Water Permeability, Strength Development And Microstructure of Activated Pulverized Rice Husk Ash Geopolymer Cement

H.H.M. Darweesh a, *

a Refractories, Ceramics and Building Materials Department, National Research Centre, Cairo, Egypt.
*Corresponding author Email: hassandarweesh2000@yahoo.com

Abstract: The activated pulverized rice husk ash (PRHA) as a pozzolanic material mixed with Portland cement (OPC) in various ratios was synthesized as geopolymer cement. The alkaline activator was prepared from a mixture of sodium hydroxide (NaOH) and sodium silicate (Na2SiO3). Effect of OPC replacement on the various properties of the synthesized geopolymers was evaluated. The results showed that the water of consistency sharply decreased with the increase of the OPC addition, while the setting times (initial and final) slightly decreased. The water absorption and apparent porosity reduced with OPC replacement at the expense of PRHA merely up to 18 wt. % content, and then increased. The bulk density as well as flexural and compressive strengths improved and enhanced also up to 18 wt. % OPC content, but then declined with any further increase. The free lime content increased up to 3 days of curing and then decreased onward due to its consumption during the pozzolanic reactions. The 18 wt. % OPC geopolymer mix is the optimum mix, where it achieved the better water absorption (6.89 %), bulk density (1.9099 g/cm³), apparent porosity (15.62 %), flexural strength (5.54 MPa) and compressive strength (58.25 MPa) at 90 days curing times. The ultrasonic pulse velocity test largely confirmed the obtained physical and mechanical characteristics. The FTIR spectra showed that the spectra of G18 geopolymer was more pronounced due to the formation of NASH geopolymer-gel needed to ensure better conformity between different constituents in the whole system that responsible for the improvements in the mechanical properties. The microstructure of the optimum G18 geopolymer mix is well-defined with no or little pores that responsible for the improving of physical properties and the enhancement of mechanical strengths, whereas the microstructure of G24 is more porous and heterogeneous matrix which was contributed to the reduction of mechanical strengths.

Keywords: Geopolymer Cement, Rice Husk Ash, Superplasticizer, Free Lime, Absorption, Density, Strength.

1. Introduction
1.1 Scope of the problem

A global problem of environmental pollution and control of waste management had been arisen, particularly in both industrial and agricultural sectors. Environmental pollution and health hazards that associated with cement and clay-bricks industries are alarming, and therefore it requires serious attention from environmentalists and governments. Environmental pollution problems associated with these industries especially in developing countries are the alternative use of some agricultural wastes that are compatible [1]. The development of sustainable construction materials reduces the associated environmental issues with the conventional cement. The production of Ordinary Portland cement (OPC) is really responsible for about 7–10% of the global CO2 emissions [2]. Recently, researchers are often concentrated to explore alternative binder materials to OPC as fly ash [3], granulated blast furnace slag [4,5], rice husk ash [6], saw dust ash [7], sugarcane bagasse ash [8], corn stalk ash [9], wheat straw ash [10], palm ash [11], physalis pith ash [12], coir pith ash [13], sun flower ash [14] and many others. These are priceless industrial and agricultural by-products, which cause disposal problems if these are not properly utilized. These wastes or byproducts can be exploited to produce Geopolymer cements and/or concretes (GPCs). These are forms of friendly/environmentally cements or concretes. These types of cements have been used in real-life projects like run ways of airport, i.e. GPCs are beneficial from both economic and environmental perspectives that can help to achieve a significant reduction in CO2 and greenhouse gas emissions [15].

Previous studies have demonstrated that GPCs improved several properties when compared to the conventional ones [16,17]. Performance of rice husk ash (RHA) based GPCs incorporating ultrafine slag and
corn stalk ash was studied [3-14]. Different fresh and hardened stage properties were tested, where it was concluded that GPCs with improving properties could be produced using agro/waste materials [1-16].

