Mechanical Characterization of New Geopolymeric Materials Based on Mining Tailings and Rice Husk Ash

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Abstract. This work presents the results of the thermomechanical evaluation of geopolymeric concrete fabricated from mining tailings, rice husk ash and fine sand. Ten types of geopolymeric concrete were studied and the relationship between the initial volumetric concentrations of the components in the mixtures and the maximum resistance in uniaxial compression under conditions of variable temperature (between ambient and 600 °C) was analyzed. The results revealed that increases in the concentration of mining tailings and fine sand lead to an increase in the value of the maximum mechanical resistance, in contrast, the increase in the concentration of rice husk ash led to a reduction in the value of the maximum mechanical resistance. Furthermore, increases in test temperature, up to 500 °C, led to systematic increases in maximum mechanical strength. Finally, the geopolymeric concretes presented a brittle-ductile transition between 500 and 600 °C showing only a ductile behavior when tested at 600 °C and only brittle up to test temperatures of 500 °C.

1. Introduction
Geopolymers are a new class of inorganic synthetic materials manufactured by geopolymerization of aluminosilicates from: industrial solid waste, calcined clays, natural minerals, among others, and an alkaline activator in aqueous solution [1]. In recent years, geopolymers are strongly attracting the attention of the international scientific community, mainly due to the variety of applications in which they can be used, derived from their excellent fire resistance, low density, low cost, ease of fabrication, stability. Thermo-chemistry and eco-friendly synthesis [1,2]. For some years geopolymers have been considered revolutionary for their possible use as a replacement for traditional Portland cement [3,4]. Several works have revealed that geopolymeric concrete has the ability to develop up to 70% compressive strength within the first 4 hours of curing at an appropriate temperature [5], in contrast to its Portland cement counterpart that takes several weeks. On the other hand, geopolymeric concrete shows very little shrinkage due to drying; it was found that after one year it presents between 5 to 7 times less shrinkage than conventional Portland cement concrete [6]. Kong et al. [7] studied the mechanical response of Portland cement and geopolymer pastes after being subjected to high temperatures, finding that while at 800 °C geopolymer paste improves its resistance to compression, Portland cement paste, at 400 °C, lost all its residual resistance, this loss of resistance of the Portland cement paste was attributed to the decomposition of Ca(OH)₂ that occurs at approximately 400 °C.

On the other hand, the generation and accumulation of large amounts of mining tailings as a consequence of mining exploitation constitutes one of the main environmental problems that the Arequipa region (Peru) supports, in addition, currently there are no methodologies for the treatment and reuse of mining tailings, which further compounds their negative environmental impact [8-10].
Therefore, in this work, several mixtures of geopolymeric concretes manufactured from mining tailings, rice husk ash and fine sand were studied, for their potential use in replacement of conventional Portland cement concretes.

2. Materials and methods

2.1. Fabrication of geopolymeric concrete
Geopolymer concrete (GCs) were fabricated by mixing mining tailings (MT), rice husk ash (RHA), fine sand (FS) and Na(OH) solution (9 molar). MT was provided by the metallurgical company CEPROMET SAC and the RHA was obtained by calcining rice husk at 300 ºC for 3 hours. Ten types of GCs were fabricated, whose volumetric concentrations are shown in table 1.

Table 1. Matrix of mixtures for the fabrication of GCs.

| Sample       | Volume (%) |
|--------------|------------|
|              | MT  | RHA  | FS  |
| GC-MT20.0RHA10.0 | 20.0 | 10.0 | 70.0 |
| GC-MT20.0RHA6.7  | 20.0 | 6.7  | 73.3 |
| GC-MT20.0RHA3.3  | 20.0 | 3.3  | 76.7 |
| GC-MT20.0RHA0.0  | 20.0 | 0.0  | 80.0 |
| GC-MT23.3RHA6.7  | 23.3 | 6.7  | 70.0 |
| GC-MT23.3RHA3.3  | 23.3 | 3.3  | 73.3 |
| GC-MT23.3RHA0.0  | 23.3 | 0.0  | 76.7 |
| GC-MT26.7RHA3.3  | 26.7 | 3.3  | 70.0 |
| GC-MT26.7RHA0.0  | 26.7 | 0.0  | 73.3 |
| GC-MT30.0RHA0.0  | 30.0 | 0.0  | 70.0 |

MT, RHA and FS were ground separately and then sieved by ASTM No. 140 mesh (106 µm). For each type of GC, and based on 12g of mixture, adequate amounts of raw material were measured (according to table 1), the dry powders were mixed for 5 minutes, then 5 ml of Na(OH) solution was added, mixing continued until a homogeneous and workable paste was obtained. All geopolymeric pastes were compacted in a 20 mm diameter steel cylindrical mold for 5 minutes and at 30 MPa. The pressed cylindrical samples were placed in airtight bags and then heat-cured at 60 ºC for 48 hours.

