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PRESERVING THE MECHANICAL PROPERTIES OF METAKAOLIN-BASED GEOPOLYMER COMPOSITE EXPOSED TO THERMAL STRESS BY USING REFRACTORY FILLER WASTES

BY

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Abstract. Metakaolin-based geopolymer composite with addition of refractory filler wastes (super-aluminous concrete and silica fire brick) recycled from heating oven demolition was designed and tested under thermal stress conditions at temperatures up to 900°C. The method of alkaline activating patented by Davidovits was applied. The originality of the work consists in choosing the super-aluminous concrete waste from the demolition as the main raw material of the process, increasing the heat treatment temperature to 90°C, and adopting the storage for a much longer period (28 days). Tests to thermal stress by exposure to 600 and 750°C showed the favourable influence of the addition of refractory fillers on preserving the mechanical stability of the geopolymer composite. The loss of compression and flexural resistance after exposure to 900°C compared to the reference sample is acceptable for using this technique in the case when the stability at high temperature is required.

Keywords: geopolymer composite, refractory filler waste, metakaolin, thermal stress, mechanical strength.

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1. Introduction

The last decade of the 20th century consecrated a new concept of environmentally friendly and economic material, based on waste or industrial by-products rich in alumina and silica. The so-called "geopolymer" conceived by the French researcher J. Davidovits as an inorganic polymer (Davidovits *et al*., 1994) allows the manufacture of new materials needed for the construction sector, practically eliminating the traditional Portland cement considered as the most used binder for the manufacture of concrete. After a long time period (over a century), in which Portland cement was industrially manufactured on a large scale under the conditions of excessive consumption of fossil fuel and the emission of huge amounts of greenhouse gases (CO_2) into the atmosphere, important restrictions appeared at the global level regarding CO_2 emissions (Reducing Carbon, 2023).

The remarkable Davidovits' invention is an excellent alternative in ecological terms to Portland cement. Numerous variants of natural (clay, kaolin, metakaolin, volcanic rock ash, rice husk ash, etc.) or recycled materials from industrial processes as by-products, rich in alumina and silica (coal fly ash, granulated blast furnace slag, red mud, etc.) (Davidovits, 2008; Nawaz and Sivakumar, 2020), activated by the addition of alkaline solutions (sodium or potassium hydroxide and silicate) (Fořt *et al*., 2022), have the ability to turn into geopolymeric products with superior mechanical properties, potential replacements of traditional concrete.

Several results of the manufacture of geopolymer concrete are already known from the literature (Mugahed Amran *et al*., 2022; Abdul Aleem and Arumairaj, 2012; Aziz and Salleh, 2022). The most frequently used alumino-silicate material in the manufacture process of geopolymers is coal fly ash with pozzolanic properties recycled as a by-product from the energy industry (Guo *et al.*, 2010). Also, granulated blast furnace slag from metallurgy industry is an alumino-silicate by-product preferentially used in these manufacturing processes, usually together with coal fly ash (Inti *et al*., 2016). Churata *et al.* (2022) have studied the effect of manufacturing geopolymer composites using different natural alumino-silicate materials together with fly ash: volcanic ash, pozzolan, metakaolin, and mining tailing. Metakaolin commonly used as an admixture or partial replacement of cement due to its most effective pozzolanic properties, improving the microstructure and strengthening the mechanical and durability properties of cement-based concrete, started to be used as a precursor in geopolymer concrete (Jindal *et al*., 2023; Duxson *et al*., 2007a; Bernal *et al*., 2011). Other research was focused on the manufacture of geopolymer composites. According to (Sata and Chindaprasirt, 2020), recycled waste such as crushed old concrete, bottom ash, residual clay brick, residual tires, and ground glass waste can be used for achieving geopolymer composites.

In general, according to the mentioned works, the mechanical characteristics of geopolymer products were at least at the level of products manufactured with Portland cement (compression strength of 28-35 MPa measured after the curing process). An increase in mechanical resistance was obtained by adding different fiber types (from steel, glass, organic polymers as well as natural fibers (vegetable or animal), which allowed high performance to be achieved (compression strength values of over 60 MPa or even higher in the case of steel fibers) (Rashad, 2020; Bhalchandra and Bhole, 2013; Korniejenko *et al.*, 2016; Saikh, 2021; Paunescu *et al.*, 2023a; Wang *et al.*, 2023).

