effect of nano-silica in early-age hydration is enhanced by the nano-silica, which accelerates the rate of hydrate nucleation [19].

During the hydration process, microstructure densifies as nano-silica reacts quickly with calcium hydroxides (Ca(OH)<sub>2</sub>), produced from the cement mineral phase Alite, Belite, Aluminate, and ferrites, hydrations. Increasing the NS concentration in cement mortar reduces the setting time, which enhances cement performance [17]. However, the NS inhibits the flow due to the filler effect and enhances the stiffness of the Portland cement matrix via better packing; homogeneity in NS-incorporated cement mortar diminishes workability [20].

Fig. 3 depicts the graphic representation of the gelling mechanism. Some small particles filled the space between cement particles, which helped to increase the compactness of the gelling system [2].

The nanoparticles of silica also have high pozzolanic properties that help increase the performance of cement and concrete due to filling the voids and their reactivity [16, 21]. The calcium ions from calcium hydroxide react with NS grains and form C-S-H [16]. The concentration of calcium hydroxides decreases and enhances the cement hydration process [18]. The nano-silica enhances the cement's consistency, setting time, and compressive strength development with and without supplementary cementitious materials [15]. Using nano-silica reduces setting time and fluidity, but water demand increases

[20]. The decrease in the compressive strength with 4% nano silica content could be due to agglomeration of high nanoparticles from nano silica and loss of surface areas [22].

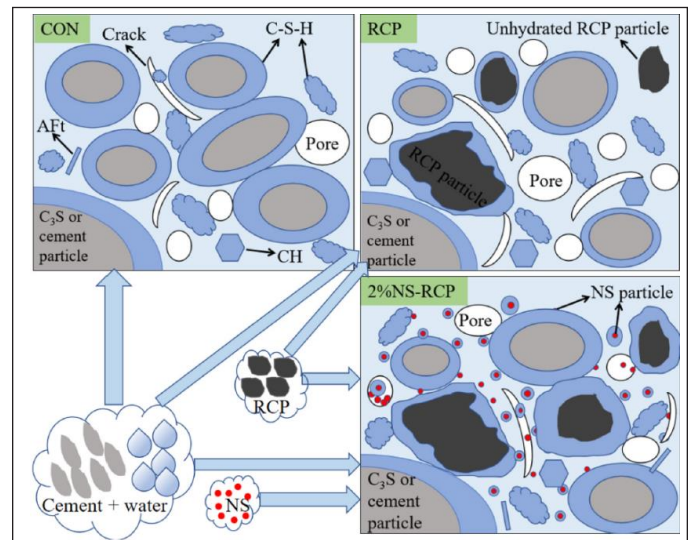


Fig. 3: Gelling Mechanism in the Presence of Nano SiO<sub>2</sub>

The early compressive strength of ordinary Portland cement pastes containing nano silica is higher at 7% of NS dose. It indicates that nano silica influences the early hydration process rather than the latter in cement pastes without fly ash [23]. Regardless of the type of cement used, the ideal replacement dosage of NS falls between 2 and 3% [16].

The cement with 25% flyash and nano-silica addition, later age compressive strength development keeps on improving, not decreasing like the cement paste without flyash with the increase of NS replacement. It can be because of NS's better dispersion and ability of less calcium flyash particles, which improves fresh mixture consistency [23].

All types of cement benefit from the nano-silica additions and the best-optimized dose of nanomaterials is found at 0.75% for OPC and Portland pozzolana cement (PPC) due to the formation of hydrated products as a result of the nucleation of the nano-silica due to its large surface area. However, over 365 days, it is observed that the strength rate for OPC and PPC with nano-silica additions is declining Fig. 4. It may be because the cement has increased C<sub>3</sub>S at the expense of C<sub>2</sub>S, whereas the rate decline rate is observed for PPC made of fly ash with nano-silica additions [24].

Steam curing can help minimize the effect of higher volume usage of supplementary cementitious materials (i.e., flyash FA) on blended cement hydration and compressive strength development [22]. With a high concentration of fly ash 40% in the blended cement with the use of nano-silica after 12 hours of steam curing, compressive strength is significantly increased by 40% by adding 3% of nano silica content but marginally reduced with 4% nano-silica content. The increase in compressive strength can be explained as a) smaller particles

of nano silica act as a seed for enhancing the hydration process, b) higher pozzolanic properties of NS and respond with calcium hydroxide to form CSH gel, c) occupying or filling the voids between fine and coarse particles and densify the paste [25], d) as fly ash also has pozzolanic characteristics, hydration of fly ash enhances in the existence of nano-silica, the mix of all above make the compact and dense microstructure which enhances compressive strengths of cement mortar [11].

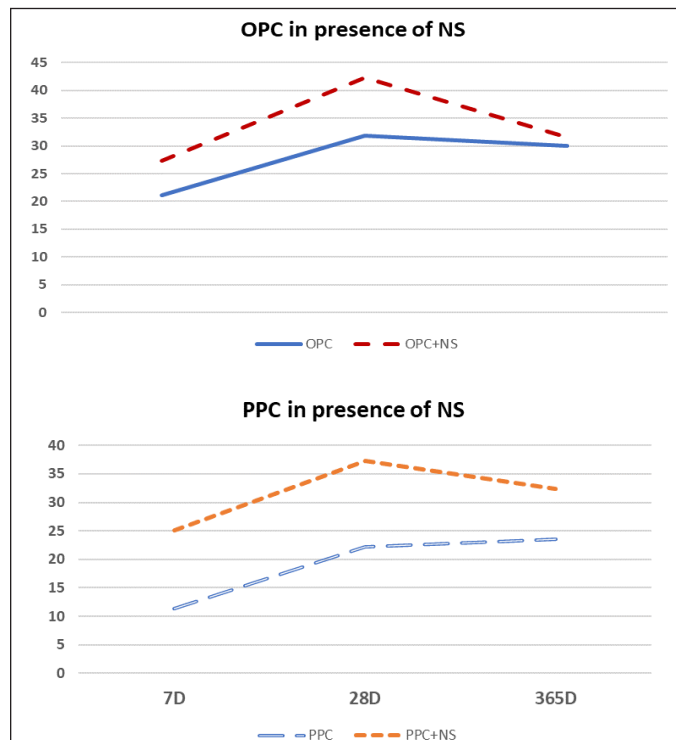


Fig. 4: Later Strength Development Trend of OPC and PPC with and without NS

In comparison to the control mix, the addition of 3% NS to FA cement concrete mix reduces the carbonation depth by 73% at 180 days. It is believed that this is because stable hydration products are created during pozzolanic reactivity, which prevents harmful ions from entering and increases the mix's durability [16].

The addition of more NS enhanced the cement mortar's resilience to sulfates. It is caused by the refinement of the pores, the reduction of pore connectivity brought about by NS, the restriction of sulphate ion entrance, and the amelioration of sulphate attack in the control sample [26].

With the addition of 2% nano-silica, Limestone Calcined Clay Cement ( $LC^3$ ) can dramatically increase its early compressive strength by 55.8%. But as age of curing increases, the influence of nano-silica to the system's strength decreases [27].

Nano-silica improved the electrical resistivity of the  $LC^3$

system, increasing its electrical resistivity. The adding of nano-silica increased the Ultrasonic Pulse Velocity (UPV) value of the system [27]. According to the accelerated carbonation trials, the carbonation degree of the  $LC^3$  system with 2% nano-silica was 11% and 7% lower than the  $LC^3$  system without nano-silica after 3 and 28 days of carbonation, respectively. It demonstrates how  $LC^3$ 's carbonation resistance is enhanced by the addition of nano-silica [27].

### B. Effect of Nano- $CaCO_3$

Cement is substituted with nano- $CaCO_3$ , the initial hydration of the cement is accelerated (Cao *et al.*, 2022), and the early development of the modulus of elasticity is boosted when the amount of nano- $CaCO_3$  used in the cement is raised. A considerable influence of the presence of nano- $CaCO_3$  particles on the hydration of  $C_3A$  and  $C_3S$  is seen, resulting in an increase of rate of setting and initial strength development in the cement [28].

