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On The Mechanical Behavior of Metakaolin Based Geopolymers Under Elevated Temperatures

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Geopolymers may be described as solid and stable synthesized aluminosilicate materials, whose properties are generally believed to provide a superior durability behavior. The work in hand presents the results of an experimental investigation on the thermomechanical behavior of geopolymer matrices composed by metakaolin (MK), silica fume (SF) and blast furnace slag (BFS). The alkaline activator solution consisted of sodium silicate and sodium hydroxide. The use of different aggregates was also investigated, by replacing natural sand with chamotte. Samples were submitted to different temperatures at predetermined intervals to a maximum of 1000ºC. Compression tests were performed, before and after the exposure to elevated temperatures. X-ray diffraction, thermal analysis (TGA and DTA) and scanning electron microscopy (SEM) were used to investigate the microstructural characteristics of the studied materials. The results showed that the presence of BFS in the geopolymer mixture significantly increases its mechanical response. However, the incorporation of SF presents inferior behavior in regular conditions and when exposed to elevated temperatures. The replacement of sand with chamotte results in higher compatibility above 500ºC, when a better tolerance to extreme environmental temperature conditions was observed.

Keywords: *Geopolymers, temperature, metakaolin*

1. Introduction

Geopolymers may be described as synthesized solid and stable aluminosilicates, derived through chemical reactions from the combination of an alkaline activator solution with aluminosilicates from a geological material, such as metakaolin, or reusable materials, such as slag. A polymerization reaction occurs in this process; so the French researcher Joseph Davidovits[1] decided in the 70s to name this complex class of materials as "geopolymers", which was firstly developed as an alternative material to withstand high temperatures.

Although much of the macroscopic characteristics of the geopolymers prepared from different sources of aluminosilicates are very similar, their microstructure, chemical and mechanical properties may vary significantly depending on the raw materials and molar ratios used in the formulations[2]. This class of materials is known to present itself as a beneficial alternative to the environment, as the industrial production of its raw materials can reduce by up to six times the release of CO_2 into the atmosphere, when compared to the production of Portland cement[3].

A study developed by researchers in Melbourne and Illinois[4] showed that the bearing capacity of the geopolymers and elastic modulus are determined mainly due to microstructural features rather than composition effects. In a complementary study, they found that the compressive strength of metakaolin-based geopolymers does not significantly changes when varying the type of alkali (sodium or potassium), or age (between 7 and 28 days). However, samples with mixtures of the two types of alkali in the composition with high Si/Al ratio showed an increase in strength. They also demonstrated that the elastic modulus is fully dependent on the type of activator. When using sodium hydroxide the modulus of elasticity increases, whereas for potassium hydroxide the effect was the opposite.

The amorphous and inorganic structure of the geopolymers generates satisfactory performance regarding thermal durability, resulting in potential applications as refractories or fire-resistant structural materials[4]. Studies developed by Davidovits mention a high resistance under extreme conditions of temperature regarding geopolymers composed by sodium silicate and metakaolin, obtaining thermal stability up to 1200°C. Barbosa[5] found that larger volumes of water and/or sodium silicate may reduce the thermal resistance of the material. It is important to notice that not all of the aforementioned studies used aggregates in their formulation, since part of the research involving geopolymers aims to investigate the material's adhesive behavior as structural reinforcement.

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The use of aggregates in a geopolymer mixture can improve its strength, durability and volumetric stability, without adding any difficulties in the processing[6]. It is important however to select an aggregate that will not react with the mixture constituents during the mixing and curing process. Previous studies have used river sand[7], refractory particles[8] and other aggregates into geopolymers. For high temperature applications the thermal stability also depends on the selection of the correct aggregate. Incompatible thermal expansion coefficients can generate unfavorable mechanical properties.

The present work evaluates the thermomechanical behavior of different geopolymer matrices when exposed to elevated temperatures. Its chemical composition varies according to the proportions of the selected aluminosilicate materials and their activator solution (consisting of sodium hydroxide and sodium silicate). Quartz sand was incorporated in three out of the four studied mortars. In a fourth matrix, sand was replaced with chamotte. The samples were subjected to compression tests, before and after being exposed to different temperatures. X-ray diffraction, thermal analysis (TGA and DTA) and scanning electron microscopy (SEM) were used to investigate the microstructure characteristics of the studied materials.

