Influence of the activating solution on the mechanical properties of compacted volcanic ash based geopolymers

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Abstract. This work studies the mechanical properties of volcanic ash based geopolymer mortars. The geopolymer mortars were made with volcanic ashes from Ubinas volcano using mixtures of Na₂SiO₃ and 12 M NaOH as alkaline activator. Solutions with different concentrations of silicate (0-25 % by wt.) were used. The geopolymer mortars were compacted at 15 MPa and cured at 80°C for three different periods of time. The results show the influence of the concentration of Na₂SiO₃ in the compression strength and wear resistance, raising highest compression strengths for 20-25% of Na₂SiO₃ while the wear resistance was higher at concentrations over 20% of Na₂SiO₃. In this optimal ratio, for 20% Na₂SiO₃, a compression strength up to 52.3 MPa was recorded at 7 days. Considering the overall performance analysis, the synthesis of geopolymers with volcanic ash promises a solution for sustainable mortar production and natural waste disposal.

1. Introduction

The volcanic ashes are vitreous pyroclastic materials produced by an eruptive volcanic action [1]. The volcanic ashes are usually grey and dark grey. They can also have a huge impact on the farmland near the volcano because during the raining season tephra and lahars falls down [2]. The composition of volcanic ashes makes them potentially attractive for the construction industry to produce geopolymers [3] [4]. Additionally, studies of volcanic ashes as fire retardant additive load on polymers has been started [5].

The geopolymer is an inorganic polymer based on alumina and silicates which is synthetized by silicon (Si) and aluminum (Al) material, that can be from geological origin [6]. There are some variables that influence geopolymerization process, such as molar concentrations of the alkali and sodium silicate,
curing temperature, liquid:solid ratio, etc. A study of the effect of Na$_2$SiO$_3$ at 24 h of curing has reported that high concentrations of Na$_2$SiO$_3$ have influence on the specimens, while those high concentrations of Na$_2$SiO$_3$ at lower temperatures of curing result in lower compression strengths [7].

However, there are not many studies about the use of volcanic ash for the production of geopolymers and the variables that influences the synthesis. As a result, this work studies the influence of different concentrations of Na$_2$SiO$_3$ as alkali activator on the mechanical properties of volcanic ash based geopolymer mortars.

2. Materials and methods

2.1. Materials

The volcanic ashes used in this work were obtained from the Ubinas volcano located in Moquegua (Peru). The volcanic ashes were ground in a planetary ball mill Fritsch 6S to obtain powder with a particle size namely under 75 µm. Figure 1 shows the particle size distribution of the volcanic ashes which was determined by a laser light scattering particle analyzer Malver MASTERSIZER 2000. The real particle size distribution ranges between 0.3 and 100 µm, with diameters of $d(50)= 25.88$ µm and $d(90)= 57.42$ µm. The density of the particles size distribution (blue curve in Figure 1) shows that powder of volcanic ash has a bimodal distribution. The first mode ranges from 0.3 to 12 µm and second mode ranges from 12 to 100 µm, being the median particle size 27.39 µm. The grounded volcanic ash has a specific gravity of 2.62 g·cm$^{-3}$ and a specific surface of 2.29 m$^2$·g$^{-1}$.

Additionally, the chemical composition of the volcanic ashes was determined by inductive plasma (ICP) mass spectrometry. Table 1 shows the presence of the main oxides such as SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$; with a molar SiO$_2$/Al$_2$O$_3$ ratio of 3.96. This composition makes the volcanic ashes appropriate as a raw material for the synthesis of geopolymers according to the basic bibliography for synthesis of geopolymers [8].

![Figure 1. Particle size distribution of the milled volcanic ashes of Ubinas.](image)
Table 1. Chemical composition (%) of Ubinas volcanic ash.

| Oxide | SiO₂  | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | K₂O  | Na₂O | P₂O₅ | MnO  | TiO₂ | LOI* |
|-------|-------|-------|-------|------|------|------|------|------|------|------|------|
| %     | 58.70 | 14.80 | 7.69  | 5.80 | 4.17 | 2.63 | 3.52 | 0.37 | 0.10 | 1.14 | 0.87 |

LOI: Loss on Ignition

The mineralogical composition of volcanic ashes was determined by a X ray diffraction (XRD). Figure 2 shows that anorthite (Ca,Na)(SiAl)₄O₈ is the main mineralogical component in volcanic ashes. In addition, the morphology of particles was determined by scanning electron microscopy (SEM). Figure 3 shows SEM images of the volcanic ashes particles at 5000x magnification; as it is shown, the morphology is irregular and varies on its shape and size. Most of the particles has an angular shape due to the grounding.

