

## The influence of ZnO nanoparticles on mechanical and early-age hydration behaviour of cement paste

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### ABSTRACT

An ultrasonic treatment was used to ensure that the nano zinc oxide abbreviated ZnO, was uniformly dispersed throughout the cement paste mixture with addition of fly ash, replacing 10% of the weight of cement. The characteristics of the cementitious mixture were investigated in this research work. The experimental work was carried out by adding nano-ZnO in increments of 0%, 0.25%, 0.5%, 0.75% and 1% by weight of cement, resulting in changes in the characteristics of the concrete paste. The quantity of nano-ZnO present in the cementitious mixture had a notable influence on the consistency of the cement. This impact was also found when the cement paste contained only 0.5% cement by weight. The electrical resistance studies found that the inclusion of nano-sized particles can both delay the hydration of blended cement mix and increase the hydration rate. The findings of experiments revealed that increasing the nano-ZnO concentrations in the cement paste resulted in greater long-term strength. Furthermore, the pore diameter distribution was optimized by the inclusion of nano-ZnO and a tight microstructure was formed in the cementitious mixture at 28 days.

**Keywords:** Zinc Oxide; Nano-particles; Compressive strength; Tensile strength; Hydration.

### 1. INTRODUCTION

The performance of cement-infused material is substantially determined by micro and nano-scale structural features. The calcium-silicate-hydrate (C-S-H) is an essential element for resilience and other qualities in cement hydration processes, with a size in the range of a few hundred nanometers (nm) [1, 2, 3]. Nano-particles (nps), as a result of its unique features [2, 3], derived from its extremely small size, offer an extensive range of potential applications in increasing the toughness and durability attributes of addition of ZnO with cement substances. These materials have significantly larger specific surface area and reactivity compared to traditional supplementary cement compounds [3, 4]. The small size dimensions of nps afford a greater interaction area for the reaction to occur [4, 5]. In general, finer particle dimensions will have a greater rate of pozzolanic activity. It has been found in nanoparticles such as nano-CaCO<sub>3</sub>, nano-SiO<sub>2</sub>, [4, 5], nano-Al<sub>2</sub>O<sub>3</sub> [5] and so on, can be employed to affect the important properties of cementitious materials. Most nanoparticles can accelerate hydration at an early age and provide C-S-H hydration nucleation sites, enhancing the microstructural density [5, 6].

Nano-ZnO, due to its distinctive visual characters and electrical attributes, has developed as a promising contender for a variety of applications, including semiconductors, catalysts, and chemical absorbent [6, 7, 8]. GARG and GARD [8] have successfully manufactured homogenous ZnO-nps with a dimension of 12 nm that may be employed in mass production. Apart from that, several ZnO nanostructures with distinct morphologies have been studied [8]. Investigations into zinc oxide's application in cementitious materials have shown its capability to modify the early age hydration of cement. From the past literature survey, it was observed that when the C<sub>3</sub>S phase is hydrated in the existence of Zn<sup>2+</sup>, a layer of Ca(Zn(OH)<sub>3</sub>)<sub>2</sub>H<sub>2</sub>O forms on the surface of the C<sub>3</sub>S phase [8, 9], which inhibits water transport to the C<sub>3</sub>S phase [9]. A variety of products and materials, including plastics, ceramics, and glass, have been augmented with nano-scale ZnO, which exhibits both semiconducting and piezoelectric capabilities. Despite this, only a few investigations on the inclusion of ZnO-nps in cement-infused materials were published so far [9, 10]. There was a significant improvement in premature strength with

the inclusion of 0.5 weight percent nano-ZnO, as expressed by GHAFARI *et al.* [11] and MOSTAFA *et al.* [12]. According to CHITTARANJAN *et al.* [13] 0.5% wt. of ZnO-nps increased the hydration of cement mortar by greater than 3 days, but the 28 days strength of concrete sample exhibited no substantial change [13]. The inclusion of ZnO-nps increased the crushing strength of concrete by 15% of weight after 28 days [13, 14], and the presence of  $\text{CaZn}_2(\text{OH})_6\text{H}_2\text{O}$  was confirmed by X-ray diffraction (XRD), which resulted in a slow-down in the hydration reaction, in a subsequent study [14]. However, there is still some uncertainty about the effectiveness of zinc oxide nano-sized particles on the initial stages of hydration.

In the past investigations, various concepts were suggested to describe the retarding impact of  $\text{Zn}_2^+$  in concrete materials, including the creation of relatively less or non-permeable zones and its toxic impact [14, 15]. However, it continues to be a contentious topic of discussion. Therefore, in this investigation, different concentrations of nano-ZnO (0.25, 0.5%, 0.75% and 1% of weight) [15] were added to cementitious material, and the characteristics of specimens were measured after 3, 7, 14, 28, and 56 days, respectively, to determine its durability [15]. Electrical resistance tests were used to analyse the premature hydration reaction of cementitious material with nano-ZnO [15, 16]. Additionally, the morphology of nano-ZnO containing cementitious materials was investigated using a scanning electron microscope (SEM) [16]. The X-ray diffraction analysis was employed to explore the effects of nano-ZnO on the cementitious matrix.

