

Fire Resistance of Geopolymer Materials—A Change in Physical and Mechanical Properties [†]

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Abstract: Geopolymers are new environmentally friendly cementitious materials that may offer an alternative to Ordinary Portland Cement. Not only do they have excellent mechanical properties, but they also have high temperature resistance. This research focuses on the high temperature exposure effect on geopolymer mortars. Two types of geopolymer mortars were prepared and exposed to different temperatures (20, 200, 400, 800 °C). The main goal of this work is to assess the changes in the mechanical and physical properties of geopolymer mortars after being exposed to a high temperature. Two types of mixtures were tested: one containing 100% fly ash (M0-K) and the other one containing 50% fly ash and ground Granulated blast furnace slag (M50-K). The paper presents an evaluation of compressive and tensile strength, density, porosity, and ultrasonic pulse velocity for both M50-K and M0-K after exposure to high temperatures.

Keywords: geopolymers; fly ash; ground blast furnace slag; high temperature; compressive and tensile strengths; ultrasound pulse velocity; density; porosity



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1. Introduction

Geopolymers are aluminosilicate materials of the Alkali-activated materials family. The geopolymerization reaction is not yet fully understood; many studies have shown that the activation of an aluminosilicate source by a highly basic alkaline solution results in the formation of amorphous materials, showing similar compressive strength to that of a traditional binder made with Ordinary Portland Cement (OPC) [1]. OPC has many disadvantages, such as excessive consumption of energy from non-renewable sources, intolerable volumes of CO₂ emissions, and questionable durability, among others. Given these facts, current environmental requirements aim to reduce the CO₂ impact of the construction industry, which is generally caused by the production of cement, one of the materials responsible for greenhouse gas emissions. Therefore, finding an alternative binder with the same strength but containing no cement is a major challenge that we are facing today. To avoid the effects of OPC on the environment, some studies have shown that geopolymers can indeed be used as binders in construction materials instead of OPC.

Fire is a frequent event that causes great damage to buildings. The degradation of physical and mechanical properties due to high temperature exposure is regarded as the primary cause of structural damage caused by fire [2]. Protecting these structures from fire is of extreme importance; therefore, the refractory materials for construction are particularly important.

This paper is focused on the (ambient and high) temperature resistance test, which is an engineering technique intended to evaluate the stability of a material under severe or unusual operating conditions. It was performed on geopolymer mortars manufactured in

the building materials research laboratory of Cracow, University of Technology. The main goal of this test was to observe the behavior of those mortars in terms of their mechanical and physical properties after their exposure to ambient and high temperature.

Poland has extensive hard coal and brown coal resources. Therefore, the power industry is mostly based on these two original energy carriers. The power plants producing heat and electric energy create combustion byproducts. These products include carbon dioxide, but mainly slags and fly ash [3].

2. Materials and Samples

Two types of mixtures were tested: one containing 100% fly ash (FA), designated as M0-K, and the second one containing 50% fly ash and ground granulated blast furnace (GGBSF) slag, designated as M50-K. In addition to the two raw materials, sand with a grain size of 0/2 mm was used in the two mixtures. The oxide composition of the raw materials is presented in Table 1.

Table 1. Oxide compositions for the Raw materials used for the research.

Oxide	FA	GGBFS
SiO ₂	52.3	39.91
Al ₂ O ₃	28.05	7.61
Fe ₂ O ₃	6.32	1.49
CaO	3.05	43.9
MgO	1.71	4.15
SO ₃	0.28	0.51
K ₂ O	2.51	0.356
Na ₂ O	0.76	0.468

Potassium Silicate (K-Sil) was used as an Alkali source, which is a commercially available liquid, and a specific amount of water was added into the mixture. The compositions of the tested mixtures are presented in Table 2.

Table 2. Composition of the two mixtures in kg per m³.