The rapid growth of C-S-H may be seen when calcium carbonate nanoparticles are seeded on the surface of  $C_3S$  particles, which explains the improvement in mechanical characteristics seen with calcium carbonate nanoparticles [28]. The heat of hydration curves from the calorimetric confirms that the pastes with nano- $CaCO_3$  produce highest peaks in the heat of hydration curves due to the hydration of  $C_3S$ . It indicates that using nano- $CaCO_3$  accelerates the rate and degree of cement hydration [17].

The workability of nano- $CaCO_3$  mortars was somewhat lower than that of control cement mortars, and flow values decreased as nano- $CaCO_3$  content increased as partial substitution for cement. The 1% nano- $CaCO_3$  shows best compressive strength, 22% and 18% greater than the control mortar at 7 and 28 days, respectively. With a rise in nano- $CaCO_3$  content of more than 2%, the compressive strength steadily decreases, which is due to the aggregation of nano- $CaCO_3$  in the wet mix due to its advanced van der Waal's forces than cement can be linked to decreased compressive strength of mortars having high nano- $CaCO_3$  concentrations [29]. 1% nano- $CaCO_3$  had the highest flexural and compressive strengths at 7 and 28 days (108.4% and 108.3% greater than the control sample, respectively, as shown in Fig. 5 [5]. Nano- $CaCO_3$  usage should be 1%-2%; beyond this threshold, mechanical characteristics decrease. At room temperature, the pure cement paste had a structure that was more highly porous than the cement paste that had been altered with  $CaCO_3$  nanoparticles [30].

Adding nano- $CaCO_3$  increases the resistivity of all concrete types due to the improved packing and enhanced microstructure with a greater amount of hydration products [28]. The adding of nano- $CaCO_3$  improved scaling resistance of all types of concrete and lowered mass loss in the consumption of  $C_3A$  at early ages to form carboaluminates [28].

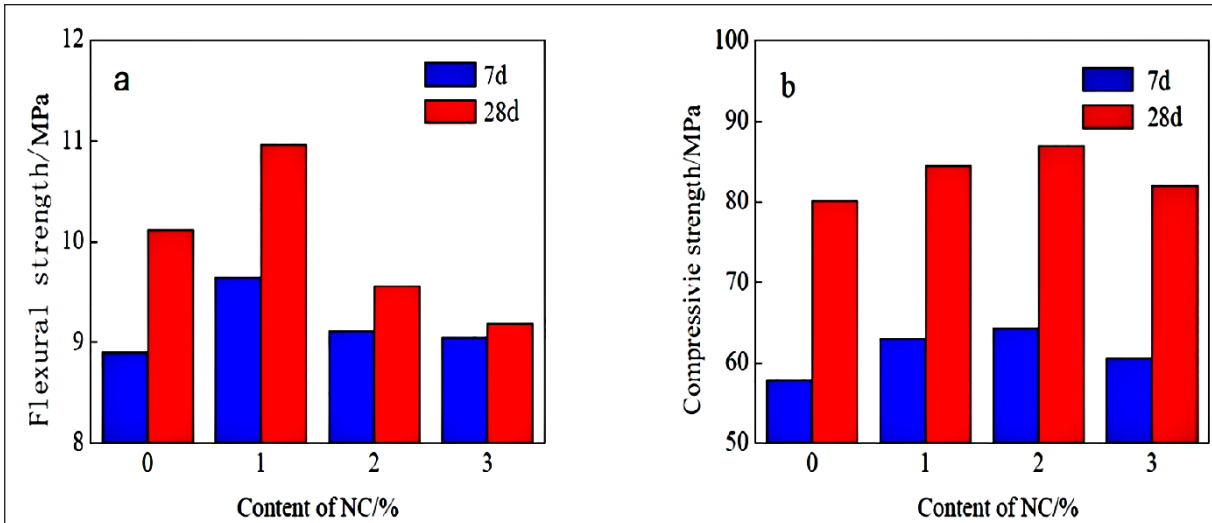


Fig. 5: Changes in Concrete's Flexural Strength (a) and Compressive Strength (b) After Adding Nano-CaCO<sub>3</sub>

### C. Effect of Nano-MgO

The strength of mortars compared with the blank sample, the compressive strength of the samples with 4% of nano-MgO at 28 days improved by 17.6%; it is due to the improvement in microstructure that occurred after nano-MgO integration. However, with the higher dosage of nano-MgO, more than 4%, the compressive strength of samples did not increase significantly at 28 and 365 days even after autoclaving, perhaps since the microstructure of the cement was disrupted through high-temperature autoclaving, micro fractures continued to develop, resulting in the deterioration of the mechanical characteristics of the mortar during the autoclaving process [31].

Magnesium oxide in the form of nanoparticles coarsened the microstructure, inhibited hydration, increased compressive strength, and reduced shrinkage with aging. The consistency of cement is affected by nano-MgO; as the amount of nano-MgO increases, the consistency of the cement gradually declines [32]. The nano-MgO also has the additional benefit of decreasing autogenous shrinkage and setting time as the nano-MgO concentration increases [33].

The greatest reduction in autogenous shrinkage was reported in mixtures containing 7.5% CaO and nano-MgO, which resulted in an 80% decrease in autogenous shrinkage after 28 days [31]. The hydration of nano-MgO occurs because of its agglomeration, resulting in the formation of a protective barrier that prevents water from accessing the agglomerates, and after autoclaving, the cement paste still has room to expand [34], and up to 70% of the extension increment is possible.

The Mg-rich hydro carbonate bridges and typical calcium-based self-healing compounds were discovered during microstructural examinations (calcite, portlandite, calcium silicate hydrates, ettringite) [31].

The samples with 6% nano-MgO SEM displayed notable broad cracks due to the volume expansion of MgO particles, resulting in expansion stress on the cement paste around them, resulting in the formation of microcracks in the cement [31].

### D. Effect of Nano Metakaolin (NMK)

Amorphous silica and alumina make up the substance known as metakaolin, which is layered long or hexagonally. Metakaolin is a highly reactive pozzolanic when compared to silica fume; metakaolin has several advantages, including the capacity to improve strength and durability through microstructure refinement, the ability to allow dependable water penetration, and the ability to be more cost-effective [35].

Although nano metakaolin is still a novel addition to concrete, the good influence of metakaolin in ultra-high-performance concrete and other types of concrete improves the concrete qualities; the addition of nano metakaolin to concrete has improved the compressive strength of mortar by about 8%-10% [36].

The increase of compressive strength is (67.3, 42.2, 26.3 & 11.29%) for ages (7, 28, 60 & 90) days respectively when using 3% NMK. While when using 5% NM this increase is (75.5, 55.8, 26.1 & 23.0%) for ages (7, 28, 60 & 90) days respectively. Finally, the increase is (86.6, 63.1, 35.5 & 23.0%) when using 10% NMK for ages (7, 28, 60 & 90) days respectively. Concrete's compressive strength increases as a result of increased Ca(OH)<sub>2</sub> consumption, enhanced pore refinement, micro-filling action, early strength growth, and stronger pozzolanic response [37].

As seen in Fig. 6, after being exposed to high temperatures, the compressive strength, tensile strength, and flexural strength of concrete containing 2% nanoclay increased. At 600 °C, the compressive strength, tensile strength, and flexural strength rose by 15%, 27%, and 106% respectively, in comparison to a control sample [5].

