Research Article

Journal of Environmental Nanotechnology

Incorporation of Nanoalumina in Potassium Feldspar-based Phosphoric Acid Activated Geopolymer Composites: A Sustainable Approach

M. Nanthini, R. Ganesan and V. Jaganathan*
Department of Civil Engineering, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences, Chennai, TN, India
Received: 11.08.2024 Accepted: 16.09.2024 Published: 30.09.2024
*jaganathanvenugopal.sse@saveetha.com

ABSTRACT

This study investigates the potential of potassium feldspar-phosphate-based geopolymer concrete as a sustainable replacement to traditional concrete, addressing the environmental concerns associated with CO_2 emissions during cement production. While geopolymer concrete offers a promising path towards sustainability, its performance often falls short of Portland cement concrete. This study investigates the use of nanoalumina in improving the performance of geopolymer concrete. A ternary mix was formulated with potassium feldspar powder, metakaolin and rice husk ash, incorporating varying percentages of nanoalumina geopolymer concrete mixes. The mechanical characteristics of the resulting geopolymer composites were assessed through compressive and split tensile strength tests. The findings revealed that a 4% nanoalumina dosage (GC-N4) yielded the most significant improvement in strength and durability. The GC-N4 mix performed superior in all metrics, demonstrating the highest compressive (41.82 MPa) and split tensile (3.7 Mpa) strengths. Reduction in water absorption and durability aspects were also optimum in GC-N4. These results highlight the potential of incorporating nanoalumina into a ternary mix of potassium feldspar powder, metakaolin and rice husk ash to significantly enhance the overall performance of geopolymer concrete, promoting its wider adoption as a sustainable construction material.

Keywords: Potassium feldspar; Geopolymer concrete; Sustainability; Nanoalumina.

1. INTRODUCTION

Because of improved mechanical qualities, less carbon footprint, and ability to use industrial byproducts of geopolymer concrete, it has become a viable substitute for conventional Portland cement-based concrete (Singh *et al.* 2020; Qadir *et al*. 2022). The alkali-activated aluminosilicate sources of fly ash, slag, and other natural minerals are the precursors of this novel material (Awoyera *et al*. 2019). In recent years, incorporating nanomaterials like nanoalumina has been shown to significantly enhance the performance of geopolymer concrete by improving its microstructure and durability (Chiranjeevi *et al.* 2023; Jindal *et al.* 2020). The utilization of potassium feldspar as a raw material for geopolymer synthesis, significantly when activated with phosphoric acid, is an encouraging breakthrough in this sector (Le-ping *et al*. 2010). This approach leverages the abundant availability of potassium feldspar and creates high-strength, chemically resistant geopolymer matrices. Recent studies have highlighted the benefits of addition of nanoalumina, including refined pore structure and increased compressive strength, making it a pivotal component in advancing geopolymer technology (Du *et al*. 2019).

Potassium feldspar and metakaolin play pivotal roles in conventional and geopolymer concrete, offering sustainable alternatives to traditional Portland cement-based materials while enhancing performance across various construction applications. Potassium feldspar, an abundant aluminosilicate mineral, has received attention for its potential in geopolymer synthesis, mainly when activated with phosphoric acid or alkalis. This activation process converts potassium feldspar into a reactive binder that can replace or supplement cement in concrete formulations, thereby reducing environmental impact and carbon emissions associated with cement production (Ma *et al.* 2022). Using potassium feldspar in geopolymer concrete not only taps into an ample natural resource but also enhances the material's chemical resistance and mechanical properties, making it suitable for diverse construction needs (Almutairi *et al*. 2021).

Metakaolin, derived from the calcination of kaolin clay, is another crucial ingredient in geopolymer concrete formulations due to its high pozzolanic reactivity. When combined with potassium feldspar, metakaolin further enhances the material's performance by improving its compressive strength, durability, and resistance to chemical attack (Juenger *et al.* 2019). This synergistic effect arises from metakaolin's ability to react with alkalis or other activating agents, forming a stable geopolymer network that binds, aggregates and enhances the overall matrix cohesion (Hattaf *et al*. 2021).

In recent years, extensive research has focused on optimizing the proportions and processing conditions of potassium feldspar and metakaolin in geopolymer concrete mixtures to achieve superior mechanical and durability properties. Studies have explored curing conditions, activator types, and particle size distributions to tailor the geopolymer's microstructure and performance characteristics (Shao *et al*. 2019). Geopolymer concrete formulations incorporating potassium feldspar and metakaolin have shown promising results in laboratory tests and practical applications. They exhibit comparable or superior mechanical properties to traditional concrete, including higher compressive strength and lower permeability, which are crucial for infrastructure durability in harsh environmental conditions (Almutairi *et al*. 2021). Compared to typical Portland cement-based concrete, these materials provide substantial environmental benefits due to their lower energy consumption and greenhouse gas emissions during production.

However, despite these advantages, the widespread adoption of geopolymer concrete, particularly in African countries, faces several challenges. These include the availability and quality of raw materials, the establishment of standardized mix design procedures, and the need for specialized equipment for large-scale production (Heidrich *et al.* 2015). To tackle these obstacles, cooperative endeavours between scholars, industry participants, and policymakers are necessary to encourage technology transfer, enhance regional infrastructure, and cultivate creativity in sustainable building methods. Research efforts continue to explore novel formulations and applications of geopolymer concrete incorporating potassium feldspar and metakaolin. A recent study focused on optimizing polymerization processes, enhancing material properties through nanotechnology, and evaluating long-term performance under various environmental exposures (Mohajerani *et al.* 2019). Integrating digital modelling and simulation techniques also plays a crucial role in predicting material behaviour and optimizing structural designs using geopolymer composites.

Potassium feldspar and metakaolin represent promising alternatives in the quest for sustainable construction materials. Combined with geopolymer concrete formulations; they can provide improved performance, less of an adverse effect on the environment, and even financial gains over traditional Portland cement-based materials. Continued research and development efforts are essential to overcoming technical barriers, expanding market acceptance, and realizing the full potential of geopolymer concrete in global construction practices.