Research on the stability of metakaolin-based geopolymer showed that these materials tend to decrease their mechanical properties at over 200°C due to high shrinkage manifested at the same time with processes of dehydration and hydrogen addition to OH^- group (forming an alkyl group), named dehydoxylation, of products resulting from the reaction (Duxson *et al.*, 2007b). At high temperatures in the range of 800-1000°C, softening and viscous sintering with a structural redistribution occur. Thus, the use of metakaolin-based geopolymer is restricted in applications where the volumetric stability is required. However, it was found that by adding suitable fillers to embrittle the matrices, the shrinkage tension can be reduced, while the breaking toughness of the made composite is improved.

Geopolymer composites have been designed and tested for several conditions to fireproof and thermal insulation properties of them (Lyon *et al.*,1997; Hammell *et al.*, 2000). Alumino-silicate resin geopolymer composites reinforced with carbon fiber were made for applications where fireproof is required. This geopolymer type has comparable strength with that of reinforced phenolic resin composites, but it has better resistance in the case of the use at higher temperature and fire exposure. Compared to steel fiber-geopolymer composites, the flexural strength, flexural modulus, and costs are decreasing, but the ability to withstand temperature is better. Reported to the density value, the high specific flexural strength, flexural modulus, temperature ability and fireproof of geopolymer composite recommend this product for fire-resistant components in aeronautics.

The well-known technique of manufacturing a geopolymer from alumino-silicate material (in the present case, metakaolinite), activated with hydroxide and silicate potassium solution, was applied by Perera and Trautman (2006) to obtain a heat-insulating material resistant for use at 1000°C. The paste resulted from mixing the metakaolinite with the alkaline solution was subjected to a curing process at 80°C for 24 hours. The geopolymer behaviour was experimentally examined during its progressive heating from the ambient temperature to over 1000°C. It was observed that at 1000°C the open porosity of the specimen was 38%, indicating obtaining a sufficiently porous material and, at the same time, a thermal insulation material resistant at the mentioned temperature (Barbosa and MacKenzie, 2003).

According to (Bernal *et al*., 2012), various alumino-silicate composites activated with alkalis, in which shards of porcelain, quartz sand or ceramic spheres with the role of reinforcement were added, led to increasing the compression strength of these composites by exposure to high temperatures due to the peculiarities of the reinforcement pieces. In this way, lumps of alumina, electrical porcelain, and ceramic spheres (Kamseu *et al*., 2010; Zuda *et al*., 2008), which have the ability to have stability in high temperature conditions, can exhibit volumetric stability at temperatures less than 1000°C.

By the experiment presented by Bernal *et al.* (2012), a metakaolin-based geopolymer was made, the size of the metakaolin grains being below 100 µm. Ground refractory brick (average grain size of 200 µm) was used as silica-rich alumino-silicate additive, recycled from the disused masonry of a laboratory muffle oven. Alumino-silica-zirconia fibers (diameter of 3.5 µm and the length between 20-35 mm) were added as reinforcement component. The alkaline solution for activating the alumina and silica-rich raw material was a sodium silicate solution (Na_2SiO_3) and solid NaOH pellets dissolved in deionized water. The preparation of geopolymer samples respected the following ratios: SiO_2/Al_2O_3 molar ratio of 3 and 3.4, Na_2O/SiO_2 ratio of 0.25 (kept constant), water in alkali activator adopted so that water/Na_2O ratio to be 12. Specimens (without reinforcing fibers) were mixed, poured into molds, and vibrated for 5 min. Particles and fibers were incorporated after the paste homogenization. The curing process was performed at 60°C for 24 hours. Then, the specimen storage was achieved at room temperature for 7 days. Testing the geopolymer behaviour at different temperatures was carried out after maintaining the specimens at 600, 800, and 1000°C for 2 hours. The results showed remarkable preservation of mechanical performances of metakaolin-based geopolymer when exposed to high temperatures by incorporating the alumino-silicate additives and fibers together. The properties improvement was observed in composites with higher additions of particles and fibers. At the same time, the volumetric product contraction was reduced. By exposure to high temperatures, the structural reorganization of the geopolymer matrix was facilitated. The densification in the interfaces between components of composite caused increasing the stiffness of this material, which became more brittle. In this way, the effect of reinforcing fibers partially loses its effectiveness.