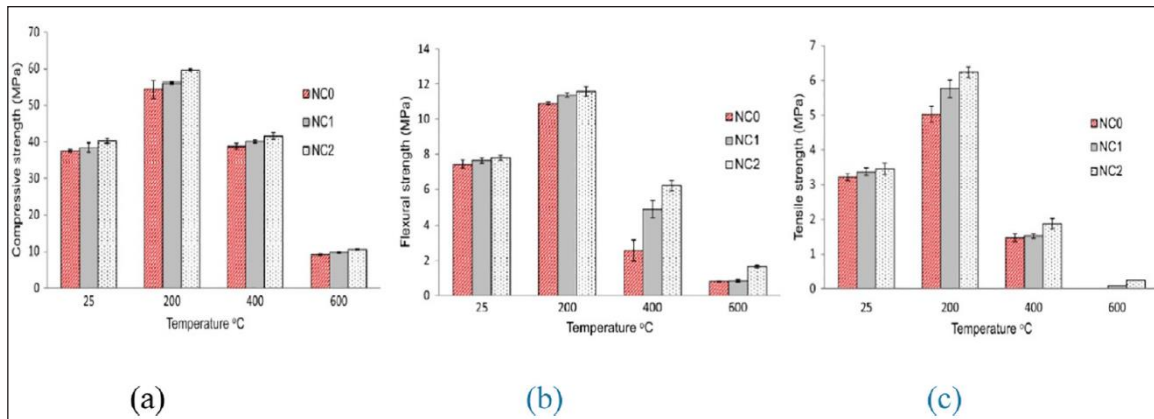


Fig. 6: Residue Properties of Nanoclay Concrete: (a) Compressive Strength, (b) Flexural Strength, (c) Tensile Strength

The optimal nano metakaolin replacement ratio (7%) results in an increase in compressive and flexural strength that, at the age of 28 days, reaches (82.6% and 59.5% respectively), when compared to the reference mix [38].

The elastic modulus is lowest when the water-to-binder ratio is 0.4 because the actual water-to-binder ratio of nano metakaolin cement mortar decreases for the small size of NMK. The hydration process of cement is influenced by moisture limitation, which causes a drop in elastic modulus in nano metakaolin cement mortar [35].

Because of its superior pore refinement, micro-filling action, and higher pozzolanic reaction, nano metakaolin has been found to greatly improve the properties of mortar mixes when it is used in greater amounts as a replacement [38].

#### IV. METAL OXIDE NANOMATERIALS

##### A. Effect of Nano $TiO_2$

The nano  $TiO_2$  increases the cement hydration process, eliminates the large pores and helps refine the pore's structure. The nano  $TiO_2$  also reduces water absorption and lowers dry shrinkage. The FTIR (Fourier transform infrared spectroscopy) study shows that the nano  $TiO_2$  enhances the growth of higher-intensity C-S-H and calcium hydroxides [39]. The high intensity of CSH is caused by the nanoparticle filling the pores. The higher density C-S-H and calcium hydroxides result in improved cement performance [40].

In the induction calorimetry curve of the hydration reaction process, the cumulative heat evolved increases as the concentration of cement with nano  $TiO_2$  increases, which confirms that the nucleation effect [41] with heterogeneous is more predominant than the concentration effect when inert  $TiO_2$  nanoparticles are put into the cement.

The water requirement of blended cement samples with nano  $TiO_2$  is greater than the reference specimen of cement [42]. It

is a higher wettability fineness and the quantity of water required with increasing concentration.

The main nano  $TiO_2$  based on photocatalytic cement or concrete [3] includes solving the air pollution problem, self-cleaning, and self-disinfection [41].

From the TG curves, cement pastes when heated between 120 °C and 900 °C, the water amount which cannot be evaporable as nano  $TiO_2$  is a non-hydraulic improver, and results show that the non-evaporable water volume enlarged with hydration duration, also indicating significant acceleration in hydration reactions based on substantially enhanced chemically bound water due to increasing dosing nano  $TiO_2$ . That confirms that role of nano  $TiO_2$  particles in hastening the initial hydration response rate and encouraging the formation and precipitation of hydration products can be established clearly [42].

The distribution of pore size and the total volume of the nanoparticles confirm that to have acted as efficient fillers for void filling. Additionally, a decrease in porosity can be assigned to accelerated hydration response rate and rapid accumulation of hydration products in the water-filled voids due to the presence of nano  $TiO_2$  nuclei [41]. The cement mortar's compressive strength indicates a significant increase at all periods by adding nano  $TiO_2$ . Because of the smaller sizes of particles and increasing concentration of nano  $TiO_2$ , it further enhanced the compressive strength [42].

Based on the evidence of the significantly enhanced degree of hydration, enhanced microstructure decreased porosity and other properties. Thus, the nano  $TiO_2$  acts as a photocatalyst to increase the cement paste performance and influence the hydration reaction of cement after adding it to cement-based materials because of its catalytic effects. Their mechanism indicated the nano  $TiO_2$  in providing a nucleation area for the hydration products accumulation but rendered them fine inert filler without any pozzolanic reactivity properties [3]. The addition of titanium dioxide nanoparticles to cement, including blended cement, increases the cement performance, such as

compressive strength and flexural strength, reduces the setting time, and adds photocatalytic self-cleaning properties [39].

Focusing on the hydration characteristics, microstructure, and dispersion of nano  $\text{TiO}_2$  integrated concrete, this overview of the development and application of nano  $\text{TiO}_2$  in the construction industry, as shown in Fig. 7 [41].

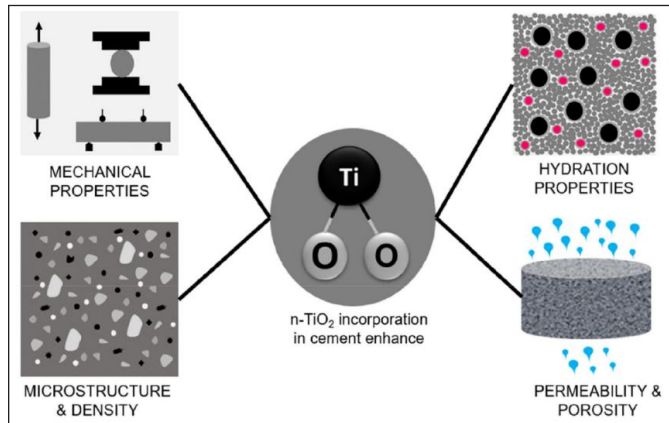


Fig. 7: Overview of the Mechanism of Nano  $\text{TiO}_2$

### B. Effect of Nano ZnO (NZ)

The two-fold properties of nano ZnO (NZ) with semiconductive and piezoelectric have been considered in several products. Including nano ZnO in cement has few adverse effects, including retarding effects on  $\text{C}_3\text{S}$  hydration, increased setting times, and reduced early compressive strengths. The cement paste shows a significantly delayed in setting times at all the duration (early and later) related to the control [43], this retarding effects on hydration through the development of a crystalline coating on hydrating species at the beginning of the hydration compound. Interestingly, the above adverse effects have been hypothesized to mainly 2 factors: the development of the lesser permeable coatings that have poisonous consequences, which are still controversial issues mainly because of conflicting results reported so far by research communities.

The incremental and cumulative heat flow curves attained from the isothermal calorimetry also indicated that compared with the blank R sample's hydration heat evolution process, adding nano ZnO significantly elongated the induction phase and increased the second hydration heat evolution peak due to exothermic reaction [43].

The compressive strength of NZ pastes distinctly reduces the initial age compressive strength of NZ pastes. When curing for 3 days, there is no compressive strength development of NZ control with 0.2% (CZ0.2) and 0.1% reduced to 44%. The compressive strength with 0.1% (CZ0.1) would be marginally higher than the control after 7 days of curing (CZ0). The compressive strength of CZ0.2 decreased as it cured, indicating that nanoscale ZnO had a super-retarded influence on cement hydration, as shown in Fig. 8 [44].

