

SYNERGETIC EFFECT OF THE ADDITION OF NANO-SILICA IN RED CLAY-BASED GEOPOLYMER PRODUCT

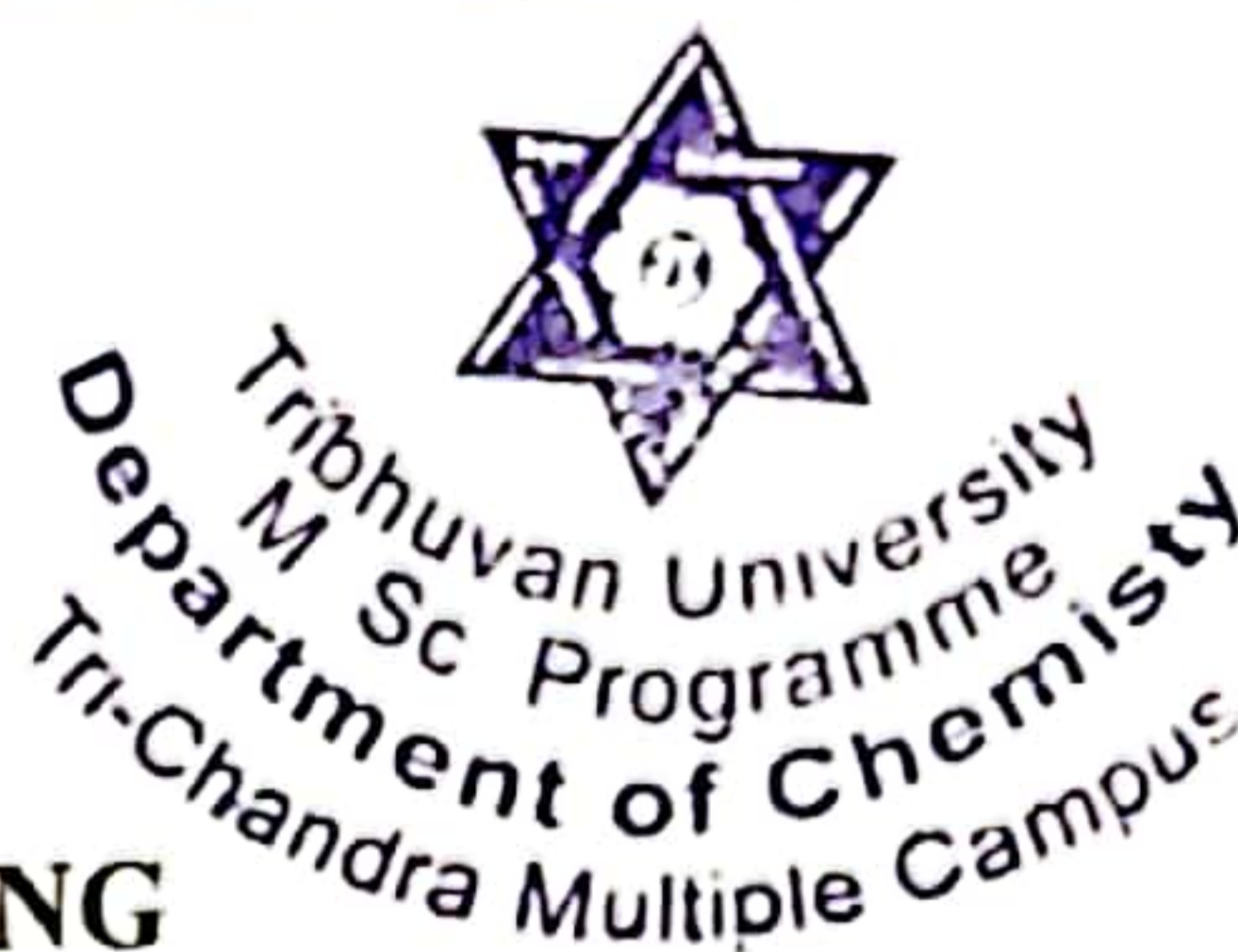
A DISSERTATION SUBMITTED FOR THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE MASTER OF SCIENCE DEGREE IN CHEMISTRY

BY

SUNIL GURUNG

SYMBOL NO.: 1853/2076

TU Registration No.: 5-2-37-498-2014



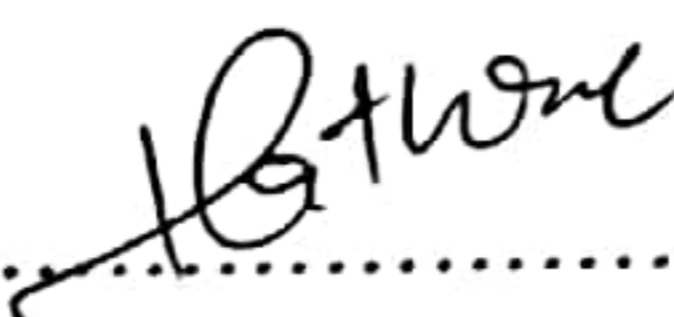
Submitted to:

DEPARTMENT OF CHEMISTRY
TRI-CHANDRA MULTIPLE CAMPUS
INSTITUTE OF SCIENCE AND TECHNOLOGY
TRIBHUVAN UNIVERSITY, KATHMANDU,
NEPAL

March, 2024

BOARD OF EXAMINERS AND CERTIFICATE OF APPROVAL

This dissertation entitled “Synergetic Effect of the Addition of Nano-Silica in Red Clay-Based Geopolymer Product” by “Sunil Gurung”, under the supervision of Assistant Prof. Dr. Arvind Pathak Department of Chemistry, Tri-Chandra Multiple Campus, Tribhuvan University, Nepal is hereby submitted for the partial fulfilment of master of Science (M.Sc.) Degree in Chemistry. This dissertation has not been submitted to any other university or institution previously for an award of a degree.


.....


Supervisor

Asst. Prof. Dr. Arvind Pathak

Department of Chemistry

Tri-Chandra Multiple Campus

Tribhuvan University, Kathmandu, Nepal


.....

Internal Examiner

Asst. Prof. Dr. Shanta Pokhrel Bhattarai

Department of Chemistry

Tri-Chandra Multiple Campus

Tribhuvan University, Kathmandu, Nepal



.....

External Examiner

Prof. Dr. Vinay Kumar Jha

Central Department of Chemistry

Tribhuvan University, Kathmandu, Nepal


.....

M.Sc. Chemistry Expert

Asst. Prof. Dr. Shanta Pokhrel Bhattarai

Department of Chemistry

Tri-Chandra Multiple Campus

Tribhuvan University, Kathmandu, Nepal


.....

Head of Department

Prof. Dr. Ashok Singh

Department of Chemistry

Tri-Chandra Multiple Campus

Tribhuvan University, Kathmandu, Nepal

Head of Department
Department of Chemistry
Tri-Chandra Multiple Campus

Date: March 27, 2024

LETTER OF RECOMMENDATION

This is to certify that dissertation work entitled “**Synergetic Effect of the Addition of Nano-Silica in Red Clay-Based Geopolymer Product**” has been carried out by **Sunil Gurung** as a partial fulfilment of the requirement of Master of Science (M.Sc.) Degree in Chemistry under my supervision. This dissertation has not been submitted to any other university or institution previously for an award of a degree.

Arvind Pathak

.....
Supervisor

Asst. Prof. Dr. Arvind Pathak

Department of Chemistry

Tri-Chandra Multiple Campus

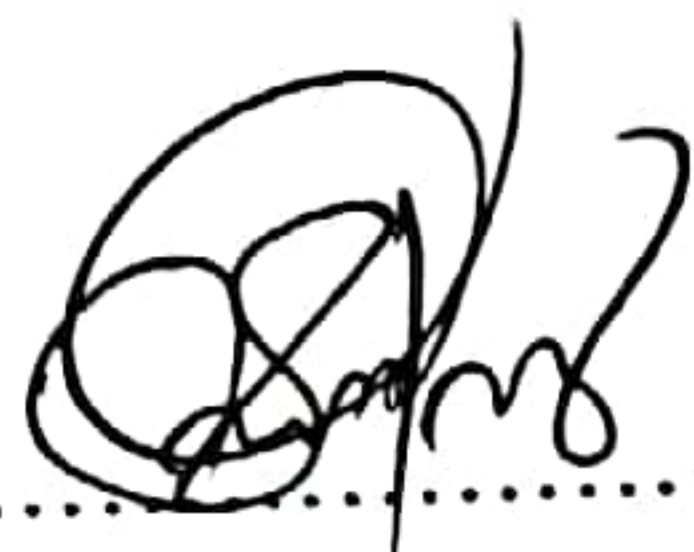
Tribhuvan University, Kathmandu, Nepal

Date: March 14, 2024



DECLARATION

I, Sunil Gurung, hereby declare that the work presented herein is genuine work done originally by me and has not been published or submitted elsewhere for the requirement of a degree program. Any literature, data, or work done by others cited in this dissertation has been given due acknowledgment and listed in the reference section.



Sunil Gurung

Date: March 14, 2024



ACKNOWLEDGEMENTS

It is an excellent opportunity for me to complete my Master of Chemistry thesis. I would like to convey my heartfelt appreciation to my supervisor, Assistant Prof. Dr. Arvind Pathak, Department of Chemistry, Tri-Chandra Multiple Campus, Tribhuvan University, for his patience, guidance, encouragement, and ongoing support during my studies.

I am highly grateful to the faculties and staff of the Department of Chemistry for providing a conducive academic environment and access to resources necessary for this research. The research facilities, library resources, and technological support have been indispensable in conducting this study.

I am thankful to Mr. Manoj Nidhi Wagle, Senior Divisional Chemist, Department of Customs, Ministry of Finance, Tripureshwor for his support in getting the Energy Dispersive X-ray diffraction results for the samples.

I would like to extend my sincere gratitude to the Department of Central Material Testing Laboratory, Pulchowk, Lalitpur for providing access to their laboratory facilities, and to Mr. Lilambar Shah for his support during laboratory work.

I am grateful to the Department of Chemistry, Amrit Campus for support in getting FTIR spectra of my samples. Also, I would like to thank NAST for its help in the X-ray diffraction measurement of samples.

Last but not least, I would like to express my gratitude to my entire family members for their invaluable assistance throughout my study. So, I consider myself fortunate to be a member of such a lovely family. Finally, I would like to express my gratitude to all contributors who assisted me throughout this work.

Sunil Gurung

Examination Roll No: 1853/ 076

ABSTRACT

This research explores the physicochemical properties and thermal behaviour of geopolymer synthesized from red clay, calcined white clay, nano-silica, and alkaline activator solution. Geopolymer is an eco-friendly alternative to Portland cement which has gained attention for its low environmental impact.

The study followed a systematic approach, starting with a variation of the amount of calcined white clay (CWC), nano-silica, and curing temperature. Based on preliminary experiments 10% CWC, 5% nano-silica, and a curing temperature of 65 °C were selected. Activator solution was prepared using sodium hydroxide solution and silica gel and used to initiate the geopolymerization process. FTIR and XRD were employed for the characterization of the sample. The addition of 5% nano-silica improved the physicochemical properties before and after exposure to the elevated temperatures. The highest compressive strength was identified within the thermal treatment range of 17.01 to 22.49 MPa on the thermal treatment of the geopolymer. The findings show that thermal treatment plays a crucial role in enhancing thermal stability, while nano-silica significantly improves the compressive strength of the geopolymer. The compressive strength of geopolymer on thermal treatment increased by up to 11.5% to 12.1% with the incorporation of 5% nano-silica.

In conclusion, this study provides a systematic understanding of the effect of the amount of CWC, nano-silica, on red clay-based geopolymers and their thermal effect. The findings help to develop sustainable construction materials with increased thermal performance, opening up possibilities for using agricultural waste in geopolymer manufacture.

Keywords: *Geopolymer; Thermal treatment; Compressive strength; Nano-silica; RHA; Red Clay; XRD; FTIR*

सार

यस अनुसन्धानले रातो माटो, क्याल्साइन सेतो माटो, नानो-सिलिका, र अल्कलाइन एक्टिभेटर घोलबाट निर्मित जियोपोलिमरको फिजिकोमेकानिकल गुणहरू र थर्मल व्यवहारको अनुसन्धान गर्दछ। पोर्टल्यान्ड सिमेन्टको पर्यावरणमैत्री विकल्पको रूपमा जियोपोलिमरले महत्त्वपूर्ण ध्यान आकर्षित गरेको छ।

यस अध्ययनमा CWC, नानो -सिलिकाको विभिन्न मात्रा भिन्न - भिन्न तापमा क्रमबद्ध रूपमा अध्ययन गरिएको छ। प्रारम्भिक प्रयोगहरूको आधारमा, 10% CWC, 5% नानो-सिलिका, र 65 °C क्युरिड तापक्रम चयन गरिएको थियो। सोडियम हाइड्रोक्साइड घोल र सिलिका जेल प्रयोग गरेर एक्टिभेटर घोल तयार गरिएको थियो र जियोपोलिमराइजेशन प्रक्रिया प्रारम्भ गर्न प्रयोग गरियो। XRD र FTIR, नमूनाको विशेषताको परीक्षण लागि उपयोगमा ल्याइएको थियो। 5% नानो-सिलिकाको मिश्रणले फिजिकोमेकानिकल गुणहरूलाई सुधार गरेको पाइयो। जियोपोलिमरलाई उच्च तापमा परिक्षण गर्दा, यसको compressive बल 17.01 देखि 22.49 MPa पाइयो। 5% नानो-सिलिकाको समावेश गर्दा 11.5% देखि 12.1% सम्म compressive बल बढेको पाइयो। उच्च तापमा जियोपोलिमरलाई परिक्षण गर्दा, यस जियोपोलिमर उत्पादनलाई अझै स्थिर बनाउन महत्त्वपूर्ण भूमिका खेलेको पाइयो।

अन्तमा, यस अध्ययनले रातो माटोमा आधारित जियोपोलिमरमा CWC, नानो-सिलिकाको थप मात्राको प्रभाव र यसको उच्च तापमा परिक्षणको क्रमबद्ध रूपमा बुझाई प्रदान गर्दछ। यस परीक्षणले ताप प्रतिरोधी दुरदर्शी निर्माण सामग्री बनाउन मदत गर्दछ। साथै, कृषिजन्य फोहोरबाट जियोपोलिमर निर्माण गर्न संभावनालाई उजागर गर्दछ।

किवोर्डहरू: : *Geopolymer; Thermal treatment; Compressive strength; Nano silica; RHA;*

