Ceramics-Silikáty 66 (4), 508-519 (2022)
www.ceramics-silikaty.cz doi: 10.13168/cs.2022.0047

INFLUENCE OF ZEOLITE ON THE CONCENTRATION OF ALKALINE ACTIVATOR IN RICE HUSK ASH BASED GEOPOLYMER MORTAR

#R. INDRAJITH KRISHNAN*, #S. NAGAN**

*Department of Civil Engineering, Thiagarajar College of Engineering, Madurai, TamilNadu, India 625015
**Department of Civil Engineering, Thiagarajar College of Engineering, Madurai, TamilNadu, India 625015

#E-mail: jith@tce.edu, nagan_civil@tce.edu

Submitted August 24, 2022; accepted September 29, 2022

Keywords: Geopolymer binder, Compressive strength, X-Ray Diffraction pattern, Fourier Transform Infra-red spectroscopy, Scanning Electron Microscope

The research aims to prepare a geopolymer mortar with rice husk ash (RHA) and zeolite. The use of RHA as a geopolymer binder that has a higher silica and low alumina content, reduces the polymerisation process. Zeolite is a natural aluminosilicate material containing the alumina content required for the polymerisation process. The compressive strength and microstructure properties of geopolymer mortar were examined for various molar concentrations and proportions of RHA and zeolite. Two different curing processes were used in this study, namely heat and ambient curing conditions. The results indicated that the compressive strength of the geopolymer mortar decreases with an increase in the proportion of zeolite. The heat curing seems to be more beneficial than the ambient curing regime. Also, an increase in the sodium hydroxide concentration increases the compressive strength of the prepared geopolymer mortar up to 12 M. The optimum percentage of zeolite replacement was found to be 10 %.

INTRODUCTION

Concrete has become a crucial component of the developing world as it has to meet the infrastructure needs of the growing world population. Thus, the demand for building the infrastructure is ever increasing and makes concrete second only to water concerning usage [1]. The use of concrete copiously increases, which, in turn, increases the need to manufacture more cement. One of the serious environmental hazards in cement manufacturing is the release of CO_2 emissions into the atmosphere [2, 3]. Thus, it has become a significant concern when considering the ecosystem. For every tonne of Ordinary Portland Cement (OPC) produced, around 640 kg of CO_2 are generated during the calcination of limestone and the combustion of fossil fuels [4]. A promising solution to mitigate the environmental impact of concrete is minimising its cement content. Accordingly, an alternative binder is needed to reduce the CO_2 emissions [5].

On the other hand, waste material disposal poses another serious environmental problem. The waste materials from industrial and agricultural sectors create environmental degradation due to the improper disposal, such as heaps of agriculture and industrial waste or the creation of landfills in rather productive lands, rendering the land useless [6]. It is feasible to utilise these waste materials as a supplementary cementitious material (SCM), an alternative to cement that has no adverse effects on the properties of concrete [7].

Developing concrete without cement is necessary for creating an eco-friendly environment by reducing the cement production and consumption [8]. In 1978, Davidovits proposed that by-products or geologically derived source materials might produce binders by a polymeric reaction of silicon and aluminium with alkaline liquids. He called these adhesives geopolymers, which are inorganic alumino-silicate polymers synthesised from materials rich in silica and alumina content. The source materials could be by-products like fly ash (FA), rice husk ash (RHA), silica fume (SF), ground granulated blast furnace slag (GGBS), etc. or natural materials like metakaolin, zeolite, clay, etc. [9]. The reaction between the source material and an alkaline solution, including sodium hydroxide and sodium silicate, results in forming a binder with a 3-D polymeric chain structure composed of Si–O–Al–O links [10]. The polymerisation process which forms the geopolymer may be assisted by heat with temperatures ranging from 60 to 90 °C for 24-48 hours. This polymer binds the aggregates and the unreacted source material to form a geopolymer concrete. Water is not a constituent of the geopolymer binder's chemical reaction; water is expelled during the curing and subsequent drying. This is in contrast to the cement hydration reactions that occur when cement is mixed with water. This property has a significant effect on the mechanical and chemical properties of geopolymer concrete. Geopolymer concrete is more resistant to heat, water ingress, alkali-aggregate reactivity and other types of the chemical attack [11].

Rice husk is one of the significant agricultural wastes created in food production. The outer covering of the rice kernel is obtained by milling the paddy. A tonne of paddy can yield roughly 200 kg of rice husk or about one-fifth of the total amount of the rice produced [12]. The rice husk can be used as fuel in the rice mill boiler, small-scale electricity generation plants, and cattle feed. Although the rice husk can be used in various ways, open field burning is the primary disposal method. During combustion, rice husk yields 22 % of RHA. RHA has high pozzolanic activity and can be used as an SCM for concrete production. Due to the lack of disposal of RHA, it is often dumped on the land and exhibits adverse effects on the environment [13].

While burning the rice husk under controlled conditions, the RHA contains a high silica composition, similar to the properties of silica fume. The idea of using RHA as a geopolymer binder has not received extensive research efforts as of yet. RHA was added to a geopolymer, enhancing compressive strength while reducing the pore size by up to 55 % [12]. It developed a dense microstructure and improved the pore blocking efficacy. As the Si/Al ratio increased, the Si–O–Si bond becomes stronger, enhancing the strength of the geopolymer. Compared to other admixtures, concrete with rice husk has better durability characteristics. Hence, RHA can be referred to as source material for geopolymer binders.

The primary component of RHA is silica (83-98 %), with only trace amounts of CaO, MgO, K_2O, Al_2O_3, Fe_2O_3, and Na_2O [12]. RHA has negligible amount of alumina; hence, a secondary source material rich in alumina is required for geosynthesis. One such source material is natural zeolite. Since ancient times, natural zeolite, a hydrated aluminosilicate of alkali and alkaline earth cations with a three-dimensional frame structure, has been used extensively in construction. However, its application as a pervasive type of natural pozzolan in the production of pozzolanic cement started in the early 20th century and its use has been increasing in recent years. Chan [14] compared the efficacy of zeolite in enhancing a concrete's performance to that of fly ash and silica fume. It is reported that zeolite is more effective than fly ash in improving the compressive strength and durability, but it is less beneficial than silica fume. A limited number of studies have been undertaken on natural zeolite-based geopolymers. Alcantara Ortega [15] used calcium hydroxide as an activator in a natural zeolite-based geopolymer. The strength of the resulting geopolymeric material was found to be influenced by the sample preparation method, alkali content, and curing conditions. Hence, this study aims to evaluate the influence of natural zeolite and RHA as a binder in a geopolymer mortar while using various molar concentrations and curing regimes.

EXPERIMENTAL

Constituents

The materials used to prepare the geopolymer mortar included RHA, zeolite, a fine aggregate, an alkaline solution, a superplasticiser and water. In this investigation, Zone II river sand that complies with the IS 383-1970 standards and has a specific gravity of 2.63 was used. The alkaline solution was composed of sodium silicate and sodium hydroxide. The sodium hydroxide flakes from the local supplier were dissolved in water to prepare the desired molar concentration. The concentration of the solution decides the amount of the NaOH solids. The sodium silicate used in this experimental study is A53 commercial grade in the form of a gel. A naphthalene-based superplasticiser was used to attain the desired workability.

Rice Husk Ash

The RHA used in this study was collected from a nearby rice mill at Madurai in Tamil Nadu. The properties of the RHA strongly depend on the combustion method and burning temperature. RHA is generally produced according to three distinct processes: grate furnace, fluidised bed and suspension/entrained combustion. The operating conditions strongly influence the physical and chemical profiles of the obtained products. The silica present in the RHA by the fluidised bed and suspension combustion samples is amorphous, and those obtained by grate furnace combustion is cristobalite. The RHA collected from the rice mill used the fluidised bed combustion method. The collected RHA samples were characterised for X-Ray Diffraction (XRD), Fourier Transform Infra-red (FT-IR) Spectroscopy, X-Ray Fluorescence (XRF) and Scanning Electron Microscope (SEM) analysis to ascertain the reactivity of the RHA.

