Long term characteristics of sustainable concrete incorporating manganese ore tailings and nano-silica as cementitious material

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Abstract. The incorporation of industrial by-products possessing latent hydration capacity as a partial cement replacement presents an effective strategy for advancing sustainable concrete production and reduction of hazardous substances in the environment. In this study, a mortar system containing ordinary Portland cement, nano-silica (NS) and Manganese Ore Tailings (MOT) was carefully designed to produce concrete. The hydration behaviour of the mortar system was examined through setting time observations. The duration of the initial hydration reaction took longer in the MOT samples, the delay increased as the MOT content increased. This could be due to the release of SO_4^{2-} ions from gypsum when MOT dissolves in water. The retardation in hydration time was significant at 25%, 30%, and 35% MOT content with delays of 2h, 3.5h, and 5.5h, respectively, compared to the control mix. Concrete mixtures with up to 10%MOT-10%NS demonstrated up to 29% improvement in mechanical properties and 37% lower shrinkage strain compared to conventional concrete. Nano-silica proved to enhance the strength and shrinkage characteristics of MOT concrete significantly due to the filler effect. Incorporating MOT in concrete offers a viable and eco-friendly solution for the safe disposal of the toxic components in MOT.
Keywords: Cement, Concrete, Compressive strength, Flexural strength, Manganese ore tailings, Nano-Silica, Shrinkage strain.

1 Introduction

The global population is growing at a rate of approximately 1% per year, adding around 80 million people annually, and is projected to reach 9.8 billion by 2050 [1]. This population growth demands the construction of millions of new homes each year, alongside other infrastructure developments. Rapid urbanization and industrialization are generating vast amounts of waste, posing significant environmental challenges. Among the most impactful waste sources from mining industries are mine tailings. The production of mine tailings has surged over the past century due to increased demand for minerals and metals, coupled with advanced extraction and processing technologies used for low-grade ores. Moreover, the volume of mined metals from the ore are usually low such that for each ton of metal mined, the tailings are usually over 100 tons [2, 3].

The environmental concerns of tailings include failure of tailing dams causing catastrophic mudflows. Also, heavy metals from tailings may leach to contaminate soil and groundwater, posing serious environmental hazards. Furthermore, tailings often emit dust causing air pollution and occupational health risk. Lastly, land degradation occurs due to large areas occupied by tailings dams and stockpiles. Consequently, the safe disposal of large quantities of such industrial waste is essential to mitigate environmental harm [2, 4].

Global warming and climate change have placed significant pressure on the construction industry to decrease cement production and develop environmentally friendly concrete using alternative materials. One promising approach to reducing cement consumption in concrete is the incorporation of industrial waste materials into concrete and mortar mixes. This practice not only addresses the shortage of natural resources but also helps resolve waste disposal challenges while promoting environmentally sustainable solutions. It reduces hazards and supports cleaner production processes. Beyond sustainability, the use of supplementary cementitious materials as a replacement for cement can enhance material rheology, long-term strength, and durability properties [5].

Mine tailings have been processed and utilized as construction materials in various applications. They have been used as substitutes for natural crushed stone, gravel, and sand in the production of mortar, bricks, and concrete [6]. Additionally, mine tailings have been applied in the construction of bases, sub-bases, and wearing courses for roads, airfields, and dams [7]. Ozen et al.[8] in their work used silica fume and fly ash with gold tailings as additives to Portland cement for mortar production. The results demonstrated that the mortar achieved compressive strength values meeting European standards for structural applications. Mehra et al. [9] explored the use of jarosite (produced from zinc extraction) in concrete as a replacement for fine aggregate, combined with fly ash. Their findings indicated that the mechanical and durability properties of jarosite-based concrete were satisfactory for structural purposes, and the leaching of heavy metals from jarosite remained within permissible limits, making it a viable alternative to traditional disposal methods.

Manganese Ore Tailings (MOT) are the fine-grained waste materials left after the extraction and processing of manganese ore in mining operations. It is a slurry by-product disposed of in tailings dams or stockpiles. Manganese is critical for steelmaking, batteries, and alloys [6], this means there is a large-scale mining activity where manganese deposit is in abundance for example South Africa, consequently resulting in large volumes of tailings in the area [10]. Manganese ore tailing is formed as a precipitate during filtration process, which separates liquid from solid waste under pressure. The solid waste is compressed into a cake-like form, often dark brown or black, containing high concentrations of iron, sulfur, and other industrial byproducts. Although MOT is typically classified as waste requiring careful disposal or treatment to mitigate environmental impacts, its composition suggests it may have potential for further processing or recycling. Unlike clay or limestone, MOT is characterized as a sandy silt, offering unique properties for potential applications in construction materials[11].