Recycled pozzolanic materials replace traditional cement in geopolymer concrete, an inventive and ecologically sustainable building material. Extensive research has underscored the potential of high-performance geopolymer concrete to revolutionize construction practices. However, in numerous third-world nations, the practical adoption of such advanced concrete remains constrained by multiple challenges. These include difficulties in refining pozzolanic materials to a satisfactory grade, absence of standardized mix design procedures, lack of field-applicable methodologies, suboptimal utilization of raw materials, and inadequate equipment for producing superior geopolymer concrete. To overcome these hurdles, integrating nanomaterials into production processes offers a promising solution. While previous studies have explored the benefits of nanoparticles in enhancing geopolymer performance, most have focused on single or dual combinations of conventional pozzolanic materials (Rashad *et al.* 2019). In contrast, current research investigates the formulation of geopolymer concrete using a blend of novel pozzolanic materials: potassium feldspar powder and metakaolin. Moreover, there needs to be more investigation into the durability and strength of geopolymer concrete when fortified with nanoalumina.

Various technologies are employed in producing nano-alumina (NA) such as, ball milling, pyrolysis, hydrothermal procedures, laser ablation, sputtering, and sol-gel processes. Its stability, hardness, insulation, and transparency are known to improve the mechanical qualities of concrete. By clogging the pores in the composite, NA enhances concrete's mechanical properties (Said *et al.* 2020).

Adding NA to geopolymer concrete (GPC) significantly improves its mechanical and microstructural properties by densifying the entire system (Çelik *et al.* 2023). Decreasing the Si/Al ratio for absorption operations is essential to increase the geopolymer material's surface area. Using crystalline Al_2O_3 can improve geopolymerization in geopolymer concrete (GC) by reducing the Si/Al ratio of the alkali activator. Additionally, NA enhances the durability of concrete by mitigating chloride attack and reducing water absorption (Amran *et al.* 2021)

While NA does not directly influence geopolymerization, it can be used as a nano-filler. It can be a crucial component and catalyst in creating geopolymer gels. In fly ash (FA)-based GC, NA acts as an accelerating agent and filler to promote polymerization, resulting in denser composites through appropriate interparticle bonding (Adewuyi *et al*. 2021). In this work, the performance of geopolymer concrete is enhanced by adding nanoalumina and pozzolanic components. The research evaluates various properties related to strength and durability across the new geopolymer concrete compositions. Incorporating nanoalumina is anticipated to enhance geopolymer concrete's specific density and compaction, improving its overall effectiveness, particularly in robustness and longevity. The delicate particulate nature of nanoalumina is expected to enhance the rigidity of geopolymer concrete, potentially reducing structural cracking according to similar studies (Jindal *et al*. 2021).

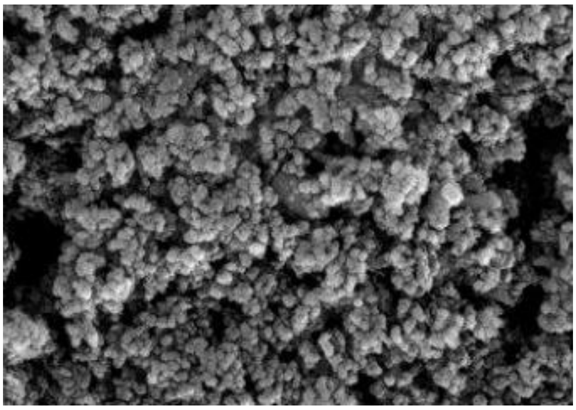

Fig. 1a: SEM Image of Nanoalumina

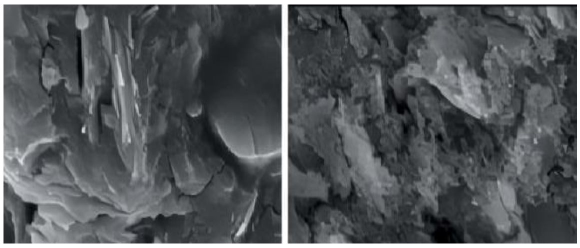

Fig. 1b: SEM image of Nanoalumina-geopolymer samples

2. EXPERIMENTAL SETUP

In order to specifically use a blend of K feldspar and metakaolin, this study involved the fabrication of eight different concrete mixes to investigate the effects of nanomaterials, K feldspar, metakaolin, and rice husk ash (RHA) on the mechanical properties of geopolymer concrete. The principal ingredients included natural fine and coarse aggregates, cementitious materials derived from an alumino-silicate source, and a pozzolanic combination activated by an alkaline solution made up of 70% metakaolin, 20% K feldspar, and 10% RHA. The mixes were modified by incorporating varying amounts of nanoalumina, ranging from 0% to 6%, to the cementitious blend. Nanoalumina particles, with a granular size of 10–9 meters, were characterized using SEM imaging, as depicted in Fig. 1.

Table 1. Mix proportions of the geopolymer concrete

Sample ID	Metakaolin (kg)	K feldspar (kg)	RHA (kg)	FA (kg)	CA (kg)	Nanoalumina (kg)	H_3PO_4 (kg)	Water (Lit)
CGC	323.8	80.95	0	595	1176	0	147	1009
GC-N0	283.325	80.95	40.5	595	1176	0	147	1009
GC-N1	283.325	80.95	40.5	595	1176	4.05	147	1009
GC-N2	283.325	80.95	40.5	595	1176	8.1	147	1009
GC-N3	283.325	80.95	40.5	595	1176	12.15	147	1009
GC-N4	283.325	80.95	40.5	595	1176	16.2	147	1009
GC-N5	283.325	80.95	40.5	595	1176	20.25	147	1009
GC-N6	283.325	80.95	40.5	595	1176	24.3	147	1009

Phosphoric acid was employed as an activator in the polymerization process. Phosphoric acid, commercially available in liquid form, was diluted with distilled water to create solutions with a 12 mol/L molar concentration. These solutions were then left stable for a full day before being used. The ternary blended pozzolanic material and the alkaline activator solution were retained at 1:0.35. A homogenization technique was utilized to ensure the even distribution of nanoparticles within the solution. The specific mix proportions of the geopolymer concrete are detailed in Table 1.