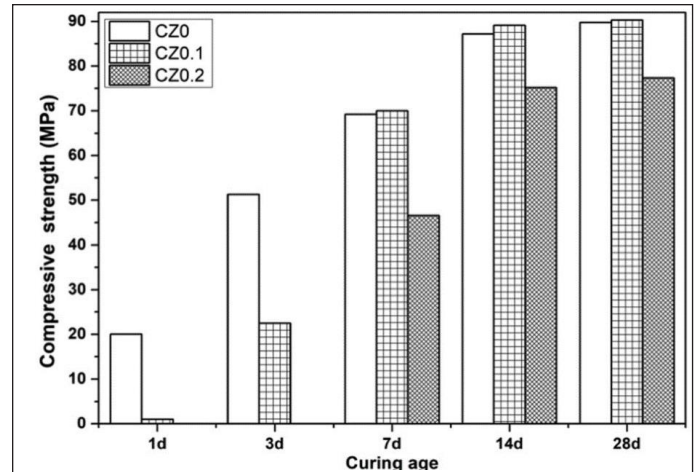


Fig. 8: Compressive Strength Behavior with Nano ZnO

The early flexural strengths also decline when adding the nano ZnO [43]. However, compressive and flexural strengths increased marginally after seven days of curing. There is no significant change in the cement compressive strengths with or without adding nano ZnO even after 72 hours of curing. The XRD examination also suggested that nano ZnO hindered the hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ ; with nano ZnO as an additional component, cement paste's initial compressive strength development was significantly reduced [43].

The said retarding effects using the layer mechanism and poison mechanism might be attributed to  $\text{Zn}^{2+}$  species for the duration of the cement hydration. Thus, in the existence of  $\text{Zn}^{2+}$ ,  $\text{Zn}(\text{OH})_2$  coating or  $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$  coating created on the cover of the cement particles then mix-up and the dissolution was hindered. Therefore, paste resistance decreased gradually. The layering process was prevalent during the dissolution phase, though the poisoning process was assumed to take over at the end of the induction phase. However, the explanation for why  $\text{Zn}^{2+}$  poisoned the nucleation sites is unknown or has no rationalization.

The release of ZnO nanoparticles after exposure to high temperatures was anticipated based on the marked decline in cement stability and disintegration. Though, the mechanical abrasion also resulted in the release of a specific amount of ZnO nanoparticles [45]. The higher amount influences the release of ZnO nanoparticles on microorganisms and exposure to weathering scenarios.

### C. Effect of Nano CuO (NC)

The using nano CuO particle up to a maximum replacement level of 2.0% improves mechanical characteristics significantly [46]. Because of the enhanced crystalline  $\text{Ca}(\text{OH})_2$  quantity at initial hydration stages, nano CuO as a partial substitute to 1% could speed up C-S-H gel development. The high activity of tiny nanoparticles raises the quantity of C-S-H gel considerably.

Furthermore, nano CuO can operate as nanofillers, restoring the pore structure of specimens by reducing pores. Because of the inappropriate dispersion of nanoparticles, increasing the CuO nanoparticles by more than 1% produces a loss in mechanical strength [47].

The incorporation of 3% NC, in the presence of SCMs such as metakaolin, increased the compressive strength as NC can act as a filler to increase the density of mortar resulting in a substantial decrease of porosity, acting as a nucleus and forming a powerful bond with C-S-H gel particles and act as Crystal-formation control and development process of  $\text{Ca}(\text{OH})_2$  crystals in the transition area can be reduced. CuO nanoparticles can provide interlocking effects between the slip planes, enhancing the toughness and flexural strengths of cement-based materials [48]. Because of the high activity of NC particles, the consumption of  $\text{Ca}(\text{OH})_2$  produced in cement hydration improves the characteristics of mixtures, including nanoparticles. Henceforth, the hydration of cement will be accelerated, and nanoparticles will diminish the size of more prominent pores.

The pore structure of CuO nanoparticle containing self compacting concrete is enhanced, and the content of all mesopores and macropores is reduced. The compressive strength of specimens increases as the nano CuO amount is raised to 4%. It is because extra hydrated products develop in the presence of CuO nanoparticles. Up to 4% CuO nanoparticles in conduction calorimetry testing could speed up the development of the first peak; the production of hydrated cement products is dependent on this process. According to thermogravimetric analysis, CuO nanoparticles might enhance the specimens' weight loss by up to 4% when partially added to cement paste. More weight loss could be due to the faster production of hydrated products in the existence of nano CuO (validated through XRD data) [46].

Nano CuO has the ability to heal itself; at 28 days of cure, 0.9% of nano-CuO was found to be 73% greater than the control sample [49].

#### *D. Effect of Nano $\text{Al}_2\text{O}_3$*

Substitution of nano alumina in the concrete, particularly UHPC (Ultra high-performance concrete), significantly impacts concrete qualities because it regulates the setting time. The purpose of nano  $\text{Al}_2\text{O}_3$  in cement is to reduce the time it takes for UHPC to start setting. Nano  $\text{Al}_2\text{O}_3$  in UHPC functions as a cement particle dispersion agent.

The effects of nano  $\text{Al}_2\text{O}_3$  on binary mixed concrete workability and compressive strength have been examined. The C-A-H (Limealumina-calcium sulfate) gel formation in concrete is the reason for utilizing  $\text{Al}_2\text{O}_3$  as a partial cement replacement. Alumina, which can be amorphous or glassy, acts at the pozzolanic component and reacts with calcium hydroxide, formed when calcium aluminates are hydrated. The amount of surface area accessible for reaction determines the rate of the pozzolanic reaction [50].

The addition of nano  $\text{Al}_2\text{O}_3$  does not result in forming a new crystalline phase within 7 days of curing, but it does result in forming a denser microstructure with bigger portlandite crystals within the cement matrix [51].

The raising of the  $\text{Al}_2\text{O}_3$  nanoparticle concentration up to 4%, due to its unique surface properties, finer grain sizes, and increased surface charge, the setting time is reduced, showing that nano  $\text{Al}_2\text{O}_3$  has a rapid hydration response rate than cement. The response rate is accelerated as these particles are extremely active and unstable [50].

The presence of nano  $\text{Al}_2\text{O}_3$  particles up to 1.5% demonstrates compressive strength enhancement, and further increase will reduce the compressive strength after curing. In the presence of a high amount of nano  $\text{Al}_2\text{O}_3$ , excess silica leaches out of the mix and causes a lack in strength since it substitutes part of the cementitious material while making no contribution to strength during the hydration process. Additionally, weak zones may be caused by flaws formed during the dispersion of nanoparticles. Consequently, as a result of the high responsiveness of nano  $\text{Al}_2\text{O}_3$  particles and the rapid consumption of  $\text{Ca}(\text{OH})_2$ , the high compressive strength of blended concrete is attributed to the quick utilization of  $\text{Ca}(\text{OH})_2$  that was generated in the cement hydration, particularly at initial stages.

The compressive strength of the nano  $\text{Al}_2\text{O}_3$  grains mixed concrete was much greater than the concrete compressive strength that did not contain nano- $\text{Al}_2\text{O}_3$  particles. The use of nano  $\text{Al}_2\text{O}_3$  particles to partially substitute cement in new concrete lowered the workability of the concrete, necessitating the use of a significant amount of superplasticizer.

#### *E. Effect of Nano-Ferric Oxide (Nano- $\text{Fe}_2\text{O}_3$ (NF))*

Nano- $\text{Fe}_2\text{O}_3$  (NF) enhances the characteristics of cement-based materials because of its enhanced dispersion, accelerated synthesis of CSH, and decreased porosity [5]. When nano- $\text{Fe}_2\text{O}_3$  is added to cement and concrete, the reaction between NF and calcium hydroxide forms the ilvaite compound has void-filling qualities similar to ettringite [5]. Calcium hydroxide and nano-ferric oxide react to produce nano-reinforcing materials that densify the microstructure of concrete [52]. Furthermore, when the nano- $\text{Fe}_2\text{O}_3$  % was raised, the workability of the composite was reduced [51], due to the nanoparticles' high surface area, which enhances water absorption and raises the water demand in the combination, a high dosage of superplasticizer is necessary [53].

The rate of exhausted heat can be increased, and the cement's hydration can be hastened by adding up to 4% NF. In addition to serving as a filler, NF also stimulates cement hydration, which reduces the  $\text{Ca}(\text{OH})_2$  crystals. The NF-modified samples filled the huge pores in the control specimen, creating a compact microstructure that showed the quick development of C-S-H gels [5]. It is possible to boost the compressive strength of concrete specimens by properly incorporating ferric oxide nanoparticles.