The chemical composition of Manganese Ore Tailings (MOT) shares similarities with Ordinary Portland Cement (OPC), particularly the presence of silicon and aluminium oxides. Consequently, MOT has emerged as a potential supplementary cementitious material for partial replacement of OPC (Bowen). Studies have reported enhanced material performance with such incorporation. Shanmugasundaram et al. [11] demonstrated that MOT–OPC blends improved the stabilization of expansive soils, achieving an unconfined compressive strength of 1179 kPa and a soaked CBR of 25.1% after 28 days. Similarly, Maurilio et al. [10] found that substituting 6–8% of cement with MOT increased concrete compressive strength and density, while reducing void ratio and water absorption.

The inherently low self-cementing and hydration activity of Manganese Ore Tailings (MOT) limits their potential for direct use as a cement substitute [10]. Nano-silica (NS), a highly reactive pozzolanic admixture, has been widely utilized to enhance the hydration kinetics and microstructural refinement of cementitious materials [12]. Owing to its high surface area and reactivity, NS rapidly reacts with calcium hydroxide ($Ca(OH)_2$) to generate additional calcium silicate hydrate (C–S–H) gel, the principal phase responsible for strength development in concrete, thereby improving both early and long-term mechanical performance [13]. In mixtures incorporating mine tailings, which typically exhibit limited pozzolanic reactivity, NS can effectively stimulate hydration and activate the latent siliceous and aluminous constituents, leading to notable strength enhancement [14]. Nevertheless, the underlying activation mechanism of NS within the MOT–OPC system and the optimal MOT replacement level remain inadequately elucidated, necessitating further investigation.

There is limited published research on the use of MOT as a construction material, either as a replacement for aggregate or cement. While previous studies have explored the use of other mine tailings in concrete and bricks as a substitute for fine aggregates, their potential as a cement replacement remains largely unexplored. Given the current environmental and climate challenges, it is crucial to assess the feasibility of using MOT as a partial substitute for cement. Understanding the mechanisms of the hydration process and changes in the microstructure of concrete incorporating MOT could provide valuable insights for advancing concrete technology.

A key challenge in utilizing mine tailings in concrete is the variability of their chemical composition, which often leads to inconsistent performance [6]. This study introduces nano-silica (NS) as a stabilizing agent to mitigate such variability and enhance the pozzolanic activity of Manganese Ore tailings (MOT). Accordingly, the objective of this work is to evaluate the performance of cement mortar incorporating MOT and to examine the influence of NS on its properties. The findings aim to advance the effective utilization of MOT in concrete production and contribute to sustainable construction practices.

2 Materials and Methodology

2.1 Manganese Ore Tailings

Manganese Ore Tailings (MOT) used in this investigation was gotten from a metal mining company. It is brown in colour and has a specific gravity of 3.24. The MOT was moist, with large particles when collected. It was air dried and milled into finer particles using a ball mill to give the final product. It was sieved sieved to create a particle size distribution ranging from 2 µm to 75µm particle sizes.

2.2 Ordinary Portland Cement, Aggregates, Water, Nano-Silica and Superplasticizer

The Ordinary Portland Cement (OPC) used in this research was Afrisam CEM I 52.5R, a high-strength, rapid-hardening Portland cement, with a specific gravity of 3.16. The coarse aggregate used was crushed granite with a maximum particle size of 14 mm, while the fine aggregate was silica sand with particle sizes ranging from 2.00 mm to 150 µm (Fig.1). The specific gravities of the coarse and fine aggregates were measured as 2.65 and 2.56, respectively. Additionally, the bulk densities of the coarse and fine aggregates were determined to be 2072 kg/m³ and 2145 kg/m³, respectively. Potable water was used for mixing the concrete.

The nano-silica (NS) used in this study possessed a specific surface area of 280 m²/g, an average particle diameter of 20 nm, and a density of 1.25 g/cm³. To facilitate uniform dispersion of the NS particles and enhance the workability of the concrete mixture, a polycarboxylate-based superplasticizer (SP) with a water-reducing capacity greater than 25% and a density of 1014 kg/m³ was added at 2% of the total weight of the cementitious materials.