2. Materials and Processing

2.1. Materials

Metakaolin (MK), silica fume (SF), and blast furnace slag (BFS) were supplied by Metacaulim do Brasil, Tecnosil and Central IBEC, respectively. Those materials are the source of silica and alumina in the systems. Their chemical compositions were obtained by X-ray fluorescence (XRF) and are reported in Table 1. The alkaline activator solution, mixed in pre-determined proportions, was composed of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). Their chemical compositions are shown in Table 2. River sand was used as a natural aggregate with density of 2.68 g/cm³, fineness modulus of 2.28 and, a maximum diameter of 1.18 mm.

Table 1. Chemical compositions of MK, SF and BFS (by mass).

Chemical Compositions	Metakaolin (MK)	Silica (SF)	Slag (BFS)
SiO_2	40.02%	93.40%	45.18%
Al_2O_3	34.00%	0.75%	10.78%
Fe_2O_3	2.00%	1.24%	2.30%
TiO_2	1.00%	0.02%	0.43%
CaO	0.10%	1.39%	32.73%
MgO	0.60%	1.02%	5.38%
K_2O	1.70%	1.25%	0.93%
Na_2O	0.10%	0.39%	0.14%
SO_3	0.10%	-	0.44%
P_2O_5	-	0.13%	0.04%
ZnO	-	0.04%	-
SrO	-	0.02%	0.12%
MnO	-	0.05%	1.38%
BaO	-	-	0.07%

Table 2. Chemical compositions of NaOH and Na_2SiO_3 (by mass).

Chemical Compositions	Sodium Silicate (Na_2SiO_3)	Sodium Hydroxide NaOH)
SiO_2	32.20%	-
Na_2O	14.70%	-
H_2O	53.10%	50.00%
NaOH	-	48.03%
SO_4	-	0.02%
Cl	-	0.005%
Na_2CO_3	-	1.94%

The particle size distribution (PSD) of MK, SF, and BFS were obtained by laser granulometry and are presented in Figure 1, along with the PSD of the sand and chamotte aggregates. As can be observed, SF and MK are significantly thinner than BFS. This difference affects the workability of the mixtures. Meanwhile, the curves presented for the aggregates demonstrated a greater fineness for the refractory material.

2.2. Processing

Four geopolymer matrices were developed in this research. The reference matrix, with a SiO_2/Al_2O_3 molar ratio equal to 3.0, resulted from the activation of a binder material consisting of 100% MK. The second and third matrices were obtained with a molar ratio SiO_2/Al_2O_3 of 3.9, and fabricated with different binders (20/80 SF/MK, and 40/60 MK/BFS). Quartz sand was the fine aggregate for the three

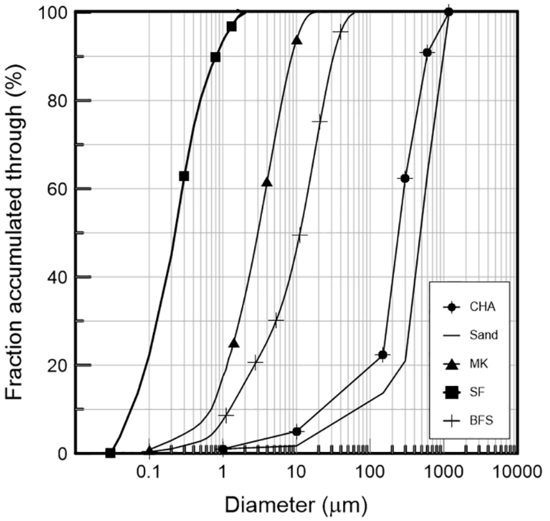

Figure 1. Particle size distribution curves of: MK, SF, BFS, sand and chamotte.

matrices, with a mass ratio of 1:1 between binders/aggregate. A fourth matrix was prepared with the substitution of the fine aggregate with a refractory one (chamotte), changing the mass ratio to 1:0.5, between binder/aggregate materials. The amounts of silicate and sodium hydroxide used in each mixture varied, in order to ensure the indicated molar ratios that are shown in Table 3: $H_2O/Na_2O = 11$ and $Na_2O/SiO_2 = 0.25$ for all mortars; and Na_2O/Al_2O_3 equal to 0.75 or 0.98, respectively for $SiO_2/Al_2O_3=3.0$ and 3.9. From all of the previously mentioned characteristics, the matrices were named 100MK, 80MK20SF, 60MK40BFS and 100MK+CHA.

