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Compressive strength and microstructural evolution of metakaolin geopolymers exposed to high temperature

O. Burciaga-Díaz[1], J. I. Escalante-Garcia[1], R. X. Magallanes-Rivera[2]

[1]Ingenieria Cerámica, Cinvestav IPN Unidad Saltillo, Av. Industria Metalúrgica No. 1062, Parque Industrial Ramos Arizpe, Coahuila, México.
[2] Building Materials, UANL. Fac. Of Civil Eng., Av.Universidad s / n, Cd. Universitaria San Nicolás de los Garza, Nuevo León.

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ABSTRACT

This research presents results of compressive strength and microstructural evolution of geopolymers exposed to high temperatures. Pastes of molar were elaborated blending metakaolin and sodium silicate solutions containing NaOH. The effect of the composition on the development of compressive strength was investigated and pastes were chosen to be exposed to 200, 500 and 800 °C, characterizing their microstructure and compressive strength. Before to high temperature exposure, the binders developed ~80MPa, and after their exposition, the loss of strength depended of the ratio SiO_2/Al_2O_3. Results of XRD, FT-IR and SEM suggest that the reorganization of the silica gel and the water evaporation reduce the thermal stability of samples exposed to high temperature.

Keywords: Geopolymers; metakaolin; thermal performance; compressive strength; microstructures.

RESUMEN

Esta investigación presenta resultados de resistencia a la compresión y evolución microestructural de geopolímeros expuestos a alta temperatura. Se elaboraron pastas, con mezclas de metacaolín y soluciones de silicato de sodio e NaOH. Se investigó el efecto de la composición química sobre el desarrollo de resistencia a la compresión; pastas con alta resistencia fueron expuestas a 200, 500 y 800°C, caracterizando su evolución microestructural y resistencia a compresión. Previo a la exposición a alta temperatura, los geopolímeros desarrollaron ~ 80MPa, y posterior a su exposición, la pérdida de resistencia dependió fuertemente de la relación SiO_2/Al_2O_3. Resultados de DRX, FT-IR y MEB sugieren que la reorganización del gel de sílice y evaporación de agua, reducen la estabilidad mecánica de los geopolímeros expuestos a alta temperatura.

Palabras clave: Geopolímeros; metacaolín; resistencia térmica; resistencia a compresión; microestructuras.

RESUMO

Esta pesquisa apresenta resultados de resistência à compressão e evolução da microestrutura de pastas geopoliméricas expostas a altas temperaturas. Foram preparadas pastas, a partir de misturas de metacaulim com soluções de silicato de sódio e NaOH. Foi então pesquisado o efeito da composição química sobre o desenvolvimento de resistência à compressão e selecionadas pastas foram expostas a 200ºC, 500ºC e 800°C, caracterizando a evolução da microestrutura e a resistência à compressão. Antes da exposição à alta temperatura, os geopolímeros alcançaram 80MPa, e pós-exposição, a perda de resistência dependeu da relação SiO_2/Al_2O_3. Os resultados de DRX, FT-IR e MEB sugerem que a reorganização do gel de sílica e a evaporação de água reduzem a estabilidade mecânica do geopolimero expostos à alta temperatura.

Palavras-chave: geopolímeros; metacaulim; resistência ao calor; resistência à compressão; microestruturas.

Corresponding author: Oswaldo Burciaga Díaz (oburciaga@itsaltillo.edu.mx)

1. INTRODUCTION

In the last decades, the geopolymers have emerged as a new alternative to replace ordinary Portland cement (OPC) in many applications, due to their high mechanical strength, improved durability and low CO_2 emissions (McLellan et al. 2011; Provis et al. 2014; Pacheco-Torgal et al. 2014; Palomo et al. 2014). Geopolymers are inorganic polymers constituted by tetrahedral units of Al and Si condensed at room temperature, that form as a result of the dissolution of amorphous raw materials (which may be industrial by-products or thermally treated clays) in the presence of highly alkaline solutions. The incorporation of alkali ions such as Na^+, K^+, and Ca^{++} balance the electric charges of the network. The condensation of polymeric structures results in a cementitious material that sets and hardens at room temperature, which also increases its mechanical properties over time (Provis et al. 2009). The main reaction products are aluminosilicate N-A-S-H (Na_2O-Al_2O_3-SiO_2-H_2O) type gels and crystalline zeolites type phases as secondary products are obtained (Provis et al. 2009; Provis et al. 2014). The preparation of the raw materials for the synthesis of geopolymers involves low energy consumption that results in lower release of greenhouse gases such as CO_2; it is considered that the CO_2 emission can be as much as 60% lower than those involved during the production of a similar volume of OPC (Kong et al. 2008).

By their ceramic-like properties, it is believed that geopolymers have good resistance at high temperatures (Kong et al. 2008; Duxson et al. 2006 A). Therefore, it is likely that in a near future these materials can be placed in a competitive position against OPC, especially in the construction of infrastructure with high fire risk, such as tunnels, bridges, housing and high-rise buildings.

Previous reports have shown that the densification and shrinkage experienced by metakaolin (MK) based geopolymers after exposure to high temperature, are strongly dependent of the Si/Al ratio and type of condensed reaction products (Duxson et al. 2006 A). The thermal resistance of the geopolymers depends of the chemical composition of the alkaline activator, nature of the MK and the curing conditions (Kong et al. 2007). A study on the effect of the alkaline cation (Na or K and their combinations) on the thermal expansion of metakaolin geopolymers (Duxson et al. 2006) concluded that the thermal shrinkage was higher for samples containing Na and lower for those with K and mixtures of Na + K. Geopolymers activated with alkaline solutions that incorporate Na undergo a shrinkage process in two stages, the first at 100°C promoted by the water evaporation and the second at around 600°C associated to structural changes inside the material (Barbosa et al. 2003; Rahier et at. 1997). Furthermore, it has been observed that geopolymer formulations exposed to high temperature undergo microstructural damage during the evaporation of water due to the low interconnectivity of the pore structure (Kong et al. 2007).

As human safety in case of fire is one a major concern for the design of buildings, it is necessary to have a deep understanding about the behavior of the materials before using them as structural elements. Therefore, this research aims to assess the structural stability of geopolymer binders exposed to high temperature through the microstructural characterization and measurement of mechanical properties.

