

COMPRESSIVE STRENGTH AND GEL FORMATION OF ENHANCED GEOPOLYMER WITH ADDITION OF NANOMATERIALS – A REVIEW

Shadman Rahman SABAB¹, U. Johnson ALENGARAM¹✉,
Chiu Chuen ONN², Saznizam Sazmee SINO¹

¹Centre for Innovative Construction Technology (CICT), Department of Civil Engineering, Faculty of Engineering, Universiti Malaya, Kuala Lumpur, 50603, Malaysia

²Department of Civil Engineering, Faculty of Engineering, Universiti Malaya, Kuala Lumpur, 50603, Malaysia

Article History:

- received 4 January 2026
- accepted 14 May 2026

Abstract. Nanomaterial reinforcement has emerged as a pivotal strategy to overcome the mechanical and durability limitations of traditional geopolymer binders. This review systematically evaluates the integration of zero- to one-dimensional nanomaterials, like graphene oxide, carbon nanotubes, and nano silica, etc., into geopolymer matrices synthesized from diverse industrial precursors such as fly ash, slag, and red mud. The fundamental mechanisms of reinforcement, specifically nucleation, matrix densification, and micro-crack bridging, are analyzed to illustrate the transition from brittle to ductile behavior. Beyond mechanical enhancement, the critical roles of dispersion techniques, particle size, and optimal dosages in mitigating workability trade-offs and agglomeration are examined. This work delineates the relationship between microstructural evolution and crack-arrest mechanisms through a systematic evaluation of SEM, XRD, and Nanoindentation results reported in recent literature. Furthermore, the review explores innovative processing trends, such as the synergy between nano-additives and rapid microwave curing, which significantly reduces energy consumption compared to conventional thermal methods. Finally, industrial scaling challenges, cost-effectiveness, and the environmental life-cycle of nano-engineered composites are addressed. By identifying critical research gaps in multi-nanomaterial synergy and standardized durability testing, this paper provides a strategic roadmap for the development of high-performance, resilient, and sustainable geopolymer infrastructure.

Keywords: geopolymer composites, nanomaterials, compressive strength, microstructure, durability, nano-silica, carbon nanotubes, graphene oxide, nano-clay, nano-titanium, nano-aluminum.

✉Corresponding author. E-mail: johnson@um.edu.my

1. Introduction

Concrete is a ubiquitous construction material whose environmental impact is often secondary to its structural necessity. These materials are the backbone of every modern structure, starting from the foundation slabs that hold the residential homes to the intricate bridges and tunnels that facilitate transport (Black et al., 2010). However, during the production of cement, the basic element in concrete, there is a significant quantity of carbon dioxide (CO₂) emissions. This is worsened by the fact that massive amounts of cement are being produced worldwide, about 33 billion tons annually, due to the rising demand for concrete to be used in urbanization and developing infrastructure (Mehta & Monteiro, 2014). The calcination of limestone, especially, releases most of the CO₂ into the atmosphere, contributing to a significant portion of the worldwide greenhouse gas emissions. This actuality shows the need to derive an alternative binding substance that can lessen the nega-

tive environmental effect while also being sustainable to be used in concrete production (Nie et al., 2022). With the need to diminish the impairment of manufacturing cement, notable research started to focus on the binder geopolymer as an eco-friendly alternative to cement. Geopolymers have become a viable alternative to the traditional Portland cement, showing a notable reduction in the emission of CO₂. The name geopolymer was given by Davidovits (1979) to describe the mineral polymers produced by geochemistry as substitute building materials. In contrast to the production of cement, which includes the calcination of limestone and releases considerable amounts of CO₂, geopolymer incorporates the industrial waste by-products or the naturally abundant aluminosilicate materials, resulting in a lower embodied carbon footprint, contributing to a friendly environmental construction industry. In addition, geopolymer binders also provide comparable

or even superior mechanical strength and durability, making them a more feasible alternative to cement in various applications of cement (Jalal et al., 2024). Geopolymer is produced by geopolymerization; synthesis through a chemical reaction involving source materials: alumina (Al^{3+}), silica (Si^{4+}), and alkaline activating solution, resulting in the formation of a stable covalently bonded structure (Provis, 2014). The strength of geopolymer concrete is heavily influenced by the curing temperature. While heat-cured specimens exhibit mechanical properties comparable or superior to ordinary Portland cement (OPC), ambient-cured formulations typically show a drastic reduction in strength due to slower geopolymerization kinetics (Deb et al., 2014, 2015).

Recent advancements in rapid activation have demonstrated that microwave curing can effectively bypass these limitations by initiating heat generation at the molecular level. For instance, Yilmazer Polat (2023) showed that microwave curing at 300W for only 10 minutes can yield a compressive strength of 67.7 MPa in fly ash-based mortars, a value comparable to results achieved after 48 hours of conventional oven curing. However, a higher calcium content in the raw materials can alter the curing regime, enabling high-strength development under ambient conditions. As recent geopolymer research utilizes higher calcium availability, the resulting reaction products transition toward calcium aluminosilicate hydrate (C-A-S-H) phases rather than sodium aluminosilicate hydrate (N-A-S-H) phases (Viola et al., 2024). Despite these advancements, challenges such as incomplete chemical reactions often persist, leading to porous microstructures that fail to reach

desired strength levels or provide adequate long-term durability. Due to these limitations, the widespread adoption of geopolymers in the construction industry remains restricted. To address these fundamental weaknesses at the sub-micron level, the integration of nanomaterials has emerged as a transformative solution.

In recent decades, nanomaterials like nano-silica or nano-alumina have been introduced to engineer the geopolymer microstructure, and could improve the fresh and hardened properties of the products (Jindal & Sharma, 2020). The nanomaterials work by enhancing chemical reactions at a nanoscale during geopolymerization, causing a denser and more compact microstructure to form. The surface area, aspect ratio, and reactivity of the nanomaterials are what affect the overall process. The aspect ratio affects the overall structural integrity, enabling improved mechanical strength and durability. The reactivity allows the formation of additional geopolymer gel. By optimizing the pore structure and minimizing permeability, these nanomaterials considerably improve the material's susceptibility against chemical attack and deterioration (Samuv-el Raj et al., 2023; Tayeh et al., 2022; Zhang et al., 2022b).

However, despite the growing body of literature, current reviews often focus on isolated material types, leaving a significant gap in the systematic understanding of how various nanomaterial geometries interact with different industrial precursors under diverse curing regimes. The current study aims to address this gap by providing a holistic review of the role of various nanomaterials in enhancing the mechanical properties and microstructural evolution of geopolymers. This paper provides critical guidelines for

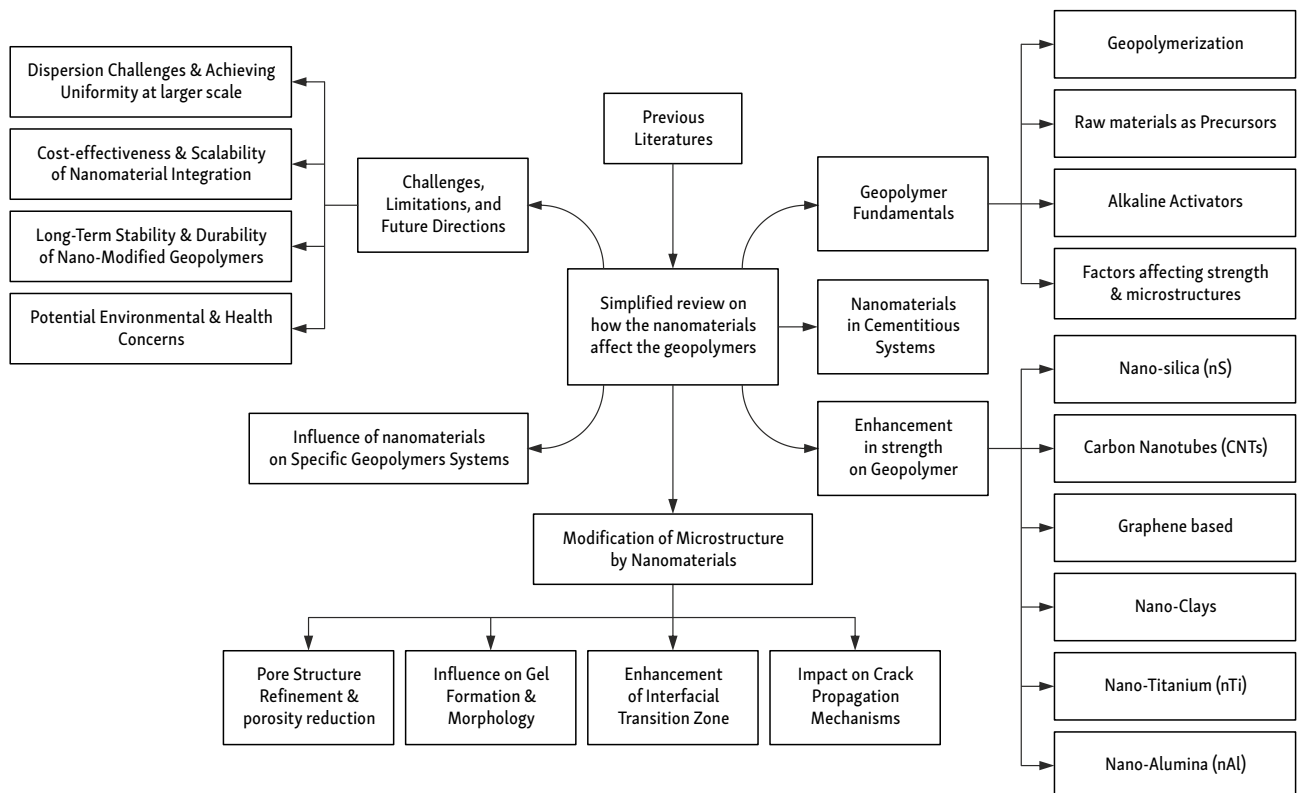


Figure 1. Structure of the current study

researchers by synthesizing data on compressive strength and advanced microstructural analysis, while also identifying the technical challenges and future research directions necessary to transition nano-engineered geopolymers from the laboratory to large-scale structural applications. Figure 1 depicts the methodology of the current study.

2. Fundamentals of geopolymers

2.1. Geopolymerization process: Dissolution, gelation, and polycondensation

Geopolymerization is an exothermic process involving the chemical synthesis of aluminosilicate oxides into a complex three-dimensional framework. This transformation proceeds through three interconnected stages: dissolution, gelation, and polycondensation.

Dissolution: Upon contact with highly alkaline activators, typically a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3), the covalent bonds (Si-O-Si and Si-O-Al) of the precursor materials are cleaved. This stage is a rate-limiting step governed by the alkalinity (pH) of the solution; a higher OH^- concentration accelerates the leaching of reactive Si^{4+} and Al^{3+} ions into the aqueous phase (Davidovits, 2008; Wallah & Rangan, 2006).

Gelation: As the concentration of dissolved species increases, the solution reaches a supersaturated state, triggering the formation of primary silicate and aluminate units. These monomers begin to orient into a coagulated gel phase. The alkalinity of the medium is critical here, as it dictates the degree of ionization and the connectivity of the initial clusters (Wallah & Rangan, 2006).

Polycondensation: In the final stage, the monomers undergo dehydration and cross-linking to form siloxo (Si-O-Si) and sialate (Si-O-Al) linkages. This stage results in a rigid, 3D macromolecular network of SiO_4 and AlO_4 tetrahedra. The final mechanical integrity and porosity of the binder are highly sensitive to the Si/Al molar ratio; a higher Si content typically yields a more cross-linked, denser

structure, whereas excessive Al can lead to faster setting but lower long-term strength (Shi et al., 2006; van Jaarsveld et al., 2002).

The complexity of this transition is further illustrated by the four-step model proposed by Sotelo-Piña et al. (2019), which maps the evolution from initial particle contact to the final hardened geopolymer matrix (Figure 2).

2.2. Key precursor materials for geopolymer synthesis

For geopolymerization to take place, the precursors used must have the key substances silica (SiO_2) and alumina (Al_2O_3). Out of various raw materials, the ones stated below are the most used.

2.2.1. Fly ash

Fly ash (FA), a spherical by-product of coal combustion, is the most widely utilized precursor in geopolymer research due to its global availability and high amorphous SiO_2 and Al_2O_3 content. While Class C FA (high CaO) can offer some ambient-curing potential, Class F FA (low CaO < 10%) remains the industry standard for geopolymerization due to its superior long-term durability and resistance to chemical attack (I. Luhar & S. Luhar, 2022; Wang et al., 2020; Watimena et al., 2017; Zhuang et al., 2016).

2.2.1.1. Reactivity and limitations

A critical limitation of Class F fly ash is its relatively low reactivity at ambient temperatures. The glassy, spherical particles revealed in SEM analysis, Rani and Gladston (2024) (Figure 3a), possess a stable surface layer that requires thermal activation (typically 60–90 °C) or high-molarity alkaline solutions to initiate the dissolution of silicate and aluminate ions. Without sufficient heat or chemical acceleration, FA-based systems often exhibit slow setting times and lower early-age strength compared to calcium-rich precursors like GGBS (Temizer & Çavdar, 2025).

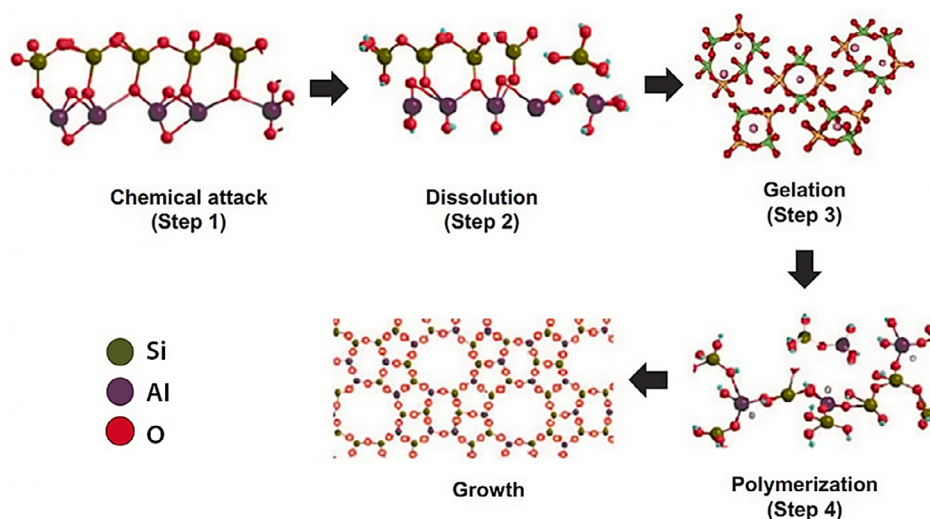


Figure 2. The process of geopolymerization (Sotelo-Piña et al., 2019)

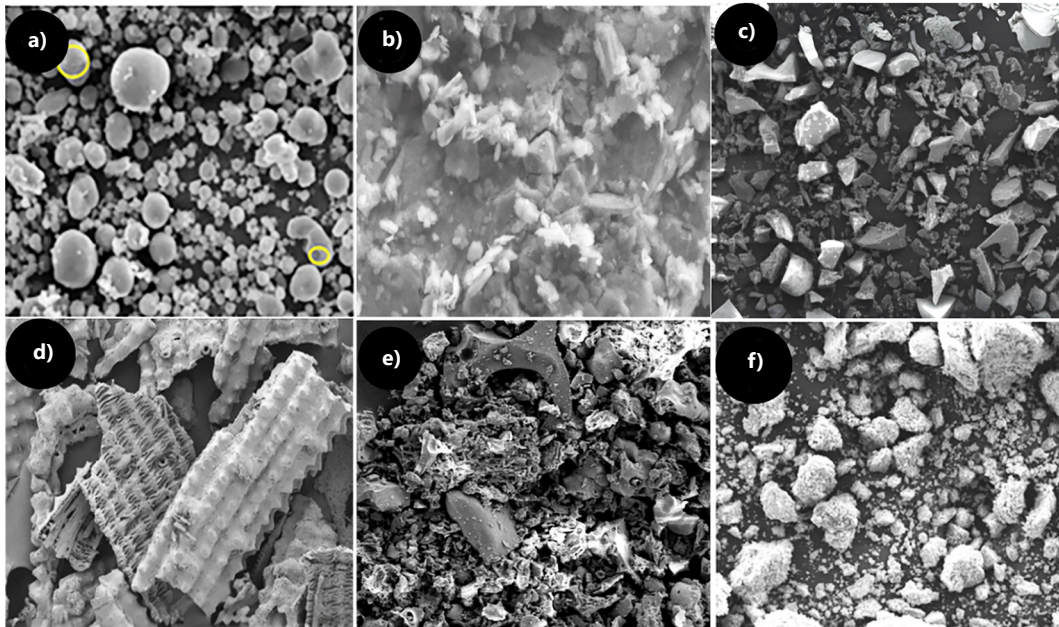


Figure 3. a – SEM analysis of FA (Rani & Gladston, 2024); b – MK (Yuan et al., 2022); c – GGBS (Tanu & Unnikrishnan, 2023); d – RCA (Somna et al., 2022), e – CBA (Lei et al., 2024); f – RM (He et al., 2013)

2.2.1.2. Compatibility with nanomaterials

Nanomaterials are particularly effective when paired with FA precursors. Because FA-based geopolymers often develop a relatively porous microstructure during early stages, the high surface area of nano-silica or carbon nanotubes acts as a “seed” for nucleation, accelerating the sluggish geopolymerization kinetics of the fly ash particles. This synergistic effect allows for a denser matrix and can potentially lower the required curing temperature, addressing one of FA’s primary industrial drawbacks (Shamsah, 2023).

