Thermal assessment of metakaolin-based geopolymer systems produced with silica fume and rice husk ash[1]

Evaluación térmica de sistemas geopoliméricos basados en metacaolín con incorporación de humo de sílice y ceniza de cascarilla de arroz

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Abstract

The effect of exposing metakaolin-based geopolymers –up to temperature of 1200 °C was assessed using as alkaline activator a mixture of potassium hydroxide with different silica sources: a commercial potassium silicate (PS), rice husk ash (RHA), and silica fume (SF). The amounts of metakaolin and activator in the mixture were adjusted to obtain molar ratios of 2.5 for SiO_2/Al_2O_3 and 0.28 for K_2O/SiO_2. The substitution of 50% PS with RHA and SF was also studied, and the resistance to compression after exposing the mixture to different temperatures between 300 and 1200 °C was assessed. The respective physical analyses, such as determination of volumetric changes, were performed, and the study was complemented with a microstructural analysis conducted by X-ray diffraction and scanning electron microscopy. At room temperature, the geopolymers presented mechanical strengths ranging between ~30 and ~36 MPa. At 1200 °C, materials originally amorphous were transformed into crystalline-type structures, specifically leucite and kalsilite. The best thermo-mechanical performance of the geopolymers was achieved by replacing 50% PS with RHA, which when exposed to 1200 °C retains 44% of its mechanical strength as compared with 26% retained by the reference material.

Key words: Geopolymers; metakaolin; rice husk ash; silica fume; leucite.

Introduction

Geopolymers are obtained from mixing, in optimal ratios, an aluminosilicate mineral, such

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as natural or calcined clays or diverse industrial products (referred to as precursor), and a highly alkaline solution (referred to as activator), which produces a cementitious material. Aluminosilicate gel (N-A-S-H) is obtained as main product and, in some cases, short-range order zeolitic phases are generated as secondary product (Duxson *et al*., 2006). Mixing the precursor and activator triggers a series of reactions (geopolymerization) that develop near-ambient temperatures, and the product obtained has properties comparable and even superior to those of traditional ceramics (Xu and Van Deventer, 2000).

The geopolymer's structure is primarily an N-A-S-H gel-type structure, formed by Si^{4+} tetrahedra partially substituted by Al^{3+}, where load balancing is achieved with the presence of the alkali cations Na^{+} or K^{+}. Sodium or potassium silicates mixed with alkali metal hydroxides are generally used as activators (Ben Haha *et al*.,2011; Duxon *et al*., 2005). However, other more environment-friendly alternative sources of silica are suggested such as rice husk ash (RHA), silica fume (SF), and micro silica, which are chemically modified with solutions of sodium or potassium hydroxide (Rodriguez, 2009; Bernal *et al*., 2011a; Zivica, 2006). By using these alternative sources of silica, more environment-friendly materials can be obtained due to the reduced consumption of commercial silicate (which is produced at temperatures above 1400 °C) as well as the use of materials considered by other industries as industrial by-products and/or waste. This paper aims to evaluate the effect of high-temperature exposure on the structure and mechanical performance of binary geopolymer systems by using a metakaolin (MK) as precursor and incorporating two sources of silica (RHA and SF) to prepare the alkali activator.

Materials and Methods

Materials

Commercial metakaolin Metamax® (MK) was used as the aluminosilicate material (geopolymer base), presenting 51.52% SiO_2 and 44.53% Al_2O_3. One of the sources of silica was mixed with potassium hydroxide (KOH) as alkali activator. Sources of silica were as follows: a solution of commercial potassium silicate (PS; $K_2O\,SiO_3H_2O$) produced by the Colombian company "Productos Químicos Panamericanos S.A."(PQP), which consisted of 13.06% K_2O, 26.38% SiO_2, and 60.56% H_2O; a commercial SF called SikaFume®; and RHA obtained by controlled heat treatment of rice husks at 600 °C. The amorphous SiO_2 content of the SF was 88.48% and that of RHA was 94%. The RHA was milled in a ball mill for 20 min until an average particle size D[4,3] of 22.84 µm was obtained. MK presents an average particle size D [4,3] of 6.57 µm.

Mixture proportions

Geopolymeric mixtures were identified with the codes PS, RHA, and FS, depending on the type of silica source used in the activator, followed by 50, which indicates the percentage of each in the mixture. In other words, RHA50 corresponds to the sample containing 50% RHA replacing commercial PS. The incorporation of the alkali activator in the mixture was adjusted to obtain geopolymer systems with total molar ratios of $SiO_2/\ Al_2O_3$ of 2.5 and $K_2O/\ SiO_2$ of 0.28.

Experimental and testing process

To prepare the geopolymer, MK was mixed with the activating solution during 7 min and then poured into cylindrical molds 30 mm in diameter and 60 mm high.