2. EXPERIMENTAL PROCEDURE

2.1 Materials.

Geopolymer pastes were fabricated using a high purity kaolinitic mineral with a mean particle size (d_{50}) of 7.64 μm and Blaine fineness of 9469 cm^2/g. The mineral had an estimated content of kaolinite ~97% and minor quartz and anatase impurities; its chemical composition as determined by X-ray fluorescence was of (wt%) 52.37 SiO_2, 44.84 Al_2O_3, 1.85 TiO_2, 0.57 Fe_2O_3, 0.11 CaO, 0.11 K_2O, and 0.11 Na_2O. The kaolin was heat treated at 750°C in air for 6 h to obtain highly reactive metakaolin (MK).The MK was chemically activated with blends of sodium silicate (SiO_2 = 29.5%, Na_2O = 14.7%, and H_2O = 55.8%) of modulus (Ms) $SiO_2/Na_2O = 2$, and sodium hydroxide flakes, both industrial grade. The pastes were elaborated at room temperature (~20°C) using purified water.

2.2 Sample preparation and test conducted.

Based on the chemical composition of MK, 36 geopolymeric formulations were elaborated. The alkaline agents were added so as to obtain overall (activator + MK) molar ratios of SiO_2/Al_2O_3 of 2.6, 2.8 and 3, and ratios Na_2O/Al_2O_3 = 0.55, 0.6, 0.65 and 0.7. The quantity of water was adjusted to achieve molar ratios H_2O/Na_2O of 9.57-13.1 (corresponding to a weight ratio H_2O/Solids = 0.53-0.57). For the manufacture of the pastes, the powders of MK and solutions were mixed for 3 min in a planetary mixer. The fresh pastes were cast in cubic molds of 2.5 cm per side and vibrated for 45 s to remove entrained air; the molds were left covered for 24 h at 20°C to avoid water losses. The demolded cubes were wrapped in plastic to prevent water losses, and cured isothermally at 20°C for up to 28 days.

Previous studies (Rovnaník. 2010; Burciaga-Díaz et al. 2012 A) reported that although the curing of samples at temperature >60°C is favorable for a rapid strength gain at early ages, curing at 20°C is more effective for the development of higher CS at later ages, as the advance of the reaction processes is promoted, which results in dense microstructures. Therefore, the curing at 20°C was supported on the hypothesis that geopolymer pastes with high degree of progress in their reaction processes (proportional to their high CS), present a better performance under exposure to thermal cycles.

Samples were tested for compressive strength with an automatized hydraulic machine at a constant loading rate of 500 N/s, each reported value corresponds to the average of four measurements. From the results, 3 high strength formulations were chosen (compositions in Table 1) to evaluate their properties at high temperature.

Table 1. Formulations tested at high temperature

Geopolymer	Molar ratios			*Ms	H_2O/Solids	Curing
	SiO_2/Al_2O_3	Na_2O/Al_2O_3	H_2O/Na_2O			
A1	2.6	0.55	12.18	1.06	0.53	20°C, por 28 d
B1	2.8	0.55	12.64	1.42	0.53	
C1	3.0	0.55	13.1	1.77	0.53	

** Ms = ratio SiO_2/Na_2O of the activator agent*

For the test, the pastes were previously cured for 28 days before exposition to high temperature. Cubic specimens of 2.5 cm per side were exposed at 200°C, 500°C and 800°C in an oven (LINDBERG BLUE, BF51828C-1) during 15 minutes. Subsequently, the samples were removed from the oven to be cooled in air during 15 minutes. This was considered as one cycle; 3 cycles were completed for each sample subjected at each temperature. The thermal stability was determined characterizing the compressive strength. The thermal cycles were chosen in order to analyze the refractory properties of the geopolymers, by means of thermal shock. The used procedure was derivated from the standard ASTM C 1171-96. No previous information was found for this type of tests applied to Portland cements.

After the mechanical testing, fragments of hardened geopolymer were ground in a planetary mill (PM 400/2; Restch, Newtown, PA), using agate media, to pass the #100 sieve. The ground powders were characterized by X-ray diffraction (DRX, Philips D-Expert) in a range of 7°-60° 2θ using a step 0.03° and time of incidence of 2 s/step, using radiation CuKα. Powders were additionally characterized by Fourier transform infrared spectroscopy (FTIR; Nicolet AVANTAR 320 FT-IR, Madison, WI), the specimen preparation involved mixing 0.005 g of sample with 0.05 g of KBr by hand using a porcelain mortar and pestle; the powders were then pressed into a disk for the analysis.

Samples were also analyzed by thermal analysis (DTA/TGA; Perkin Elmer, Pyris Dymond) to evaluate their behavior at high temperature. The heating rate was of 10 °C/min until 900°C. Fragments of fractured cubes were also mounted in resin and polished using diamond pastes down to 1/4 microns. Carbon coating was necessary to make the samples conductive under the scanning electron microscope (SEM; Philips XL30) operated at an accelerating voltage of 20 kV.

3. RESULTS

3.1 CS of geopolymers before exposition at high temperature.

Figure 1, shows 28 day CS results as a function of the molar ratios SiO_2/Al_2O_3, Na_2O/Al_2O_3, and water content. In general, regardless of the chemical composition and water content, the geopolymers reached values of CS > 40MPa; the highest CS were developed by binders with ratio $SiO_2/Al_2O_3 = 3.0$, reaching up to 81 MPa for a ratio water/solids = 0.53. For geopolymer with $SiO_2/Al_2O_3 = 3$, the increase of the ratio Na_2O/Al_2O_3 from 0.55 to 0.70 did not significantly affect the CS; however, the increase of the ratio water/solids to 0.5 and 0.57 reduced the CS to 71 and 55 MPa respectively. It was noteworthy that the CS reduced more markedly when the water content and the ratio Na_2O/Al_2O_3 increased simultaneously.

For geopolymers with ratio $SiO_2/Al_2O_3 =2.8$, the CS was of 55–75 MPa using a ratio $Na_2O/Al_2O_3 = 0.55$; higher Na content decreased the CS. This suggest that the content of Na, supplied by the NaOH, in the alkaline solutions has a strong influence in the strength, so it is possible that for ratios $Na_2O/Al_2O_3 > 0.60$ while keeping constant the ratio $SiO_2/Al_2O_3 =2.8$, the provided Na was excessive and instead being incorporated into the reaction products, it remained free weakening the microstructure after the formation of carbonates, as previously reported (Burciaga-Díaz et al. 2010).

