Influence of the Activating Solution and Aggregates in the Physical and Mechanical Properties of Volcanic Ash Based Geopolymer Mortars

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Abstract. The physical, mechanical and microstructural properties of volcanic ash based geopolymer mortars by alkaline activation (with NaOH and Na(OH) + Na₂SiO₃ solutions) using different aggregates (Peruvian sand and standard sand) were studied. For the synthesis of geopolymers, a liquid:solid ratio of 0.1 and an ash:sand ratio of 1:1 were selected, and 25% of sodium silicate was added to the Na(OH) solution. The samples were compacted, toughened and cured at 80°C for 48 h. The dissolution of volcanic ash particles and the formation of the geopolymeric matrix increase with Na(OH)+Na₂SiO₃ solution and standard sand while the local sand promotes better geopolymerization with NaOH solution. The compression strength of volcanic ash based geopolymer mortar reported values from 18.93 MPa to 23.28 MPa at 6 months of curing, which determines the use of these geopolymers as a construction material.

1. Introduction

Geopolymers, known as inorganic polymers or zeolite precursors, are aluminosilicate materials with attractive properties causing a variety of studies to replace Portland cement because the production of Portland cement results in an excessive carbon dioxide emissions (which are 6-7% of the worldwide emissions) [1]. These inorganic polymers have good physical and mechanical properties, such as stability at high temperatures and high compression strength [2]. These properties rely on a variety of parameters, such as the type of precursor materials, mineralogical and chemical compositions of the aluminosilicate sources, temperature and curing time, alkaline composition of the solution, the liquid:solid and aggregate ratios [3]. Additionally, a variety of studies has revealed that volcanic ashes, metakaolin and different aluminosilicates can be used as precursor materials for the synthesis of geopolymers.

Volcanic ashes contain a large amount of silica and alumina which make them suitable for the production of geopolymers [4]. These vitreous materials also have a certain amount of innocuous and inactive minerals such as magnetite, quartz and mica, leading into an important challenge to understand the reaction of phases during and after the hydration process. Nowadays, there have been
developed studies concerning volcanic ashes as a replacement of Portland cement. Volcanic ashes are widely available in the south area of Peru. The Ubinas volcano is considered as the most active volcano in Peru because of its 25 events of high fumarolic activities followed by ashes and rocks emissions since XVI century [5]. The distribution of ashes around the volcano, determined by the influence of winds, allowed the formation of stockpiles, which are reachable and it can contribute into easy extraction followed by economic and environmental benefits to the country.

The current investigation has studied the physical, mechanical, mineralogical and microstructural properties of volcanic ashes based geopolymer mortars, using different types of aggregates such as local sand (LS) and standard sand (SS). The geopolymer mortars were under evaluation for 6 months, with an ash:sand ratio of 1:1. The alkaline activation had a liquid:solid ratio of 0.1, with sodium hydroxide (NaOH) and sodium silicate + sodium hydroxide (NaOH+Na$_2$SiO$_3$) solutions, this last in a concentration of 75%-25% (w/w), and both solutions were in 12 M concentration.

2. Experimental procedure

2.1. Materials
Volcanic ashes (VA) were collected from Ubinas volcano, whose geographical coordinates are 297608 of latitudes, 8196158 length and 4600 meter above sea level (Moquegua, Peru). The aggregate of local sand (LS) was from Arequipa, and the aggregate of standard sand (SS) was standardized CEN-NORMSAND (according to DIN EN 196-1 standard), with a particle size ranging between 0.08 and 2 mm. The volcanic ashes were ground in a planetary ball mill Fritsch 6S for 25 min at 450 rpm in order to get fine particles (<75 µm). The volcanic ashes and aggregates were dried in Memmert Universital Oven UN55 at 105 °C for 6 h. Portland cement from Yura IP (YC) was used for comparison to the geopolymer mortars.

2.2. Method of synthesis of geopolymeric mortars
The synthesis of geopolymer mortars was made by alkali activation. Volcanic ashes and aggregates were in a ratio of 1:1. They were dissolved in an alkaline solution with a liquid:solid ratio of 0.1. The solutions of (NaOH) and (NaOH+Na$_2$SiO$_3$) were in 12 M concentration, and NaOH+Na$_2$SiO$_3$ was in a proportion of 75%-25%. The samples were mixed according to the UNE-196-3 standard, dumped into cylindrical molds of 28 mm diameter and followed by compression at 15 MPa. The samples were covered with a plastic film to be cured at 80° C for 48 h in a Memmert Universal Oven UN-50. After curing, the samples were placed in a Memmert Incubator IF-110 at room temperature and high relative humidity (>90%) until the compression test day (7, 14, 28, 90 and 180 days).