In Egypt, the rice production is concentrated in a limited agricultural area around the Nile Delta, where nearly about 8-10 million tons of rice is produced annually. This is creating a large volume of rice byproducts. Often, an uncontrolled burning of rice husk was done for its disposal. Random burning of either rice or even barely husks creates what is known as “Black Cloud” which is very dangerous to the environment. The seasonal and highly localized massive burning usually generated an excessive air pollution that lowers air quality in the surrounding megacity of Cairo. This has become a serious health concern for citizens and authorities [18-20]. Since 2-3 decades, the pozzolanic cements are widely used all over the world. Such cements are employed for their economical, ecological and technological importance, i.e. reduction of energy consumption and CO2 emission [15,21].

GPCs using RHA and GbfS investigating its strength development, microstructure and permeability characteristics were evaluated [22]. This study reported that the highest compressive strength of 69 MPa was achieved when 15% RHA and 85% GbfS were used. In another study, the microstructure of RHA in GPCs was conducted [23]. A decrease in the width of the interfacial transition zone among aggregates and the paste was noticed for GPCs, which helped to decrease the water absorption. FA/GPCs containing RHA as a partial replacement was produced [24]. The compressive and bond strengths of GPCs were studied. It was concluded that RHA promoted the growth of the geopolymer gels, refined the pore structure, densified the geopolymer framework and enhanced the bond strength of GPCs. The effect of RHA addition on the properties of GbfS / GPC was studied [25], where the mechanical properties were improved and enhanced. Moreover, a denser microstructure was noted with the addition of RHA and better results were observed for 5% RHA if compared with the other levels.

Mechanical and durability performance of GbfS/GPC with RHA as a replacement of 10, 20 and 30% GbfS were exhibited [26]. An enhancement in strength was observed with up to 10% RHA, where a significant improvement in the durability properties such as chloride penetration and sorptivity was observed as RHA reduced the sorptivity and the chloride permeability. Many studies focused on using RHA as a secondary binder.

1.2. Objectives of the Study

The current investigation aimed to produce GPCs using PRHA with the partial substitution of OPC at the expense of PRHA. A series of experimental tests were carried out to evaluate the water of consistency, setting times, water absorption, bulk density, apparent porosity, free lime contents, flexural strength and compressive strength. The obtained results were confirmed with ultrasonic pulse velocity, FTIR spectra and SEM-EDAX analysis at 90 days for the optimum GPC batch comparing with that of the control.

2. Experimental Program

2.1. Raw Materials

The used raw materials in the current study are Ordinary Portland cement (OPC Type I- CEM I 42.5 R) and rice husks (RH). The OPC sample with a Blaine surface area of 3400 cm²/g was delivered from Sakkar cement factory, Giza, Egypt, and its commercial name is known as “Asmant El-Montaz”. The RH sample was provided from a local plant, Giza, Egypt. Firstly, the RH sample was processed and washed with running water for 20 minutes, and then washed with distilled water, well dried under open air and direct sun for two days. It was then burned in a suitable furnace at 800 °C for 2 hours soaking time to produce what is known as rice husk ash (RHA). The furnace was left to cool overnight. Then, the RHA was screened to pass through 200 mesh sieves (63 μm).

| Chemical oxide composition of the raw materials, wt. % |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                | SiO₂            | Al₂O₃          | Fe₂O₃          | CaO            | MgO            | Na₂O           | K₂O            | SO₃            | LOI            |
| OPC            | 20.12           | 5.25           | 1.29           | 63.13          | 1.53           | 0.55           | 0.3            | 2.54           | 2.64           |
| RHA            | 77.17           | 8.83           | 1.29           | 1.26           | 0.11           | 0.03           | 1.06           | 0.02           | 0.84           |
The chemical analysis of the OPC and PRHA using the X-ray fluorescence (XRF) technique is shown in Table 1, while the mineralogical phase composition of the OPC sample [27,28] is summarized in Table 2. The physical properties of the raw materials and the composition of sodium silicates (Na$_2$SiO$_3$) are recorded in Tables 3 and 4, respectively.