On the other hand, for binders of ratio $SiO_2/Al_2O_3 = 2.6$, the CS was of 62 MPa, and similarly to pastes with ratio $SiO_2/Al_2O_3 =3.0$, the increased water content reduced the strength to 40 MPa in some cases. Moreover, the increase of the ratio Na_2O/Al_2O_3 from 0.55 to 0.6 resulted in the loss of CS, which later increased for samples with $Na_2O/Al_2O_3 = 0.7$.

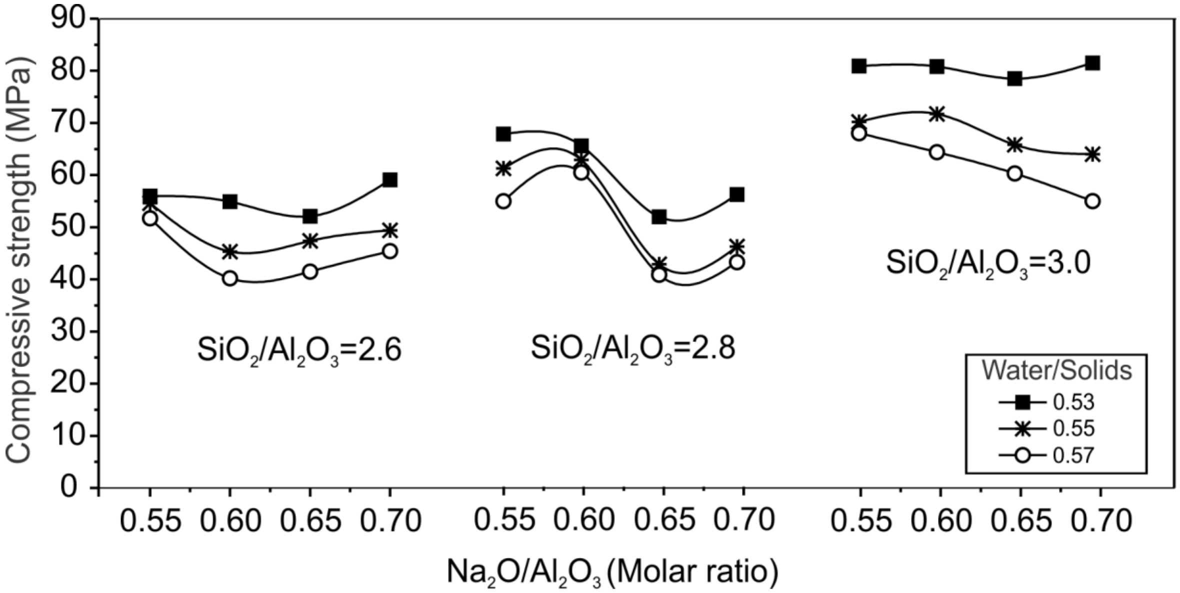

Figure 1. CS of geopolymers after 28 days as a function of the ratios SiO_2/Al_2O_3, Na_2O/Al_2O_3 and water/solids

3.2 Loss of CS as a function of the temperature.

Based on the previous results, 3 pastes of geopolymers were chosen (A1, B1 y C1; see Table 1) to evaluate their performance at high temperature. Figure 2 shows the results of strength changes after exposure at 200°C, 500°C and 800 °C after 28 days of curing at 20 °C.

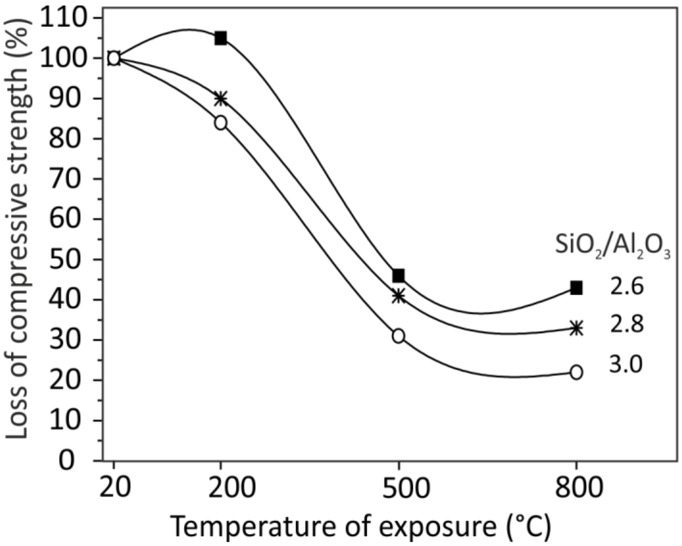

Figure 2. Loss of CS of geopolymers as a function of the ratio SiO_2/Al_2O_3 and temperature

It is noteworthy that binders of SiO_2/Al_2O_3 =2.6 exposed at 200°C showed a gain of CS of ~ 5%; the increased temperature had possibly reactivated and enhanced the geopolymerization reactions of remnant unreacted material, favoring the strength, which is consistent with previous observations (Pan et al. 2010). In contrast, samples with SiO_2/Al_2O_3 =2.8 and 3.0, showed CS losses of 9 and 15%, respectively at 200°C. Increasing the temperature to 500°C resulted in a significant drop of CS for all mixtures; the most pronounced effect corresponded to geopolymer with ratio SiO_2/Al_2O_3 = 3.0 which lost 65% of its initial CS. Between 500 and 800°C the CS for the latter binder was stabilized in losses of 85%, while that for binders with SiO_2/Al_2O_3 = 2.6 and 2.8, minor CS losses of 52 and 65% were observed, respectively.

3.3 Thermogravimetric analysis.

Figure 3, shows thermograms of geopolymers with ratios SiO_2/Al_2O_3 = 2.6, 2.8 and 3.0 after 28 days of curing. The binder with SiO_2/Al_2O_3 = 2.6 showed the lowest weight losses of 11.2% at 200°C and 17.1% at 800 °C. The binder B1 showed the next low weight losses of 13.1%, 17.3% and 18.7 % at 200°C, 500°C and 800°C, respectively. Finally the geopolymer with a ratio SiO_2/Al_2O_3 = 3.0 showed the highest weight losses of 12% at 200°C and 19% at 800°C. In all cases the highest weight was lost between ambient temperature and 200°C as a result of the release of water molecules present in the structure, which possibly results in the formation of structural defects such as porosity and cracking (Provis et al. 2009).