Recent studies have expanded the use of FA-based systems from binders to full-scale composite mixtures. For example, Rao et al. (2024) demonstrated that fly ash-based geopolymer concrete can successfully incorporate up to 40% recycled concrete aggregates (RCA) for pavement applications. This research indicates that while RCA replacement increases water absorption, the robust FA matrix maintains structural integrity and compressive strengths (33–38 MPa) suitable for rigid pavements, illustrating a viable path for large-scale environmental footprint reduction.

2.2.2. Metakaolin

Metakaolin (MK), produced through the controlled calcination of kaolinitic clay, is widely regarded as a high-purity aluminosilicate precursor for geopolymer synthesis. Unlike FA, MK is an engineered material, which ensures a consistent chemical composition and a high amorphous content, primarily consisting of Al_2O_3 and SiO_2 in a reactive state.

2.2.2.1. Reactivity and performance comparison

In contrast to the spherical, glassy particles of fly ash, MK exhibits a flaky, plate-like morphology, according to Yuan et al. (2022) (Figure 3b). This structural difference leads

to significantly higher reactivity at ambient temperatures; MK-based geopolymers typically achieve superior early-age mechanical properties without the need for thermal curing. However, the high specific surface area and layered structure of MK result in a much higher water demand compared to FA-based systems. This often leads to increased shrinkage and a more brittle matrix, which are the primary technical limitations of pure MK geopolymers.

2.2.2.2. Compatibility with nanomaterials

The integration of nanomaterials with Metakaolin presents unique challenges and opportunities compared to other precursors. While MK provides a highly reactive environment for geopolymerization, its high viscosity can hinder the uniform dispersion of nano-additives like carbon nanotubes or graphene oxide.

However, when effectively dispersed, nanomaterials serve a dual purpose in MK systems:

- a) **Crack Bridging:** The flaky nature of MK makes the matrix prone to micro-cracking during drying; 1-D nanomaterials are particularly effective at bridging these gaps and enhancing fracture toughness.
- b) **Pore Refinement:** Nano-silica can react with the abundant alumina in MK to further refine the pore structure, mitigating the characteristic permeability and shrinkage issues associated with this precursor (Aboulayt et al., 2018; Gómez-Casero et al., 2022; Han et al., 2023; Sujjavanich et al., 2017; Yuan et al., 2022; Zhang et al., 2014, 2021, 2022a, 2023).

2.2.3. Ground granulated blast furnace slag (GGBS)

Ground Granulated Blast Furnace Slag (GGBS) is a calcium-rich byproduct of steel manufacturing that occupies a unique position among geopolymer precursors due to its

dual cementitious and pozzolanic nature. Unlike the aluminosilicate-dominated fly ash or metakaolin, GGBS contains significant quantities of calcium oxide (CaO), which fundamentally alters the geopolymerization pathway.

2.2.3.1. Reactivity and performance comparison

The primary distinction of GGBS lies in its ability to undergo hydration and polycondensation at ambient temperatures. While FA requires external heat to initiate reaction, the high calcium availability in GGBS facilitates the simultaneous formation of calcium aluminosilicate hydrate (C-A-S-H) and calcium silicate hydrate (C-S-H) gels alongside the traditional geopolymer (N-A-S-H) network. This hybrid gel structure results in a significantly denser matrix with higher early-age strength and lower porosity compared to FA-based systems. However, a major limitation of GGBS is its rapid setting time and high autogenous shrinkage, which can lead to micro-cracking if not carefully controlled.

2.2.3.2. Compatibility with nanomaterials

The interaction between GGBS and nanomaterials is highly dynamic due to the accelerated reaction kinetics.

- a) **Nucleation and Acceleration:** Because GGBS already reacts quickly, the addition of high-reactivity nanomaterials like nano-silica can lead to “flash setting”. This necessitates precise control over mixing sequences to ensure the nanomaterials are dispersed before the matrix hardens.
- b) **Mitigating Brittleness:** While GGBS produces a very strong and dense matrix, it is often more brittle than MK or FA systems. The integration of 1-D nanomaterials (such as carbon nanotubes) is particularly beneficial here, as they provide internal reinforcement and bridge the micro-cracks formed during the rapid hydration of the slag particles.
- c) **Morphological Advantage:** SEM analysis by Tanu and Unnikrishnan (2023) (Figure 3c) shows that GGBS particles are angular with uneven surfaces. This high roughness provides a superior mechanical interlock with nanomaterials compared to the smooth, spherical surface of fly ash, leading to a stronger interfacial transition zone (ITZ) (Amar et al., 2023; Shahmansouri et al., 2020; Xie et al., 2019; Zheng et al., 2022).

2.2.4. Rice husk ash

Rice Husk Ash (RHA) is an agricultural by-product obtained from the controlled combustion of rice hulls. It stands out from mineral-based precursors due to its exceptionally high amorphous silica content, which makes it a potent supplementary source for geopolymerization.

2.2.4.1. Reactivity and performance comparison

Unlike the glassy spheres of FA or the dense angular particles of GGBS, RHA is characterized by a “hull-like” structure with high internal porosity and cellular units, as evi-

denced by SEM analysis by Somna et al. (2022) (Figure 3d). This unique physical structure imparts a significantly higher specific surface area compared to FA, leading to rapid silica dissolution. However, the cellular nature of RHA results in the highest water demand among all precursors, even exceeding that of MK. This high demand can lead to workability issues and significant drying shrinkage if the liquid-to-binder ratio is not carefully optimized.

2.2.4.2. Compatibility with nanomaterials

The synergy between RHA and nanomaterials is primarily driven by the “Silica-on-Silica” effect.

- a) **Pore Refinement:** While RHA improves the chemical resistance of the matrix, its cellular remnants can leave behind microscopic voids. The addition of nano-silica (nS) or nano-alumina (nA) is highly effective in filling these intra-particle pores, creating a “multi-scale” packing effect that RHA alone cannot achieve.
- b) **Chemical Balancing:** Because RHA is silica-rich but alumina-poor, it is often used in “hybrid” systems. When nanomaterials like nano-alumina are added to an RHA-based geopolymer, they provide the necessary aluminum ions to balance the Si/Al ratio, facilitating a more robust and faster-forming polycondensation network.
- c) **Dispersion Challenges:** Like MK, the high-water absorption of RHA can lead to a very dry mix, which increases the risk of nanomaterial agglomeration. Consequently, the use of high-range water reducers (superplasticizers) is almost always mandatory when combining RHA with nano-additives to maintain a uniform distribution (Hossain et al., 2021; Kaur et al., 2018; Mulapeer & Omar, 2025; Nuaklong et al., 2020; Somna et al., 2022; Valenzuela et al., 2025; Verma et al., 2024).

2.2.5. Coal bottom ash

Coal Bottom Ash (CBA) is a coarser, heavier by-product of coal combustion that settles at the base of furnace boilers. While it shares a similar chemical profile with FA, comprising primarily of SiO_2 , Al_2O_3 , and Fe_2O_3 , its physical characteristics and processing requirements create distinct challenges for geopolymerization.

2.2.5.1. Reactivity and performance comparison

In its raw state, CBA is physically coarse and largely non-reactive compared to the fine, glassy spheres of FA. As shown in the SEM analysis (Figure 3e), CBA particles exhibit highly irregular, angular shapes and a significantly more porous internal structure (Lei et al., 2024). To achieve a level of reactivity suitable for geopolymerization, CBA requires intensive mechanical grinding to increase its specific surface area. While this grinding process activates the material, CBA-based geopolymers often exhibit higher water demand and lower early-age strength than FA or GGBS-based systems due to the retention of porous cellular remnants.

2.2.5.2. Compatibility with nanomaterials

The integration of nanomaterials with CBA is a strategic necessity to compensate for the precursor's inherent porosity.

- a) **Internal Curing and Pore Filling:** The porous nature of CBA particles can act as a reservoir for alkaline solutions. When nanomaterials like nano-silica are introduced, they can penetrate these surface pores, promoting localized geopolymerization and “plugging” the voids that would otherwise weaken the matrix.
- b) **Mechanical Interlocking:** The irregular and rough surface of ground CBA provides a superior mechanical “grip” for 1-D nanomaterials, such as carbon nanotubes or nano-clays. This results in a more robust interfacial transition zone (ITZ) compared to the smooth surfaces found in FA systems.
- c) **Overcoming Grinding Limitations:** Because grinding CBA to a very fine level is energy-intensive, adding highly reactive nanomaterials allows the use of coarser CBA particles without sacrificing the final mechanical performance of the composite (Bheel et al., 2024; Dong et al., 2019; Geragop & Mokhtar, 2023; Gulam et al., 2021; Ping et al., 2022; Lei et al., 2024; Singh et al., 2022b; Yashwanth Reddy & Harihanandh, 2023).

2.2.6. Red mud

Red mud (RM), a highly alkaline bauxite residue from the Bayer process, presents both significant environmental challenges and unique chemical opportunities for geopolymerization. Characterized by a high pH (10.5–13), RM is rich in iron oxide (Fe_2O_3) and aluminosilicate phases, though its chemical profile is often imbalanced for standalone geopolymer synthesis.

2.2.6.1. Reactivity and performance comparison

The primary chemical distinction of RM is its exceptionally low Si/Al ratio and high iron content, which differentiates it from mineral-based precursors like FA or MK. As shown in the SEM analysis taken from He et al. (2013) (Figure 3f), RM consists of irregularly shaped, porous aggregates formed by the clustering of ultrafine particles. While its inherent alkalinity can assist in the activation process, using RM in high proportions typically leads to extended setting times and a high risk of alkali leaching. Furthermore, the high iron content can interfere with the formation of a continuous aluminosilicate network, often resulting in lower compressive strength if not blended with high-silica sources like RHA or Nano-silica.

2.2.6.2. Compatibility with nanomaterials

The integration of nanomaterials is essential for stabilizing RM-based geopolymers and addressing their structural deficiencies.

- a) **Chemical Balancing and Seeding:** Since RM is silica-deficient, the addition of nano-silica is highly effective.

It not only provides the necessary silicate ions to correct the Si/Al ratio but also acts as a nucleation site to accelerate the sluggish reaction kinetics typical of RM-rich blends.

- b) **Immobilization of Heavy Metals:** RM contains trace heavy metals that pose leaching risks. Nanomaterials with high adsorption capacities, such as nano-clays or carbon nanotubes, can help physically and chemically immobilize these ions within the geopolymer matrix, enhancing the environmental safety of the composite.
- c) **Countering Porosity:** The porous aggregates of RM can lead to high water absorption. Nanomaterials provide a densification effect that “plugs” these micro-voids, significantly reducing permeability and improving resistance to chemical attack (Bai et al., 2023; Hai et al., 2024; He et al., 2013; Li et al., 2019; Mudgal et al., 2021; Sarde et al., 2024; Singh et al., 2018; Ye et al., 2016).

The inherent limitations of individual precursors, such as the low reactivity of FA, the high shrinkage of MK, or the alkalinity of RM, necessitate a synergistic blending approach. By combining diverse precursors, researchers can optimize the chemical environment for geopolymerization. For instance, Yilmaz et al. (2023) demonstrated that a quaternary blend of MK, FA, GGBS, and RM could produce high-performance geopolymers capable of incorporating 100% recycled aggregates. In such complex systems, the role of nanomaterials becomes even more critical; they act as the ‘bridge’ between different reaction phases (e.g., C-A-S-H from slag and N-A-S-H from FA), ensuring a unified and resilient microstructural framework even in highly heterogeneous mixtures.

Figure 4 highlights the fundamental divergence in chemical composition among major precursors, revealing that geopolymerization kinetics are governed by a sliding scale of calcium (CaO) versus aluminosilicate ($\text{Al}_2\text{O}_3 + \text{SiO}_2$) content. The data consolidate precursors into three primary categories that dictate the resulting matrix microstructure: (i) High-Calcium systems (represented by GGBS and RM), which contain 20–40% CaO and promote a rapid-setting C-A-S-H gel; (ii) Pure Aluminosilicate systems (represented by MK and RHA), which are nearly CaO -free (< 1%)

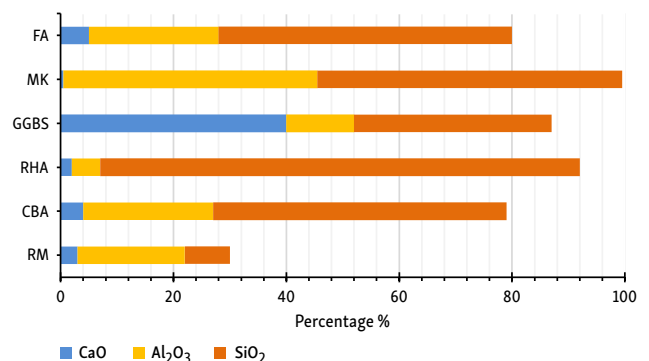


Figure 4. Chemical composition of major geopolymer precursor materials

and form a distinct 3-D N-A-S-H network; and (iii) Blended systems (represented by FA and CBA), which exhibit an intermediate CaO content (5–25%) that can form complex, hybridized gels. This visualization of the ‘oxide ratio trade-off’ is critical for later sections (4.1–4.6), as it explains why chemically active nanomaterials, such as nano-alumina or nano-silica, must be carefully matched to the precursor: they function as reactive templates that modify these inherent oxide ratios to optimize matrix densification.

2.3. Alkaline activators: Type and influence

Alkaline activators critically control geopolymer synthesis, initiating precursor breakdown and accelerating gel formation. Typically composed of NaOH, KOH, and Na_2SiO_3 , these activators directly influence geopolymer mechanical and durability properties through molarity and type selection. For example, Helvacı and Görhan (2025) demonstrated that increasing NaOH molarity from 4M to 12M enhanced compressive strength in calcined zeolite-based mortars. Błaszczyński and Król (2017) confirmed that the activator type produces varied compressive strength and microstructural characteristics. These findings emphasize the critical importance of alkaline activator selection and optimization for tailoring geopolymer properties (Helvacı & Görhan, 2025; Khattab et al., 2023; Prochon et al., 2020). While commercial sodium silicate is a standard activator, its high carbon footprint is a significant drawback. Recent studies have explored “green” alternatives; for instance, Lazarus et al. (2025) successfully synthesized an in-house sodium silicate (IHS) from RHA and treated POFA. Using this waste-derived activator in fly ash/slag-based pervious geopolymer concrete resulted in structural performance comparable to commercial variants, significantly reducing the overall embodied CO_2 of the material.

2.4. Factors influencing geopolymer strength and microstructure

Multiple parameters critically affect geopolymer strength and microstructure: Si/Al ratio, alkaline activator type and concentration, curing conditions, and water content/workability. These factors govern geopolymerization kinetics, gel formation (N-A-S-H, C-A-S-H), and resulting matrix porosity and viscosity.

2.4.1. Si/Al ratio

Silica-to-alumina ratio critically influences geopolymer gel network properties. Lower ratios, 1.0 to 2.0, produce rigid aluminosilicate structures, while higher ratios, 3.0 to 4.5, improve workability and densification but reduce strength. Optimal Si/Al ratio of about 3.45 in silica fume/red mud blends achieves compressive strengths exceeding 30 MPa after 28-day curing, as demonstrated by Ye et al. (2016).

2.4.2. Activator concentration and type

Alkaline activator concentration (NaOH, KOH, sodium silicate) directly affects precursor dissolution (Bai et al., 2023;

Mudgal et al., 2021). Higher NaOH concentrations (10–14 M) enhance early strength but risk efflorescence or microcracking without silica balance. Helvacı and Görhan (2025) demonstrated that 12M NaOH combined with sodium silicate produces higher compressive strength mortars. Błaszczyński and Król (2017) confirmed that alkali type (NaOH or KOH) influences pore structure and phase composition.