Mixtures	M0-K	M50-K
K-Sil + Water	330.7	347.5
FA	734.9	386.1
GGBFS	0.0	386.1
Sand 0/2 mm	1102.4	1158.3

A procedure involving the preparation of the binder was applied to the manufacture of geopolymer mortars. First, an alkaline-activating solution was prepared. The amount of liquid silicate was measured, then water was added into this liquid to obtain the assumed water/binder ratio of 0.3. Subsequently, FA was mixed with an Alkaline-activating solution for 10 min. Then, GGBFS was added, and mixing continued for 5 min. Next, the rotary mixer was switched off for 1 min while the binder mixing continued to remove the solids stuck onto the container. Finally, at a low mixing speed, sand was gradually added to the mixture for 3 min. The total mixing time was approximately 20 min. The manner of preparation was selected based on reports in the literature and optimized following the team's previous experience in the propagation of geopolymer blends.

The geopolymer mortars were cast into prismatic 40 × 40 × 160 mm specimens, as shown in Figure 1a. The samples were compacted on a shaking table and covered with plastic lids. Twenty-four hours after casting, the specimens were removed from the molds and stored at room ambient temperature with a relative humidity of about 75%. Plastic was used to protect them from water evaporation and to limit moisture exchange with the environment.



Figure 1. (a) Samples after being heated and cooled down, (b) Electric Furnace NABETHERM.

3. Testing Procedures

3.1. Heating Procedures

After 21 days of curing, the samples were heated in an electrical furnace with a heating rate of $1\text{ }^{\circ}\text{C}/\text{min}$ at a set temperature of 200, 400, 600, 800 and $1000\text{ }^{\circ}\text{C}$, Figure 1b. The heating rate followed RILEM recommendations [4] to minimize stress due to the temperature differences between hotter surfaces and the cooler inner parts of the sample. Concrete and mineral materials such as geopolymers are suitable for these heating conditions for evaluating the impact of temperature. Maintaining the temperature for 1 h until homogenization in the entire cross-section of the sample is required when the set temperature in the range of $200\text{--}1000\text{ }^{\circ}\text{C}$ has been reached. After temperature homogenization, the samples were cooled down and their physical and mechanical properties were measured.

3.2. Physical and Mechanical Properties

The following properties of mortars were evaluated after temperature exposure.

3.2.1. Mechanical Properties

The compressive strength and tensile strength, tested in bending, were measured for the undamaged materials and for the materials after high-temperature exposure.

Firstly, the mortar samples were tested in a three-point bending test using the control testing machine. The loading rate applied was 50 N/s , as this is recommended in PN-EN 196-1 for testing cement mortars. Apart from the bending test, the compressive strength was evaluated according to the remaining prisms ($40 \times 40 \times \text{approx. } 80\text{ mm}$) produced by bending or three-point tests. The load was applied at a loading rate of 2400 N/s for the compressive strength, according to PN-EN 196-1.

The specimens after compressive and bending tests are presented in Figure 2.

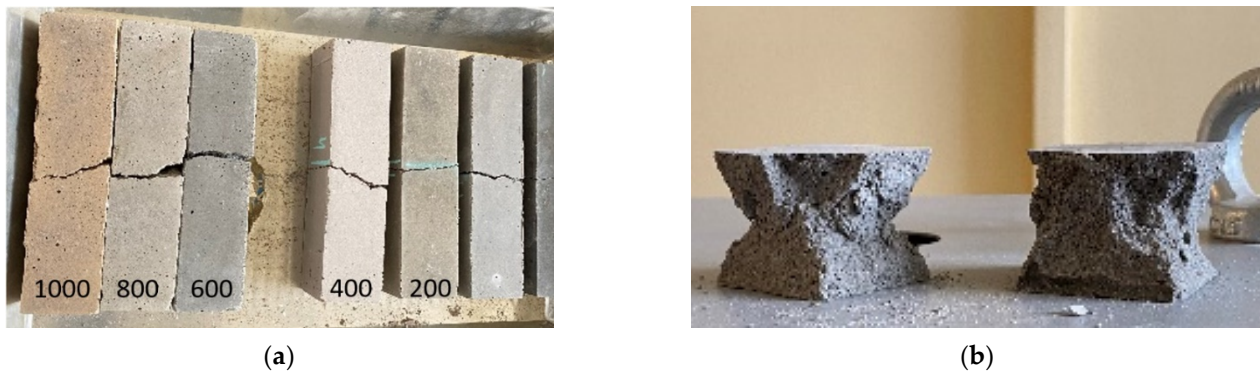


Figure 2. Samples after mechanical tests: (a) after bending tests, (b) after compressive tests.