Other experiment presented in the literature (Sevim *et al*., 2023) refers to making a geopolymer composite type resistant to relatively high temperature conditions (up to 800°C) by introducing into its composition some fillers containing metallurgical slag and fire brick waste from building demolition. Elevated temperatures at which flexural and compression strength as well as mass loss of composite were determined, fell within the limits of 300-800°C. Results showed that the improvement of compression and flexural strength of geopolymer specimens was obtained in the temperature range of 300-800°C by comparison with the reference sample, in the case of using the weight ratio of fillers of 30% and carrying out the tests in the range of 300-600℃.

The current paper contains the results of tests conducted by authors aiming at an objective almost similar to that in the work (Bernal *et al.*, 2012). This objective is keeping the mechanical properties of a geopolymer composite under the conditions of its exposure to relatively high temperatures (up to 900℃). Previously, except for metakaolin used as the main alumino-silicate cementitious binder, particles and fibers with refractory properties were introduced into the mix formed by metakaolin and the alkaline activator. As particles, lumps of refractory brick recycled from oven lining were used and the reinforcing fibers were of alumina-silica-zirconia type, having also refractory properties. The originality of the current work consisted in the simultaneous use, together with metakaolin, of two refractory wastes (refractory concrete and brick), of which super-aluminous refractory concrete recycled from the masonry of a metallurgical heating oven for the first time, without using refractory reinforcing fiber, whose effect could lose effectiveness due to densification by exposure to rising temperature.

2. Materials and Methods

The basic raw material used in this experiment was metakaolin. Metakaolin ($Al_2Si_2O_7$) is a largely amorphous dehydration product of the clay mineral kaolinite, which exhibits strong pozzolanic activity, having the role of supplementary cementitious material. The known advantages of metakaolin are: increasing compression and flexural strength, increasing resistance to chemical attack, increasing durability, reducing permeability, reducing effects of alkali-silica reactivity, reducing shrinkage, and improving workability (El-Diadamony *et al*., 2018). It was chosen as the main cementitious binder in the material mixture for the manufacture of geopolymer. The oxide composition of metakaolin includes: 55.10% SiO_2, 34.10% Al_2O_3, 5.24% Fe_2O_3, 0.28% CaO, 0.25% MgO, 0.10% Na_2O, 0.02% K_2O, 2.00% TiO_2, 1.00% P_2O_5, 0.01% SO_3, and 1.50% LOI (Mo *et al*., 2014). The pore size of white metakaolin for construction (origin China) selected for the experiment was less than 50 µm.

The aim of the research, whose results are presented in the current paper, was preparing relatively high-strength geopolymer, whose mechanical properties to be affected within low limits by exposing the composite to sufficiently high temperatures (up to 900℃). Therefore, the content of alumina and silica in the geopolymer mass was supplemented by the implementation of some waste rich in these chemical compounds with the role of additives. Two types of recycled refractory waste from the demolition of a metallurgical heating oven from the Metallurgical Research Institute of Bucharest (Romania) were used: broken super-aluminous refractory concretes and silica fire brick lumps, both advanced grinding, so that their grain size to be under 150 µm.

Chemical composition of the super-aluminous refractory concrete recovered from the lining furnace contains: 4.1% Al_2O_3, 0.3% Fe_2O_3, 2.5% CaO, 0.2% SiO_2, 0.01% MgO, 0.07% Na_2O, and 0.06% K_2O. This composition was determined (Paunescu *et al*., 2022) with X-ray fluorescence spectrometer (SR EN ISO 12677). Also, the same determination procedure allowed to identify the chemical composition of silica fire brick lump (ASTM C27-98): 30.1% Al_2O_3, 64.8% SiO_2, 1.5% Fe_2O_3, 0.3% MgO, 0.3% CaO, and 2.0% TiO_2.