2.3 Mix Design

A total of six concrete mixes were prepared, including a control mix as given in Table 1. The mix design followed an M20 grade of concrete with a proportion of 1:2:4 (Cement/MOT: Sand: Granite) and a water-to-binder ratio of 0.3. The control mix consisted of Ordinary Portland Cement (OPC), natural fine aggregates, natural coarse aggregates, and water. Manganese Ore tailings (MOT) was used to partially replace OPC at replacement levels of 0%, 5%, 10%, 15%, and 20% by weight of cement. Nano-silica was incorporated for all mixes except the control mix, at a constant percentage of 10% of cementitious content based on recommendations by Adetukasi et al.[15]. Seventy-two concrete cubes (150 x 150 x 150 mm) were cast for density and compressive strength tests (Fig. 1) which were conducted after curing periods of 7, 14, 21 and 28 days, thirty-six short concrete beams (750 x 150 x 150 mm) for flexural strength tests (Fig. 2), and eighteen concrete prisms (100 x 100 x 500 mm) for shrinkage measurements up to 90 days.

Mix (% MOT content)	Sand (kg)	Water (kg)	Granite (kg)	Cement (kg)	MOT (% of Cement)	NS (% of cement)
Control	840	210	1680	420	0	0
0%MOT-10%NS	840	210	1680	420	0	10
5%MOT-10%NS	840	210	1680	399	5	10
10%MOT-10%NS	840	210	1680	378	10	10
15%MOT-10%NS	840	210	1680	357	15	10
20%MOT-10%NS	840	210	1680	336	20	10

Fig. 1. Concrete cubes for compressive strength test

Fig. 2. Concrete beam under flexural strength test

3 Results and Discussions

3.1 Setting Time of MOT Concrete

The setting time results for mortar samples with varying MOT replacement percentages are presented in Fig. 3. The longest initial setting time, recorded for the 20% MOT sample, was 202 minutes. It was observed that the initial and final setting time increased as the MOT content increased, with the control concrete (0% MOT, 0% NS) having the shortest initial setting time at 98 minutes. The control concrete and the 5% MOT concrete had the same final setting time of 159 minutes. The addition of NS increased the setting times only by 3% compared to the control mix.

The prolonged setting time in MOT concrete may be attributed to the reduced solubility of the cement paste due to the presence of sulphate ions from gypsum in the MOT. XRD analysis [11] revealed that MOT contains 71.58% gypsum ($CaSO_4 \cdot 2H_2O$). When gypsum reacts with calcium aluminate in its natural form, it forms ettringite, which inhibits the formation of calcium silicate hydrates (C-S-H), the primary compound responsible for the hardening of concrete. This delay in C-S-H formation slows the setting process, preventing the concrete from hardening too quickly after mixing. Additionally, a higher cement content leads to more tightly packed cement particles, which facilitates greater interparticle contact and accelerates setting time.

Open time, defined as the difference between the initial and final setting times, was found to be lowest for the 20% MOT concrete, with an open time of 21 minutes. As the MOT percentage in the concrete increased, the open time decreased. This finding supports previous research suggesting that mine tailings, when used in appropriate amounts, can act as an effective set-retarding admixture in concrete [12].

