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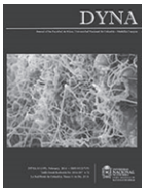

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Mechanical and thermal performance of a geopolymeric and hybrid material based on fly ash

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Abstract
This article presents an evaluation of the thermal behavior of a hybrid (FA/OPC) and geopolymer (FA100) material. The FA100 system is based on fly ash (FA), which has an elevated content of unburned material (14.8%). The FA/OPC system is comprised of a mixture of fly ash and ordinary Portland cement (OPC) at a proportion of 80/20. The thermal performance was evaluated by several tests, such as exposure to high temperatures (up to1000°C) and direct flame resistance. In addition, the effect of cyclic exposure was studied at 700°C for 10 cycles. FA/OPC hybrid material retains 92% of its initial strength and FA100 retains 113.3% of its initial strength at 700°C. Both materials can withstand 10 exposure cycles with a strength loss of less than 45%. In direct flame exposure, a temperature gradient of about 500°C was observed. These results indicate that these types of materials could possibly be used as fire-resistant materials in civil structures.

Keywords: fly ash; geopolymer; hybrid material; fire resistance

Comportamiento mecánico y térmico de un geopolímero y un material híbrido basado en ceniza volante

Resumen
Este artículo presenta la evaluación del comportamiento térmico de un material hibrido (FA/OPC) y un geopolimero (FA100). El sistema FA100 está basado en ceniza volante (FA) con un alto contenido de material orgánico (14,8%). El sistema FA/OPC se compone de la mezcla de FA y cemento portland (OPC) en proporción de 80/20. El desempeño térmico se evaluó mediante diferentes ensayos, exposición a altas temperaturas (hasta 1000°C) y resistencia a la llama directa. Adicionalmente se estudió el efecto de la exposición cíclica del material a temperatura de 700°C durante 10 ciclos. FA/OPC y FA100 retienen el 92%y el 113,3% respectivamente de su resistencia inicial a 700°C. Ambos materiales soportaron 10 ciclos y reportan una pérdida de resistencia menor del 45%. Respecto a la llama directa, se identificó un gradiente del orden de 500°C. Estos resultados indican que este tipo de materiales pueden ser utilizados en estructuras civiles resistentes al fuego.

Palabras claves: ceniza volante; geopolimero; material hibrido; resistencia al fuego

1. Introduction

Fly ash (FA) is a byproduct obtained from electricity generation via carbon in thermoelectric plants and boilers in several industries. This material has become one of several solid wastes that are generated in large volumes worldwide (on the order of 600 million tons reported), primarily due to the growing global energy demand. The large volume generated, its effect on the environment, and the excessive costs for handling and disposal have led numerous researchers to focus their attention on looking for solutions to this problem. However, although the potential markets are known, the decision to use the material in specific applications implies strict quality control, and the resulting material must demonstrate its competitive power against the natural resource or raw material that is to be replaced [1].

The primary variability of fly ash according to the source of origin is attributed to the reduced control over system

variables during coal burning processes; this lack of control is more critical in industrial boilers, where the main FA impurity is unburned carbon (abbreviated as "unburned"), which can reach values of up to 35% [2]. Temuujin et al. [3] investigated the effect of a thermal treatment (500-800°C) on ash to reduce the unburned levels and reported that it affects the vitreous phase at the surface level by 10% due to the crystallization of the mullite and hematite phases. Thus, its reactivity decreases, and the geopolymer mechanical strength decreases by approximately 20%. Lee et al. [4] used the flotation technique to reduce the carbon levels present in the ash and obtained positive results.

Fernández-Jiménez A. et al. [5] studied a group of F-type Spanish fly ash to determine the effect of their physicochemical characteristics on the mechanical strength of alkali-activated materials. The authors reported that the mechanical strength depends on the following factors: proportion of reactive silica and alumina, vitreous phase content, and particle size distribution. Adequate control of these characteristics allows compressive strengths of up to 70 MPa at 1 day of curing to be attained [6]. Additions of other supplementary materials to FA-based geopolymers to form binary mixtures, such as bottom slag, granulated blast furnace slag, and metakaolin, have also been investigated [7-9]. In relation to this, it has been reported that mixtures blended with granulated blast furnace slag (GBFS) are more resistant than those that contain metakaolin (MK) and that the optimum mixture percentages vary with the addition. Recently, hybrid systems have emerged [10], where a portion of the FA is replaced by a clinker or ordinary Portland cement (OPC) in orders of up to 30%); in this case, in addition to the aluminosilicate-type (N-A-S-H) gel characteristic of the alkali-activated FA, a (N-C)-A-S-H-type substitute gel is generated [11]. These types of hybrid materials are part of the currently so-called "*Alkali-activated Portland Cement-based Blended Cements*" [12].