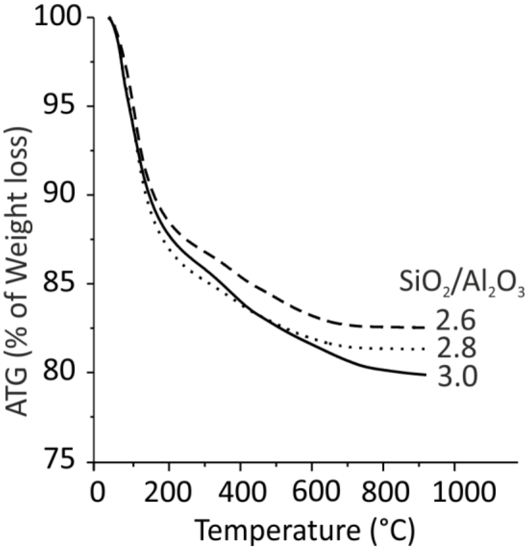

Figure 2. Thermogravimetric analysis of geopolymers exposed to temperatures of up to 900°C

In relation to the differential thermal analysis results, these were not included since no exothermic or endothermic events were noted as the related to the occurrence of reaction processes or crystallization of some phases during the thermal treatment.

3.4 X-ray diffraction (XRD).

Figure 4, shows XRD results of geopolymers A1, B1 and C1 after 28 days and after exposition at 200, 500 and 800ºC. The reaction products after the geopolymerization before thermal treatment were of amorphous nature, as noted by the amorphous hump around 15-35 °2θ, the position of the hump, shifted to higher angles relative to the unreacted MK, suggesting that the products are N-A-S-H type gels (Provis et al. 2009; Burciaga-Díaz et al. 2012). Reflections of quartz and anatase corresponding to the impurities in the MK were also present. The features of the reaction products in the XRD patterns were similar regardless of the chemical composition and mechanical properties of the various binders.

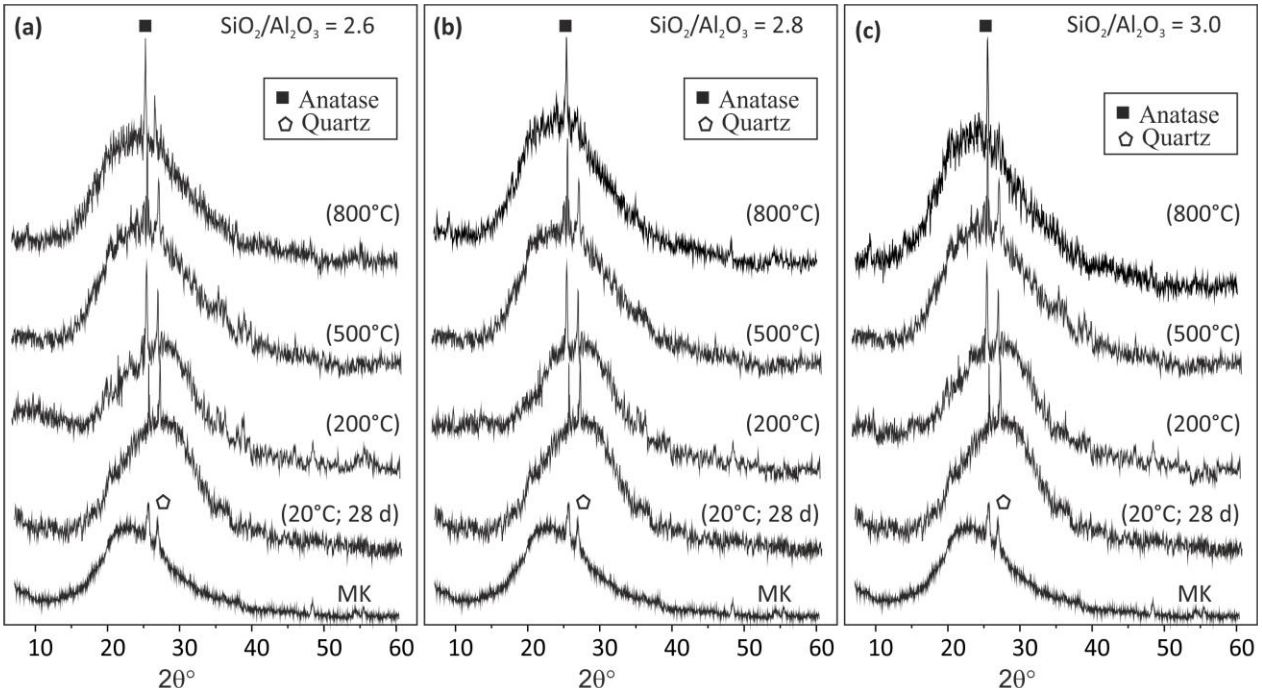

Figure 4. XRD results of geopolymer pastes with composition SiO_2/Al_2O_3 = 2.6, 2.8 and 3.0 after 28 days of curing at 20°C and after exposition at 200°C, 500°C and 800°C

Comparing the XRD patterns of samples subjected at 200°C and 500°C with those non thermally treated, it was observed that the quartz reflections (26.6 and 45.7 °2θ) and anatase (TiO_2 in 25.3, 48.03 and 55.05 °2θ) remained, as well as the amorphous hump (between 15-30°2θ). However, at 500°C the amorphous shifted slightly towards lower angles relative to the non-thermally treated geopolymers and to those treated at 200°C. At 800 °C the amorphous hump remained similarly as for 500°C; also, the quartz and anatase reflections remained, suggesting that these phases were inert during the exposure to high temperature.

The results indicate that at 200°C the geopolymers still have structural stability; however, higher temperatures (500 and 800°C) cause structural disturbance manifested by the collapse of the mechanical properties. Moreover, the shift of the amorphous hump towards lower angles after 500°C also indicates a microstructural reorganization in the geopolymers possibly associated with a rearrangement or flow of atomic species as Si and Al present in the structure of the N-A-S-H gel.