Table 3. Solid materials (mass) and molar ratios for each geopolymer matrix (with 1000g as reference).

Matrix	Mass (g)				Molar Ratios			
	MK	SF	BFS	Sand/Chamotte	SiO_2/Al_2O_3	H_2O/Na_2O	Na_2O/SiO_2	Na_2O/Al_2O_3
100MK	1000	-	-	1000	3	11	0.25	0.75
80MK20SF	800	200	-	1000	3.9	11	0.25	0.98
60MK40BFS	600	-	400	1000	3.9	11	0.25	0.98
100MK + CHA	1000	-	-	500	3	11	0.25	0.75

The preparation of the geopolymer mixtures was performed in a 5L capacity planetary mixer. The mixture process is described as follows: (i) manual mixing of the dry materials (sand/chamotte, MK, SF and/or BFS) with a metallic spatula, to achieve maximum homogeneity in the mixture of solids; (ii) addition of the alkaline activator solution, comprising of sodium hydroxide and sodium silicate (premixed) for 1 minute; (iii) mixture during 4 minutes at 136 rpm in the planetary mixer; (iv) turning off the planetary mixer for removal of trapped solids on the walls of the container; (v) and finally homogenization of the mixture for 3 minutes at 281 rpm.

The flow table test was carried out according to the ASTM C143[9]. The results are presented in Table 4. It is observed that as the amount of metakaolin decreases and the volume of slag increases, the matrix becomes more fluid. This is due to the fact that metakaolin is much finer, and require a larger amount of water to be incorporated into the activator solution.

Table 4. Flow table test spreading.

Matrix	Standard Consistency (mm)
100MK	127.5
80MK20SF	163.5
60MK40BFS	201.0
100MK + CHA	175.5

Cylindrical specimens with the height of 100 mm and diameter of 50 mm were produced for compression tests. Due to the fluid consistency of the mortar, it was not necessary to perform any type of consolidation. All specimens were prepared and cured at room temperature (25 ± 2°C), demolded after 24 hours and wrapped in plastic bags to prevent moisture loss and cracking during the subsequent curing of 7 days.

3. Testing Methods

X-ray diffraction (XRD) was performed to characterize the crystalline phases of the used materials (metakaolin, blast furnace slag and silica fume) and geopolymer mortars (100MK, 80MK20SF, 60MK40BFS and 100MK+CHA). XRD was carried out using a Shimadzu diffractometer model XRD-7000 with copper radiation (Cu-Ka, $\lambda = 1.5418$ Å) operating at 40 kV and 30 mA. Scans were performed with an angular velocity of 0.02º per second and measuring the interval between Bragg angles of (2θ) 5° and 80° in order to determine the crystalline phases.

Thermal analysis (TGA and DTA) was conducted using a Shimadzu DTG-60H equipment, to accurately measure the weight loss while the specimens were gradually exposed to elevated temperatures. In the analysis, the equipment operated at a heating rate of 10°C/min from room temperature to approximately 1200°C under nitrogen atmosphere and log flow of 100 mL/min. The tests were carried out in platinum crucibles. This equipment was able to make the two analysis simultaneously: thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

Compression tests were performed on cylindrical specimens (100 mm height and 50 mm diameter) at 7 days, using a MTS testing equipment, model 810, with load capacity of

500 kN. The tests were performed at a displacement rate of 0.5 mm/min. The axial displacements were measured by two LVDTs, with length of 70 mm, coupled with acrylic rings positioned around the specimen. The displacement result was the average value of the displacements obtained by the transducers. Figure 2.a shows the test setup.

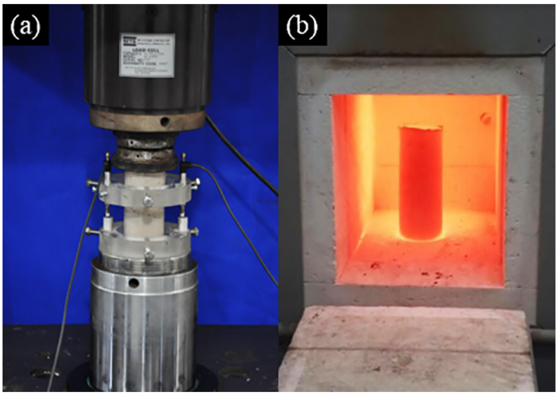

Figure 2. (a) Arrangement of compression test setup and (b) sample heating in a muffle furnace.