The performance of these materials in aggressive environments and to the phenomenon of leaching has been reported as highly satisfactory [13, 14]. Rostami et al. [15] claim that this new type of binder could revolutionize the concrete industry and ceramics in general because its properties are excellent: a strength development of 90% in the first 24 hours, an ultimate strength of up to 110 MPa, excellent resistance to acid media, such as sulfuric, nitric, hydrochloric, and organic acids in general, and elevated frost resistance, which validates its use in high-performance structural applications. Because these alternative binders have an application in the civil industry, the study of its behavior against temperature, specifically in the event of a fire, has been an object of study. In general, reports have shown a better performance of these materials compared with traditional OPC-based materials, and several authors attribute this to structural transformations at high temperatures that lead to the formation of crystalline phases of greater thermal stability [16,17].

The objective of the present study is to evaluate the fire behavior of a 100% FA geopolymer and an FA/OPC 80/20 hybrid type material produced from FA with a high-unburned level. To accomplish this, the materials were exposed to different temperatures up to 1000°C and to thermal cycles at a temperature of 700°C, and the effect on the compressive strength was evaluated. Additionally, a direct flame exposure test was performed. The study is expanded on with a microstructural evaluation of the materials using the following techniques: XRD, FTIR, and SEM.

2. Methodology and experimental techniques

2.1. Materials

To synthesize the geopolymeric material, FA from the Termopaipa thermoelectric power station was used as the aluminosilicate precursor. The FA particle size was determined by laser granulometry using a Mastersizer 2000 instrument, which indicated a mean size D(4.3) of 63.9 μm; after a milling process (ball mill) for 90 minutes, the mean size decreased to 19.5 μm. To obtain the hybrid binder, OPC was used as a source of calcium. Table 1 shows the chemical composition of the corresponding materials, it was measured by an X-ray fluorescence (XRF) technique using MagixPro PW-2440 X-ray fluorescence spectrometer, equipped with a Rhodium tube with a maximum output of 4.0 KW and 0.02% of sensitivity. The elevated loss on ignition (14.8%) for FA as a consequence of the organic material present (unburned carbon) is noteworthy; likewise, OPC has a reported 9.6% loss on ignition, which is attributed to the addition of limestone in the final stage of the cement production process. Fernández-Jiménez A. et al. [5] determined the factors that affect the quality of the material fabricated with alkali-activated fly ash and reported the following as the main characteristics of fly ash: an unburned percentage below 5%, a Fe_2O_3 content below 10%, a low content of CaO, and a reactive silica content between 40 and 50%. Regarding grain size, it is claimed that at least 80-90% of the grains must be smaller than 45 μm in size; finally, large amorphous-phase content is recommended. When comparing the physicochemical characteristics of the FA used in the present investigation, it is observed that the ultimate criterion for the unburned level is not met. According to the chemical composition data (Table 1), the SiO_2/Al_2O_3 molar ratio of the ash is 4.25, and according to the standard ASTM C618 [18], the ash is of type F.

Fig. 1 shows the morphology of the fly ash grains obtained by scanning electron microscopy (SEM). The images show the presence of spherical grains, some of which are compact and some hollow; the latter contain smaller spheres in their interior,

Table 1.
Chemical composition of the raw materials.

Compound (% wt)	FA	OPC
SiO_2	53.7	20.2
Al_2O_3	21.5	7.0
Fe_2O_3	4.5	4.8
CaO	0.8	58.4
TiO_2	1.0	-
K_2O	1.4	-
S	0.6	-
MgO	0.6	-
P_2O_5	0.5	-
Na_2O	0.3	-
Loss on Ignition (950°C)	14.8	9.6

Source: The authors

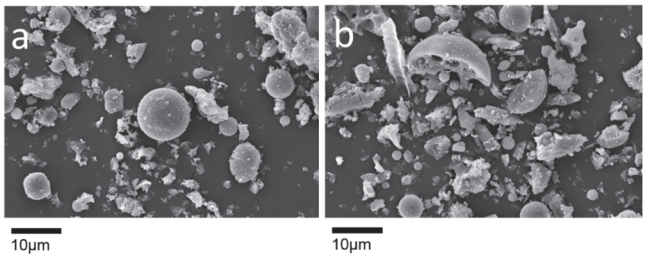

Figure 1. a) Fly ash before milling, b) Fly ash after milling
Source: The authors

which are comprised of the so-called cenospheres and plerospheres [19]. The milling process reduces the fraction of spherical grains, where rupture increases the specific area and, consequently, increases the reactivity of the material [20].