2.4.3. Curing conditions (temperature, humidity, duration)

Curing temperature, humidity, and duration critically affect early strength development and matrix compactness. Low-calcium precursors, such as FA and MK, require elevated temperatures of around 60 to 85 °C to accelerate aluminosilicate dissolution and early strength gain. Bai et al. (2023) demonstrated that 60 °C curing achieves RM-FA geopolymer compressive strengths exceeding 60 MPa within 28 days. Conversely, calcium-rich precursors like GGBS develop adequate strength under ambient curing conditions at 20 to 30 °C due to their intrinsic hydraulic activity, requiring no thermal activation. Long et al. (2024) confirmed that slag/FA/RM-based geopolymer mortars achieve superior strength compared to cement mortars under ambient curing, demonstrating ambient curing viability. In a recent study, Balapanov et al. (2024) demonstrated that microwave curing can produce hybrid geopolymer mortars with physical and mechanical properties comparable to those cured in conventional ovens for 24 hours.

2.4.4. Water content and workability

Water-to-solid ratio critically affects flowability, ion mobility, and final porosity. Adequate water enables precursor dissolution and ion transport during geopolymerization, but excess causes increased porosity and reduced mechanical performance. This can be observed from the work of Ye et al. (2016), demonstrated that lowering the water-to-solid ratio to 0.45 in red mud-based geopolymers increased compressive strength while reducing pore volume.

3. Role of nanomaterials in cementitious systems: A brief overview

Nanomaterials are transformative additives in cementitious systems, modifying hydration, microstructure, and mechanical performance through high surface area, reactivity, and nanoscale dimensions. Key materials include nano-silica, CNTs, GO, nano-alumina, and nano-clays.

Nano-silica (nS) functions as filler and pozzolanic agent: it fills voids, refines pore structure, and accelerates C-S-H formation, enhancing compressive strength (up to 30%) while reducing water absorption and porosity at < 3% by weight. High reactivity improves packing density and early-age strength through nucleation effects (Ranjana et al., 2024).

CNTs and GO reinforce crack-bridging, load transfer, and microstructural enhancement. High-aspect-ratio CNTs

arrest crack propagation, enhancing tensile and flexural strength, while GO improves matrix-aggregate interfacial bonding. CNT dosages of 0.05% to 0.2% by weight significantly increase flexural strength without compromising workability (Qin et al., 2021).

Nano-alumina (Al_2O_3) accelerates hydration and matrix densification by producing additional aluminate hydrates, enhancing early-strength development, and reducing water absorption and chloride permeability (Xiong et al., 2021).

Nano-clays modify fresh-mix rheology and act as fillers, nucleation sites, and reactive pozzolans. They consume $\text{Ca}(\text{OH})_2$, promote C-S-H formation, reduce permeability and shrinkage, and create denser, more homogeneous microstructures (Mansi et al., 2022).

3.1. Critical analysis of nano-integration in OPC

While the studies highlight the theoretical benefits of nano-additives, a critical evaluation reveals several practical inconsistencies. First, the “pore-filling” vs. “chemical-reactivity” trade-off: while nano-silica (nS) and nano-clays are praised for densification, their high specific surface area significantly increases water demand. This often necessitates higher dosages of superplasticizers, which, if not carefully calibrated, can lead to delayed setting or air-entrainment, potentially negating the strength gains (Mansi et al., 2022; Ranjan et al., 2024).

3.2. The divergence in reinforcement mechanisms

A comparison between 0-D particles (nS) and 1-D/2-D filaments (CNTs/GO) suggests that while oxides focus on matrix densification, carbon-based nanomaterials specialize in energy dissipation. However, the effectiveness of CNTs is highly sensitive to the “dispersion threshold”. Studies show that beyond 0.2% by weight, the probability of “clumping” increases exponentially, transforming the reinforcement from a bridge into a localized defect (Qin et al., 2021).

3.3. The scale of observation

Much of the existing literature focuses on small-scale paste or mortar samples. There is a critical research gap in translating these “micro-successes” to full-scale concrete, where the presence of large aggregates creates a complex Interfacial Transition Zone (ITZ) that nanomaterials must effectively penetrate to provide real-world structural value.

4. Enhancement of geopolymer strength by nanomaterials

The incorporation of nanomaterials into conventional cement is expanding due to their role in improving the mechanical performance and durability. They have also brought attention to many significant research works

on integrating them into geopolymer. Typically, geopolymers have amorphous aluminosilicate gel networks, which, when nanomaterials are added, can improve their characteristics. Nanomaterials can improve gel formation, refine microstructure, and alleviate the inherent brittleness of the structure. Nanoparticles like nano-silica, nano-alumina, carbon nanotubes, graphene-based materials, and nano-clays interact with geopolymer precursors and alkaline activators to accelerate geopolymerization, densifying the matrix and bridging microcracks (Zaid et al., 2024).

While the mechanical benefits of these nano-additives are substantial, their practical implementation is governed by significant hurdles in dispersion and cost-effectiveness. A detailed critical analysis of these industrial limitations and health concerns is provided in Section 7.

4.1. Nano-silica (nS)

Nano-silica (nS) is among the most investigated nanomaterials for geopolymer enhancement. High reactivity, ultrafine particle size, and large specific surface area significantly alter geopolymerization and microstructure. Nano-silica inclusion consistently improves compressive, flexural, and tensile strengths through enhanced polymerization kinetics, improved packing density, and refined pore structures (Algaifi et al., 2021; Goyal et al., 2024; Wang et al., 2018). TEM analysis shown in Figure 5a taken from Gao et al. (2018) reveals angular-shaped nano-silica particles.

4.1.1. Mechanisms of compressive, flexural, and tensile strength enhancement

Nano-silica strength enhancement in geopolymer matrices occurs through three primary mechanisms: (i) the filler effect, wherein nano-silica particles occupy interstitial spaces between aluminosilicate particles, reducing porosity and increasing matrix density; (ii) nucleation, where nS particles serve as active gel formation sites, accelerating geopolymerization and early-age strength (Arif et al., 2023; Wang et al., 2018); (iii) chemical interactions; pozzolanic nano-silica facilitates additional gel formation and bonding within the network. These combined effects significantly improve compressive, flexural, and tensile strengths (Lu et al., 2024).

4.1.2. Influence of nS Particle Size, Surface Area, and Dosage

Nano-silica effectiveness in geopolymer composites depends on particle size, specific surface area, and dosage. Smaller particles <20 nm provide higher surface area, enhancing chemical reactivity and physical filling effects, improving strength significantly (Gao et al., 2017; Goyal et al., 2024). Extremely small particles may agglomerate, limiting matrix dispersion and uniformity. Optimal dosages range from 1 to 3% by weight of binder. Dosages exceeding optimal levels cause agglomeration and increased viscosity, negatively affecting workability and mechanical properties (Lu et al., 2024).

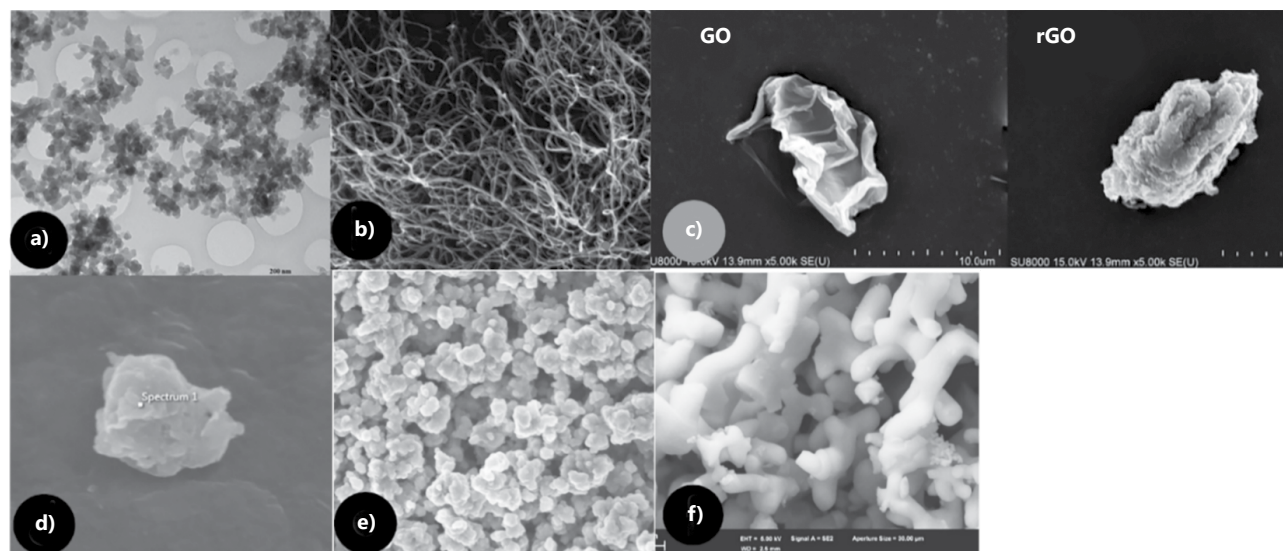


Figure 5. a – TEM of nano-Silica (Gao et al., 2018); b – SEM of Carbon nanotube (Jittabut & Horpibulsuk, 2019); c – SEM of GO and rGO sheets (Liu et al., 2020); d – electron image of nano-clay (Assaedi et al., 2016); e – morphology of nano-titanium (Luo et al., 2021a), f – SEM of nano-alumina (Assaedi & Olawale, 2022)

4.1.3. Effect of Dispersion Techniques on Strength Performance

Effective nano-silica dispersion is critical for uniform matrix distribution and full potential realization. Common techniques, such as ultrasonication, high shear mixing, surfactants, and superplasticizers, improve particle distribution and enhance strength and homogeneity (Lu et al., 2024). Ultrasonic dispersion combined with surfactants achieves the highest nS dispersion, significantly boosting compressive strength and mitigating agglomeration issues (Gao et al., 2018). Furthermore, the sequence of incorporation, specifically whether the nS is pre-dispersed in the alkaline activator or dry-blended with the precursor, significantly dictates the extent of the nucleation effect and the resulting homogeneity of the N-A-S-H gel.

4.1.4. Strength Enhancement in Different Geopolymer Matrices

Nano-silica effectively enhances various geopolymer systems: FA-based, slag-based, and blended precursors. FA-based geopolymers show substantial compressive and flexural strength increases through improved gel structure and lower porosity. Slag-based geopolymers benefit from accelerated C-A-S-H gel formation, achieving rapid strength gain and enhanced durability. Blended precursor systems exhibit synergistic effects, producing superior strength and durability compared to single-precursor systems (Algaifi et al., 2021; Arif et al., 2023; Wang et al., 2018).

4.1.5. Optimal nS dosage ranges and potential drawbacks at high concentrations

Optimal nano-silica dosage ranges from 1–3% by binder weight, maximizing mechanical properties while maintain-

ing workability and cost-effectiveness. Within this range, nano-silica enhances early and long-term strength, reduces permeability, and improves durability. Dosages exceeding 4–5% cause severe agglomeration, increased viscosity, reduced workability, and decreased strength from non-uniform nanoparticle dispersion. High nano-silica contents also significantly elevate production costs, reducing practical viability for large-scale applications (Gao et al., 2017; Goyal et al., 2024; Lu et al., 2024). Consequently, the “optimal” dosage is not a static value but a dynamic equilibrium between maximum microstructural densification and the rheological limits of the geopolymer paste. While Table 1 highlights a consensus around the 1–3% range, it also underscores a critical research gap: the need for standardized surfactant-to-nanoparticle ratios that can stabilize higher concentrations without compromising the alkaline activation process. Moving forward, transitioning from empirical “trial-and-error” dosage testing toward predictive modeling of particle packing could mitigate these concentration-dependent drawbacks.

4.2. Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs), with exceptional mechanical, electrical, and thermal properties, are promising geopolymer reinforcement nanomaterials. CNT incorporation enhances mechanical properties and durability through effective load transfer, microcrack bridging, and improved microstructure. Recent studies examine CNT performance factors: reinforcement mechanisms, type, dispersion methods, and dosage optimization (Ahmadi et al., 2022; da Luz et al., 2019; Li et al., 2021a, 2021b; Oualit & Irekti, 2022; Yang et al., 2021, 2023; Zhong et al., 2024). Figure 5b taken from Jittabut and Horpibulsuk (2019) shows the irregularly shaped nanotubes.

Table 1. Factors and difficulties associated with recent studies on nano-silica

References	Aspects Covered	Mechanisms and Improved Durability	Microstructure Analysis	Optimal Dosage	Drawbacks at High Dosage
Goyal et al. (2024)	Portland-slag cement with nSiO ₂ + nCuO; antimicrobial & structural performance	nSiO ₂ offsets hydration-retardation of nCuO, accelerates C-S-H formation; compressive strength rises, water penetration decreases, effective antibacterial & antialgal properties	Pore Refinement, Dense interfacial transition zone	1–3%	nSiO ₂ greater than 1% was not evaluated
Arif et al. (2023)	M20 concrete; strength vs. permeability using 0 to 2% nSiO ₂	Significant improvement in compressive & flexural strengths, Enhanced density & lower permeability at optimal doses	Refined pore structure; smaller pores	1–3%	Severe agglomeration; reduced strength
Lu et al. (2024)	Recycled concrete aggregate with accelerated carbonation + nano-silica treatment	High early strength gains; enhanced flexural properties, improved durability via refined gel structure	Accelerated gel formation; reduced voids	1–3%	Workability and dispersion issues
Algaifi et al. (2021)	Optimization of GBFS, FA, and bottle glass waste nano-silica powder (BGWNP)	Ultra-filler effect reducing porosity; nucleation sites for gel formation; compressive, tensile, and flexural strength increases	Increased gismondine and albite phases; reduced quartz intensity	BGWNP 8.4%	BGWNP greater than 10% causes strength reduction
Gao et al. (2017)	Olivine-nanosilica used as a green activator in slag-fly-ash blends	Soluble Si supplied by olivine-nSiO ₂ forms C-A-S-H gels comparable to waterglass; 20 to 29% lower CO ₂ ; strength about 95% of control; slightly higher workability	shows dense matrix, minor porosity rise	Best mechanical balance at activator modulus (Ms) about 1.4	Higher Ms, greater than 1.4 extra shrinkage and porosity; slight strength loss
Wang et al. (2018)	Waste-based alkali-activated binder; efflorescence control, strength	nSiO ₂ accelerates hydration, cuts carbonate ion release by 40 to 60%, and raises 28-d strength to 15%	compact gel network	2% of the binder	Greater than 2% causes agglomeration, flow loss, and no further efflorescence benefit
Gao et al. (2018)	Full replacement of water-glass by eco-olivine nSiO ₂	Alternative silicate gives equal strength, better flow, and lowers CO ₂	Improved matrix density; reduced porosity	Activator with Ms 1.4	High Ms 1.8 increases shrinkage & porosity; slightly lower strength

4.2.1. Reinforcement mechanisms and improved fracture toughness

CNTs enhance geopolymers matrices through bridging mechanisms that arrest crack propagation, improving fracture toughness and mechanical integrity. Li et al. (2021a) showed functionalized MWCNTs in FA and GGBS-based geopolymers dramatically improve compressive and flexural strengths via crack bridging and microstructural densification. Similarly, Ahmadi et al. (2022) reported MWCNTs in MK-RM composites increase strengths by over 36% through crack-bridging and pore-filling. Additionally, da Luz et al. (2019) confirmed flexural strength improvements up to 66% from strong CNT-matrix bonding, refining porosity, and enhancing crack resistance. Oualit and Irekti (2022) demonstrated improved mechanical properties in MK-based geopolymers from crack bridging and porosity reduction (Li et al., 2021a, 2021b).

4.2.2. Influence of CNT type (SWCNTs, MWCNTs), aspect ratio, and dispersion

CNT reinforcement effectiveness depends on type: single-walled CNTs (SWCNTs) vs. multi-walled CNTs (MWC-

NTs), aspect ratio, functionalization, and dispersion quality. Functionalized MWCNTs provide superior reinforcement compared to pristine CNTs through improved dispersion and interfacial bonding (Sekkal & Zaoui, 2022; Zhu et al., 2022). da Luz et al. (2019) showed functionalized MWCNTs increase compressive strength up to 46.6%, while pristine MWCNTs showed less improvement. Similarly, Zhu et al. (2022) demonstrated that silica-coated MWCNTs enhance dispersion and bonding, significantly improving mechanical properties. Oualit and Irekti (2022) and Yang et al. (2021, 2023) emphasized suitable dispersion techniques: ultrasonication, surfactants, and proper aspect ratios as critical for final composite performance. Recent breakthroughs in nanotube technology have moved toward functionalization to overcome dispersion barriers. A study by Kirgiz et al. (2025) utilized silver nanoparticles-functionalized multi-walled carbon nanotubes (Ag-PM-WCNT) in combination with carbon quantum dots (CQD). This hybrid approach resulted in a more compact matrix, with the functionalized nanotubes significantly enhancing the shear and bending strength of geopolymer reinforced-composite beams. Silver functionalization facilitates superior interfacial bonding, ensuring that the mechanical benefits

are sustained over extreme durations (up to 4370 days), which underscores the long-term structural reliability of these composites.