3.2.2. Physical Properties

➤ *Specific and apparent density*

The material's specific density and its drop after thermal exposure were determined using a helium pycnometer ULTRAPYCNOMETR 1000, Quantachrome, while the apparent density was determined by the geometrical method, using an electronic caliper (measuring accuracy up to 0.01 mm) and a RADWAG analytical balance, with a measurement accuracy of 0.001/0.01 g.

➤ *Porosity*

Based on the specific and apparent densities, porosity can be evaluated by the formula 1:

$$P = 1 - \frac{\rho_0}{\rho} \quad (1)$$

where ρ_0 and ρ are, respectively, apparent and specific density.

➤ *Ultrasonic Pulse Velocity (UPV)*

Ultrasonic pulse velocity (UPV) testing was used to determine the integrity and quality of the mortar, structure concrete, or stone (up to 6 feet thick) by measuring the speed and attenuation of an ultrasonic wave passing through the specimen being tested. The method consists specifically of measuring the time of travel of an ultrasonic pulse passing through the sample being evaluated as per EN 12504-4:2021 [5]. Comparatively a higher velocity is obtained when material quality has sufficient density, uniformity, homogeneity, etc.

Determining the time as well as the distance the wave was sent through the sample in formula 2 allows us to determine the value of UPV used.

$$V_p = \frac{d}{t} \text{ m/s} \quad (2)$$

where t and d are, respectively, the travel time and the distance. The UPV (V_p) is expressed in m/s.

4. Results and Discussion

4.1. Mechanical Properties

In general, a decrease in mechanical properties was observed (except for an increase observed at 200 °C for M0-K due to the geopolymerisation progress). For compressive strength, the reference value (at 20 °C) for M0-K equaled 11.16 MPa, and after exposure to 800 °C was 6.77 MPa, while for M50-K, the reference value was 74.4 MPa and at 800 °C was 11.50 MPa. A decrease of 39.33% and 84.54%, respectively, in compressive strength for the M0-K and M50-K was noted at 800 °C.

Above 400 °C, it is reported that the mechanical properties of mortar significantly decrease compared to undamaged samples. This is ascribed to the movement of physically bonded water and OH groups, phase transformation of geopolymers, the development

of anhydrous products, and the sintering process [6,7]. At elevated temperatures, non-uniform recrystallization occurred, which resulted in the formation of large cracks that consequently reduced the strength [8,9].

Considering the mechanical properties of the two tested mortars, it can be highlighted that replacing 50% of FA with GGBSF resulted in an increase of over 700% in compressive strength and over 350% in tensile strength. Nevertheless, the drop in compressive strength in the M50-K was more significant at 800 °C, reaching the same level as the M0-K. Similarly, the tensile strength of the M50-K dropped suddenly after being exposed to 200 °C and continued to decrease, reaching the same value as M0-K at 800 °C. It seems that the geopolymer bond created by GGBSF is very sensitive to high temperature exposure and is susceptible to damage at temperatures over 200 °C.

The changes in compressive strength and tensile strength for the M0-K and M50-K are presented in Figure 3.