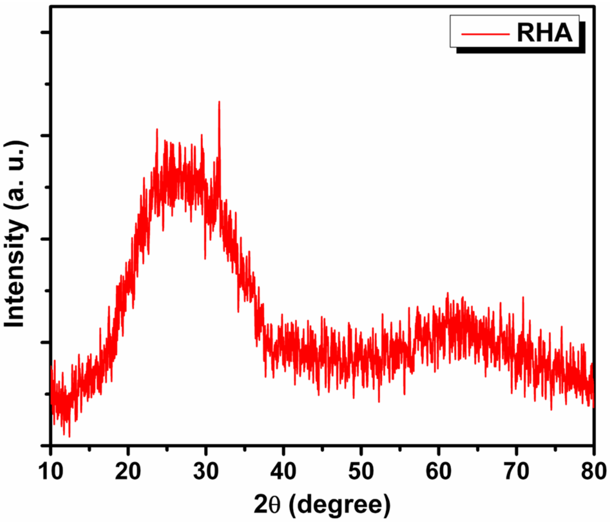
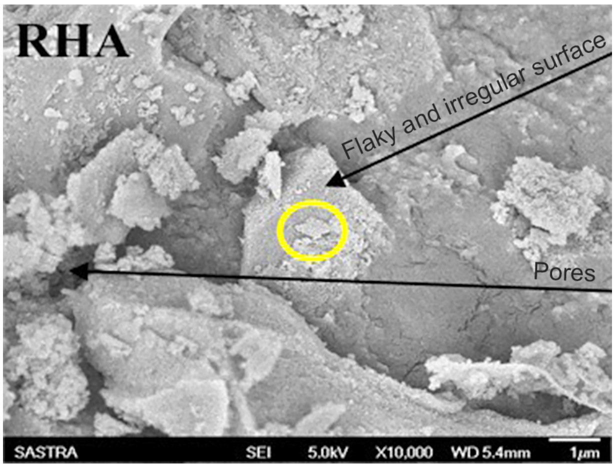
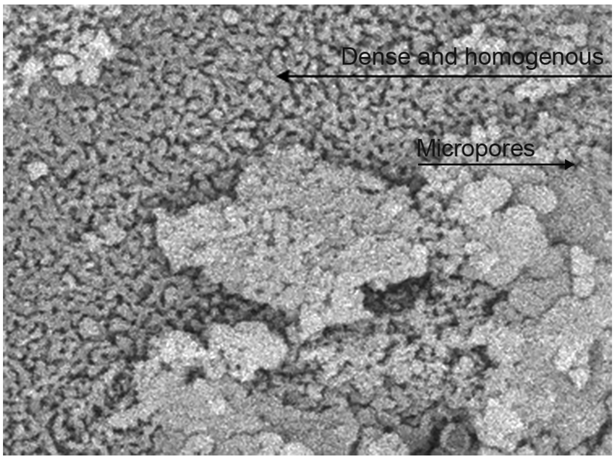


Figure 1. X-Ray Diffraction pattern for the RHA.

As shown in Figure 1, the collected RHA sample is highly amorphous from the XRD pattern. The XRF analysis in Table 1 shows the presence of silica as the only primary constituent in the RHA and other metal compounds, such as Al, Ca, Fe, Ti, K, P and S, as minor constituents. The investigation into the microstructure of the powdered RHA samples from the SEM analysis, as shown in Figure 2a, revealed that the RHA particles are flaky and have micropores leading to the material having a more specific surface area and the ability of the RHA to increase the water absorption. It was also observed from the magnified image shown in Figure 2b that the surface area is homogeneous and denser. It was observed from the SEM images that the RHA is untreated based on the pore sizes of approximately 40-50 nm. Hence, the other binding materials can blend easily within the pore size of the RHA to form a matrix. The chemical bonding formation of the collected RHA sample was found using FT-IR spectroscopy and is shown in Figure 3. From the FT-IR analysis, the RHA particles have no preformed bonds, and they contain metal oxide bonds. The specific surface area of the RHA was found using Blaine's air permeability test having a value of 655 $m^2 \cdot kg^{-1}$.



a)



b)

Figure 2. SEM analysis of the RHA (a) and magnified SEM analysis of the indicated area – 100 nm (b).

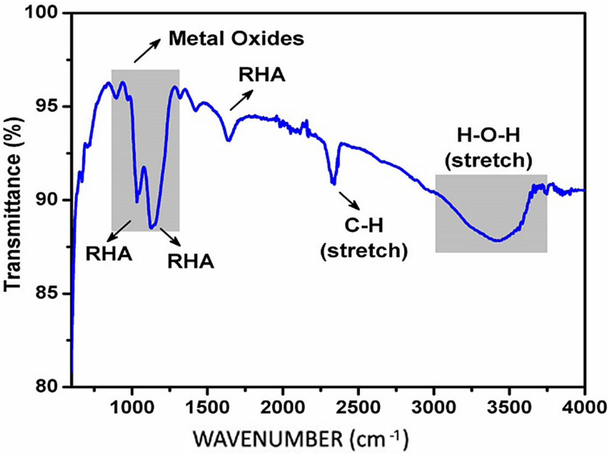


Figure 3. FT-IR spectrum of the RHA.

Zeolite

Zeolite is an alkaline earth cation-containing crystalline, hydrated alumino-silicate with infinite 3-D structures. Due to the significant content of reactive SiO_2 and Al_2O_3, natural zeolite exhibits pozzolanic activity, similar to other pozzolans. The zeolite powder used in this study is clinoptilolite of natural origin and was characterised by XRD, XRF, SEM and FT-IR analysis. From the XRD graph shown in Figure 4, the zeolite is multi-crystalline, and the peaks seen in the graph confirm JCPDS #00-071-0962 and #00-086-1110. The XRF analysis in Table 2 shows that the primary constituent of zeolite is silica, alumina, as a secondary constituent, and metal oxides, such as Fe, Ca, Na, Mg, K, Mn and Ti, as minor

Table 1. RHA chemical constituents from the XRF analysis.

Compounds	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O	P_2O_5	SO_3	LOI
RHA (wt. %)	91.45	0.70	0.26	0.90	0.12	1.87	0.61	0.04	4.03

Table 2. Zeolite chemical constituents from the XRF analysis.

Compounds	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	TiO_2	MgO	K_2O	MnO	LOI
Zeolite (wt. %)	74.62	7.72	2.76	0.17	0.36	0.02	1.92	0.66	1.06	10.71