4.2.3. Effect of CNT dosage on strength properties

CNT dosage significantly affects geopolymer composite mechanical properties, with optimal concentrations between 0.05 to 0.5% by weight. Excessive dosage causes severe agglomeration, compromising performance. Li et al. (2021a) and Zhong et al. (2024) identified 0.1% MWCNT dosage as optimal, achieving about 18% strength improvements. Similarly, da Luz et al. (2019) reported optimal performance at 0.1% pristine CNT dosage (flexural strength $\pm 28.7\%$), with detrimental effects at 0.2% from increased porosity and agglomeration. Yang et al. (2021) confirmed that very low dosages of about 0.045% significantly improve properties, while exceeding optimal levels notably reduces performance.

4.2.4. Challenges in dispersion and achieving homogeneity

Achieving uniform CNT dispersion and homogeneity remains the primary challenge in geopolymer systems.

Strong van der Waals interactions cause CNTs to agglomerate, adversely affecting mechanical and durability properties. Effective techniques, such as ultrasonication, surfactants, and chemical functionalization, are critical for uniform distribution (Abbasi et al., 2016; da Luz et al., 2019; Yang et al., 2021). Abbasi et al. (2016) confirmed that ultrasonication and chemical functionalization improve uniform distribution. da Luz et al. (2019) showed that functionalized CNTs achieve significantly better dispersion and interfacial bonding than pristine CNTs, improving homogeneity and mechanical properties. Yang et al. (2021, 2023) emphasized surfactant type and dosage importance, warning that inappropriate dispersants cause foaming and strength loss. Oualit and Irekti (2022) stressed ultrasonic dispersion combined with chemical dispersants to maximize CNT reinforcing benefits. Table 2 depicts the characteristics and influence of the different CNT types. The data reveal MWCNTs outperform pristine CNTs, optimal dosages cluster around 0.1 to 0.2%, and functionalized CNTs with proper dispersion techniques are essential for achieving homogeneous composites and maximizing mechanical benefits while minimizing agglomeration-related performance losses.

Table 2. Aspects and challenges of various recent research on CNT

References	Aspects Covered	Mechanisms and Improved Durability	Influence of CNT Types	Optimal Dosage	Challenges
Ahmadi et al. (2022)	Reinforcement in MK-RM geopolymer	Crack bridging, improved compressive & flexural strengths	MWCNTs are effective in crack bridging	0.1–0.2%	Agglomeration at higher dosages
Abbasi et al. (2016)	Dispersion methods and CNT reinforcement	Enhanced dispersion, significant strength enhancement	MWCNT, functionalization improved dispersion	0.5%	CNT dispersion challenges and agglomeration
da Luz et al. (2019)	Comparison of pristine vs functionalized CNTs	Strong bonding, porosity refinement, and flexural strength increase (66%)	Functionalized CNTs are notably superior to pristine CNTs	0.1% optimal, negative effects above 0.2%	Pristine CNT agglomeration and increased porosity at higher dosages
Oualit and Irekti (2022)	Effect of CNT reinforcement on MK-based geopolymer	Crack bridging, porosity reduction, and improved mechanical strength	MWCNT optimal, functionalization beneficial	0.2% optimal	Dispersion difficulty, agglomeration at high dosage
Yang et al. (2021, 2023)	Dispersion methods, CNT reinforcement, and durability aspects	Crack bridging, improved durability, and porosity reduction	Functionalized CNTs significantly improved dispersion	0.045–0.1%	Surfactant-related foaming and agglomeration at improper dosages
Li et al. (2021a, 2021b)	CNT reinforcement, dispersion, and optimal dosage in slag/FA geopolymers	Improved microstructure, crack bridging, and strength enhancement	Functionalized MWCNTs have superior dispersion and bonding	0.1%	Dispersion difficulties at higher CNT concentrations
Zhong et al. (2024)	Effect of CNT dosage on mechanical properties	Enhanced compressive strength via optimal dosage and dispersion	MWCNT (functionalized) optimal mechanical performance	0.1%	Agglomeration beyond optimal dosages
Zhu et al. (2022)	Influence of silica-coated CNTs on geopolymer properties	Enhanced interfacial bonding and dispersion quality	Silica-coated CNT superior dispersion and bonding	0.1–0.2%	Potential agglomeration without silica coating
Kirgiz et al. (2025)	Incorporating Hybrid Ag-PM-WCNT & CQD	Increased shear and bending strength. Extreme long-term structural reliability.	Dual-filling effect with CQDs and CNTs	0.5–0.75% Ag-PM-WCNT & 2.5% CQD	Reduction in fresh fluidity

When viewed in the broader context of geopolymer modification, the transition from Section 4.1 to 4.2 highlights a fundamental divergence in reinforcement strategy: whereas nano-silica primarily densifies the matrix to prevent crack initiation, CNTs are specifically tailored to arrest crack propagation once initiated. This shift from chemical densification to mechanical bridging underscores the necessity of selecting nano-additives based on the specific structural requirements of the application.

4.3. Graphene-based nanomaterials (Graphene oxide (GO), Reduced graphene oxide (rGO))

Graphene-based nanomaterials, such as GO and rGO, are promising geopolymer reinforcements due to their extraordinary mechanical strength, excellent flexibility, and high surface area. Their incorporation improves mechanical, durability, and microstructural properties (Arpitha & Parthasarathy, 2023; Karupaiyan & Jeyalakshmi, 2024; Li et al., 2022b; Li & Shi, 2025; Liu et al., 2020; Tang et al., 2023; Vishnu et al., 2021; Yan et al., 2016). Figure 5c taken from Liu et al. (2020) reveals that these materials exhibit contrasting morphologies: GO consists of smooth, flat sheets with well-defined edges, while rGO displays wrinkled, folded, and crumpled surfaces.

4.3.1. Exceptional mechanical properties and load transfer

GO and rGO demonstrate superior mechanical reinforcement through efficient load transfer across matrices, attributed to high aspect ratio and robust intrinsic strength. Liu et al. (2020) reported 25% flexural strength increase at 0.3 wt.% GO in FA-based composites. Similarly, Li et al. (2022b) found significant mechanical improvements at elevated temperatures, with GO enhancing residual compressive strength by approximately 25% at 600 °C. Furthermore, Yan et al. (2016) reported rGO nanocomposites achieve a 61.5% toughness enhancement at 0.5 wt.% through crack deflection, pull-out, and bridging.

4.3.2. Influence of GO/rGO nanosheet size, layering, and reduction degree

The effectiveness of these nanosheets depends on their lateral size, exfoliation degree, and the extent of reduction. Tang et al. (2023) found silane-modified GO surface functionalization improves dispersion and mechanical strength, achieving a 110% tensile improvement. Liu et al. (2020) showed that nanosheet size directly affects geopolymer gel formation and homogeneity. Additionally, Karupaiyan and Jeyalakshmi (2024) demonstrated well-dispersed GO forms robust, uniformly distributed silico-aluminate networks, enhancing compressive strength by approximately 20% compared to unmodified MK-based geopolymers.

4.3.3. Effect of dosage and dispersion on strength enhancement

Dosage and dispersion are the primary factors influencing the strength and durability of these composites. Maglad

et al. (2022) found an optimal 0.25 wt.% GO increases compressive strength by 37.5% and reduces chloride permeability by 35.3%. In contrast, Yan et al. (2016) showed that rGO content exceeding 0.3% causes agglomeration and reduced performance. Li and Shi (2025) demonstrated that appropriate GO dosages enhance freeze-thaw resistance by refining the microstructural integrity and improving the degree of polymerization.

4.3.4. Potential for functionalization and multi-scale reinforcement

GO and rGO enable multi-scale reinforcement through versatile surface chemistry and functionalization. Tang et al. (2023) found that silane-functionalized GO facilitates stronger matrix interactions, reinforcing both the nano- and microscales. Arpitha and Parthasarathy (2023) reviewed GO/rGO potential, showing functionalization enhances compatibility and dispersion for robust multi-scale reinforcement addressing geopolymer brittleness. Moreover, Vishnu et al. (2021) demonstrated significant mechanical improvements from multi-scale compatibility with additives like wollastonite and slag.

Table 3 presents a comprehensive overview of eight GO/rGO-geopolymer studies. Key findings show GO/rGO optimal dosages cluster at 0.2–0.5%, with functionalized variants consistently outperforming pristine materials; silane-functionalization and uniform dispersion are critical; multi-scale reinforcement potential is significant, but agglomeration limits performance at high dosages.

While nano-silica acts primarily as a chemical densifier and CNTs as a 1-D crack-bridging filament, graphene-based materials represent a “2D barrier” strategy. Their plate-like geometry creates a tortuous path for invading ions and crack propagation alike. However, the critical divergence for GO lies in its oxygen-rich functional groups, which, unlike the inert surface of pristine CNTs, allow for a chemical bond with the geopolymer gel. This suggests that GO is not merely a physical reinforcement but a reactive template that dictates the morphology of the resulting N-A-S-H or C-A-S-H framework.

4.4. Nano-clays (Montmorillonite (MMT), Kaolinite nanoparticles)

Nano-clays, MMT, and Kaolinite nanoparticles are gaining significant attention for geopolymer enhancement due to their distinctive layered structure, high surface area, and chemical reactivity. Their incorporation significantly improves mechanical strength, reduces shrinkage, and enhances durability through direct interactions with geopolymeric gels and extensive pore structure modification (Abdalla et al., 2022; Gadkar & Subramaniam, 2021; Hassaan et al., 2015; Khater et al., 2013; Li et al., 2022a; Mahboubi et al., 2019; Ravitheja & Kumar, 2019; Zhang et al., 2024). Figure 5d taken from Assaedi et al. (2016) shows the electron image of nanoclay, revealing particles with irregular, roughly rectangular shapes and sharp, defined edges.

Table 3. Aspects and challenges of various recent research on graphene-based nanomaterials

References	Aspects Covered	Mechanical and Durable Properties	Influence on Particle Size & Functionalization	Optimal Dosage	Challenges & Potentials
Liu et al. (2020)	Mechanical enhancement in FA geopolymer	25% increase in flexural strength	Optimal nanosheet size crucial for strength enhancement	0.3%	Dispersion difficulties; potential for enhanced load transfer
Li et al. (2022b)	High-temperature performance with GO addition	Enhanced residual strength at high temperatures	Uniform dispersion critical, improved strength at nanoscale	0.2–0.5%	Agglomeration at high temperatures; improved thermal stability potential
Tang et al. (2023)	Functionalized GO nanosheets in geopolymers	Up to 110% improvement in tensile strength	Silane-functionalized GO improves dispersion and strength	About 0.1–0.3%	Challenges in uniform dispersion; high potential for functionalization
Maglad et al. (2022)	Influence of GO dosage on geopolymer performance	37.5% increase in compressive strength, 35.3% reduction in chloride permeability	Optimal GO dispersion achieved at the nanoscale	0.25%	Dispersion and agglomeration at high dosage; improved durability potential
Yan et al. (2016)	Mechanical properties enhancement using rGO	61.5% toughness increase	Optimal dispersion with rGO is crucial for effectiveness	0.3–0.5%	Agglomeration beyond optimal dosage; significant mechanical improvement potential
Karuppaiyan and Jeyalakshmi (2024)	Role of GO in MK-based geopolymers	20% compressive strength improvement	Functionalized GO significantly improved dispersion	0.2–0.4%	Dispersion challenges, potential for increased durability
Vishnu et al. (2021)	Multi-scale reinforcement in geopolymer concrete	Improved compressive and tensile strengths, enhanced durability	GO compatibility with other additives enhances reinforcement	0.02–0.06%	Compatibility and dispersion issues; improved multi-scale reinforcement potential
Li and Shi (2025)	Freeze-thaw resistance and carbonation durability	Enhanced freeze-thaw durability and residual compressive strength	Effective dispersion enhances the polymerization degree	0.1–0.3%	Potential agglomeration, significant freeze-thaw resistance enhancement potential

4.4.1. Lamellar structure and improved interlayer bonding

Montmorillonite (MMT) nano-clays possess unique lamellar structures of layered aluminosilicate sheets with interlayer cations undergoing ion exchange and intercalation. These structures enhance geopolymer strength by improving interlayer bonding and promoting dense packing. As-saedi et al. (2016) demonstrated that these lamellar structures enhance both compressive and flexural strengths through effective interlayer reinforcement and densification. Similarly, Li et al. (2022a) reported layered nano-clays promote the formation of a dense, stable gel, which effectively reduces micro-cracking and enhances structural integrity.

4.4.2. Influence of clay type, surface modification, and exfoliation

The effectiveness of nano-clays is heavily dependent on the clay type (MMT vs. Kaolinite), surface modification, and the degree of exfoliation. MMT generally shows superior effects due to its higher reactivity and ease of exfoliation, which enables better dispersion within the binder. Gadkar and Subramaniam (2021) found that MMT transforms geopolymer paste rheology from Maxwell flow to yield-type responses, significantly improving yield stress and gel stability. Ravitheja and Kumar (2019) confirmed MMT and nano-clay enhance ambient-cured FA-based geopolymer strength with optimal dosage, boosting early-

age compression and densification. Furthermore, Hassaan et al. (2015) showed that thermally activated nano-kaolin improves mechanical properties by accelerating the geopolymerization rate and enhancing microstructural densification.

4.4.3. Effect of nano-clay dosage on strength and workability

Optimal nano-clay dosage critically affects geopolymer performance. Excessive amounts cause agglomeration, reduce workability, and affect mechanical properties. Mahboubi et al. (2019) found 3% nano-clay enhances compressive strength and acid resistance, indicating an optimal range of 2 to 3% by weight. While Abdalla et al. (2022) suggested that moderate dosages of 1 to 2% balance strength enhancement and workability, with higher dosages causing severe agglomeration and performance loss. Zhang et al. (2024) achieved near-zero shrinkage and excellent performance at 3% to 4% dosage, emphasizing careful optimization to maintain geopolymer workability.

Table 4 presents a comprehensive overview of nine nano-clay geopolymer studies. Key findings: MMT consistently outperforms other clays; optimal dosages cluster at 2% to 3%; thermal activation enhances performance; 1% to 2% provides optimal strength-workability balance; dosages exceeding 3% risk severe agglomeration; optimal range avoids workability loss while maximizing mechanical benefits.

Table 4. Aspects and challenges of various recent research on nano-clays

References	Aspects Covered	Mechanical and Durable Properties	Influence of Clay Type & Modification	Optimal Dosage	Challenges & Potentials
Assaedi et al. (2016)	Mechanical properties enhancement via lamellar structure	Improved compressive and flexural strength significantly	Lamellar structure provided effective interlayer reinforcement	2–3%	Dispersion challenges, significant mechanical potential
Khater et al. (2013)	Influence of nano-clays on geopolymer composite performance	Enhanced durability and mechanical performance	Enhanced geopolymer performance with MMT addition	2–3%	Potential agglomeration at high dosages; improved durability
Li et al. (2022a)	Effect of nano-clays on geopolymer gel densification	Dense, stable geopolymer gels; reduced micro-cracks	Improved densification and gel stability	2–4%	Dispersion difficulty, high potential for reduced cracking
Zhang et al. (2024)	Shrinkage reduction and strength enhancement using nano-clay	Near-zero shrinkage, high mechanical strength	Optimal dosage is critical for shrinkage reduction	3–4%	High dosage agglomeration issues; potential for zero shrinkage
Gadkar and Subramaniam (2021)	Rheological behavior improvement with MMT	Improved yield stress, stable gel formation	MMT transformed the rheological properties effectively	1–2%	Agglomeration at higher dosage; potential for rheological improvement
Mahboubi et al. (2019)	Compressive strength and durability enhancement	Enhanced compressive strength and acid resistance	Enhanced mechanical performance through optimal nano-clay addition	3%	Dispersion and agglomeration issues at higher dosages
Hassaan et al. (2015)	Thermal activation and surface modification of nano-kaolin	Significantly improved mechanical properties and microstructure	Thermal activation enhanced dispersion and reactivity	1–3%	Agglomeration and workability reduction at higher dosages
Abdalla et al. (2022)	Optimal dosage for improved geopolymer properties	Enhanced strength and optimized workability	Moderate dosage (1 to 2%) effectively improved strength	1–2%	Dosage sensitivity, balance between workability and strength
Ravithija and Kumar (2019)	Nano-clay enhancement in ambient-cured geopolymers	Increased early-age compressive strength and density	MMT improved early-age strength in ambient curing	2–4%	Agglomeration beyond optimal dosage; ambient curing potential
Assaedi et al. (2017)	Nano-clay effect on geopolymer mechanical and microstructural properties	Enhanced compressive strength and reduced micro-cracks	Effective reinforcement due to nano-clay dispersion	2–3%	Potential agglomeration, significant improvement in mechanical properties

Distinct from the inert mechanical reinforcement of CNTs or the 2-D physical barrier of GO, nano-clays exhibit a “chemical-structural” convergence. Because they are aluminosilicate-based, they participate directly in the geopolymerization process through ion exchange, effectively becoming a reactive nucleus rather than just an additive. This chemical affinity explains their superior ability to control autogenous shrinkage, a major limitation of pure geopolymer systems. However, their high-water absorption remains a critical hurdle; whereas nano-silica primarily influences the reaction kinetics, nano-clays dominate the rheological evolution, suggesting their role is as much about controlling the “fresh state” behavior as it is about the “hardened state” performance.