Three cylindrical specimens of each formulation (in room temperature) were initially subjected to compression tests. Three other specimens of each formulation were exposed to different temperatures (100, 300, 500, 700 and 1000ºC) in a muffle furnace (Figure 2.b) at an incremental rate of 10ºC/min. Once the desired temperature was attained, the system was maintained in the same temperature for 1 hour. After this procedure the specimens were allowed to cool naturally inside the furnace. The compression tests were performed after the samples were cooled down.

SEM was used to visualize the microstructures of the different mixtures produced. The analysis was carried out in a FEI Quanta400 Scanning Electron Microscope operating at 20 kV. Samples were cut, mounted in a resin, ground and polished to obtain a smooth surface.

4. Results and Discussion

Figure 3 shows the X-ray diffractograms for MK, BFS and SF. Figures 3.a and 3.b, for blast furnace slag and metakaolin, respectively, show the presence of aluminosilicates, mostly amorphous. BFS has crystalline peaks for minerals gehlenite and akermanite, the first normally found in iron slag. Metakaolin contains quartz, muscovite, kaolinite and illite peaks, demonstrating the presence of impurities and incomplete calcination of kaolinite. In Figure 3.c it is possible to see that silica fume is an amorphous material, so it does not show peaks for crystalline materials.

Figure 4 shows the X-ray diffractograms for the geopolymer matrices. It is possible to observe that all of the matrices

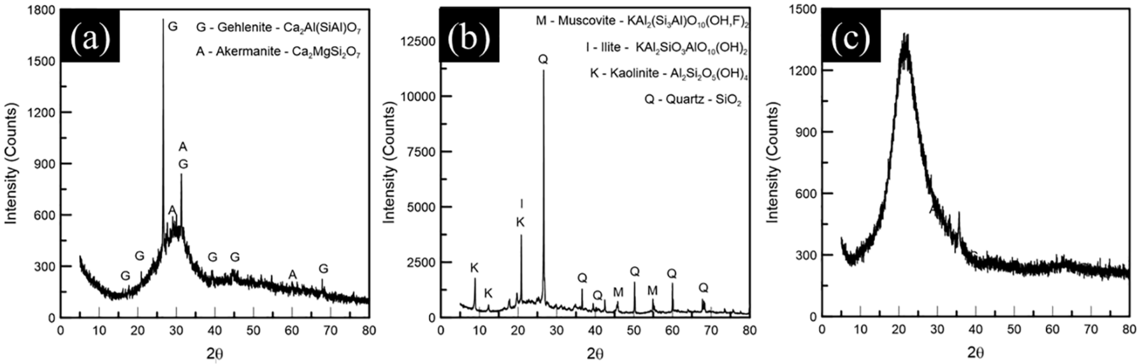

Figure 3. Diffractograms of: a) blast furnace slag; b) metakaolin; and c) silica fume.

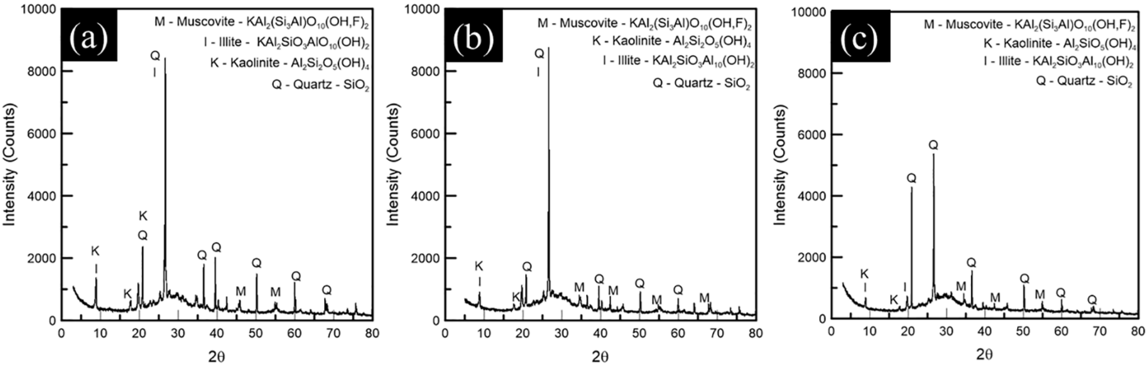

Figure 4. Diffractograms of: (a) 100MK; (b) 80MK20SF; and (c) 60MK40BFS.

still present crystalline phases from metakaolin. Again, metakaolin contains peaks for quartz, muscovite, illite and kaolinite, and the latter does not react to form geopolymer gel (refer to Figures 4.a, 4.b and 4.c). It is also possible to visualize that the amorphous structure of the silica fume did not change the geopolymer crystalline behavior in Figure 4.b.