Initially, the dry ingredients (fine aggregate, coarse aggregate, and blended pozzolanic materials) were well mixed. Following this, the prepared activator was added to the dry mix. After combining all components in their fresh state, a slump cone test was performed to assess the workability. The desired cubes and cylinders were then cast from the mixture, with the samples being de-moulded after 24 hours and subsequently cured in an oven at 105 °C for up to 90 days. Each concrete mix had three samples cast to facilitate laboratory testing corresponding to the thermal curing periods.

Experiments were carried out on fresh and hardened concrete to assess the impact of nanoparticles on the performance of the concrete. The following tests were conducted to evaluate the properties and performance of geopolymer concrete mixes incorporating varying percentages of nanoalumina: workability test, compressive strength test, split tensile strength test, rapid chloride penetration test (RCPT), sulphate resistance test, water absorption test and X-ray diffraction (XRD) analysis. These tests assess the enhancements of incorporating nanoparticles into the geopolymer concrete mix.

3. RESULTS AND DISCUSSION

The effects of rice husk ash and nanoalumina on the durability and strength of geopolymer concrete based on K feldspar and metakaolin were investigated. Two critical components are introduced in this research: nanoalumina, added externally to the pozzolanic mixtures in amounts of up to 6%, and rice husk ash, which replaced pozzolanic material up to 10% of the time. The geopolymer concrete's pozzolanic ingredient was a mixture of metakaolin and K feldspar.

There were two primary findings: The first examined how rice husk ash affected metakaolin and K feldspar's pozzolanic activity. The second observation examined how nanoalumina improved the geopolymer concrete's packing density. Fresh and hardened concrete tests were conducted on the newly mixed geopolymer concrete to gain a complete understanding.

3.1 Slump and Density

The relative slump values of the designed geopolymer concrete mixes, based on a flow test involving 25 tamps, are presented in Table 2. It is essential to highlight that all mixes demonstrated excellent flowability, regardless of their composite types. Introducing nanoalumina and rice husk ash into the geopolymer mixtures significantly enhanced the relative slump values.

The slump height increased by 50% when rice husk ash was added to 10% of the pozzolanic material. The enhanced ball-bearing action in the geopolymer concrete and the decreased flocculated pozzolanic particles in the blend are responsible for this improvement. Moreover, the blend's slump height increased by 69% when 1% nanoalumina was added. This raise resulted from increased packing density. The porosity was decreased, and the mix's workability was improved due to the filling of fine nanoalumina particles in the pores.

Table 2. Slump test results of mixes

Mix	Slump value	Density (kg/m³)
CGC	-	1778
GC-N0	1.51	1762
GC-N1	1.69	1759
GC-N2	2.28	1785
GC-N3	2.54	1764
GC-N4	2.73	1735
GC-N5	2.24	1720
GC-N6	2.21	1638

Up to 4% of nanoalumina was added, maintaining the trend of raising slump height. The pozzolanic mix's total surface area was decreased, the packing density was increased, and the higher nanoalumina concentration noticeably enhanced the flowability of the concrete.

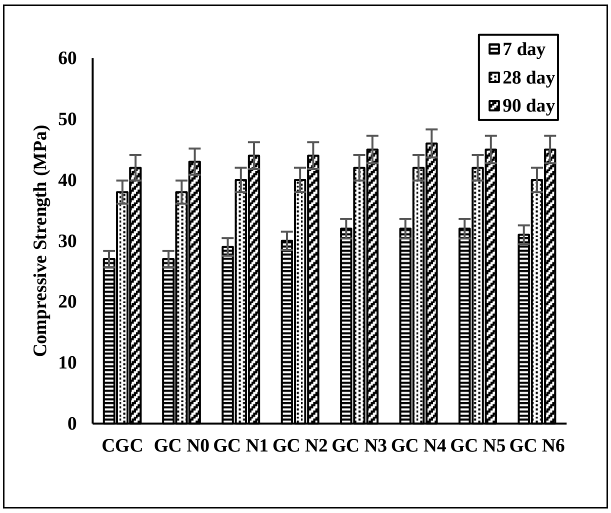

Fig. 2: Compressive strength of GC-NA mixes

During the mixing process, the granular shape of nanoalumina enhances mobility by acting as a ball-bearing between the mixed particles. However, because rice husk ash and nanoalumina have lower specific gravity than K feldspar and metakaolin, adding them to the concrete gradually reduces its density. Higher nanoparticle content in lightweight geopolymer composites had decreased flowability; in particular, the slump of the mix containing 5% nanoalumina was 20% less than that of the mix containing 4% nanoalumina. More nanoalumina further reduced the slump height, indicating that a percentage higher than 4% would result in more voids in the geopolymer concrete. The fineness of nanoalumina makes it more water-retentive than other nanoparticles, which hinders the flow of the mortar. This is explained by the hydrophilic character of the nanoparticles, which have a vast surface area and absorb water. In addition, the non-uniform particle size of the nanoalumina and the direct interaction between the nanoalumina sol and pozzolanic materials led to a decrease in flowability.

3.2 Compressive Strength

The compressive strengths of geopolymer concrete specimens with different nanoalumina percentages (0% to 6%) at 7, 28, and 90 days are shown in Fig. 2.

The compressive strength of the geopolymer concrete and nanoalumina combinations grew over time. Specifically, after 28 days of thermal curing, the compressive strengths of conventional and geopolymer concrete incorporating rice husk ash (GPC-RHA) were determined at 40.71 MPa and 41.82 MPa, respectively. With the addition of 1% nanoalumina, the mixture's compressive strength improved by 12%, and with the addition of 4%, it increased by 16.12%.