2.2. Specimen preparation

Two cementitious specimens were prepared, one composed of a fly ash-based geopolymer (FA-100) and an FA/OPC 80/20 hybrid system, which contained 20% OPC as a replacement for the fly ash.

Table 2 shows the composition of the mixtures according to the following factors: molar ratios of SiO_2/Al_2O_3 and Na_2O/SiO_2 and the FA/FA+OPC ratio; the same table includes the liquid/solid ratio and the applied curing system. The l/s ratio corresponds to the water ratio in the alkali-activator and free water, and *s* refers to the sum of the proportions of precursors and the anhydrous activator fraction. Sand from Ottawa and a binder:sand ratio of 1:2.75 were used to prepare the mortars. A mixture of sodium hydroxide (Merck analytical grade reactant) and sodium silicate (32.4% SiO_2, 13.5% Na_2O, 54.1% H_2O) was used as the alkali-activator to obtain the molar ratios shown in Table 2.

2.3. Testing techniques

The microstructure and mechanical strength were evaluated in the paste-type specimens, and the thermal performance of the mortar specimens was analyzed. The mechanical strength was evaluated at early ages of 7 and 28 days of curing using a Universal INSTRON 3369 press at a displacement rate of 1 mm/min. The thermal behavior was Table 2 shows the composition of the mixtures according to the following factors: molar ratios of SiO2/Al2O3 and Na2O/SiO2 and the FA/FA+OPC ratio; the same table includes the liquid/solid ratio and the applied curing system. The l/s ratio corresponds to the water ratio in the alkali-activator and free water, and s refers to the sum of the proportions of precursors and the anhydrous activator fraction. Sand from Ottawa and a binder:sand ratio of 1:2.75 were used to prepare the mortars. A mixture of sodium hydroxide (Merck analytical grade reactant) and sodium silicate (32.4% SiO2, 13.5% Na2O, 54.1% H2O) was used as the alkali-activator to obtain the molar ratios shown in Table 2.

Table 2.
Geopolymeric mixtures produced.

System	SiO_2/Al_2O_3	Na_2O/SiO_2	l/s	Curing
FA-100	4.4	0.2	0.4	24 hours at 65°C, ~90% RH
	5.3	0.2		
	6.0	0.15-0.2-0.3		
FA/OPC 80/20	4.4	0.2	0.4	In humid chamber, ~80% RH
	5.3	0.2		
	6.0	0.15-0.2-0.3		

Source: The authors

evaluated to determine the residual strength after exposure of the specimens at 400, 700, and 1000°C at a heating rate of 2°C/min and a holding time of 1 hour at each temperature. Additionally, a direct flame resistance test was performed for 30 minutes; in addition to the flame temperature data, this text identified the temperature transmission of the material during heating. Finally, a study of the effect of cyclic exposure was performed at 700°C with a holding time of 1 hour and cooling in the oven; the procedure was executed for 10 cycles. Microstructural and morphology analysis were conducted by a scanning electron microscopy (SEM) using a JEOL JSM-6490 LV instrument. This device contains an INCAPentaFETx3 detector (brand OXFORD INSTRUMENTS, Model 7573); before examination, the samples were coated with gold by deposition in a Denton Vacuum Desk IV vacuum unit, mineralogical compounds were identified by X-ray diffraction using a X'Pert PANalytical MRD instrument with a CuKα1 tube operated at 45 kV and 40 mA, for which the scan was performed for 30 minutes in the 2θ range of 4-60°.