3. Characterization techniques of materials and geopolymeric mortars

3.1. X-ray Fluorescence Spectroscopy (XRF)
The chemical composition of precursor materials was determined by an X-ray Fluorescence Spectrometer (XRF) Spectro Xepos.

3.2. X-ray Diffraction (XRD)
The mineralogical composition of precursor materials and geopolymer mortars was analyzed by X-ray diffraction, Bruker (DRX) D8, with a radiation or CuKα ($\lambda = 0$, 1542 nm), voltage of 40 kV and current of 40 mA, the angle 2θ was in arrange of 10° to 80° with a scan speed of 2 °/min.

3.3. Absorption, and bulk density
The bulk density was determined by gravimetric method (UNE-EN 1015-11:1999), Archimedes method (ASTM C-20) and the absorption analysis by ASTM C-642.
3.4. Compression strength
The compression strength of geopolymer mortars was determined at 7, 14, 28, 90 and 180 days of curing according to UNE-EN 12390-3:2003. It was carried out in a hydraulic compression machine ELE International. Five tests were made for each condition.

3.5. Scanning Electron Microscopy (SEM)
The morphological characteristics of geopolymer mortars were analyzed by a Scanning Electron Microscope Hitachi SU8230 with back scattered electron (BSE). The images were taken at 5kX.

4. Results and discussion

4.1. Materials characterization

4.1.1. X-ray Fluorescence Spectroscopy (XRF). The chemical composition of precursor materials used in this work are shown in table 1. They are mainly composed of SiO\(_2\), Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\). The composition is favorable as the values are ranged into the main requirements in precursor materials for the production of geopolymers [6].

|       | YC   | VA   | LS   | SS   |
|-------|------|------|------|------|
| SiO\(_2\) | 31.68| 45.26| 45.33| 93.90|
| Al\(_2\)O\(_3\) | 6.32 | 13.40| 14.47| 4.04 |
| Fe\(_2\)O\(_3\) | 3.28 | 6.72 | 8.03 | 1.38 |
| CaO    | 29.86| 5.18 | 5.23 | 0.58 |
| MgO    | 0.43 | 3.58 | 2.73 | 0.01 |
| K\(_2\)O | 1.48 | 1.48 | 1.17 | -    |
| TiO\(_2\) | 0.17| 1.08 | 0.74 | 0.06 |
| P\(_2\)O\(_5\) | 0.17| 0.37 | 0.21 | 0.02 |
| Na\(_2\)O | 0.01| 0.26 | 1.44 | -    |
| MnO    | 0.04| 0.10 | 0.08 | 0.01 |
| LOI\(^a\) | 26.56| 22.57| 20.57| -    |

\(^a\) Loss on ignition

The hydraulic cement (YC) is formed by 29.86% of calcium oxide (CaO), 31.68% of silicon dioxide (SiO\(_2\)), and low quantities of aluminum oxide (Al\(_2\)O\(_3\)) and iron oxide (Fe\(_2\)O\(_3\)).

Regarding the chemical composition of volcanic ash (VA), it shows SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio of 5.73. These components are the major constituent in precursor materials for the production of geopolymers and their values match those reported by Davidovits [7] and Palomo [8]. It is well known that the small amounts of calcium oxide influence significantly in the properties of geopolymer cements. In this case, CaO is 5.18%. The chemical composition confirms that volcanic ashes are predominantly constituted of silica followed by aluminum, iron, calcium and sodium oxides. The amount of (SiO\(_2\)+Al\(_2\)O\(_3\)) %wt is beneficial for the synthesis of geopolymers. Therefore, volcanic ash based geopolymer can be effective [7] and its alumina composition is beneficial for the mitigation of efflorescence [9].

The chemical composition of the aggregates was also analyzed, LS showing 45.33% of SiO\(_2\). On the other hand, SS has a high amount of SiO\(_2\) (93.91%), which is similar to the dune sand reported by Chuah [10] on his studies of the properties of fly ash based geopolymer mortars.