PATHAK and TIWARI [17] explored the physical and durability aspects of cement-infused materials using 60 nanometer sized zinc oxide nanoparticles. The results of the experiments revealed that utilizing ZnO-nps up to a maximum substitution level of 1.0% results in concrete with increased strength when used in conjunction with cement [17, 18]. For partial cement substitution, nano ZnO ranging from 0% to 1.0% was used [17, 18]. According to the results of the experimental study, it was observed that ZnO nanoparticles increases the cement hardening time, while the addition of these nano-ZnO particles to the binding agent affects concrete pourability, necessitating the use of a super plasticizer [18]. ZHANG *et al.* [18] revealed that the nano-ZnO particles, when added to concrete at a concentration of 1%, increase the compressive strength by 18%. Additionally, the durability of concrete mixtures has enhanced. Nano particles were used as an additive to enhance the unit weight of concrete, resulting in a substantial reduction in the concrete pores [19, 20, 21]. Once the proportion of nano-ZnO in concrete is increased above 1% the hardness of the concrete reduces [21]. Detailed literature survey on the subject revealed that there are very few studies related to addition of ZnO in cementitious materials documented. Therefore, the proposed research aims to examine the effectiveness of cement – fly ash combination along with ZnO in cement concrete to partially replace cement, with the goal of enhancing sustainability and cost effectiveness.

## 2. MATERIALS AND METHODS

For this project, OPC of grade 43 was used. There were no lumps in the cement, which was grey in colour and its chemical constituents are revealed in Table 1. Zinc oxide (ZnO) falls within the category of inorganic substance [21]. ZnO, a white substance highly soluble in water, is often used as an ingredient in a variety of products [21, 22]. Energy dispersive X-ray spectroscopy (EDS) was used to find the chemical composition of cement and fly-ash, which is listed in Table 1 and the physical parameters of zinc oxide is listed in Table 2. ZnO-nanoparticles have been added to cement composites to enhance performance and durability [21, 22]. Furthermore, fly ash is added at 10% by weight of the cement content offers a balanced approach towards improving workability, durability, sustainability, and cost-effectiveness of concrete structures [22, 23].

Fine aggregate was collected from locally available sandy soil containing particles lesser than 0.5 mm size, with a particle fineness of 2.35 and a specific gravity of 2.5. A coarse aggregate sample of crushed stone with diameter approximately 20 mm or larger [22, 23] has a specific gravity of 2.6. This sample was preserved for laboratory testing.

### 2.1. Specimen preparation

ZnO is relatively environmentally friendly. It can contribute to the sustainability of construction projects by reducing the need for additional materials or maintenance over the lifespan of the structure. The mix design of concrete was formulated for M35 grade, and based on the material properties, the mix ratio was determined as 1:2.08:2.72 (Cement with flyash: FA: CA) with water cement ratio adopted as 0.4%, according to IS 456-2000.

Two sets of mixes were prepared in the laboratory studies. The N Series mixes were used to make control mix of samples. These mixes consisted of cement, fly ash, natural coarse and fine aggregates, and water. A Z series of ZnO-nps, ranging in size from 15 nm was prepared by changing the percentage of ZnO-nps [23, 24]. The cement substitutions were 0.25%, 0.5%, 0.75% and 1.0% by weight [23, 24]. For all combinations, the w/c

**Table 1:** Properties of cement and flyash.

OXIDES	COMPOSITION (%)	
	CEMENT	FLYASH
CaO	60.1	3.18
SiO <sub>2</sub>	21.2	60.29
Al <sub>2</sub> O <sub>3</sub>	3.2	24.65
Fe <sub>2</sub> O <sub>3</sub>	2.9	6.10
MgO	1.9	1.78
Na <sub>2</sub> O	0.8	0.52
K <sub>2</sub> O	0.6	2.45
SO <sub>3</sub>	2.1	0.4
LOI	1.5	3.24

**Table 2:** Properties of nano-ZnO.

DESCRIPTION	PROPERTY
Colour	White
Particle size	15 nm
Purity	99%
pH value	9.0

**Table 3:** Mix proportions of cement blended with flyash and nanoparticles.

MIX GROUP	CEMENT (%)	FLYASH (%)	W/C RATIO (%)	NANO-ZINC OXIDE (%)
N	90	10	0.4	0.00
NZ1	89.75	10	0.4	0.25
NZ2	89.50	10	0.4	0.50
NZ3	89.25	10	0.4	0.75
NZ4	89.00	10	0.4	1.0

ratio was chosen as 0.40%. The aggregates used in the mixture, 30% of that weight would be sand, while the remaining 70% would be coarse aggregate of the total weight. Table 3 shows the ratios of the various mixes.

It was decided to combine cement with nano-ZnO particles in a laboratory cement mixer to obtain the NZ series combinations. Only cement powder was used in the N series combinations. They were combined for 2 minutes under dry conditions and then for another 3 minutes after water was added to the mixture [25].

Cube mould of 150\*150\*150 mm and cylinder mould of 150 × 300 mm sizes were selected as per the IS 456-2000 to determine the compressive strength and split tensile strength of concrete at 3, 7, 14, 28, and 56 days after curing. IS 516-2021 [25, 26] specifies for smaller size test specimen ratio of diameter of specimen to maximum size of aggregate of not less than 3 to 1. Based on the literature review [25, 26, 27], the test specimens for compressive test of cement mortar (cube of size 50 × 50 × 50 mm) and flexural tests (prism of size 50 × 50 × 200 mm) align with the recommendations of IS 516-2021 [25, 26, 27]. All the specimens were kept in a standard drying chamber for 24 hours with the surface layers confined by plastic cover to avoid loss of moisture content. The concrete specimens were examined for compressive strength at 3, 7, 14, 28, and 56 days after curing.

## 2.2. Setting time and strength

The initial and final consistency periods of cement pastes were assessed utilizing a manual Vicat device, following the methods described in IS: 9597-2008 [27]. The onset and completion of setting were determined by assessing the intrusion of the Vicat needle into cementitious mixture at depth of 32 mm and 0.5 mm, respectively.