### 2.2. Activating Solution

A solution mixture of sodium hydroxide (NaOH) and sodium silicate (Na$_2$SiO$_3$) was prepared as an alkaline activator. The NaOH solution with a molarity of 8M was prepared by mixing 97–98% pure pellets with distilled water. The Na$_2$SiO$_3$ solution was composed of 25.7% SiO$_2$, 10.2% Na$_2$O, and 64.1% H$_2$O with a bulk density of 1370 kg/m$^3$. The prepared batch was kept at room temperature for 24 hours [29].

### 2.3. Preparation and Methods

The activator solution was then gradually poured to the GPC mixes. Also, the polycarboxylate ether (PCE) (Figure 1) was used as a superplasticizer to improve and enhance the workability of the prepared geopolymers [30]. It is a white powder which is completely soluble in water and it is a high-water reducing admixture. Its solid content, density and pH-value are 98.0±1.0, 600±5.0 and 9.0±1.0, respectively. The control GPC mix was prepared as recommended in a previous study [29-31].
The GPC batches were partially substituted by OPC at the expense of PRHA as RHA: OPC are 100:0, 94:6, 88:12, 82:18 and 76:24 % having the symbols G0, G6, G12, G18 and G24 as summarized in Table 5. The blending process of the various geopolymer cement batches was done in a porcelain ball mill using three balls for two hours to assure the complete homogeneity of all cement mixes. The standard water of consistency [32] and setting time [33] of the various cement pastes were directly measured using Vicat Apparatus, and then the water of consistency could be calculated from the following relation:

\[ WC, \% = A / C \times 100 \]  \hspace{1cm} (1)

Where, A is the amount of water taken to produce a suitable paste, C is the amount of cement mix (300 g).

Pellets of sodium hydroxide, NaOH with high purity (98 %) were dissolved in normal water to form an acticated solution of 12 M NaOH concentration. Then, it was well mixed with sodium silicate, Na2SiO3 solution for about 5 minutes. During mixing, 1 % of both the alkali activated solution and superplasticizer was added with the correct predetermined w/c-ratio (water of consistency), and poured into the prepared cement portion inside the mixer step by step, and then the mixer was run for 5 minutes at an average speed of 10 rpm in order to have perfect homogenous pastes. Before casting of cement cubes, the moulds were covered with a thin film of a motor engine oil, to facilitate the release of the cement cubes from the moulds during the de-moulding. The cement pastes were then casted into one-inch cubic stainless steel moulds (2.5 x 2.5 x 2.5 cm³) using about 500 g from the cement batch, vibrated manually for three minutes, and then on a mechanical vibrator for another three minutes to remove all air bubbles tapped inside the cement pastes. The moulds were filled to the top surface and smoothed with a flat stainless-steel trowel or a suitable spatula to obtain a flat and smooth surface [34]. After casting, they were covered with a wet sheet during the first 24 hours to prevent moisture loss. The moulds were then kept in a humidity chamber for 24 hours under 95 ± 1 relative humidity and room temperature (23 ± 1). The moulds were demoulded in the following day. The specimens were soon placed in a suitable dryer at 60 °C for 24 hours for heat curing to achieve the highest compressive strength for all mixes [22]. Thereafter, the specimens were cured by the total immersion in water at an ambient laboratory temperature till the time of testing at 1, 3, 7, 28, 56 and 90 days. This is necessary for the cement cubes as it facilitates the proper hydration of cement phases. These GPC batches were subjected to investigate its effects on the strength modification and permeability.

The water absorption, bulk density and apparent porosity of the different hydrated geopolymer batches [7,6,27,28,34-38] were determined from the following relations: -

\[ WA, \% = W1-W2/W2 \times 100 \]  \hspace{1cm} (2)

\[ B.D, (g/cm3) = W1/(W1–W2) \times 1 \]  \hspace{1cm} (3)

\[ A.P, \% = (W1–W3)/(W1–W2) \times 100 \]  \hspace{1cm} (4)

Where, W1, W2 and W3 are the saturated, suspended and dry weights, respectively.