The thermal stability of the matrices was studied using the thermogravimetric and differential thermal analysis. Thermograms (TGA), the derivative thermogravimetric curves (DTG), and differential thermal analysis (DTA) are shown in Figure 5. As the temperature increases, all geopolymers presented endothermic peaks followed by weight losses. An average loss of 12% after exposure to 200ºC was recorded for the 100MK+CHA sample, presenting the lower result of all mixtures containing sand as aggregate. The mixture 60MK40BFS showed an average mass reduction of 13.5%, while the other two, 100MK and 80MK20SF, presented reductions of 16% and 30% in this range of temperature, respectively. These weight losses, occurring between 50ºC and 200ºC, are presumed to be related to the dehydration of the structures present in the correspondent aluminosilicate gels of the geopolymers[7].

The rest of the water contained in the matrices is more strongly bound or less able to diffuse to the surface, and continues to gradually evolve to about 500°C[7]. The formulation containing SF showed the highest degradation behavior between 50 and 500ºC. This response is attributed to the incomplete dispersion of the SF during the mixing, forming small clusters, increasing significantly the porosity and reducing the thermal stability.

Although it is not possible to clearly distinguish it in the resulting curves, it is known that quartz exhibits thermal expansion around 500ºC[10]. This degradation is usually associated with the elastic properties of the aggregate and matrix, modifying significantly the mechanical behavior of the mixtures[11]. In the range of 500 to 1000°C, the geopolymers are stable, showing small reductions related to the shrinkage of the samples that occur due to the densification of the matrices, resulting from the crystallization. After their exposure, up to 500ºC, these structures were fully dehydrated, but did not undergo full structural collapse.

The results of the compressive tests for the four matrices are shown in Figure 6 and Table 5. In tests with specimens at ambient temperature (25ºC), there was a significant increase in the compressive strength (σ_{max}) for the matrix containing BFS. In fact, the partial substitution of MK by BFS increases the mechanical strength because of the additional gel formation of $CaO-Al_2O_3-SiO_2-H_2O$ (C-A-S-H) due to the presence of calcium from the BFS. This gel fills the voids in the geopolymer matrix $Na_2O-Al_2O_3-SiO_2-(H_2O)$(N-A-S-(H)), reducing porosity[12] and permeability[13]. It is noted, however, that the partial replacement of MK by SF reduced the compressive strength, and increased its strain capacity; this fact can be attributed again to the incomplete dispersion of the SF during the mixing of materials, which increases the porosity and decreases the mechanical strength. The elastic modulus was computed in the linear elastic region of the curve up to 40% of the maximum strength.