Red Clay; XRD; FTIR

LIST OF ABBREVIATIONS

Abbreviated form	Detail of Abbreviations
RHA	Rice Husk Ash
RC	Red Clay
CWC	Calcined White Clay
FTIR	Fourier Transform Infrared
EDX	Energy Dispersive X-ray Fluorescence
XRD	X-ray Diffraction
MPa	Mega Pascal
OPC	Ordinary Portland Cement
GPC	Geopolymer Concrete
AAS	Alkali-Activated Slag
SF	Silica Fume
MK	Metakaolin
BRHA	Black Rice Husk Ash
RM	Red Mud
GGBS	Ground Granulated Blast Furnace Slag

LIST OF FIGURES

	Page
Figure 1: Molecular structure of geopolymer (Laskar, 2020).....	1
Figure 2: Schematic diagram of geopolymer formation (Raja et al., 2021)	3
Figure 3: Comparison of Portland cement and geopolymer (Nicholson et al., 2005)	4
Figure 4: Formation structure of Geopolymer (Kabir et al., 2015).....	7
Figure 5: Red Clay	14
Figure 6: Rice Husk	15
Figure 7: Structure of Kaolinite (Barani and Kalantari, 2018)	16
Figure 8: Rice Husk Ash.....	17
Figure 9: Red Clay	18
Figure 10: Calcined White Clay.....	18
Figure 11: Schematic representation of the preparation of Silica.....	19
Figure 12: Schematic representation of geopolymer synthesis.....	21
Figure 13: Casting sample.....	22
Figure 14: Preparation of geopolymer cubes (RC-2).....	22
Figure 15: FTIR Spectrometer	24
Figure 16: SLF 9 Load Frame.....	24
Figure 17: XRD patterns of (a) raw materials and their geopolymer products (b) nano-silica extracted from RHA	27
Figure 18: FTIR Spectra of raw materials (a) and its geopolymer products (b).....	29
Figure 19: Plot of compressive strength of geopolymer product with CWC% variation.	30
Figure 20: Plot of compressive strength of geopolymer product with Nano-silica % variation	31
Figure 21: Plot of compressive strength of RC-2 with temperature variation.....	32
Figure 22: Plots of compressive strength of geopolymer products with a curing time	33
Figure 23: Plot of compressive strength of RC-1 and RC-2 at 300 °C and 400 °C.....	34

LIST OF TABLES

	Page
Table 1: Sample Designation of geopolymer products	20
Table 2: Chemical composition of raw materials (%)	26
Table 3: Physical properties of geopolymer product 28 days	35

TABLE OF CONTENTS

	Page
Board of Examiners and Certificate of Approval	i
Letter of Recommendation	ii
Declaration.....	iii
Acknowledgements.....	iii
Abstract.....	v
संक्षेप.....	vi
List of Abbreviations	vii
List of Figures	viii
List of Tables	ix
CHAPTER 1: INTRODUCTION.....	1
1.1. General Background.....	1
1.2. Statement of the Problem	6
1.3. Objectives of Study.....	6
1.3.1. General Objective	6
1.3.2. Specific Objectives	6
CHAPTER 2: LITERATURE REVIEW.....	7
2.1. Raw Materials Used to Make Geopolymers	13
2.1.1. Red Mud	13
2.1.2. Red Clay	14
2.1.3. Rice Husk Ash (RHA).....	14
2.1.4. White Clay (Kaolinite)	15
2.1.5. Ground Granulated Blast Furnace Slag (GGBS).....	16
CHAPTER 3: MATERIALS AND METHODS	17
3.1. Materials.....	17
3.2. Preparation of Rice Husk Ash.....	17

3.3. Preparation of Red Clay	17
3.4. Calcination of white clay.....	18
3.5. Preparation of Nano-silica from RHA	18
3.6. Preparation of Alkaline Activator Solution.....	19
3.7. Sample Designation.....	20
3.8. Sample Preparation	21
3.9. Characterization Techniques:.....	23
3.9.1. Energy Dispersive X-ray Fluorescence (EDX) Analysis	23
3.9.2. XRD Analysis.....	23
3.9.3. Fourier Transform Infrared (FTIR) Analysis	23
3.10. Compressive Strength of the Geopolymer Products	24
3.11. Physical Properties of the Geopolymer Products	25
CHAPTER 4: RESULTS AND DISCUSSION	26
4.1. Energy Dispersive X-ray Fluorescence (EDX) Analysis	26
4.2. X-Ray Diffraction (XRD) Analysis	27
4.3. FTIR Analysis	28
4.4. Mechanical Properties of the Geopolymer Products.....	30
4.4.1. Variation of Calcined White Clay (CWC)	30
4.4.2. Variation of Nano-silica	31
4.4.3. Variation of temperature.....	31
4.4.4. Variation the Curing period.....	32
4.4.5. Thermal stability of geopolymer products.....	34
4.5. Physical properties of geopolymer products	35
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS.....	36
5.1. Conclusions	36
5.2. Recommendations	36
REFERENCES.....	37

APPENDIX I	45
Photo plates	45

CHAPTER 1

1. INTRODUCTION

1.1. General Background

Davidovits invented the term “geopolymer”(Davidovits 1989). The prefix “geo” denotes an aluminosilicate derived from geological materials, which, upon reacting with an alkaline solution, forms a binder through polycondensation. Geopolymer, is an aluminosilicate compound that is derived from pulverized coal fly ash. Enhancing the stability of frame-like polymerization structure within a geopolymer through a newly developed technique may support conserving energy and reducing carbon emissions. This generation of green materials may eventually replace traditional cement and concrete (Korniejenko et al. 2020). Geopolymers are new environmentally beneficial materials containing fly ash and red mud. Geopolymers provide a practical solution for replacing Portland Cement (PC) products as construction supplies for various applications (Kaze et al. 2021).

Geopolymer is made up of SiO_4 and AlO_4 tetrahedrons that share oxygen atoms, resulting in a Si-O-Al closed frame structure similar to Zeolite. The hardening mechanism is comparable to that of traditional cement. It is an inorganic polymerization of the system colloid particles. One type of early-strength material hardens in about 1.5 to 2.0 hours at room temperature. Geopolymers are made up of two main components: source materials and alkaline liquids. Silicon and aluminum should be used as starting materials for geopolymers based on aluminum-silicate (El-Kholy et al. 2018).

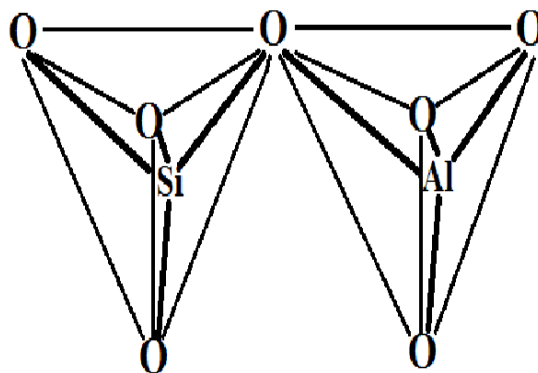
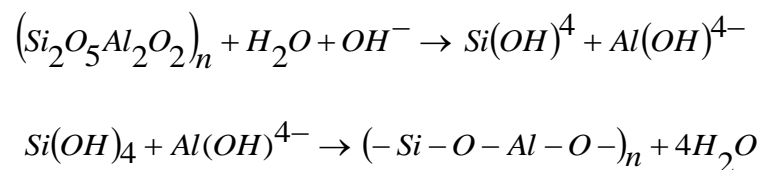


Figure 1: Molecular structure of geopolymer (Laskar, 2020)

Silica, characterized by its tetrahedral structure comprising interconnected SiO_4 units, is a polymer of silicic acid and is denoted by the chemical formula SiO_4 . It occurs naturally in the form of sand, glass, quartz, and so on. Synthetically produced silica is typically

amorphous, while naturally occurring silica is crystalline. Chemical applications require silica, which is produced using silicate solution or silane reagents (Jal et al. 2004). Nano-silica, commonly known as silicon dioxide nanoparticles. It was produced rapidly and effectively by a chemical preparation technique using paddy husk ash (PHA). The nanomaterials known as nano silica find extensive usage in various applications such as polymers, fiber optic strands, inks, adhesives, and cement-based building materials (Premaratne et al. 2013). Nano-SiO₂ has been shown to have higher pozzolanic activity than silica fume, which is a typical additional cementitious material. Nano-silica shows reduced porosity and enhances pozzolanic reactivity with Ca (OH)₂ (Güneyisi et al. 2016). Nano-SiO₂ has gained attention in comparison to conventional mineral admixtures because of its enhanced capabilities in concrete. Using Nano-silica as a cement alternative saves concrete costs and CO₂ emissions.

Various methods can be employed to prepare potential non-cement materials, all of which involve the substitution of cement with environmentally friendly alternatives. Non-cementitious materials, generated through the utilization of various precursors and alkalis, (Chindaprasirt et al. 2007) or through material blending, can undergo reactions, ultimately resulting in the formation of a solid matrix with satisfactory mechanical performance. The utilization of waste materials such as GGBS, red mud, and fly ash in geopolymers has attracted significant attention as an eco-friendly substitute for Portland cement. (Bajpai et al. 2020). Solid aluminosilicate powder reacts with alkali silicate or alkali hydroxide to produce geopolymers (Davidovits 1991). Geopolymerisation occurs under very alkaline conditions when reactive aluminosilicates dissolve and liberate free (SiO₄) and (AlO₄) tetrahedral units into solution. Polymeric Si-O-Al-O linkages are formed when the tetrahedral units share an oxygen atom with a polymeric precursor. (Komnitsas 2011). During geopolymerisation, the following reaction occurs:



Geopolymer formation involves mixtures of solid and liquid.

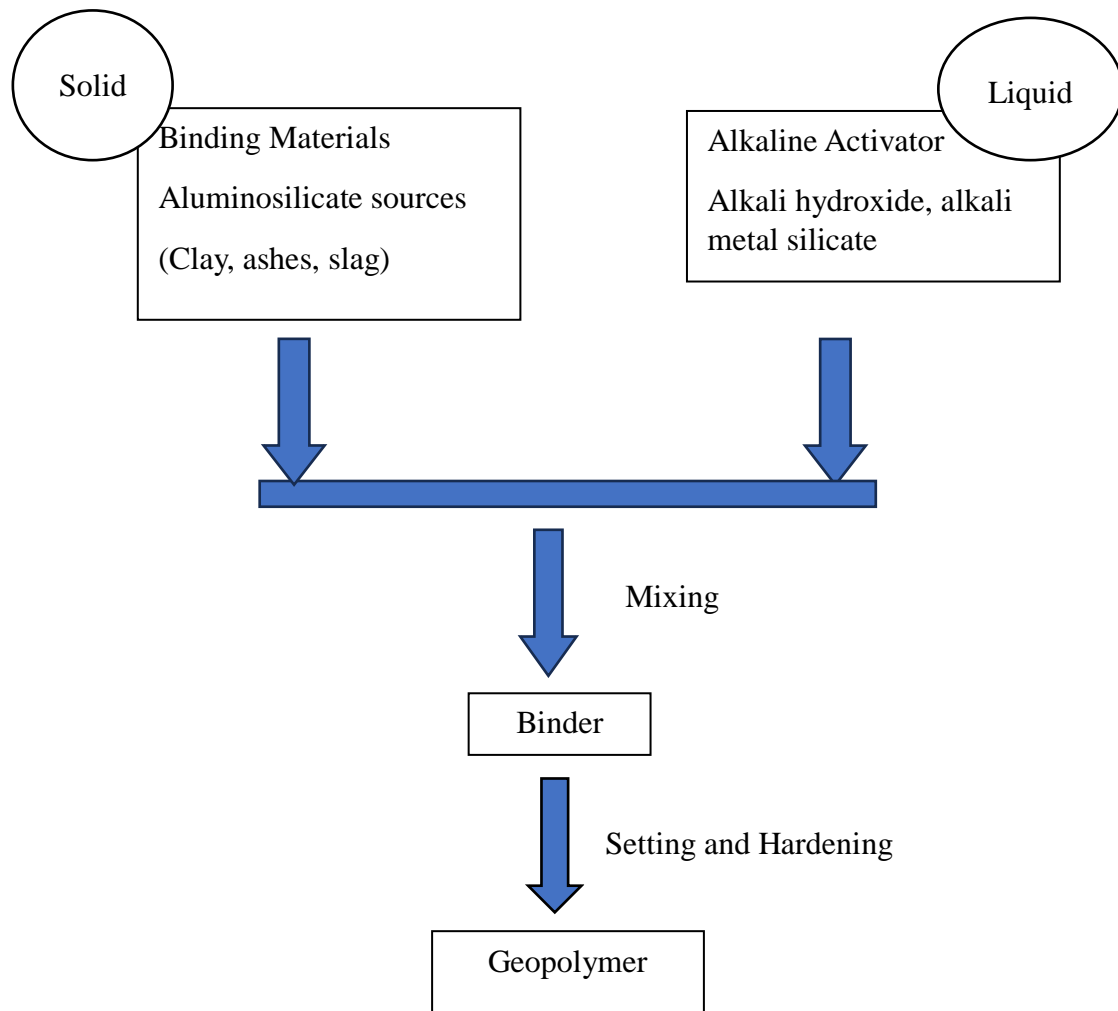


Figure 2: Schematic diagram of geopolymer formation (Raja et al., 2021)

Geopolymer concrete is a construction material that consists of an aluminosilicate and an alkali solution and has mechanical qualities equivalent to standard Portland cement concrete. Geopolymer concrete (GPC) development has attracted a lot of interest in recent years as an alternative for energy-saving, shrinkage, material cost, ecologically friendly, thermal stability, thermal conductivity, long-lasting, and more efficient cement materials than today's Portland cement (PC). The durability mechanism is greatly impacted by the calcium content. It is roughly 10-30% more resistant to chemical attacks (Al-mashhadani et al. 2018). Because of increased industrialization, vast amounts of trash are being generated, causing environmental and ecological difficulties as well as occupying large areas of prime cultivable land. There are several disadvantages to manufacturing Portland cement. Some of the primary disadvantages include massive consumption of natural

resources and energy, emission of greenhouse gases, and so on. Atmospheric CO₂ also reacts with the hydration products, causing the structure to degrade. The utilization of geopolymer binders presents a promising alternative for various applications, offering the potential to replace Ordinary Portland Cement (OPC) with notable environmental and technical advantages. These advantages include a significant decrease in CO₂ emissions by 80-90% and enhanced resistance against corrosive chemicals and elevated temperatures. (Duxson et al. 2007; Rapazote et al. 2011). OPC production and use are the largest anthropogenic cause of climate change, accounting for around 8% of global CO₂ emissions. These days OPC's more widespread use is endangering all living on the planet.