2.2. Physical, structural, microstructural and mechanical characterization
The real density of the raw material was determined by helium pycnometry (Functional Characterization Laboratory, CITIUS, University of Seville, Spain). X-ray diffraction analysis was performed on the starting powders, using a Bruker D8 Advance A25 X-ray diffractometer with Cu Kα radiation and Ni filter (X-Ray Laboratory, CITIUS, University of Seville, Spain). Microstructural characterization was performed by scanning electron microscopy (SEM) (Microscopy Laboratory, CITIUS, University of Seville, Spain). The thermomechanical characterization of the CGs was performed on 5x5x10 mm parallelepipedes and using a MICROTEST EM1/50/FR universal testing machine (Spain). The tests were carried out at temperatures between ambient and 600 ºC, in an air atmosphere and with a constant compression rate of 0.05 mm/min.

3. Results and discussion

3.1 Density, phases and morphology
The real average density found for FS, MT and RHA was 3.07, 2.83 and 2.23 g/cm³, respectively. Regarding the structural analysis, diffraction peaks of up to five phases were identified in FS: Albite (Na(Si3Al)O8), Gypsum (CaSO4*2H2O), Quartz (SiO2), Potassium Magnesium Aluminum Fluoride Silicate (KMg(Si3Al)O10F2) and Fluoro-edenite (NaCa3Mg5Si7AlO22F2)., nine-phase diffraction peaks in MT: Muscovite (KAi2Si3), Quartz (SiO2), Orthoclase (KAlSi3O8), Pyrite (FeS2), Calcite (CaCO3),...
Sulfur (S), Actinolite (Ca$_2$(Mg,Fe$^{+2}$)$_5$Si$_8$O$_{22}$(OH)$_2$), Hydrogen Arsenate Hydrate (As$_5$O$_5$$^*$4H$_2$O) and Arsenolite (As$_2$O$_3$); and a completely amorphous baseline for RHA, without the presence of diffraction peaks.

Figure 1 shows SEM micrographs of powder from FS (figure 1(a)), MT (figure 1(b)) and RHA (figure 1(c)), significant differences were found in particle sizes, those of FS being those of larger, it is also observed that the shape of the FS particles are mostly angular and those of MT and RHA rounded.

![Figure 1. SEM micrographs of raw material powder (a) FS, (b) MT and (c) RHA.](image)

Figures 2(a) and 2(b) show SEM micrographs of polished surfaces of GCs with 70 and 80 vol.% FS, respectively. For all the GCs studied, two differentiated phases were found: a continuous phase that corresponds to the geopolymer (mixture of MT and RHA activated alkaline) and another dispersed phase of FS particles located within the continuous phase of geopolymer. Greater grain cohesion has been observed in GCs with 70 vol.% FS (figure 2(a)), compared to poor grain cohesion of the GC with 80 vol.% FS (figure 2(b)).

![Figure 2. SEM micrographs of polished surfaces of GCs with (a) 70 vol.% and (b) 80 vol.% FS.](image)

3.2. Compressive strength

Figure 3 shows curves of maximum compression stress vs. test temperature. A systematic increase in mechanical resistance could be seen by increasing the temperature up to 500 °C, from this temperature an evolution in mechanical behavior occurs, which suggests the activation of microscopic mechanisms of plastic deformation, which led the samples to enter in a state of steady creep with mechanical strengths below 8 MPa in all cases.
Figure 3. Compressive stress as a function of test temperature.

Figure 4 shows the relationship between the maximum mechanical response in compression and the volumetric fraction of FS, when the volumetric fraction of MT is kept constant. An increase in mechanical resistance is observed as the volumetric fraction of FS increases, this relationship is valid up to approximately 76.7 vol% of FS, since from this volumetric fraction the mechanical resistance begins to decrease, this decrease in mechanical resistance is It can be attributed to the limited cohesion of the sand particles due to the excessive volumetric concentration of fine sand particles in relation to the volumetric concentration of binder phase (MT and RHA).

Figure 4. Compressive stress as a function of volume fine sand and keeping the volume of mining tailings constant.

4. Conclusions
Geopolymeric concretes were successfully fabricated by geopolymerization of mining tailings powder, rice husk ash, fine sand, and an aqueous solution of sodium hydroxide (9 molar). Geopolymeric concrete presented two phases: a continuous phase of geopolymer and another dispersed phase of fine sand particles located within the continuous phase of geopolymer.
It was determined that increases in the concentration of mining tailings or fine sand in geopolymeric concretes, leads to increased values of maximum mechanical resistance, in contrast, increases in the concentration of rice husk in geopolymeric concretes, leads to decrease of the values of maximum mechanical resistance.

The increase in temperature in mechanical compression tests, up to 500 °C, lead to systematic increases in maximum mechanical resistance. Geopolymeric concrete presented a brittle-ductile transition between 500 and 600 °C, showing ductile behavior when tested at 600 °C and brittle to temperatures below 500 °C.

5. References

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