Moreover, as mentioned, the structure of geopolymers contain tetrahedral SiO_4 and AlO_4 units randomly distributed along of polymeric chains, interconnected forming cavities of sufficient size to accommodate alkaline ions and water molecules weakly bounded (Temuujin et al. 2011). Therefore, when the structure is subjected to temperatures above 500°C, the water molecules retained in the cavities suddenly acquire high kinetic energy. When the movement of the molecules increases, the retained water begins to escape from the structure as steam producing a high internal pressure that generates expansive forces within the microstructures. The generated forces cause the internal and surface cracking of the samples and produce the partial collapse of the geopolymeric network contributing with the distortion of the microstructures which is manifested by the displacement of the hump registered in the XRD patterns.

3.5 Infrared spectroscopy (FT-IR).

Figure 6 shows the FT-IR spectra for the MK and the binders A1, B1 and C1 after 28 days of curing at 20°C and after the exposition at 200°C, 500°C and 800°C. The MK spectrum shows a wide shoulder at 1083 cm^{-1} denoting the presence of asymmetric stretching vibrations Si–O–Si and Al–O–Si within the TO4 (T = Si or Al) tetrahedral typical of an amorphous aluminosilicate. The band at 800 cm^{-1} is directly related to the presence of Al–O vibrations in the tetrahedrally coordinated AlO_4 molecule (Lee y van Deventer. 2003). The band in the region of 462 cm^{-1} corresponds to the Si–O–Si and Si–O bonds located in the structural chains (Criado et al. 2007).

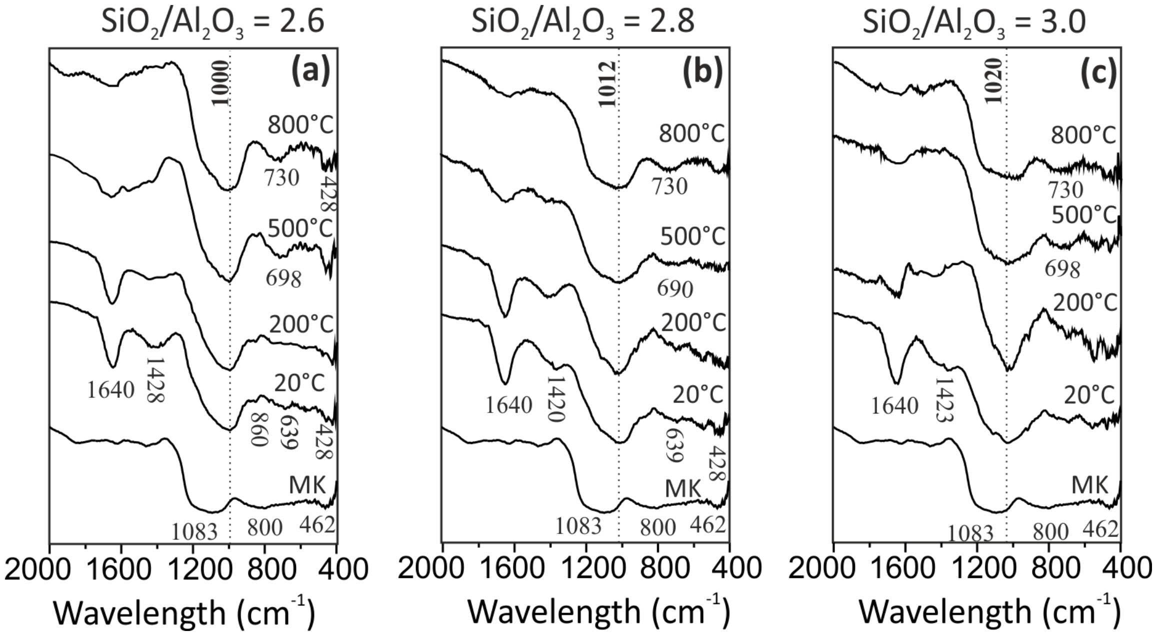

Figure 3. FT-IR results of MK and geopolymers A1 (a) B1 (b) and C10 (c) cured at 20°C by 28 days and exposed to thermal shock at 200, 500 and 800°C.

The spectra of the geopolymers cured 28 days at 20°C (A1, B1 y C1) show significant differences relative to that of MK, evidencing the formation of new products. The vibrational band with a maximum at 1083 cm^{-1} was found to shift towards lower frequencies for geopolymers of ratio SiO_2/Al_2O_3 = 2.6, 2.8 and 3.0, whereas that at 800 cm^{-1} disappeared after the alkaline activation of the MK. Both events indicate that the original aluminosilicate structure of the MK was significantly depolymerized and dissolved by the alkaline solution, resulting in the condensation of new products as the N-A-S-H. These bands showed a broad shape due to the overlapping of various types of bonds which include Si-O, Si-O-Si, Si-O-Al and probably Si-O-Al-(Na), resulting from the fine intermixing of phases (Burciaga-Díaz et al. 2012 B).

For formulation SiO_2/Al_2O_3 = 2.6, after treatment at 200, 500 and 800°C, the typical band of geopolymeric materials (Si-O-Si, Al-O-Si, Si-O-Si and O-Si-O) remained, indicating that such temperatures did not significantly affect the structure of the binder, which correlated with the lowest percentage of CS loss already described.

Previous studies (Burciaga-Díaz et al. 2010; Burciaga-Díaz et al. 2012 B) have reported the condensation of silica gel in geopolymers by energy dispersive spectroscopy (EDS). It has been observed that the value of the ratio Si/Al measured by EDS in microstructures of pastes tends to be higher than the nominal ratios (those initially considered during the formulation of geopolymers assuming a 100% reaction between alkaline solution and MK). The silica gel condenses finely intermixed with the N-A-S-H gel, and also favors the mechanical properties. The silica gel is more prone to condense when alkaline solutions of ratio $SiO_2/Na_2O > 2.8$ (with low alkalinity) are used. In this context, for formulations B1 and C1 with molar ratio $SiO_2/Al_2O_3 = 2.8$ and 3.0, respectively, it can be seen that the bands of transmittance at 1012 cm^{-1} and 1020 cm^{-1} attributed to the presence of Si-O-Si and Si-O-Al bonds, appeared widened after exposure to 500°C. This suggests that in these formulations an important restructuring of the reaction products occurred as a result of the diffusion of Si, Al and Na species present possibly in unreacted silica gel and also contained in the structure of the N-A-S-H gel. The changes in the transmittance bands correlated with the CS losses described for these binders.