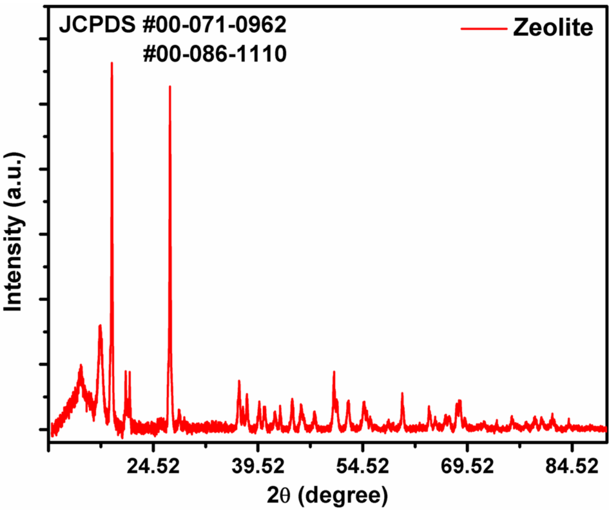
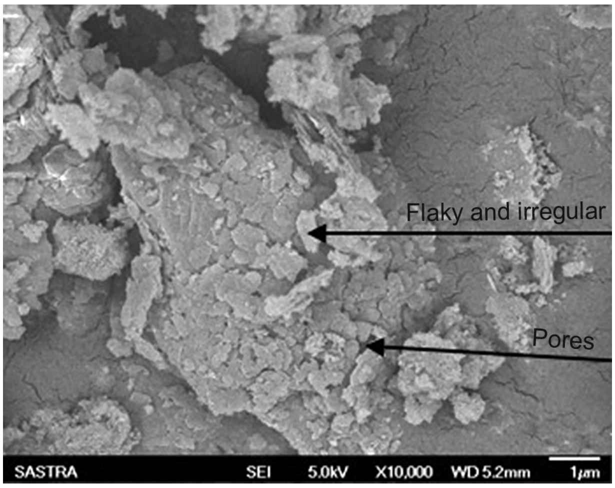
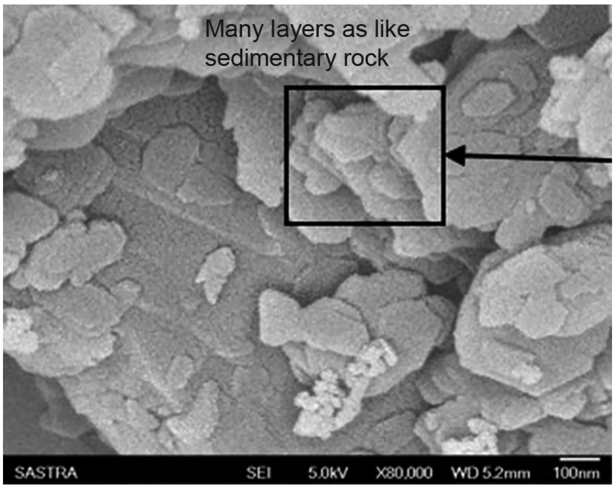


Figure 4. X-Ray Diffraction pattern for the zeolite.



a)



b)

Figure 5. SEM analysis of the zeolite (a) and magnified SEM analysis of the zeolite (b).

constituents. The SEM image in Figure 5 indicates that the zeolite is flaky and irregular. The enlarged SEM image shows that the particles are made of many layers, like sedimentary rocks, which tend to attract and retain the molecules that come into contact with it. From the SEM image in Figure 5a, the powdered zeolite shows random cracks on the surface. Additionally, the downward peaks in the FT-IR analysis shown in Figure 6 suggest the presence of an Si–O–Si bond in the zeolite, which means the alumina is not bonded with the silica and is available for polymerisation. The specific surface area of the zeolite was found using Blaine's air permeability test having a value of 483 $m^2 \cdot kg^{-1}$.

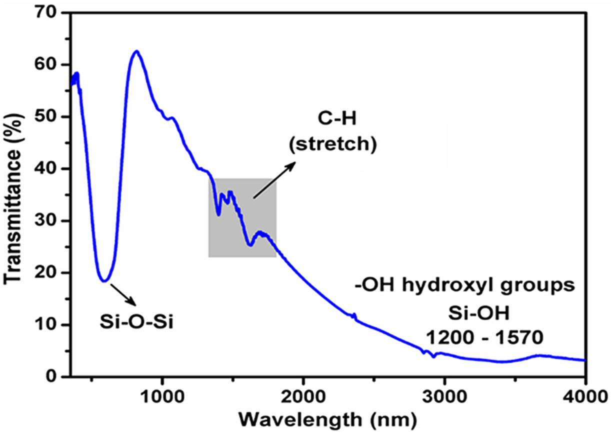


Figure 6. FT-IR spectrum of the zeolite.

Mix composition
and Specimen preparation

The geopolymer mortar was prepared by replacing the RHA with 10 %, 20 %, 30 %, and 40 % of zeolite. Table 3 indicates the mixture proportions for the geopolymer mortar. The letter Z in the mix designation indicates zeolite, and the numbers in the mix identification show the zeolite incorporation percentage. Moreover, C displays a control mixture with only RHA as a binder for the geopolymer mortar.

The alkaline solutions were prepared one day before casting. The mortar mixture was prepared using a Hobart mixer machine. The dry materials were mixed until homogeneity was obtained. Then alkaline solutions were added and mixed for 5 minutes, followed by adding a superplasticiser and extra water, if any. The mortar was filled into cube-shaped moulds of 70.7 mm and compacted by table vibration. The cast specimens were kept in the moulds for 24 hours at room temperature. After demoulding, one-half of the specimens were kept at room temperature for Ambient Curing (AC) till the date of testing. The remaining half of the specimens were placed in a Heat Curing (HC) chamber maintaining 60 °C for 24 hours and then kept at room temperature till testing.

Table 3. Geopolymer mortar mixture proportions.

Materials (in kg·m^{-3})	Mix Identification				
	C	Z10	Z20	Z30	Z40
RHA	348.17	313.35	278.53	243.71	208.9
Zeolite	–	33.34	66.68	100.03	133.38
Sand	1456	1456	1456	1456	1456
Sodium Hydroxide	59.43	59.43	59.43	59.43	59.43
Sodium Silicate	148.57	148.57	148.57	148.57	148.57
Super plasticiser (% by weight of cementitious material)	1.5	1.5	1.5	1.5	1.5

Tests on Geopolymer mortar

A slump flow test was used to find the flowability of the fresh geopolymer mortar. The superplasticiser dosage was kept constant to evaluate the influence of the zeolite with the different replacement percentages on the workability of the mix. The 70.7 mm cube-shaped specimens were used to determine the compressive strength of the mortar mixtures complying with IS 516-1959. The microstructure analysis was ascertained using SEM and FT-IR on the fractured samples.

RESULTS AND DISCUSSION

Workability

The effect of the zeolite addition on the flow characteristics of the geopolymer mortar was evaluated by a mini flow table test. These test results indicate the quality of the mortar towards its consistency. Figure 7 present the flow value in mm for the different mortar mixes. The test results show a negative impact on the workability of the mortar mixes due to the incorporation of the zeolite. It can be identified from Figure 7 that with the initial replacement, i.e., at 10 % replacement, the workability was on par with the control mix. However, with an increase in the zeolite content, there was a significant decrease in the workability of the mortar mixes. This aspect may be due to the high absorption property due to the microporous structure of the zeolite [16]. Also, it was found from the results that the workability becomes reduced with an increase in the molar concentration and similar results were also reported by Detphan [17], Hadi [18] and Patankar [19]. The percentage decrease in the flow for 10 %, 20 %, 30 % and 40 % of the RHA replacement with the zeolite were 2.7 %, 13.6 %, 27.3 % and 45.5 %, respectively, for the 12 M concentration.

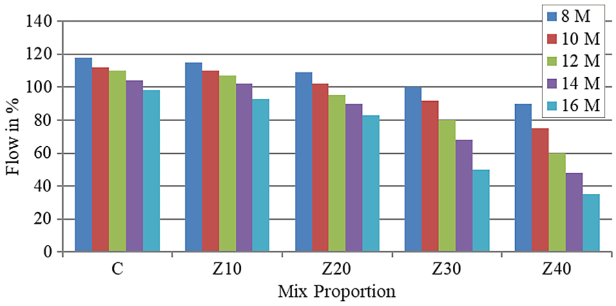


Figure 7. Workability of the geopolymer mortar mix.

Table 4. Geopolymer mortar's compressive strength.