As nanoalumina's volume fraction in the composite rises, so does its availability for reaction, leading to this strength growth. The higher amount of nanoalumina in the mixture speeds up the reaction rate as compared to mixes without it. Researchers attribute this acceleration to the presence of reactive silica since it regulates the polymerisation reaction and encourages the formation of alumina-silica gel, which is required to build material strength. Particularly, in ternary blended geopolymer concrete, there is a greater synthesis of potassium aluminosilicate hydrate (K-A-S-H) gel.

Increased K-A-S-H gel production is made possible by interactions with the potassium in feldspar, such as those involving nanoalumina, which enhances matrix packing and microstructure. Following 7, 28, and 90 days of heat curing, the absorbance capacity and compressive strength of the geopolymer concrete cubes increased by 15%, 12%, and 6% due to these interactions. These findings suggest that nanoalumina is essential for the early-age strength development of concrete. Nanoalumina accelerates the polymerization process by acting as nucleation sites and promoting the creation of gel phases. A denser and more linked aluminosilicate network is created by this quick reaction, which improves mechanical qualities and lowers porosity.

The advantages of adding nanoalumina do, however, have a limit. Compressive strength decreases when the nanoalumina content is raised above the ideal threshold. The leading cause of this decrease is the accumulation of too many nanoalumina particles, which can lead to matrix imperfections such as pores or unreacted particles. These flaws result from unreacted components in the specimen. Additionally, the decline in compressive strength observed beyond a 6% nanoalumina addition can be attributed to the replacement of more robust materials, such as K-feldspar and metakaolin, with weaker materials, like rice husk ash, which lacks significant pozzolanic activity in the ternary mix.

Furthermore, unhydrated cement coated with excess phosphoric acid, produced by adding more than 4% nanoalumina, may slow the hydration process. This excess phosphoric acid can impede the adequate hydration of cementitious components, thereby reducing the strength properties of the geopolymer concrete.

In conclusion, including nanoalumina in geopolymer concrete significantly enhances compressive strength, particularly at early ages, by promoting the formation of additional K-A-S-H gel and improving the microstructure. However, careful optimization is required to avoid excessive nanoalumina content, which can lead to aggregation, defects, and reduced strength. The balance between the reactive components and the optimization of nanoalumina content is crucial for achieving the desired mechanical properties in geopolymer concrete.

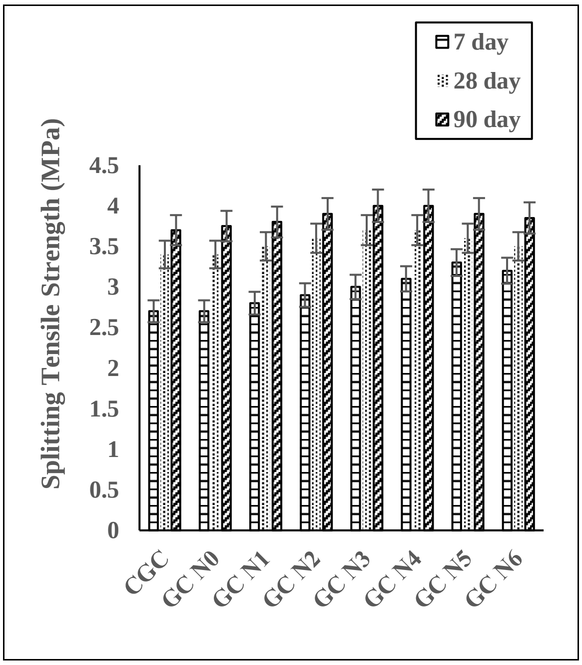

Fig. 3: Split tensile strength of GC-NA mixes

3.3 Split Tensile Strength

Fig. 3 illustrates the split tensile strengths of various geopolymer concrete samples (GC-N0 to GC-N6) after 7,28, and 90 days, with tensile strengths ranging from 3.49 MPa to 3.7 MPa after 28 days and 2.5 MPa to 3.4 MPa after seven days. Notably, the tensile strength of geopolymer concrete increased in a pattern similar to that of compressive strength as the nanoparticle dosage increased, with the GC-N4 mix demonstrating the highest improvement (18.9%) after seven days. In a detailed study involving metakaolin, rice husk ash, and K-feldspar, these materials were used in proportions of

70%, 10%, and 20%, respectively, with varying nanoparticle dosages. The split tensile strength of these geopolymer composites followed a similar increasing trend (Paruthi et al. 2023). Specifically, the GC-N4 sample, which comprised 70% metakaolin, 10% rice husk ash, 20% K-feldspar, and 4% nanoparticles, exhibited the highest strength increase. This mix improved 26.87% and 27.4% in split tensile strength after 7,28 and 90 days, respectively.

Numerous synergistic variables are responsible for the observed increase in tensile strength up to a 4% addition of nanoalumina. Because of its high surface area and high reactivity, nanoalumina is well-known for improving the geopolymerization process. When introduced into the geopolymer matrix, nanoalumina provides an additional source of reactive silica, which facilitates the formation of a denser and more interconnected aluminosilicate network. This improved network structure is critical for enhancing the geopolymer concrete's mechanical properties and durability.

Moreover, nanoalumina particles serve as nucleation sites for forming gel phases, accelerating the polymerization process. This results in faster setting and hardening of the geopolymer concrete, contributing to its early-age strength development. The presence of nanoalumina also leads to a more homogeneous and densely packed microstructure, significantly reducing porosity and improving the overall integrity of the material.