The compressive strength of nano-Fe<sub>2</sub>O<sub>3</sub> particles in blended concrete was much greater than that of concrete that did not contain nano-Fe<sub>2</sub>O<sub>3</sub> particles; also, the flexural tensile strength. The addition of NF encourages the formation of extra CSH nucleation sites, which quickens the growth of hydration products in the pores and voids of the concrete components.

The NF develops into a smart structural material with enhanced diagnostic capabilities that can self-monitor stress. In comparison to regular Portland cement concrete, concrete composite containing 2% NF displayed the highest gamma radiation shielding capacity [54]. Comparatively to mortars containing mixed nanosilica and NF, the capillary permeability of concrete decreases. An increase in electrical resistance decreases the likelihood of corrosion. With an increase in NF and a significant increase in electrical resistivity as concrete ages, particularly at lower water-to-binder ratios, the electrical resistivity value rises.

As calcium hydroxide and nanomagnetite combine to generate the Fe-ettringite phase, which decreases porosity, the fast chloride permeability decreases by 44% with the 2% NF and improves resistance to sulfate attack.

## V. CARBON-BASED NANOMATERIALS

### A. Effect of Carbon Nanotubes (CNTs)

The benefit of employing CNTs in UHPC is that it allows for greater flexibility, which raises the system's overall strength. Comparing CNTs to other nanomaterials, CNT is the most effective nanomaterial in enhancing flexibility and increasing strength in ultrahigh-performance computing. Most importantly, as compared to other nanomaterials, CNT has a smaller volume and size. The primary response of CNT in UHPC is to increase the tension and compression capacities of the material. Several nanostructured Carbon cement additives, polymeric cement additives, and ionic cement additives can be used to make high performance concrete (HPC), functionalized concretes, and coating materials. The most promising methods to make cement nanocomposites are CNT and graphene functionalization. With the addition of nanoparticles, cement for building construction can be made stronger [55].

CNT particles are prone to aggregation due to their huge specific surface area and the powerful van der Waals forces revealed by their aspect ratio. NaOH solution can be used to clean up the oxidation debris on the CNT surface, which enhances dispersion. By acting as a surfactant, the alkaline solution can enhance deagglomeration. Even a small amount of CNT greatly enhances the mechanical characteristics. CNT has both macro and micro effects, such as a bridging influence that aids in load transfer and crack prevention [56].

The MWCNT improves nucleation sites, notably in geopolymer concrete, and accumulation of MWCNT produces C-S-H gel, which has high hardness, improved pore topologies, control

over nanoscale fractures, and reduced drying shrinkage. Furthermore, the GGPC's extremely compact development is a result of the CNT's well-dispersed and homogeneous distribution, which significantly improves the particle packing of GGPC. These actions prevent fracture growth, bridge existing fractures, and prevent crack propagation, which increases resistance to chloride penetration [56]. The effects of CNTs on the UHPC are summarized in Fig. 9.

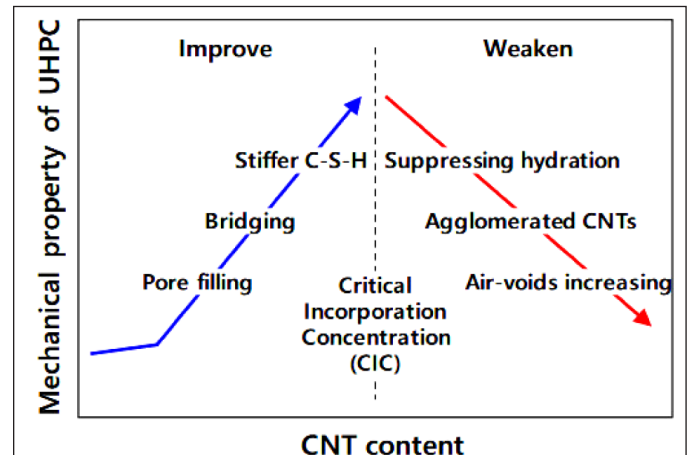


Fig. 9: The Effects of CNTs on Ultrahigh-Performance Concrete (UHPC) Performance

Carbon nanotubes are used as additions to various structural materials because of their exceptional mechanical characteristics, thermal conductivity, and electrical qualities. Carbon molecules have peculiar features that make them useful in various sectors, such as nanotechnology, electronics, optics, and various branches of materials science and technology. Carbon nanotubes have the potential to reduce the formation of nano-cracks in concrete [7]. The mechanical properties of C-S-H composites, such as the shear and bulk modulus, elastic constants, and Poisson ratio, are influenced by the carbon nanotubes (CNTs). The cement paste's overall performance was enhanced by the use of CNT, which increased cement paste stability and density [7]. The CNTs cement-based composites exhibit strain-sensing behavior; they can measure their electrical properties when subjected to external loads [51].

The amount of Multi wall CNTs, (MWCNTs) improves the compressive toughness of specimens with water curing. From the images from scanning electron microscope images, a large distribution network of MWCNTs, enhances the mechanical characteristics of concrete. With the addition of 0.25%, the MWCNTs amount showed the highest compressive strength by 39.2% compared to the specimen without MWCNTs.

The blend of 0.50% MWCNT + 0.50% Carbon Fiber offers abroad range of resistivity for load failure. This combination of nanofiller sensors has great electrical and mechanical qualities. Therefore 0.50% MWCNT + 0.50% carbon fiber has the optimal results for cement-based nanosensors. The 0.50% of MWCNT + 0.50% of CF is the best dose to attain better self-

sensing properties of concrete, and the sensor can be installed for the important location of buildings and infrastructures [57].

### B. Effect of Carbon Nano Fibers (CNF)

No substantial difference was observed in compressive strength by the addition of carbon nano fibers but, (CNFs) were able to counteract the effects of faults caused by pockets of (CNFs) agglomerates by acting as a buffer. Instead of acting as an activator or a delay of the hydration products, CNFs operate as a nanofiller and a crack-bridging agent in cement composites [58]. Pore size distribution experiments revealed that adding CNFs improved pore and increased pore capacity in the 6-200 nm pore size scale, indicating they enhanced pore refinement. Because of the presence of the (CNF) pockets, the water porosity increased even at modest (CNF) loading levels. Due to the obstruction caused by the (CNFs) and ball-like structures,

the total volume of accessible pores was reduced for the 2% CNF loading, resulting in more water penetration resistance for the material [59].

### C. Effect of Graphene-Based Nanomaterials - Graphene Oxide (GO)

Beginning with  $C_2S$ ,  $C_3S$ ,  $C_3A$ ,  $C_4AF$ , and  $CaSO_4 \cdot 2H_2O$ , the hydration process can be initiated by the oxygen-containing functional groups on the surface of GO reacting with these minerals to create growth points for hydrated crystals. From Fig. 10 [44] the vast number of oxygen-containing functional groups that are present on the surface of GO can serve as growth sites for the production of GO hydration goods and services, leading to the development of many gel pores during the hydration process [60].

