Research Article

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Investigation of Microstructural Properties of Nano-modified Concrete for Sustainable Environment

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ABSTRACT

The creation and evaluation of Nano-modified concrete, with an emphasis on its microstructural characteristics, is the main goal of this extensive study. The inclusion of nanosilica and nanoclay not only enhances the characteristics of concrete but also contributes to mitigating soil pollution. By adding nanosilica and nanoclay as additional cementitious materials, the study intends to assess the structural integrity of nano-modified concrete using cutting-edge techniques like Scanning electron microscopy, Transition electron microscopy and X-ray diffraction. Four different concrete compositions with variable amounts of nanosilica and nanoclay additions (0%, 5%, 10% and 15% of nano additives by weight of fine aggregate) and a 3% cement replacement rate were cast and evaluated throughout the experimental phase. A comparison with regular concrete revealed significant improvements in microstructures, demonstrating the efficacy of nano-modified concrete without sacrificing necessary characteristics. Slump values increased with the addition of nano-silica and nanoclay, indicating better workability and smoother concrete surfaces. The study's findings indicate that the development of Nano-modified concrete has great potential as an advanced building material. In addition to providing instant structural gains, the use of nanosilica and nanoclay enhances the long-term performance of concrete buildings and creates new opportunities for creative and long-lasting building techniques.

Keywords: Nanosilica; Nanoclay; SEM; TEM and XRD.

1. INTRODUCTION

Nanotechnology, with its focus on particles at the nanometer scale (10^{-9} m), has garnered significant scientific attention. The inclusion of nanomaterials acts as a filter against improper soil stabilization and as a good filter for water adsorption character. The minute size of nanoparticles can lead to substantially enhanced properties compared to conventional materials with similar chemical composition and larger grain size. Despite this potential, there is a paucity of reports on the integration of nanoparticles into cement-based building materials (Byung *et al*. 2007). Axial strength rises with higher replacement percentages in their experiments. They introduced nano-silica in 0%, 1%, 2%, 3%, and 5% increments, which resulted in significant enrichments in strength across all testing ages. Notably, the optimal enhancement occurred at a 5% replacement of cement, highlighting its efficacy in bolstering axial strength (Ye *et. al*. 2007).

Amorphous particles with sizes ranging from 1 to 500 nm make up colloidal nano-silica, which has unique chemical and physical characteristics when compared to coarser particle admixtures. Compared to materials with bigger particles, the tiny size range offers distinctive properties that highlight its effectiveness in a variety of applications (Björnström *et al.* 2004). When cement mortar containing nano SiO_2 particles was examined experimentally, blended mortars showed increased strength after 7 and 28 days. According to a microstructure study, SiO_2 enhances microstructure and also acts as an activator to aid in the pozzolanic reaction, which improves the material's performance even more (Naveen, *et al*. 2023a).

When SF and metakaolin were added to the mixture, the shrinkage of plain concrete was minimized at an early age. Higher doses (15%) of each additional mineral admixture were found to have a stronger impact at 45 days of age as well as at earlier ages, particularly during the first week of curing (Ganesh *et. al.* 2023). Other theories for the lower shrinkage rate included the filling effect and pores shrinking to smaller sizes. Through its chemical and physical effects on the structure, nano-silica strengthens cement systems. With its natural reactivity and its ability to serve as nucleation sites for quick C-S-H production, it chemically improves pozzolanic C-S-H creation in two steps. In terms of physical function, nanoparticles operate as fillers, compacting and strengthening the partly hydrated cement paste, to create a more robust microstructure (Arasu *et. al*. 2023).

Numerical modeling and experimental analysis may be utilized to forecast various system characteristics and comprehend system performance. In order to assess the chemical influence of nano-silica on the cement system, this work offers a quantitative examination of scanning electron microscopic pictures of cement pastes with varying amounts of cement substitution with nano-silica (Aly *et al.* 2012). Nano-silica is acknowledged as a pozzolanic material, engaging in a reaction with the calcium hydroxide (CH) generated during cement hydration. This reaction leads to the formation of a secondary type of calcium-silicate-hydrate (C-S-H) within the paste. Comparisons between the nano-modified samples and the conventional paste serve as an indicator of the pozzolanic reactivity of nano-silica within the paste.