However, the benefits of nanoalumina addition have a limit. When the nanoalumina content exceeds 4%, the tensile strength decreases. This decline is primarily due to the agglomeration of nanoalumina particles, which creates inhomogeneity in the uncured resin zones. These agglomerations increase the material's porosity, leading to weaker regions within the matrix. As a result, the effectiveness of the nanoalumina diminishes, and the split tensile strength of the geopolymer concrete is adversely affected. Another critical aspect of using nanoalumina in geopolymer concrete is its impact on the water-binder ratio. Nanoalumina reduces this ratio, creating a denser mortar matrix and a better-defined interfacial transition zone. This zone, typically the weakest link in concrete composites, becomes more resilient with the optimal addition of nanoalumina. However, when more than 4% nanoalumina is used, this zone becomes prone to crack formation due to the increased porosity and inhomogeneity caused by particle agglomeration.

Including nanoalumina in geopolymer concrete significantly enhances split tensile strength, mainly when used in optimal amounts. The combination of metakaolin, rice husk ash, and K-feldspar, with an optimal 4% nanoalumina addition, results in a robust geopolymer matrix with superior mechanical properties. However, exceeding this optimal dosage leads to diminishing returns due to agglomeration and increased porosity, highlighting the importance of precise material optimization in geopolymer concrete formulations.

3.4 Rapid Chloride Permeability Test (RCPT)

The study focused on assessing the impact of nanoalumina on the resistance of geopolymer concrete to chloride penetration, a crucial factor for concrete durability in corrosive environments. Fig. 4 illustrates the charge transmission of various geopolymer concrete samples (GC-N0 to GC-N6). Results indicated a notable improvement in chloride resistance with the inclusion of nanoalumina compared to conventional mixes. For instance, without nanoalumina and rice husk ash, the control mix exhibited a charge transmission of 1058 coulombs, indicating a low level of chloride penetration. In contrast, mixes containing nanoalumina showed significantly enhanced performance, with a charge transmission of 956 coulombs, categorized as extremely low chloride penetration. This represented a 28.61 % increase in resistance compared to the control.

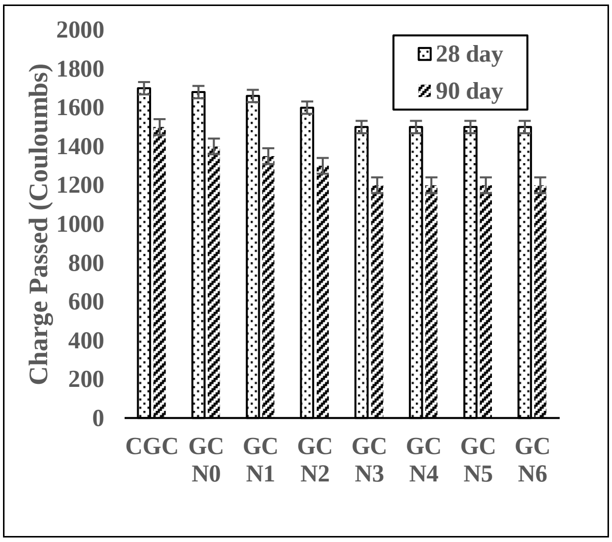

Fig. 4: RCPT test results on mixes

The observed enhancement aligns with established literature (Lv *et al*. 2022), highlighting the role of nanoparticles in improving the resistance of concrete to chloride diffusion. This improvement is attributed to nanoalumina's nucleation effect, which enhances mechanical properties. The study also noted that well-dispersed nano dispersions improved particle packing within the geopolymer matrix, resulting in a microstructure characterized by increased compactness and density. The spherical morphology of nanoalumina and rice husk ash further enhanced the packing density.

Furthermore, the study found that 90-day cured geopolymer concrete exhibited lower charge transmissions than those cured for 28 days across all nanoalumina mixes. This can be attributed to the ongoing densification of the microstructure over time due to adding nanoalumina, refining pore structures and compacting the matrix. Previous research supported these findings, demonstrating nanoalumina's efficacy in reducing chloride ion penetration and improving concrete durability (Mohseni *et al.* 2019).

Furthermore, because nanoalumina contains more crystalline components, the introduction of nanoalumina in a geopolymer mortar based on K feldspar and metakaolin decreased the values of the Rapid Chloride Penetration Test (RCPT). These methods improve the material's resistance to chloride diffusion by aiding in fracture arrest and crack bridging.

Overall, the results underscore the potential of nanoalumina in enhancing the durability of geopolymer concrete against chloride penetration. The findings highlight improved resistance from enhanced mechanical properties, optimized particle packing, and refined microstructure. These insights emphasize nanoalumina's role as a promising additive in geopolymer concrete formulations that extend service life and enhance performance in harsh environmental conditions rich in chlorides.

3.5 Water Absorption

When evaluating concrete's long-term durability, water absorption is crucial in determining the material's structural integrity and the longevity of implanted reinforcements. This test aims to assess the concrete's resistance to moisture infiltration, which is significantly impacted by capillary suction and pressure head. Because it reflects the concrete structure's resistance to moisture penetration, the water absorption coefficient obtained from these tests is a prediction indication for the service life of concrete structures.

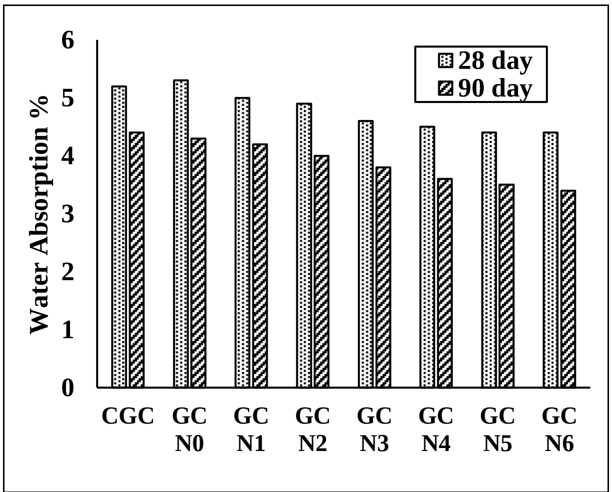

Fig. 5: Water absorption test results on mixes

Fig. 5 presents insights into how water absorption rates vary by including nanoalumina and rice husk ash in geopolymer concrete. As the proportion of nanoalumina increased, water absorption consistently decreased. Specifically, significant differences were observed when comparing blends using K feldspar and metakaolin as binders versus blends incorporating rice husk ash and nanoalumina. For example, during 28 days of thermal curing, the GC-N0 mix showed a 5.5% water absorption, which decreased to 4.5% after 90 days.