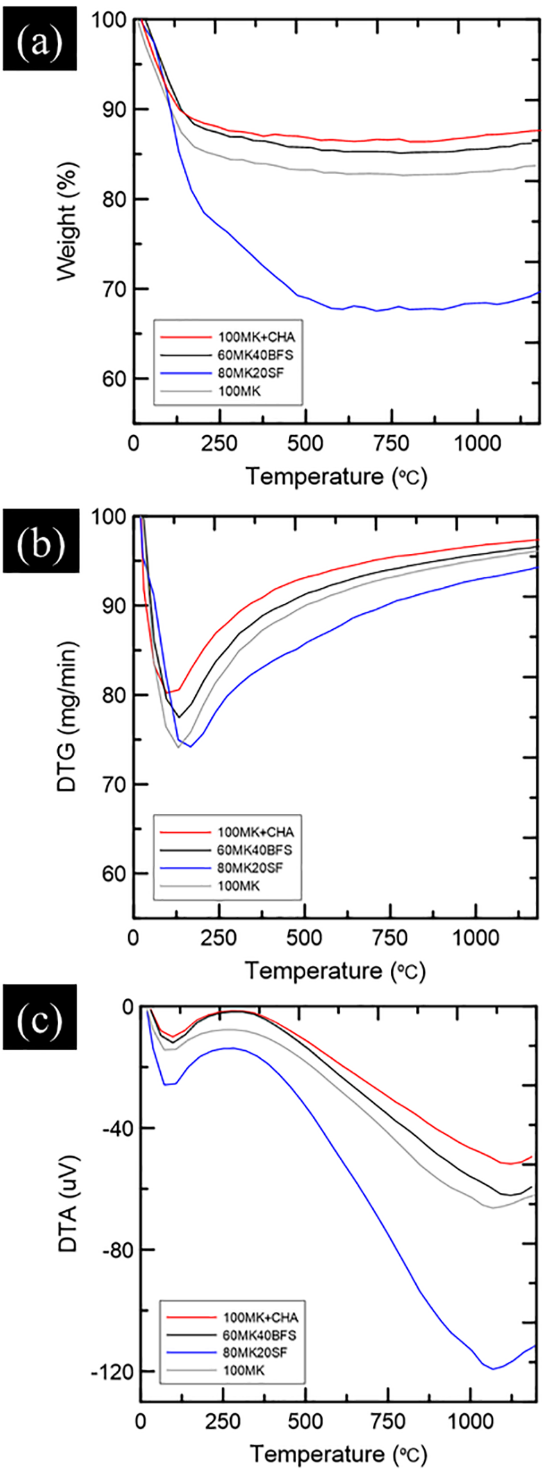

Figure 5. (a) TGA; (b) DTG; and (c) DTA of: 80MK20SF, 60MK40BFS, 100MK and 100MK + CHA.

As presented in Figure 6 and 7, and also with the results shown in Table 5, all geopolymer matrices suffered a strength