Various experimental techniques commonly employed to investigate cementitious materials encompass X-ray powder diffraction (XRPD), Backscatter electron (BSE) image analysis, Thermal gravimetric analysis (TGA), Nuclear Magnetic Resonance (NMR) techniques, small angle neutron and X-ray scattering, atomic force microscopy and Nano indentation (Arasu *et. al.* 2018). Among these methods, TGA and XRPD stand out as reliable approaches for predicting the pozzolanic reaction extent. These techniques are capable of providing precise analyses of the pozzolanic reaction based on the calcium hydroxide content of the paste. TGA and XRPD offer more accurate insights into the pozzolanic reaction extent compared to image-based techniques (Naveen *et al.* 2023).

Reusing various by-products, such as fly ash, silica fume, and nano-silica, is an appealing alternative given the growing expectations for sustainability. Several studies have demonstrated that using industrial byproducts enhances concrete's varied qualities and creates environmentally beneficial materials (Sobolev *et. al.* 2009). Nanotechnology is now widely used in all scientific fields. The gel porosity in the cement matrix or the nano-size dimensions of the calcium silicate hydrates (C-S-H) particles have a significant impact on the performance of concrete (Vivek *et. al.* 2020).

The scanning electron microscope (SEM) micrographs provided a detailed insight into the concrete's microstructure, revealing a more sophisticated and densely packed pore arrangement in specimens incorporating admixtures as they progressed through extended curing periods. This observed refinement in pore structure played a pivotal role in augmenting the strength and durability characteristics of the High-Performance Self-Compacting Concrete (HPSCC) specimens (Mostafa Jalal *et. al.*, 2015). The integration of admixtures contributed to the overall improvement of the material's performance over time, highlighting the potential for enhanced longevity and robustness in practical applications (Vivek *et. al.* 2018). Examinations through SEM and XRD unveiled the substantial positive impact of nanoparticles on concrete quality. While the enhancement in mechanical characteristics was deemed less noteworthy, the authors emphasized a significant reduction in chloride ion penetration and a concurrent increase in electrical resistivity. These findings present viable options for effectively controlling corrosion in reinforced concrete structures (Eskandaria *et al*. 2015).

Using methods from XRD and AFM, the microstructural characteristics of concrete were evaluated. A total of forty concrete mixes containing 0, 2, 4 and 6 weight percent (wt. %) of nanosilica in the cement and three different types of reinforcing fibers (0.2, 0.3, and 0.5 v% for steel, 0.1, 0.15, and 0.2 v% for polypropylene, and 0.15, 0.2, and 0.3 v% for glass) were assessed. The appropriate percentages of both nanosilica and reinforcing fibers were found by the authors to enhance bonding (Akshana *et al*. 2020)

2. MATERIALS

2.1 Cement

Cement's specific gravity of 3.15, as determined by measurement, complies with IS:1727-1967 requirements. The standard consistency of 31% complies with IS:4031-1968 part-4 requirements. Soundness is evaluated using a 0.94 mm Le-Chatelier apparatus displacement, as per IS:4031-1968 criteria. A well-balanced formulation was found in the cement's chemical composition examination, with significant quantities of calcium oxide (CaO) suggesting strong strength potential. Important for mechanical qualities, silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) aid in the development of hydration products. A stable composition is suggested by moderate quantities of alkalis, magnesium oxide (MgO), sulfur trioxide (SO_3), loss on ignition (LOI) and lime saturation factor (LSF). Reduced chloride levels improve durability, and the information serves as a basis for better concrete compositions.

2.2 Fine Aggregate

The fine aggregate exhibits qualities that are vital for the formulation of a concrete mix. It is compatible with fine aggregate standards, having a maximum particle size of 2.36 mm, and helps create a concrete mix that is properly graded. A water absorption rate of 1.20% denotes a moderate level of moisture absorption, which affects durability and workability.

2.3 Coarse Aggregate

The coarse aggregate exhibits specified characteristics crucial for concrete performance. With a maximum particle size of 12.5 mm, it meets the required size criteria for effective concrete compaction. Low water absorption of 0.46% signifies its moisture resistance, crucial for maintaining concrete durability. The Los Angeles abrasion test result of 15% indicates moderate resistance to abrasion, ensuring enduring structural integrity. A crushed value of 16% demonstrates suitable strength. The angularity number of 9.5 denotes a well-graded aggregate, contributing to optimal interlocking in the concrete matrix.