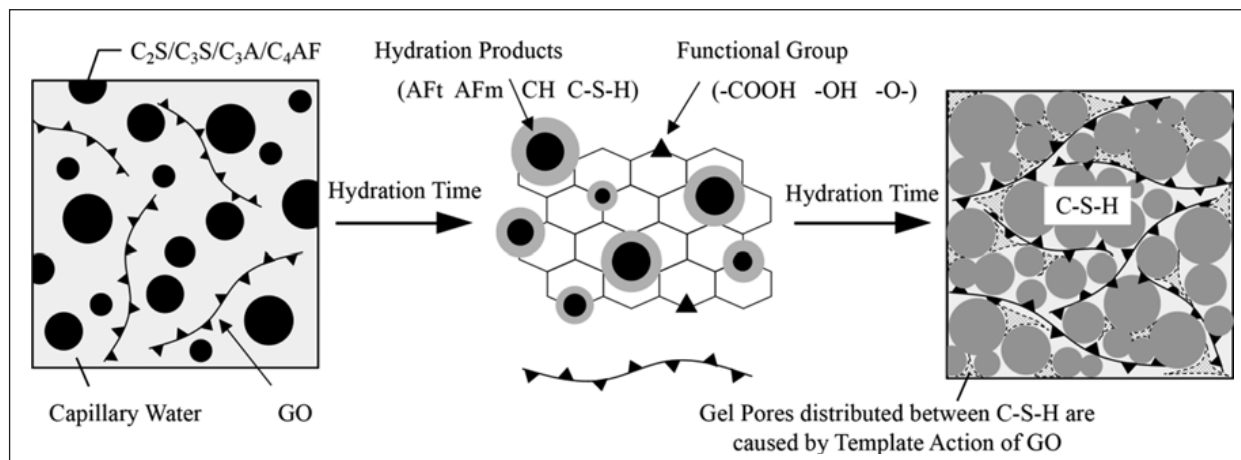


Fig. 10: Schematic Diagram of the Action Mechanism of GO

The nanostructures made of graphene exhibit outstanding electrical, mechanical, chemical, and thermal properties. Cement-based materials reinforced with graphene-based nanoparticles can therefore have improved structural strength and toughness, as well as the capacity to have self-cleaning surfaces and self-sensing capabilities [61].

The removal of the aggregation of GO in the pore solution was aided by the nano-silica coating on GO, which led to a finer surface structure and enhanced dispersion. The nano-silica-coated GO helped CSH build up and develop, which enhanced the cement mixture's microstructure and increased its macro-mechanical properties [61].

Compared to plain cement, the nano silica, Graphene oxide reinforced cement composites enhanced their compressive strength at curing times 1, 3, 7 and 28 days, up to 120.6%, 124.1%, 126.7% and 133% respectively. The compressive strengths of the GO-reinforced cement composites without nano

silica at curing times 1, 3, 7, and 28 days increase to 106.0%, 106.7%, 112.2% and 113.6% respectively. The compressive strengths of the cement mortars when the dosage is increased; both strengths initially gain in value and then drop in value [51].

Because the free water needed to hydrate the cement particles was sufficient under various w/c ratios at the first stage of hydration when there was no variation in reaction rates, the chemical shrinkage increases as the w/c ratio rises. Calcium hydroxide (CH) and calcium silicate hydrate (C-S-H) were two hydration products with comparable yields. The absolute volume shrinkage brought on by high-density hydration products was comparable to the chemical shrinkage that occurred during the hydration of cement. However, as the GO in the composite cement hydrated, the free water was gradually consumed, and the relative humidity gradually dropped [60].

The general characteristics of concrete and cement in the presence of different nanomaterials are outlined in Table II.

TABLE II: OVERALL PROPERTIES OF CEMENT AND CONCRETE IN THE PRESENCE OF VARIOUS NANOMATERIALS

Nano Materials	Properties in Cement and Concrete
Al <sub>2</sub> O <sub>3</sub>	Increased serviceability
CNT	Crack prevention Mechanical durability Decreases the concrete's final setting time
TiO <sub>2</sub>	Offers self-sensing and self-cleaning properties to concrete structures Increase degree of hydration Increases the abrasion resistance of concrete
SiO <sub>2</sub>	Rapid hydration, reinforcement of mechanical strength Contributes to reduced emissions of CO <sub>2</sub> , as the addition of 1 kg micro silica reduced almost 4 kg cement
CuO	Formability, corrosion Resistance
Fe <sub>2</sub> O <sub>3</sub>	Abrasion-resistant Increased compressive strength
Clay	Increased surface roughness and Compressive strength
GO	Enhancing impermeability, freeze thaw resistance, and CO <sub>2</sub> resistance Enhancing impermeability and chloride ion resistance, chloride ion resistance, and sulfuric acid and hydrochloric acid resistance

## VI. CONCLUSION

Nanomaterials are utilized in regular Portland cement to compensate for each ingredient's shortcomings, provide advantages of one or more of the others, and improve the product qualities of cement-based materials. Nanomaterials can change the fundamental of cement properties to improve their physical and chemical application capabilities, including fresh properties, microstructure, mechanical, and durability. The microstructure of concrete is improved, internal voids are decreased, and the durability of concrete is increased by the use of nanoparticles. Most of the problems can be overcome by using concrete that contains the right ratios of a variety of nanomaterials. Dispersion is the greatest obstacle to the effective use of nanomaterials. An emerging area of research is the usage of nanoparticles in concrete. Adding nanoparticles to concrete could enhance the environment because they can make different types of durable concrete. Supplementary cementitious material has sluggish early hydration product development; adding nanoparticles can overcome drawbacks. By reducing

the fundamental size of concrete structures and lowering CO<sub>2</sub> emissions, the inclusion of nanoparticles to the concrete mix transforms concrete into an environmentally friendly building material. The cost of nanoparticles is a topic of interest; the effect of nanomaterials on construction needs to be investigated along with economic analysis.

*Data Availability Statement:* The authors confirm that the data supporting the findings of this study are available within the article.

## REFERENCES

- [1] S. P. Dunuweera, and R. M. G. Rajapakse, "Review article: Cement types, composition, uses and advantages of nanocement, environmental impact on cement production, and possible solution," *Advances in Materials Science and Engineering*, vol. 2018, 2018, Art. no. 4158682, doi: <https://doi.org/10.1155/2018/4158682>.
- [2] X. Liu, L. Liu, K. Lyu, T. Li, P. Zhao, R. Liu, Z. Zuo, F. Fu, and S. P. Shah, "Enhanced early hydration and mechanical properties of cement-based materials with recycled concrete powder modified by nano-silica," *Journal of Building Engineering*, vol. 50, p. 104175, 2022, doi: <https://doi.org/10.1016/j.jobbe.2022.104175>.
- [3] A. M. Castro-Hoyos, M. A. Rojas Manzano, and A. Maury-Ramírez, "Challenges and opportunities of using titanium dioxide photocatalysis on cement-based materials," *Coatings*, vol. 12, p. 968, 2022, doi: <https://doi.org/10.3390/coatings12070968>.
- [4] A. Khan, M. A. Sikandar, M. T. Bashir, S. A. A. Shah, B. Zamin, and K. Rehman, "Assessment for utilization of tobacco stem ash as a potential supplementary cementitious material in cement-based composites," *Journal of Building Engineering*, vol. 53, p. 104531, 2022, doi: <https://doi.org/10.1016/j.jobbe.2022.104531>.
- [5] J. A. Abdalla, B. S. Thomas, R. A. Hawileh, J. Yang, B. B. Jindal, and E. Ariyachandra, "Influence of nano-TiO<sub>2</sub>, nano-Fe<sub>2</sub>O<sub>3</sub>, nanoclay and nano-CaCO<sub>3</sub> on the properties of cement/geopolymer concrete," *Cleaner Materials*, vol. 4, p. 100061, 2022.
- [6] S. Du, J. Wu, O. AlShareedah, and X. Shi, "Nanotechnology in cement-based materials: A review of durability, modeling, and advanced characterization," *Nanomaterials*, vol. 9, p. 1213, 2019, doi: <https://doi.org/10.3390/nano9091213>.
- [7] H. Saleem, S. J. Zaidi, and N. A. Alnuaimi, "Recent advancements in the nonmaterial application in concrete and its ecological impact," *Materials*, vol. 14, p. 6387, 2021, doi: <https://doi.org/10.3390/ma14216387>.
- [8] K. Scrivener, A. Ouzia, P. Juilland, and A. K. Kunhi Mohamed, "Advances in understanding cement