3. Discussion of results

3.1. Compressive strength and microstructural characterization

Fig. 2 shows the compressive strength results obtained for the pastes of the two systems, FA100 and FA/OPC 80/20, as a function of the molar ratios of SiO_2/Al_2O_3 and Na_2O/SiO_2 and curing age. Here, it should be noted that in both evaluated systems, the optimum molar ratio for SiO_2/Al_2O_3 and Na_2O/SiO_2 correspond to 6 and 0.2, respectively. However, the strengths drastically differed for each system. FA/OPC 80/20 exhibited a compressive strength of up to 2 and 3.8 times that of the FA100 geopolymer at 28 and 360 days of curing, respectively. It should be noted that the presence of OPC in the geopolymeric mixture, in addition to increasing the strength, contributes to eliminate the thermal curing stage (~70°C) primarily for simple fly ash systems, which is in accordance with results from other researchers [21]. It is inferred that the cement hydration heat favors the dissolution of SiO_2 and Al_2O_3 species of the geopolymeric precursor. Palomo A. et al. [22] reported a compressive strength of 38 MPa at 28 days for a fly ash hybrid dosed with 30% OPC, whereas in the present investigation, it was possible to obtain a strength of 55.6 MPa with 20% OPC. Furthermore, an increasing strength development was observed for the hybrid system, whereas in the geopolymeric system (FA100), the strength reached at 7 days is similar to that exhibited by the material at 360 days

(approximately 22 MPa); the strength reported for the hybrid material at the same curing age was 85.5 MPa.

Fig. 3 shows the X-ray diffractograms for FA and the geopolymers, FA-100 and FA/OPC 80/20, after 28 days of curing with a SiO_2/Al_2O_3 molar ratio of 6 and a Na_2O/SiO_2 molar ratio of 0.2. It was observed that the FA presented a high content of crystalline phase, as evidenced by the presence of quartz (Q, ICSD: 062404), mullite (M, ICSD: 100805), and hematite (H, ICSD: 082137). The increase in the base line in the 2θ region of 15-30° is associated with the presence of the vitreous phase. The diffractograms corresponding to FA100 and FA/OPC 80/20 indicate that the crystalline phases characteristic of FA and OPC remain unaltered, i.e., the Q, M, and H of FA and calcite ($CaCO_3$; ICSD: 16710) in the OPC, which confirms that these phases do not participate in the alkali-activation process. In addition, the formation of Trona (ICSD: 062200) ($Na_3H(CO_3)22H_2O$) was identified in the FA100, which is due to the characteristic peaks at 33.84 (100%) and 29.05 (80%) and can be attributed to the action of CO_2 in the environment.

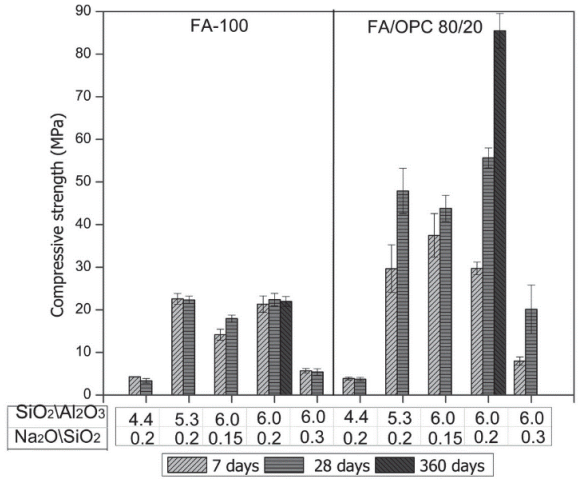

Figure 2. Compressive strength as a function of the molar ratios and curing age.
Source: The authors

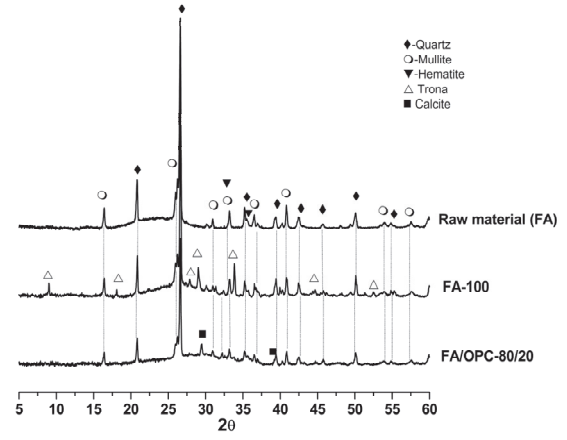

Figure 3. Diffractogram of the alkali-activated systems after 28 days of curing.
Source: The authors

The formation of portlandite was not observed in the hybrid material, which indicates that calcium ions must be part of the amorphous gels formed in the geopolymerization; this result suggests the presence of (N,C)-A-S-H-type gels in this system [23,24]. The amorphous halo between 20-35° 2θ, which is associated with the vitreous phase, is greater for the FA100 geopolymer.