Portland cement undergoes hardening through the hydration of Calcium Silicate, forming Calcium Di-Silicate hydrate (CSH) and Lime Ca (OH)₂. On the other hand, geopolymer cement achieves hardening through the polycondensation reaction of sodium/potassium oligo-(sialate- siloxo), resulting in the formation of a crosslinked network of sodium/potassium poly (sialate-sioloxo). The comparison between Portland cement and geopolymer cement is given below.

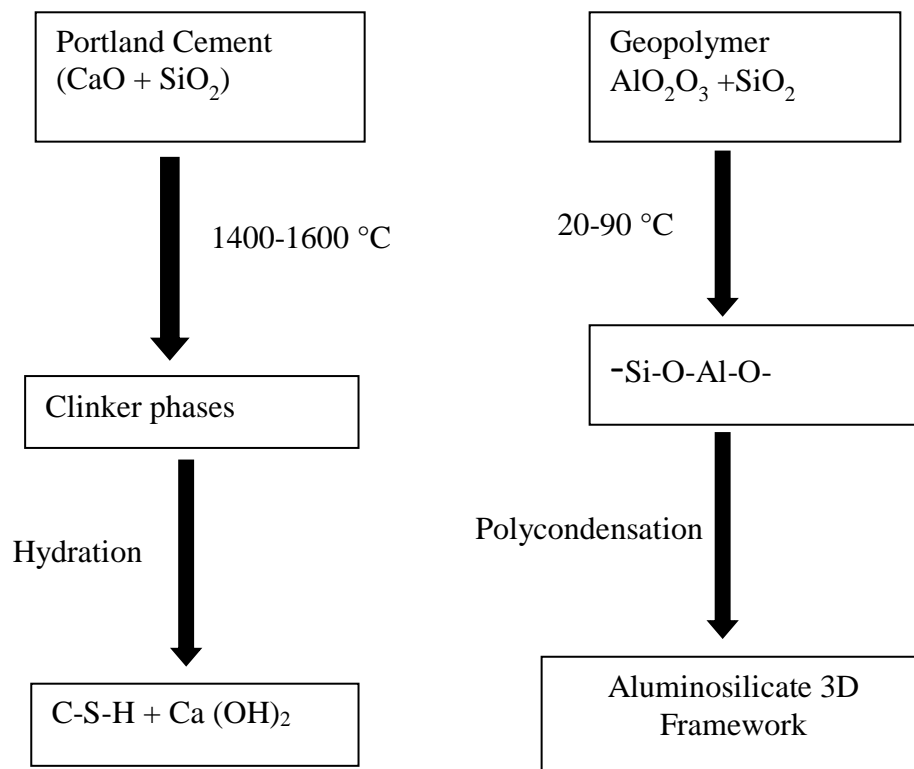


Figure 3: Comparison of Portland cement and geopolymer (Nicholson et al., 2005)

Geopolymers exhibit remarkable heat resistance, making them suitable for exposure to elevated temperatures. They possess a high tolerance for heat, as they are non-combustible, do not emit gases or fumes, and are non-toxic. In recent times, these inorganic polymers have attracted due to their performance level compared to Portland cement (Hardjito 2004). The majority of the research has shown that geopolymer is innovative waste-based concrete that has great durability uses less energy, and a preference over conventional Portland cement. (Davidovits 1991, 1994)

In comparison to cement-based composite materials, geopolymers have the following benefits:

- ✓ Exceptional durability
- ✓ Acid resistance
- ✓ Minimal shrinkage
- ✓ Resilience to high temperature
- ✓ Resistance to corrosion
- ✓ Resistance to fire
- ✓ Cold and quick setting
- ✓ Cost-effective production methods
- ✓ Reduction in greenhouse gas emissions
- ✓ Low energy consumption.
- ✓ Abundant availability of raw materials.

Because of these properties, polymeric materials are being considered as an alternative to OPC for multiple industrial applications such as construction, transportation, road building, aerospace, mining, and metallurgy (Martin et al. 2010).

The main aim of this study is to find the synergetic effect of the addition of nano-silica in red clay-based geopolymer products and to investigate their thermal stability at high temperatures.

1.2. Statement of the Problem

The construction of buildings in rural and urban areas necessitates a massive amount of cement, which is produced in our country every day. On average, the production of each ton of cement necessitates raw materials of approximately 1.5 tons, resulting in the emission of nearly 1 ton of CO₂ gas into the environment (Kong and Sanjayan 2008).

Crude steel production is also increasing. This has resulted in mining activity, which is responsible for the generation of waste, which can endanger the environment and its inhabitants. However, there is a significant potential for these wastes to be utilized in the construction sector as source material for sustainable and eco-friendly development (Das et al. 2020).

1.3. Objectives of Study

1.3.1. General Objective

Investigation of the synergetic effect of the addition of nano-silica on the physicomechanical properties and thermal behaviour of red clay-based geopolymer composites.

1.3.2. Specific Objectives

- ✓ Examination of the impact of nano-silica contents on the compressive strength of red clay-based geopolymers.
- ✓ Investigation of the impact of curing temperature and duration of curing on the geopolymer composites.
- ✓ Study the effects of thermal treatment on the thermal stability and mechanical properties of red clay-based geopolymer composites enriched with nano-silica.

CHAPTER 2

2. LITERATURE REVIEW

Davidovits invented the term “geopolymer” (Davidovits 1989). He proposed geopolymers as an inorganic polymer with non-combustible, non-flammable, and heat resistance to address plastic-related fires in France. The prefix “geo” denotes an aluminosilicate derived from geological materials, which, upon reacting with an alkaline solution, forms a binder through polycondensation. Geopolymerization requires an alkaline chemical activator to initiate the reaction in the formation of a mineral polymer structure. Geopolymerization is a relatively rapid chemical reaction that occurs under alkaline conditions with Si and Al minerals, resulting in a three-dimensional polymeric chain and ring structure of Si-O-Al-O- linkages. The geopolymer is made up of 3 classes of inorganic polymers that are based on the silica/ alumina ratio and are made up of the following three, monomeric units (He et al. 2013).

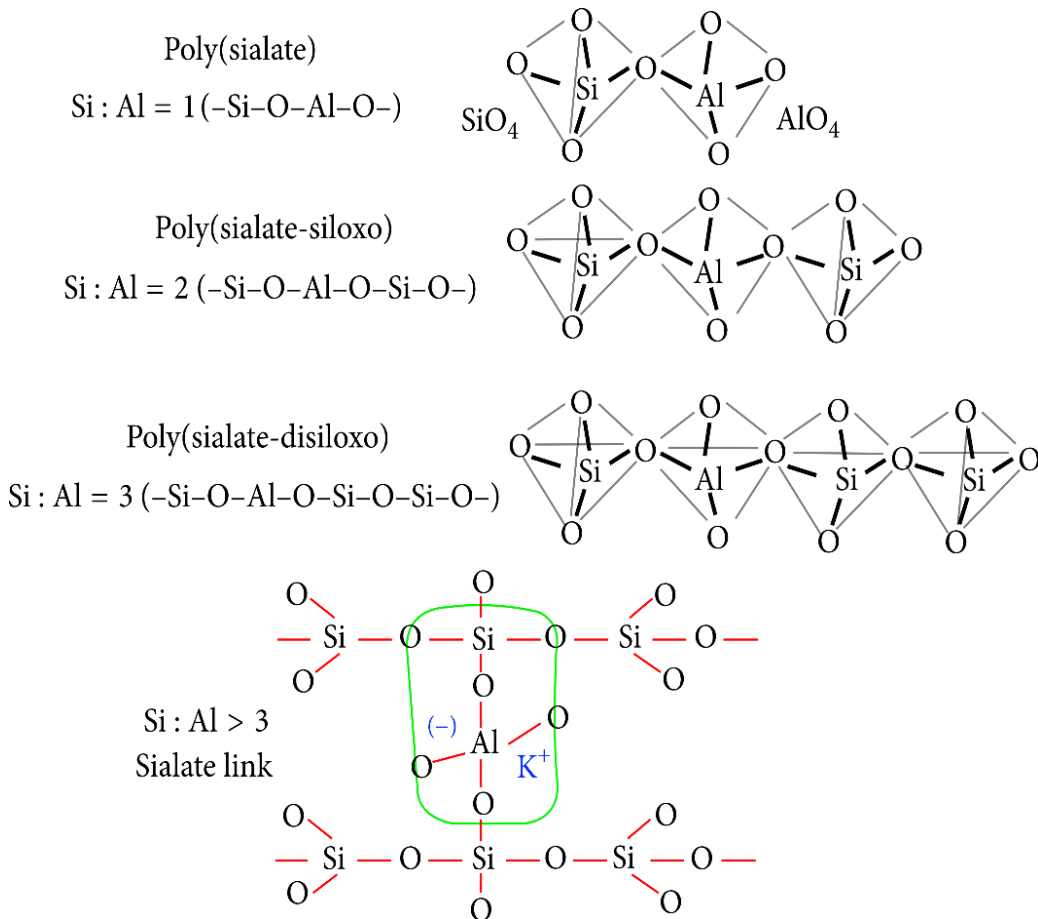


Figure 4: Formation structure of Geopolymer (Kabir et al., 2015)

Ancient constructions like the Egyptian pyramids, were constructed by casting blocks and allowing them to solidify, resulting in artificial zeolitic rock. Experimental research has revealed a new family of mineral binders known as “geopolymer” because it was related to organic condensation polymers (Davidovits 1994). Geopolymer concrete (GPC) development has attracted a lot of interest in recent years as an alternative for energy-saving, shrinkage, material cost, ecologically friendly, thermal stability, thermal conductivity, and long-lasting, (Duxson et al. 2007) more efficient cement alternatives than OPC available today.

Sapute et al. (2012) found that the curing temperature and curing time affect the compressive strength of geopolymer concrete based on fly ash. They concluded that curing temperature and duration are the critical factors in the activation process. Curing time of 6-24 hours results in greater compressive strength. However, after 20 hours, strength gain is minimal.

One of the most critical parameters for geopolymerisation is the curing temperature. Curing parameters, including temperature, curing duration, and relative humidity, affect the microstructure and mechanical properties (Kornjienović et al. 2010) of alkaline-activated fly ash. After 4 days of curing at 65 °C, the geopolymer sample had a maximum strength of 33 MPa. Compressive strength decreases when the curing period extends beyond four days. The compressive strength briefly decreased after more than 8 days of curing. Geopolymer samples’ compressive strength declined as they cured at temperatures over 65 °C.

In geopolymer composite of rice husk ash (RHA) and red mud (RM), the compressive strength of the geopolymer products has been reported to range from 3.2 to 20.5MPa for the synthesized geopolymers with nominal Si/Al ratios of 1.68- 3.35 (He et al. 2013). This variation in compressive strength highlights the effect of material composition and Si/Al ratio on the mechanical properties of geopolymer composites.

Many studies show that pure amorphous silica can be made from a cheap rice husk. The goal of adding nano-silica to the cement mixture is to boost durability because micro-silica and nano-silica particles may fill the spaces between cement particles. Because of its pozzolanic reaction and the influence of pore-filling, nano-silica is the most extensively utilized mineral in cement and concrete to increase performance (Rahmawati et al. 2021).

Givi et al. (2010) observed that nano-silica particles with an average size of 15nm resulted in increased concrete strength at early ages compared to particles sized at 80nm. However, concrete with 80nm nano-silica particles exhibited higher compressive strength at 90 days.

Zhang et al. (2012) discovered that the large capillary porosity declined with increasing nano-silica dosage, alongside decreases in both critical pore diameters and threshold, which notably dropped at 2% nano-silica.

Rezania et al. (2019) showed that the permeability decreased with increasing nanoparticle concentration because of the difficulties of dispersing them in concrete at larger dosages. The use of nanoparticles in alkali-activated slag (AAS) concrete led to an unwanted increase in water penetration depths; whereas, the utilization of micro-silica lowered permeability.

Patankar et al. (2014) studied the impact of curing duration and temperature on the compressive strength of fly ash-based geopolymer concrete. They discovered that, at all temperatures, the compressive strength of geopolymer concrete increases with increasing concentration of sodium hydroxide at all temperatures, however, the rate of strength improvement at and above 60°C is not noticeable.

The strength of geopolymer concrete made from black rice husk ash and ground granulated blast furnace slag increases with an increase in curing temperature (Venkatesan and Pazhani 2015). Coal fly ash geopolymer of compressive strength 41.7 MPa with an increase in curing period of up to 28 days has been reported (Pathak and Jha 2012).

The maximal compressive strength of geopolymer products from brick dust was reported at 11.43 MPa (Pathak et al. (2014)). Geopolymers made from sand cement dust, brick dust, and a mix of sand cement and brick dust with an alkaline activator solution were found to have maximum compressive strengths of 36.3, 45.1, and 43.2 MPa respectively (Pathak et al. 2014).

Das et al. (2020) discovered that the compressive strength and workability of geopolymer decrease as the amount of RHA increases. However, the geopolymer containing 10% RHA demonstrated a compressive strength of 25MPa. This grade of concrete is

commonly used for the majority of building projects, hence expanding the use of RHA for a more environmentally friendly binder synthesis via geopolymerization.

Xu and Deventer (2000) investigated a variety of aluminosilicate minerals to create geopolymers. As an alkaline activator, they used sodium or potassium hydroxide. They discovered that adding sodium silicate solution. They discovered that the reaction between the solution and source material was improved by adding sodium silicate solution to sodium hydroxide solution as the alkaline activator. They discovered that the sodium hydroxide solution caused more mineral dissolution than the potassium hydroxide solution.

Gleize et al. (2003) investigated the microstructural consequences of replacing 10% of PC with silica fume (SF) in a lime, sand, and cement mix proportion by volume in 1:16:1 for masonry mortar. They found that silica fumes reduce overall porosity and boost compressive strength only at later ages and that the pore structure of silica fume mortar is finer than that of non-silica fume mortar.

Khater (2013) measured compressive strength and performed scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR) analysis to investigate the effect of adding silica fume (SF) to the waste concrete from demolition projects and the geopolymer made from the alkaline activation of alumina-silicates metakaolin. According to their findings, the compressive strength of geopolymer mixes containing SF increased up to 7% substitution, then reduced up to 10% but remained higher than the control mix. However, increasing the SF level decreases the mechanical properties of the reaction result

According to (Das et al. 2020) the concept of using pozzolanic by-products from the industry, such as RHA, SF, fly ash, GGBS, and many more, sustainably should be encouraged in the manufacturing of modern concrete. Additionally, as cement production poses a significant environmental hazard due to its large carbon emissions that contribute to global warming, the old traditional way of making concrete using OPC should be progressively reduced. Thus, creating and implementing newer building materials that will improve strength and durability is the main task of those concrete makers.