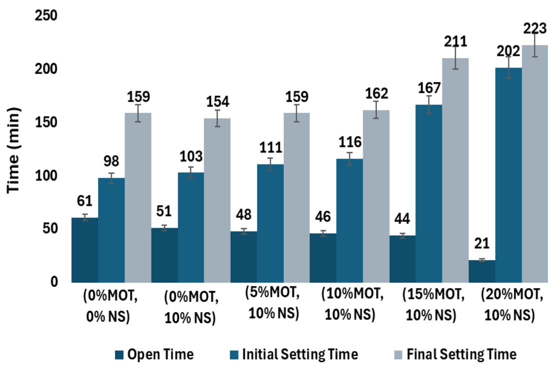

Fig. 3. Setting and Open Time Result of MOT Mortar

3.2 Workability of MOT Concrete

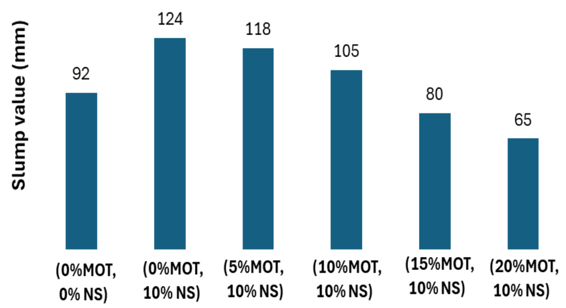

Fig. 4. Slump values of MOT Concrete Mixes

The slump flow results shown in Fig. 4 for the MOT Concrete mixes indicated that the incorporation of MOT in concrete reduced slump flow, thereby reducing workability. As the amount of MOT in the mix increased, the slump flow reduced. Up to 15% replacement level, the mixes exhibited a true slump, with values ranging from 80mm for the 15% MOT mix to 118mm for the 5% MOT mix. Addition of NS and the superplasticizer improved the slump value significantly from 92mm which was observed for the control concrete (0% MOT, 0%NS) to 124mm, observed for the 0% MOT-10%NS mix. This explains the higher slump value observed for the 5% and 10% MOT samples, meaning addition of NS and SP helped to reduce the adverse effects that MOT may have on concrete workability.

3.3 Density of MOT Concrete

Fig. 5 presents the density of concrete with varying MOT replacement levels. The mix with 20% MOT recorded highest wet and dry densities of 2241kg/m^3 and 227kg/m^3 respectively while the control concrete had the lowest wet and dry densities of 2132 kg/m^3 and 2124kg/m^3 respectively. Both the wet and dry densities of MOT concrete increased as MOT content increased, which can be attributed to the higher specific gravity of MOT compared to cement. Addition of NS proved to make the concrete denser, this is as expected as the particles of NS are very fine, able to fill the voids in the concrete matrix. At all replacement levels, the wet density was found to be higher than the dry density. This difference is due to the mass of water used in mixing the concrete and the temporary expulsion of air during the mixing process. As the concrete cures, some of the water either chemically reacts with the cement (during hydration) or evaporates. This loss of excess water leads to a reduction in overall mass, resulting in a lower density in the hardened state. The differences between the wet and dry densities of concrete with the same MOT content in all the MOT mixes are greater than that observed in conventional concrete, which may indicate a higher loss of mix water in the MOT concrete samples.

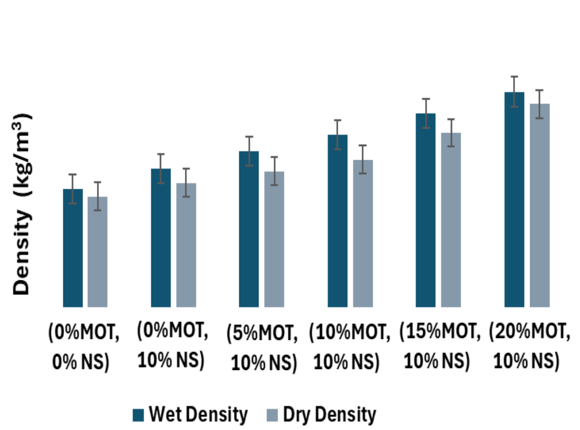

Fig. 5. Density of Concrete Containing Manganese Ore Tailings and Nano-Silica

3.4 Compressive Strength of MOT Concrete

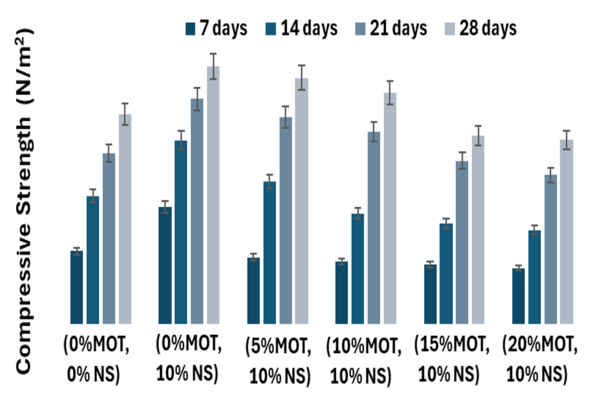

Fig. 6. Compressive Strength Result of MOT Concrete at Different Ages

Fig. 6 presents the compressive strength of MOT concrete at 7, 14, 21 and 28 days of curing. At all replacement levels, the concrete showed strength improvements with age, indicating that the presence of

MOT did not hinder the hydration process. At day-7, the mix containing 0%MOT-10%NS had the highest compressive strength of 13.72 N/mm², followed by the control concrete (0%MOT-0%NS) and the MOT concretes where strength decreased as MOT content increased. However, at 14-day test, the 5% MOT concrete exhibited higher compressive strength than the control concrete (11%↑) and at 21-day test, the 10% MOT attained higher compressive strength (12%↑) than the control concrete. This confirms the retardation observed in MOT samples from the calorimetry results.