4.5. Nano-titanium (nTiO₂)

Nano-titanium dioxide (nTiO₂) is widely studied for geopolymer enhancement. Synthesized in anatase or rutile phases, nTiO₂ exhibits high chemical stability, photocatalytic activity, and a large surface area: 60 to 87 m²/g with particle sizes ranging from 10–80 nm. When incorporated, nTiO₂ acts as a physical filler and a potent nucleation agent, accelerating geopolymerization while densi-

fying the microstructure. Addition improves mechanical performance and imparts self-cleaning and antimicrobial functionalities (Ghanim et al., 2023; Gopala Krishna Sastry et al., 2021; Maraş, 2021; Mashout et al., 2023; Sivasakthi et al., 2021; Tuntachon et al., 2019; Zawrah et al., 2025). Figure 5e taken from Luo et al. (2021a) illustrates the morphology of nano-titanium, revealing roughly spherical to angular particle morphologies.

4.5.1. Mechanisms of compressive, flexural, and tensile strength enhancement

The reinforcement provided by nTiO₂ operates through four primary mechanisms: (i) Filler effect: nTiO₂ fills micropores and nanopores, densifying the matrix and refining pore structures; (ii) Nucleation: nTiO₂ accelerates geopolymerization, promoting C-S-H, C-A-S-H, and N-A-S-H gel formation; (iii) Microstructure Densification: While less reactive than nano-silica, nTiO₂ promotes a more connected gel network, improving compressive and flexural strengths; (iv) Interfacial enhancement: nTiO₂ improves fiber-matrix adhesion, enhancing toughness by limiting crack propagation at the interfacial transition zone (ITZ) (Ghanim et al., 2023; Maraş, 2021).

4.5.2. Influence of nTi particle size, surface area, and dosage

The efficacy of nTiO₂ depends heavily on particle size and dosage. Smaller particles (< 50 nm) yield better reactivity and dispersion. Ziada (2024) found 15 to 30 nm particles provide excellent nucleation-driven strength gains. Zawrah et al. (2025) reported an optimal dosage range of 1% to 3% by weight; exceeding this limit results in severe agglomeration, which introduces localized defects and reduces overall homogeneity.

4.5.3. Effect of dispersion techniques on strength performance

Proper dispersion is crucial for realizing the benefits of nTiO₂. Wang and Zha (2020) identified that combining ultrasonication with polycarboxylate superplasticizers effectively improves particle distribution, leading to higher compressive and flexural strengths. Tuntachon et al. (2019) confirmed that high-energy dispersion is necessary to mitigate the natural tendency of nTiO₂ to cluster in high-molarity alkaline solutions.

4.5.4. Strength enhancement in different geopolymer matrices

nTiO₂ shows versatility across FA, MK, and slag-based systems. Gopala Krishna Sastry et al. (2021) observed enhanced FA-based geopolymer compressive strength. Sivasakthi et al. (2021) showed nTi improves strength through enhanced geopolymerization and denser microstructures. Mashout et al. (2023) gained enhanced resistance to sulfates and radiation, while Ghanim et al. (2023) found that waste clay-based geopolymers exhibit up to 35% compressive strength improvements at a low dosage of 0.3%.

4.5.5. Optimal nTi dosage ranges and potential drawbacks at high concentrations

Optimal nTiO₂ dosage ranges from 0.5% to 3.0% by weight of binder. Within this range, strength and durability improve through effective pore refinement and matrix densification (Maraş, 2021; Mashout et al., 2023; Zawrah et al., 2025). Dosages exceeding 3% to 4% cause pronounced agglomeration, increased viscosity, reduced workability, and compromised performance (Wang & Zha, 2020). Ghanim et al. (2023) found high dosages negatively affected geopolymer integrity due to reduced homogeneity and increased porosity from agglomeration.

Table 5 summarizes the findings of recent studies on nTiO₂ in geopolymer composites. The consolidated data indicate that optimal dosages cluster between 0.5% and 3.0%, with strength gains ranging from 5% to 50% depending on the precursor.

While the previously discussed nSiO₂ and nano-clays contribute to the matrix through direct chemical reactivity, nTiO₂ represents a “functional-physical” convergence. It acts as a highly stable nucleation template that accelerates the geopolymerization kinetics without being con-

sumed by the reaction. This makes nTiO₂ uniquely valuable for applications in aggressive environments (such as radiation shielding or sulfate-rich soils) where chemical stability is paramount. However, the divergence observed here is that nTiO₂ is often selected for its secondary “smart” properties, such as photocatalysis, which sets it apart from the purely structural reinforcements like CNTs or graphene. This highlights a shift in research priority: moving from merely increasing strength to engineering multifunctional “living” materials.

4.6. Nano-alumina (nAl₂O₃)

Nano-alumina (nAl) attracts significant interest as a geopolymer additive due to its dual role as an efficient physical filler and a highly reactive chemical constituent. Unlike inert nano-fillers, nAl participates directly in the geopolymerization process, facilitating the creation of denser, more homogeneous aluminosilicate matrices (Alomayri, 2019; Zidi et al., 2019, 2021). Widely utilized in FA, MK, and RHA-based systems, nAl improves compressive, flexural, and tensile strengths while enhancing durability through reduced water absorption and improved environmental resistance (Reddy & Ramujee, 2022; Arshad et al., 2024; Mohseni et al., 2019; Rani & Gladston, 2024). Figure 5f taken from Assaedi et al. (2022) shows the SEM of nano-alumina, which reveals a coral-like structure with spherical and rod-like porous networks.

4.6.1. Mechanisms of compressive, flexural, and tensile strength enhancement

The enhancement provided by nAl operates through two primary mechanisms: (i) Nanofiller and Nucleation effect, which physically densifies the microstructure and serves as a nucleation template that promotes uniform gel growth and improved stress transfer across the matrix; (ii) Chemical promotion; actively promotes the development of the gel phase. SEM and XRD analyses confirm that this leads to a more compact, less-porous network by providing additional aluminum ions necessary for the polycondensation of silicate monomers. Strength improvements are typically optimized at a 2% dosage; beyond this threshold, the increased surface energy leads to agglomeration, which diminishes the reinforcement’s effectiveness (Alomayri, 2019; Arshad et al., 2024; Assaedi & Olawale, 2022; Zidi et al., 2019, 2021).

4.6.2. Influence of particle size, surface area, and dosage

Commercial particles typically feature diameters of 40 to 60 nm and high specific surface areas. Research suggests that an optimal dosage of approximately 2% by binder weight yields the highest mechanical performance in MK and FA-based systems. Dosages exceeding 3% significantly reduce workability and introduce localized weak points due to particle clustering (Alomayri, 2019; Arshad et al., 2024; Assaedi & Olawale, 2022; Rani & Gladston, 2024; Zidi et al., 2019).

Table 5. Aspects and challenges of various recent works on nano titanium

References	Aspects Covered	Mechanical & Durability Results	Influence of Particle Size & Dosage	Dispersion Techniques & Effects	Optimal Dosage & Drawbacks
Gopala Krishna Sastry et al. (2021)	FA-based GPC with nano-TiO ₂ ; strength, durability	Max compressive and flexural strength increased, improved sulfate/chloride resistance	20–80 nm; 1 to 5% tested; 5% best	Manual mixing, superplasticizer	5% optimal; greater than 3% increases permeability/agglomeration
Sivasakthi et al. (2021)	FA-based mortars; thermal resistance	Compressive strength increases by 31 to 50%; better thermal stability	Commercial nTiO ₂ ; 1% to 3% tested; 2% best	Manual mixing	1–3%; reduced strength beyond the optimal range
Mashout et al. (2023)	Slag/basalt geopolymers; fire, sulfate, gamma resistance	Compressive strength increased by 5 to 15%; improved fire/sulfate durability	20–80 nm; 0.5–1% tested	Ultrasonication improved particle dispersion	0.5–2%; agglomeration and reduced performance at higher dosage
Maraş (2021)	Fiber-reinforced geopolymer	Enhanced tensile and compressive strengths significantly	Particle sizes 8 to 10 nm; effective at low dosages 0.5–2%	Fiber-matrix adhesion significantly improved	Optimal range 0.5–2%; high dosage results in reduced strength
Ziada (2024)	MK-slag geopolymer; high-temp resistance	Compressive strength increased by 3.8–32.6%	13 nm; 1–2% tested	Manual mixing	2% optimal; higher not tested
Luo et al. (2021a)	FA geopolymer, 2% nTiO ₂ ; micromechanics	Compressive strength increased by 10.5%; improved gel properties	20 nm; 2% tested	Superplasticizer & sonication	2% optimal; higher not tested
Raza et al. (2023)	Micro-carbon fiber FA geopolymer, 1 to 4% nTiO ₂	Compressive strength, flexural strength, and impact increased by 23%, 40%, and 53%	20 nm; 1 to 4% tested; 2 to 3% best	High-speed mixing	2–3% optimal; greater than 3% reduces strength
Wang and Zha (2020)	CDG-slag geopolymer paste, 0 to 2% nTiO ₂	Compressive and flexural strength increases by 10% and 13%	20–30 nm; 0–2% tested	Dry mixing	2% optimal; higher not tested
Ahmed et al. (2023)	FA/MK geopolymer, 2.5% nTiO ₂	compressive strength increases, improved dye removal, and antimicrobial	21 nm; 2.5% tested	Manual mixing	1–3%; reduced performance beyond optimal dosage
Wang et al. (2024)	Ceramic waste-slag geopolymer with nano-SiO ₂ -TiO ₂ coating;	45.6 MPa compressive 7 days at 40% ceramic waste; 5.8 % coating gave max hydrophobicity and self-cleaning	Nano-TiO ₂ /SiO ₂ in coating: 3.7–7.0%; 5.8% best for self-cleaning	Dip-coating with silane, epoxy, polyamide	5.8% SiO ₂ -TiO ₂ optimal for coating; higher amount has no added benefit
Tuntachon et al. (2019)	FA geopolymer paste with nano-TiO ₂	Enhanced resistance to algae and fungi, minor mechanical improvement	20 nm nTiO ₂ ; 1 to 5% by binder; Particle size 20 nm; dosages up to 5% beneficial for microbial resistance	Good distribution via conventional mixing methods	Optimal dosage 5% for microbial resistance; minor strength reduction at higher levels
Zawrah et al. (2025)	Waste clay-based geopolymers with nano-TiO ₂	Compressive strength increased by 24–35%	Particle size 50 to 200 nm; optimal dosage around 0.3%	Chemical synthesis and dispersion; effective microstructure improvement	0.3 % optimal; greater than 0.3%: agglomeration, slight strength drops
Ghanim et al. (2023)	FA-based UHPC with nano-TiO ₂	Compressive strength enhanced, chloride resistance improved	Smaller particle sizes are highly beneficial; optimal dosage 0.4–2%	Ball milling highly effective; optimal duration: 30 min	Optimal dosage around 1.2%; high dosages reduce workability

4.6.3. Effect of dispersion techniques on strength performance

Uniform distribution is essential for maximizing the reactive surface area of nAl. Techniques such as high-shear mechanical stirring, ultrasonication, and the use of specific surfactants have been shown to improve homogene-

ity (Xavier & Rahim, 2022; Zidi et al., 2019, 2021). For instance, Xavier and Rahim (2022) used homogenization to ensure that the coral-like clusters are sufficiently broken down, leading to consistent microstructural densification. Inadequate dispersion causes particle agglomeration, reducing active surface area and reinforcement effectiveness.

4.6.4. Strength enhancement in different geopolymer matrices

In FA and GGBS systems, it enhances resistance against acid and salt attack by refining the capillary pore network (Reddy & Ramujee, 2022; Rani & Gladston, 2024). In MK and RHA systems, nAl improves microstructure and mechanical properties, producing denser matrices and enhanced fracture resistance (Alomayri, 2019; Mohseni et al., 2019; Zidi et al., 2019). Microfiber- and fiber-reinforced geopolymers show synergistic nAl-fiber effects, further boosting mechanical performance (Arshad et al., 2024; Assaedi & Olawale, 2022). Recent studies into multi-scale reinforcement have demonstrated a synergy between nAl and nano-limestone in FA-MK blends, achieving compressive strengths up to 64.3 MPa. In these hybrid systems, nAl promotes chemical polycondensation while the limestone acts primarily as a physical nucleation site (Alwan & Fathi, 2026).

4.6.5. Optimal nAl dosage ranges and potential drawbacks at high concentrations

Optimal nAl dosage is 2% by binder weight, maximizing compressive, flexural, and tensile strengths. Exceeding this level reduces workability and mechanical performance due to nAl agglomeration and poor dispersion. Excessive nAl increases water demand and decreases setting time, limiting practical applicability (Alomayri, 2019; Arshad et al., 2024; Assaedi & Olawale, 2022; Rani & Gladston, 2024; Zidi et al., 2019, 2021).

Table 6 provides a comprehensive summary of recent experimental investigations into nAl-modified geopolymers. The data consistently point to a 2% dosage as the “sweet spot” for mechanical gain, with particle sizes between 20 and 50 nm yielding the most reliable results.

In conclusion, the role of nAl provides a critical chemical counterpoint to nSiO₂. While nano-silica focuses on increasing the silicate concentration to speed up initial gelation, nano-alumina ensures the structural balance of the resulting 3-D network by providing the necessary aluminate units for high-strength sialate (Si-O-Al) linkages. This highlights a fundamental “chemical convergence” between these two oxides: whereas carbon-based (CNTs) and functional (nTiO₂) nanomaterials act as external reinforcements, nAl and nSiO₂ function as internal geopolymerization accelerators. This distinction is vital for future research; it suggests that the most resilient geopolymer composites will likely arise not from a single nano-additive, but from the simultaneous use of reactive nano-oxides to densify the “gel” and fibrous nanomaterials to bridge the cracks.

Figures 6, 7, and 8 illustrate the maximum strength gains, optimal dosages, and durability improvements achieved through nanomaterial reinforcement. A comparative analysis of compressive strength enhancement (Figure 6) reveals that while all studied nanomaterials improve mechanical performance, their effectiveness varies significantly. Nano-silica (nSiO₂) exhibits the highest

peak enhancement (≈80%), likely due to its dual role as a high-surface-area filler and a chemical reactant. In terms of dosage (Figure 7), a clear convergence is observed in the ‘optimum threshold’ behavior; all nanomaterials show a parabolic relationship where strength increases up to a specific percentage before declining due to agglomeration. However, the materials diverge at the location of this peak. Carbon-based materials (CNTs and GO) reach their maximum effectiveness at much lower dosages (< 0.5%) compared to oxides like nTiO₂ or nSiO₂ (2.0–3.0%). This suggests that 1-D and 2-D nanomaterials are more susceptible to entanglement and van der Waals clustering, requiring stricter dosage control than 0-D nanoparticles. Regarding durability (Figure 8), the effects of nanomaterials converge on Freeze-Thaw resistance and Sulfate resistance, with Graphene Oxide (GO) showing consistent improvements across these metrics. A notable divergence is seen in water absorption and thermal stability. Nano-alumina (nAl₂O₃) and Nano-clays excel in reducing water absorption by refining the capillary pore network. In contrast, CNTs provide superior thermal stability by acting as a ‘bridge’ that maintains structural integrity during heat-induced micro-cracking.

To provide a holistic and critical evaluation of the nanomaterials discussed, Table 7 synthesizes the comparative performance, primary reinforcement mechanisms, and documented technical limitations of each additive. While the individual Sections 4.1–4.6 detail specific laboratory successes, this synthesis reveals a clear divergence in material behavior based on precursor chemistry and geometric dimensionality. Specifically, it highlights the “performance-workability” trade-off inherent in high-surface-area oxides versus the “dispersion-dependency” of carbon-based filaments. By contrasting these conflicting findings, the table underscores that nanomaterial effectiveness is not universal but is highly contingent upon the chemical compatibility between the additive and the specific geopolymeric activator used.