- hydration mechanisms,” *Cement and Concrete Research*, vol. 124, p. 105823, 2019.
- [9] D. C. Chu, J. Kleib, M. Amar, M. Benzerzour, and N. Abriak, “Determination of the degree of hydration of Portland cement using three different approaches: Scanning electron microscopy (SEM-BSE) and Thermogravimetric analysis (TGA),” *Case Studies in Construction Materials*, vol. 15, p. e00754, 2021.
- [10] T. Dorn, O. Blask, and D. Stephan, “Acceleration of cement hydration - A review of the working mechanisms, effects on setting time, and compressive strength development of accelerating admixtures,” *Construction and Building Materials*, vol. 323, p. 126554, 2022, doi: <https://doi.org/10.1016/j.conbuildmat.2022.126554>.
- [11] L. G. Li, Z. H. Huang, J. Zhu, A. K. H. Kwan, and H. Y. Chen, “Synergistic effects of microsilica and nano-silica on strength and microstructure of mortar,” *Constr. Build. Mater.*, vol. 140, pp. 229-238, Jun. 2017, doi: <https://doi.org/10.1016/j.conbuildmat.2017.02.115>.
- [12] G. Singh, and B. Saini, “Nanomaterial in cement industry: A brief review,” *Innov. Infrastruct. Solut.*, vol. 7, p. 45, 2022, doi: <https://doi.org/10.1007/s41062-021-00649-z>.
- [13] C. O. Nwankwo, G. O. Bamigboye, I. E. E. Davies, and T. A. Michaels, “High volume Portland cement replacement: A review,” *Construction and Building Materials*, vol. 260, p. 120445, 2020.
- [14] D. Y. Yoo, T. Oh, and N. Banthia, “Nanomaterials in ultra-high-performance concrete (UHPC) - A review,” *Cement and Concrete Composites*, vol. 134, p. 104730, 2022, doi: <https://doi.org/10.1016/j.cemconcomp.2022.104730>.
- [15] A. A. Raheem, R. Abdulwahab, and M. A. Kareem, “Incorporation of metakaolin and nanosilica in blended cement mortar and concrete - A review,” *Journal of Cleaner Production*, vol. 290, p. 125852, 2021, doi: <https://doi.org/10.1016/j.jclepro.2021.125852>.
- [16] K. Gayathiri, and S. Praveenkumar, “Influence of nano silica on fresh and hardened properties of cement-based materials - A review,” *Silicon*, vol. 14, pp. 8327-8357, 2022, doi: <https://doi.org/10.1007/s12633-021-01598-z>.
- [17] Y. Sargam, and K. Wang, “Influence of dispersants and dispersion on properties of nano silica modified cement-based materials,” *Cement and Concrete Composites*, vol. 118, p. 103969, 2021.
- [18] H. Sun, X. Zhang, P. Zhao, and D. Liu, “Effects of nano-silica particle size on fresh state properties of cement paste,” *KSCE Journal of Civil Engineering*, vol. 25, no. 7, pp. 2555-2566, 2021, doi: <https://doi.org/10.1007/s12205-021-0902-3>.
- [19] S. Bai, X. Guan, and L. Guoyu, “Early-age hydration heat evolution and kinetics of Portland cement containing nano-silica at different temperatures,” *Construction and Building Materials*, vol. 334, p. 127363, 2022.
- [20] R. Garg, R. Garg, M. Bansal, and Y. Aggarwal, “Experimental study on strength and microstructure of mortar in presence of micro and nano-silica,” *Materials Today: Proceedings*, vol. 43, part 2, pp. 769-777, 2020, doi: <https://doi.org/10.1016/j.matpr.2020.06.167>.
- [21] N. B. Singh, M. Kalra, and S. K. Saxena, “Nanoscience of cement and concrete,” *Materials Today: Proceedings*, vol. 4, no. 4, part E, pp. 5478-5487, 2017. [Online]. Available: [www.materialstoday.com/proceedings](http://www.materialstoday.com/proceedings)
- [22] M. Baoguo, M. Junpeng, T. Hongbo, L. Hainan, L. Xiaohai, J. Wenbin, and Z. Ting, “Effect of nano silica on hydration and microstructure characteristics of cement high volume fly ash system under steam curing,” *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, vol. 34, pp. 604-613, 2019, doi: <https://doi.org/10.1007/s11595-019-2094-y>.
- [23] A. Ehsani, M. Nili, and K. Shaabani, “Effect of nanosilica on the compressive strength development and water absorption properties of cement paste and concrete containing fly ash,” *KSCE Journal of Civil Engineering*, vol. 21, no. 5, pp. 1854-1865, 2017, doi: <https://doi.org/10.1007/s12205-016-0853-2>.
- [24] M. Ghosal, and A. K. Chakraborty, “Impact of nano silica on the cementitious systems of built environment,” *Materials Today: Proceedings*, vol. 65, part 2, pp. 758-763, 2022.
- [25] R. Abhishek, and R. R. Nayaka, “Overview on evaluation of the mechanical, durability properties and microstructure of nano-silica assimilated cement composites (Nano SAC),” *Materials Today: Proceedings*, vol. 58, pp. 1431-1435, 2022.
- [26] Q. Huang, X. Zhu, L. Zhao, M. Zhao, Y. Liu, and X. Zeng, “Effect of nano silica on sulfate resistance of cement mortar under partial immersion,” *Constr Build Mater*, vol. 231, p. 117180, 2020, doi: <https://doi.org/10.1016/j.conbuildmat.2019.117180>.
- [27] R. S. Lin, S. Oh, W. Du, and X. Y. Wang, “Strengthening the performance of limestone-calcined clay cement (LC<sup>3</sup>) using nano silica,” *Construction and Building Materials*, vol. 340, p. 127723, 2022.
- [28] L. Poudyal, K. Adhikari, and M. Won, “Nano calcium carbonate (CaCO<sub>3</sub>) as a reliable, durable, and environment-friendly alternative to diminishing fly ash,” *Materials*, vol. 14, p. 3729, 2021, doi: <https://doi.org/10.3390/ma14133729>.