According to (Rangan et al. 2008) geopolymer concrete has a high compressive strength when compared to normal concrete. For the same mix, it is approximately 1.5 times

higher. Geopolymer concrete also demonstrated very good workability in comparison to standard concrete.

Kaur et al. (2018) studied the impact of RHA-based geopolymer's alkali activator on the binder (AAB) ratio and alkaline activator's molarity. The results revealed that after 28 days, the highest compressive strength of 39.95 N/mm² was reached. Compressive strength is a direct function of the molarity of the alkali activator solution as well as the Alkali Activator to Binder (AAB) ratio. Microstructure becomes quite dense as molarity rises; this is likely due to a high degree of geopolymerization.

Hossain et al. (2021) examined the use of waste RHA for the more environmentally friendly manufacture of geopolymer. The implications of RHA addition on important characteristics such as compressive strength, setting time, durability, and workability were discussed. After analyzing RHA's impact on geopolymer, it was determined that adding 10–20 weight percent of RHA improved both the geopolymer's short- and long-term qualities. As a result, the building industry's use of RHA is environmentally responsible and sustainable.

Phoongernkham et al. (2017) examined the effects on strength improvement of PC and fly ash-based Geopolymer Mortar (GM) of a mixture of sodium silicate and sodium hydroxide solutions. The production of extra CSH strengthened the compressive and shear bond strengths of GMs as PC concentration increased. The 15% PC/SHSS mixture had the best shear bond and compressive strengths.

Mohammad et al. (2023) used NaOH/sodium silicate to produce and analyze metakaolin (MK)-based GC with different amounts of nano-silica (NS) (1.5, 3.0, 4.5, 6.0, and 7.5% by weight of MK content). According to the study, the flexural, compressive, and tensile strength of the GC steadily increased up to 6.0% NS; however, mechanical properties decreased with any additional increases in the ratio. The study found that adding 6.0% NS to MK-based GC improves compressive strength by 34.3% when compared to the control GC mix, as well as 39 and 37% in flexural and split tensile strength when compared to control GC strength. Moreover, the statistical analysis supports the remarkable impact of nano-silica on the mechanical properties of geopolymer concrete, underlining its significance in boosting performance and sustainability in comparison to cement-based materials.

According to Phoongernkham et al. (2014), using nano-SiO₂ as a fly ash addition reduced the setting time while using nano-Al₂O₃ resulted in only a minor reduction. When 1-2 percent of nanoparticles are added to the geopolymer matrix, more sodium aluminosilicate hydrate (NASH), geopolymer gel, and calcium silicate hydrate (CSH) or calcium aluminosilicate hydrate (CASH) are formed. This improves the compressive strength, flexural strength, and elastic modulus of pastes. Furthermore, the shear bond strength between the geopolymer and concrete substrate is strengthened by the inclusion of both nano-SiO₂ and nano-Al₂O₃.

The chemical characterisation of red mud changes depending on the bauxite ore and the refining technique (sintering/ bayer process). Iron and alumina oxide are crucial components in the sintering process. But calcium oxide and silica oxide play significant roles in the Bayer process. The passivating layer on the reinforcement bar in concrete is strengthened by red mud's high content of iron oxide (Fe₂O₃) and aluminum oxide (Al₂O₃), which are both extremely alkaline and resistant to carbonation and chloride ion assault (Ruben et al. 2019).

Lingyu et al. (2021) examined the mechanisms and developments in the study of geopolymer concrete's permeation properties, frost resistance, structural fire resistance, corrosion resistance, and carbonation resistance. Hydrostatic and osmotic pressure theories are the main basis of the freezing-thawing failure mechanism of geopolymer concretes. Less than 75 freezing-thawing cycles are allowed in GPC, and its resistance to frost is limited.

Ridtirud et al. (2011) studied the effects of NaOH concentration, sodium silicate-to-NaOH ratio, liquid-to-ash ratio, curing temperature, and curing duration on shrinkage. The study determined that the utilization of higher molarity NaOH as an alkaline activator resulted in both a notable impact on early strength and greater compressive strength. Since geopolymer concrete may generate compressive strengths beyond 60 °, it is also the ideal choice for precast concrete products.

Buchwald et al. (2009) researched the thermal characteristics of geopolymer binders, examining both sodium and potassium variants, along with their corresponding geopolymer composites. Their findings revealed that geopolymer derived from calcined kaolinite demonstrated structural stability up to 1200 °C.

Li et al. (2021) investigate the impact of silica fume, especially at concentrations of 2% and 4%, on the thermomechanical behavior of fly ash geopolymer. Their findings indicated that the geopolymer's strength was maintained at temperatures as high as 1000 °C by adding 2% silica fume.

Lemougna et al. (2013) investigated how the stability and thermos-mechanical properties of geopolymers were affected by the composition of the activating solution. Geopolymers produced using potassium silicate solutions exhibited greater thermal stability compared to those synthesized with sodium silicate solutions. Some investigations have explored the thermos-mechanical characteristics of composites or geopolymer binders at high temperatures.

Assaedi et al. (2019) discussed the effect of nano-silica on the mechanical performance and durability of geopolymer composites reinforced with flax fabric. After the samples were kept for 32 weeks at room temperature, the durability experiments were carried out. The investigation's findings demonstrated that the inclusion of nano-silica improves the mechanical and physical properties. The degradation of flax fiber was slowed down by the presence of NS, which also lowered the system's alkalinity and sped up the geopolymeric reaction

2.1. Raw Materials Used to Make Geopolymers

2.1.1. Red Mud

Red Mud (RM) is the residue left over from the Bayer process' digestion of bauxite ores with caustic soda to produce alumina. Every ton of alumina produced yields 1.5–1.6 tons of red mud. Approximately 120 million of them have a high alkalinity. An estimated 2.7 billion tons of industrial waste with an average pH of 11.3+ 1.0 are produced globally. Because of the high alkalinity and superfine particle size of RM, proper disposal is challenging, hence it is usually disposed of through land storage (Kong et al. 2018).

Red mud, also referred to as red sludge, is an industrial waste generated by Bayer technology, which is primarily utilized in the bauxite refining process to generate aluminum. Red mud is one of the most hazardous wastes in the aluminum smelting sector, which is a mixture of solid and metallic impurities (Adesanya and Raheem 2009; Le et al. 2018).

2.1.2. Red Clay

Red clay is an insoluble clay mineral that is mostly composed of clay minerals and is generated by a variety of rocks composed in the earth's crust in humid, hot climates. Red clay has a large void ratio, a high liquid limit, and a high natural water content; however, its compatibility is poor when employed as a filling material (Yanzhao et al. 2020).



Figure 5: Red Clay

Reig et al. (2013) demonstrated that by utilizing NaOH and sodium silicate solution as activators, red clay brick waste may be converted into alkali-activated cement pastes and mortars. Zeolitic structures are produced, as demonstrated by thermogravimetric analysis, however, they tend to disappear as the concentration of the alkaline solution rises. After seven days of curing, the optimum combination was 45/7.0/1.60, which produced compressive strengths that were almost 30 MPa.

2.1.3. Rice Husk Ash (RHA)

Rice Husk (RH) is a byproduct of rice milling whereas Rice Husk Ash (RHA) is produced through the combusting of Rice Husk at high temperatures in a controlled environment. In countries like Southeast Asia, the United States, China, India, and Brazil, RH and RHA are widely available. To produce energy, RH has therefore been recycled through burning. This produces RHA, which has a high concentration of amorphous silica (85-95%). Hossain et al. (2018) provide a complete description of nano-silica processing using RH/RHA. They found that amorphous silica from RHA or RH is an available substitute for quartz for producing value-added ceramics in practical applications.



Figure 6: Rice Husk

Rice Husk Ash (RHA) is a type of sustainable biomass energy that is created by burning rice husks to generate electricity. Rice husk is an agricultural byproduct from rice paddy processing, and is typically 20% of the weight of rice paddy. It is the hard shell that protects rice grains. When rice husk is burned, 25% of its weight is turned into ash, which is known as Rice Husk Ash (RHA). It can be found all around the world, but especially in developing countries. According to Chindaprasirt et al. (2007), its composition is approximately 40% cellulose, 30% lignin, and 20% silica. RHA is made up of amorphous silica and highly porous particles with a low density and a large internal specific surface area.

The RHA is a reactive substance that can be utilized as a volcanic ash filler (Kaur et al. 2018). The use of rice husk has the advantage of not only creating precious silicas but also of lowering disposal and pollution issues. Many studies show that pure amorphous silica can be made from a cheap rice husk. The goal of adding nano-silica to the cement mixture is to boost durability because micro-silica and nano-silica particles may fill the spaces between cement particles.

2.1.4. White Clay (Kaolinite)

Kaolin, China clay, or white clay are names for rocks that are high in kaolinite. Traditionally, porcelain has been made using kaolin, a fine, white clay material. The term kaolin is assumed to be originated from the Chinese word kaolin.

Kaolinite is an aluminosilicate with a 1:1 uncharged dioctahedral layer structure (Habert et al. 2011). Each layer is composed of a sheet of $\text{AlO}_2(\text{OH})_4$ octahedra building six-membered aluminate rings, and a sheet of SiO_4 and a sheet of tetrahedra forming six-membered silicate rings joined by common oxygen atoms. These electrically neutral sheets are kept together by hydrogen bonds and van der Waals forces. These connections are strong enough to prevent water from penetrating the interlayer gaps and generating swelling.

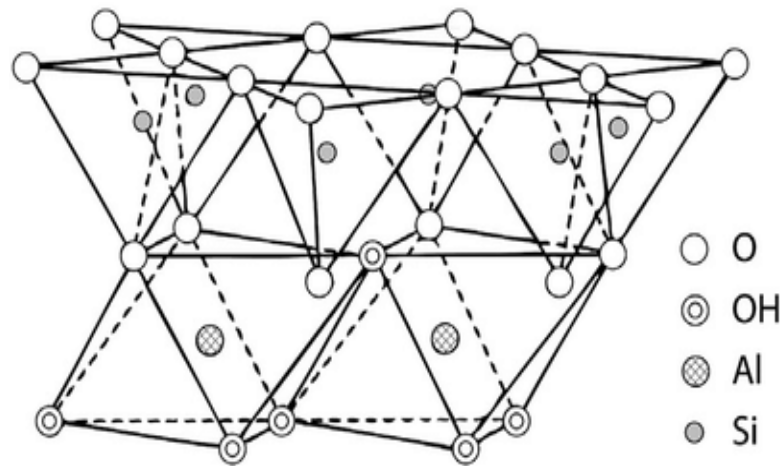


Figure 7: Structure of Kaolinite (Barani & Kalantari, 2018)

2.1.5. Ground Granulated Blast Furnace Slag (GGBS)

Ground granulated blast furnace slag (GGBS) is an effective aluminosilicate source because of its high alumina and silica concentration, which is required for the geopolymerization reaction (Kumar et al. 2018). It is a byproduct of the iron industry and is often used as an assistive or cement replacement material to enhance the mechanical properties and durability of concrete. GGBS not only promotes sustainable construction but also reduces CO_2 emissions from Portland cement use (Saludung et al. 2018).

GGBS is essentially a calcium aluminosilicate framework material with an excessive charge balance. The chemical is primarily $\text{CaO}-\text{SiO}_2-\text{MgO}-\text{Al}_2\text{O}_3$. Glass networks are mainly formed by Si^{4+} and Al^{3+} cations, with divalent Ca^{2+} and Mg^{2+} acting as network modifiers, as well as any alkalis (Li et al. 2010).

CHAPTER 3

3. MATERIALS AND METHODS

3.1. Materials

The key materials used for the geopolymer synthesis encompass Rice Husk Ash (RHA), White Clay (WC), and Red Clay (RC), which were locally sourced from Madhyanepal -7 Lamjung District.

3.2. Preparation of Rice Husk Ash

The Rice Husk Ash was prepared from the rice husks which were sun-dried in open air to reduce the moisture, and underwent heating to transform into RHA. The prepared RHA was enclosed inside the muffle furnace at a temperature of 450 °C for 3 hours to thoroughly eliminate the carbonaceous material. Thus, obtained rice husk ash was ready for sample preparation.



Figure 8: Rice Husk Ash

3.3. Preparation of Red Clay

Red clay was exposed in the oven for 2 hours at 120 °C to remove any moisture and contaminants. Subsequently, the dried red clay was carefully sealed in an air-tight plastic bag.



Figure 9: Red Clay

3.4. Calcination of white clay

White clay was subjected to the muffle furnace for 3 hours at 750 °C to effectively eliminate impurities and moisture in the absence of oxygen. Hence, 474.15 g of calcined white clay was obtained from the initial 500 g of white clay.



Figure 10: Calcined White Clay

3.5. Preparation of Nano-silica from RHA

First of all, 200 g of RHA and 500 mL of 5M NaOH were mixed. Then the solution was agitated in magnetic stirrer for 4 hrs at 80 °C and left for 2 days. Again, the solution was agitated in a magnetic stirrer for 1 hr at the previous temperature, and then the solution was filtered with the help of the Buchner funnel. The filtrate was mixed with 20 mL 2% starch solution. 2N H₂SO₄ was added dropwise to solution till filtrate reached a pH of

around 8. Then precipitate was collected and dried in an oven. Thus, the obtained precipitate (Nano-silica) was ready for further procedure.