Modulus of elasticity of the different hydrated geopolymer batches was determined due to the specifications of ASTM-C649 [39], where it gives an idea on the rigidity of the structure and the load-deformation behavior.

The mechanical properties in terms of flexural and compressive strengths were carried out in accordance with ASTM-C293 [40] and ASTM-C109M [41], respectively. The rod-shaped samples were subjected to flexural strength (FS, MPa) using a simple beam with three points loading system (Figure 2), which was determined from the following equation:

\[ F. S, \text{ kg/cm}^2 = (PL)/2(b)(d) / 10.2\text{MPa} \]  \hspace{1cm} (5)

Where, where, B: the load of rupture, kg, S: span or the distance between the two lower beams (5cm), W: width of sample, cm and T: thickness of sample, cm.
The Compressive Strength (CS) of the various hardened cement pastes was measured using a suitable Piston as follows:

\[
CS = \frac{L (KN)}{S_a (cm^2)} \times 102 (Kg/cm^2)/10.2 (MPa)
\]

Where \(L\) is the load taken, \(S_a\) is the surface area. Thereafter, about 10 grams of the broken specimens after the compressive strength test was first well ground, dried at 105 °C for 30min. Then, it was placed in a solution mixture of 1:1 methanol: acetone to stop the hydration [14,35-37].

The free lime content (FLn) of the hydrated samples pre-dried at 105 °C for 24 hours was also determined. About 0.5g sample + 40ml ethylene glycol → heating to about 20 minutes without boiling. About 1-2 drops of pH indicator were added to the filtrate and then titrated against freshly prepared 0.1N HCl until the pink color disappeared. The 0.1N HCl was prepared using the following equation:

\[
V_1 = N \times V_2 \times W (7) \times 100/D \times P \times 1000
\]

Where, \(V_1\) is the volume of HCl concentration, \(V_2\) is the volume required, \(N\) is the normality required, \(W\) is the equivalent weight, \(D\) is the density of HCl concentration and \(P\) is the purity (%). The heating and titration were repeated several times until the pink color did not appear on heating. The free lime content [27,28,34-37] was calculated from the following relation:

\[
FLn, \% = \frac{(V \times 0.0033/1) \times 100}{V}
\]

Where, FLn and V are the free lime content and the volume of 0.1N HCl taken on titration, respectively. The final value for each parameter was reported by taking the average value of three specimen results.

The obtained results were confirmed with Ultrasonic Pulse Velocity (USPV) test, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) supported with EDAX analysis. The USPV test is one of the prominent Non-Destructive Testing (NDT) methods. It is mainly carried out to assess the uniformity and relative quality of existing structures and specimens [41, 42]. The test was carried out on 1, 3, 7, 28, 56 and 90 days for some selected samples. The FT-IR spectra were done by Perkin Elmer FT-IR spectrometer in transmittance mode in a wavenumber range of 4000-500 cm\(^{-1}\) and a resolution of 500 cm\(^{-1}\). The microstructure of some selected GPC samples hydrated at 90 days was investigated using JEOL–JXA–840 electron analyzer at accelerating voltage of 30 kV. The fractured surfaces were fixed on Cu-ka stubs by carbon paste and then coated with a thin layer of gold. The SEM images are supported with EDAX analysis.

3. Results and Discussion

3.1. Water of Consistency and Setting Times

Figure 3 demonstrates the water of consistency and setting times (initial and final) of the various geopolymer cement mixes. The water of consistency of the blank GPC was 31.46. This value was sharply decreased by the gradual substitution of OPC at the expense of PRHA. This is mainly due to the presence of the high-water reducing superplasticizer (PCE) [3,8,9-11,16]. The chemical formula and structure of the used superplasticizer showed a lot of free hydroxyl groups (OH\(^{-}\)) which supplied the geopolymer cements with water. Accordingly, the w/c ratios were largely reduced [27,28]. On the other side, the setting times (Initial and final) displayed the same trend as in water of consistency. This may be contributed to the same cause [16,27,28].