It is also important to mention that after exposure at 200°C the intensity of bands attributed to the vibrations H-O-H at frequencies of 3000 cm^{-1} (not shown in the FT-IR spectra in Figure 5) decreased; moreover, the higher the temperature of exposure, the lower the intensity of such vibrations, indicating an increased water losses. Under these circumstances a microstructural collapse was originated resulting in a microporous structure with low mechanical properties.

The results correlated well with the above explanations and to the relationship between the strength losses, weight changes in the samples and to the evaporation of water produced by the high temperature. Therefore, the FT-IR spectra confirm the hypothesis that the structural changes in the geopolymers are produced by the loss of water as well as by the viscous flow of silica gel and geopolymeric gel.

3.6 Scanning Electron Microscopy (SEM).

Figure 6, presents microstructures of geopolymer A1 ($SiO_2/Al_2O_3 = 2.6$ and $Na_2O/Al_2O_3 = 0.5$) after 28 days at 20°C and after exposure at 200, 500 and 800°C. After curing at 20°C, the microstructure appeared dense and with low porosity with only a few trapped bubbles, which explains the relatively high CS (59.6 MPa). Based on the XRD results, the microstructures consist of amorphous aluminosilicate gel N-A-S-H derived from the reactions and which is identified by the gray darker tone. The brightness of the features in the microstructures observed by backscattered electron images is directly proportional to the average atomic number of the irradiated zone; thus, it was considered that the incorporation of water into such a gel reduces the mean atomic number, making it appear darker.

After exposure to 200°C the matrix of reaction products was denser with less unreacted MK particles suggesting that the temperature favored the advance of the reactions, in agreement with the increase in CS (59 to 62.8 MPa). However, after treatment at 500°C the porosity increased and the CS decreased until 28 MPa. After 800°C the micrographs showed an increase in the density of the matrix and the tone of the microstructure became clearer due to the reduced water content, which increased the average atomic number. The releasing of water causes structural defects (cracks and pores) associated with the structural collapse of the mechanical properties, although the corresponding micrographs at 800°C did not show such defects, the defects were evident at macrostructural level.

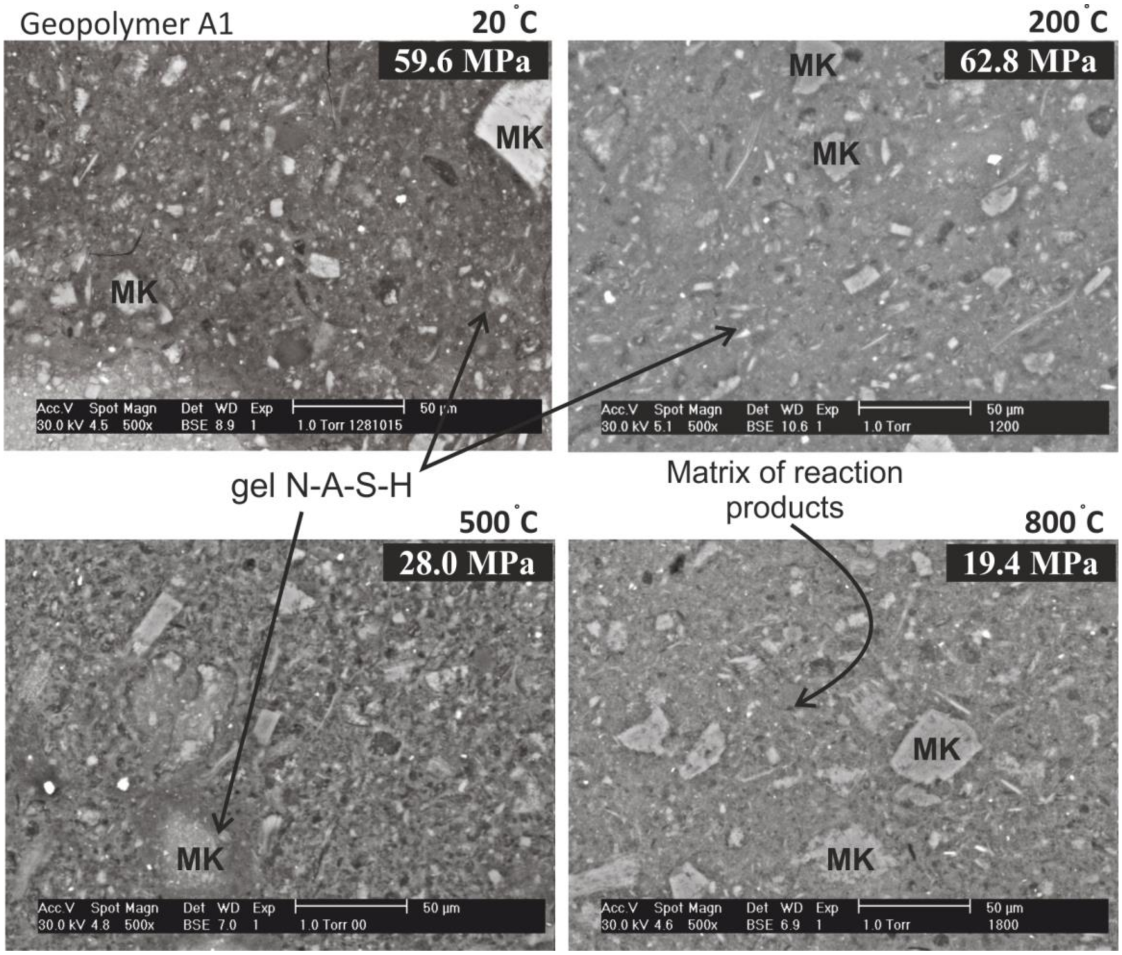

Figure 4. Microstructures of geopolymer A1 after 28 days at 20°C and exposed at 200, 500 and 800°C.