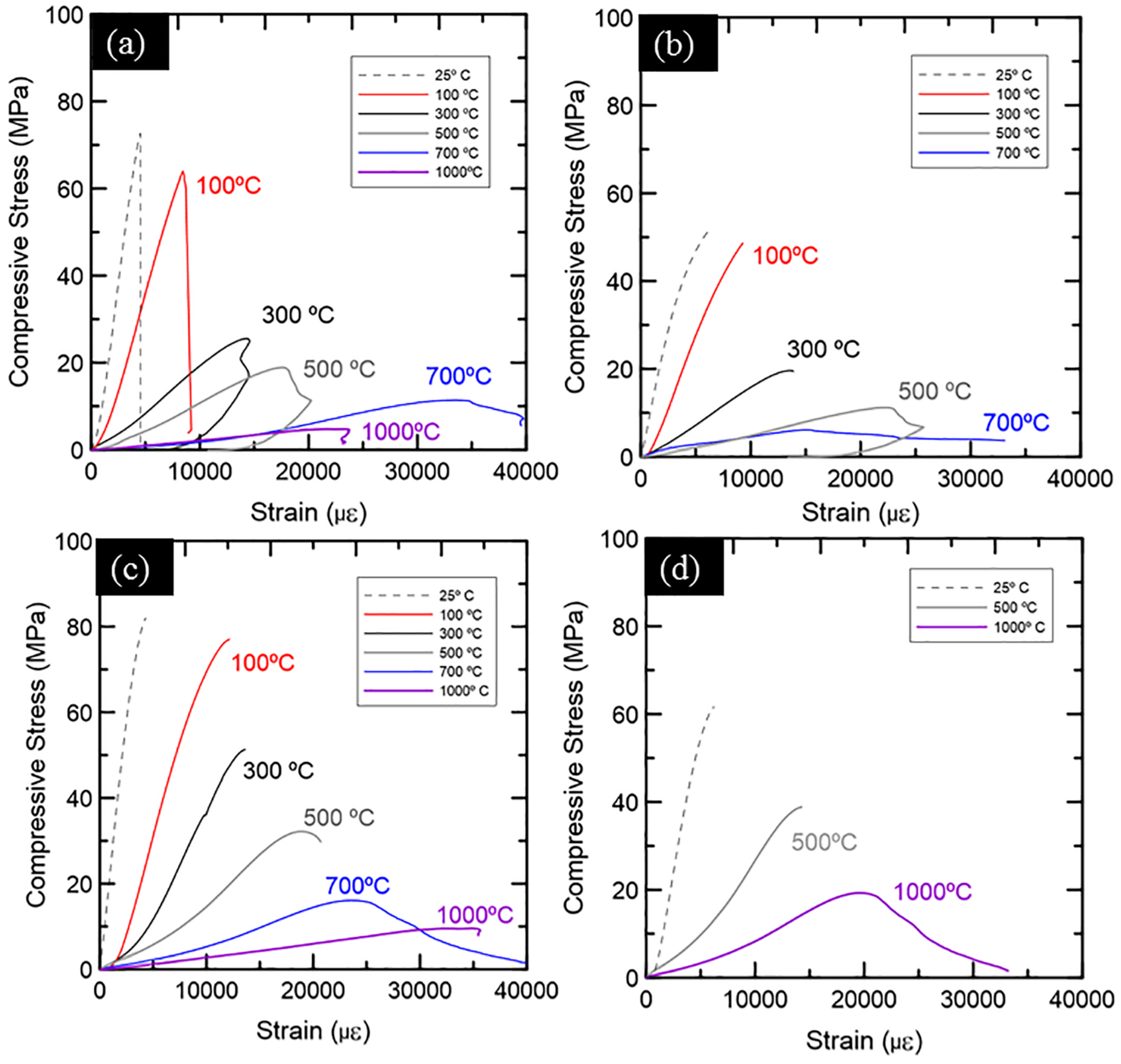

Figure 6. Influence of elevated temperatures on the compressive behavior of (a) 100MK, (b) 80MK20SF, (c) 60MK40BFS, and (d) 100MK + CHA.

Table 5. Results of compressive tests performed in four different matrices submitted to temperatures up to 1000ºC (values in parentheses refer to standard deviation).

Matrix	Compressive Tests											
	25ºC		100ºC		300ºC		500ºC		700ºC		1000ºC	
	σ_u (MPa)	E_t (GPa)	σ_u (MPa)	E_t (GPa)	σ_u (MPa)	E_t (GPa)	σ_u (MPa)	E_t (GPa)	σ_u (MPa)	E_t (GPa)	σ_u (MPa)	E_t (GPa)
100MK	72.70 (2.1)	14.26	64.00 (3.6)	11.01	25.53 (2.0)	2.91	18.88 (3.5)	1.63	11.42 (4.1)	0.43	4.82 (1.8)	0.35
80MK20SF	51.24 (1.4)	12.05	48.65 (2.3)	8.32	19.45 (2.9)	2.13	11.21 (3.9)	1.02	6.76 (2.1)	0.89	-	-
60MK40BFS	81.98 (3.2)	23.94	77.00 (3.8)	12.31	51.31 (3.2)	5.04	32.17 (5.0)	2.34	16.08 (3.3)	0.93	9.51 (2.7)	0.47
100MK + CHA	61.73 (2.9)	14.7	-	-	-	-	38.86 (3.3)	3.99	-	-	19.82 (3.5)	1.35

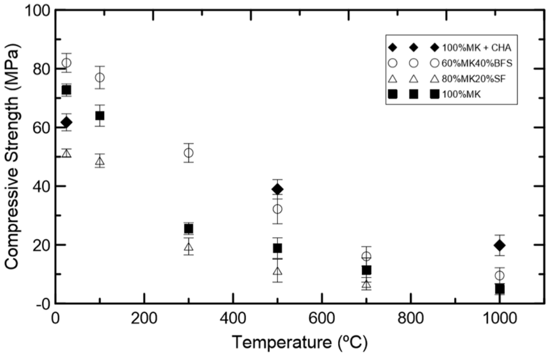

Figure 7. The effect of exposure to elevated temperatures on the compressive strength of the geopolymer matrices (error bars indicate standard deviation).

loss after the exposure to elevated temperatures. However, they indicate different behaviors at selected points. At 100ºC the samples demonstrated a slightly reduction in the compressive strength, with significant drops of the modulus of elasticity, resulting from the loss of free water in the pores of the matrices. At 300ºC it is possible to note that the samples of 100MK and 80MK20SF showed lower results when compared to the mixture 60MK40BFS. These samples underwent a higher rate of water loss than the BFS+MK geopolymer. This is believed to be one of the causes for the lower performance obtained, after exposure to elevated temperatures. At 500ºC all matrices reinforced with sand presented a higher degradation than the one incorporated with the refractory aggregate. This problem occurs due to the deterioration after 500ºC of the natural aggregate (sand)[11]. At 700ºC and 1000ºC, matrices made with MK and MK+SF demonstrate minimum capacity to withstand loads, while the mixture containing BFS register a relatively higher behavior. The matrix reinforced with chamotte indicated the best mechanical behavior in aggressive temperature environments, reaching 19.82 MPa at 1000ºC.