2.4 Nano Silica

The features of the nano-silica under investigation are notable. Its strong surface reactivity, with a specific surface area of 202 m^2/g, helps to improve the cementitious qualities of concrete. 2.28 specific gravity indicates a lightweight composition. For concrete admixtures, a pH of 4.15, which is somewhat acidic, is acceptable. The low readings for ignition loss (0.66) and drying loss (0.47) suggest that much volatile or flammable material is not present. Fine particle size is demonstrated by the little filter residue at 0.02. Its low carbon (0.06%) and chloride (0.009%) contents guarantee that there are few impurities, while the high SiO_2 percentage (99.88%) highlights its purity. The material's exceptional purity is confirmed by trace levels of Fe_2O3 (0.001), TiO_2 (0.004), and Al_2O3 (0.005), which makes it a useful addition for maximizing the qualities of concrete. Its high flowability, indicated by its tamped density of 44 g/l, makes it simple to include into concrete mixes.

2.5 Nanoclay

The substance exhibits a composition comprising 45.00% SiO_2, 36.00% Al_2O3, 0.70% Fe_2O3, 0.15% CaO, 0.17% MgO, 0.15% TiO_2, 14.00% Loss on Ignition (L.O.I.), 0.10% K_2O, and 0.10% Na_2O. While SiO_2 and Al_0O_3 dominate, considerations for Fe_2O_3 and L.O.I. are essential for applications involving color and high-temperature stability. The material displays a specific gravity of 2.6, indicating moderate density. With a brightness level of 78 and a whiteness value of 80, it exhibits good light reflectance properties. The acid solubility of 1.2 suggests its susceptibility to acidic conditions. Water absorption at 36 ml/100 gm indicates a moderate capacity to absorb moisture. These characteristics collectively define the material's physical and chemical attributes, influencing its potential applications in various industries such as paints, coatings, or construction materials.

3. Methodology

Mix design was carried out in accordance with the specifications and a directive published by IS norms, IS 10262: 2009, to fulfill the M40 standards. The qualities of fine gravel, coarse aggregate, nano silica, nanoclay, and cement 53 grade were utilized. Table 1 shows the mix designations.

Table 1. Mix designations

Mix No.	Mix Representation				
	Nano Silica	Cement	Nanoclay	Fine Aggregate	Carse Aggregate
T1	3%	97%	0%	100%	100%
T2	3%	97%	5%	95%	100%
T3	3%	97%	10%	90%	100%
T4	3%	97%	15%	85%	100%

4. RESULTS AND DISCUSSION

4.1 SEM Analysis

The examination of the morphology, structure, and surface characteristics of polymer surfaces is commonly conducted through Scanning Electron Microscopy (SEM). In SEM, secondary electrons generated by a thermal or field-emitting cathode are employed. The electron beam, produced by the cathode, undergoes attenuation through a condenser and an objective electromagnetic lens. In the back-focal plane of the objective lens, electromagnetic coils are strategically positioned to scan the electron beam. Subsequently, an electron detector is often employed to collect the signal generated by secondary electrons. This comprehensive process allows for the detailed observation and analysis of the topography and features of polymer surfaces.

The SEM micrograph of the unmodified concrete (NMC) sample is displayed in Fig. 1. This image makes it evident that the C-S-H gel is dispersed throughout the particles, leaving many empty spaces between them, which might have an impact on the concrete's strength.

The SEM image of concrete specimens devoid of 3% nanoclay and 5% nano-silica is displayed in Fig. 2. It is evident that although C-S-H gel is not enough in between the particles, the nanoparticles that occupy the gel's holes provide a superior structure. The SEM image of a concrete specimen containing 10% nanoclay and 3% nano-silica is displayed in Fig. 3. In comparison to Figures 1 and 2, it is evident that the C-S-H gel formation is likewise good, with a homogeneous microstructure and relatively few pores between the particles.