3.2. Thermo-mechanical behavior

3.2.1. Exposure at high temperatures

The thermal behavior of both FA-100 and FA/OPC-80/20 was evaluated by exposing the mortars to different temperatures (400, 700, and 1000°C). Table 3 shows the percentage weight loss and the volumetric change with respect to the initial value (positive values (+) represent expansion, and negative values (-) represent contraction). The weight loss in both materials at 400°C was similar (12.7%), which is attributed to the evaporation of surface water located in the pores, the physical binding of water to the reaction products, and the partial volatilization of organic matter (carbon) provided by FA [24]. At higher temperatures, this loss is attributed to a dehydration process of the structure [26, 27, 17], and to the decomposition of the carbonates present, i.e., the sodium and calcium carbonates identified by XRD. Weight loss at 1000°C for the two evaluated systems was different by approximately 2%, which can be associated with the limestone content present in the cement used (OPC); this result occurs because, based on the OPC chemical composition shown in Table 1, the incorporation of 20% OPC into the system leads to a 1.96% loss on ignition, which is equivalent to the CO_2 of the decomposition of the limestone present in this cement fraction. Regarding the volumetric change in the material, contraction and expansion changes occurred. The physical appearance of the specimens after heating at 1000°C corroborates the transformation of a dense matrix into a porous matrix with a sponge-like appearance and partial surface vitrification (Fig. 4)

The mechanical strength values of the mortars were 18.3 MPa and 31.34 MPa at 28 curing days for the FA100 and FA/OPC-80/20 systems, respectively. After heating at 700°C, a strength increase of 13.3% was observed in the FA geopolymer, whereas a reduction of 7.8% was observed in the FA/OPC hybrid. These results are comparable to the results presented by other researchers [27]. At 1000°C, due to the excessive expansion of the test samples, it was not possible to evaluate mechanical strength. None of the systems contained cracks (Fig. 4). Authors such as *Kong et al.* [27,28] associated this behavior with the presence of hollow particles in the ash, facilitating the escape of water vapor, thus avoiding severe cracking in the material. Heating at the different temperatures modified the color of the test samples; at the end of the test, a grey coloration with small red dots was obtained in FA100. In FA/OPC, the specimens become orange, which is attributed to the loss of carbon and to the oxidation of iron (Fig. 4); other researchers have reported similar results [29].

3.2.2. Exposure to thermal cycles

The exposure to thermal cycles was performed at a temperature of 700°C for 10 cycles. At the end of each cycle,

Table 3.
Weight changes and volume loss with respect to temperature

Mixture	Property	400°C	700°C	1000°C
FA-100	Weight loss, %	12.64	12.92	18.25
	Volumetric Change, %	-29.38	-5.69	73.95
FA/OPC 80/20	Weight loss, %	12.75	14.94	20.01
	Volumetric Change, %	-34.72	5.08	132.12

Source: The authors

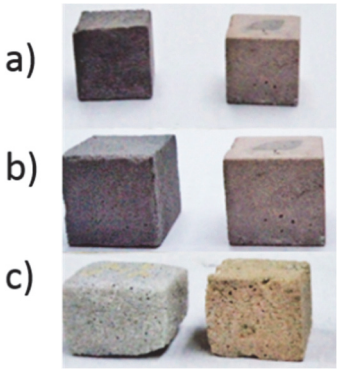

Figure 4. Thermal exposure (from left to right: FA-100, FA/OPC 80/20) - a) 400°C, b) 700°C, and c) 1000°C
Source: The authors

Table 4.
Weight losses and volumetric changes associated with thermal cycles at 700°C ((-) contraction, (+) expansion)

System	Cycle N°	Weight loss, %	Volume change, %
FA-100	2	12.92	(+) 6.59
	6	11.56	(+) 5.40
	10	11.36	(+) 5.17
FA/OPC 80/20	2	14.94	(+) 2.98
	6	12.80	(+) 2.90
	10	12.07	(-) 3.35

Source: The authors

the test samples were removed to determine their weight, volumetric change, and residual strength. Table 4 shows the values associated with weight loss and volumetric change of each system at the end of cycles 2, 6, and 10.