According to IS: 679-1989 [28], compression and bending strength tests were performed at various curing days, with six specimens created for each group.

### 2.3. Electrical resistivity

An electrodeless fresh cement resistivity analyzer was used to measure the electrical resistivity of ZnO-nps. The newly prepared cement mixture was poured into the mould at a predetermined position for the experiment. The mould was then carefully shaken by finger in order to eliminate air from the mixture. Finally, a plastic cover was placed over the mould, and the resistivity of cementitious material was measured for 3-days. The measurement tool was kept in a thermostatically regulated environment with a steady ambient condition of 20°C and fluctuations in the resistive properties of the concrete were recorded as per the IS 516-2021 [29] recommendations.

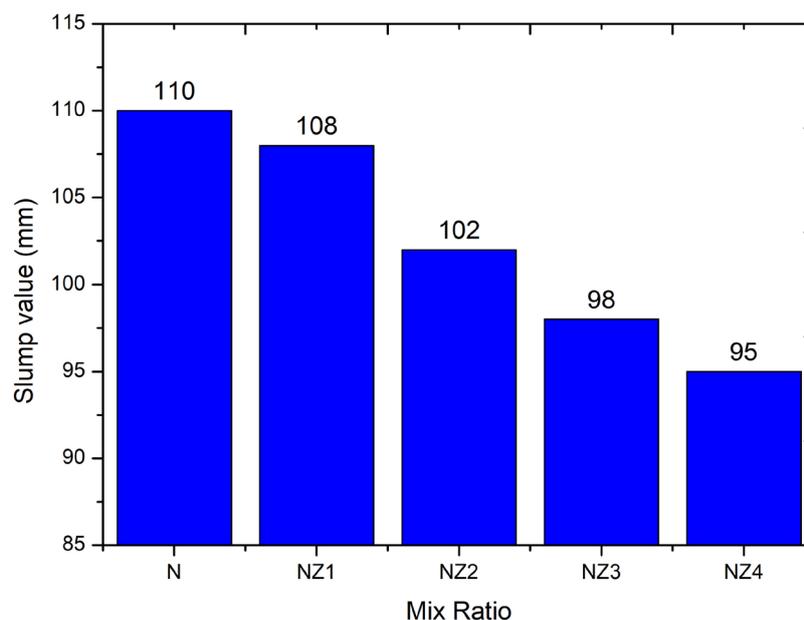
### 2.4. SEM and XRD

The crushed pieces of specimens were collected for microscopic characterization during the compressive strength test. For the SEM research, samples of various ages were chosen, and the specimens underwent gold coating for SEM analysis. The test was conducted using Auto Pore IV 9500, capable of detecting pore diameters of up to 3 nm under high pressure, and utilized for analyzing the porous structure and distribution of pore sizes within the samples [30]. X-ray spectrometer with monochromatic Cu-K $\alpha$  electro-magnetic radiation was used to perform XRD studies and identify the hydrated compounds at different curing periods.

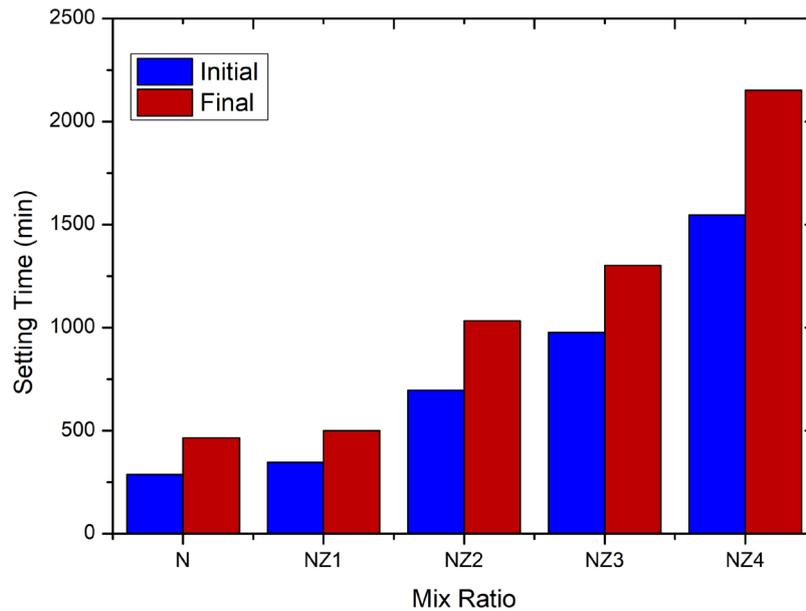
## 3. RESULTS AND DISCUSSIONS

### 3.1. Workability and setting time

The viscosity of the fresh cement mixture was not noticeably affected by the existence of nano-ZnO. Due to its nano-scale size, the surface area of nano-ZnO is significantly larger than that of cement particles. Consequently, the cement mixture became more difficult to work with due to increased water adsorption. Figure 1 demonstrates that as the amount of ZnO-nps increased, the fluidity of the cement mixture decreased [30]. Nano-ZnO, with measurements in nanometers, is smaller than the cement particle, which are measured in micrometers. Due to its extensive specific surface area, nanoparticles generally lead to a decline in the workability of cement paste [30]. The hardening period for the cementitious mixture with ZnO-nps is shown in Figure 2. In the control mix, the setting process commenced after 288 minutes, and the setting was fully completed after 465 minutes. Throughout the study, the cement paste modified with nano-ZnO exhibited longer durations for both the commencement and completion of setting compared to the standard control mix [30]. Table 4 displays the consistency period of the cement mixture with zinc oxide.