Unlike the research aiming at an almost similar objective carried out by Bernal *et al.* (2012), the current work did not test the use of reinforcing fibers introduced into the mixture at the same time together with the mentioned alumino-silicate wastes (refractory concrete and brick). The reason is that due to the increase of the geopolymer stiffness caused by densification at high temperature in the interface areas between the components, the effectiveness of reinforcing fibers decreases.

The usual method of alkaline activation of alumino-silicate materials with the mix of Na_2SiO_3 aqueous solution and NaOH pellets dissolved in distilled water was adopted. The alkaline activator was constituted so that SiO_2/Al_2O_3 molar ratio to be 3.5 and Na_2O/SiO_2 molar ratio to be 0.25. The water amount in the activator composition was measured for obtaining the water/Na_2O ratio of 11.8. The alkaline solution favours the development of geopolymerization reaction (Davidovits *et al*., 1994), forming the geopolymer composite.

Previously, the authors of this work experimentally observed that metakaolin-based geopolymer unreinforced with refractory materials is disadvantaged in terms of mechanical resistance compared to geopolymers reinforced with such additives, whose high temperature-strength (up to 900°C) is about two times higher. For this reason, the current experiment was focused only on metakaolin-based geopolymer reinforced with broken refractory wastes.

The working method adopted included firstly preparation of the alkaline activator mixture containing sodium silicate solution (Na_2SiO_3) and water-soluble NaOH pellets dissolved in distilled water. After the homogenization of the activator, the metakaolin as well as broken refractory wastes (super-aluminous concrete and silica fire brick) were mechanically processed. Weight proportions adopted for the solid components were kept constant during the entire experiment (16% refractory concrete, 12% silica fire brick, and 72% metakaolin).

The technique chosen for mixing the solid and liquid components was pouring the liquid alkaline activator over the ground metakaolin and mix them together until a paste was formed. The ground refractory additions were later introduced into this paste, the mixing being continued for 30 min. Next, the paste was poured in cubical molds for determining the compression strength and respectively, in prismatic molds for measuring (in three points) the flexural strength. The molds were placed in a laboratory electric oven and heated to 90°C for 24 hours. Then, the specimens were removed from the molds and stored at room temperature for 28 days before performing the mechanical determinations.

The behaviour of specimens at relatively high temperatures (600, 750, and 900°C) was identified by heating them to these temperatures (with low rates below 5°C/min) and maintaining them at the mentioned values for 2 hours. The temperature of the thermal treatment of the paste (90°C) was chosen at the upper level of the usual range and the time of the curing process (storage at room temperature) was extended up to 28 days, compared to 7 days practiced by Bernal *et al.* (2012). Also, solid component proportions of the mix were no longer used in experiments, according to the literature.

The reference sample manufactured by the same technique described above was represented by the geopolymer composite not subjected to temperature conditions in the range of 600-900°C, determining its characteristics being carried out only after the storage at room temperature (25°C).

Usual methods were applied for characterizing the geopolymer composite specimens. Bulk density was determined by applying the water intrusion method (Archimedes' method) in conformity with ASTM D792-20 standard. 100 kN-compression fixture Wyoming Test Fixture was used for the identification of compression strength value of the geopolymer composite (A practical guide, 2018), while the flexural strength was measured by conducting the three-point bend test on the sample according to SR EN ISO 14125:2000. Modulus of rupture was determined using the standard center point loading test (ASTM C 293). The volumetric contraction of specimens was determined by measuring their volume before and after exposure to temperature and calculating the variation percentage of results (Bernal *et al*., 2012). The well-known method of immersing the sample under water (ASTM D570) was used for measuring the water-absorbing ability. Microstructural features of specimens were investigated with Biological Microscope MT5000 model (1000 x magnification).

3. Results and Discussion

Applying the adopted experimental method, the geopolymer composite specimens stored at room temperature (about 25°C) and under the conditions of a humidity of 60-70% for 28 days were separately tested immediately in the case of reference sample and respectively, after maintaining at constant temperatures of 600, 750, and 900°C in a laboratory electric oven for 2 hours, to determine the behaviour of specimen characteristics under conditions of exposure to these temperatures. The duration of storage to complete the curing process of material was adopted at 28 days, applying the own experience of hardening the geopolymer concrete (Paunescu *et al.*, 2023a; Paunescu *et al.*, 2023b; Păunescu *et al*., 2023c).