At 28-day test, the 0%MOT-10%NS mix had the highest compressive strength of 30.18 N/mm2. This was followed by the 5%MOT-10%NS and 10%MOT-10%NS concrete mixes with compressive strengths of 28.84 N/mm2 and 27.08N/mm2 respectively. After 28 days of curing, the control concrete only has compressive strength higher than the 15% MOT-10%NS and 20% MOT-10%NS mixes. This suggests that at lower MOT replacement levels, the pozzolanic properties of MOT enhance the hydration process. At higher MOT content, the increased heavy metal content competes for the calcium silicate hydrate (C-S-H) gel responsible for strength development, instead of developing more hydration materials, it is used to stabilize the heavy metals in MOT. The fine particles of MOT, which help fill the pores in the concrete, may have contributed to the compressive strength of MOT concretes. This may explain why MOT samples achieved satisfactory strength even at a 20% replacement level (21.56 N/mm²). Similar to investigation by Liu et al. [6] on mine tailings, compressive strength was found to reduce with higher content of mine tailings in the mix.

The analysis indicates that MOT exhibit low early-age hydration activity, contributing minimally to the cement hydration process during the initial curing period. However, the reactivity of MOT was observed to increase progressively with extended curing time, suggesting a delayed but sustained pozzolanic response. Incorporation of NS proved to be effective at enhancing the compressive strength of both normal and MOT concrete. An improvement of compressive strength of 23% was observed between the control concrete and concrete containing 10% NS incorporation. Due to its nanometric particle size, NS can fill voids within the cement matrix, refining the pore structure and reducing porosity. This densification improves the interfacial transition zone (ITZ) between the cement paste and aggregates, which is typically the weakest link in concrete microstructure. This provides enhanced strength, stiffness, and overall durability of concrete.

3.5 Flexural Strength of MOT Concrete of MOT Concrete

Fig. 7 illustrates the variation in flexural strength of MOT concrete with varying curing age (7 and 28 days) and MOT replacement levels (0%, 5%, 10%, 15%, and 20%). The highest flexural strength was recorded on the concrete mix 0%MOT-10%NS confirming the effectiveness of NS in enhancing concrete strength. This is further reflected in the flexural strength results for the MOT concrete samples. The 5% MOT concrete exhibited higher flexural strength, with values of 2.63 N/mm² at 7 days and 4.13 N/mm² at 28 days, representing a 29% increase compared to the control concrete. This is similar to the compressive strength result and confirms the ability of NS to enhance pozzolanic activity in MOT. At 15% MOT content, the flexural strength was comparable to the control concrete at 28 days and even exceeded it at 7 days of curing. However, the 20% MOT demonstrated lower flexural strength at 28 days when compared to the control concrete.

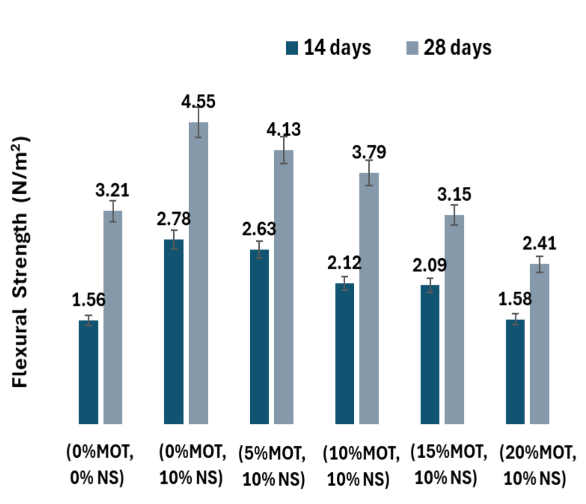

Fig. 7. Flexural Strength Result of Manganese Ore Tailings Concrete at Different Ages

3.6 Drying Shrinkage of Manganese Ore Tailings Concrete

Concrete shrinkage occurs due to the loss of water from the cement paste. It is essential to measure shrinkage in order to control cracking. Drying shrinkage refers to the deformation that happens as free water evaporates from the concrete, influenced by temperature and humidity. This shrinkage is affected by factors such as the water-cement ratio, cement composition, aggregate type, degree of hydration, curing conditions, curing temperature, relative humidity, moisture content, and the drying duration [15].