Interestingly, this trend was reversed when rice husk ash replaced 10% of metakaolin and K feldspar in blending, indicating a slower hydration reaction at 28 days but subsequent pore filling with K-A-S-H gel at 90 days, reducing water absorption.

The introduction of nanoalumina further improved water resistance in geopolymer concrete. With nanoalumina levels reaching up to 6%, water absorption decreased consistently at 28 and 90 days of thermal curing compared to controlled geopolymer concrete. This reduction amounted to 0.5% and 0.8% decreases in water absorption, respectively, highlighting the additive's effectiveness in densifying the concrete matrix. This densification was facilitated by the pozzolanic action of nanoalumina and rice husk ash, which filled the pore structure of geopolymer concrete with fine-grained particles, thereby reducing capillary pores and enhancing overall compactness.

The fine particle size of nanoalumina played a crucial role in filling the pores of the bulk pozzolanic paste, significantly reducing capillary absorption and consequent strength gains. Moreover, higher doses of nanoalumina correlated with improved concrete density, a primary factor influencing lower water absorption rates. This phenomenon underscores the pivotal role of nanoalumina in minimizing water ingress, thereby enhancing concrete durability.

Overall, this experiment underscores the beneficial impact of nanoalumina and rice husk ash on mitigating water absorption in geopolymer concrete. By refining the pore structure and enhancing overall compactness, these additives contribute to a more resilient concrete matrix capable of withstanding moisture-induced degradation over prolonged periods. The findings emphasize the potential of nanoalumina as a strategic additive in optimizing concrete performance in various environmental conditions, ultimately supporting sustainable infrastructure development through enhanced durability and longevity.

3.6 Sulphate Resistance Test

The sulphate resistance test assessed the impact of Na_2SO_4 exposure on geopolymer concrete specimens, measuring gradual mass loss over increasing immersion durations. Fig. 6 illustrates that higher percentages of nanoalumina corresponded to reduced mass loss. Introducing rice husk ash into K feldspar and metakaolin mixes resulted in a 2% lower mass loss in blends. However, adding nanoalumina further decreased mass loss in concrete mixes. For instance, 4% nanoalumina in ternary concrete mixes reduced mass loss to 6%.

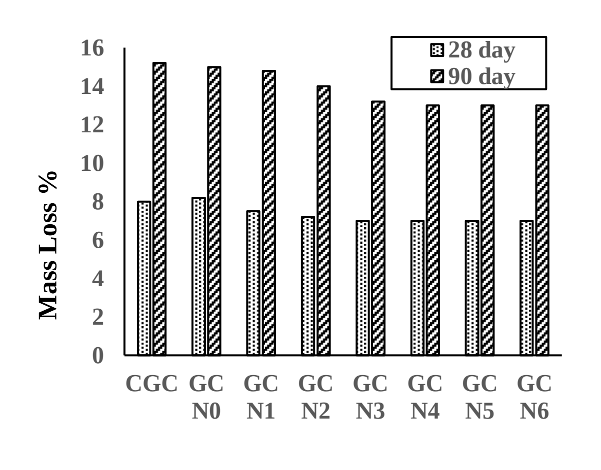

Fig. 6: Mass loss % on GC-NS mixes

The large surface area and ultrafine grain size of geopolymer concrete with nanoalumina are responsible for its superior mechanical qualities and durability. By efficiently filling in the tiny spaces between pozzolanic materials like metakaolin and K feldspar, nanoalumina helped to create a denser structure. Phosphoric acid, husk ash, and nanoalumina interacted during hydration to promote more K-A-S-H gel formation. By improving the surface of the microstructure, this secondary gel strengthened the geopolymer concrete and prevented sulfate ion penetration.

Further additions of nanoalumina did not significantly alter mass loss beyond 6%, suggesting a threshold effect in enhancing sulphate resistance. Acid attacks can break Si–O–Al/Si bonds within the geopolymer network structure. Geopolymer concrete specimens cured at elevated temperatures may exhibit reduced density, potentially facilitating acid penetration and increasing surface area vulnerability to damage. Including up to 10% rice husk ash increased the reactive phase content, enhancing its effectiveness. Additionally, metakaolin contributed to higher thermal curing temperatures, generating internal heat during hydration and geo-polymerization dissolution, which is crucial for binder phase formation. The sample GC-N6 demonstrated superior resistance to acidic media than GC, indicating a denser and more robust matrix.

This experiment underscores nanoalumina's pivotal role in augmenting sulphate resistance in geopolymer concrete. By optimizing microstructure density and enhancing chemical interactions among constituents, nanoalumina effectively mitigates mass loss under sulfate exposure. These findings highlight nanoalumina as a promising additive for improving geopolymer concrete's durability and performance in harsh environmental conditions, supporting sustainable infrastructure development. Future research may explore optimal nanoalumina dosages and additional additives to enhance geopolymer concrete's resilience against chemical degradation, extending its service life in challenging applications.

3.7 X-ray Diffraction

This prepared concrete samples were ground to fine powders for XRD analysis. This process is critical to ensure uniformity and reduce sample loss. The grinding process was carried out in a liquid media, such as methanol or ethanol, to prevent structural damage and guarantee precise measurement of crystalline phases. Then, the finely ground powders were pushed into smooth-surfaced sample holders angled 45° with respect to the incident X-ray beam for ideal diffraction.