Both in the case of the reference sample and in the case of samples subjected to the behaviour test of their characteristics after exposure to 600, 750, and respectively, 900°C, the following features were determined: bulk density, water-absorbing, compression strength, flexural strength, modulus of rupture, volumetric contraction, and peculiarities of microstructural appearance of specimens.

Table 1

Characteristics of geopolymer composite specimens after exposure to high temperature

Characteristic	Exposure temperature (°C)			
	25	600	750	900
Bulk density (g·cm^{-3})	2.16	2.24	2.31	2.34
Water-absorbing (vol. %)	5.3	5.6	5.1	4.9
Compression strength (MPa)	35.8	38.0	35.6	27.8
Flexural strength (MPa)	11.8	12.5	12.1	10.1
Modulus of rupture (MPa)	8.3	5.2	5.4	8.0
Volumetric contraction (%)	4.0	9.8	11.2	11.6

According to the work (Bernal *et al*., 2012), geopolymer composite specimens exposed to relatively high temperatures exhibit decreasing the shrinkage with the increase of the refractory filler content added to the mixture mass, maintaining in the same time high mechanical strength. Increasing the volumetric stability of composite through exposure to temperature, due to the capacity of refractory fillers that interact with the matrix to deflect the crack and to densify the interface matrix-fillers, also contributes to increasing the material rigidity.

In the case of the current work, the two fillers with refractory properties (concrete and fire brick wastes) represent 28% of the total solids, i.e. more than the fillers used by Bernal *et al.* (2012). Exposure to 750°C showed a volumetric contraction of 11.2%, higher compared to that measured at 600°C (9.8%). By exposure to 900°C, the contraction continued to increase, but more easily (11.6%). Analysing Table 1, it can be seen that at 900°C there are different trends between the evolution of compression strength (decreasing) and that of volumetric contraction (increasing). During the densification, silicate gel contraction takes place, which leads to high tendency of shrinkage. The presence of OH^- groups reduces the silicate gel viscosity, favouring a better structural redistribution by exposing the composite to high temperature as well as during the solidification through the final cooling.

The flexural strength variation in the reference sample and in the three exposures to temperatures between 600-900°C shows an apparent value constancy. It increases slightly from 11.8 MPa (in the case of reference sample) to 12.5 MPa (at 600°C) and 12.1 (at 750°C), registering a more obvious decreasing up to 10.1 MPa (at 900°C). In terms of values, the level of flexural strength is high for this type of material, even at 900°C.

By comparison with the value corresponding to the reference sample (8.3 MPa), the modulus of rupture decreases in the case of specimens with the addition of refractory fillers, tested after exposure to 600 and 750°C (5.2 and 5.4 MPa) and approaches the initial value (8.0 MPa) for the sample exposed to 900°C.

Frontal images of metakaolin-based geopolymer specimens, including the reference sample and the samples prepared with the addition of refractory fillers after exposure to temperatures of 600, 750, and 900°C, are shown in Fig. 1.