**Figure 1:** Slump test results.



**Figure 2:** Consistency period of cement paste with and without nano-ZnO.

**Table 4:** Effect of nano-ZnO in the consistency of cementitious mixture.

MIX GROUP	SLUMP VALUE (mm)	SETTING TIME OF CEMENT (mm)		RELATIVE RETARDATION (%)	
		INITIAL	FINAL	INITIAL	FINAL
N	110	288	465	1	1
NZ1	108	347	499	1.20	1.07
NZ2	102	697	1033	2.42	2.22
NZ3	98	976	1302	3.39	2.80
NZ4	95	1574	2152	5.37	4.63

The establishment of a systematic structure at the beginning of hydration products generally slows hydration rate when ZnO is present. The concentration of nano-ZnO hindered the hydration of  $C_3S$  and  $C_2S$  in the cementitious material, as indicated by hydration heat and XRD data, leading to delayed initiation time and increased setting time [30]. Furthermore, it was noted that the curing durations of the cement paste at the commencement and conclusion of the experiment substantially increased with the addition. As shown in Figure 2, the retardation times in relation to the N mix are shorter. The longest settings time was found for the NZ4 mix, which required 2152 and 1574 minutes for final and initial setting, respectively.

### 3.2. Mechanical property

The strength properties of the samples were examined after 3, 7, 14, 28, and 56 days, with a minimum of three samples averaged for each set at each time period studied. Figure 3 illustrates the typical compression force of the cementitious mixture at various curing periods. Enhancement in strength was noted in the mixes containing nano-ZnO as the curing time progressed [30]. However, after 3 days of curing, the studies showed that the addition of nano-ZnO significantly reduced mechanical properties. This reduction was attributed to nano-ZnO impeding the initial cement solidification process [30], resulting in longer final and initial curing period in concrete [31]. Therefore, the presence of nano-ZnO negatively impacted the initial strength development of the concrete [31] and minimized the flow condition of the cement paste due to its large exposed surface area, leading to improved early hardening periods relative to the conventional mix. Furthermore, as the concentration of nano-ZnO increased, the hardening time was further prolonged.

After 3 days of curing, the properties of mixture with and without nano-ZnO are nearly identical. Comparing the NZ1 and NZ2 groups after 7 days, the compressive force of NZ2 was found higher than that of NZ1,

and similarly, NZ2 was higher than NZ3 and NZ4. NZ1, NZ2, NZ3 and NZ4 all exhibited increases in 7-day flexural strength of 17%, 8%, 11% and 10% respectively, as illustrated in Figure 4. The split tensile strength of cementitious mixture with nano-ZnO had improved by 25% to 30% after 7 days compared to the control mix (N) [32], as shown in Figure 5. Cement paste containing 0.5% by weight of nano-ZnO had compressive, split tensile and flexural strengths that were 6.5%, 5% and 11.6% greater than those of the control group after 56 days.

### 3.3. Heat evaluation

It is possible to use the quantity of heat emitted during the hydration reaction, known as the heat of hydration, to estimate the onset of the early stage hydration. Figure 6 and 7 shows the curves of progressive and cumulative heat flow vs hydration time. It was demonstrated in Figure 6 that the inclusion of nano-ZnO particles in the hydration heat evolution process increased the time required to influence the induction peak and the exothermic rate.

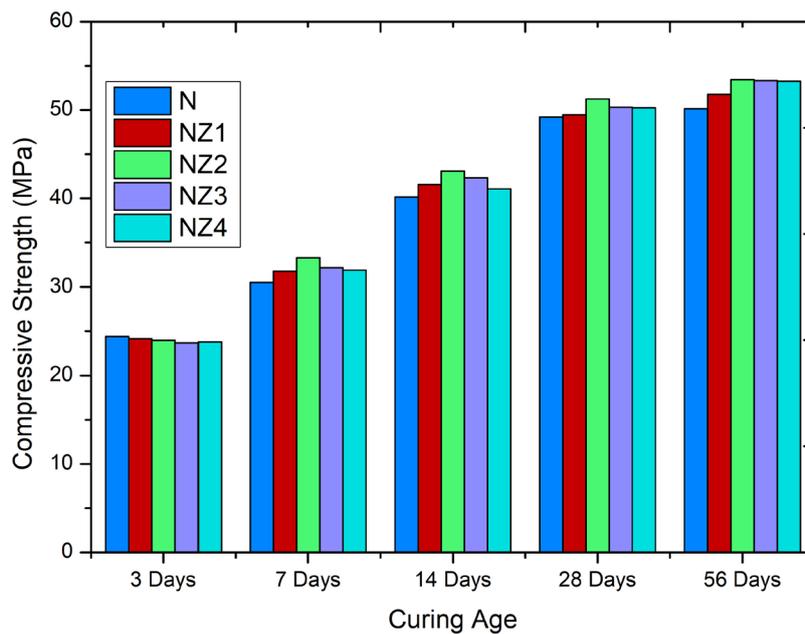


Figure 3: Comparing the compressive strength of cement paste containing nano-ZnO.