3.2. Water Absorption

The results of water absorption of the various geopolymer cement mixes hydrated are represented as a function of curing times up to 90 days in Figure 4. The water absorption of the control was the highest at all curing times.
Figure 3. Water of consistency and setting times of the various geopolymer cement mixes.

Figure 4. Water absorption of the various geopolymer cement mixes hydrated up to 90 days.
The water absorption of the control was the highest at all curing times. It was continuously increased with the replacement of OPC at the expense of PRHS, and also at all curing ages. This is essentially attributed to the pozzolanic reactions of the PRHA constituents with the evolved Ca (OH)$_2$ from the hydration of C$_3$S and C$_2$S of the OPC [43,44]. Moreover, the temperature curing improves the bond characteristics, with the aid of the activator used [45]. This was only continued till 18 wt. % OPC (G18), and then reduced with further addition of OPC as occurred with G24. However, it was little lower than those of the blank. Thus, the G18 mix exhibited the optimum water absorption data.

### 3.3. Bulk Density and Apparent Porosity

The data of bulk density and apparent porosity of the various geopolymer cement mixes are drawn as a function of curing times up to 90 days in Figures 5 and 6, respectively. The bulk density of the control GPC mix improved and increased with the gradual substitution of the PRHA by OPC only up to 18 wt. % (G18), and then decreased with more substitution. The increase of bulk density is principally contributed to the activation action by OPC through the pozzolanic reactivity of the released Ca (OH)$_2$ resulting from the normal hydration of the calcium silicate phases of the OPC with the PHSA to form CSH. The new formed CSH phases deposited in the pore structure and hence decreased the porosity of the hardened samples, this in turn reflected positively on the bulk density [16,46-48], in addition to the positive action by the activator solution. The decrease of bulk density may be due to the open pore volume that happened by the further substitution of OPC. So, the G18 achieved the highest values of bulk density at all curing ages. Though the bulk density results of G24 decreased at all curing times, it was still higher than those of the blank (G0). The results of apparent porosity confirmed those of the water absorption.

The apparent porosity of the blank was the maximum at all curing stages. It was decreased with the increase of OPC addition. This was continued up till 18 wt. %, and the increased. The decrease of apparent porosity is principally due to the gradual deposition and precipitation of the formed CSH in the pore structure leading to the reduction of the porosity of the hardened samples [49-52], while the increase of the apparent porosity may be contributed to the formation of open pore volume. Hence, the G18 mix recorded the highest values of bulk density nearly at all curing periods. In spite of the increase of the apparent porosity of G24, its values of apparent porosity were still better than those of the blank (G0).

![Figure 5. Bulk density of the various geopolymer cement mixes hydrated up to 90 days.](image-url)
Figure 6. Apparent porosity of the various geopolymer cement mixes hydrated up to 90 days.

The results of bulk density are inversely proportion with those of apparent porosity. These results can be attributed to the formation of the geopolymerisation products such as NASH gel. So, the densification parameters of the geopolymer matrix were improved [53]. The increase of the OPC content more than 18 wt. %, diminished the bulk density, and enhanced the apparent porosity, which was related [46,51] to the creation of weak zones due to the occurrence of new mineral phases in the geopolymer matrix. Therefore, it was affecting the mechanical properties of the synthesized geopolymers.

3.4. Free Lime Content

The free lime contents of the various geopolymer cement mixes are plotted as a function of curing times up to 90 days in Figure 7. The free lime content of the blank is zero. As soon as the OPC was added to the GPC, the free lime started to release, but it soon consumed through the pozzolanic reactivity of the PRHA. As a result, the free lime content was at its minimum, i.e. no free lime was detected in the various GPC mixes. This is an advantage for the cement which reflected positively on their physical, chemical and even mechanical characteristics.