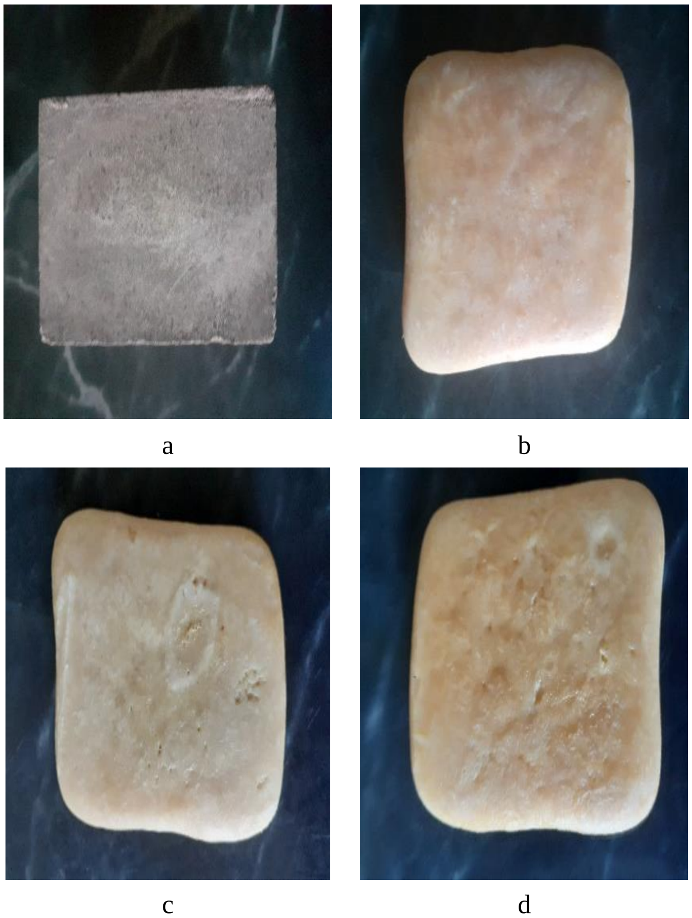

Fig. 1 – Metakaolin-based composite tested at different temperature
a – 25°C; b – 600°C; c – 750°C; d – 900°C.

Microstructural appearance of the same metakaolin-based geopolymer specimens is presented in Fig. 2.

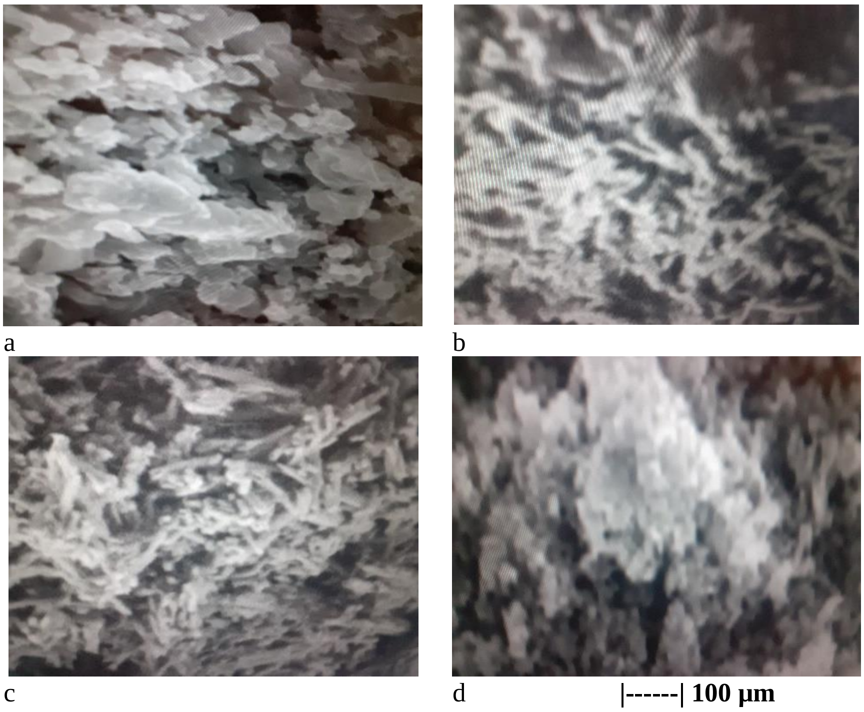

Fig. 2 – Microstructural appearance of composite specimens
a – at 25°C; b – at 600°C; c – at 750°C; d – at 900°C.

As a result of exposing the specimens to temperatures up to 900°C, the viscosity of the sodium silicate gel used as an alkaline activator is reduced. Consequently, the geopolymer matrices underwent reorganization and redistribution at the microstructural level, favouring the composite resistance to thermal stresses. The pictures in Fig. 2 shows the appearance of these changes starting from the microstructure image of reference sample (a).