4.1.2. X-ray Diffraction (XRD). The X-ray diffractograms of precursor materials in an angle range of 10\(^\circ\) to 80\(^\circ\) of 2\(\theta\) are shown in figure 1. The cement shows the major peaks of tricalcium silicate (3CaO.SiO\(_2\)) or trico (C\(_3\)S), bicalcium silicate (3CaO.SiO\(_2\)) or belite (C\(_2\)S), tricalcium aluminate (3CaO.Al\(_2\)O\(_3\)) or C\(_3\)A), and tetracalcium ferritoaluminate (4CaO.Al\(_2\)O\(_2\).Fe\(_2\)O\(_3\)) or (C\(_4\)AF). According
to other studies, the crystalline system of C₃S and C₂S phases is monoclinic, C₃A is cubic and C₄AF is orthorhombic [11], [12]. There are also another phases such as calcium oxide or lime, magnesium oxide and alkaline sulfates [11].

The XRD of volcanic ashes shows peaks of augite, muscovite, anortite, forsterite, quartz, feldspars, magnetite, sodium diopside, and aluminum diopside [9], [13],[14]. Unlike other studies, this volcanic ash has a prominent peak between angles 50° and 55°, which corresponds to the presence of diopsides. The characterization and classification of volcanic ashes is based on the mineralogical composition. The aggregates show peaks of quartz and alpha quartz, as well as a high amount of calcite [15].

![Figure 1. DRX patrons of cement (YC), volcanic ash (VA), local sand (LS), and standard sand (SS).](image)

4.2. Physical and mechanical tests of mortars

4.2.1. Water absorption and bulk density. Table 2 shows the water absorption, Archimedes density and bulk density (%) for samples cured at 28 days. The water absorption varies from 8.54% to 12.96% where samples VA-SS-1 and VA-SS-2 have the lowest values. Although those values are slightly above the reported in other studies like Djobo [9], it is well known that water absorption correlates with the values of apparent porosity which is the result of water that could not react during the geopolymization. Therefore, the higher water absorption, the higher porosity in mortars. The bulk and Archimedes’ densities range from 1.92 to 2.11 g/cm³ and 1.74 to 2.05 g/cm³ respectively, showing VA-SS-1 and VA-SS-2 samples the highest values. Density also correlates to the apparent porosity. Porosity decreases when the density increases and vice versa affecting the mechanical properties of mortars [16]. Thus, good results on compression strength are expected for volcanic ash based geopolymor mortars activated with Na(OH)+Na₂SiO₃, better than YC-LS samples. Additionally, the influence of the aggregates and alkaline solution in samples with LS solution causes higher values of density using NaOH solution, resulting in less porosity. In contrast, samples with SS have higher density values when using NaOH+ Na₂SiO₃ solution, indicating this solution has reacted much better with SS-containing mortars than with LS ones. According to the chemical composition of aggregates, the higher amount of silica contributes to a better polycondensation [13].
Table 2. Absorption, density, and bulk density of volcanic ash based geopolymer mortars

| Mortar   | Activator            | Absorption % | Bulk density (g/cm³) | Archimedes density (g/cm³) |
|----------|----------------------|--------------|----------------------|----------------------------|
| YC-LS    | H₂O                  | 11.66        | 1.96                 | 1.84                       |
| VA-LS-1  | Na(OH)               | 12.64        | 1.95                 | 1.80                       |
| VA-LS-2  | Na(OH)+Na₂SiO₃       | 12.96        | 1.92                 | 1.74                       |
| VA-SS-1  | Na(OH)               | 10.90        | 2.02                 | 1.96                       |
| VA-SS-2  | Na(OH)+Na₂SiO₃       | 8.54         | 2.11                 | 2.05                       |

4.2.2. Compression strength. The evolution of the compression strength of volcanic ash based geopolymer mortars with time (from 7 days to 180 days) is reported in table 3. The maximum strength for sample VA-SS-2 is 38.84 MPa at day 7th which decreases over time until 23.24 MPa on day 180. However, this sample with Na(OH) solution has the minimum strength with values of 16.94 MPa, 23.62 MPa and 11.81 MPa at days 7, 90 and 180 respectively. Apart from that, sample VA-LS-1 shows better strengths with Na(OH)+Na₂SiO₃ for each curing time. According to different studies, the gradual decrease on the strength of geopolymer mortars in comparison with cement Portland is accredited to the presence of calcium, porosity or an unfinished geopolymerization [9], [17], [18]. Additionally, the compressive strength can be related to the characteristics of the aggregates and their bind with the polymer gel [19], along with the absorption and density properties [9]. Therefore, it can be inferred that the values of compressive strengths for samples VA-LS are accredited to an unfinished geopolymerization, contrary to the samples VA-SS which may have a complete geopolymerization.