3.5. Flexural Strength

Figure 8 illustrates the flexural strength results of the various geopolymer cement mixes hydrated up to 90 days. The flexural strength displayed the same trend of the compressive strength, i.e. with OPC substitution up to 18 wt. %, a gradual and progressive increase in the strength was noted, but with further increase of OPC content the flexural strength tends to decline. Also, the flexural strength continuously improved and enhanced with the curing times up to 90 days, i.e. as the curing time proceeds, the flexural strength increased too. The improvement and enhancement in strength with up to 18 wt. % OPC content is attributed to the formation of higher quantities of CSH gel, which refined the pore structure and filled up the voids [6-9,27,28]. Because of this filler effect of CSH gel, the OPC helped to bridge the cracks, block the separation at the crack interface whenever cracks were formed. As soon as the crack started to form, the crack begins to reduce step by step due to the micro/filler action of the CSHs, i.e. stable matrix structure could be formed. As a result, strong bonds were created between the GPC constituents. Therefore, this should be positively reflected on the strengths.

With higher OPC content, a matrix of non-homogeneous structure was arisen.
This may be due to the poor dispersion of OPC particles. So, the excess content of the OPC may also lead to the extra evolution of heat after the hydration has taken place. The later trend was mainly responsible for crack formation. Hence, the formation of a weaker matrix structure with a lower strength could be expected [4,26,27,30,54]. The hydration process of OPC, heat was evolved during hydration. If water was not sufficiently available for hydration, the homogeneity of the matrix would be disturbed.
Accordingly, more water would be available for proper mixing at higher cement contents as in the present research, but if not some particles of OPC might have been left unreacted. This in turn could be decreased the strength of the GPC matrix, i.e., a poor matrix structure due to higher amount of heat released.

3.6. Compressive Strength

The compressive strength results of the various geopolymer cement mixes hydrated up to 90 days are shown in Figure 9. The compressive strength improved and enhanced with the increase of OPC content only up to 18 wt. %, and then slightly decreased gradually with any further increase of OPC content. This trend was occurred at all curing ages of hydration. GPC mixes exhibited the higher compressive strength values after 90 days of hydration. This is essentially attributed to the smaller size particles of both OPC and PRHA which filled the pore structure of the hardened samples. This is often resulting in a denser and more compact microstructure [6-10,27,28]. In contrast, with more than 18 wt. % OPC content, a marginal decrease in the compressive strength was observed. The GPC mix containing 24 wt. % OPC exhibited the lower compressive strength values at all curing ages of hydration. Yet, the strength achieved with 24 wt. % of OPC substitution was still considered satisfactory.

For the control mix with zero OPC content, the content of alumina is the least. Hence, the formation of either CASH or NASH gels is too limited. Moreover, mixing PRHA with the activator, the CSH gel could be generated due to the occurring of pozzolanic reactions between the constituents of PRHA and the free lime, Ca (OH)2 that resulting from the hydration of tri-and dicalcium silicate of OPC [5,16,56]. Mixes with higher OPC content, CSH, NASH and CASH gels were expected from the mixes. Furthermore, the smaller particle size OPC helps in filling the pore volume and voids. As a result, the reduction of pore system by disconnecting the capillaries was produced. This was reflected positively on the strength characteristics [22].

3.7. Ultrasonic Velocity Test

Ultra-sonic pulse velocity test (USPV) is mainly carried out to assess the uniformity and relative quality of structures and specimens. Hence, the ultrasonic pulse velocity graph of the blank geopolymer mix (G0), the optimum geopolymer cement (G18) and G24 is graphically drawn versus the hydration ages up to 90 days in Figure 10.
Figure 10. Ultrasonic pulse velocity of some selected geopolymer cement mixes (G0, G18 and G24) hydrated up to 90 days.