SEM images of binder B1 (SiO_2/Al_2O_3 =2.8) cured at 20°C and exposed at 200, 500 and 800°C are shown in Figure 7. Without thermal treatment, some particles of unreacted MK were observed after 28 days, together with some pores and cracks distributed heterogeneously. The pore formation is due to the incomplete elimination of entrapped air during the vibration of the fresh paste because the viscosity of the binder was high. Unlike to paste A1, at 200°C a high content of unreacted MK particles was noted and the matrix of reaction products was less dense and more porous. At 500°C the microstructures showed dehydration and larger pores with respect to the microstructures obtained after treatment to 200°C. After 800°C, the tone of the reaction products became brighter due to the elimination of water physically and chemically bounded, which promoted the increase of the nominal atomic number of the reaction products. Furthermore, the amount of pores was higher than for the sample exposed at 500°C, which resulted in a decreased CS.

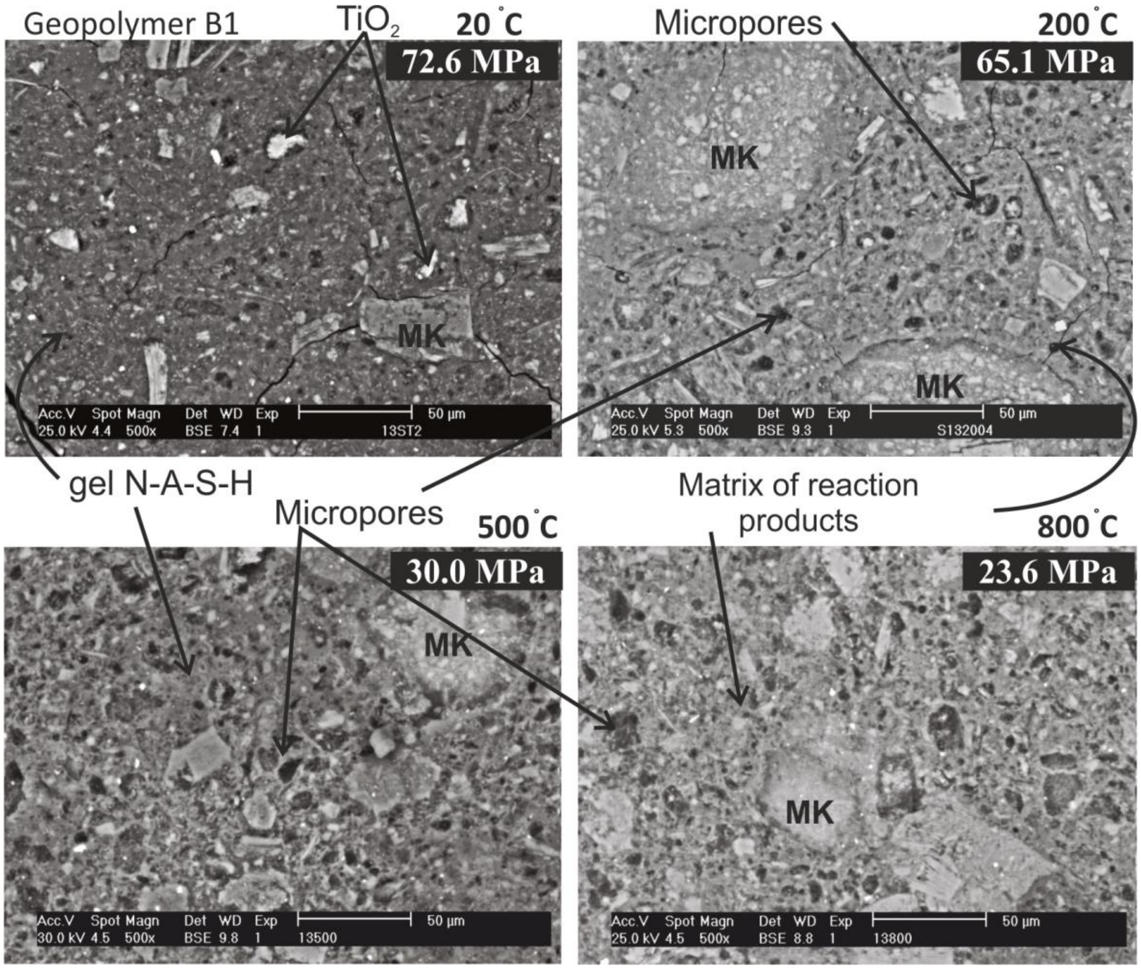

Figure 7. Microstructures of geopolymer B1 after 28 days at 20°C and exposed at 200, 500 and 800°C.

Figure 8 shows the microstructures of geopolymer C1 (SiO_2/Al_2O_3 =3.0; 81 MPa) cured at 20°C and thermally treated. Particles of TiO_2 and unreacted MK were observed after only curing at 20°C, in a dense matrix of geopolymeric products, in agreement with the high CS. It is important to mention that although the precipitation of silica gel (from sodium silicate) densifies significantly the matrix, this promotes the weakening of the microstructures after exposure to high temperatures. After treatment at 200°C the contrast of the particles and the reaction products is low, suggesting that the samples began to dehydrate leading to the formation of cracks as observed in the microstructures. After treatment at 500 and 800°C a severe damage on the microstructure was noted; the amount and size of pores increased and water was lost, which was evidenced by the reduced contrast between the reaction products and MK particles. Finally the registered values of CS were lower than those reached by the geopolymers A1 and B1.