It shows that the cement and nanoparticles are reacting to improve the binding and increase strength. The SEM image of a concrete specimen containing 3% nano-silica and 15% nanoclay is displayed in Fig. 4. In comparison to Fig. 3, the C-S-H gel formation is similarly impacted by the huge lumps that are created owing to the excess quantity of nano-silica, even though a better-packed microstructure between the concrete and nanomaterials can be observed here. It also has an impact on concrete's strength.

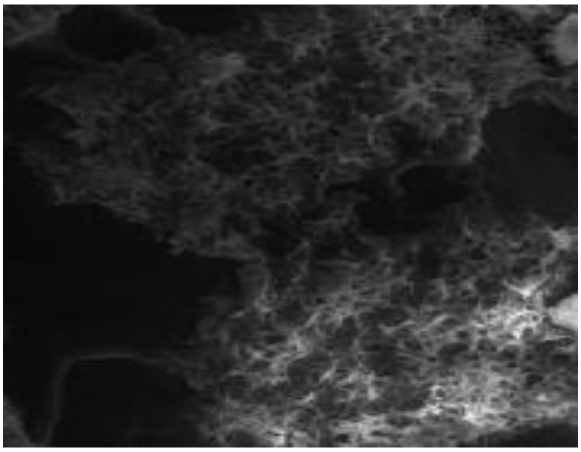

Fig. 1: SEM image of T1 mix (3% Nano-silica + 97% Cement & 0% Nanoclay + 100% Fine Aggregate + 100% Coarse Aggregate)

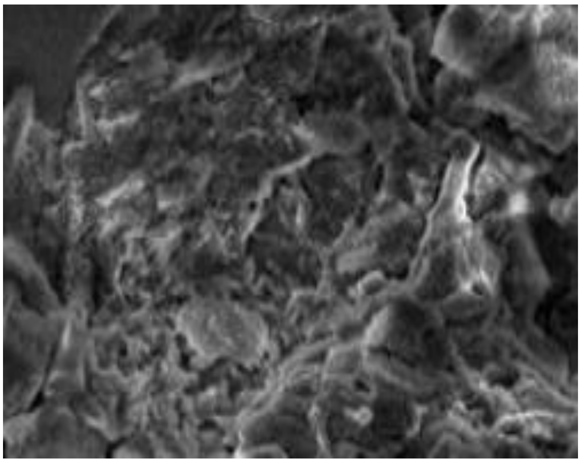

Fig. 2: SEM image of T2 mix (3% Nano-silica + 97% Cement & 5% Nanoclay + 95% Fine Aggregate + 100% Coarse Aggregate)

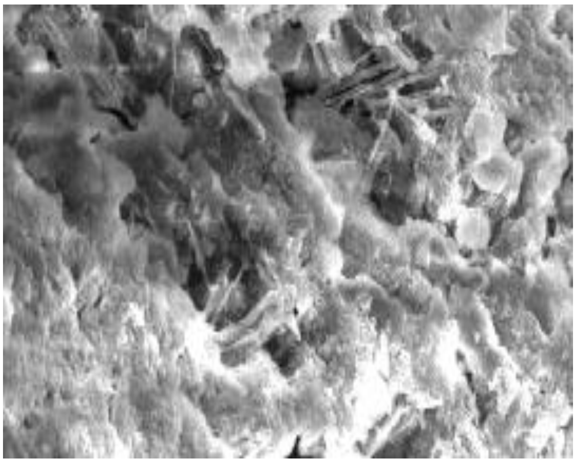

Fig. 3: SEM image of T3 mix (3% Nano-silica + 97% Cement & 10% Nanoclay + 90% Fine Aggregate + 100% Coarse Aggregate)

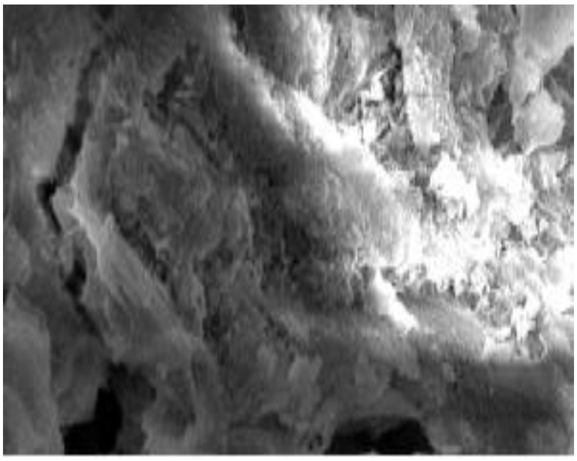

Fig. 4: SEM image of T4 mix (3% Nano-silica + 97% Cement & 15% Nanoclay + 85% Fine Aggregate + 100% Coarse Aggregate)