5. Modification of geopolymer microstructure by nanomaterials

5.1. Pore structure refinement and porosity reduction

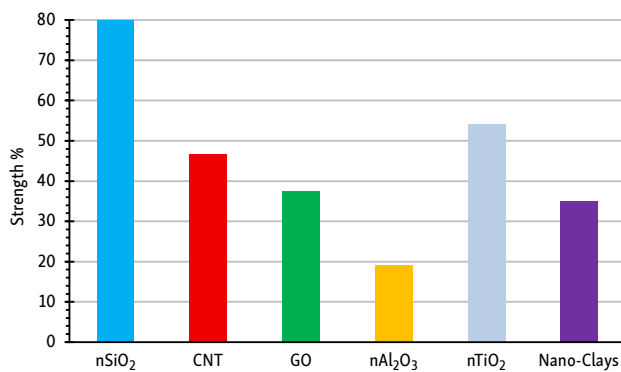
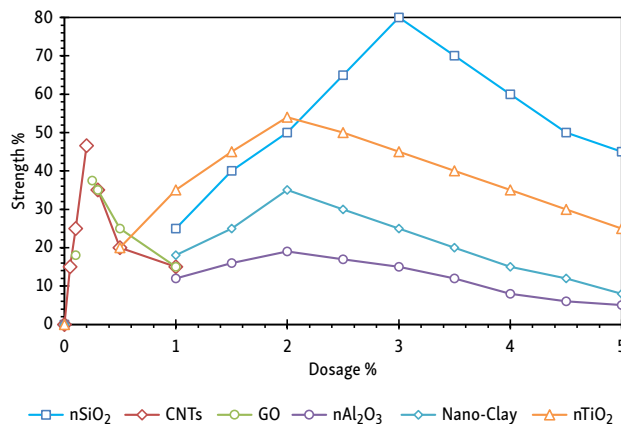
Nanomaterial incorporation fundamentally alters geopolymer microstructure through pore structure refinement and porosity reduction (Chiranjeevi et al., 2023). Microstructural modification occurs via complex physical and chemical nanoparticle-matrix interactions (Drabczyk et al., 2023). Nanoscale dimensions enable molecular-level interactions with aluminosilicate networks, producing compact, dense microstructures compared to conventional geopolymers (Al-Baldawi et al., 2025). Various nanomaterials, nS, nAl₂O₃, nTiO₂, consistently reduce total porosity and refine pore size distribution in composite sites (Kishore et al., 2023; Yi et al., 2024).

Table 6. Aspects and challenges of various recent works on nano alumina

References	Aspects Covered	Mechanical & Durability Results	Influence of Particle Size & Dosage	Dispersion Techniques & Effects	Optimal Dosage & Drawbacks
Zidi et al. (2019)	MK-based geopolymer with nano-alumina	2% nano-alumina: compressive increase; porosity decreased; denser matrix; water absorption decreased	300–500 nm; 1–3% tested; 2% best	High-speed stirring, ultrasonication in the activator	2% optimal; greater causes agglomeration, microcracks, lower strength
Assaedi and Olawale (2022)	FA-based geopolymer with PVA fibers and nano-alumina; mechanical and microstructure	2% nano-alumina: compressive, flexural strength, and impact increased; denser microstructure	50 nm; 0–3% tested; 2% best	Dry mixing, then with an alkaline solution and fibers	2% optimal; more forms crack, and lower strength
Mohseni et al. (2019)	RHA-based lightweight geopolymer	20% nano-alumina by binder; high compressive and flexural strength, less water absorption; improved chloride resistance	20 nm; 20% of binder (high for RHA-based system)	Dispersed in an alkaline solution, then mixed	20% used; higher not tested
Xavier and Rahim (2022)	FA/laterite geopolymer compressive, FTIR, TGA	0.75–1% nano-alumina: compressive strength increased; greater than 1%: workability and strength decreased due to agglomeration	0.02–6% tested; 0.75–1% best	Homogenizer mixing	0.75–1% optimal; greater than 1%: agglomeration, poor fluidity
Zidi et al. (2021)	MK-based geopolymer comparison of nano-silica, nano-alumina, and nano-zinc oxide	2% nano-alumina: compressive rises; porosity falls; best pore reduction	1–3% tested; 2% best	High-speed mixing, ultrasonication	2% optimal; more causes agglomeration, lower strength
Rani and Gladston (2024)	FA-GGBS geopolymer concrete	2% nano-alumina: compressive, split tensile, flexural strength increases; water absorption decreases; acid/salt resistance rises	20–50 nm; 0–4% tested; 2% best	Dry mixing, then with an alkaline solution	2% optimal; greater causes strength and durability decline
Reddy and Ramujee (2022)	FA-GGBS geopolymer and OPC concrete	2% nano-alumina: increase in compressive 17% (GPC), 19% (OPC); flexural 36% (GPC), 54% (OPC); split tensile 28% (GPC)	60 nm; 1–3% tested; 2% best	Added to the activator, then mixed with solids	2% optimal; increase 2%: agglomeration, lower strength
Alomayri (2019)	FA-based geopolymer paste	2% nano-alumina: compressive, flexural, impact, hardness increases; denser, less porous matrix	50 nm; 1–3% tested; 2% best	Added to the activator, then mixed with FA	2% optimal; greater causes agglomeration, and cracks
Arshad et al. (2024)	FA-based geopolymer with micro-carbon fiber and nano-alumina	3% nano-alumina + 0.5% fiber: compressive, flexural, impact increases; denser matrix, better C-S-H formation	40–50 nm; 0–4% tested; 3% best with fiber	Dispersed with fiber, then mixed	3% optimal (with fiber); greater than 3%: not tested, risk of agglomeration
Alomayri et al. (2025)	FA-based geopolymer with nano-alumina and micro steel fibers;	2% nano-alumina + 0.5% steel fiber: compressive, flexural, impact, fracture toughness increases; denser, less porous matrix	50 nm; 1–3% tested; 2% best	High-speed mixing, nano-alumina in the activator, then with fibers	2% optimal; more causes agglomeration, microcracks, lower strength
Alwan and Fathi (2026)	Nano-Alumina (nAl) & Nano-Limestone (nL) added to FA-MK based geopolymer	Ternary blends with nAl and nL achieved peak compressive strength, split tensile, and flexural strength up to 90 days	nAl: 70nm; 2% optimal nL: 70nm; 3% optimal	Both nAl and nL were added to water, then dispersed using a hand mixer before adding into the geopolymer	Higher nano particle >3% dosage increases water demand, leading to self-desiccation and micro-crack formation

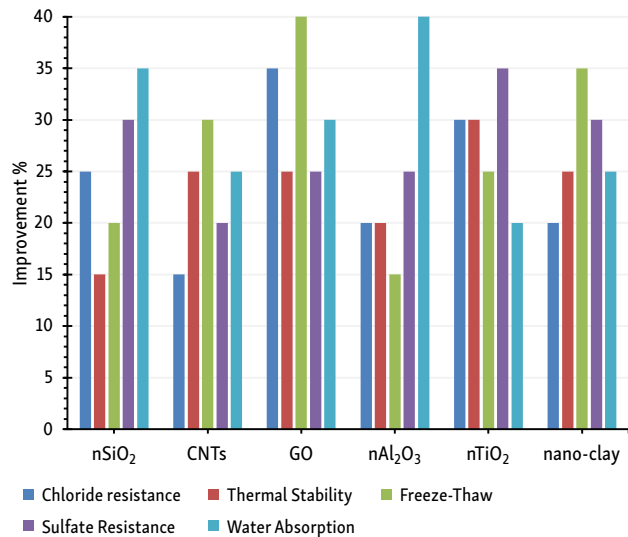
Table 7. Comparative synthesis of nanomaterial impacts, optimal dosages, and documented technical challenges in geopolymer composites

Nanomaterial	Primary Precursor	Typical Dosage	Consensus on Strength	Long-Term / Durability Focus	Conflicting Findings / Limitations
Nano-Silica	Fly Ash / Slag	1–3%	High (up to 80%)	Excellent Chloride & Sulfate resistance	Performance drops in high-calcium systems due to rapid setting/agglomeration
CNTs	Metakaolin / FA	0.05–0.1%	Moderate (Flexural focus)	Improves thermal stability & crack resistance	Significant strength loss if ultrasonic dispersion is insufficient
Graphene Oxide	Slag / FA	0.2–0.5%	High (Multiscale)	Significant reduction in chloride permeability	High cost; potential for reduction (rGO) in extremely alkaline environments
Nano-Clays	FA / Slag	2–4%	Moderate	Best for shrinkage control	Drastic reduction in workability; requires high water-to-binder ratios
Nano-TiO ₂	FA / Waste Clay	1–3%	Moderate	Imparts self-cleaning & photocatalytic properties	Generally, chemically inert; lacks the pozzolanic “bond” seen with nSiO ₂
Nano-Alumina (nAl ₂ O ₃)	Metakaolin / RHA	1–2%	High (20–40%)	Improved acid resistance & matrix density.	Limitation: Significantly increases water demand; excessive dosages lead to porous “islands” rather than densified gel

**Figure 6.** Maximum compressive strength enhancement by different nanomaterials in geopolymer composites**Figure 7.** Dosage-dependent compressive strength enhancement for different nanomaterials in geopolymers

5.1.1. Role of nanoparticles as fillers in interstitial spaces

Nanoparticles serve dual functions in geopolymer systems: physical fillers and nucleation sites for gel formation (Xu et al., 2021). With sizes typically ranging from 1–100 nm, particles penetrate and fill the smallest interstitial spaces between larger precursor particles like FA, MK (Kishore

**Figure 8.** Durability property improvements achieved by different nanomaterials in geopolymers

et al., 2023). High surface area provides numerous nucleation sites for additional hydration products, C-S-H and N-A-S-H gels, contributing to matrix densification (Al-Baldawi et al., 2025; Indwar et al., 2024). Properly dispersed nano-silica fills micro-voids between FA particles, creating denser phases that fill pore spaces (Kishore et al., 2023). Nano-silica accumulation creates dense phases, significantly reducing capillary pore volume and improving system packing density (Kishore et al., 2023; Yi et al., 2024).

Filler effectiveness depends heavily on dispersion quality (Xu et al., 2021). Properly dispersed nanoparticles bridge gaps between larger particles, creating interconnected networks (Drabczyk et al., 2023). Bridging enhances mechanical properties and reduces permeability by creating load transfer pathways while blocking aggressive substance transport (Yi et al., 2024). Optimal filler effects occur with uniform nanoparticle distribution throughout the matrix, preventing agglomerates that create weak zones or increase porosity (Indwar et al., 2024; Xu et al., 2021).

5.1.2. Impact on permeability and durability

Pore structure refinement through nanomaterial incorporation profoundly affects permeability and long-term durability (Chiranjeevi et al., 2023; Mahboubi et al., 2019). Reduced porosity and refined pore size distribution decrease permeability coefficients, preventing aggressive substance ingress of chloride ions, sulfates (Fong et al., 2025; Jin et al., 2022). Geopolymer concrete with 4% nano-silica exhibits minimal fast chloride permeability, much lower water absorption, and reduced sulfate attack mass loss (Chiranjeevi et al., 2023).

Enhanced durability is particularly evident in chloride-rich environments, where refined microstructure reduces chloride penetration (Fong et al., 2025; Jin et al., 2022). Nano-silica reinforced geopolymer maintains better mechanical properties under coupled wet-thermal and chloride salt environments (Jin et al., 2022). Optimal nano-silica dosages significantly reduce the chloride diffusion coefficient, with machine learning analysis identifying nano-silica content and mix parameter combinations achieving the lowest chloride penetration depths (Fong et al., 2025). This chloride resistance improvement stems from a densified microstructure, limiting capillary pore connectivity and reducing chloride ion diffusion pathways (Jin et al., 2022; Mahboubi et al., 2019).

Water absorption shows marked improvement with nanomaterial incorporation (Mahboubi et al., 2019; Moradikhou & Esparham, 2021). Refined pore structure reduces water-accessible pore volume and decreases water penetration rate into the matrix (Moradikhou & Esparham, 2021). Nano-clay and nano-silica additions provide increased acidic media stability with reduced weight loss, demonstrating superior chemical resistance (Mahboubi et al., 2019). Thermal stability is also enhanced, with nano-silica providing greater stability, confirmed by thermogravimetric analysis (Dudek & Sitarz, 2020; Sikora et al., 2018).

5.1.3. Characterization using Mercury Intrusion Porosimetry (MIP) and other techniques

Mercury Intrusion Porosimetry (MIP) is the primary technique for quantifying the effects of nanomaterials on geopolymer pore structure (Luna-Galiano et al., 2016). MIP measures total porosity, pore size distribution, and connectivity via mercury intrusion under controlled pressure. The Washburn equation ($d = -4\gamma\cos(\theta)/P$) enables precise pore size determination from nanometers to micrometers (Xu et al., 2022). MIP consistently demonstrates that the incorporation of nanomaterials reduces total porosity and shifts the pore distribution toward finer pores (Luna-Galiano et al., 2016; Zidi et al., 2020).

MIP analysis shows optimal nano-silica additions reduce total intrusion volume from 0.165 to 0.095 mL·g⁻¹ and decrease average pore diameter from 0.246 to 0.077 μm in FA-based geopolymers (Luna-Galiano et al., 2016). Nano-enhanced geopolymers exhibit increased mesopore fractions (84–94%) with average pore diameters reduced

to 7 to 10 nm (Xu et al., 2022). These quantitative measurements evidence microstructural densification and correlate with improved mechanical properties and durability (Luna-Galiano et al., 2016; Zidi et al., 2020).

Complementary techniques, SEM, XRD, and FTIR, provide additional microstructural insights. SEM reveals denser, more homogeneous structures with reduced cracks and improved interfacial bonding (Dudek & Sitarz, 2020). XRD confirms additional amorphous phase formation and enhanced geopolymerization, while FTIR spectroscopy evidence increased polycondensation degrees in nano-modified systems (Yi et al., 2024). Thermogravimetric analysis demonstrates enhanced thermal stability and modified decomposition patterns (Sikora et al., 2018). Combined techniques provide a comprehensive understanding of how nanomaterials alter geopolymer microstructural architecture, leading to enhanced performance (Dudek & Sitarz, 2020; Zidi et al., 2020).

5.2. Influence on geopolymer gel formation and morphology

5.2.1. Nanoparticles as nucleation sites for gel precipitation

Nanoparticles provide heterogeneous nucleation sites that fundamentally alter geopolymer gel precipitation and growth mechanisms. High specific surface area increases with decreasing particle size, providing numerous nucleation sites for hydration product formation during geopolymerization (Kishore et al., 2023). These sites reduce nucleation activation energy and accelerate gel formation (Jindal & Sharma, 2020).

Nucleation occurs through alkaline solution immobilization around nanoparticles, creating localized high-reactivity zones where aluminosilicate species condense into initial gel structures (Drabczyk et al., 2023). Carbon nanotubes offer additional nucleation sites, with enhanced gel formation, improving mechanical properties (Jindal & Sharma, 2020). Nano-silica provides highly reactive surfaces, facilitating additional aluminosilicate bonds, creating nucleation centers for N-A-S-H (sodium aluminosilicate hydrate) gel network development (Ma et al., 2024).

Nanoparticle nucleation effectiveness depends on surface chemistry and reactivity. Nano-silica's high surface area and energy enrich surrounding phases and accelerate geopolymerization through enhanced precursor dissolution. Experimental verification shows nanoparticle addition eliminates the typical geopolymerization lag phase, supporting the heterogeneous nucleation model (Drabczyk et al., 2023).

5.2.2. Alterations in gel density and homogeneity

Nanomaterial incorporation significantly enhances geopolymer gel density and homogeneity through multiple mechanisms. Nanoparticles densify gels by filling interstitial spaces and promoting additional binding phase formation, creating compact, uniform matrix structures. En-

hanced C-S-H gel formation from nanomaterial addition reduces porosity and improves overall composite density (Abbass & Singh, 2022).

Nano-silica demonstrates superior performance in creating dense, homogeneous gel structures. High surface area and reactivity provide abundant nucleation sites, leading to accelerated gel precipitation, fine pore filling, and reduced overall porosity. The compact microstructure exhibits reduced crack formation, improving mechanical strength and durability. Nano-silica addition promotes well-integrated geopolymer networks through aluminosilicate and calcium silicate hydrate gel growth. SEM and Mercury Intrusion Porosimetry (MIP) analyses consistently demonstrate nS yields denser, more homogeneous matrices than unmodified systems. Optimal 2% to 5% nS content produces pronounced pore volume and microcrack reductions; excessive addition causes agglomeration and material degradation (Ma et al., 2024).

Homogeneity improvements are evident in more uniform gel phases. Optimal nano-silica additions increase N-A-S-H gel presence compared to reference mixtures. nS's high reactivity provides additional nucleation sites and accelerates precursor dissolution (Ma et al., 2024). Calcium-containing hydrated gels form from calcium content interweaving with the geopolymer gel, filling voids and creating uniform matrices (Li et al., 2024).

5.2.3. Analysis using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

SEM and TEM provide comprehensive insights into microstructural modifications from nanomaterial incorporation. SEM reveals denser, more homogeneous microstructures with reduced crack formation and improved interfacial bonding, demonstrating nanomaterial contributions to microstructural densification through transition from porous, heterogeneous to compact, uniform matrices (Jindal & Sharma, 2020).