- [29] S. W. M. Supit, and F. U. A. Shaikh, "Effect of nano-CaCO<sub>3</sub> on compressive strength development of high-volume fly ash mortars and concretes," *Journal of Advanced Concrete Technology*, vol. 12, pp. 178-186, 2014.
- [30] F. Shaikho, and S. Supit, "Mechanical and durability properties of high volume fly ash (HVFA) concrete containing calcium carbonate (CaCO<sub>3</sub>) nanoparticles," *Constr Build Mater*, vol. 70, pp. 309-321, 2014.
- [31] Y. Ye, Y. Liu, T. Shi, Z. Hu, L. Zhong, H. Wang, and Y. Chen, "Effect of nano-magnesium oxide on the expansion performance and hydration process of cement-based materials," *Materials (Basel)*, vol. 14, no. 13, p. 3766, 2021, doi: <https://doi.org/10.3390/ma14133766>.
- [32] P. P. Giannakopoulou, A. Rogkala, P. Lampropoulou, M. Kalpogiannaki, and P. Petrounias, "Evaluation of cement performance using industrial byproducts such as nano MgO and fly ash from Greece," *Appl. Sci.*, vol. 11, p. 11601, 2021, doi: <https://doi.org/10.3390/app112411601>.
- [33] R. Polat, R. Demirboğça, and F. Karagöl, "The effect of nano-MgO on the setting time, autogenous shrinkage, microstructure and mechanical properties of high performance cement paste and mortar," *Mag. Concr. Res.*, vol. 156, pp. 208-218, 2017.
- [34] T. Zhang, B. Ma, H. Tan, H. Qi, and T. Shi, "Effect of sodium carbonate and sodium phosphate on hydration of cement paste," *Journal of Building Engineering*, vol. 45, p. 103577, 2022, doi: <https://doi.org/10.1016/j.jobe.2021.103577>.
- [35] G. Xiaoyu, F. Yingfang, and L. Haiyang, "The compressive behavior of cement mortar with the addition of nano metakaolin," *Nanomaterials and Nanotechnology*, vol. 8, 2018, doi: <https://doi.org/10.1177/1847980418755599>.
- [36] M. M. S. Norhasri, M. S. Hamidah, and A. M. Fadzil, "Applications of using nano material in concrete: A review," 2017, doi: <http://dx.doi.org/10.1016/j.conbuildmat.2016.12.005>.
- [37] S. A. Al-Mishhadani, A. M., Ibrahim, and Z. H. Naji, "The effect of nano metakaolin material on some properties of concrete," *Diyala Journal of Engineering Sciences*, vol. 6, no. 1, pp. 50-61, 2013.
- [38] M. A. Al-Wahab Ali, M. J. Kadhim, and I. F. Nasser, "Some properties of cement mortar incorporating micro and nano-metakaolin materials," *Materials Science Forum*, vol. 1021, pp. 231-240, 2021, doi: <https://doi.org/10.4028/www.scientific.net/msf.1021.231>.
- [39] A. T. Akono, "Effect of nano-TiO<sub>2</sub> on C-S-H phase distribution within Portland cement paste," *J Mater Sci*, vol. 55, no. 11106-11119, 2020, doi: <https://doi.org/10.1007/s10853-020-04847-5>.
- [40] E. Grebenişan, A. Hegyi, A. V. Lăzărescu, H. Szilagy, and C. Florean, "Influence TiO<sub>2</sub> nanoparticles addition on the physico-mechanical performances of micro-concrete," In: L. Moldovan, and A. Gligor (Eds.), *The 15th International Conference Interdisciplinarity in Engineering. Inter-Eng 2021. Lecture Notes in Networks and Systems*, vol. 386, Springer, Cham, 2022, doi: [https://doi.org/10.1007/978-3-030-93817-8\\_17](https://doi.org/10.1007/978-3-030-93817-8_17).
- [41] M. Devasena, and V. Sangeetha, "Implications of nano-titanium dioxide incorporation in cement matrix: A review," *J. Inst. Eng. India Ser. D*, vol. 102, no. 2, pp. 567-573, 2021, doi: <https://doi.org/10.1007/s40033-020-00247-w>.
- [42] J. Chen, S. Kou, and C. Poon, "Hydration and properties of nano-TiO<sub>2</sub> blended cement composites," *Cement & Concrete Composites*, vol. 34, pp. 642-649, 2012.
- [43] J. Liu, H. Jin, C. Gu, and Y. Yang, "Effects of zinc oxide nanoparticles on early-age hydration and the mechanical properties of cement paste," *Construction and Building Materials*, vol. 217, pp. 352-362, 2019.
- [44] X. Li, J. Li, Z. Lu, and J. Chen, "Properties and hydration mechanism of cement pastes in presence of nano-ZnO," *Construction and Building Materials*, vol. 289, p. 123080, 2021.
- [45] A. Augustyniak, J. Jablonska, K. Cendrowski, A. Głowacka, D. Stephan, E. Mijowska, and P. Sikora, "Investigating the release of ZnO nanoparticles from cement mortars on microbiological models," *Applied Nanoscience*, vol. 12, pp. 489-502, 2022, doi: <https://doi.org/10.1007/s13204-021-01695-w>.
- [46] A. Nazari, and S. Riahi, "Effects of CuO nanoparticles on compressive strength of self-compacting concrete," *Sadhana*, vol. 36, part 3, pp. 371-391, Jun. 2011.
- [47] A. S. Mohammadzadeh, F. Nasiri, M. Arabani, and A. K. Haghi, "Effects of nanoCuO particles on mechanical properties of soil-cement mixtures," *Proceedings of the 5th International Conference on Nanostructures (ICNS5)*, Kish Island, Iran, 2014.
- [48] A. Ghanei, F. Jafari, M. M. Khotbehsara, E. Mohseni, W. Tang, and H. Cui, "Effect of nano-CuO on engineering and microstructure properties of fibre-reinforced mortars incorporating metakaolin: Experimental and numerical studies," *Materials*, vol. 10, p. 1215, 2017, doi: <https://doi.org/10.3390/ma10101215>.
- [49] A. J. Choobasti, and M. Valizadeh, "The effect of nano-CuO on mechanical, microstructural, and self-healing properties of clayey sandy soils," *Arab J Geosci*, vol. 15, p. 1346, 2022, doi: <https://doi.org/10.1007/s12517-022-10621-5>.

- [50] A. Nazari, S. Riahi, S. Riahi, S. F. Shamekhi, and A. Khademno, "Influence of  $\text{Al}_2\text{O}_3$  nanoparticles on the compressive strength and workability of blended concrete," *Journal of American Science*, vol. 6, no. 5, pp. 6-9, 2010.
- [51] K. P. B. Gutierrez, A. L. H. May, J. M. S. López, A. H. Moreno, and S. A. Z. Castro, "Recent progress in nanomaterials for modern concrete infrastructure: Advantages and challenges," *Materials 2019*, vol. 12, p. 3548, 2019, doi: <https://doi.org/10.3390/ma12213548>.
- [52] M. Heikal, M. E. Zaki, and S. M. Ibrahim, "Characterization, hydration, durability of nano- $\text{Fe}_2\text{O}_3$ -composite cements subjected to sulphates and chlorides media," *Constr. Build. Mater.*, vol. 269, p. 121310, 2021.
- [53] A. Joshaghani, M. Balapour, M. Mashhadian, and T. Ozbakkaloglu, "Effects of nano- $\text{TiO}_2$ , nano- $\text{Al}_2\text{O}_3$ , and nano- $\text{Fe}_2\text{O}_3$  on rheology, mechanical and durability properties of self-consolidating concrete (SCC): An experimental study," *Constr. Build. Mater.*, vol. 245, p. 118444, 2020.
- [54] S. A. Abo-El-Enein, F. I. El-Hosiny, S. M. El-Gamal, M. S. Amin, and D. M. Ramadan, "Gamma radiation shielding, fire resistance, and physicochemical characteristics of Portland cement paste modified with synthesized  $\text{Fe}_2\text{O}_3$  and ZnO nanoparticles," *Constr. Build. Mater.*, vol. 173, pp. 687-706, 2018.
- [55] A. S. Dahlan, "Impact of nanotechnology on high performance cement and concrete," *Journal of Molecular Structure*, vol. 1223, p. 128896, 2021, doi: <https://doi.org/10.1016/j.molstruc.2020.128896>.
- [56] F. A. Shilar, S. V. Ganachari, V. B. Patil, T. M. Y. Khan, N. M. Almakayeel, and S. Alghamdi, "Review on the relationship between nano modifications of geopolymer concrete and their structural characteristics," *Polymers*, vol. 14, p. 1421, 2022, doi: <https://doi.org/10.3390/polym14071421>.
- [57] A. K. Roopa, and A. M. Hunashyal, "Evaluate the optimum dosage of nano materials on self-sensing properties of nano cement composites," *Materials Today: Proceedings*, vol. 49, pp. 2197-2204, 2022.
- [58] D. Lu, and J. Zhong, "Carbon-based nanomaterials engineered cement composites: A review," *Infrastruct Preserv Resil*, vol. 3, 2022, Art. no. 2, doi: <https://doi.org/10.1186/s43065-021-00045-y>.
- [59] R. K. Ibrahim, R. Hamid, and M. R. Taha, "Nanomaterials in civil engineering," Conference Paper, Jun. 2012. [Online]. Available: <https://www.researchgate.net/publication/268075169>
- [60] Y. Miao, Y. Zhang, B. Li, L. Chai, and G. Ma, "Effect of graphene oxide on chemical shrinkage behaviour of cement-based composite paste," *KSCE Journal of Civil Engineering*, vol. 26, no. 4, pp. 1858-1879, 2022, doi: <https://doi.org/10.1007/s12205-021-1013-x>.
- [61] Y. Suo, R. Guo, H. Xia, Y. Yang, B. Zhou, and Z. Zhao, "A review of graphene oxide/cement composites: Performance, functionality, mechanisms, and prospects," *Journal of Building Engineering*, vol. 53, no. 2, p. 104502, 2022, doi: <https://doi.org/10.1016/j.job.2022.104502>.