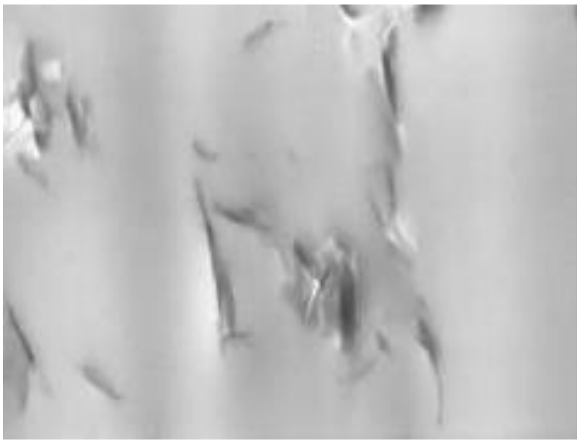

Fig. 5: TEM image of T1 mix (3% Nano-silica + 97% Cement & 0% Nanoclay + 100% Fine Aggregate + 100% Coarse Aggregate)

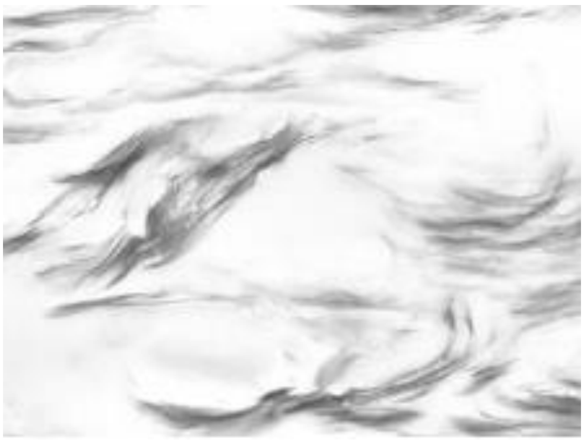

Fig. 6: TEM image of T2 mix (3% Nano-silica + 97% Cement & 5% Nanoclay + 95% Fine Aggregate + 100% Coarse Aggregate)

4.2 TEM Analysis

An electron beam is sent across the material being examined in TEM, a sophisticated microscopy method. The sample is placed carefully on a holder so that electrons may travel through and interact with the substance. The TEM image of a concrete specimen containing 0% nanoclay and 3% nano-silica is displayed in Fig. 5, 5% nanoclay and 3% nano-silica in Fig. 6 and 10% nanoclay and 3% nano-silica in Fig. 7. Similarly, the TEM image of a concrete specimen containing 15% nanoclay and 3% nano-silica is displayed in Fig. 8. A picture is created as a result of the contact, and linked computers then gather and capture it. Scientists may investigate the internal structure and fine features of specimens at the nanoscale thanks to this sophisticated imaging technique. To get a better knowledge of the content and characteristics of compounds with complex internal structures, such as biological samples, nanoparticles and different crystalline structures, TEM is very helpful. The captured photos have a major impact on the progress of science in many different domains.

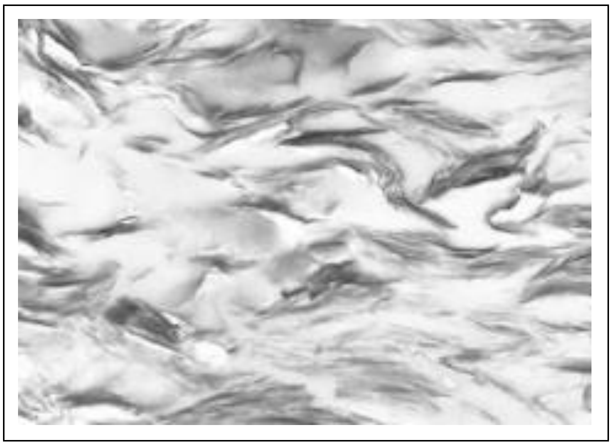

Figure 7. TEM image of T3 mix (3% Nano-silica + 97% Cement & 10% Nanoclay + 90% Fine Aggregate + 100% Coarse Aggregate)