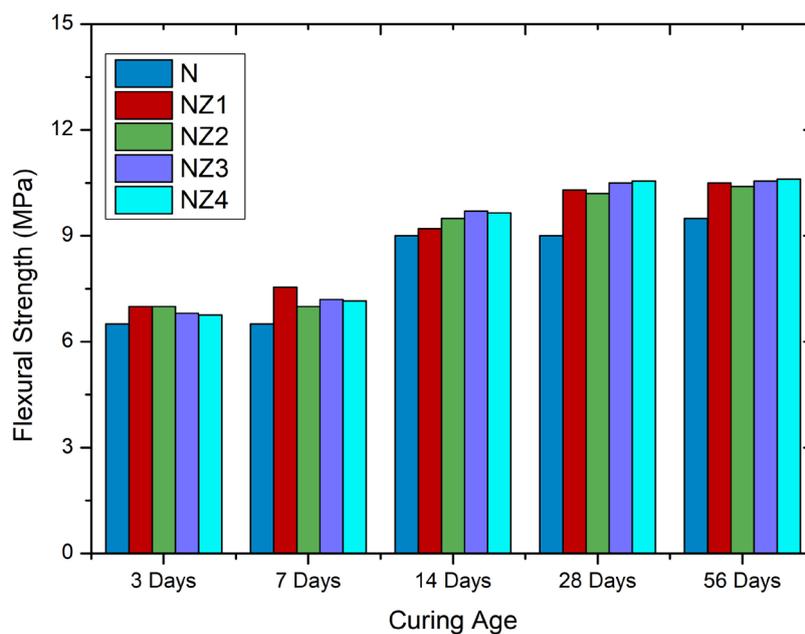


Figure 4: Comparing the flexural strength of cement paste containing nano-ZnO.

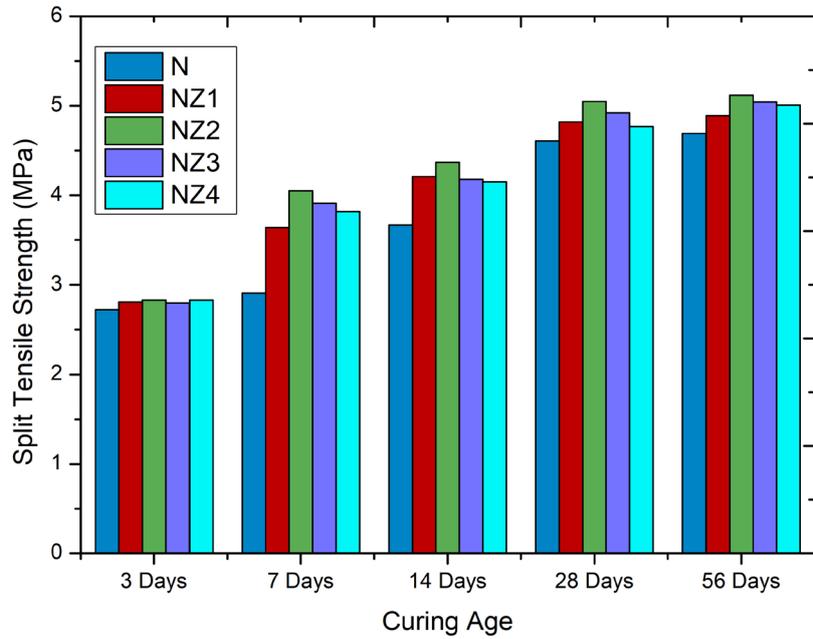


Figure 5: Comparing split tensile strength of cement paste containing nano-ZnO.

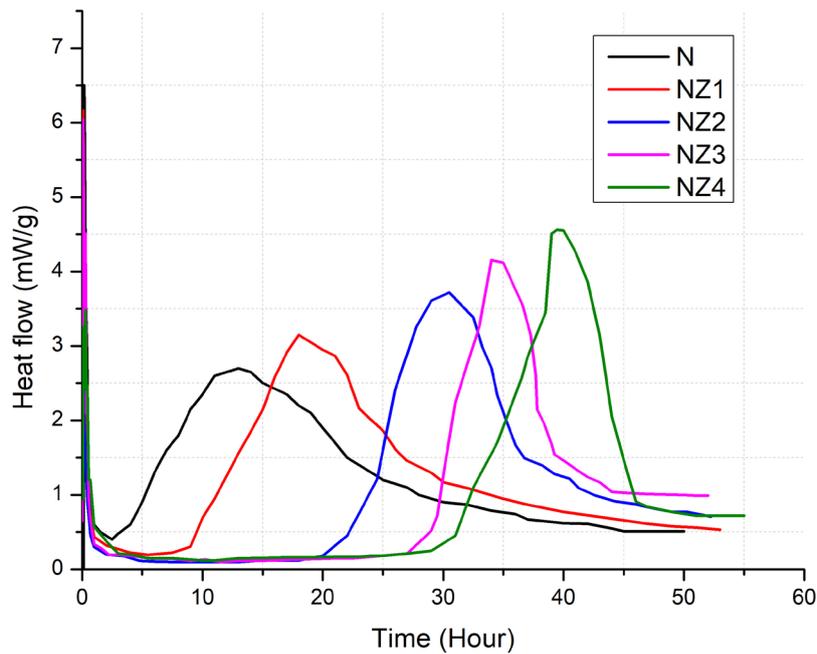


Figure 6: Heat flow of cement paste with and without nano-ZnO.

The acceleration time for the N sample began approximately 2.5 hours after the addition of water and ended roughly 12 hours later. The appearance of the hydration peak was delayed as the concentration of zinc oxide nanoparticles increased, ranging from 0% to 0.5% by weight. The acceleration period for the NZ4 mixture started at 1650 minutes and completed at 2340 minutes. The time span of the beginning stage was significantly prolonged.