The XRD experiments were conducted using CuKα radiation from a diffractometer operating at specific parameters: 45 kV and 40 mA. The diffractometer was configured in a Bragg–Brentano θ–2θ geometry, standard for analyzing crystalline materials. A beam knife and a 1° receive anti-scatter slit were utilized to cut down on background noise. A linear position sensing X-ray detector (X'Celerator) was used to collect the data. It was able to capture diffracted X-rays with a step size of 0.017° throughout a range of 2θ angles, from 8° to 60°, with reliability.

The XRD analysis revealed several crystalline phases present in the geopolymer concrete samples (Fig. 7). Quartz (SiO_2), traces of potassium feldspar ($KAlSi_3O_8$), mullite ($Al_6Si_2O_{13}$), and hematite (Fe_2O_3) were among the identified phases. Each phase was characterized by its distinct diffraction pattern, represented by peaks at specific 2θ angles. For instance, quartz typically peaks at approximately 34.73° (CuKα).

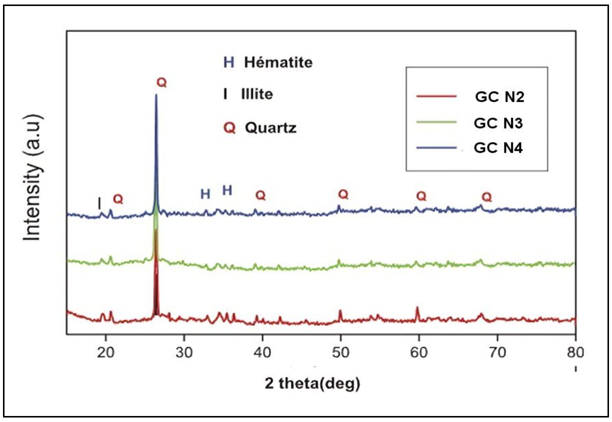

Fig. 7: XRD patterns for different mixes

The XRD analysis revealed that the geopolymer matrix displayed similar XRD patterns with or without NA. Quartz and mullite particles in the ternary mix, contributing to an AS gel formation in geopolymer complexes, were indicated by an irregular peak between 16° and 27°. Additionally, the XRD profiles of ternary mixes containing NA were comparable, suggesting these components remained inactive during the polymerization process. However, these filler materials were present in the final geopolymer matrix. Consequently, it can be concluded that NA functions as a nanocomposite, improving the morphology by filling pores, but it has no discernible effect on the polymerization reaction. NA can, therefore, be added in small amounts to improve the microstructure of the geopolymer matrix because of its capacity to fill pore spaces and its role in the geopolymerization process.

Adding nanoalumina to geopolymer concrete mixes significantly influenced the crystalline phase composition and microstructure. Nanoalumina, characterized by its ultrafine particle size and high surface area, was crucial in improving the concrete's performance. Adding nanoalumina increased quartz content, which is one noteworthy finding from the XRD measurements. Crystall-phase quartz is well-known for being inert and long-lasting; it enhances concrete's mechanical strength and chemical resistance. The denser microstructure resulting from nanoalumina addition contributed to reduced permeability and enhanced durability against chemical attacks, such as sulfate ions.

The hydration process, influenced by adding alumina silicate materials like metakaolin and K feldspar, proceeded differently in the presence of nanoalumina. Traditionally, aluminium silicates react with alkalis to form geopolymer gels, but nanoalumina accelerated these reactions, promoting additional hydration products. This evident phenomenon filled voids and improved the concrete's mechanical properties. The XRD results underscored the positive impact of nanoalumina on geopolymer concrete's durability and mechanical strength. By enhancing hydration kinetics and promoting the formation of dense microstructures, nanoalumina mitigated pore formation and reduced permeability. This reduction in permeability is critical for resisting chloride and sulfate ion penetration, which are common causes of concrete deterioration in aggressive environments.

Moreover, the mineral phases improved chemical resistance and minimized mass loss when exposed to aggressive substances like sodium sulfate (Na_2SO_4). The findings suggest that optimizing nanoalumina dosages and combining them with suitable alumino silicates can tailor geopolymer concrete formulations for specific environmental conditions, enhancing their service life and sustainability.

4. CONCLUSION

Geopolymer concrete compositions using a ternary blend of K feldspar, metakaolin and rice husk ash exhibited superior performance compared to blends like K feldspar and metakaolin alone. This ternary mixture encouraged the development of secondary K-A-S-H gel, which is essential for improving the durability and strength of the concrete. Incorporation of nanoalumina boosted the concrete's structural, mechanical and chemical properties. The enhanced properties of nanoalumina-modified geopolymer concrete make it suitable for various structural applications, including bridges, buildings, and infrastructure exposed to aggressive environmental conditions. Despite potentially higher material costs, nanoalumina-enhanced geopolymer concrete offers economic benefits through reduced maintenance and extended service life, offsetting initial investment costs over the structure's life cycle. Future research could optimize nanoalumina dosages, explore new nanomaterials, and investigate the long-term behaviour of nanoalumina-modified geopolymer concrete under varying environmental conditions to advance its application and performance further.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

REFERENCES

Adewuyi, Y. G., Recent Advances in Fly-Ash-Based Geopolymers: Potential on the Utilization for Sustainable Environmental Remediation, *ACS Omega,* 6(24), 15532–15542 (2021) https://doi.org/10.1021/acsomega.1c00662

Almutairi, A. L., Bassam, A. T., Adeyemi, A., Haytham, F. I. and Abdullah, M. Z., Potential Applications of Geopolymer Concrete in Construction: A Review, *Case Stud. Constr. Mater.,* 15, e00733 (2021). https://doi.org/10.1016/J.CSCM.2021.E00733

Amran, M., Amin, A., Chu, S. H., Roman, F., Sani, H., Afonso, A. and Nikolai, V., Long-Term Durability Properties of Geopolymer Concrete: An in-Depth Review, *Case Stud. Constr. Mater.,* 15, e00661 (2021) https://doi.org/10.1016/J.CSCM.2021.E00661