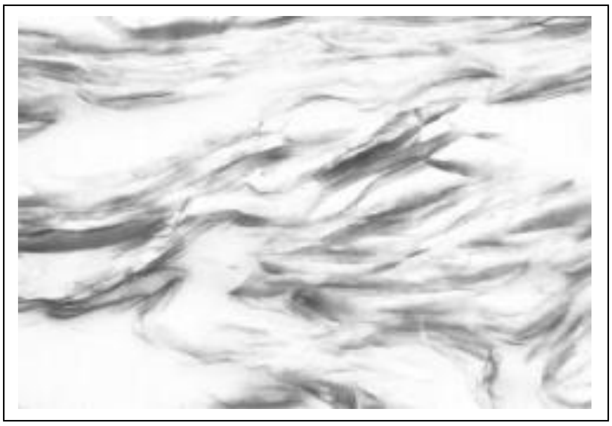

Fig. 8: TEM image of T4 mix (3% Nano-silica + 97% Cement & 15% Nanoclay + 85% Fine Aggregate + 100% Coarse Aggregate)

4.3 XRD Analysis

One of the most used methods for examining phase analysis, both quantitative and qualitative, is XRD, which also yields information about individual components. The powder diffraction study of the material about the structure of allotropic transformation revealed the substance's purity. Phase transitions and the attainment of substance purity are achieved. Fig. 9 shows the XRD picture of a concrete specimen with 3% nano-silica and 0% nanoclay, Fig. 10 - 5% nanoclay and 3% nano-silica, Fig. 11 - 10% nanoclay and 3% nano-silica and Fig. 12 - 15% nanoclay and 3% nano-silica. Outperforming other mixes, the addition of nano-silica at 3% by weight of cement and nanoclay at 10% by weight of fine aggregate yields superior outcomes. For the ideal nano mix, the Si peaks also rise significantly. The presence of nano-silica and nanoclay in concrete is also enhanced by the cement's hydration process. The Si peaks decreased for the other mixtures, indicating that more nano-modifiers were added due to the loosening of the concrete's strength.

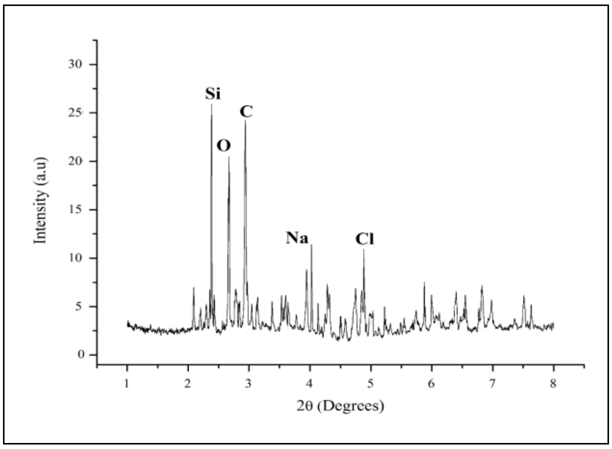

Fig. 9: XRD image of T1 mix (3% Nano-silica + 97% Cement & 0% Nanoclay + 100% Fine Aggregate + 100% Coarse Aggregate)

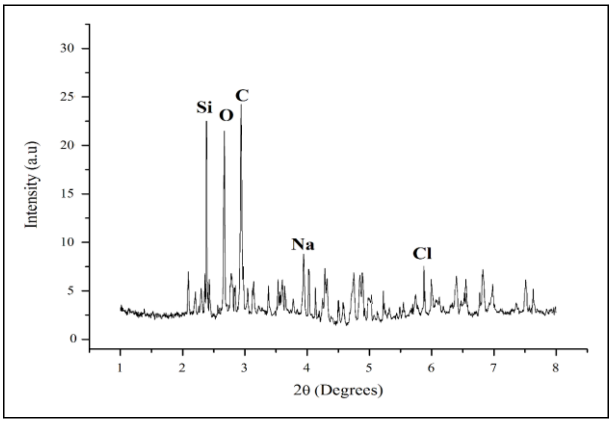

Fig. 10: XRD image of T2 mix (3% Nano-silica + 97% Cement & 5% Nanoclay + 95% Fine Aggregate + 100% Coarse Aggregate)