The computation of the consistent component of the speed-up phase in the slope, as shown in Figure 7, demonstrates that increasing ZnO particles results in a better acceleration rate, and ZnO nano-particles function as delayed accelerators. With the addition of more nanoparticles, the subsequent thermal reaction becomes shorter in duration and higher in intensity. Although the peak level after retardation increased when zinc oxide was included, the total heat of nano-ZnO-containing specimens was marginally lesser than that of the N sample

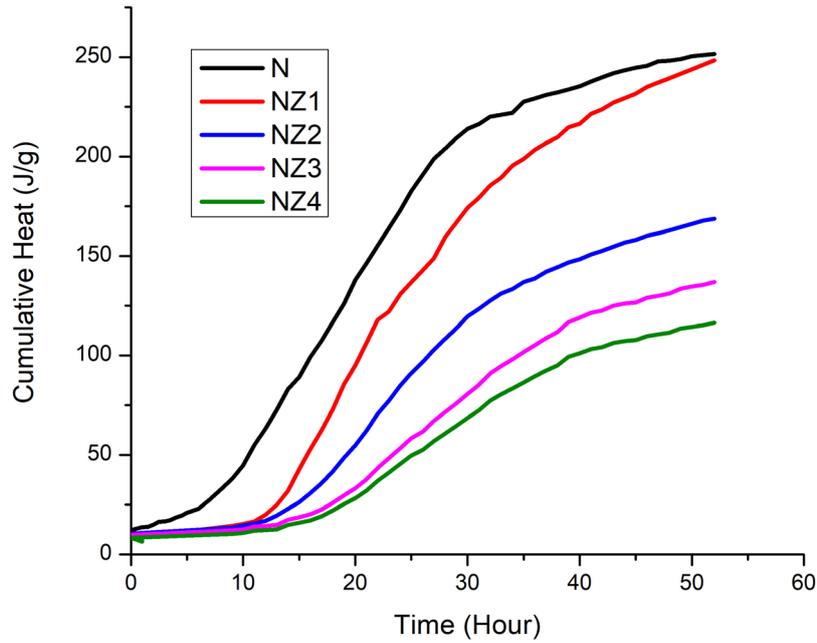


Figure 7: Cumulative heat flow hydration.

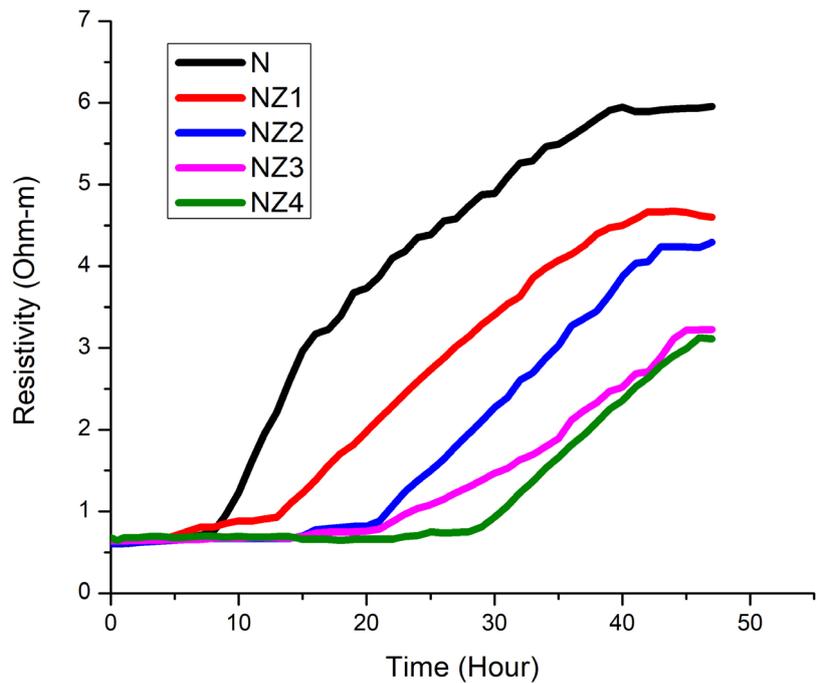


Figure 8: Time-Resistivity curve for blend of cement with nano-ZnO.

shown in Figure 7. Therefore, using nano-ZnO to delay the heat reaction and reduce heat evolution in the beginning stage of hydration could be beneficial.

### 3.4. Electrical resistivity

It is possible to use the resistivity of newly batched cement paste to indicate the early stages hydration because it changes as the cement paste hydrates. The resistivity time plots of cementitious mixture with various nanoparticles are presented in Figure 8, along with the setting time calculated using the Vicat needle. Because the electrical resistivity of the cementitious mixture containing nano-ZnO was smaller than that of the control set (N) at the same age, it appears that the acceleration phase was delayed when nano-ZnO was added.

It is obvious that the inclusion of nano-ZnO greatly extends the dissolving periods. Over time, the addition of nano-ZnO reduces the amount of time spent in the NZ1 state. It can be inferred that the inclusion of nano-ZnO prolongs cement particle disintegration. The beginning and final setting periods of the nano-ZnO cement paste were similarly delayed. As hydration products' concentration increases over time to form skeletons, the substantial electrical resistivity of this mixture is enhanced by blocking ion movement pathways using these substances. Consequently, the increase in electrical resistance can be compared to the time it takes the cement paste to set.

### 3.5. X-ray diffraction analysis

XRD was utilized to examine the crystal phase of the cement paste after 3 and 28 days of exposure to various nano-ZnO concentrations. The analysis after 3 days revealed that the un hydrated cement phase constituted the majority of the N and NZ2 mixtures. Nano-ZnO slowed down the hydration reaction, resulting in greater diffraction peak intensities of  $C_3S$  and  $C_2S$  in the NZ2 sample compared to the control mix. The 3 days XRD peak of the NZ2 mix did not reveal the formation of the ZnO phase, possibly due to the minimum addition of ZnO-nps in this research. The  $Ca(OH)_2$  phase was also found in the N and NZ2 samples after 3 and 28 days, respectively [33]. The XRD scattering patterns of N and NZ2 were nearly identical after 28 days, indicating that the inclusion of nano-ZnO had no substantial influence on the hydration level of the cementitious material at a later time. Figure 9 depicts the XED pattern of concrete with a zinc oxide mixture.