The USPV of the blank (G0) increased up to 7 days, and then enhanced very slightly up to 90 days, i.e. the various constituents of blank (G0) did not affect by the ultrasonic pulse velocity [57,58]. It is good mention that the same trend was displayed by the optimum batch (G18) and G24. Furthermore, the values of USPV of G18 are the lowest, while those of G0 and G24 are the highest. As a result, the USPV test proved that the matrix conformities of G18 are well sticky and with good quality than those of the blank or even G24, i.e. good uniformity with no cracks [58]. The gradual increase of pozzolanic reactions of PRHA with the resulting free lime from the hydration of calcium silicate phases of OPC is the essential factor responsible for the high quality and uniformity of G18 [58,59]. Therefore, the results of USPV confirmed largely the obtained results.

3.8. FT-IR analysis

The FT-IR spectra of the prepared geopolymer mixes G0, G18 and G24 are graphically plotted in Figure 11. The absorption band at wave number 3644-3642 cm\(^{-1}\) as detected with G24 is contributed to the free OH\(^{-}\) group coordinated to Ca\(^{2+}\), i.e. free lime or Ca (OH)_2, which is the essential factor to reduce its mechanical properties at all curing times. The large absorption bands located at 3565-3560 cm\(^{-1}\) and the less pronounced one at 1652-1646 cm\(^{-1}\) on the spectra of optimum G18 mix are assigned to the vibration bands of O-H bonds related to water. The absorption bands situated at 1443-1386 cm\(^{-1}\) are linked to the C-O stretching band of CO\(_3^{2-}\) [60] due to the reaction among Na\(^+\) into the geopolymer matrix with CO\(_2\) of the atmosphere [61,62]. The absorption bands occurring around 1044-1039 cm\(^{-1}\) in all spectra are linked to the vibration modes of Si-O-Al bonds [63,64]. The two absorption bands nearly at 1710-1680 and 1560-1250 cm\(^{-1}\) are related to the main silicate band involve Si-O stretching vibration bands of CSH. The three absorption bands at 1265-750 cm\(^{-1}\) are characterizing to CO\(_3^{2-}\) and SO\(_4^{2-}\), respectively are due to the rate of carbonation and sulfonation of CSH and/or CAH. Hence, the presence of reactive SiO\(_2\) in PRHA permitted the formation of high content of Si- that made this band shifted. This was also noted by some researchers [60,65], where they used reactive silica from PRHA to improve the formation of iron silicate compounds from raw iron-rich laterites cured at 80 °C. In G18 geopolymer, this band is more pronounced and showed the formation of NASH geopolymer-gel needed to ensure better conformity between different constituents in the whole system that responsible for the improvements in the mechanical properties.
3.9. SEM-EDAX Analysis  

Figure 12 illustrates the SEM images supported by EDAS (Energy-Dispersive X-ray Spectroscopy) of the blank (G0), the optimum geopolymer (G18) and G24 hydrated up to 90 days, respectively. The G18 containing 18 wt. % OPC demonstrated a microstructure of high and dense homogeneity with few or nearly no pores or cracks. This was evidently confirmed by EDAS spectra showing the existence of high percentage of SiO₂, Al₂O₃, but Na⁺ or K⁺ as minor elements, which was close to the optimum ratio for the NASH-gel [66]. Significantly, it contributes to the improve of the mechanical properties [66,67]. The microstructure of G24 shows more porous and heterogeneous matrix when compared with that of G18, or even G0. Consequently, this caused the reduction of mechanical properties of the prepared geopolymers containing high ratio of OPC [68].

![Figure 11. FTIR spectra of G0, G18 and G24 hydrated up to 90 days.](image)
4. Discussion

The improvements in mechanical properties with up to 18 wt. % OPC replacement (G18) could be attributed to the formation of additional Ca products (CSH) due to the presence of OPC. The OPC was rich in CaO content (66.33%), which often accelerated the polymerization process and was also responsible for additional CSH and CASH gels. These were responsible for the improvements and enhancing the mechanical strengths at all curing times. Furthermore, they imparted the strength development as compacting filler, covering and refining the pore structure, and also densifying the matrix by filling up the voids [23,69-71]. As the CASH gel has a spongy appearance, it helped in the formation of a denser microstructure. Also, as the bulk density of OPC was higher than PRHA, the stiffness of the hardened samples was increased, and so exhibited higher densities [23,72,73].