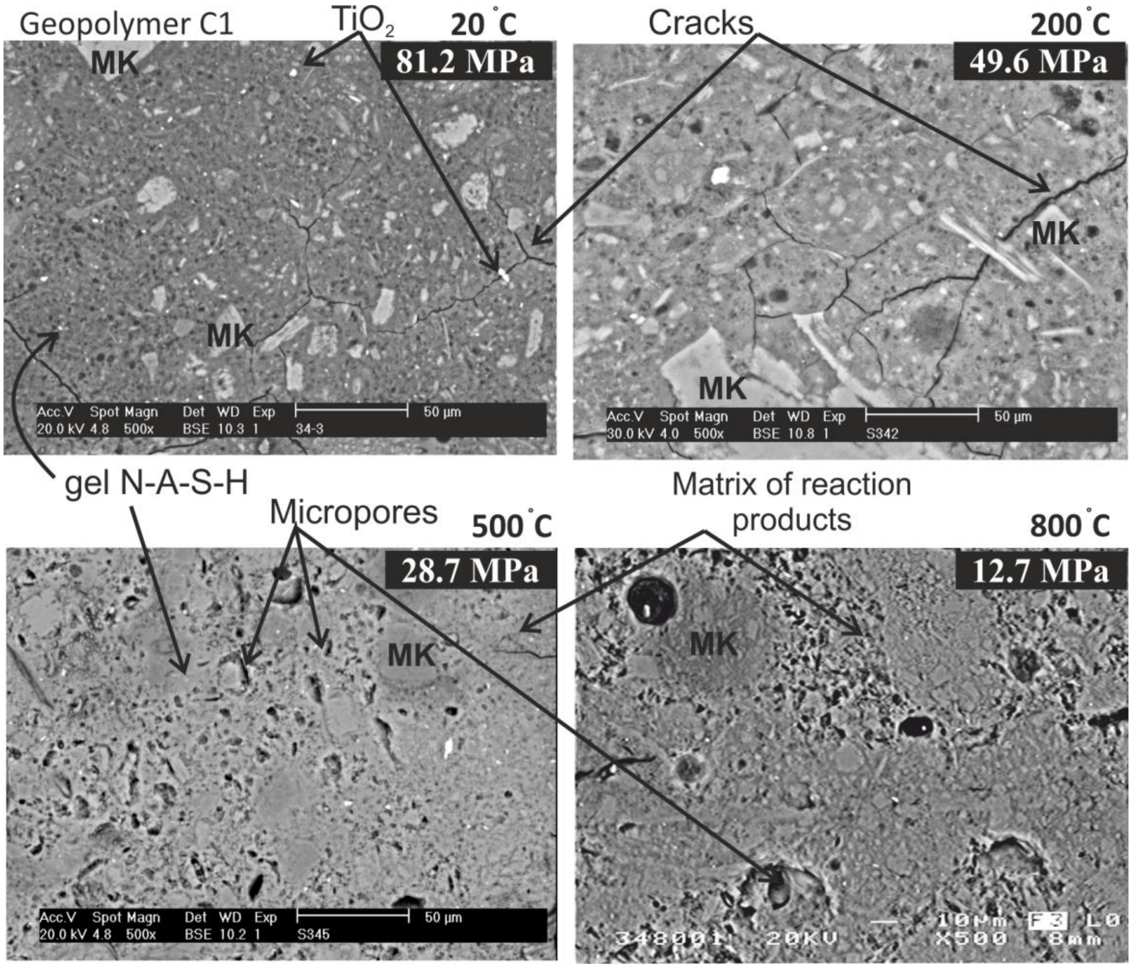

Figure 8. Microstructures of geopolymer C1 after 28 days at 20°C and exposed at 200, 500 and 800°C.

4. DISCUSSION

The results showed that geopolymers may have thermal stability up to 200°C, with strength losses of up to 14 % by weight (geopolymer B1). The weight loss at temperatures >200°C is related to the loss of water in form of steam according to the following equation: ΔT = gradient of temperature at 200°, 500°C and 800°C.

$$\mathrm{Mn\{\text{-}(Si\text{-}O_2)\ z\text{-}Al\text{-}O\}n\ .\ wH_2O} \xrightarrow{\Delta T} \mathrm{Mn\{\text{-}(Si\text{-}O_2)z\text{-}Al\text{-}O\}n + wH_2O\ (\uparrow)}$$

The produced steam has a higher volume than that occupied by the same amount of liquid water, creating internal forces, which produces internal pressures promoting expansive forces inside the geopolymers. Additionally, based on SEM results and previous reports (Barbosa et al. 2003; Burciaga-Díaz et al. 2012 B), the structure of the geopolymers includes finely intermixed silica gel condensed from the activating solution which does not incorporate into the reaction geopolymerization products. When the water is removed by dehydration of silica gel by the following equation, there is a release of energy.

$$Si(OH_4) \xrightarrow{\Delta T} SiO_2 + 2H_2O\ (\uparrow)$$

Typically the condensed silica gel in the matrix of reaction products, releases about 20-100 J/g as a result of the releasing of water during the dehydroxilation process (Duxson. 2006 B). The water loss stimulates the decrease of the free energy of the system. When the materials are subjected to different gradient of temperature (ΔT = 200, 500 and 800ºC), the decrease in free energy, generates thermodynamically stable structures as structural relaxation occurs in the system. The structural relaxation leads to a process of densification of the silica gel. The intermixing of N-A-S-H and silica gel is a bi-continuous medium water-solids which dehydrates and shrinks at high temperature favoring the formation of defects. Under these conditions, the water and its distribution are a function of the gel structure. The release of water is a function of the temperature and of the heating rate, which in turn cause a strong lineal shrinkage. The shrinkage occurring during the dihydroxylation process promotes the cracking weakening the structure of the geopolymer (Duxson. 2006 B). Since water occupies a volume within the microstructures, its output forms cavities, cracks and pores by the effect of expansion and contraction forces acting in the interior of the samples. The resulting morphology is a microporous amorphous material with low mechanical properties. Additionally, the broadening observed previously in the transmittance bands at 1012 cm^{-1} and 1020 cm^{-1} in the FT-IR spectra for samples SiO_2/Al_2O_3 = 2.8 and 3.0 exposed to temperatures > 500°C suggest that such formulations experienced a reorganization of the reaction products related to the migration of Si species contained in unreacted silica gel. In contrast geopolymer A1 (with ratio SiO_2/Al_2O_3 = 2.6) showed the best resistance to high temperature, as it was the binder in which there were probably fewer water molecules and condensation of silica gel in the matrix of reaction products.

5. CONCLUSIONS

The results suggest that the deterioration of the CS of geopolymer samples exposed to temperatures in the range of 20-800°C, is not only related to the loss of weight promoted by evaporation, it also depends on the microstructural rearrangement of the geopolymeric N-A-S-H gel. The shrinkage that occurs during the process of dehydroxilation and densification of the gel, results in the formation of pores and cracking weakening the structure of the binders. The good performance of geopolymer A1 is related with the good structural stability of the formed reaction products and possibly with the poor condensation of silica gel during the reaction processes. Therefore, for applications that involve exposition to high temperature, it is desirable to synthesize materials containing in their structure a minimal amount of water molecules, also, all of the sodium silicate solution supplied by the activating solution must to take part in the reaction processes to limit the condensation of unreacted silica gel.

6. ACKNOWLEDGMENTS

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