### 3.6. Scanning electron microscope with ZnO mixture

The SEM images reveal that the prepared ZnO nanoparticles exhibited non-uniformity in size and a nearly spherical morphology, along with aggregate of nano-crystallites, as shown in Figure 10 [34, 35]. Observations indicate agglomeration, with the ZnO nanoparticle size measured at approximately 85 nm, consistent with

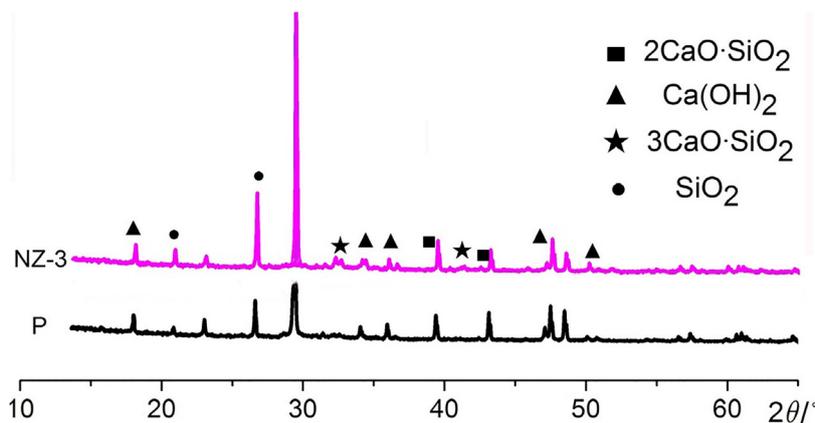


Figure 9: XRD pattern of concrete with ZnO mixture.

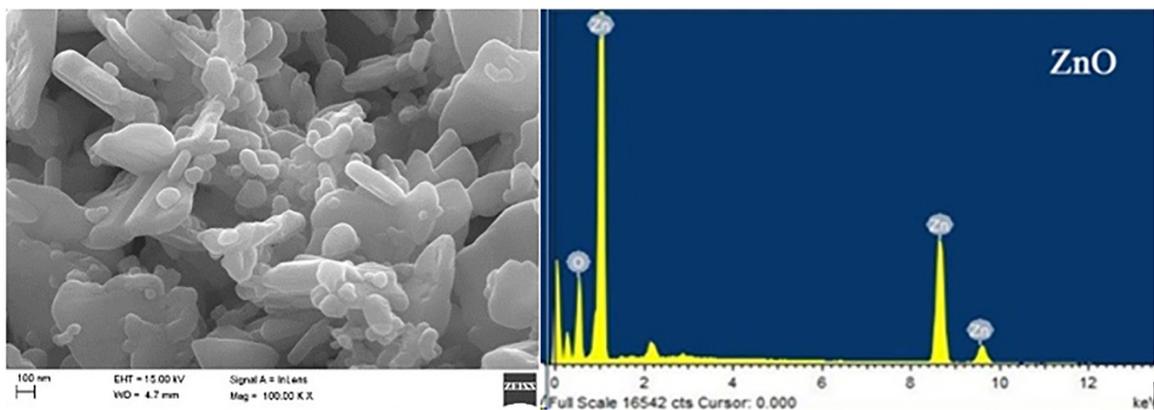


Figure 10: SEM and EDX images of ZnO.

EDX analysis. This allows for the identification of agglomerates and an understanding of the degree of particle agglomeration, as it can influence properties such as surface area, reactivity, and dispersion in a matrix.

The SEM method often conducts thorough examinations of microstructures, as depicted in the Figures 11 (a) and 11 (b), which present SEM visuals of both the control and NZ2 samples after 28 days. In the control mix sample, numerous pores of significant size are observed. In contrast, the nano-samples exhibit a reduced number of pores spaces compared to control mix [34, 35]. In the absence of ZnO, small crystalline structures accompanied by interconnected capillaries of calcium hydroxides were observed. Subsequently, with the addition of ZnO, a proportional reduction in the occurrence of pore spaces was noted. The micro graphical study using Sem revealed characteristic phases of the sample’s microstructure, with the darkest phase representing pores within the structure and a less dark phase indicating calcium hydroxide in the form of hexagonal plates. Conversely, the brightest phases, with fewer pore spaces, corresponding to the C-S-H gel. The mechanical strength of these sample increased due to the presence of C-S-H gel flakes indicates in Figures 11 (a) and 11 (b).

Mapping images for the control and NZ2 specimens subjected to 28 days of immersion in fresh tap water, along with their corresponding EDX spectra, are presented in Figures 12 (a1) & 12 (b1). Table 5 shows the chemical compounds of the specimen at 28 days curing period. Figure 12 illustrates the anticipated chemical compounds and their individual components for the respective specimens. Based on these findings, it is evident that the calcium percentage in the nano-ZnO blend is lesser than that in the control mixture, indicating an extension of setting time.

The primary reason for conducting EDX analysis on these samples was the superior mechanical properties observed after 28 days of curing, surpassing those of specimen with different nanoparticle compositions. Figure 12 (a1) and (b1) illustrate that the samples’ chemical compositions primarily consisted of oxygen, silicon, carbon, calcium, manganese and alumina nanoparticles. EDX investigations indicated that cement paste samples incorporating nanoparticles exhibited a more even distribution and a higher nanoparticle concentration compared to control cement pastes.