It should be noted that no significant changes were observed in weight loss as the number of 700°C cycles increased. In relation to volumetric change, the FA-100 geopolymer was transformed into a porous, foamed material with an expansion of approximately 5-6% with respect to the initial dimensions of the specimen (before being subjected to 700°C). In contrast, FA/OPC presented a lower expansion during the first two cycles (2.98%); subsequently, FA/OPC contracted by approximately 3%. It should be noted that after the 10 thermal cycles, the materials changed color, and even though they maintained their physical integrity, a 56% decrease in mechanical strength was observed for the FA-100 system, and a 40% decrease was observed for the FA/OPC 80/20 system (Fig. 5). These results can be attributed to the increased in porosity and to microstructural transformations, as mentioned in other studies [30]. The residual strength in the first case was 9.4 MPa, and the second was approximately twice that value (17.65 MPa). These values were determined for specimens exposed to fire after 28 days of curing, whose initial strength values were 18.3 MPa and 31.34 MPa for FA100 and FA/OPC 80/20, respectively.

Fig. 6 shows the SEM images of the two materials at the end of the 10 thermal cycles, where the formation of cavities or pores can be observed; thus, when the densified, continuous structure characteristic of the geopolymeric and hybrid materials disappeared, the irregularities became critical points that weakened the structure [26]. Strength losses of the same order (52%) have also been reported in other studies of fly-ash-based geopolymeric mortars exposed to 800°C [31]. It is claimed that, in general, these materials exhibit a greater thermal stability than that of Portland concretes, which lose their structural integrity at temperatures of around 700 and 800°C due to calcium silicate hydrated (CSH) decomposition. In contrast, in systems that are alkali-activated with sodium silicates, increasing temperature can contribute to generating new crystalline phases, such as Na-feldspars, nepheline ($NaAlSiO_4$), or albite ($NaAlSi_3O_8$), which contribute to a greater thermal stability at high temperatures [29,32]. Fernández-Jiménez et al. (2008) [33] reported the presence of a nepheline phase at temperatures above 600°C and the presence of albite at temperatures of approximately of 1000°C in an FA-based geopolymer [30].

3.2.1. Direct flame resistance

Fig. 7 shows a plot of the values obtained in the direct flame resistance test. The temperature of the flame emitted by the torch incident on the surface of the FA-100 and FA/OPC 80/20 specimens remained stable after the first four minutes at approximately 820°C until the end of the thermal test (30 minutes). The temperature, which was measured with a thermocouple and is associated with the temperature transferred through the material in the FA/OPC 80/20 and FA-100 systems, was significantly lower than the flame temperature. A temperature gradient of approximately 500°C was observed in FA/OPC 80/20, and a slightly lower temperature was observed in the FA-100 geopolymer, which indicates that these materials act as thermal insulators; it is

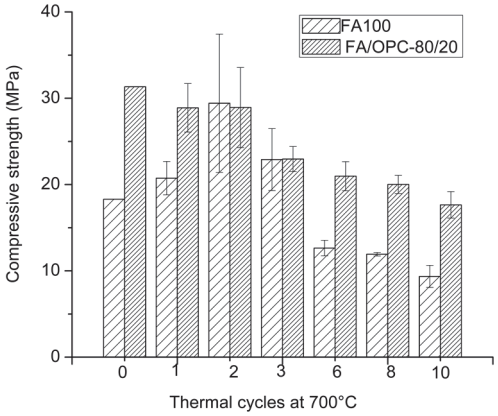

Figure 5. Compressive strength after each exposure cycle
Source: The authors

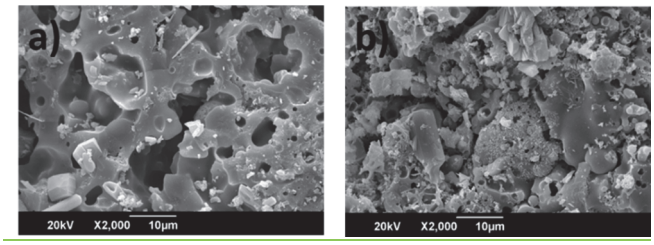

Figure 6. SEM microphotograph. Specimen after 10 thermal cycles. a) FA-100, b) FA/OPC 80/20.
Source: The authors