With higher substitution levels of >18% OPC (G24), the compressive strength slightly decreased. This is mainly contributed to the excessive CSH gels, which often resulted in the release of a higher quantity of heat, and consequently, higher chances of cracking were expected. This always causes the deterioration with further increase in OPC content, resulting in larger size voids, and a looser matrix structure. This case of a loose network of GPC, due to the poor bonding among various constituents, has a lower density and weaker zones, i.e. open pores and cracks. This gives a big opportunity for the declined characteristics. The PRHA needs high water amounts [22,45], and the extra water absorbed by PRHA led to an increase in the overall water requirements for proper hydration of GPC ingredients. This usually formed a matrix with lower strength. The increase of the strength with curing period could be mainly due to that the dissolution of higher amounts of the formed aluminosilicates (CSH and CAH), and also their polycondensation often led to the increase of the strength [22,23,69]. The results indicated that the activated PRHA based GPC with 18 wt. % OPC addition can be used as a building material for construction purposes like roadway and runway building constructions.

Many studies [23,70-72] reported that the formed CSH gel which is the main product resulting from the hydration of OPC with water, was responsible for the strength improvement, developing and the hardening of the matrix. Also, the structure improved by time, where a compact and denser matrix structure with fewer pores was formed due to the combined action of CSH, CASH and NASH gels as in G18. This often improved the overall mechanical performance. In addition, CSH gel formed a network of nanoparticles refining the matrix pore structure, allowing dense packing and reduction in porosity of the matrix. According to the relatively higher SiO$_2$/Al$_2$O$_3$ molar ratio and the amorphous nature of PRHA compared to other pozzolana, the reactive SiO$_2$ and Al$_2$O$_3$ contents could be in turn increased in the reaction media. Consequently, the formation of more geopolymerization products, which could be mainly sodium aluminosilicate hydrate gel (NASH) due to the low Ca$^{2+}$ content [48,73,74]. Hence, the decrease in compressive strength beyond 18 wt. % OPC may be related to the appearance of zeolitic phases in the geopolymer matrix, leading to the formation of a heterogeneous structure. Thus, the decrease in the overall mechanical properties was occurred as in G24 mix [23,75,76].

5. Conclusions

The synthesis of geopolymers-based PRHA was experimentally carried out. The prepared PRHA-based geopolymers (G0) showed poor structured products
with low physical and mechanical properties at all curing times. The partial replacement of OPC up to 18 wt. % at the expense of PRHA significantly improved all characteristics of the synthesized geopolymers, while the addition of > 18 wt. % OPC decreased both physical and mechanical properties, i.e. the optimum replacing content of PRHA by OPC was 18 wt. %. This brought more Al2O3 and reactive SiO2 which promoted the formation of amorphous NASH-gel and the geopolymerization reactions. This was considered as the main reason responsible for the better physical and mechanical properties of the synthesized geopolymers. With more than 18 wt. % OPC, all characteristics were declined. The obtained results are largely confirmed by ultrasonic pulse velocity test (USPV). G18 demonstrated a microstructure of more compacted with a high dense homogeneity matrix with nearly few or no pores or cracks when compared with that of G24 or even G0. The FTIR as well as the SEM-EDAX spectra proved that the optimum geopolymer mix (G18) had more pronounced with NASH geopolymer-gel needed to ensure better conformity between the different ingredients of the whole system that responsible for the modification and development in both physical and mechanical properties. The activated PRHA-OPC geopolymer could be used as a sustainable building material. It also could be developed the resources of the geopolymers and environmental protection in the sector of building and construction.

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