TEM provides superior resolution for investigating nanoscale geopolymer gel features and nanoparticle interactions. Al_2O_3 containing nanoparticles range from 5 to 10 nm in diameter, while larger crystallites span 30 to 80 nm within the matrix. TEM characterizes unique geopolymer structures, including spherical formations dispersed throughout sponge-like microstructures with nano-sized pores (Knežević et al., 2023).

Time-resolved cryo-TEM reveals particularly valuable nucleation and growth mechanisms. N-A-S-H gel nucleation and growth follow a multistep process: prenucleation clusters form within the first geopolymerization minute, agglomerate into partially polymerized globules, then transform into stable, highly polymerized N-A-S-H gel. This demonstrates gel formation follows non-classical nucleation theory with intermediate phases preceding final geopolymeric network formation (Tang et al., 2022).

The SEM and TEM combination proves essential for understanding geopolymer gel morphological evolution. SEM provides a broader microstructural context on poros-

ity, crack formation, and matrix density, while TEM offers detailed nanoscale particle distribution, gel network structure, and nanoparticle-matrix interactions. Energy-dispersive spectroscopy (EDS) combined with both techniques enables chemical composition analysis, confirming geopolymer network formation and successful nanomaterial incorporation (Knežević et al., 2023).

5.3. Enhancement of the Interfacial Transition Zone (ITZ)

5.3.1. Improved bonding between aggregates and the geopolymer matrix

The interfacial transition zone (ITZ) between aggregates and the geopolymer matrix critically influences mechanical performance and durability. Geopolymer concrete exhibits fundamentally different ITZ characteristics than Portland cement concrete. Unlike traditional concrete with weak ITZs exhibiting high porosity and calcium hydroxide crystals, geopolymer concrete microstructure does not present weak ITZs near aggregates (Alanazi, 2022). In one study, Lakew et al. (2023) added steel fibers to inhibit the propagation of cracks that originate in the porous interfacial transition zones (ITZ) of recycled aggregates, enabling the production of high-strength structural geopolymer concrete from 100% waste materials.

Nanomaterials, particularly nS and nTiO_2 , significantly improve aggregate-matrix bonding through multiple mechanisms. These create denser, more durable microstructures with enhanced interfacial bonding. Enhancement is attributed to additional binding phase formation and interfacial pore refinement, creating continuous, interconnected networks between matrix and aggregates. Nanoindentation tests reveal that geopolymer concrete demonstrates high matrix bond strength with no clear weak zones around aggregates with lower modulus, unlike typical Portland cement ITZs (Alanazi, 2022; Chiranjeevi et al., 2023; Zeyad et al., 2024).

Microscopic examination confirms improved interfacial bonding. SEM analysis shows no clear differences between microstructures in the vicinity of large aggregates and matrix phase microstructures, with no obvious voids around aggregate particles. Nanoparticle presence leads to nano-sized porosity at the ITZ, creating refined, cohesive interfaces between aggregates and cement paste (Shilar et al., 2022).

5.3.2. Reduction of weak zones and microcracks

Nanomaterial incorporation effectively reduces weak zones and microcracks through microstructural densification and enhanced gel formation. Nanoparticles create homogeneous matrix structures, minimizing weak points at aggregate-matrix interfaces. Unlike traditional concrete with weak ITZ regions containing pores and microcracks, nano-enhanced geopolymer concrete does not present weak zones near aggregates (Alanazi, 2022; Valente et al., 2021).

Weak zone reduction is achieved through nanoparticle filler effects, which fill micro-voids and create denser phas-

es, reducing pore spaces (Chiranjeevi et al., 2023). Densification eliminates crack initiation sites and reduces overall porosity. Nano-silica particles effectively fill pores and tiny cracks, making internal structures more compact and improving crack formation and propagation resistance under loading (Jin et al., 2022).

Additional hydration products: C-S-H and N-A-S-H gels further enhance weak zone reduction (Valente et al., 2021). These binding phases create continuous matrices bridging weak points and providing enhanced load transfer. Mercury Intrusion Porosimetry confirms that nanomaterial incorporation significantly reduces total porosity and shifts pore size distributions toward finer ranges, effectively eliminating larger pores serving as stress concentration points (Jin et al., 2022).

5.3.3. Role of nanomaterials in bridging interfaces

Nanomaterials provide crucial bridging at interfaces within geopolymer composites, creating enhanced connectivity between phases. Nanoparticles' extremely small size enables penetration of the smallest interfacial regions, creating physical bridges between the matrix and aggregates (Drabczyk et al., 2023). This bridging enhances load transfer capabilities and prevents interface debonding under stress.

Carbon-based nanomaterials, carbon nanotubes, and graphene nanosheets demonstrate exceptional bridging capabilities due to high aspect ratios and excellent mechanical properties. Carbon nanotubes act as reinforcing fillers through crack-bridging effects (Valente et al., 2021). Bridging involves percolating nanoparticle networks spanning weak interfaces, creating multiple load transfer pathways, and improving composite toughness.

Nanomaterial bridging extends beyond mechanical reinforcement to chemical bonding enhancement. Graphene nanosheets establish secondary chemical bonds with aluminosilicate chain oxygen atoms, creating strong interfacial adhesion (Valente et al., 2021). Combined physical and chemical bridging ensures effective stress distribution and increased toughness at break. High nanomaterial surface area provides numerous contact points for matrix interaction, creating an integrated, cohesive composite structure.

To illustrate, Figure 9 highlights the functional divergence among different nanomaterial geometries. nSiO₂ and nTiO₂ are dominated by the filler effect and nucleation, making them ideal for densifying the geopolymer matrix. Conversely, CNTs and GO diverge from the oxides by showing peak performance in crack bridging and load transfer. This indicates a fundamental shift in reinforcement strategy: while nano-oxides chemically and physically densify the "gel" phase, carbon-based nanomaterials mechanically reinforce the "composite" structure. This divergence suggests that "hybrid" systems, combining a 0-D oxide with a 1-D carbon filament, could offer a convergent path to maximizing both matrix density and fracture toughness.

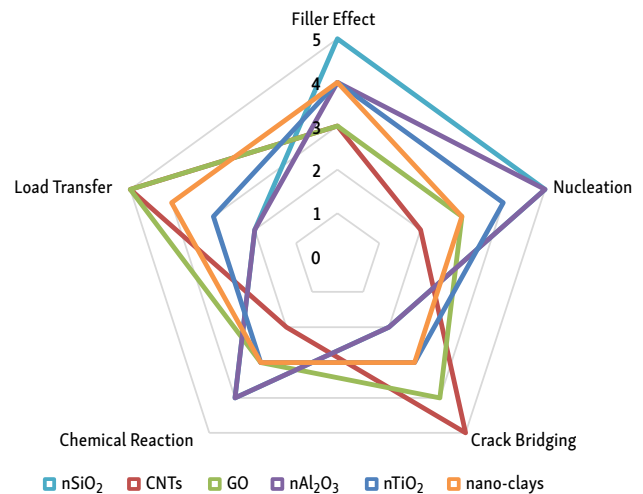


Figure 9. Comparative effectiveness of enhancement mechanisms for different nanomaterials

5.4. Impact on crack propagation mechanisms

5.4.1. Nanomaterials as crack arrestors and deflection agents

Nanomaterials function as effective crack arrest and deflection agents through multiple toughening mechanisms. Nanoparticles create physical barriers, forcing cracks to deflect from their original path, increasing the energy required for advancement. This deflection transforms failure from simple tensile crack propagation to mixed-mode failure involving tensile and shear components.

Crack-arresting effectiveness depends on nanoparticle size, distribution, and interfacial bonding. Carbon nanofibers provide dual strengthening mechanisms: porosity refinement and material densification, plus crack bridging effects. Crack bridging involves nanoparticles spanning crack surfaces, providing resistance to crack opening and increasing fracture toughness (Valente et al., 2021).

Nano-silica demonstrates particularly effective crack-arresting capabilities due to its high surface area and strong matrix bonding. Nano-silica is most suitable for crack resistance and toughness in geopolymer concrete (Jin et al., 2022). The crack-arresting mechanism forms tortuous crack paths requiring significantly more propagation energy than straight advancement. Nanoparticles force cracks to navigate around or through nanoscale reinforcements, increasing fracture surface area and energy dissipation.

5.4.2. Improved fracture toughness and resistance to microcracking

Nanomaterial incorporation in geopolymer systems substantially improves fracture toughness and microcracking resistance through enhanced matrix properties and modified failure mechanisms. Fracture toughness increases by 38% to 45% compared to unreinforced composites, at-

tributed to synergistic matrix densification, crack bridging, and deflection (Valente et al., 2021).

Carbon-based nanomaterials show particularly pronounced improvements. Carbon nanofibers increase fracture toughness by 38%, 40%, and 45% at 0.1%, 0.2%, and 0.5% by weight, respectively, with accompanying 83%, 72%, and 74% fracture energy increases (Valente et al., 2021). High aspect ratio nanofibers promote tensile failure resistance through crack-bridging mechanisms.

Nano-silica also demonstrates significant fracture toughness improvements. Enhanced toughness from good nanoparticle dispersion throughout the matrix operates through pore refinement, increased gel formation, and improved interfacial bonding (Rahmawati et al., 2021). Nano-silica distinctly improves geopolymer concrete impact resistance, with optimized nano-silica content yielding improvements in impact toughness, initial crack numbers, and ultimate failure (Jin et al., 2022).

5.4.3. Analysis using microscopy and fracture mechanics testing

Advanced microscopy combined with fracture mechanics testing reveals mechanisms by which nanomaterials enhance crack resistance in geopolymer composites. Scanning electron microscopy (SEM) shows denser, more homogeneous microstructures with reduced crack formation and improved interfacial bonding when nanoparticles are incorporated, demonstrating the transition from porous, heterogeneous to compact, uniform matrices (Knežević et al., 2023).

Transmission electron microscopy (TEM) provides superior nanoscale resolution of geopolymer gels and nanoparticle interactions. TEM reveals Al_2O_3 -containing nanoparticles with 5 to 10 nm diameters and larger crystallites ranging from 30 to 80 nm within the matrix (Knežević et al., 2023). This technique characterizes unique geopolymer structures and clarifies nanoparticle distribution and integration.

Fracture mechanics testing (three-point bending, single-edge notched beam tests) quantifies fracture property improvements from nanomaterial incorporation. Digital image correlation (DIC) monitors crack propagation in real-time, revealing three cracking stages: initiation, stability, and instability (Rezaei Lori & Mehrali, 2024). Nanomaterial-enhanced composites show significantly extended stability stages, yielding more stable propagation and improved toughness.

Nanoindentation combined with microscopy characterizes nanoscale mechanical properties and interfacial transition zone behavior. Studies show nanomaterial-incorporated geopolymer concrete exhibits no clear weak aggregate zones with lower modulus, indicating improved interfacial bonding and enhanced load transfer (Alanazi, 2022). These advanced techniques collectively demonstrate how nanomaterials fundamentally alter fracture behavior at multiple length scales.

6. Influence of nanomaterials on specific geopolymer systems

6.1. Nanomaterial enhancement in fly ash-based geopolymers

Fly ash-based geopolymers are extensively studied for nanomaterial enhancement due to environmental benefits and improved performance potential. Nanomaterial incorporation addresses inherent limitations, including slower ambient-temperature strength development and reduced workability compared to Portland cement (Alanazi, 2022). Nano-silica is most effective: 2% nano- SiO_2 addition increases compressive strength by up to 80% at room temperature (Drabczyk et al., 2023).

Enhancement mechanisms involve accelerated geopolymerization, pore refinement, and additional binding phase formation. Nano- SiO_2 enhances FA activity, accelerating geopolymerization, increasing C-S hydrogen gel chain length, and providing particle-filling effects. High nano- SiO_2 surface area and energy accelerate geopolymerization, particularly beneficial for FA systems typically requiring elevated-temperature curing (Han et al., 2022; Rahmawati et al., 2021).

Nano- TiO_2 demonstrates significant effectiveness in FA systems. At 5%, nano- TiO_2 improves compressive strength by 54.31% over controls. Optimal dosage ranges from 3 to 5%, with maximum performance at around 10% before declining at higher concentrations. Nano-silica addition to high-volume FA-slag concrete reduces initial and final setting times, improving construction applicability (Chiranjeevi et al., 2023; Syamsidar et al., 2017).

Nano-enhanced FA geopolymers show marked durability improvements, particularly chloride resistance and freeze-thaw performance. At 4%, nano-silica exhibits minimum rapid chloride permeability, significantly reduced water absorption, and decreased sulfate attack mass loss compared to unmodified systems (Chiranjeevi et al., 2023). Refined microstructure from nanomaterial incorporation creates impermeable matrices resisting aggressive environmental conditions (Han et al., 2022).

6.2. Nanomaterial enhancement in MK-based geopolymers

Metakaolin-based geopolymers benefit significantly from nanomaterial incorporation through mechanical enhancement and microstructural densification. MK's high reactivity creates an ideal matrix for nanomaterial integration, producing synergistic effects exceeding other geopolymer systems. Nano-silica shows exceptional performance: 1% addition increases compressive strength from 43.7 to 68.4 MPa (Cheng et al., 2019; Gao et al., 2013).

Nano-silica improves mechanical and durability properties more pronouncedly than nano-clay due to its high surface area and reactivity. At 5%, nano-silica in MK mortar achieves compressive and tensile strengths of 36 MPa and 3.5 MPa, respectively, with the lowest water absorp-

tion of 4.65%. At 2% by weight, nano-silica increases compressive strength by 22%, flexural strength by 82%, and fracture toughness by 82% (Rahmawati et al., 2021; Zidi et al., 2020).

XRD and SEM analyses confirm denser microstructures in nano-enhanced MK geopolymers with increased N-A-S-H gel presence. Nano-silica's high reactivity provides nucleation sites and accelerates MK dissolution, forming denser, interconnected networks through additional aluminosilicate bonds and nucleation centers (Kamal et al., 2025; Zidi et al., 2020).

Optimal nano-silica dosage ranges from 2% to 5% depending on the specific application. Excessive nanomaterial content causes agglomeration, creating weak zones and reducing performance. Nanomaterial incorporation significantly reduces setting time through accelerated geopolymerization reactions (Rahmawati et al., 2021).

6.3. Nanomaterial enhancement in slag-based geopolymers

Ground granulated blast furnace slag (GGBS) based geopolymers demonstrate excellent compatibility with nanomaterials, with significant mechanical and durability improvements. Calcium content enables unique nanomaterial interactions through C-A-S-H and N-A-S-H gel formation. Nano-TiO₂ addition up to 3% improves compressive strength: $\pm 21.5\%$, split tensile strength: $\pm 17.5\%$, and flexural strength: $\pm 14.76\%$ over control mixtures (Wang et al., 2024).

Nanomaterial incorporation enhances C-A-S-H gel formation, achieving compressive strength increases of up to 19.2% at 90 days. Calcium-containing hydrated gels interweave with geopolymer gel, filling voids and creating uniform matrices. This dual gel mechanism is pronounced in slag systems due to the inherent calcium content (Chiranjeevi et al., 2023; Shaikh & Hosan, 2019).

Slag incorporation significantly enhances workability and reduces setting times. Replacing 10% volcanic tuff with slag reduces setting times from 48 hours to 435 minutes. Up to 30% slag addition achieves 92.08% flow time reduction, improving practical applicability. Under 80 °C curing for 48 hours, 28-day strength reaches 15.03 MPa at 30% slag incorporation (Boumaza et al., 2025).

Nano-enhanced slag geopolymers show improved pore structure and densification. Additional hydration products, including calcium silicate hydrate and sodium aluminosilicate hydrate gels, enhance structural integrity. Mercury Intrusion Porosimetry confirms significant porosity reductions and shifts toward finer pore distributions with optimal nanomaterial incorporation (Xiao et al., 2024).

6.4. Nanomaterial enhancement in RM-based geopolymers

Red mud-based geopolymers present unique opportunities for nanomaterial enhancement due to distinctive chemical composition and alkaline nature. High Fe₂O₃, Al₂O₃, and residual alkalinity create specific nanomaterial

interaction mechanisms. Strategic nanomaterial incorporation mitigates strength decreases with increasing red mud content while maintaining environmental benefits (Ai et al., 2021).

Rice husk ash (RHA) incorporation compensates for red mud's low SiO₂/Al₂O₃ ratio, driving microstructural refinement. As RHA loading increases from 0% to 60%, BET surface area rises from 19.2 to 29.5 m²/g while BJH pore diameter decreases from 6.68 to 5.76 nm, indicating a denser network. Methylene blue uptake capacity increases from 6.59 to 10.74 mg/g at pH 8 after 180 min, reflecting enhanced adsorption sites. RHA's nanostructured silica framework and red mud's aluminosilicate matrix synergistically produce superior surface characteristics and improved dye-removal performance (Nguyen et al., 2023).