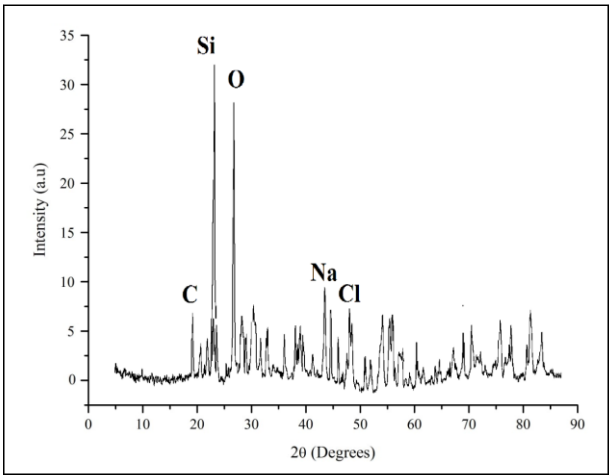

Fig. 11: XRD image of T3 mix (3% Nano-silica + 97% Cement & 10% Nanoclay + 90% Fine Aggregate + 100% Coarse Aggregate)

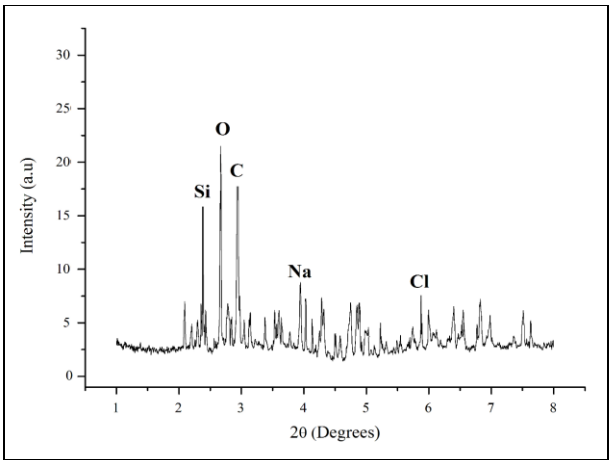

Fig. 12: XRD image of T4 mix (3% Nano-silica + 97% Cement & 15% Nanoclay + 85% Fine Aggregate + 100% Coarse Aggregate)

5. CONCLUSION

The SEM analysis conducted on fractured surfaces of diverse NMC samples has provided valuable insights into morphological changes within internal structures. This revelation suggests a robust interfacial adhesion between nano-silica and nanoclays with cement, potentially contributing to the observed enhancement in tensile strength. The TEM and SEM images depicting 3% nano-silica with 10% nanoclay loadings showcase distinctive moderate structures, indicating the successful formation of optimal nanocomposites. These structures play a pivotal role in augmenting properties across various replacement rates of nanocomposites. XRD analysis further supports these findings, revealing the disappearance of peaks in T3 nanocomposites, signifying the separation of silica and clay layers and the development of interpolated structures. The TEM studies provide compelling evidence confirming the optimal replacement of nanocomposites. The synergy between nano-silica and nanoclays at the microscopic level underscores the effectiveness of these additives in enhancing concrete properties. The formation of well-defined structures not only strengthens the interfacial bonds but also influences the overall performance of the material. This comprehensive microscopic examination not only validates the effectiveness of the nanocomposites but also sheds light on the intricate mechanisms underlying their influence on concrete properties. The results of these advanced microscopy and analytical techniques contribute significantly to our understanding of NMC behavior. The confirmation of optimal nanocomposite replacements in the TEM studies holds promise for the development of high-performance concrete, emphasizing the importance of precise nanomaterial integration for improved structural characteristics. Incorporating nano-silica and nanoclay not only enhances the properties of concrete but also mitigates soil pollution. This research provides a crucial foundation for further advancements in Nano-modified concrete technology, facilitating the development of more durable and resilient construction materials.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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