Awoyera, P. and Adeyemi, A., A Critical Review on Application of Alkali Activated Slag as a Sustainable Composite Binder, *Case Stud. Constr. Mater.,* 11, e00268. (2019) https://doi.org/10.1016/J.CSCM.2019.E00268

Çelik, A. İ., Yasin, O. Ö., Alireza, B. and Ibrahim, Y. H., Mechanical Performance of Geopolymer Concrete with Micro Silica Fume and Waste Steel Lathe Scraps, *Case Stud. Constr. Mater.,* 19, e02548 (2023) https://doi.org/10.1016/J.CSCM.2023.E02548

Chiranjeevi, K., Marykutty, A., Badrinarayan, R. and Praveenkumar, T. R., Enhancing the Properties of Geopolymer Concrete Using Nano-Silica and Microstructure Assessment: A Sustainable Approach, *Sci. Rep.,* 13(1), 17302 (2023). https://doi.org/10.1038/s41598-023-44491-y

Du, S., Junliang, W., Othman, A. and Xianming, S., Nanotechnology in Cement-Based Materials: A Review of Durability, Modeling, and Advanced Characterization, *Nanomater.* 9(9), 1213 (2019) https://doi.org/10.3390/nano9091213

Hattaf, R., Abdelilah, A., Azzedine, S., Nouha, L., Mohamed, O. T., Moussa, G. and Redouane, M., Reusing Geopolymer Waste from Matrices Based on Metakaolin or Fly Ash for the Manufacture of New Binder Geopolymeric Matrices, *Sustainability,* 13(14), 8070 (2021). https://doi.org/10.3390/su13148070

Heidrich, C., Jay, S., Berndt, M. L., Stephen, F. and Kwesi, S. C., Pathways and Barriers for Acceptance and Usage of Geopolymer Concrete in Mainstream Construction, 2015 World of Coal Ash (WOCA) Conference in Nasvhille, TN, (2015).

Jindal, B. B. and Rahul, S., The Effect of Nanomaterials on Properties of Geopolymers Derived from Industrial Byproducts: A State-of-the-Art Review, *Constr. Build. Mater.,* 252, 119028 (2020). https://doi.org/10.1016/J.CONBUILDMAT.2020.119028

Juenger, M. C.G., Ruben, S. and Susan, A. B., Supplementary Cementitious Materials: New Sources, Characterization, and Performance Insights, *Cem. Concr. Res.,* 122, 257–73. (2019) https://doi.org/10.1016/j.cemconres.2019.05.008

Le-ping, L., Cui X., Qiu, S., Yu, J. and Zhang, L., Preparation of Phosphoric Acid-Based Porous Geopolymers, *Appl. Clay Sci.,* 50(4), 600–603 (2010) https://doi.org/10.1016/J.CLAY.2010.10.004

Lv, Z., Maohua, Z. and Yanyu, S., Research on The Chloride Diffusion Modified Model for Marine Concretes with Nanoparticles under The Action of Multiple Environmental Factors, *J. Mar. Sci. Eng.,* 10(12), 1852 (2022). https://doi.org/10.3390/jmse10121852

Ma, S., Zhang, Z. and Liu, X., Comprehensive Understanding of Aluminosilicate Phosphate Geopolymers: A Critical Review, *Mater.,* 15(17), 5961 (2022). https://doi.org/10.3390%2Fma15175961

Mohajerani, A., Lucas, B., John, V. S., Halenur, K., John, M., Arul, A., Suksun, H. and Aeslina, A. K., Nanoparticles in Construction Materials and Other Applications, and Implications of Nanoparticle Use, *Mater.* 12(19), 3052 (2019). https://doi.org/10.3390/ma12193052

Mohseni, E., Mahyar, J. K., Mahdi, K., Behnam, Z. and Babak, B., Evaluation of Mechanical and Durability Properties of Fiber-Reinforced Lightweight Geopolymer Composites Based on Rice Husk Ash and Nano-Alumina, Construction and Building Materials, 209, 532–540 (2019). https://doi.org/10.1016/J.CONBUILDMAT.2019.03.067

Paruthi, S., Ibadur, R., Asif, H., Afzal, H. K., Ana, M. M. S. and Ehab, S., A Comprehensive Review of Nano Materials in Geopolymer Concrete: Impact on Properties and Performance, *Dev. Built Environ.,* 16, 100287 (2023). https://doi.org/10.1016/J.DIBE.2023.100287

Rashad, A., Effect of nanoparticles on the properties of geopolymer materials, *Mag. Concr. Res.,* 71(24), 1283-1301 (2019). http://dx.doi.org/10.1680/jmacr.18.00289

Said, S., Mikhail, S. and Riad, M., Recent Processes for the Production of Alumina Nanoparticles, *Mater. Sci. Energy Technol.,* 3, 344–363 (2020) https://doi.org/10.1016/J.MSET.2020.02.001

Shao, Q., Keren, Z., Xuejin, Z., Jin, Z. and Xiaohui, Z., Enhancement of Nano-Alumina on Long-Term Strength of Portland Cement and the Relation to Its Influences on Compositional and Microstructural Aspects, *Cem. Concr. Compos.,* 98, 39–48 (2019). https://doi.org/10.1016/J.CEMCONCOMP.2019.01.016

Singh, N. B. and Middendorf, B., Geopolymers as an Alternative to Portland Cement: An Overview, *Construction and Building Materials,* 237, 117455 (2020). https://doi.org/10.1016/J.CONBUILDMAT.2019.117455

Qadir, A., Laith, A., Frayyeh, J. Q. and Osama, A. A. A., Geopolymer as a Green Concrete Alternative to Portland Cement Concrete: Article Review, *Journal of Al-Farabi for Engineering Sciences*, 1, (2022). https://doi.org/10.59746/jfes.v1i1.16