Mix identification	Molar concentration (M)	Compressive Strength in MPa			
		AC		HC	
		7 days	28 days	7 days	28 days
C	8	4.29	5.56	9.14	9.87
	10	5.17	7.1	9.55	10.21
	12	6.56	8.15	11.38	11.54
	14	4.54	6.82	9.81	10.08
	16	4.48	6.21	9.25	9.83
Z10	8	9.52	11.54	14.54	15.62
	10	10.52	13.9	16.88	17.95
	12	12.24	15.12	21.63	23.29
	14	11.49	14.55	21.1	22.78
	16	10.97	13.25	19.68	21.61
Z20	8	8.52	11.08	13.86	14.3
	10	9.83	12.35	16.3	17.8
	12	10.23	13.7	19.47	21.82
	14	9.52	12.5	17.95	19.3
	16	8.82	11.29	15.19	17.17
Z30	8	7.36	10.71	11.65	12.8
	10	8.13	11.85	13.37	14.52
	12	9.91	13.37	17.72	18.49
	14	8.39	11.5	16.17	17.5
	16	7.99	10.96	14.35	15.8
Z40	8	7.04	10.03	10.52	11.87
	10	7.6	11	11.9	13.22
	12	8.01	11.39	14.8	16.63
	14	7.56	10.9	12.9	14.5
	16	6.8	9.86	11.95	13.1

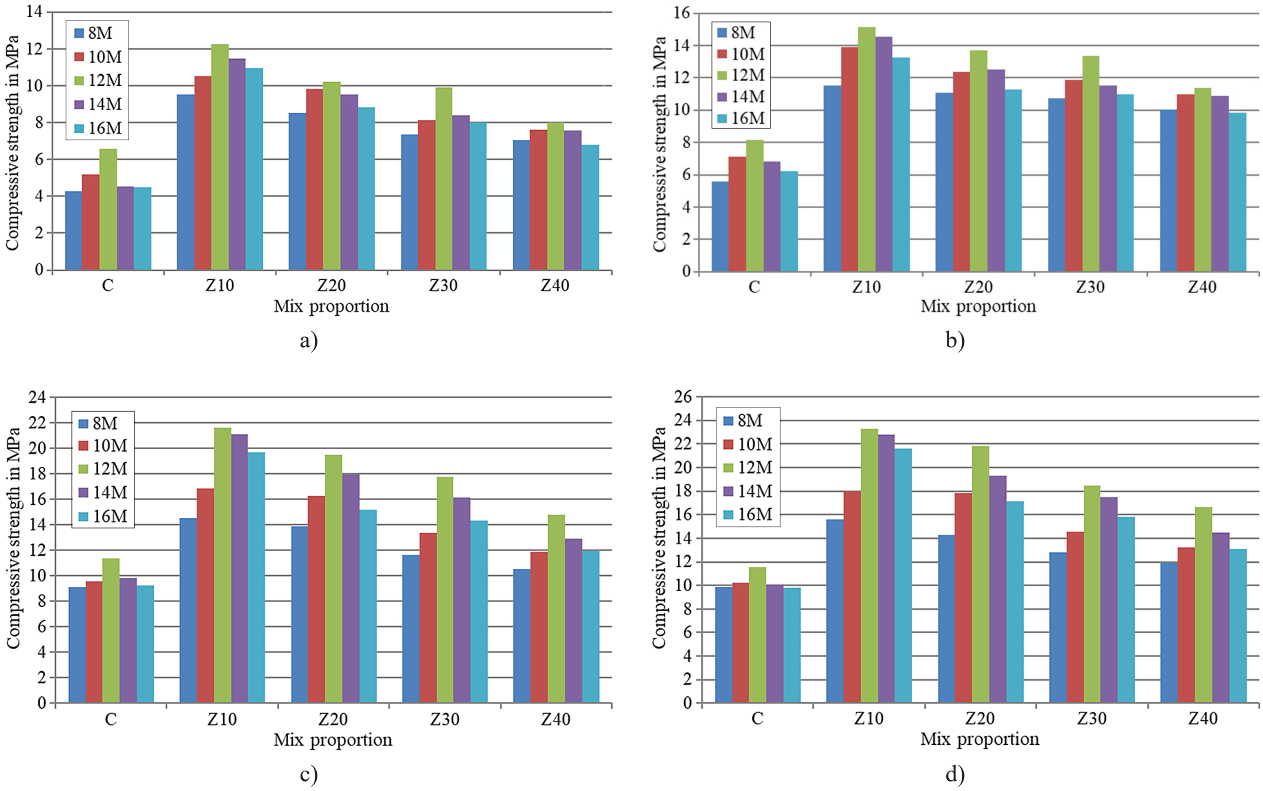
Compressive strength of the geopolymer mortar

The mortar cubes were cast for various RHA and zeolite percentages for five different molar concentrations of NaOH solution. The mortar cubes were placed in both ambient curing and heat curing conditions. The compressive strength of the mortar cube specimens was tested at 7 days and 28 days after casting, and the results are presented in Table 4.

Effect of zeolite on compressive strength

It can be seen in Table 4 that the compressive strength of the geopolymer mortar increased with the inclusion of zeolite by replacing the RHA up to 10 %. The statement above is endorsed by the results shown in Figure 8a-d. The increase in the strength with the inclusion of zeolite is due to the chemical composition of the zeolite as it contains crystalline hydrated aluminosilicates. It has a silicon (SiO_4) and aluminium (AlO_4) tetrahedral structure linked by one oxygen atom. In synthesising the geopolymer, the end product is the formation of a pseudo zeolite, which is responsible for the strength development in the geopolymer. Hence, the use of natural zeolite enhances the strength of the geopolymer. The Z10 mortar mix achieved a higher compressive strength than the other mix proportions. The percentage increase in the compressive strength varies from 58 % to 126 %, irrespective of the molar concentration and curing regime. The reason may arise due to the dissolution of the natural zeolite in the alkaline solution, which produces a sodium aluminosilicate gel, enhancing the mortar's strength. However, a further increase in the proportion of zeolite beyond 10 % decreases the compressive strength of the geopolymer mortar, but it is found to be higher than the control mortar containing 100 % RHA. This is ascribed to the incomplete dissolution of the zeolite in the alkaline solution, which leads to brittle and weaker gel formation at higher zeolite proportions. The same was also reported by Valipour [20]. Ahmadi [21] stated that the optimum percentage of zeolite for cement replacement is 15 %.

Furthermore, the control mortar mix containing 100 % RHA has a lower strength than the other mix proportions. RHA is rich in silica and contains a negligible amount of alumina. The strength reduction is attributed to the low alumina content in the RHA, which results in more unreactive silica in the geopolymer matrix. The alumina content plays a vital role in the polymerisation process, which contributes to the strength development in the geopolymer by reacting with the silica in a highly concentrated alkaline solution and producing an aluminosilicate gel. The formation of an aluminosilicate gel, as a result of the polymerisation process, is responsible for the setting and hardening of the binder. It, thus, contributes to the strength of the geopolymer mortar.



a) b) c) d)

Figure 8. Geopolymer mortar's compressive strength at: a) 7 days – AC, b) 28 days – AC, c) 7 days – HC, d) 28 days – HC.

Hence, the low alumina content in the RHA affects the geopolymerisation reaction and weakens the microstructure of the geopolymer mortar, thereby subsequently reducing the strength [22].

Effect of the molar concentration

The results from Table 4 indicate that the compressive strength of the geopolymer mortar can be varied by varying the molar concentration. The compressive strength of the mortar increases up to 12 M concentration, beyond which the strength of the mortar becomes reduced. The maximum compressive strength of the geopolymer mortar is obtained at a 12 M concentration, and the percentage increase in the compressive strength varies from 14 % to 47 % under ambient curing and 17 % to 53 % under heat curing compared to the mortar specimens prepared with the 8 M concentration. It may be because of the better dissolving ability of the Si and Al ions from the source material at the 12 M concentration, consequently increasing the inter-molecular bonding strength of the geopolymer mortar [23,24].