Silica-rich nanomaterials enhance red mud geopolymerization through additional binding phases. FT-IR analysis confirms geopolymer formation with Si-O-T (T = Si or Al) bond formation (Nguyen et al., 2023). Silica fume and diatomite incorporation improve fluidity and create compact structures with better pore characteristics (Chen & Li, 2023).

Environmental considerations for red mud-based geopolymers focus on both pollutant immobilization and structural performance. Studies of FA-RM blends show that polymerization transforms heavy metals, like mercury, into stable mineral fractions, yielding leachates that meet regulatory limits, for instance, Hg reduced to 0.0004 mg/L, while achieving 28-day compressive strengths up to 10.78 MPa at optimal formulations (Luo et al., 2026). Further, incorporating up to 50% red mud into one-part geopolymers produces strengths as high as 36.3 MPa under autoclave curing (Ai et al., 2021), though red mud's high alkalinity means some elements, such as chromium and vanadium, can remain more mobile and require careful process control to immobilize effectively. These findings demonstrate that red mud geopolymers can both valorize a hazardous by-product and deliver construction-grade materials while safeguarding environmental and human health.

6.5. Nanomaterial enhancement in blended precursor geopolymers

Blended precursor geopolymer systems demonstrate synergistic effects when enhanced with nanomaterials, often exceeding single-precursor performance. Binary combinations of FA and GGBS show significant improvements with nano-silica incorporation, with ternary mixtures containing 25% GGBS, 65% FA, and 10% bagasse ash demonstrating optimal performance. Complementary reaction mechanisms between different precursors and nanomaterials enhance gel formation and microstructural development (Chiranjeevi et al., 2023).

Incorporation of 4% nano-silica achieves the greatest improvements in blended systems: compressive strength of 41.33 MPa and split tensile strength of 2.91 MPa. Nano-enhanced blended systems minimize chloride permeability, water absorption, and sulfate attack mass loss, indicating superior durability (Chiranjeevi et al., 2023).

MK-FA and slag-metakaolin blends show particularly promising results with nanomaterial enhancement, often exceeding single-precursor performance. Different precursor dissolution rates and reaction kinetics create opportunities for staged gel formation optimized through strategic nanomaterial addition. Nano-silica and nano-clay, up to 2% by weight, significantly enhance geopolymerization rate, reduce setting times, and improve hardened properties (Gómez-Casero et al., 2022).

Microstructural analysis reveals complex gel networks combining N-A-S-H, C-A-S-H, and additional binding phases (Indwar et al., 2024). Carbon nanotubes and nano-TiO₂ enhance geopolymerization by providing nucleation sites, while nano-alumina more prominently reduces porosity. X-ray diffraction studies confirm increased peaks indicating additional hydration products, consistent with SEM observations of densified microstructures.

Nanomaterial dosage optimization requires consideration of precursor combination and desired performance. Nanomaterial inclusion densifies microstructure and produces high mechanical strength, with durability studies showing enhanced geopolymerization prevents micro-pore interconnectivity through the formation of denser geopolymer gel matrices (Jindal & Sharma, 2020).

7. Challenges, limitations, and future directions

7.1. Dispersion challenges and achieving uniformity at larger scales

Nanomaterial dispersion in geopolymer systems represents a critical technical challenge limiting commercial application. Due to large specific surface area and surface activity, nanomaterials agglomerate through Van der Waals forces, creating uneven distribution and reducing performance. Agglomeration creates localized high-concentration zones while leaving other areas deficient, compromising mechanical and durability enhancements (Kishore et al., 2023).

Ultrasonic dispersion is the most effective approach for uniform distribution, with sonication providing strong shear forces to break agglomerates and enhance nanoparticle suspension. Well-dispersed nanoparticles act as efficient fillers, densify the microstructure, and accelerate early geopolymerization. However, drawbacks include time-consuming procedures, operational complexity, and high equipment costs, limiting large-scale production viability. The high alkalinity (pH > 13) of geopolymer activators presents a unique challenge for dispersion; many common surfactants used in cement chemistry degrade in such harsh environments, causing nanoparticles to re-agglomerate even after successful sonication. Alternative techniques, such as high-speed mechanical mixing and dispersing agents, exist, but each presents challenges in achieving consistent results across different batch sizes and conditions (Guo et al., 2020; Luo et al., 2021b).

Characterizing dispersion quality in hardened geopolymers remains problematic due to the difficulty of

separating reaction products from reacting nanomaterials. Scanning electron microscopy, though commonly used, experiences interference from active particles during geopolymerization, limiting assessment reliability. Indirect evaluation methods based on mechanical strength and water absorption lack sufficient detail to confirm their reliability as dispersion indicators (Du et al., 2019).

Scaling from laboratory to industrial production requires specialized equipment handling the unique rheological properties of nano-enhanced mixtures while maintaining consistent dispersion across larger volumes. In a laboratory setting, high-energy ultrasonication is often employed to break van der Waals forces in nanomaterials like CNTs or nS; however, this approach proves energy-intensive and thus impractical for large-scale construction applications. To address this limitation, industrial processes should transition to high-shear in-line dispersion systems or incorporate pre-dispersed masterbatch liquid slurries. These slurries minimize the health risks associated with handling dry nano-powders while ensuring that the high surface area of the particles is utilized without re-agglomeration during the bulk mixing process. Moreover, the accelerated reaction kinetics induced by the nucleation effect of nanoparticles, which can mitigate or eliminate the characteristic lag phase in geopolymerization, necessitate precisely calibrated retarders to ensure adequate workability (slump) for industrial transport and casting. Standardized mixing protocols and quality control procedures, such as real-time rheological monitoring, are essential for commercial viability, yet current practices lack the systematic approach necessary for reliable implementation at the ready-mix plant scale (Utomo et al., 2023; Xu et al., 2021).

7.2. Cost-effectiveness and scalability of nanomaterial integration

Nanomaterial-enhanced geopolymers face significant economic challenges due to high nanomaterial costs and complex production processes. Nanotechnology complexity and specialized equipment substantially increase material costs compared to conventional additives (Saleem et al., 2021). Current market prices for nano-silica and engineered nanomaterials are prohibitively expensive for large-scale construction, with premium pricing not consistently justified by performance gains alone.

However, economic assessment must consider long-term benefits beyond initial costs (Saleem et al., 2021). Enhanced durability and extended service reduce lifecycle costs through minimized repair and replacement frequencies. Nanoparticles enable cost savings via reduced labor, eliminated distribution and storage expenses, and decreased maintenance requirements.

Strategic cost management optimizes economic benefits while managing increased fixed costs (Ali et al., 2022). Manufacturing process optimization and economies of scale are expected to reduce nanomaterial costs as fabrication technologies progress and global production increases (Saleem et al., 2021).

Scalability of commercial nanomaterial production remains critical for cost-effectiveness and market adoption. Laboratory successes require significant capital investment in specialized equipment and quality control systems for commercial volumes. While lab-scale synthesis often utilizes high-purity chemical reagents, industrial application necessitates the use of technical-grade nanomaterials to remain economically viable. The current market price for engineered reinforcements like CNTs and GO remains prohibitively high, often increasing the raw material cost of the geopolymer binder by several orders of magnitude without a linear increase in performance. Large-scale production using optimized manufacturing processes can achieve commercial viability, though initial investments and expertise requirements may initially limit widespread adoption (Nandiyanto et al., 2022; Suet, 2024). To counter these initial capital hurdles, a shift toward Life Cycle Cost Analysis (LCCA) is essential; the “premium” initial cost of nano-enhanced geopolymers is offset by extended service life, reduction in chloride permeability, and significantly lower maintenance and repair frequencies in aggressive environments. Future cost-effectiveness will likely depend on “economies of scale” and the development of lower-cost “green” synthesis methods for nanomaterials, such as producing nano-silica from agricultural waste like RHA (Moosa & Saddam, 2017).

7.3. Long-term stability and durability of nano-modified geopolymers

Long-term stability and durability of nano-modified geopolymers remain critical for structural applications, though comprehensive long-term service data is limited. Short-term studies demonstrate significant mechanical and durability improvements, but extended environmental performance requires further investigation.

Nanomaterial incorporation enhances durability against thermal diffusion, acid, sulfate infiltration, and chloride penetration through denser microstructures with reduced porosity and improved pore connectivity. However, multi-decade stability requires validation via accelerated aging and field monitoring (Alghrairi et al., 2025).

Nano-enhanced geopolymers exhibit superior resistance to sulfate attack, acid exposure, and freeze-thaw cycles compared to unmodified systems. Nanomaterial-modified composites show significantly better residual strength after aggressive environment exposure, with reduced mass loss and maintained structural integrity (Al-Saffar et al., 2023; Bautista-Gutierrez et al., 2019).

Environmental stability concerns require careful assessment, particularly given the aggressive alkaline environment inherent to geopolymer matrices. Environmental aging can significantly alter nanoparticle physicochemical properties and mobility, changing morphology and chemical state as functions of aging time and conditions (Kuchibhatla et al., 2012). For carbon-based nanomaterials like CNTs and Graphene Oxide, long-term exposure to the high-pH pore solution of geopolymers can lead to

surface functional group degradation, potentially weakening the interfacial bond between the nanomaterial and the aluminosilicate gel over time. While nanoparticles form protective barriers preventing moisture and chemical ingress, release dynamics depend on material composition and specific degradation scenarios encountered during service life (Singh et al., 2022a). In outdoor infrastructure, oxidative environment exposure can cause nanoparticle structural rearrangement and chemical transformation, with aging potentially accelerated by ambient light, oxygen, and moisture (Peng et al., 2010). Furthermore, the “leaching potential” of nanomaterials during the eventual decommissioning or recycling of nano-enhanced geopolymer structures remains a critical research gap. Future durability studies must transition from short-term (28-day) strength testing to accelerated aging protocols that simulate 50-year service lives, focusing on the carbonation resistance and sulfate attack stability of the nano-densified interfacial transition zone (ITZ) (Arab et al., 2025).

7.4. Potential environmental and health concerns related to nanomaterials

Nanomaterial incorporation in geopolymer systems raises significant environmental and health concerns requiring resolution before widespread commercialization (Hirose et al., 2011). Limited research on prolonged nanoparticle exposure and nano-enhanced product use creates uncertainty about long-term effects on human health and ecological systems.

Occupational health hazards during nano-enhanced geopolymer handling require immediate attention. According to OSHA, primary safety risks include fire, explosion, and unexpected reactions during material handling and processing. Laboratory evidence indicates that nanoparticles can cause asbestos-like symptoms, including lung inflammation and potential DNA damage (Shvedova et al., 2014). Release of nanomaterials during construction activities poses challenges for establishing appropriate safety protocols and exposure limits (Mohajerani et al., 2019).

Environmental release pathways include atmospheric emissions during production and construction, manufacturing waste streams, and potential structure leaching during service and demolition. Nanomaterials may contaminate soil, migrate into groundwater systems, or reach aquatic environments via waste transport and runoff. Primary concerns stem from transportation spillages and diffuse releases from wear and erosion of nano-enhanced structures (Ferreira et al., 2023).

Regulatory frameworks and safety guidelines for construction applications remain underdeveloped, hindering industry adoption and worker protection (Ferreira et al., 2023). Current knowledge gaps in nanomaterial exposure assessment and construction-environment risk management require comprehensive protocols for handling, use, and disposal. Essential interventions include control banding strategies, personal protective equipment requirements, and worker health surveillance programs (Macías-Silva et al., 2024; West et al., 2016).

7.5. Knowledge gaps and areas for future research

Significant knowledge gaps persist in understanding the behavior of nanomaterials within geopolymer systems, particularly regarding their long-term performance and optimization strategies. The lack of comprehensive mathematical modeling and artificial intelligence applications for predicting nanomaterial-geopolymer behavior presents a major research opportunity. Limited understanding of nanomaterial interactions with various geopolymer precursor systems remains a critical constraint (Drabczyk et al., 2023).

Current research inadequately addresses optimal nanomaterial dosages across different geopolymer compositions. Developing predictive models to determine optimal nanomaterial selections and dosages based on precursor composition and application requirements is essential. Integrating machine learning and artificial intelligence could significantly enhance optimization efficiency and reduce experimental demands (Ly, 2025).

Interdisciplinary collaboration between materials scientists, manufacturing engineers, and environmental specialists is crucial for developing cost-effective nano-enhanced geopolymers while addressing carbon emissions reduction. The synergy between sustainability goals and nanotechnology applications in construction offers potential for breakthrough, eco-friendly, high-performance materials (Drabczyk et al., 2023).

Practical implementation challenges require systematic attention: standardized production protocols, quality control procedures, and field application guidelines remain underdeveloped. Scaling from laboratory success to commercial production faces obstacles, including process scaling, quality consistency across batch sizes, and field-relevant testing methods (Al-Baldawi et al., 2025). Priority research should focus on industry-ready solutions that maintain laboratory-demonstrated performance characteristics while meeting real-world construction requirements (Gamal et al., 2021; Teizer et al., 2012).

8. Conclusions

This comprehensive review has established that the integration of low-dimensional nanomaterials represents a fundamental paradigm shift in the design of sustainable geopolymer binders. By bridging the gap between microscopic chemical kinetics and macroscopic structural integrity, nanotechnology transforms geopolymers from simple industrial by-product binders into sophisticated, multi-functional engineered composites.

8.1. Synthesis of core findings and material performance

The critical evaluation of the existing literature yields several decisive conclusions regarding the performance boundaries of nano-enhanced geopolymers:

- Nanomaterial influence is governed by a “three-tier reinforcement” hierarchy. Nano-silica (nSiO_2) and na-

no-alumina (nAl_2O_3) serve as primary chemical accelerators that optimize the ratio and polycondensation kinetics. Nano-clays and nano-titanium (nTiO_2) function as rheological stabilizers and nucleation templates. Conversely, CNTs and graphene-based materials act as mechanical anchors, transitioning the failure mode from brittle fracture to energy-dissipative crack bridging.

- A universal performance limit was identified across all systems. Optimal mechanical and durability gains consistently cluster within the 0.1–3.0% range. Beyond these specific thresholds, high surface energy leads to van der Waals-induced agglomeration, which converts potential reinforcement sites into localized structural defects, effectively negating the chemical benefits of the additive.
- The effectiveness of nano-additives is deeply contingent upon precursor chemistry. Fly ash systems exhibit the most dramatic strength gains (up to 80%) when paired with nSiO_2 , as it compensates for the slow dissolution rates of glassy fly ash spheres. In contrast, slag-based systems derive significant durability benefits from nano-clays, which mitigate the autogenous shrinkage characteristic of calcium-rich geopolymer gels.

8.2. Strategic directions for future research

To transition nano-modified geopolymers from laboratory successes to standardized construction materials, the research community must pivot from empirical observation to mechanistic optimization:

- Future studies should prioritize the development of alkaline-stable surfactants and silane-coupling agents. Research must specifically address the stability of dispersants in high-pH environments (> 13) to prevent post-sonication re-agglomeration.
- Investigation should shift toward “hybrid” systems that combine 0-D nanoparticles (for matrix densification) with 1-D or 2-D filaments (for crack bridging). This approach offers “all-stage” protection, arresting cracks at both the initiation (nanoscale) and propagation (microscale) stages.
- The vast, heterogeneous data landscape of geopolymer chemistry is ideally suited for Machine Learning (ML) optimization. Future research should implement predictive models (e.g., Random Forest or Neural Networks) to determine optimal nano-dosages based on the specific oxide composition of local precursors, reducing the reliance on trial-and-error experimental campaigns.
- There is a critical lack of multi-decade service data. Research must focus on standardized accelerated aging tests to evaluate carbonation resistance, alkali-silica reaction potential, and the leaching stability of heavy metals in nano-densified matrices over a 50-year simulated lifespan.

8.3. Framework for industrial implementation

To facilitate the commercial adoption of these advanced binders, the following roadmap is proposed:

- Transitioning from the handling of raw nano-powders to pre-dispersed liquid nano-slurries. This addresses occupational health risks (toxicity) while ensuring uniform dispersion at the ready-mix plant scale.
- A shift in economic evaluation is required. The high initial cost of nanomaterials must be quantified against reduced maintenance cycles, lower carbon-tax liabilities, and the extended service life of the infrastructure to provide a compelling case for stakeholders.
- Exploiting the secondary functional properties of nanomaterials, such as the photocatalytic activity of nTiO_2 and the piezoresistive sensing capabilities of CNTs, to engineer “smart” pavements and self-sensing structural components capable of real-time health monitoring.

Acknowledgements

The authors extend their appreciation to the University of Malaya for providing research and technical support through research grant IMG 003-2024 (Circular Production Route for Sustainable Geopolymer Mortar: Utilizing Waste from Mineral Wool Production for 3D Printing).

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