Strength and fire resistance characteristics of geopolymers synthesized from volcanic ash, red clay and waste pen shells

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Abstract. This study utilized volcanic ash and red clay, as well as calcined waste pen shell (Baluko) in the production of geopolymer-based materials. The geopolymers were formed by activating the mixture of these raw materials (as the alumina-silica rich materials) with activating solution of 12M NaOH/Na₂SiO₃ (w/w: 2.5:1). Two sample types, a cube type and a slab type, were used in the study in order to conform to test standards for compressive strength and fire resistance test. The cube type molds were for the compressive strength tests while the slab type was used for the fire resistance tests. Material testing such as Fourier Transform Infrared (FTIR) spectroscopy was used to analyze the chemical characteristics of both the raw materials and the geopolymer specimens. The mixture containing 45% volcanic ash-45% red clay-10% calcined waste pen shell powder (by weight) was observed to have the highest compressive strength out of all the samples tested. The fire resistance of the geopolymers formed from a ternary mixture of 16% volcanic ash-66.67% red clay-16% calcined waste pen shell powder (by weight) was also observed to be comparable to that of ordinary Portland Cement (OPC). Furthermore, the FTIR results of both raw materials and geopolymer showed evidence that geopolymerization occurred in the samples, indicating that the selected precursors are viable for use in the formation of geopolymers.

Keywords: Geopolymer, volcanic ash, red clay, waste pen shell.

1. Introduction
Geopolymers, also referred to as alkali-activated cement, geocement, hydroceramic, etc., are inorganic polymers synthesized by the addition of an alkali solution to an aluminosilicate-rich precursor material. It is dubbed as a next-generation cement but with a lower carbon footprint and embodied energy as compared to ordinary Portland cement (OPC) [1-3]. Some of its properties are high compressive strength, good chemical resistance and high temperature resistance attributed to its three-dimensional structure of aluminate and silicate tetrahedra joined by oxygen corners [4, 5]. Some recent studies show
that geopolymers could also be utilized for wastewater treatment, as a heavy metal adsorbent, and as a heterogeneous catalyst [6-9].

Geopolymer technology allows for waste valorization of industrial and agro-industrial by-products and waste materials that have high concentration of alumina and silica. These include coal ash, rice hull ash, red mud, blast furnace slags, among others [10-12].

Volcanic ashes, natural pozzolans rich in alumina and silica, have been used in geopolymer studies [13-14]. In this study, red clay, which is also naturally rich in minerals, is combined with volcanic ash as the aluminosilicate raw material mixture in the geopolymer synthesis. The addition of calcined Baluko shells, a type of pen seashells rich in calcium, is done in consideration of the calcium-silicate-hydrate, \( \text{CaO-SiO}_2\cdot\text{H}_2\text{O} \) or \( \text{C-S-H} \), reaction path in the presence of water [15, 16]. \( \text{C-S-H} \) is the primary product of hydration of silica and calcium and is the major factor in the strength of OPC-based concrete.

Thus, this study explores the Philippine-locally available materials of volcanic ash, waste pen shells, and red clay to form geopolymer-based materials. These three materials were sourced from the Bicol Region where Mayon Volcano is located, red clay is abundant and Baluko (Pinnidae) pen shell meat is a local delicacy. Seashells, such as Baluko shells, are good sources of calcium and the calcined shell has been utilized to make a composite geopolymer with fly ash [17]. The use of such indigenous resources and waste (as are the Baluko pen shells) as raw materials for geopolymer precursor mitigates not only the waste’s environmental footprint but also contributes towards producing eco-friendly materials.

2. Materials and Method

2.1 Preparation of raw materials

The three materials, volcanic ash, red clay and waste pen shells (Baluko), sourced from Bicol region in the Philippines, are shown in Figure 1. The volcanic ash and red clay, being initially damp, rocky, and clumped together, underwent drying and grinding to achieve a particle size of not greater than 150 \( \mu \)m. The waste pen shells had to be washed first with sodium hypochlorite to remove contaminants that cling onto the shell before oven drying at 110°C. The dried shells were then calcined at 700°C in a muffle furnace.