Table 3. Compression strength (MPa) of volcanic ash based geopolymer mortars.

| Mortar   | Activator            | 7 days      | 14 days     | 28 days     | 90 days     | 180 days   |
|----------|----------------------|-------------|-------------|-------------|-------------|------------|
| VA-LS-1  | Na(OH)               | 27.49±8.91  | 27.57±6.28  | 24.57±1.72  | 23.15±5.12  | 18.93±1.49 |
| VA-LS-2  | Na(OH)+Na₂SiO₃       | 17.46±6.69  | 12.67±2.62  | 14.15±2.33  | 16.75±1.08  | 11.81±1.02 |
| VA-SS-1  | Na(OH)               | 16.94±1.82  | 14.99±1.88  | 20.21±7.31  | 23.62±5.91  | 11.81±2.81 |
| VA-SS-2  | Na(OH)+Na₂SiO₃       | 38.84±2.57  | 31.835.67   | 26.30±5.67  | 21.58±8.26  | 23.28±5.14 |
| YC-LS    | H₂O                  | 27.45±3.44  | 28.03±4.77  | 29.36±2.57  | 27.36±0.56  | 25.10±7.96 |

4.3. Mineralogical characterization of mortars

4.3.1. X-ray Diffraction (XRD). X-ray diffraction patterns of volcanic ash based mortars are shown in Figure 2. The diffraction patterns for samples YC-LS and VA-LS are similar and there are no variations. On the other hand the diffraction pattern for sample VA-SS shows a slightly shift of its major peak located at the angle of 28°. As mentioned in the studies developed by Baenla [20], minerals present in volcanic ashes have not been affected by the alkaline activation except muscovite, arcanite and calcite, suggesting an incomplete dissolution of crystalline phases in precursor materials [14]. Also, it is worth mentioning that the dissolution of muscovite is marked by the decrease of its peak followed by an increase of bents between angles 18° and 30° in the diffraction patterns of mortars compared to the volcanic ash. However, the diffraction pattern of volcanic ash based geopolymer mortars also shows the appearance of sodium aluminum silicate hydroxide hydrate Na₈(AlSiO₄)₃(OH)₄·2H₂O at angles between 20° and 25°. This can be related to the nature of the precursor materials, curing temperature and the concentration/composition of the alkaline solution [14].
4.4. Microstructural analysis of mortars

4.4.1. Scanning Electron Microscopy (SEM). Microstructural characteristics of volcanic ash based geopolymer mortars by alkaline activation and different aggregates are shown in figure 3. The images reveal that dissolution of volcanic ash particles and geopolymeric matrix increases with sodium silicate in NaOH solution 12M. Additionally, the images show the presence of micropores and bubbles of water (holes), which influence the compression strength of mortars. According to different studies, it can be inferred that there are areas with unfinished geopolymerization due to the agglomeration of volcanic ash particles which also have influence on the compression strengths of mortars [21], [14] and is reported in this work. Therefore, the high compression strength of VA-SS samples could be related to a better geopolymerization than VA-LS samples.
Figure 3. SEM images of volcanic ash based geopolymer mortars (a) VA-LS-1, (b) VA-LS-2, (c) VA-SS-1, and (d) VA-SS-2.

5. Conclusions
The synthesis of volcanic ash based geopolymer mortars was accomplished using different aggregates such as local sand and standard sand with two alkaline solutions, NaOH and Na(OH)+Na₂SiO₃, those initial materials influence on the properties of the geopolymer mortars. The chemical composition analysis of precursor materials confirms the presence of silicate, alumina and calcite, which have no variation on the diffraction patterns of the geopolymer mortars.

The physical properties and the compression strengths for volcanic ash geopolymer mortars are more attractive than cement mortars, allowing the use of volcanic ashes for the production of geopolymers in construction. Samples with NaOH+Na₂SiO₃ have lower density due to an excessive alkaline solution followed by an unfinished geopolymerization.

According to the gradual decrease on compression strength of volcanic ash based geopolymer mortars, it can be inferred that the aggregates have also influence on the properties due to the different values of samples with LS and SS. It is also considered that the compression strength is related to the presence of calcite, porosity and agglomeration of volcanic ash that could not react to the alkaline solution which can be noticed in the SEM images.

6. References
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