Samples were then cured over a 20-h period at 75 °C and 90% RH. Prior to high-temperature exposure,– samples were dried at 50 °C until a constant weight was reached. Study temperatures were 300, 600, and 1200 °C. Thermal stability of geopolymers was determined based on compressive strength and dilatometry. Microstructural analysis was also performed, using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

Dilatometry measurements were conducted on samples 4.6 mm in diameter and 25 mm long. Each sample was placed within a horizontal dilatometer, and tests were performed in N_2 inert atmosphere with a gas feeding rate of 100 ml/min and a load of 30 CN. Sapphire was used as reference standard. Samples were heated to 1000 °C and cooled naturally inside the dilatometer.

A JEOL scanning electron microscope (JSM-6490LV) was used under high-vacuum conditions (3x10-6 torr) to observe particle morphology. Photomicrographs magnified 10 000X were taken. The equipment has an INCAPentaFETx3 detector (Oxford Instruments Model 7573). Samples were materialized on a gold-coated cover slip in a Denton Vacuum Desk IV chamber, which was placed over the samples. X-ray diffraction (XRD) analysis was performed on a RINT2000 wide-angle goniometer, using the Cu Kα1 signal at 45 kV and 40mA. A 0.02° pass was used within a range of 5°–70° at a rate of 5°/min.

Results and Discussion

Compressive Strength

The variation in compressive strength at 28 days curing is shown in Figure 1 for each of the mixtures after being exposed to the different test temperatures. At room temperature, the matrix with 100% commercial silicate (PS100) recorded 32 MPa, while the mixture in which 50% sodium silicate had been substituted by RHA (RHA50) recorded a compressive strength of 30 MPa, which is only a 7.8% decrease. The use of SF in equal proportions increased strength to 36 MPa. These results indicate that, at room temperature, substituting 50% PS with alternative sources of silica (RHA and SF) does not significantly affect mechanical performance.

Increasing the temperature to 300 °C significantly decreased residual compressive strength in all samples, the most noticeable being that of the PS-activated sample. The highest cracking was observed in solid samples containing commercial silicate, cured in plastic tubes sealed at 75 °C for 20 h (Figure 2). Samples submitted to temperatures of 600 °C were accordingly not tested for compression. However, exposure to 1200 °C triggered a strong increase in residual compressive strength for all the mixtures under study. RHA50 retained 44% of its compressive strength at room temperature and FS50, 28%—both values higher than those recorded by the check sample (26%).

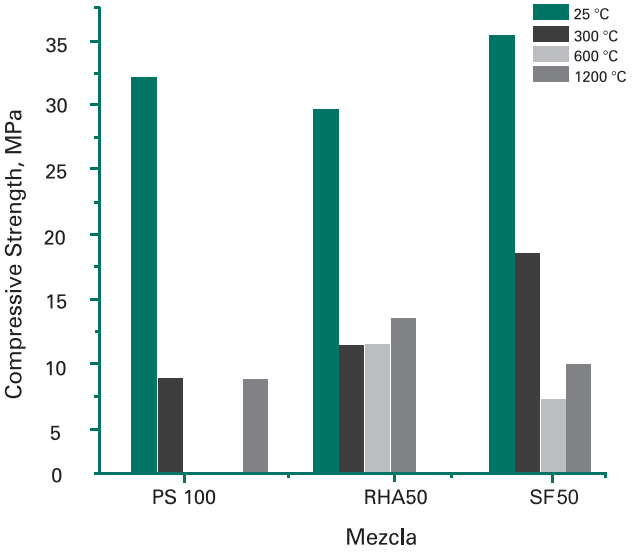


Figura 1. Resistance to compression of geopolymer pastes.

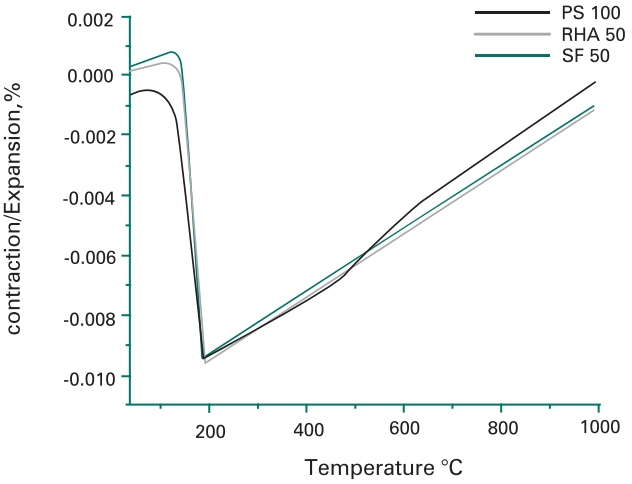


Figura 2. Dilatometry curves of geopolymer pastes.