The compressive strength of geopolymer mortar decreased at a lower molar concentration. It may be attributed to the slow dissolution rate of the silica and alumina compounds at the low molar concentration [25]. Singh [26] stated that a gel formed at a low molar concentration does not undergo polycondensation, but leaves as a co-precipitate. Furthermore, above a 12M concentration, the compressive strength of the geopolymer mortar decreases because silica and other components dissolve more readily at higher molar concentrations. Hence, it leads to excess silica in the solution and results in silicic acid (H_2SiO_3) formation, which is responsible for the reduction in the strength of the binder.

Influence of the curing regime and curing age

The curing conditions significantly influence the microstructures, properties, and rate of the geopolymerisation of the geopolymers. Under an ambient temperature, the rate of dissolution of the monomers and the rate of the polymerisation of the aluminosilicate gel are both low, resulting in a weaker geopolymer. The curing temperature affects the hardening and geopolymerisation process in the geopolymer matrix by accelerating the reaction [25]. The accelerated reaction improves the bond between the aggregate and the geopolymer matrix, increasing the inorganic gel formation and leading to a more compact and denser microstructure. Thus, it enhances the strength of the geopolymer binder. An accelerated reaction and strength improvement was observed on the geopolymer specimens cured at 40 to 80 °C. It is crucial to note that the influence of the temperature depends on the curing duration. Heat curing for a shorter period did not result in substantial changes in the strength development [27].

In contrast, a longer heat curing time of at least 20 hours caused a noticeable rapid reaction rate and early strength. However, elevated temperatures above 80 °C, especially at the initial stage, results in the formation of larger pores in the specimen, which eventually affects the mechanical strength. According to Nath [28], if heat curing were not applied, the chemical reaction rate of the geopolymers would be slow. The heat curing accelerates the rate of dissolution and polymerisation and improves the strength due to the thermodynamic effect. This is because the energy required to dissolve the source materials is an endothermic process [29]. Hence, the curing temperature and duration were considered 60 °C for 24 hours in this investigation based on the pertinent literature.

Heat-cured specimens exhibit higher compressive strength than those cured under ambient curing. The test results are consistent with the previous research results mentioned above. Regardless of the molar concentration and mix proportion, heat curing improves the compressive strength at 28 days between 19 % and 78 % compared to ambient curing. The increment in the strength at elevated temperatures is due to the increase in the degree of geopolymerisation, which results in the formation of a higher amount of reaction products [30]. Rovnaník [31] reported that the geopolymerisation reaction takes place only at the surface layer of the source material to form a primary geopolymer gel. Any further reaction depends on the diffusion of hydroxide and silicate ions through the primary geopolymer gel, which is influenced by the curing temperature at an early stage of the reaction. The raw materials require thermal activation to accelerate the geopolymerisation reaction to achieve a high strength geopolymer binder. The lower compressive strength at ambient curing is due to the higher amount of unreacted source materials.

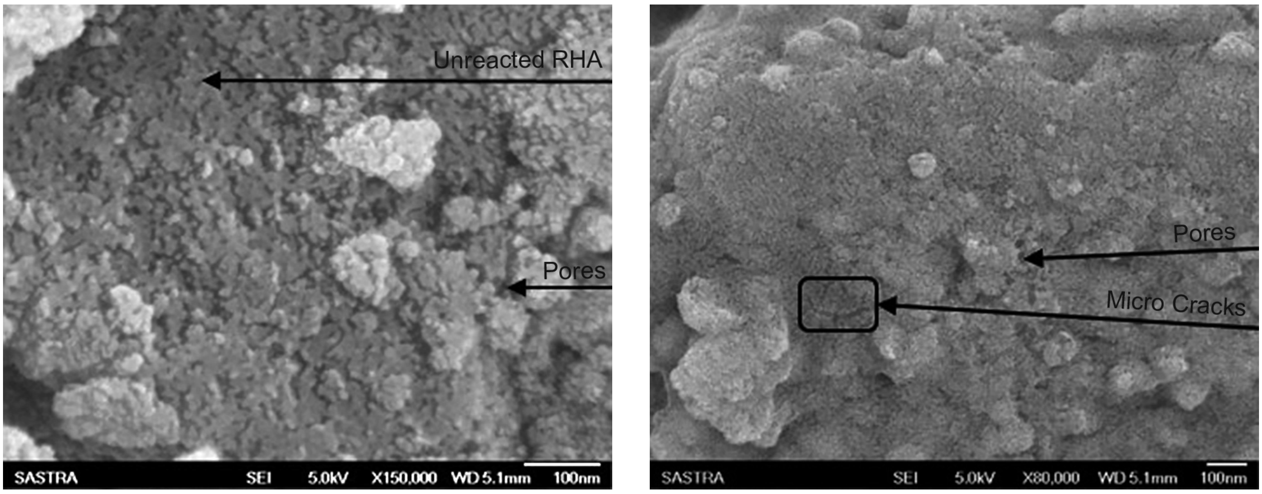
Furthermore, the rate of the strength gain under heat curing is found to be lower than the ambient cured samples. It implies that the specimens subjected to heat curing attain strength at an early stage, and there is no significant development in the strength at later stages and the same was also reported by Punurai [32]. However, in the ambient cured specimens, the strength development is continuous and gains its maximum compressive strength at 28 days.

SEM analysis for the mortar specimens

After the compressive strength test, the core samples of the mortar cubes were collected and tested to find the microstructural properties. Figure 9a to j shows the SEM analysis results.

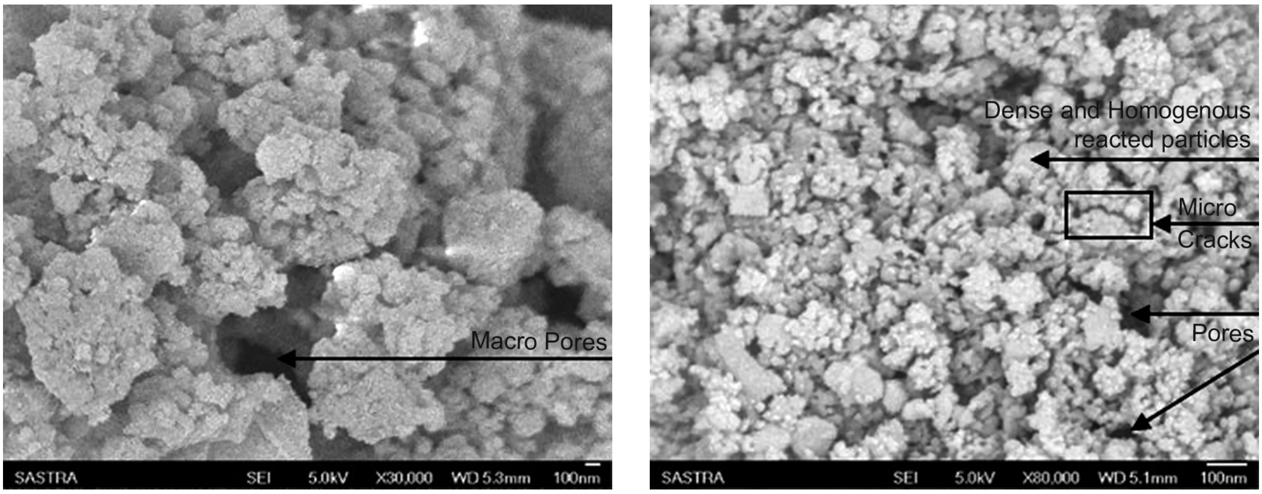
Figure 9a shows the SEM image of the control mortar mix under ambient curing conditions. It can be seen from Figure 9a that there are more unreacted RHA particles and more micropores. Figure 9b shows the control mix under the heat curing conditions, and it is clear from the image that the amount of unreacted RHA particles becomes reduced. Furthermore, microcracks and pores are present, which have irregular porous structures. The 10 % zeolite replacement mix is seen in Figure 9c and Figure 9d under ambient and heat curing conditions, respectively; where the mortar exhibits more microporous structures. Thus, the obtained strength is higher in the 10 % zeolite replacement due to the microstructural porous nature, which aids in the strength development. If the RHA is treated with acid, the strength may increase even with the 10 % zeolite compared to the untreated RHA. This is because the pores in the treated RHA samples may increase uniformly to attract more zeolite particles to aid the strength development. Particles are observed agglomerated in Figure 9c, where the pore size is approximately 0.5 µm. In Figure 9d, the particles seem spherical, with an average pore size of 30 nm. It can also be seen from the image in Figure 9d that the structure is porous, homogeneous and denser, which increases the strength of the mortar. However, microcracks are formed. Figure 9e and Figure 9f depict the mortar mix with a 20 % zeolite replacement under ambient and heat curing conditions, respectively, when the zeolite proportion increases, the pore size of the mortar also increases. The strength of the mortar decreased with an increase in the size of the pores. In Figure 9e, unbounded zeolite was observed on the surface. From Figure 9f, the Z20 mortar mix under heat curing, the unbounded zeolite may split into small pieces randomly throughout the surface compared with the ambient curing. At any further higher percentage replacement by zeolite, it can be visualised that the zeolite accumulates, as in Figures 9g and 9h, compared with the Z20 mix. Thus, it does not properly react with the RHA owing to the strength reduction. Figure 9h shows macrocracks under heat curing conditions.