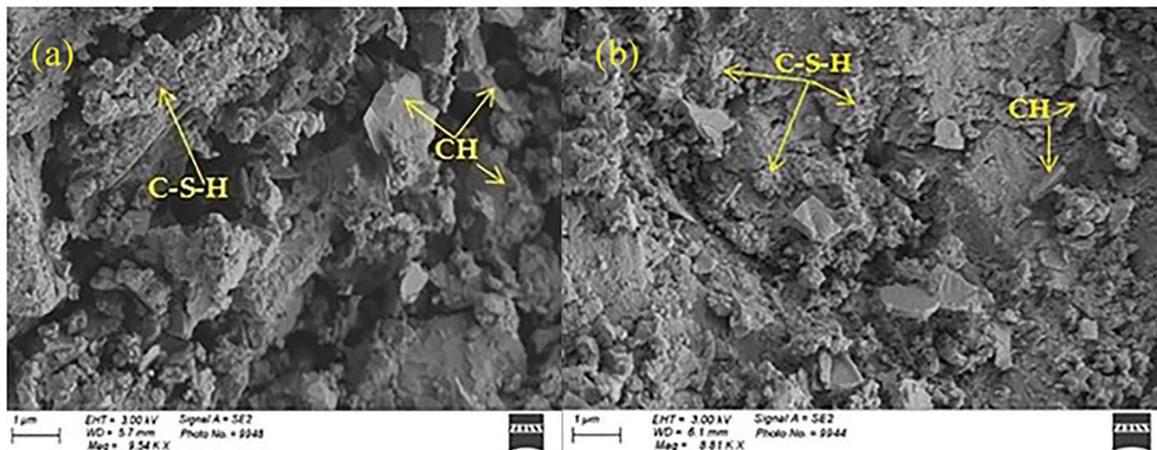


Figure 11: SEM micrographs of (a) control mix (b) ZnO specimen at 28 days of curing age.

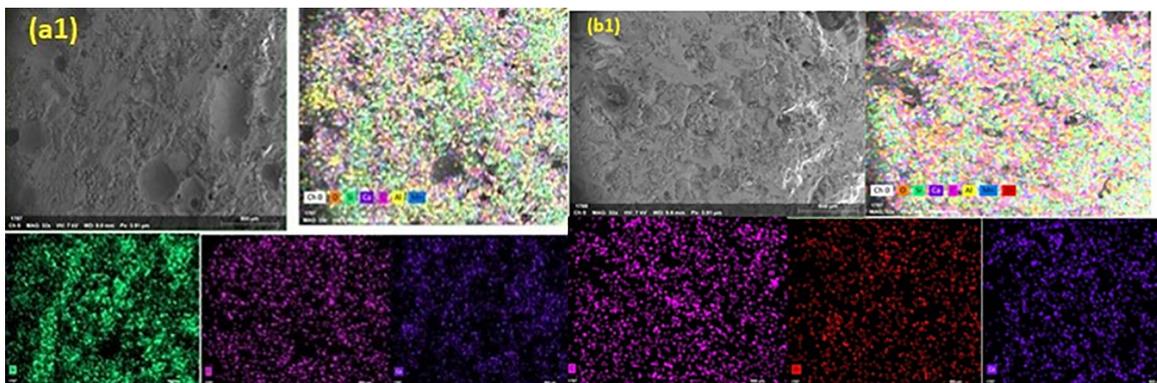


Figure 12: EDX and mapping analysis for (a1) nominal mix (b1) ZnO specimen at 28 days of curing age.

**Table 5:** Chemical compounds of the specimen at 28 days curing age.

ELEMENT	WEIGHT (%)		ATOMIC (%)	
	N	NZ	N	NZ
Oxygen	38.02	42.52	51.54	52.54
Silicon	35.01	33.11	26.21	27.61
Carbon	6.15	6.59	9.52	11.65
Calcium	13.50	8.56	8.62	5.05
Aluminium	1.15	1.78	1.20	0.91
Manganese	6.17	7.25	2.91	2.15
Zinc	–	0.19	–	0.09

#### 4. CONCLUSIONS

Based on the comprehensive investigation conducted on the addition of nano-ZnO particles in cementitious materials, several significant conclusions can be drawn.

- The inclusion of nano-ZnO resulted in the formation of a crystalline layer formation at the initial hydration, which slowed the hydration rate and prolonging setting times. Higher concentrations of nano-ZnO intensifying these effects.
- The mechanical properties, notably compressive, flexural, and split tensile strengths, showed significant improvement with curing, particularly after 7 days, surpassing those of the control mix. This enhancement persisted up to 56 days, with the cement paste containing 0.5 wt. percent nano-ZnO exhibiting noteworthy improvements in strength relative to the control group.
- The inclusion of nano-ZnO in hydration prolonged onset time and exothermic rate, resulting in delayed heat peaks and extending initiation duration, indicating its role as a delayed accelerator, potentially benefiting early-stage hydration reactions.
- The inclusion of nano-ZnO prolonged dissolving periods and delayed setting times, while increasing hydration product concentrations strengthened skeletons and improved electrical resistivity, correlating with setting time.
- The XRD analysis revealed that nano-ZnO slowed down the hydration reaction, resulting in higher diffraction peak intensities of un-hydrated cement phases associated with the control mix.
- The SEM analysis indicated that the inclusion of nano-ZnO reduced the pore spaces in cementitious materials compared to the control mix, resulting in denser microstructures.

#### 5. ACKNOWLEDGMENTS

Authors are grateful to Kongunadu College of Engineering and Technology.

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