Contraction and thermal expansion

Figure 2 also shows the thermal expansion curves for the pastes under study. The three mixtures studied show an expansion up to ~170 °C, followed by a strong contraction up to ~200 °C and then expand. Contraction occurring up to ~200 °C is related to the dehydration of the weakly bonded (free) water of the geopolymeric gel. Mixtures to which RHA and SF had been added presented contraction, unlike PS which presented the greatest expansion and a change in slope at ~503 °C, suggesting further expansion of the sample over a narrow temperature range. All samples show expansion up to 1000 °C; however, sintering and viscous flow compress the structure, making it impossible to visualize the contraction of samples at 1200 °C. Weight loss in PS100 exposed

to 1200 °C was 11.15% as compared with 10.42% in RHA50 and 9.92% in SF50. Because most of the water of these materials exists as weakly bound (free) water, it is believed to have little effect on sample expansion as can be observed in the dilatometry curves (Temuujin *et al*., 2011).

Table 1 indicates that as temperature increases, the percent of volumetric contraction also increases as a result of increased gel surface energy due to the release of water from the surface and small pores, which causes a partial collapse of the porous gel network (Kong *et al*., 2008). Values of 45–48% were reached at a temperature of 1200 °C, which are similar to those found by Bernal et al. (2011b). This probably induces microcracking, as also observed by Fernández *et al*. (2010) in geopolymeric pastes exposed to high temperatures, which serve as stress concentrator and reduce the load-bearing capacity of pastes. No significant differences were observed between study samples. However, PS samples showed higher cracking, while the surface of samples containing RHA and SF was smoother and less cracked.

Tabla 1. Percentage volumetric contraction

Mixture	Temperature		
	300 °C	600 °C	1200 °C
PS100	8.75	15.11	46.43
RHA50	7.92	13.35	48.65
SF50	8.69	13.76	45.06

Microstructural analysis

Figure 3 shows the diffractograms of the different geopolymer systems studied, at different temperature exposure. Materials that had not been exposed to high temperatures (25 °C) presented a 25–35° deviation from the baseline at angle 2q, attributable to the highly structurally disordered geopolymeric gel and the presence of anatase (TiO_2) corresponding to impurities found in the starter MK.

Exposing materials to temperatures of 1200 °C led to the transformation of the K-A-S-H gel by structurally reorganizing and subsequently crystallizing leucite ($KAlSi2O_6$)- and kalsilite ($KAlSiO_4$)-type structures for each system under study (PS, RHA, SF). As a result, the degree of amorphicity decreased significantly, evidenced by the disappearance of the deviation from the baseline in the diffractograms of materials exposed to 1200 °C. Data recorded also evidenced MK anatase peaks in materials after exposure to high temperatures. These results are consistent with those found by Tie-Song *et al*., (2009) and He *et al*.. (2010), who found that leucite formation may be enhanced in systems with alkali metals of higher atomic weight and high SiO_2 content (Bell et al., 2009).

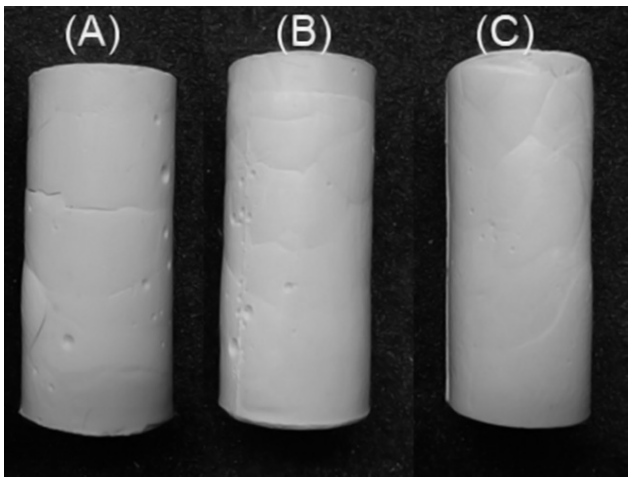


Figura 3. Samples exposed to 1200 °C: (A) PS100; (B) RHA50; and (C) SF50.

Micrographs of each geopolymer system that hadn't been exposed to 1200 °C (Figure 4) reveal the presence of non-reacting MK particles embedded into the gel. As a result, the material obtained is highly porous. With increasing exposure temperature, structural densification is generally observed, caused by the dehydration of formed products and the structural changes generated. Cracking increased in the FS50 system at 1200 °C, caused by capillary contraction during material dehydration and hydroxylation. These cracks may decrease mechanical strength significantly, and can be controlled by incorporating particles with high thermal stability such as alumina or zirconium (Kamseu *et al*., 2010) as well as the inclusion of ceramic fibers (Bernal *et al* ., 2012).