SEM micrographs for 100MK, 80MK20SF and 60MK40BFS are shown in Figure 8. Presence of pores and unreacted MK and SF particles are shown in both micrographs (Figures 8.a and b). The image obtained for the 60MK40BFS mixture shows a much more denser structure (Figure 8.c). This formulation presented a lower porosity, that can also justify the higher values obtained in the compression tests.

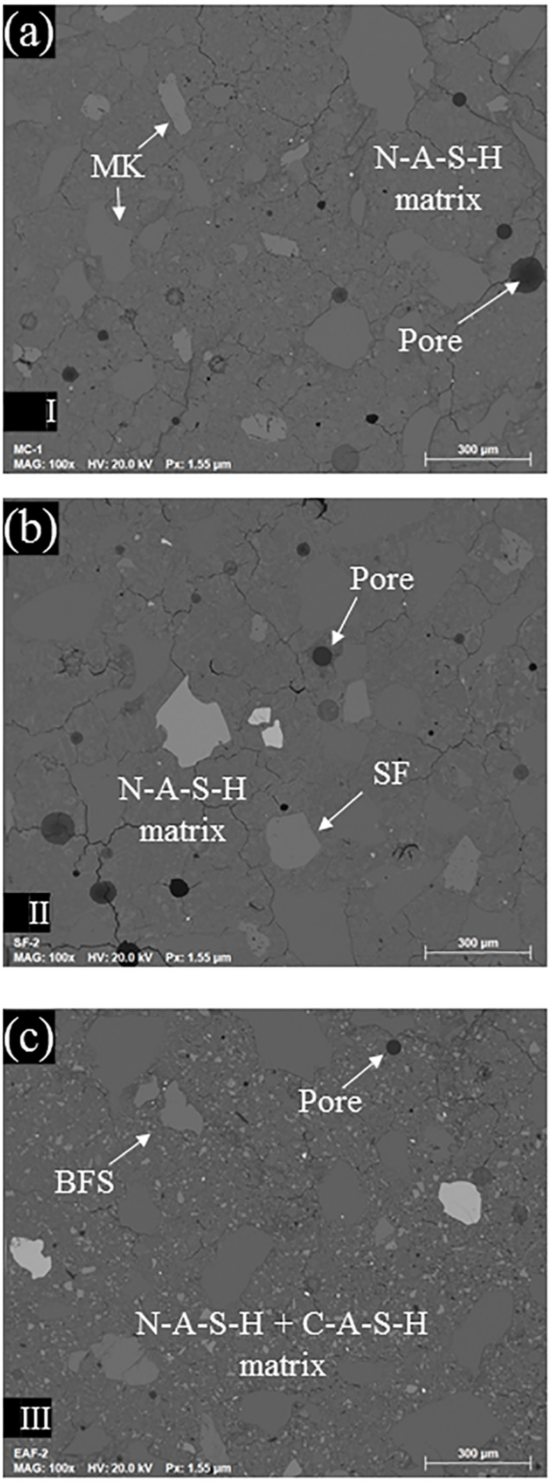

Figure 8. SEM micrographs showing the microstructure of polished samples of: (a) 100MK, (b) 80MK20SF and (c) 60MK40BFS.

5. Conclusions

Modifications in the MK based matrix compositions through its partial replacement by BFS and SF changes the physical and mechanical behavior of the mortars. The presence of BFS significantly increases the compressive strength due to the additional gel formation $CaO-Al_2O_3-SiO_2-H_2O$ (C-A-S-H). A high silica fume content is more detrimental to the performance of the geopolymer matrices due to their incomplete dispersion in the material. However, all three geopolymer mortars exhibited high compressive strength, reaching values as high as 82 MPa at 7 days.

TGA results showed that SF and MK based-geopolymers presented significantly higher weight loss than those produced with BFS+MK. Higher water losses may be associated with the degradation presented in the results of the compression tests. The thermal incompatibility between the geopolymer matrix and its aggregate is the most likely cause of strength loss after exposure to temperatures up to 450ºC. This is proven by the results presented with the replacement of the natural aggregate (sand) by the refractory one (chamotte). Even though their initial strength obtained was 11 MPa lower, the replacement showed beneficial characteristics to the geopolymer matrix, achieving satisfactory results at 1000ºC.

With all these statements, it is possible to conclude that the incorporation of the refractory aggregate in geopolymer matrices can significantly modify their brittle behavior when exposed to elevated temperatures, improving the reliability of this material in extreme temperature conditions.

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