From Figure 9i and Figure 9j, more unreacted zeolite can be found on the surface of the specimen, reducing the strength. The heat-cured samples exhibit a higher strength than the ambient-cured samples. Heat curing reduces the water content in the pores of the mortar, thus increasing the micropores in the mortar, and



a) C – AC

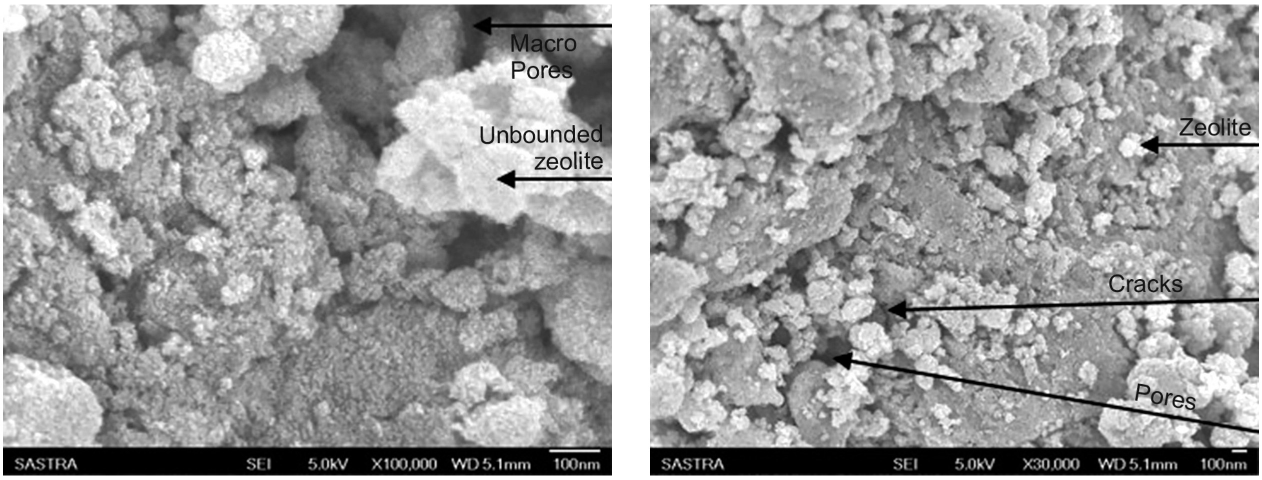
b) C – HC



c) Z10 – AC

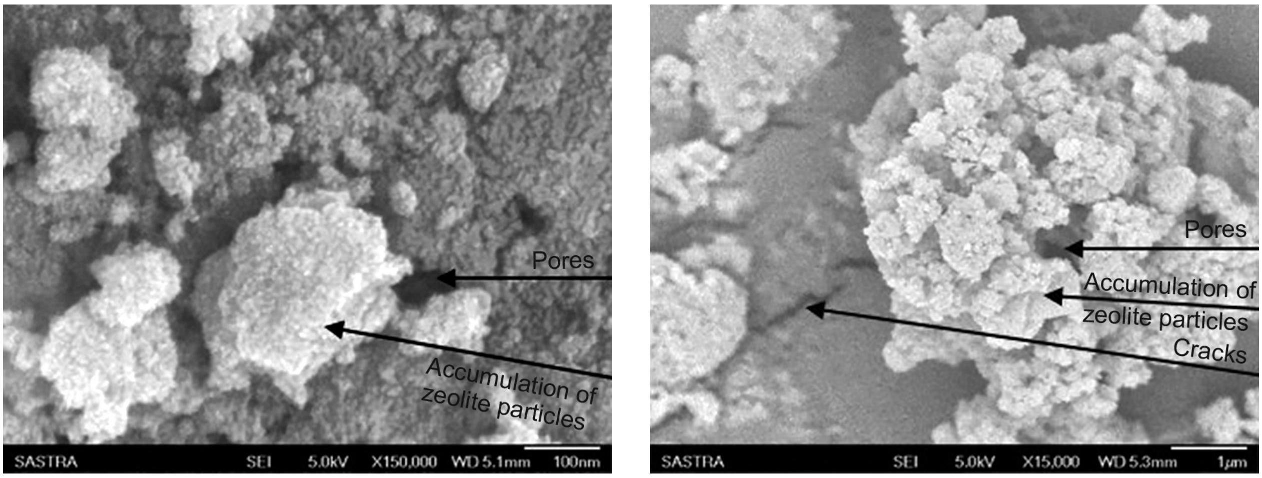
d) Z10 – HC

Figure 9. SEM analysis images of the mortar samples. *(Continue on next page)*



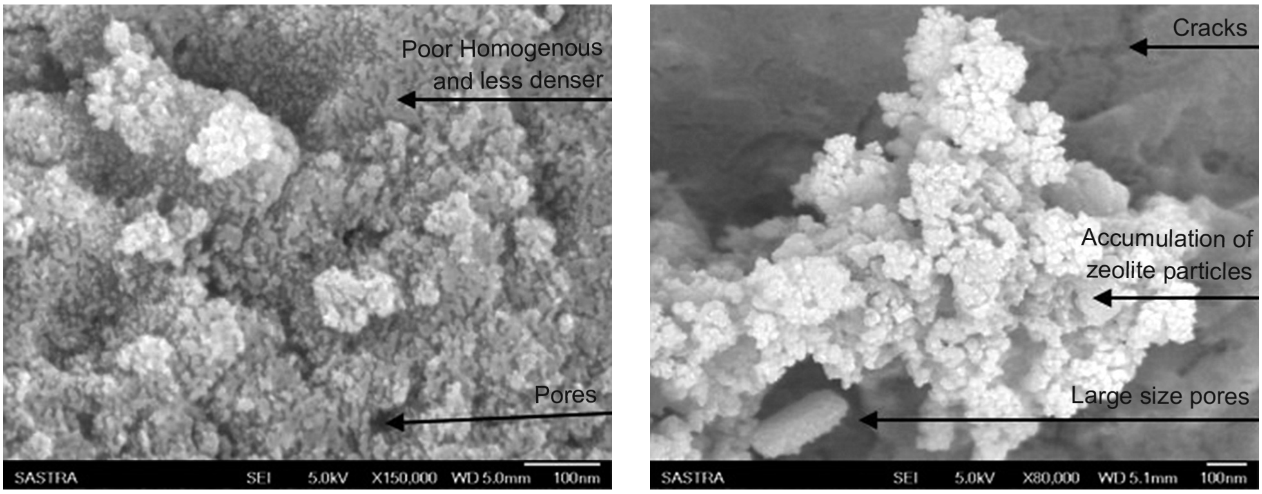
e) Z20 – AC

f) Z20 – HC



g) Z30 – AC

h) Z30 – HC



i) Z40 – AC

j) Z40 – HC

Figure 9. SEM analysis images of the mortar samples.