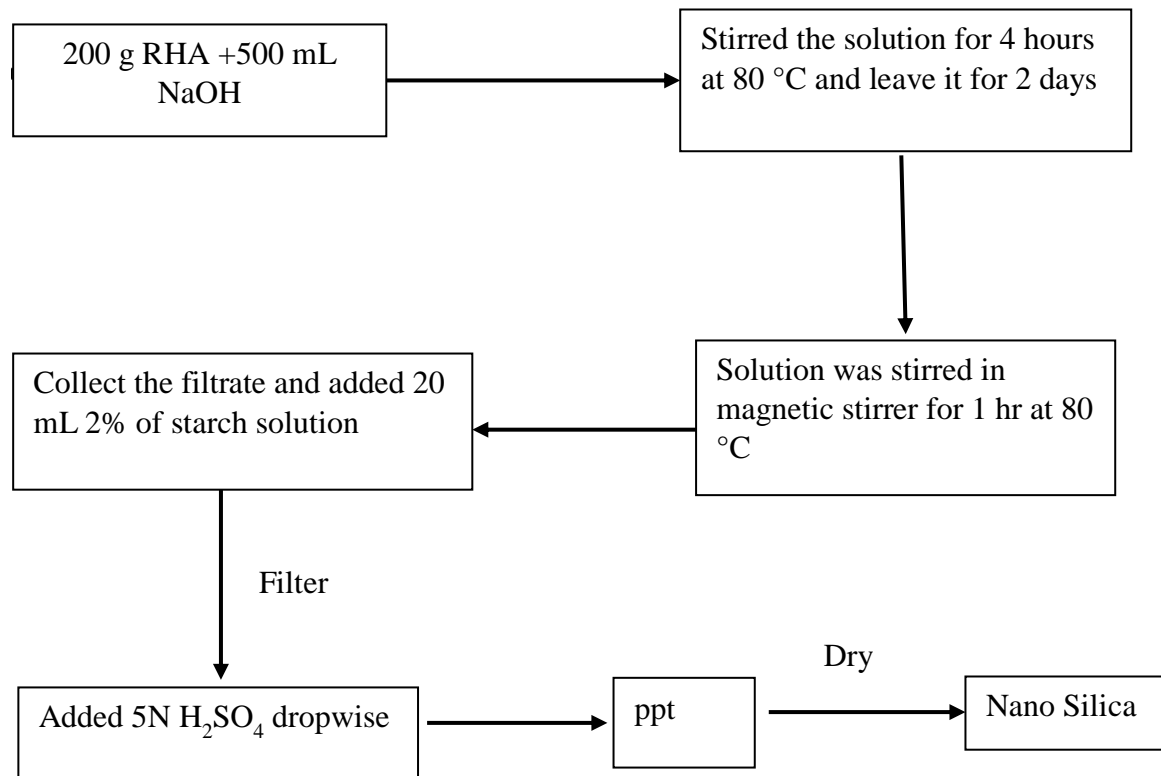


Figure 11: Schematic representation of the preparation of Silica

3.6. Preparation of Alkaline Activator Solution

An alkaline activator solution holds significant importance in the geopolymerization process. In this experiment, the alkaline activator solution was a mixture of sodium hydroxide and sodium silicate.

To prepare sodium hydroxide solution, first, dissolve 29.894 g of NaOH pellets in 150 mL of water, then 40.54 g of silica gel was dissolved and mixed for 3 hours at 80 °C using a magnetic stirrer. The activator solution was prepared one day before the sample preparation.

3.7. Sample Designation

Table 1: Sample Designation of geopolymer products

Sample	Red Clay (%)	Calcined White Clay (%)	Nano Silica (%)	Lime (%)	Sand (%)
RC-1	90	10	0	0	0
RC-2	85.5	9.5	5	0	0
RC-3	83.79	9.31	4.9	2	0
RC-4	34.2	3.8	2.0	0	60

Where,

RC-1 represents the mixture of Red Clay (90%) and 10 % of Calcined White Clay

RC-2 represents the mixture of red clay (85.5%), Calcined White Clay (9.5%), and Nano -Silica (5%)

RC-3 represents the mixture of red clay (83.79%), Calcined White Clay (9.31%), Nano - Silica (4.9%), and lime (2%)

RC-4 represents the mixture of red clay (34.2%), Calcined White Clay (3.8%), Nano - Silica (2.0%), and Sand (60%)

3.8. Sample Preparation

The powders of RC, CWC, and Nano-silica of different percentage variations were combined and an activator solution was added. Thus, produced samples were heated at different temperatures for 2 hours and their compressive strength was measured after they were allowed to cure at room temperature for seven, fourteen, twenty-one, and thirty-eight days.

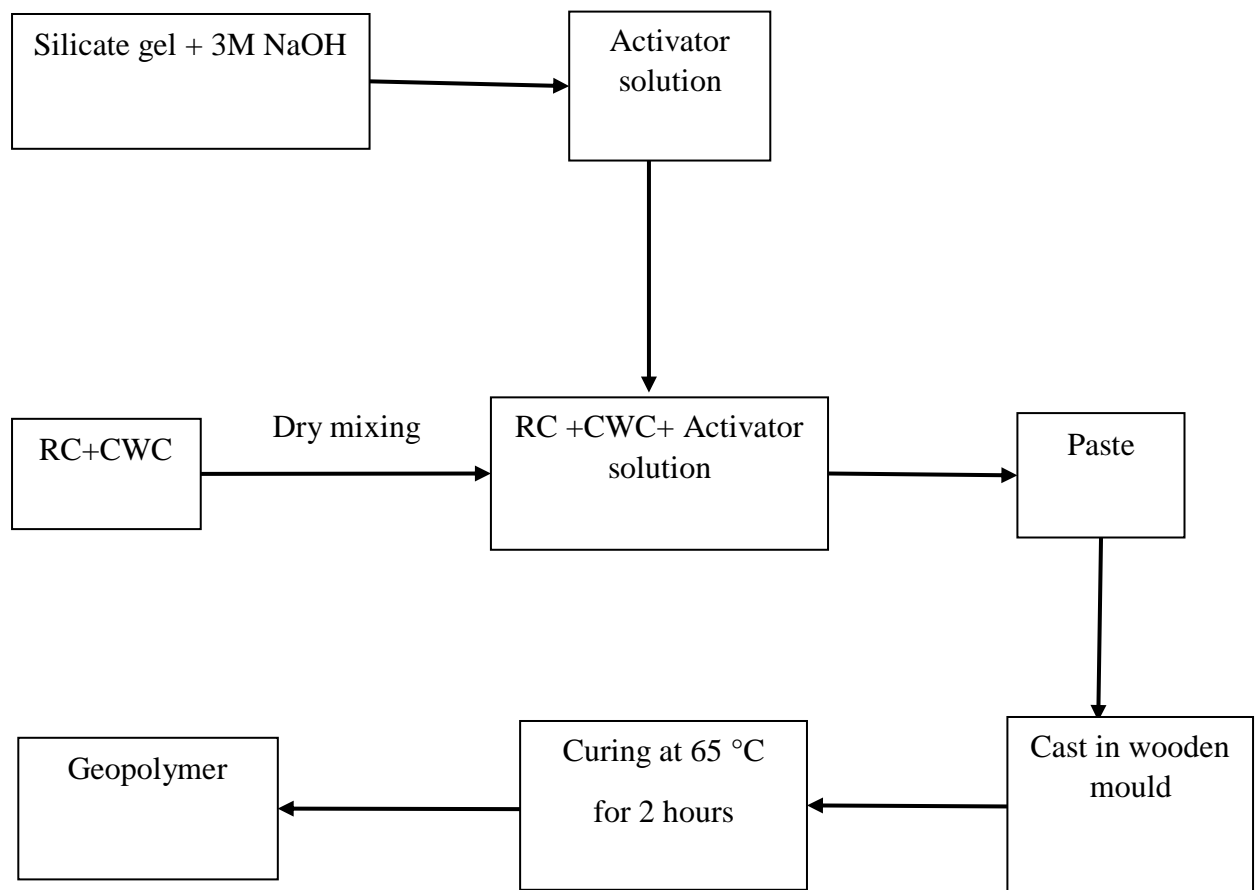


Figure 12: Schematic representation of geopolymer synthesis



Figure 13: Casting sample



Figure 14: Preparation of geopolymer cubes (RC-2)

3.9. Characterization Techniques:

3.9.1. Energy Dispersive X-ray Fluorescence (EDX) Analysis

Energy Dispersive X-ray Fluorescence (EDX) analysis of the raw materials and geopolymer sample was performed using an EDX spectrophotometer (EDX-8000, Shimadzu) at the Department of Customs, Tripureshwor, Kathmandu.

In EDX analysis, X-rays are utilized to excite the atoms in a sample, causing them to generate X-ray fluorescence light. The emitted X-ray's energy is then measured and analyzed to identify the sample's elemental composition.

3.9.2. XRD Analysis

XRD experiments are conducted using an X-ray diffractometer. It is a typical common method employed to analyze the composition or crystalline structure of a sample. CuK α radiation (Bruker D8) was used to record XRD patterns on an X-ray diffractometer at the National Academy of Science and Technology (NAST), Khumaltar, Kathmandu.

The sample being tested is usually in the form of fine powder. The diffraction pattern is studied to determine the crystallographic phases present in the material. This is usually accomplished by comparing the observed diffraction pattern to reference patterns from a database of known crystal structures. The diffraction peak positions and intensities are utilized to determine the lattice parameters, crystal symmetry, and other structural features of the material.

3.9.3. Fourier Transform Infrared (FTIR) Analysis

The study, which was conducted at the Amrit campus in Lainchaur, used FTIR analysis (Spectrum Two, Perkin Elmer Spectrum IR 10.6.2) in the frequency range of 4000 to 450 cm⁻¹.

FTIR operates on the basis that different chemical bonds absorb infrared radiation at specific frequencies, resulting in distinct absorption bands in the FTIR spectrum. The FTIR spectrum shows peaks and troughs that represent the sample's absorption of infrared light.

The functional groups and chemical bonds found in the sample are represented by these absorption bands.



Figure 15: FTIR Spectrometer

3.10. Compressive Strength of the Geopolymer Products

The compressive strength of the prepared geopolymer was determined using an SLF 9 load frame machine at Tribhuvan University's Central Material Testing Laboratory, Institute of Engineering Pulchowk Campus.



Figure 16: SLF 9 Load Frame

Compressive strength is an important attribute of all concrete since it is affected by curing temperature. The curing temperature causes an increase in compressive strength.

The compressive strength is defined as the uniaxial force exerted per square meter. It refers to the sort of pressure applied. The compressive strength of a material or structure

refers to its ability to endure loads that cause it to shrink. The sample was crushed using a load and the results were recorded. The equation is used to calculate compressive strength measurement.

$$Force = \frac{Factor \times Load}{Area} \text{-----(1)}$$

$$F, 1Kg/mm^2 = 9.80655 N/mm^2 \quad (1 \text{ N/mm}^2 = 1 \text{ MPa})$$

3.11. Physical Properties of the Geopolymer Products

The physical characteristics of the geopolymer products (bulk density, apparent specific gravity, water absorption, and apparent porosity) were determined following ASTM-373 standards. Initially, the geopolymer underwent a drying process in an oven at 105 °C for 2 hours, and its weight in the dry state was recorded. Subsequently, the geopolymer was subjected to boiling in a water bath for 3 hours and left to soak for an additional 24 hours before its weight was measured.

1. Exterior Volume V:

$$V, cm^3 = W - S \text{-----(2)}$$

2. Apparent Porosity, P:

$$P, \% = \frac{(W - D)}{V} \times 100 \text{-----(3)}$$

3. Water Absorption, A:

$$A, \% = \frac{(W - D)}{D} \times 100 \text{-----(4)}$$

4. Apparent Specific Gravity, T:

$$T, \% = \frac{D}{D - S} \times 100 \text{-----(5)}$$

5. Bulk Density, B:

$$B, g / cm^3 = \frac{D}{V} \text{-----(6)}$$

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1. Energy Dispersive X-ray Fluorescence (EDX) Analysis

Energy Dispersive X-ray Fluorescence (EDX) analysis is shown in the following Table (2).

Table 2: Chemical composition of raw materials (%)

Raw materials	Si	Fe	K	Ti	Mn	Cu	Zn	Others
Red clay	89.637	5.886	3.713	0.648	0.035	0.015	0.008	0.058
CWC	86.28	6.062	6.863	0.589	0.068	0.009	0.02	0.109
Silica	99.152	0.028	0.719	-	0.037	0.009	0.013	0.042

This table represents the chemical composition of three raw materials (Red clay, CWC, and Silica). The Red clay consists mostly of predominantly Silicon with a small amount of Iron, Potassium, Titanium, Manganese, Copper, and Zinc. The CWC consists of a lower percentage of Silicon compared to red clay but contains higher percentages of Iron, Potassium, and Titanium along with minor amounts of Manganese, Copper, and Zinc. Silica is almost entirely composed of Silicon with trace amounts of other elements like Iron, Potassium, Manganese, Copper, and Zinc.

4.2. X-Ray Diffraction (XRD) Analysis

The XRD pattern of Red Clay and their geopolymer products is shown in Figure 17.

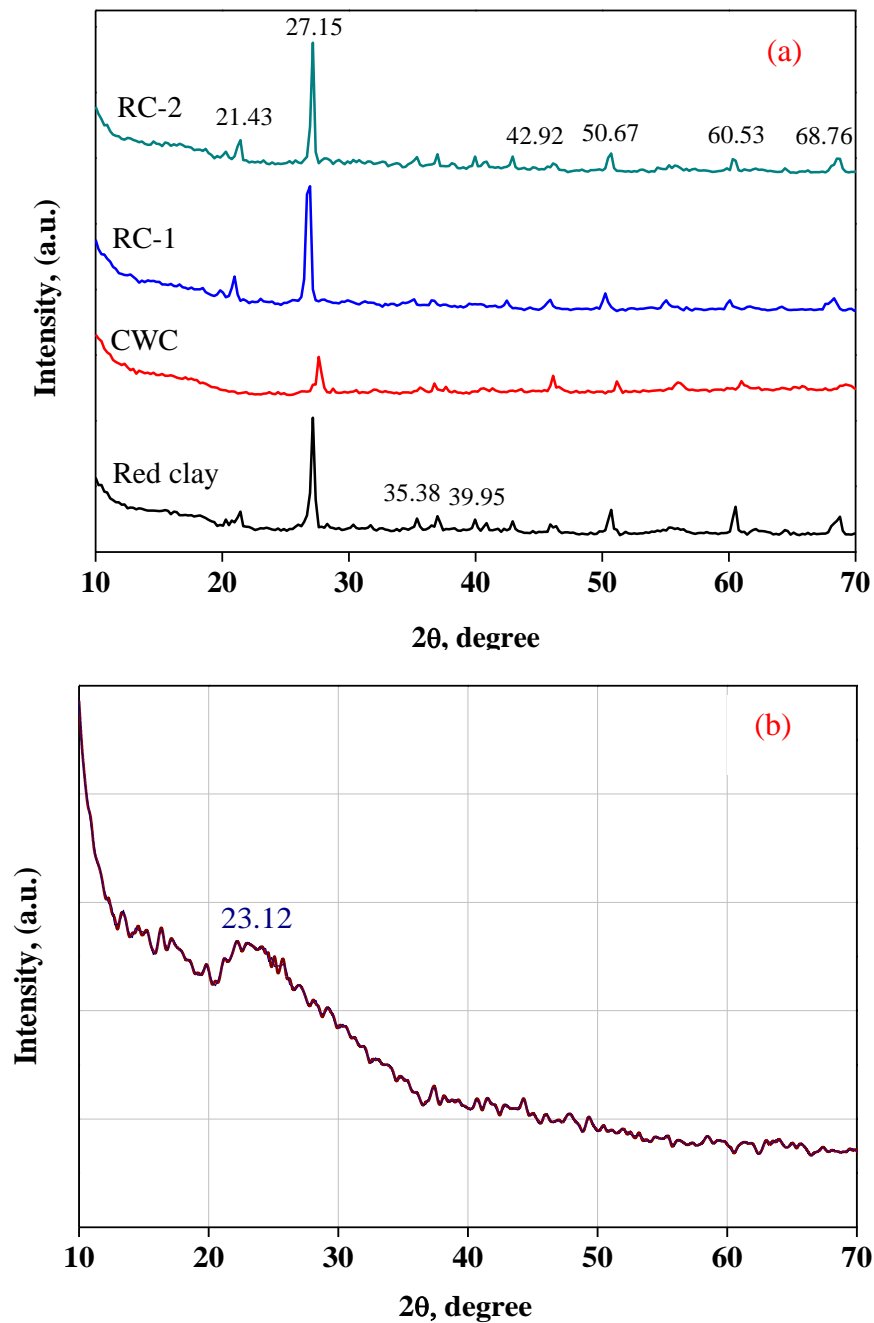


Figure 17: XRD patterns of (a) raw materials and their geopolymer products (b) nano-silica extracted from RHA

The sample's XRD patterns were plotted between 20 to 70 °. The major peaks at $2\theta = 21.43, 27.15, 35.38, 50.67, 60.53, 68.76$ °. The peak around $2\theta = 21, 27$ denotes the material's dominant silica phases. The diffraction pattern is primarily amorphous, with few crystalline silica peaks. The hump in the region of $2\theta = 21-40$ indicates the changes

of crystalline to amorphous raw materials into geopolymer products. The XRD pattern of nano-silica figure (17b) shows a significant broad peak centered at a 2θ angle of 23.12° , indicating its amorphous nature. The particle size of nano-silica was found to be 10.37 nm.