Fig. 8 illustrates the shrinkage strain of concrete containing MOT at various replacement levels over a 90-day observation period. All the concrete samples had a steady increase in shrinkage strain at early ages (0-30days) and a gradual increase afterwards. The 0%MOT-10%NS mix has the lowest total shrinkage strain of 73 mm/m after 90 days. This is followed closely by the 5%MOT-10%NS mix with a shrinkage strain of 78mm/m. The control sample (0%MOT-0%NS) recorded total shrinkage strain of 124 m/mm, this is lower than the 15% and 20% MOT (with 10%NS) samples which recorded 152mm/m and 165 mm/m respectively.

It was observed that shrinkage increased in the samples with increased MOT content. The addition of NS improved the resistance of the samples to shrinkage as the normal concrete with NS significantly has lower shrinkage strain compared to the control concrete without NS. It also improved the shrinkage characteristics of concrete with lower MOT content (up to 10%) as they have lower shrinkage strain compared to the control concrete. This is in alignment with results from compressive and flexural strength tests. This means that addition of NS to MOT concrete improves both strength and structure of the concrete.

The increased shrinkage observed in concrete containing higher percentages of MOT (15% and 20%) may be due to the high sulphates content contributed by higher MOT content, which react with tricalcium aluminate to form ettringite and gypsum. This reaction causes the cement paste to expand and creates pores. As the concrete ages, the water within these pores evaporates, leading to increased drying shrinkage.

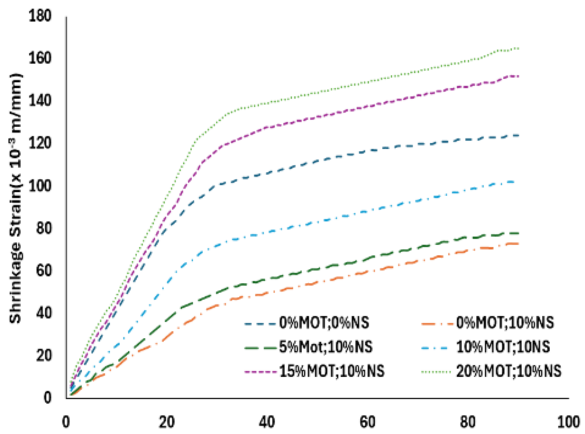

Fig. 8. Shrinkage Strain of MOT Concrete at Different Replacement Levels

4 Conclusion

This study provides a thorough analysis of the performance of Manganese Ore Tailings (MOT) as a partial substitute for cement and the incorporation of nano-silica in the production of sustainable concrete. It was observed that the initial and final setting time increased as the MOT content increased. The control concrete (0% MOT-0% NS) had the shortest initial setting time at 98 minutes. The longest initial setting time was recorded for the 20% MOT sample, as 202 minutes. The high percentage of gypsum contained in MOT contributed to the extended setting time of MOT mortar. The addition of NS increased the setting times by 3% compared to the control mix. Open time was found to be lowest for the 20% MOT concrete, with an open time of 21 minutes. As the MOT percentage in the concrete increased, the open time decreased. This confirms that MOT, when used in appropriate amounts, can act as an effective set-retarding admixture in concrete.

Both the wet and dry densities of MOT concrete increased as MOT content increased, which can be attributed to the higher specific gravity of MOT compared to cement. Addition of NS proved to make the concrete denser, this is as expected as the particles of NS are very fine, able to fill the voids in the concrete matrix. The 5%MOT-10%NS and 10%MOT-10%NS mixes recorded improved compressive strength over the control concrete by 17% and 10% respectively. The same trend was observed for the flexural strength of MOT concretes. Addition of NS improved the flexural strength of normal concrete by 32% and the compressive strength by 23%, consequently contributing to the higher strength recorded in the MOT samples.

MOT concrete at lower replacement levels (up to 10%) showed lower shrinkage strain by 37% and 18% for the 5%MOT-10%NS and 10%MOT-10%NS respectively compared to the control concrete but at higher replacement levels (15 and 20%), higher shrinkage strains were recorded.

Finally, nano-silica proved to enhance the strength and shrinkage characteristics of MOT concrete significantly. Incorporation of MOT in concrete offers a viable and eco-friendly solution for the safe disposal of the toxic components in MOT. This study suggests that MOT holds potential as a partial replacement for ordinary Portland cement.

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