The experiment presented in this paper highlighted the fact that the geopolymer exposure to relatively high temperatures (600-900°C) facilitates the structural reorganization of matrix as well as the densification in the interface area between components of the geopolymer composite. These structural changes could cause an increase in the stiffness of the metakaolin-based material, reducing the effective effect of using reinforcing fibers with refractory properties. For this reason, the current experiment avoided the introduction of fibers into the composite mass, limiting itself to increasing the amount of refractory fillers (waste of super-aluminous concrete and silica fire brick) up to 28% (of which 16% concrete waste and 12% brick waste).

Tests to thermal stress under the conditions of exposure to relatively high temperatures, showed the favourable influence of the addition of refractory fillers in the weight ratios mentioned above on maintaining the mechanical stability of the geopolymer composite.

Especially, exposure to 600 and 750°C confirmed this technical observation. The compressive strength (having in the reference sample a good value of 35.8 MPa due to the curing process at ambient temperature extended to 28 days) registered a slight increase to 38.0 MPa corresponding to the exposure to 600°C and then, practically, a return to the initial value in the case of exposure to 750°C. The exposure of the geopolymer specimen to 900°C showed a sudden reduction of the compression strength value to 27.8 MPa, indicating diminishing the effect of refractory filler utilization.

An almost similar evolution was also constated in the case of flexural strength. Compared to the value of the reference sample (11.8 MPa), the flexural strength of samples exposed to 600 and 750°C slightly increased and remained at high value (12.5 and 12.1 MPa), falling to 10.1 MPa in the case of the sample exposed to 900°C.

Comparing the experimental results of the current work with other results in this research field (Bernal *et al*., 2012), it was observed that the attempt to keep unaffected the mechanical properties of the geopolymer composite exposed to temperatures of 900-1000°C did not have the desired success. However, the loss of compression resistance (22.3%) and especially, of flexural resistance (14.4%) in the case of exposure to 900°C compared to the reference sample, are acceptable values for using the technique presented in the paper in the situation where the stability at high temperature is required.

4. Conclusions

The objective of the work was to preserve the high mechanical properties of the metakaolin-based geopolymer composite under the conditions of exposure to relatively high temperatures up to 900°C. The practical solving of this aiming was achieved by introducing into the geopolymer composition two filler types with refractory abilities recovered from the demolition of masonry of some heating ovens in metallurgical industry: broken super-aluminous concrete and silica fire brick lumps. The use of highly refractory concrete waste constitutes the main element of the paper originality, not being tested in other similar works. On the other hand, reinforcing fibers from refractory materials were not applied because the structural changes due to exposure to high temperatures can cause an increase in the material stiffness. The results showed remarkable improvements in the compression and flexural strength of geopolymers exposed to 600 and 750°C as well as losses of strength (14.4-22.3%) compared to the reference sample by exposure to 900°C, still acceptable for the use of the composite when the stability at high temperature is required.

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PĂSTRAREA PROPRIETĂȚILOR MECANICE ALE COMPOZITULUI DIN GEOPOLIMER PE BAZĂ DE METACAOLIN EXPUS SOLICITĂRILOR TERMICE PRIN UTILIZAREA DEȘEURILOR DE UMPLUTURI REFRACTARE

(Rezumat)

A fost proiectat și testat în condiții de solicitare termică la temperaturi până la 900°C un compozit din geopolimer pe bază de metakaolin cu adaos de deșeuri de umpluturi refractare (beton superaluminos și cărămidă refractară silicioasă) reciclate din demolarea cuptoarelor de încălzire. A fost aplicată metoda activării alcaline brevetată de Davidovits. Originalitatea lucrării constă în alegerea deșeului de beton superaluminos din demolări ca materie primă principală a procesului, creșterea temperaturii tratamentului termic la 90°C și adoptarea stocării pentru o perioadă de timp mult mai mare (28 de zile). Teste la solicitări termice prin expunerea la 600 și 750°C au arătat influența favorabilă a adaosului umpluturilor refractare asupra conservării stabilității mecanice a compozitului din geopolimer. Pierderea rezistenței la compresiune și încovoiere după expunerea la 900°C prin comparație cu proba de referință este acceptabilă pentru utilizarea acestei tehnici în cazul în care este cerută stabilitate la temperatură înaltă.