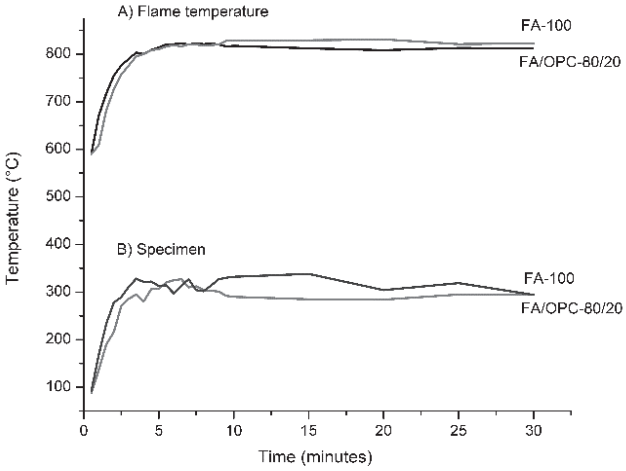

Figure 7 Temperature transfer vs exposure time. A) flame temperature of FA/OPC 80/20 (black) and FA-100 (gray), B) Sepecimen temperature FA/OPC 80/20 (gray) and FA-100 (black)
Source: The authors

inferred that, with the use of these materials as binders in prefabricated elements (panel-type) or as binders in concrete, the structure would be protected in the case of a fire, providing time that could positively contribute to avoiding the catastrophic failure of the structure and the resulting human impact. Cheng et al. [34] produced panels from the alkali-activation of steel slags, which were exposed at 1100°C (flame temperature); after 35 minutes, the temperature on the panel side was approximately 350°C, a reduction in the order of 700°C, which corresponds to the behavior reported here. Several researchers have suggested the use of these materials as thermal insulators on both ceramic and metallic substrates [35,36].

Fig. 8 shows the test samples before and after flame exposure. In the FA/OPC-80/20 system, cracking was observed on the surface that was directly exposed to the flame, and the initial coloration of the material transitioned from black to a lighter color in the direct exposure region, while its surroundings became light pink. In contrast, no cracks were observed in the FA-100 geopolymer, although coloration changes did occur. In samples 3 and 4, which correspond to the opposite and lateral surfaces of the two materials, no effects were observed, which is indicative of the good performance of the materials.

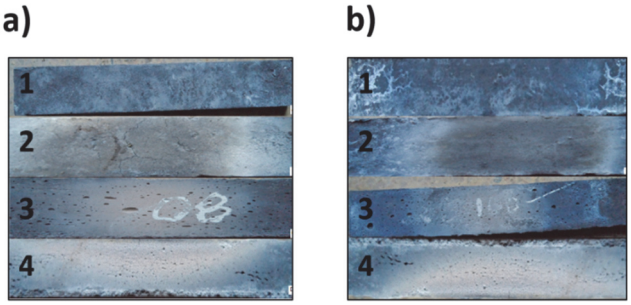

Figure 8. a) FA/OPC 80/20, b) FA-100. 1= before exposure 2= side of direct exposure, 3=opposite side, 4= lateral view of the test sample.
Source: The authors

4. Conclusions

- The results of this study indicate that fly ash containing unburned material of around 15% does not affect the long-term strength (360 days) or thermal exposure performance of the resulting material, which enables the use of lower quality FA to produce geopolymers and hybrid materials.
- A 20% addition of OPC to the FA100 geopolymer increases its mechanical strength by up to 150% and 288% at curing ages of 28 and 360 days, respectively. In addition, FA/OPC 80/20 does not require thermal curing. These are significant advantages of the hybrid material compared with the geopolymer.
- In general, FA-100 and FA/OPC-80/20 exhibited good thermal performance. The residual strength at a high temperature (700°C) was 92% of the initial strength in the hybrid material and 113.3% that of the geopolymer. The two evaluated materials are capable of withstanding 10 heating/cooling cycles at 700°C with less than 45% loss of mechanical strength at the end of 10 cycles.
- The behavior of the materials against a direct flame with a thermal gradient of approximately 500°C from the internal side of the panel was good.
- Based on these results, these materials could represent an alternative that can protect or reinforce structures in the case of fires due to their good mechanical behavior and thermal isolation capacity.

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