![Figure 1. Raw materials: A volcanic ash, B red clay and C Baluko pen shells](image)

X-ray Fluoroscopy (XRF) analysis show the composition of the component materials in Table 1. The volcanic ash and the red clay contain high alumina (63.91% and 65.55%, respectively) and silica (17.06% and 26.48%, respectively) and the calcined Baluko shell is 84.37% calcium oxide (\( \text{CaO} \)).
Table 1. Composition of raw materials (percentage by mass).

| Component     | Volcanic Ash | Red Clay | Baluko pen shell |
|---------------|--------------|----------|------------------|
| SiO₂          | 63.91        | 65.55    | 8.01             |
| Al₂O₃         | 17.06        | 26.48    | 4.12             |
| Fe₂O₃         | 8.61         | 7.77     | 0.71             |
| Na₂O          | 2.46         | 0.06     | 2.12             |
| MgO           | 3.15         | 0.02     | 0.67             |
| CaO           | 4.81         | 0.12     | 84.37            |
| Total         | 100.00       | 100.00   | 100.00           |

2.2 Synthesis and testing of geopolymer samples
The activating solution was prepared by mixing 12M sodium hydroxide (NaOH) solution with water glass solution (Na₂SiO₃) in a ratio of 2.5:1. The solid-to-liquid ratio of 0.25 by mass was maintained in all mixtures following the mix design described in Table 2. The fresh mix was then placed in the appropriate molds to form 50 mm x 50 mm x 50 mm cubical samples and 200 mm x 200 mm x 50 mm slab type samples. The cube type samples were subjected to compressive strength tests while the slab type samples were used for the fire resistance tests. One set of samples was pre-cured at 80°C for one day and then fully cured for a total of 28 days. The other set was cured at ambient conditions for the full 28 days. Compressive strength was measured using a Universal Testing Machine (UTM) whereas the fire resistance was evaluated following ASTM E119: Standard Test Methods for Fire Tests of Building Construction and Materials (Standard Fire Test).

Table 2. Mix proportions of the geopolymer samples (percentage by mass).

| Mixture Code | Volcanic Ash (VA) | Red Clay (RC) | Baluko shells (BS) |
|--------------|-------------------|---------------|--------------------|
| UCL008       | 75                | 25            | 0                  |
| UCL009       | 50                | 50            | 0                  |
| UCL010       | 45                | 45            | 10                 |
| UCL011       | 66.67             | 16.67         | 16.67              |
| UCL012       | 16.67             | 66.67         | 16.67              |
| UCL013       | 75                | 0             | 25                 |
| UCL014       | 25                | 75            | 0                  |
| UCL015       | 0                 | 75            | 25                 |

3. Results and Discussion

3.1 Fourier Transform Infrared (FTIR) spectroscopy analysis
Figure 2 shows the infrared spectrum of the red clay. The values indicated in the waveforms are the peaks in which there are bonds and minerals essential in geopolymerization. The peaks from 3624 -3693 cm⁻¹ indicate that kaolinite is present. Kaolinite, Al₂Si₂O₅(OH)₄, is a major constituent of red clay which gives sharp absorption bands in the 3600-3700 cm⁻¹ region [18]. The band at 1040 cm⁻¹ is due to asymmetric stretching vibrations of silicate tetrahedron [18]. The peak at 793 cm⁻¹ indicates the presence of quartz which is explained by the Si-O stretching vibration. On the other hand, the peak at 677 cm⁻¹ indicates a Si-O symmetric bending vibration due to low level of Al for Si substitution. The band at 538 cm⁻¹ is due to the presence of hematite. It overlaps into one broad adsorption band centered at 535 cm⁻¹ assignable to Fe-O present in kaolinite [18]. The region between 2850 - 3000 cm⁻¹ indicates that there is a presence of organic matter. More specifically, the peaks at 2860 and 2927 cm⁻¹ correspond to the C-H stretching vibrations of some organic contribution [19].
Figure 2. FTIR spectrum of red clay