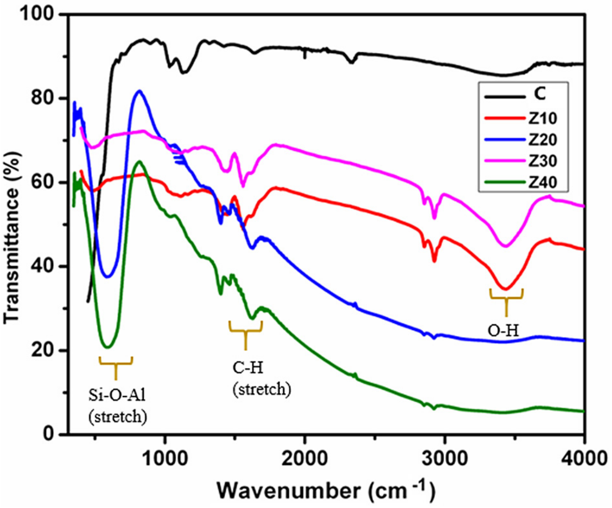
similar findings were also reported by Bouguermouh [33]. Also, visible microcracks are formed under the heat curing conditions, as observed from the SEM images; this may be due to the material drying. However, if the aggregate and geopolymer binder are strongly bonded, it strengthens the microcrack path and considerably increases the mortar strength [27]. The SEM images under ambient curing conditions showed a high degree of accumulation and a slightly porous nature. This could be due to the presence of the natural zeolite in the mix.

However, the aggregation of zeolite particles is less under the heat curing conditions for a lower zeolite proportion, of up to 20 % replacement.

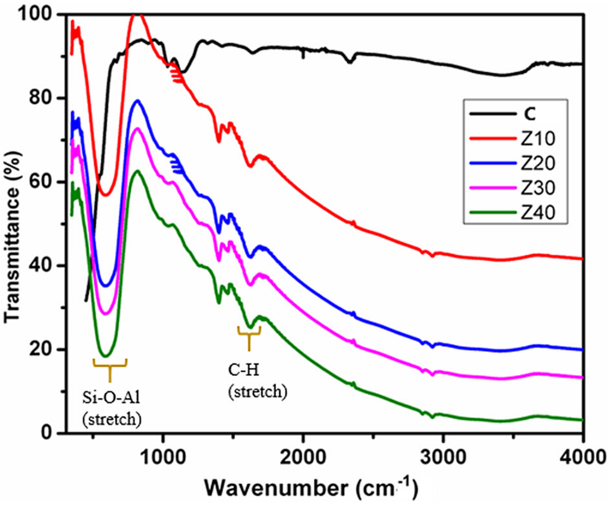
FT-IR analysis of the geopolymer mortar

The mortar samples were analysed for their chemical bond formation characteristics using an FT-IR test. Both the heat and ambient cured samples were tested for their chemical bonds, and the results are shown in Figure 10a and Figure 10b.

The graph of Figure 10a shows the FT-IR test results of the mortar samples under ambient curing conditions, and Figure 10b illustrates the FT-IR test results of the mortar under heat-cured conditions. The peak at 700 cm^{-1} may be attributed to the stretching frequency of the Si–O–Al bonds [34]. In Figure 10a, the peak around 3500 cm^{-1} is responsible for the OH of water in the mortar samples [34]. The peak shows an IR frequency around 1500 cm^{-1}, possibly due to the C–H (stretching) functional group in the geopolymeric chain links [34]. The absence of a peak at 3500 cm^{-1} in Figure 10b indicates the loss of water molecules under heat curing. The downward peaks in the 700 cm^{-1} range show the presence of Si–O–Al bonds. These peaks are found in all the mortar samples with zeolite, but they are not observed in the control sample. This is because the addition of zeolite increases the geopolymerisation reaction due to the formation of Si–O–Al bonds. The decrease in the transmittance percentage signifies the increase in the concentration of the bond. Figures 10a and 10b show the decrease in transmittance percentage for the increase in the proportion of zeolite. Though the quantity of the polymer bond increases with the increasing percentage of zeolite, the accumulation of zeolites at higher percentage replacements provides reduced strength. While comparing the heat and ambient cured samples, the heat-cured specimens exhibit a higher presence of Si–O–Al bonds.



a) AC



b) HC

Figure 10. FT-IR analysis of the geopolymer mortar: a) AC, b) HC.

CONCLUSION

This paper addressed the application of natural zeolite and rice husk ash as a binder material in a geopolymer mortar. In this study, the fresh and hardened properties of a geopolymer mortar made by partially replacing the RHA with natural zeolite were investigated and the results are compared with a mortar containing 100 % RHA and without zeolite. The following conclusions can be drawn from this investigation:

- The porous structure and high surface area of natural zeolite resulted in a significant decrease in the mortar workability.
- The natural zeolite reacts with the addition of an activator alkaline solution to give rise to the geopolymer formation. This is in agreement with the FTIR and SEM characterisation.
- The compressive strength of the mortar containing natural zeolite was higher than that of the control mortar at all ages and curing regimes which can be attribute to the dissolution of the zeolite in the alkaline solution and the formation of alumina silicate gel. However, the strength of the mortar becomes reduced with an increase in the zeolite proportion. The optimum percentage of zeolite replacement is 10 %.
- The compressive strength of the geopolymer mortar increases with an increase in the molar concentration of sodium hydroxide and the maximum strength is obtained at a 12 M concentration.
- The material synthesised under heat curing conditions exhibits a higher compressive strength. This indicates that the source material needs thermal activation to obtain a geopolymer with high compressive strength.

- The mortar under ambient curing conditions requires a long curing time in order to generate a significant increase in strength.

Acknowledgements

The Chairman and Principal of the Thiagarajar College of Engineering in Madurai, India, are gratefully acknowledged by the authors for their assistance in conducting the research. Here, the aid of the Material Testing Laboratory's teaching and non-teaching staff is also appreciated.