Figure 2. X-ray diffraction analysis of Ubinas volcanic ash

Figure 3. SEM micrograph of Ubinas volcanic ash. 5000x

2.2. Geopolymer synthesis

The geopolymers were obtained by an alkali activation of the volcanic ashes, using a liquid/solid ratio of 0.2, with an alkali activator solution [3]. It is reported that activating solutions with both sodium silicate and sodium hydroxide increase the geopolymerization process and improve the strength of mortars [9]. The concentration of sodium hydroxide and the proportion of Na₂SiO₃/NaOH influence the properties of fresh and strengthen geopolymer mortars [10].

The alkali solution was then based on sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH), in a concentration of 12M NaOH with a mass percentage Na₂SiO₃ of 0, 5, 10, 15, 20 and 25%. Each solution was denominated as G0, G5, G10, G15, G20 and G25 respectively. The geopolymer paste was mixed for 5 min. Then, it was poured into cylindrical molds of 28 mm diameter, followed by a compression at 15 MPa; this action reduces the amount of alkali solution to be used in the geopolymerization concerning the cost. The specimens were immediately removed from the mold, covered with plastic film and cured at 80 °C for 48 h in a Memmert brand forced convection oven.

2.3. Characterization techniques

The bulk density of dried mortars was determined according to the ASTM C140, which calculates the density after 28 days of curing. The water adsorption was determined by the ASTM C-642 and the compression strength was studied at 7, 14 and 28 days of curing according to the ASTM C39 using an automatic compression testing machine (ELE International, England).
The wear resistance was determined in a Microtest pin-on-disc machine according to the ASTM G99-03 using a stainless steel ball (AISI 316) of 6 mm diameter, applying a load of 15 N at 60 rpm.

3. Results and discussion

Figure 4 shows the density of geopolymer mortars and the water adsorption at different mass concentrations of Na$_2$SiO$_3$ (0, 5, 10, 15, 20 and 25%). The bulk density of the cured/hardened geopolymer samples ranges from 1.78 to 2.06 g·cm$^{-3}$. The results indicate that the density of volcanic ashes based geopolymer pastes increases from 5 to 25% with increasing Na$_2$SiO$_3$. More than the fact that Na$_2$SiO$_3$ - NaOH solutions have higher density than water which makes the activation solution denser, the Si present in the solution enhances the polymerization process, thus increasing the density of the gel formed (probably N-A-S-H gel) in the mortar [11].

Increasing the concentration of sodium silicate has a small but noticeable effect on water adsorption, because water adsorption decreases with the increasing of sodium silicate. Water adsorption is clearly related to porosity in the samples, which is opposite to density [12]. The increases of density shown in Figure 1 are in accordance with the reduction of water absorption. This behavior was observed in [12], where the increase of sodium silicate reduces the water adsorption until 17, 13 and 15%.

![Figure 4. Bulk density of geopolymers (main y-axis) and water adsorption (secondary y-axis) related to the amount of sodium silicate in the activating solution.](image_url)

Figure 5 shows the compression strength at 7, 14 and 28 days of curing of the geopolymers with different concentrations of Na$_2$SiO$_3$ and NaOH. It is shown that the compression strength increased at 28 days of curing with the increasing mass of Na$_2$SO$_3$ with values of 32, 33, 41, 44 and 51 MPa for samples G0, G5, G10, G15, G20 and G25 respectively. Therefore, increasing the amount of sodium silicate the compression strength will increase. For samples G0 and G5 (which have less viscous activation solution), the compression strength is higher at 7 and 14 days of curing which can be attributed to the concentration of Na$_2$SiO$_3$ which increase the viscosity in the activation solution. The viscosity of the solution influences the wettability, therefore the geopolymer samples need more quantity of solution to achieve a complete geopolymerization and, as a consequence, the compression strength can be reduced. The addition of soluble silicates affects the polymerization of the composite, the setting time and viscosity; furthermore, it is necessary to consider the concentration of the alkali in order to have the enough concentration for a balance in the substitution of the silicon tetrahedron by the aluminum and...
avoid the lixiviation and its reaction with CO$_2$. The CO$_2$ will result in a formation of carbonates or hydrogen carbonates in an efflorescence form or precipitations decreasing the compression strength [13].