Figure 3 shows the infrared spectrum of the uncalcined Baluko shell and the calcined Baluko shell. For the uncalcined Baluko shell, a broad absorption around 3421.55 cm\(^{-1}\) is caused by the O–H stretching vibration. The peak at 3642.18 cm\(^{-1}\) indicates a sharp O–H stretching band upon calcination. The peak at 1453.6 cm\(^{-1}\) indicates a bending vibration of the O-Ca-O functional group. The Baluko shells, being primarily composed of calcium carbonates, only act as aggregates and do not fully contribute to the geopolymerization process [15]. On the other hand, FTIR pattern from the calcination process indicates a new peak which appears at 3,620 cm\(^{-1}\). This indicates the formation of basic OH groups which attached to the calcium atoms, which could make the calcined clay more reactive to form cementitious-like structure [20].

Figure 3. FTIR spectra of uncalcined and calcined Baluko pen shells.

Figure 4 shows the infrared spectrum of the volcanic ash. The bands at 726 cm\(^{-1}\) and 592 cm\(^{-1}\) indicate ring vibrations of Si-O bonds of the silicate network. The main band related to the vibration of SiO/Al–O bond of aluminosilicate framework is located at around 1014 cm\(^{-1}\). The peaks at 2926 - 2959 cm\(^{-1}\) and 2860 cm\(^{-1}\) may relate to C–H vibrations bond of methane. The bands observed at 3420 and 1631 cm\(^{-1}\) are characteristic of stretching and bending vibrations, respectively, of O–H bonds from silanol group and water molecules [21].
Figure 4. FTIR spectrum of volcanic ash.

Figure 5 shows spectra of some of the geopolymer specimens produced from this experiment. The peak at around 1600-1630 cm\(^{-1}\) indicate a H-OH bending vibration and is typical for polymeric structures including aluminosilicate [22]. At around 1400 cm\(^{-1}\), O-C-O stretching of carbonates occur. The peaks ranging from 950-1200 cm\(^{-1}\) indicate that there is a T-O-Si asymmetric stretching, in which T can either be Al or Si. The key feature of the spectra are the bands around 1000 cm\(^{-1}\) to 900 cm\(^{-1}\) which indicates the presence of geopolymeric structure. As far as evidence of C-S-H reaction, the presence of the absorption hump at 970–1100 cm\(^{-1}\) due to polymeric silica and at 800-970 cm\(^{-1}\) due to the dissolution of calcium silicate, is correlated with the development of water bending vibration bands (1500–1700 cm\(^{-1}\)) due to the formation of calcium silicate hydrate, C-S-H [23, 24].
3.2 Thermogravimetric analysis (TGA) of Baluko seashells

As shown in Figure 6, the Baluko shells experienced a minimal loss of mass from 0℃-420℃ of the test. However, at within the 500℃ range, the weight of the sample began to decrease. At about 690℃, a dramatic reduction of weight can be observed. The decrease in mass was due to the thermal decomposition reaction that occurred when CaCO₃ was exposed to extreme temperatures, which resulted in the production of the compounds calcium oxide (CaO) and carbon dioxide (CO₂). At about 700℃, a chemical reaction occurred converting CaCO₃ into CaO.

![Thermograph of Baluko seashell](image)

**Figure 6.** Thermograph of Baluko seashell.

3.3 Unconfined compressive strength

The mean compressive strengths of the geopolymer samples produced varied over a range of 0.06MPa to 3.61MPa for the samples cured at ambient conditions, whereas the mean compressive strengths of the samples pre-cured at 80℃ varied over a range of 0.25MPa to 7.19MPa. These results indicate that the pre-curing of the samples at an elevated temperature has resulted in an overall gain in the mean compressive strength of the geopolymers [22]. The results of compressive strength test are summarized in Figure 7.

![Unconfined compressive strength of geopolymer samples](image)

**Figure 7.** Unconfined compressive strength of geopolymer samples.
Moreover, the samples formed from ternary mixtures of volcanic ash, red clay, and calcined Baluko seashell were observed to have higher mean compressive strengths when compared to the samples formed from binary mixtures. It can be observed that the mean compressive strength of the ternary geopolymer binder mixtures ranges from 4.3MPa to 7.19MPa, attaining the highest recorded value when equal parts of volcanic ash content (45%) and red clay (45%) content are incorporated into the mixture, with an amount of calcined Baluko seashell not exceeding 10% of the whole mixture. This implies that the addition of calcined Baluko shells contribute to increasing the strength.