After applying sodium pellets, the raw materials' XRD peaks decrease due to the dissolution of alumino-silicate and the formation of geopolymeric products. The same crystalline (Silica) transforms into semicrystalline phases and remains as silica after geopolymerisation.

4.3. FTIR Analysis

The FTIR spectra of silica, calcined white clay, and red clay are shown in following figure 18. The main absorption peaks at 570, 793, 952, 1060, 1463, 1642, 2853, 2925, 3382, 3446, 3696 cm^{-1} respectively. The peak band within the 600 - 900 cm^{-1} range appears due to the existence of Si-O/Al-O and bending vibrations of octahedrally coordinated Al is present. The product's broad absorption band around 1004-1027 cm^{-1} may be caused by the conversion of asymmetric stretching vibrations of Si-O-Al bonds into symmetric bonding, where Al is four-fold coordinated (Chindaprasirt et al. 2009). The absorption band at 1427- 1642 cm^{-1} indicates stretching vibrations of the C-O bond of CO_3^{2-} ions caused by the reaction of atmospheric CO_2 with alkali hydroxide (Phair and Deventer 2002) The absorption bands at 3382-3696, and 2925, cm^{-1} correspond to the stretching and bending vibrations of O-H and H-O-H bonds of water molecules.

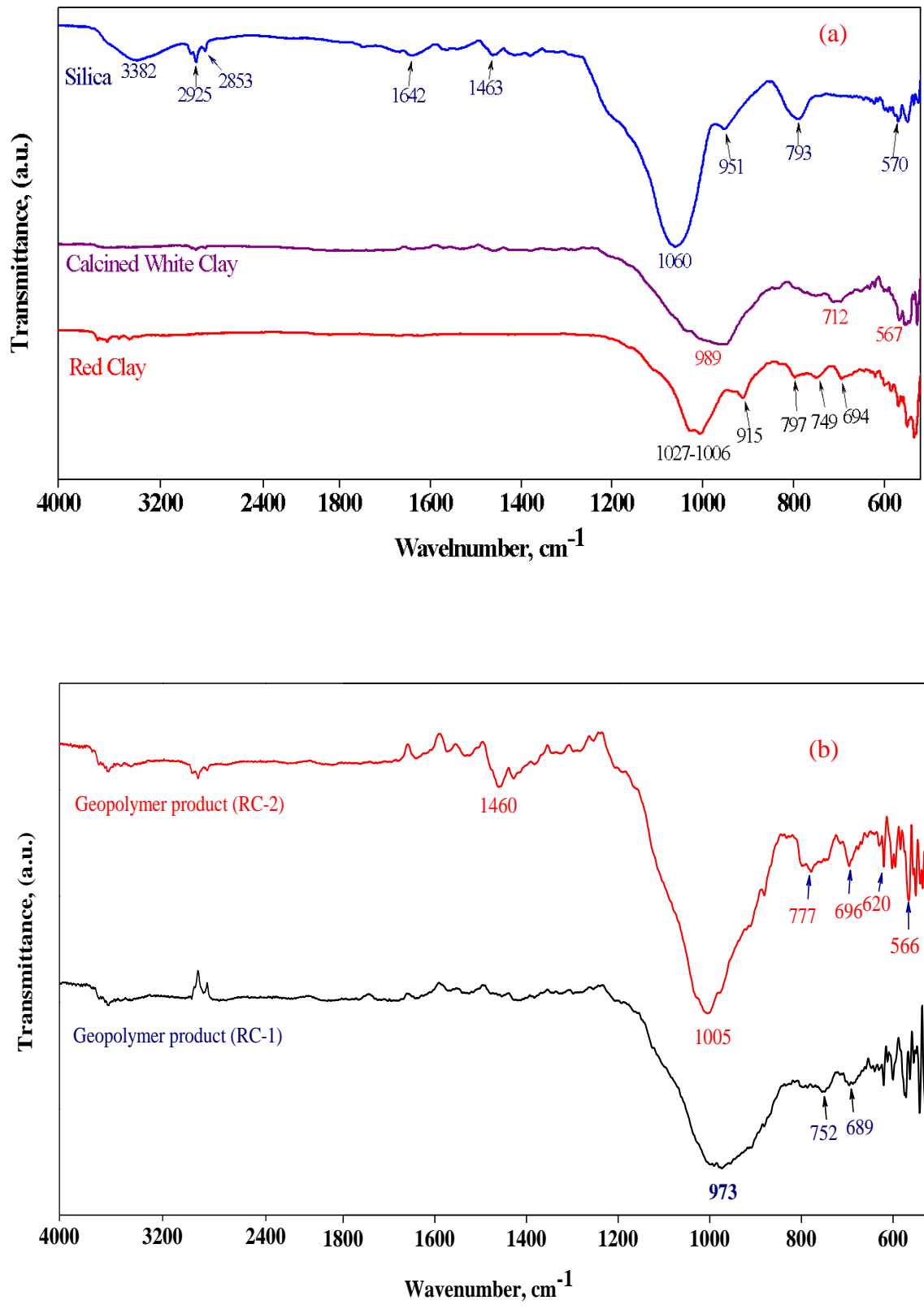


Figure 18: FTIR Spectra of raw materials (a) and its geopolymer products (b)

4.4. Mechanical Properties of the Geopolymer Products

4.4.1. Variation of Calcined White Clay (CWC)

The compressive strength of geopolymer products prepared by the red clay and with the variation of Calcined White Clay (CWC) is shown in the Figure (19).

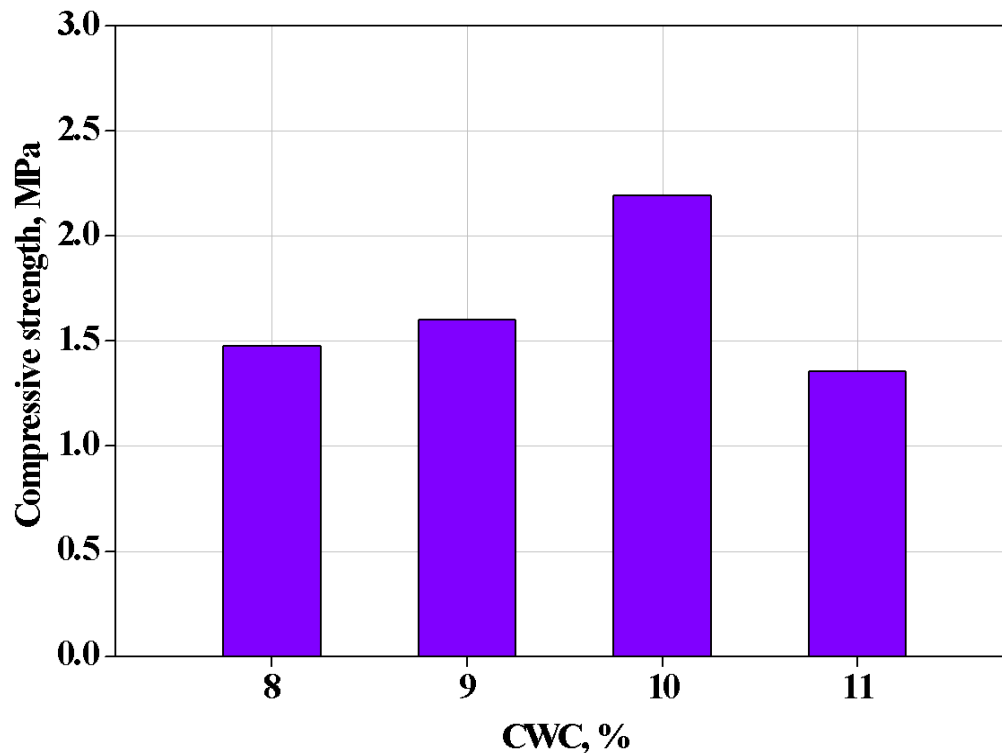


Figure 19: Plot of compressive strength of geopolymer product with CWC% variation

At 7 days of curing, the compressive strength values of geopolymer products were 1.48, 1.60, 2.19, and 1.36, MPa for CWC % equal to 8, 9, 10, and 11% respectively. The maximum compressive strength value of 2.19 MPa was discovered in 10% of the CWC% variations. The calcined white clay's pozzolanic reactivity may be responsible for the increase in compressive strength value (Yanguatin et al. 2017).

4.4.2. Variation of Nano-silica

After the selection of 10% Calcined White Clay (CWC), the geopolymer product was prepared by mixing red clay and calcined white clay with nano-silica at different percentage variations as shown in Figure 20.

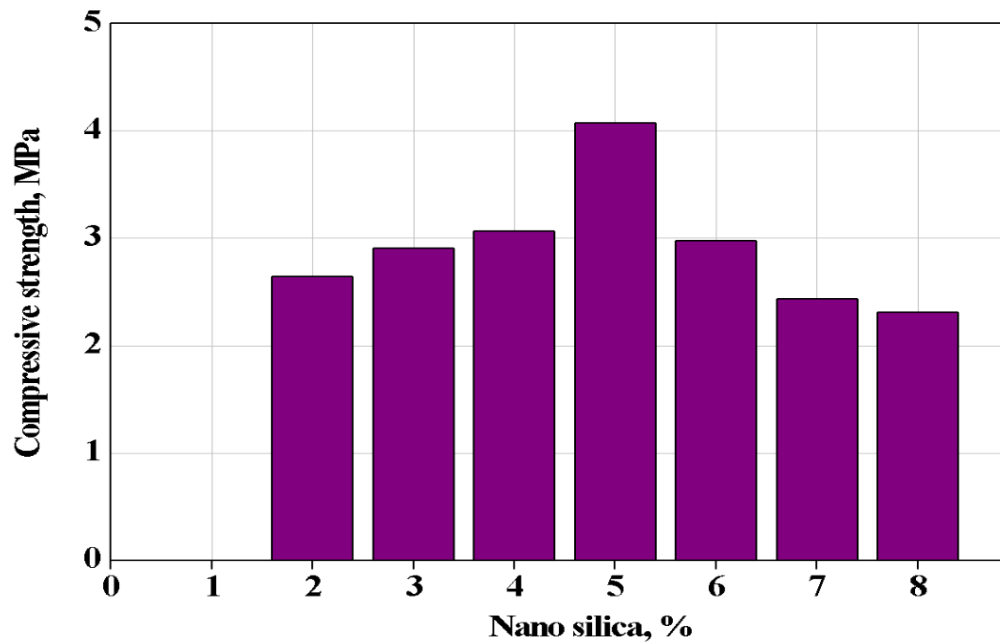


Figure 20: Plot of compressive strength of geopolymer product with Nano-silica % variation

The compressive strength values of nano-silica geopolymer were 2.64, 2.91, 3.07, 4.07, 2.97, 2.43, and 2.31 MPa for nano-silica concentrations equal to 2, 3, 4, 5, 6, 7 and 8 % respectively with 7 days of curing. The highest compressive strength value 4.07 MPa was found in 5% of the nano-silica % variations.

4.4.3. Variation of temperature

The compressive strength of geopolymer products (RC-2) with temperature variation is shown in Figure (22). The compressive strength values of geopolymer products were 2.57, 2.58, 4.00, 4.35, and 4.35 MPa at 50, 60, 65, 70 and 80 °C respectively. The compressive strength of geopolymer rises with temperature. This is because the

polymerization process increases as temperature rises (Nagral et al. 2014). Furthermore, the synthesis of geopolymer depends significantly on the curing temperature.