REFERENCES

1. Deb A.(1994): Building materials – the Indian scenario: Wide ranging analysis of traditional and new materials in the Indian context highlighting the need to restructure. *Building Research & Information, 22*, 252–260. doi: 10.1080/09613219408727398
2. Kibert C.J., Bosch G.(1998): Green Buildings Materials '96. *Building Research & Information, 26*, 190–198. Doi: 10.1080/096132198369968
3. Gowram I., Beulah M., Sudhir M.R., Mohan M.K., Jain D. (2021): Efficacy of Natural Zeolite and Metakaolin as Partial Alternatives to Cement in Fresh and Hardened High Strength Concrete. *Advances in Materials Science and Engineering*, 2021, 4090389. doi: 10.1155/2021/4090389
4. Zhang P., Zheng Y., Wang K., Zhang J. (2018): A review on properties of fresh and hardened geopolymer mortar. *Composites Part B: Engineering, 152*, 79–95. doi: 10.1016/j.compositesb.2018.06.031
5. Tong K.T., Vinai R., Soutsos M.N. (2018): Use of Vietnamese rice husk ash for the production of sodium silicate as the activator for alkali-activated binders. *Journal of Cleaner Production, 201*, 272–286. doi: 10.1016/j.jclepro.2018.08.025
6. Vigneshwari M., Arunachalam K., Angayarkanni A. (2018): Replacement of silica fume with thermally treated rice husk ash in Reactive Powder Concrete. *Journal of Cleaner Production, 188*, 264–277. doi: 10.1016/j.jclepro.2018.04.008
7. Yilmaz A. (2021): Mechanical and durability properties of cement mortar containing waste pet aggregate and natural zeolite. *Ceramics – Silikaty, 65*, 48–57. doi: 10.13168/cs.2021.0001
8. Amran M., Al-Fakih A., Chu S.H., Fediuk R., Haruna S., Azevedo A., Vatin N., (2021): Long-term durability properties of geopolymer concrete: An in-depth review. *Case Studies in Construction Materials,15*, e00661. doi: 10.1016/j.cscm.2021.e00661
9. Tian Q., Sun S., Sui Y., Wang Y., Lv Z. (2021): Effects of composition of fly ash-based alkali-activated materials on compressive strength: A review. *Ceramics – Silikaty, 65*, 9–23. doi: 10.13168/cs.2020.0037
10. Papa E., Medri V., Amari S., Manaud J., Benito P., Vaccari A., Landi E. (2018): Zeolite-geopolymer composite materials: Production and characterization. *Journal of Cleaner Production, 171*, 76–84. doi: 10.1016/j.jclepro.2017.09.270
11. Khan M.Z.N., Shaikh F. uddin A., Hao Y., Hao H. (2016): Synthesis of high strength ambient cured geopolymer composite by using low calcium fly ash. *Construction and Building Materials, 125*, 809–820. doi: 10.1016/j.conbuildmat.2016.08.097
12. Patel Y.J., Shah N. (2018): Enhancement of the properties of Ground Granulated Blast Furnace Slag based Self Compacting Geopolymer Concrete by incorporating Rice Husk Ash. *Construction and Building Materials, 171*, 654–662. doi: 10.1016/j.conbuildmat.2018.03.166
13. Mehrotra S.O., Masood I. (1992): Pozzolanic behaviour of bagasse ash: A derivative of sugar cane distillation, bagasse ash, has properties that might be suitable for use in building materials. *Building Research & Information, 20*, 299–304. doi: 10.1080/09613219208727228
14. Chan S.Y.N., Ji X. (1999): Comparative study of the initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes. *Cement & Concrete Composites, 21*(4), 293-300. doi: 10.1016/S0958-9465(99)00010-4
15. Alcantara Ortega E., Cheeseman C., Knight J., Loizidou M. (2000): Properties of alkali-activated clinoptilolite. *Cement and Concrete Research, 30*(10), 1641-1646. doi: 10.1016/S0008-8846(00)00331-8
16. Tran Y.T., Lee J., Kumar P., Kim K.H., Lee S.S. (2019): Natural zeolite and its application in concrete composite production. *Composites Part B: Engineering,165*, 354–364. doi: 10.1016/j.compositesb.2018.12.084
17. Detphan S., Chindaprasirt P. (2009): Preparation of fly ash and rice husk ash geopolymer. *International Journal of Minerals, Metallurgy and Materials, 16,* 720–726. doi: 10.1016/S1674-4799(10)60019-2
18. Hadi M.N.S., Farhan N.A., Sheikh M.N. (2017): Design of geopolymer concrete with GGBFS at ambient curing condition using Taguchi method. *Construction and Building Materials, 140*, 424–431. doi: 10.1016/j.conbuildmat.2017.02.131
19. Patankar S. V., Ghugal Y.M., 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. doi: 10.1155/2014/938789
20. Valipour M., Pargar F., Shekarchi M., Khani S. (2013): Comparing a natural pozzolan, zeolite, to metakaolin and silica fume in terms of their effect on the durability characteristics of concrete: A laboratory study. *Construction and Building Materials, 41*, 879–888. doi: 10.1016/j.conbuildmat.2012.11.054
21. Ahmadi B., Shekarchi M. (2010): Use of natural zeolite as a supplementary cementitious material. *Cement and Concrete Composites, 32*, 134–141. doi: 10.1016/j.cemconcomp.2009. 10.006
22. Hwang C.L., Huynh T.P. (2015): Effect of alkali-activator and rice husk ash content on strength development of fly ash and residual rice husk ash-based geopolymers. *Construction and Building Materials, 101,* 1–9. doi: 10.1016/j.conbuildmat.2015.10.025
23. Wang H., Li H., Yan F. (2005): Synthesis and mechanical properties of metakaolinite-based geopolymer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 268*, 1–6. doi: 10.1016/j.colsurfa.2005.01.016
24. Parveen S., Pham T.M., (2020): Enhanced properties of high-silica rice husk ash-based geopolymer paste by in-

corporating basalt fibers. Construction and Building Materials,245, 118422. doi: 10.1016/j.conbuildmat.2020.118422

25. Zaidahtulakmal M.Z., Kartini K., Hamidah M.S. (2019): Rice husk ash (RHA) based geopolymer mortar incorporating sewage sludge ash (SSA). in: *Journal of Physics: Conference Series*, (Vol. 1349, No. 1, p. 012022), Institute of Physics Publishing. doi: 10.1088/1742-6596/1349/1/012022
26. Singh B., Rahman M.R., Paswan R., Bhattacharyya S.K. (2016): Effect of activator concentration on the strength, ITZ and drying shrinkage of fly ash/slag geopolymer concrete. *Construction and Building Materials, 118*, 171–179. doi: 10.1016/j.conbuildmat.2016.05.008
27. Nurruddin M.F., Haruna S., Mohammed B. S., Sha´aban I.G. (2018): Methods of curing geopolymer concrete: A review. *International Journal of Advanced and Applied Sciences, 5*, 31–36. doi: /10.21833/ijaas.2018.01.005
28. Nath P., Sarker P.K. (2014): Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition. *Construction and Building Materials, 66*, 163–171. doi: 10.1016/j.conbuildmat.2014.05.080.
29. Bakharev T. (2005): Geopolymeric materials prepared using Class F fly ash and elevated temperature curing. *Cement and Concrete Research, 35*, 1224–1232. doi: 10.1016/j.cemconres.2004.06.031.
30. Noushini A., Castel A. (2016): The effect of heat-curing on transport properties of low-calcium fly ash-based geopolymer concrete. *Construction and Building Materials, 112*, 464–477. doi: 10.1016/j.conbuildmat.2016.02.210
31. Rovnaník P. (2010): Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer. *Construction and Building Materials, 24,* 1176–1183. doi: 10.1016/j.conbuildmat.2009.12.023
32. Punurai W., Kroehong W., Saptamongkol A., Chindaprasirt P. (2018): Mechanical properties, microstructure and drying shrinkage of hybrid fly ash-basalt fiber geopolymer paste. *Construction and Building Materials, 186*, 62–70. doi: 10.1016/j.conbuildmat.2018.07.115
33. Bouguermouh K., Bouzidi N., Mahtout L., Pérez-Villarejo L., Martínez-Cartas M.L. (2017): Effect of acid attack on microstructure and composition of metakaolin-based geopolymers: The role of alkaline activator. *Journal of Non-Crystalline Solids, 463*, 128–137. doi: 10.1016/j.jnoncrysol.2017.03.011
34. Aissa Bouaissi, Long-yuan Li, Mohd Mustafa Al Bakri Abdullah, Quoc-Bao Bui (2019): Mechanical properties and microstructure analysis of FA-GGBS-HMNS based geopolymer concrete. *Construction and Building Materials, 210*, 198–209. doi: 10.1016/j.conbuildmat.2019.03.202.