Conclusions

At room temperature, substituting 50% PS with alternative sources of silica such as RHA and SF 0% did not significantly affect compressive strength.

Exposure to a temperature of 600 °C triggered losses in residual compressive strength in all the mixtures studied, losses being more pronounced in

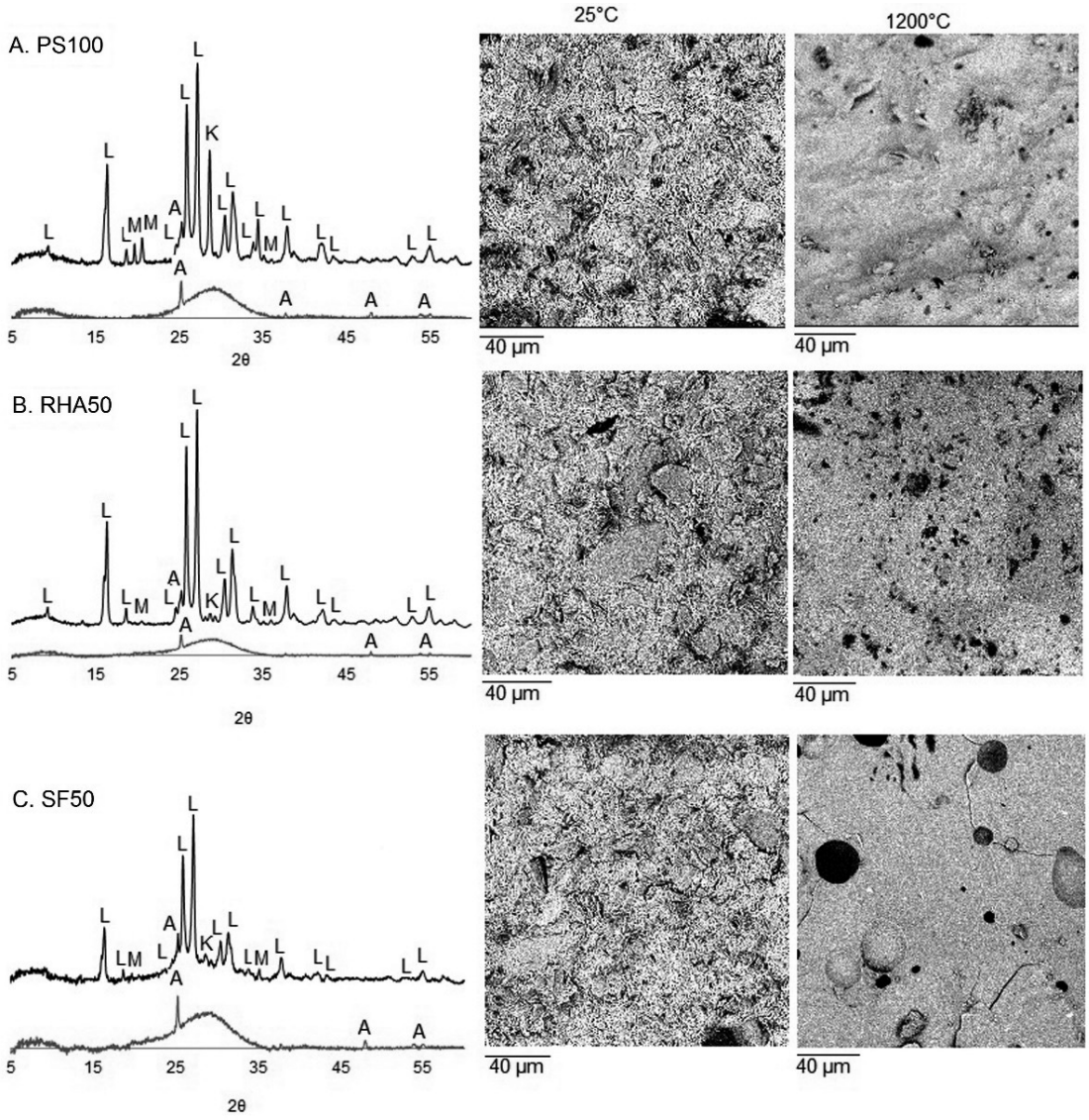


Figura 4. DRX diffractograms and electronic micrographs of samples at 25 °C and post-treatment at 12000 °C.

the PS100 and SF50 systems.

In general, the increased compressive strength at 1200 °C in all mixtures is attributed to the formation of new, stable crystalline components, such as leucite and kalsilite, at this temperature.

The sample in which 50% commercial silicate (PS) had been substituted with RHA (RHA50) presented the best thermomechanical performance and retained 44% of its initial compressive strength after exposure to 1200 °C.

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