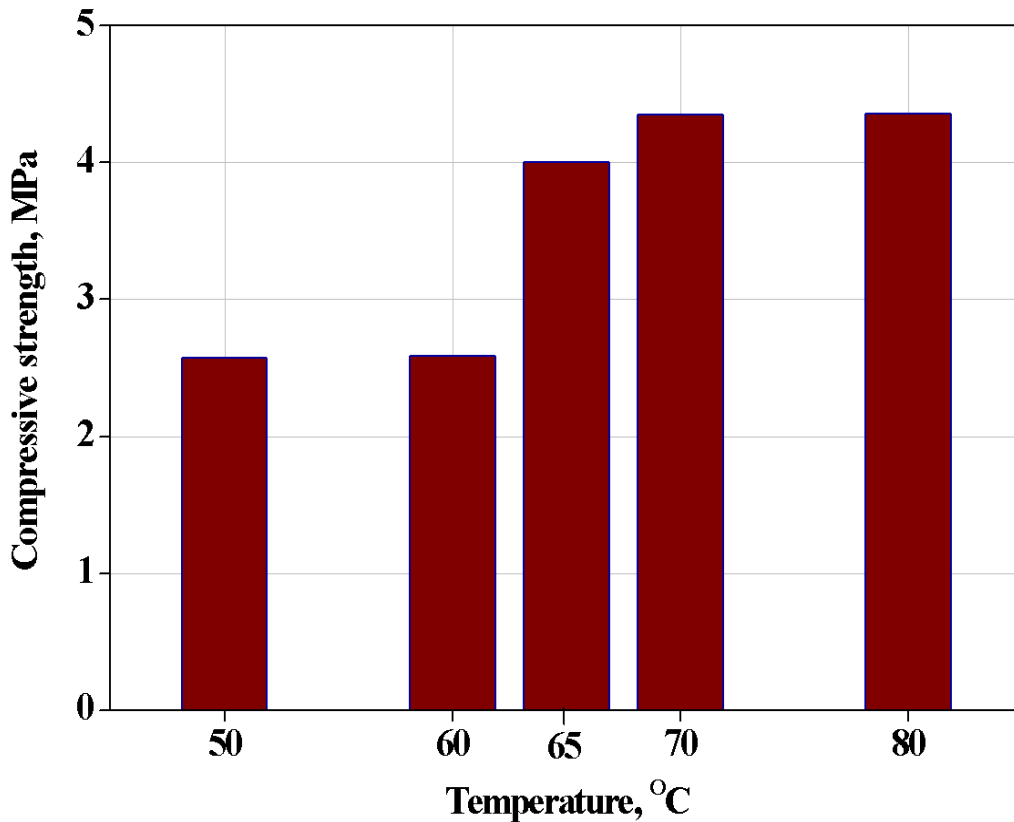


Figure 21: Plot of compressive strength of RC-2 with temperature variation

4.4.4. Variation the Curing period

After selecting 10% Calcined White Clay (CWC), (RC-1), 5% nano-silica (RC-2), 2% lime (RC-3), 20% sand (RC-4). Geopolymer products were cured for 7-28 days at 65 °C, as illustrated in the Figure below.

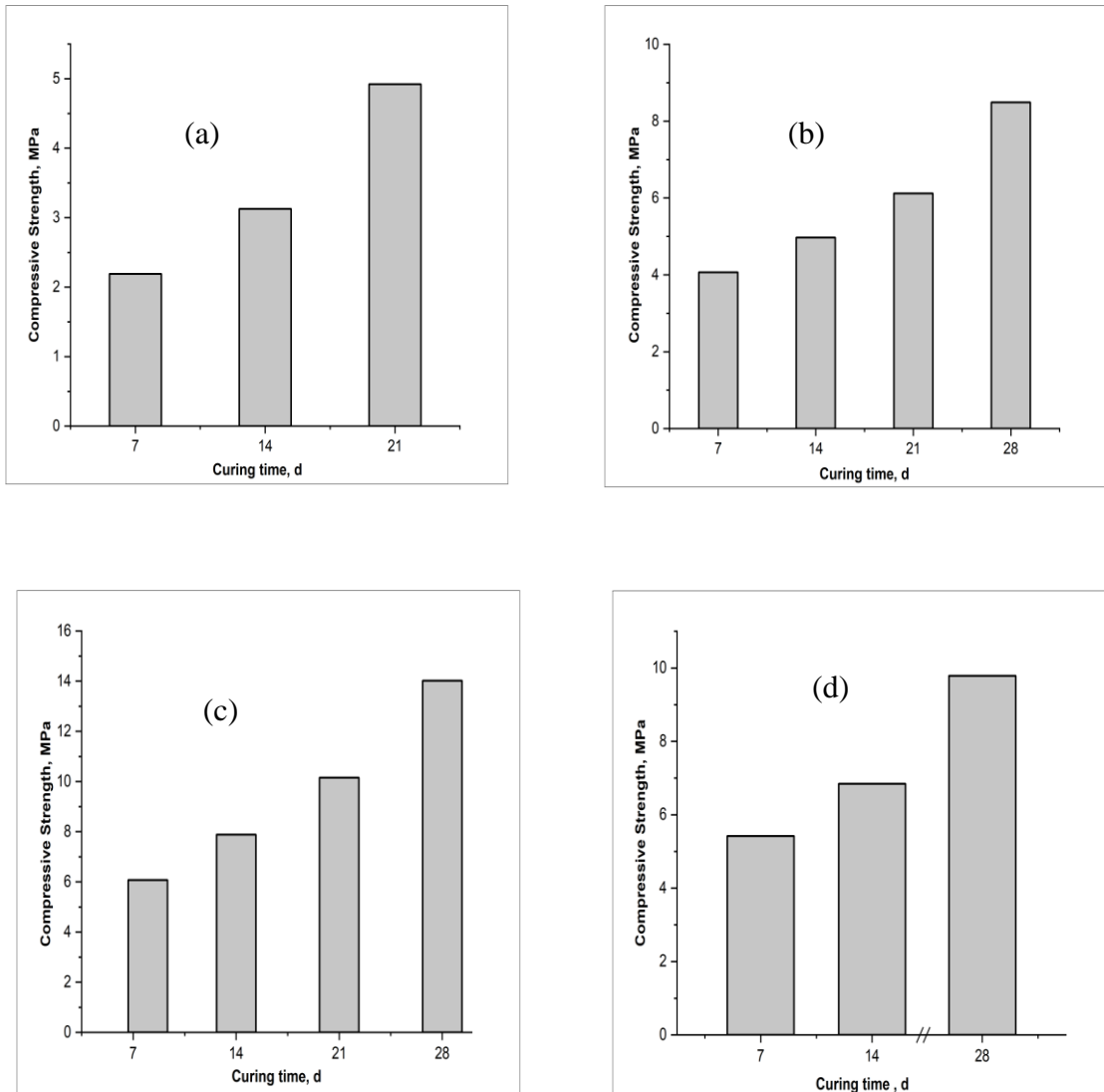


Figure 22: Plots of compressive strength of geopolymer products with a curing time RC-1 (b) RC-2 (c) RC-3 (d) RC-4

The compressive strength values of geopolymer products of RC-1 RC-4 were found to be 2.19, 3.13, 4.92 MPa 5.42, 6.85, 9.79 MPa at 7, 14, 21 and 28 days of curing time respectively at the temperature of 65 °C. Similarly, RC-2 and RC-3 were found to be 4.070, 4.97, 6.12, 8.49 MPa and 6.07, 7.88, 10.15, 14.02 MPa at 7, 14, 21 and 28 days of curing time respectively at the temperature of 65 °C.

The compressive strength values increase with the curing period in all RC-1, RC-2, RC-3, and RC-4 plots. From the above figure, the compressive strength values were found higher in the RC-3 plot. Similarly, the lowest compressive strength values were found in

the RC-1 plot. At low temperatures, geopolymer precursors condense, and water molecules evaporate, avoiding the formation of voids and cracks and enhancing compressive strength (Kani and Allahverdi 2009) This suggests that the cure for synthesizing geopolymers with higher compressive strength requires a longer period at a lower temperature

4.4.5. Thermal stability of geopolymer products

After 56 days, geopolymer products RC-1 and RC-2 were subjected to a thermal stability test at 300 and 400 °C. The compressive strength of RC-1 and RC-2 heated at 300 °C and 400 °C is shown in Figure (23). The compressive strength values of geopolymer products RC-1 were 17.01 and 20.18 MPa at 300 and 400 °C whereas, the compressive strength of geopolymer products RC-2 were 19.06 and 22.49 MPa at 300 and 400 °C. The compressive strength values increase with an increase in temperature.

This graph shows that the compressive strength of RC-2 is more than RC-1. The inclusion of nano-silica may account for the greater compressive strength values of RC-2. The goal of adding nano-silica to the cement mixture is to boost durability because nano-silica particles may fill the spaces between cement particles. Also, the inclusion of nano-silica increased the compactness of reaction products. Nano-silica contributes to a compact, dense microstructure with improved interlocking morphology, leading to increased compressive strength (Deb et al. 2015).

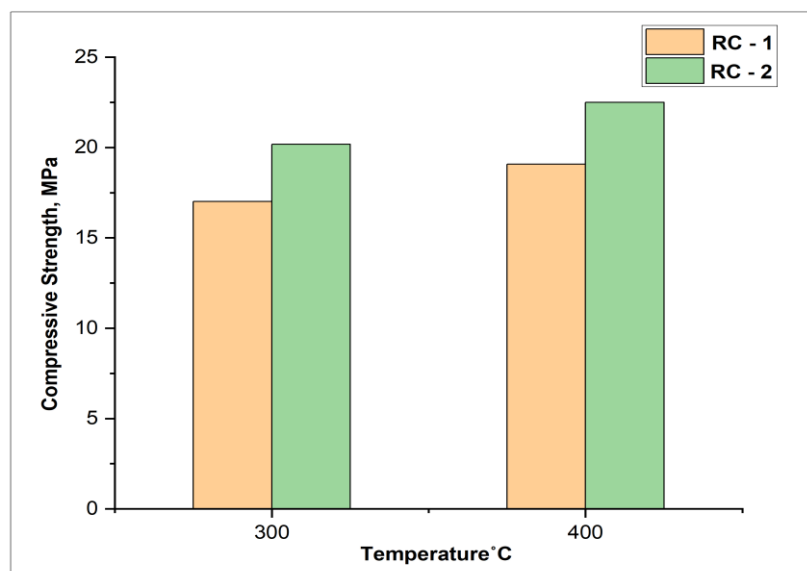


Figure 23: Plot of compressive strength of RC-1 and RC-2 at 300 °C and 400 °C

4.5. Physical properties of geopolymer products

Water absorption is a significant impact on building material's durability. Lower water absorption values indicate greater resistance to water infiltration and environmental harm. The physical characteristics of the geopolymer products (bulk density, apparent specific gravity, water absorption, and apparent porosity) were measured over 28 days. The apparent porosity and water absorption were found higher in RC- 4 while lower in RC- 3.

Table 3: Physical properties of geopolymer product 28 days

Samples	Apparent Porosity (%)	Water Absorption (%)	Apparent Specific Gravity (%)	Bulk Density (g/cm³)
RC-1	11.46	5.92	2.18	1.93
RC-2	10.79	5.60	2.18	1.94
RC-3	4.41	2.32	1.98	1.90
RC-4	12.68	6.49	2.24	1.96
RC-2 heated at 300 °C for 1 hour	8.62	5.07	2.76	1.71

CHAPTER 5

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this work, the impact of various factors on the properties of geopolymers was investigated to optimize their performance for possible uses in construction materials. Systematic experiments were performed to assess the effects of CWC content, nano silica content, temperature, curing period, and thermal treatment on properties of geopolymers. Among different CWC variations, 10% CWC concentration produced the maximum compressive strength. The addition of nano-silica improves mechanical properties and durability, indicating its potential as an important additive in geopolymer compositions. Among different nano-silica variations, the highest compressive strength was observed with 5% nano-silica content. Furthermore, it is found that temperature and curing period have a significant impact on the development of geopolymer strength, with higher temperatures and longer curing periods often resulting in improved properties.

The highest compressive strength, 22.94 MPa, was recorded on thermal treatment of the RC-2 at 400 °C. On thermal treatment at 300 °C, the compressive strength of RC-2 increased by 12.13%, and similarly on thermal treatment at 400 °C, the compressive strength of RC-2 increased by 11.49%. The compressive strength of RC-1 and RC-2 on thermal treatment (300 °C and 400 °C) shows that the compressive strength of RC-2 is more than RC-1. The higher values of compressive strength of RC-2 may be due to the addition of nano-silica. From this, it is concluded that thermal treatment is crucial in enhancing the thermal stability of geopolymer, and the using of nano-silica further enhances the quality of the geopolymer.

5.2. Recommendations

This technique is confronted with numerous obstacles. The construction industry is conservative by nature, there are no long-term durability data, and there is no standard technique to assess the performance of geopolymers. It becomes a viable substitute for OPC if red clay can be used to make a geopolymer with a comparable compressive strength.

REFERENCES

- Abhilash, P. P., Nayak, D. K., Sangoju, B., Kumar, R., and Kumar, V. **2021**. Effect of nano-silica in concrete; a review. *Construction and Building Materials*, 278, 1-19.
- Adesanya, D. A., and Raheem, A. A. **2009**. A study of the workability and compressive strength characteristics of corn cob ash blended cement concrete. *Construction and Building Materials*, 23(1), 311–317.
- Al-mashhadani, M. M., Canpolat, O., Aygörmez, Y., Uysal, M., and Erdem, S. **2018**. Mechanical and microstructural characterization of fiber-reinforced fly ash-based geopolymer composites. *Construction and Building Materials*, 167, 505–513.
- Assaedi, H., Alomayri, T., Shaikh, F., and Low, I. M. **2019**. Influence of nano-silica particles on the durability of flax fabric reinforced geopolymer composites. *Materials*, 12(9), 1459.
- Bajpai, R., Choudhary, K., and A Srivastava. **2020**. Environmental impact assessment of fly ash and silica fume-based geopolymer concrete. *Journal of Cleaner Production*, 254, 120147.
- Barani, K., and Kalantari, M. **2018**. Recovery of kaolinite from tailings of Zonouz kaolin-washing plant by flotation-flocculation method. *Journal of Materials Research and Technology*, 7(2), 142–148.
- Behfarnia, K., and Rostami, M. **2017**. Effects of micro and nanoparticles of SiO₂ on the permeability of alkali-activated slag concrete. *Construction and Building Materials*, 131, 205–213. <https://doi.org/10.1016/J.CONBUILDMAT.2016.11.070>
- Buchwald, A., Vicent, M., Kriegel, R., Kaps, C., Monzó, M., and Barba, A. **2009**. Geopolymeric binders with different fine fillers - Phase transformations at high temperatures. *Applied Clay Science*, 46(2), 190–195.
- Chindaprasirt, P., Homwuttiwong, S., and Jaturapitakkul, C. **2007**. Strength and water permeability of concrete containing palm oil fuel ash and rice husk-bark ash. *Construction and Building Materials*, 21(7), 1492–1499.