![Graph showing the influence of Na$_2$SiO$_3$ concentration on the compression strength of geopolymers at 7, 14, and 28 days of curing.](image)

**Figure 5.** Influence of the increasing Na$_2$SiO$_3$ in the activation solution over the compression strength of geopolymers at 7, 14 and 28 days of curing.

In order to study the effects of the geopolymers curing time on the compression strength, compression tests were carried out at 60, 90, 120 and 150 curing days. Under the 28 days of curing the effect of Na$_2$SiO$_3$ concentration on the compression strength was similar to the studied in figure 5 [7]. Figure 6 shows that the compression strength for sample G15 decrease followed by samples G20 and G25. The maximum value for sample G15 was 49.74 MPa at 7 days of curing, for sample G20 was
52.35 MPa at 7 days of curing and for sample G25 was 57.1 MPa at 28 days of curing. The chemical reaction of the geopolymer in the geopolymerization process is fast, the geopolymer achieve the 70% of its strength in the first 3-4 h of curing. It is expected that the compression strength will not vary with time due to the 24 hours of accelerated thermal curing employed. However, this work reveals a decreasing compression strength starting the 28 days of curing which can be attributed to an excess of NaOH that is shown as an efflorescence form and can be cracking the samples. Additionally, the durability of the active alkali conglomerates depends on the microstructure of the reaction products on the system which rely on the prime material, nature and concentrations of the activator and curing time [13].

The ASTM G99-03 standard was used to calculate the wear rate (Figure 7). It is possible to determine the lowest wear rate which means a highest durability in sample G20 as it is shown. The combination of the activator geopolymer in sample G20 has shown good results on the compression strength test, so it can be inferred that the combination of 20% de Na$_2$SiO$_3$ and 12 M de NaOH promotes better reaction and hence better mechanical properties; on the other side, the wear strength is more than two orders of magnitude lower than a sample of cement (CEM IV) (6.62×10$^{-5}$ mm$^3$/N·mm) after 28 days of curing. For sample G0 (12 M NaOH activating solution), the wear strength compared to the same conventional cement is also lower. However, for samples G5, G10, G15 and G25 there is a decrease on the wear strength compared to other tested geopolymers.

![Figure 7. Wear behavior in the different materials tested (CEM IV and geopolymeric pastes activated with 12 NaOH at different amounts of Na$_2$SiO$_3$).](image)

4. Conclusions

This work has studied the behavior of the volcanic ashes based geopolymer mortar from the Ubinas volcano located in Peru, which had different concentrations of the Na$_2$SiO$_3$ in the activation solution, leading to the following conclusions:

- The amount of Na$_2$SiO$_3$ in the activator alkali is a critic parameter related to the compression strength and wear resistance of geopolymer samples. Another parameter such as the curing time of samples has affect the compression strength. The best composition of alkali activation solution was obtained for 20% Na$_2$SiO$_3$ with 12 M NaOH.
- The 12 M NaOH as an alkali activator along with different concentrations of Na$_2$SiO$_3$ generates a high mechanical performance at short periods. The composition of the alkali solutions plays an essential role on the dissolution of silicon and aluminum from volcanic ashes. The wear
durability of the volcanic ashes alkali activated with different concentrations suppose an increase of 99.8% on the wear strength compared to a sample of cement.

Acknowledgements
We wish to express our gratitude to Luis Cesar Perez Huamaní. This study was funded by the Ministerio de Ciencia, Innovación y Universidades of Spain through project RTI2018-096428-B-I00 and through regional project HORATSO-UC3M-CM.

Article I.

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