3.4 Fire resistance tests

The fire resistance tests were conducted following the Fire Test Standard ASTM E119 which exposes one side of the samples to a prescribed temperature vs. time profile as shown in Figure 8. According to the ASTM E119, the material is considered to have failed if the temperature of the unexposed surface has risen 140°C above its initial temperature. Material failure is also considered if visual cracking takes place. The time at which material failure has occurred is taken as the material fire resistance rating (FRR) [25, 26].

![Figure 8. Time-temperature curve for the fire resistance test according to ASTM E119 [23].](image)

In the fire resistance tests, the sample UCL 010 (45-45-10 VA-RC-BS) showed the fastest increase in temperature reaching its failure temperature within 17 minutes of direct fire exposure. The samples UCL 011 (66.67-16.67-16.67 VA-RC-BS) and UCL 012 (16.67-66.67-16.67 VA-RC-BS) have approximately 30 minutes fire resistance rating as shown in Table 3. It is seen here that the samples with higher calcined seashell content produces geopolymers with comparable fire resistance rating to OPC concrete and also with higher percentage of residual strength as seen in Table 4. Figure 9 seems to indicate that higher volcanic ash content has a higher fire resistance than red clay based on the actual temperature vs. time profile of the unexposed side of the samples and on the physical appearance of the unexposed surfaces before and after fire testing, as shown in Figure 10, which shows more visible cracks for the sample with higher red clay content.
Table 3. Fire resistance ratings of geopolymer samples vs standard concrete.

| Sample (50 mm thickness) | Mix Proportion (VA-RC-BS) | Mean Fire resistance rating (FRR) |
|-------------------------|---------------------------|-----------------------------------|
| UCL 010                 | 45-45-10                  | 17 minutes                        |
| UCL 011                 | 66.67-16.67-16.67         | 28.5 minutes                      |
| UCL 012                 | 16.67-66.67-16.67         | 32.75 minutes                     |
| OPC Concrete            | with Type A aggregate     | 31.3 minutes                      |
| NZS 3101-1              | (standard for 50 mm thick concrete) | 30 minutes                      |

Figure 9. Temperature vs time of unexposed side of selected geopolymer specimens during fire resistance tests.

Figure 10. Unexposed surfaces of geopolymer pre-firing (top), post-firing (bottom).

Table 4. Residual strength after fire resistance test

| Sample   | Mix Proportion (VA - RC - BS) | Mean compressive strength before fire test | Mean compressive strength after fire test |
|----------|-------------------------------|--------------------------------------------|------------------------------------------|
| UCL 010  | 45-45-10                      | 5.96 MPa                                    | 5.30 MPa                                 |
| UCL 011  | 66.67-16.67-16.67             | 2.10 MPa                                    | 2.62 MPa                                 |
| UCL 012  | 16.67-66.67-16.67             | 8.14 MPa                                    | 7.84 MPa                                 |
4. Conclusions
Volcanic ash, red clay and waste Baluko shell were used to produce geopolymer-based materials. A mix proportioning which contains 45% volcanic ash- 45% red clay-10% calcined waste shell was observed to have the highest compressive strength out of all the samples. The fire resistance of the geopolymers formed from a ternary mixture of 16% volcanic ash-66.67% red clay- 16% calcined waste shell powder was observed to be comparable to that of OPC. Furthermore, the FTIR results showed evidence that geopolymerization occurred from the activation of these raw materials indicating that the selected precursors are viable for use in the formation of geopolymers. Also, better strength properties were observed for the samples that contain higher calcined waste seashells which may be attributed to the C-S-H reaction path.

With these results, it is envisioned that more studies will look into naturally occurring mineral-rich materials such as volcanic ash and red clay as additional alternative or replacement materials in the production of eco-friendly binders for the building sector. Thus, moreover, in this specific formulation, future work will investigate further the optimization of the properties of the geopolymer product.

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