- Chindaprasirt, P., Jaturapitakkul, C., Chalee, W., and Rattanasak, U. **2009**. Comparative study on the characteristics of fly ash and bottom ash geopolymers. *Waste Management*, 29(2), 539–543.
- Das, S. K., Mishra, J., Singh, S. K., Mustakim, S. M., Patel, A., Das, S. K., & Behera, U. **2020**. Characterization and utilization of rice husk ash (RHA) in fly ash-blast furnace slag-based geopolymer concrete for a sustainable future. *Materials Today: Proceedings*, 33, 5162–5167.
- Das, S. K., Singh, S. K., Mishra, J., and Mustakim, S. M. **2020**. Effect of rice husk ash and silica fume as strength-enhancing materials on properties of modern concrete—A Comprehensive Review. *Lecture Notes in Civil Engineering*, 61, 253–266.
- Davidovits, J. **1989**. Geopolymers and geopolymeric materials. *Journal of Thermal Analysis*, 35(2), 429–441.
- Davidovits, J. **1991**. Geopolymers: inorganic polymeric new materials. *Journal of Thermal Analysis and Calorimetry*, 37(8), 1633–1656.
- Davidovits, J. **1994**. Geopolymers: man-made rock geosynthesis and the resulting development of very early high-strength cement. *Journal of Materials Education*, 91–91.
- Deb, P. S., Sarker, P. K., and Barbhuiya, S. **2015**. Effects of nano-silica on the strength development of geopolymer cured at room temperature. *Construction and Building Materials*, 101, 675–683.
- Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G. C., Palomo, A., and Van Deventer, J. S. J. **2007**. Geopolymer technology: The current state of the art. *Journal of Materials Science*, 42(9), 2917–2933.
- El-Kholy, S., Hasan, H., and AG Asran. **2018**. Experimental studies on effects of alkaline solution type on behavior of zeolite & red-mud based geopolymer mortar. *Lifesciencesite.Com*, 15(4), 31–39.
- Givi, A. N., Abdul Rashid, S., Aziz, F. N. A., and Salleh, M. A. M. **2010**. Experimental investigation of the size effects of SiO₂ nano-particles on the mechanical properties of binary blended concrete. *Composites Part B: Engineering*, 41(8), 673–677.

- Gleize, P. J. P., Müller, A., and Roman, H. R. **2003**. Microstructural investigation of a silica fume-cement-lime mortar. *Cement and Concrete Composites*, 25(2), 171–175.
- Güneyisi, E., Gesoglu, M., Azez, O. A., and Öz, H. Ö. **2016**. Effect of nano-silica on the workability of self-compacting concretes having untreated and surface treated lightweight aggregates. *Construction and Building Materials*, 115, 371–380.
- Habert, G., D’Espinoze De Lacaillerie, J. B., and Roussel, N. **2011**. An environmental evaluation of geopolymer based concrete production: Reviewing current research trends. *Journal of Cleaner Production*, 19(11), 1229–1238.
- Hardjito, D. **2004**. On the development of fly ash-based geopolymer concrete: *ACI Materials*. 467-472
- He, J., Jie, Y., Zhang, J., Yu, Y., and Zhang, G. **2013**. Synthesis and characterization of red mud and rice husk ash-based geopolymer composites. *Cement and Concrete Composites*, 37(1), 108–118
- Hossain S. K.S., Mathur Lakshya, and Roy P. K. **2018**. Rice husk/rice husk ash as an alternative source of silica in ceramics: A review. *Journal of Asian Ceramic Societies*, 6(4), 299–313.
- Hossain, S. S., Roy, P. K., and C. J. **2021**. Utilization of waste rice husk ash for sustainable geopolymer: A review. *Construction and Building Materials*, 310, 125218
- Jal, P. K., Sudarshan, M., Saha, A., Patel, S., and Mishra, B. K. **2004**. Synthesis and characterization of nano-silica prepared by precipitation method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 240(1–3), 173–178.
- Kabir, S. M. A., Alengaram, U. J., Jumaat, M. Z., Sharmin, A., and Islam, A. **2015**. Influence of molarity and chemical composition on the development of compressive strength in POFA-based geopolymer mortar. *Advances in Materials Science and Engineering*, 2015.
- Kani, E. N., and Allahverdi, A. **2009**. Effects of curing time and temperature on strength development of inorganic polymeric binder based on natural pozzolan. *Journal of Materials Science*, 44(12), 3088–3097.

- Kaur, K., Singh, J., and Kaur, M. **2018**. Compressive strength of rice husk ash based geopolymer: The effect of alkaline activator. *Construction and Building Materials*, 169, 188–192.
- Kaze, C. R., Adesina, A., Laure Lecomte-Nana, G., Sontia Metekong, J. V., Van Essa KamgaSamen, L., Kamseu, E., and Melo, U. C. **2021**. Synergetic effect of rice husk ash and quartz sand on microstructural and physical properties of laterite clay based geopolymer. *Journal of Building Engineering*, 43, 103229.
- Khater, H. M. **2013**. Effect of silica fume on the characterization of the geopolymer materials. *International Journal of Advanced Structural Engineering*, 5, 1-10.
- Komljenović, M., Bašćarević, Z., and Bradić, V. **2010**. Mechanical and microstructural properties of alkali-activated fly ash geopolymers. *Journal of Hazardous Materials*, 181(1–3), 35–42.
- Komnitsas, K. A. **2011**. The potential of geopolymer technology towards green buildings and sustainable cities. *Procedia Engineering*, 21, 1023–1032.
- Kong, I.N.G., Khoo, K. M., and O Buddrick. **2018**. Synthesis and characterization of red mud and sawdust-based geopolymer composites as potential construction material. *Materials Science Forum*, 923, 130–134.
- Kong, D. L. Y., and Sanjayan, J. G. **2008**. Damage behavior of geopolymer composites exposed to elevated temperatures. *Cement and Concrete Composites*, 30(10), 986–991.
- Korniejenko, K., Lin, W. T., and Šimonová, H. **2020**. Mechanical Properties of Short Polymer Fiber-Reinforced Geopolymer Composites. *Journal of Composites Science*, 4(3), 128.
- Kumar, P., Pankar, C., Manish, D., and Santhi, A. S. **2018**. Study of mechanical and microstructural properties of geopolymer concrete with GGBS and Metakaolin. *Materials Today: Proceedings*, 5(14), 28127–28135.
- Laskar M. Sulaem. **2020**. Alternate materials for sustainable construction technology a state-of-the-art report. In *Department of Civil Engineering*. 1-36

- Le, V., Do, Q. M., Hoang, M. D., Pham, V. T. H. Q., Bui, T. H., and Nguyen, H. T. **2018**. Effect of Alkaline Activators on Engineering Properties of Geopolymer-Based Materials Synthesized from Red Mud. *Key Engineering Materials*, 777, 508–512.
- Lemougna, P. N., ChinjeMelo, U. F., Delplancke, M. P., and Rahier, H. **2013**. Influence of the activating solution composition on the stability and thermo-mechanical properties of inorganic polymers (geopolymers) from volcanic ash. *Construction and Building Materials*, 48, 278–286.
- Li, C., Sun, H., and Li, L. **2010**. A review: The comparison between alkali-activated slag (Si + Ca) and metakaolin (Si + Al) cement. *Cement and Concrete Research*, 40(9), 1341–1349.
- Li, O. H., Yun-Ming, L., Cheng-Yong, H., Bayuaji, R., Abdullah, M. M. A. B., Loong, F. K., Jin, T. S., Teng, N. H., Nabialek, M., Jež, B., and Sing, N. Y. **2021**. Evaluation of the effect of silica fume on amorphous fly ash geopolymers exposed to elevated temperature. *Magnetochemistry*, 7(1), 1–14.
- Lingyu, T., Dongpo, H., Jianing, Z., and Hongguang, W. **2021**. Durability of geopolymers and geopolymer concretes: A review. *Reviews on Advanced Materials Science*, 60(1), 1–14.
- Liu, X., Jiang, J., Zhang, H., Li, M., Wu, Y., Guo, L., Wang, W., Duan, P., Zhang, W., and Zhang, Z. **2020**. Thermal stability and microstructure of metakaolin-based geopolymer blended with rice husk ash. *Applied Clay Science*, 196, 105769.
- Martin, S., Miroslava, K., Ivana, K., Frantiska, M., & Maria, P. **2010**. The evaluation of geopolymer properties prepared by alkali activation of black coal ashes with high content of loss on ignition. *Citeseer*, 15, 277–282.
- Mohmmad, S. H., Shakor, P., Muhammad, J. H., Hasan, M. F., and Karakouzian, M. **2023**. Sustainable alternatives to cement: synthesizing metakaolin-based geopolymer concrete using nano-silica. *Construction Materials*, 3(3), 276–286.
- Nagral, M. R., Ostwal, T., and Chitawadagi, M. V. **2014**. Effect of curing temperature and curing hours on the properties of geo-polymer concrete. *International Journal of Computational Engineering Research*, 04(9), 2250–3005.

- Nicholson, C., Fletcher, R., Miller, N., and Stirling, C. **2005**. Building innovation through geopolymer technology. *Chemistry in New Zealand*, 69(3), 10.
- Patankar, S. V., Ghugal, Y. M., and Jamkar, S. S. **2014**. Effect of concentration of sodium hydroxide and degree of heat curing on fly ash-based geopolymer mortar. *Indian Journal of Materials Science*, 2014, 1–6.
- Pathak, A., and Jha, V. K. **2012**. Synthesis of geopolymer from inorganic construction waste. *Journal of Nepal Chemical Society*, 30, 45–51.
- Pathak, A., Kumar, S., and Jha, V. K. **2014**. Development of building material from geopolymerization of construction and demolition waste (CDW). *Transactions of the Indian ceramic society*, 73(2), 133–137.
- Pathak, A., Pokharel, N., and Jha, V. K. **2014**. A Green Building Material from Demolition Waste. *IOE Graduate Conference*, 127–130.
- Phair, J. W., and Van Deventer, J. S. J. **2002**. Effect of the silicate activator pH on the microstructural characteristics of waste-based geopolymers. *International Journal of Mineral Processing*, 66(1–4), 121–143.
- Phoongernkham, T., Chindaprasirt, P., Sata, V., Hanjitsuwan, S., and Hatanaka, S. **2014**. The effect of adding nano-SiO₂ and nano-Al₂O₃ on properties of high calcium fly ash geopolymer cured at ambient temperature. *Materials and Design*, 55, 58–65.
- Phoongernkham, T., Hanjitsuwan, S., Damrongwiriyanupap, N., and Chindaprasirt, P. **2017**. Effect of sodium hydroxide and sodium silicate solutions on strengths of alkali-activated high calcium fly ash containing Portland cement. *KSCE Journal of Civil Engineering*, 21(6), 2202–2210.
- Premaratne, W., Priyadarshana, W., Gunawardena, S., Alwis, A. DE, and Premaratne W. **2013**. Synthesis of nanosilica from paddy husk ash and their surface functionalization. *Journal of science, University of Kelaniya*, 8, 33–48.
- Rahmawati, C., Aprilia, S., Saidi, T., and Aulia, T. B. **2021**. Current development of geopolymer cement with nano-silica and cellulose nanocrystals. *Journal of Physics: Conference Series*, 1783(1), 012056.

- Raja, V. K. B., Raj, S. K., Sairam, M. D., Kasyap, A. V. R. S., Kumar, V. G., Padmapriya, R., Baalamurugan, J., and Sonawane, P. D. **2021**. Geopolymer green technology. *Materials Today: Proceedings*, *46*, 1003–1007.
- Rangan, B. V., Rangan, B. V., Fieaust, P., and Faci, C. **2008**. *Fly ash-based geopolymer concrete*.
- Rapazote, G., Laginhas J, and A. Teixeira-Pinto. **2011**. Development of building materials through alkaline activation of construction and demolition waste (CDW)-Resistance to acid attack. *Advances in Science and Technology*, *69*, 156–163.
- Reig, L., Tashima, M. M., Borrachero, M. V., Monzó, J., Cheeseman, C. R., and Payá, J. **2013**. Properties and microstructure of alkali-activated red clay brick waste. *Construction and Building Materials*, *43*, 98–106.
- Rezania, M., Panahandeh, M., Razavi, N., and Berto, F. **2019**. Experimental study of the simultaneous effect of nano-silica and nano-carbon black on permeability and mechanical properties of the concrete. *Theoretical and Applied Fracture Mechanics*, *104*, 102391.
- Ridtirud, C., Chindaprasirt, P., and Pimraksa, K. **2011**. Factors affecting the shrinkage of fly ash geopolymers. *International Journal of Minerals, Metallurgy and Materials*, *18*(1), 100–104.
- Ruben, N., Venkatesh, C., Sri, M., Chand, R., and Nerella, R. **2019**. a state of the art on red mud as a substitutional cementitious material. *In Annales de Chimie Science Des Materiaux*, *43*(2), 99-106.
- Saludung, A., Ogawa, Y., and Kawai, K. **2018**. Microstructure and mechanical properties of FA/GGBS-based geopolymer. *MATEC Web of Conferences*, *195*, 1-8.
- Sapute M. B., Wakchaure Madhukar R., and Patankar Subash V. **2012**. Effect of duration and temperature of curing on compressive strength of geopolymer concrete. *International Journal of Engineering and Innovative Technology*, *1*(5), 152-155.
- Venkatesan, R. P., and Pazhani, K. C. **2015**. Strength and durability properties of geopolymer concrete made with Ground Granulated Blast Furnace Slag and Black Rice Husk Ash. *KSCE Journal of Civil Engineering* *20*, 2384–2391.

- Xu, H., and Deventer, V. J. S. J. **2000**. The geopolymerisation of alumino-silicate minerals. *International Journal of Mineral Processing*, 59(3), 247–266.
- Yanguatin, H., Tobón, J., and Ramírez, J. **2017**. Pozzolanic reactivity of kaolin clays, a review Reactividad puzolánica de arcillascaoliníticas, unarevisión. *RevistaIngenieria de Construccion*, 32(2), 13–24.
- Yanzhao, Z., Pu, S., Li, R. Y. M., and Zhang, J. **2020**. Microscopic and mechanical properties of undisturbed and remolded red clay from Guiyang, China. *Scientific Reports*, 10(1), 1–14.
- Zhang, M. H., Islam, J., and Peethamparan, S. **2012**. Use of nano-silica to increase early strength and reduce the setting time of concretes with high volumes of slag. *Cement and Concrete Composites*, 34(5), 650–662.

APPENDIX I

Photo plates



Wet mixing of raw materials



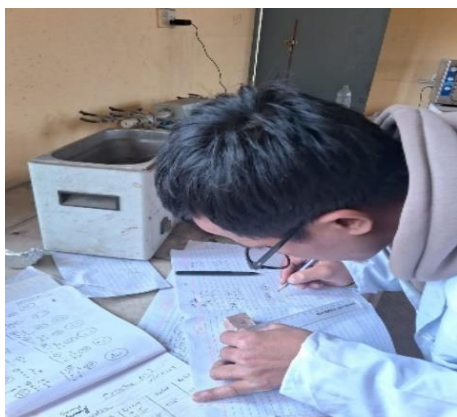
Casting geopolymer sample



Casting Sample



Geopolymer cubes (RC-1)



Measuring the geopolymer cube



Weighing the suspended sample