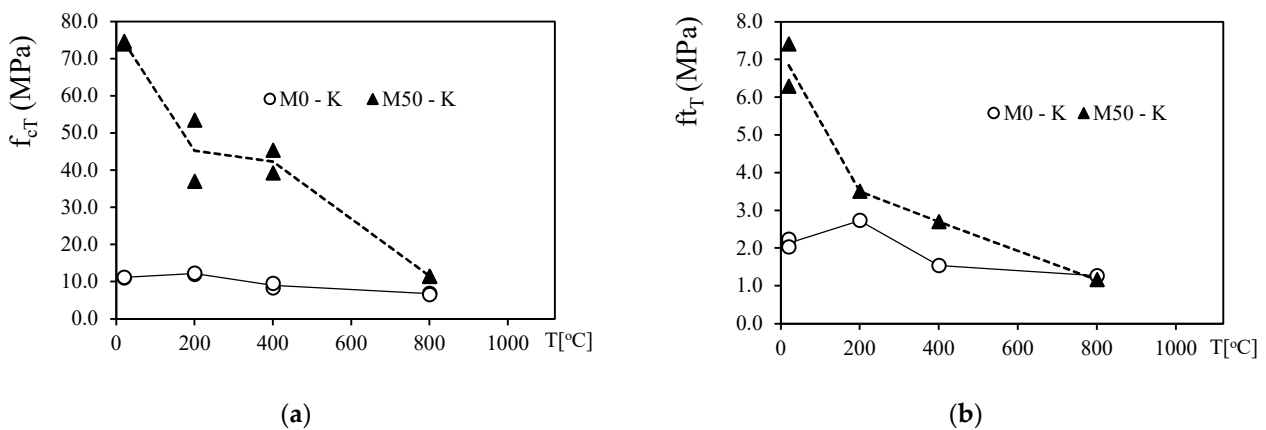


Figure 3. The changes of compressive and tensile strength with temperature (T) for M0-K and M50-K: (a) compressive strength f_{cT} , (b) tensile strength, f_{tT} .

4.2. Physical Properties

The initial (20 °C) apparent densities were 1825 kg/m³ for M0-K and 2070 kg/m³ for M50-K, and their true (specific) densities evaluated with a helium pycnometer were, respectively, 2490 kg/m³ and 2475 kg/m³. Samples containing 50% (M50-K) of FA and Metakaolin had a higher apparent density compared to those containing 100% of FA (M0-K), as shown in Figure 4. The evaluated total porosities reflected this observation. The porosity of the M0-K was 40% and that of M50-K was 27% (Figure 5). The lower apparent density of M0-K was attributed to a more significant number of pores in the material and their larger size. This also affects the differences in the initial mechanical properties.

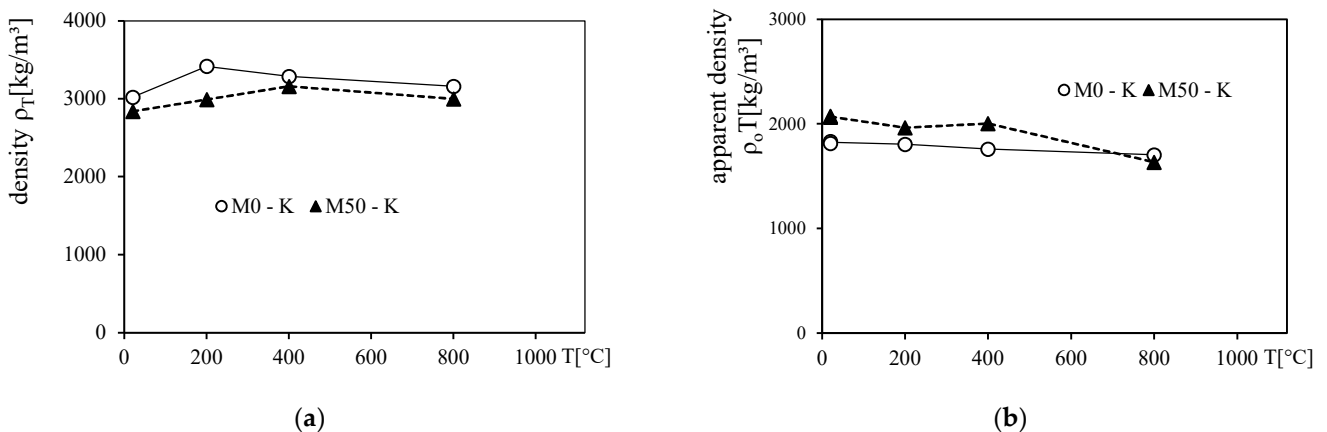


Figure 4. (a) Specific density ρ_T and (b) apparent density ρ_{0T} in kg/m³ of heated samples.

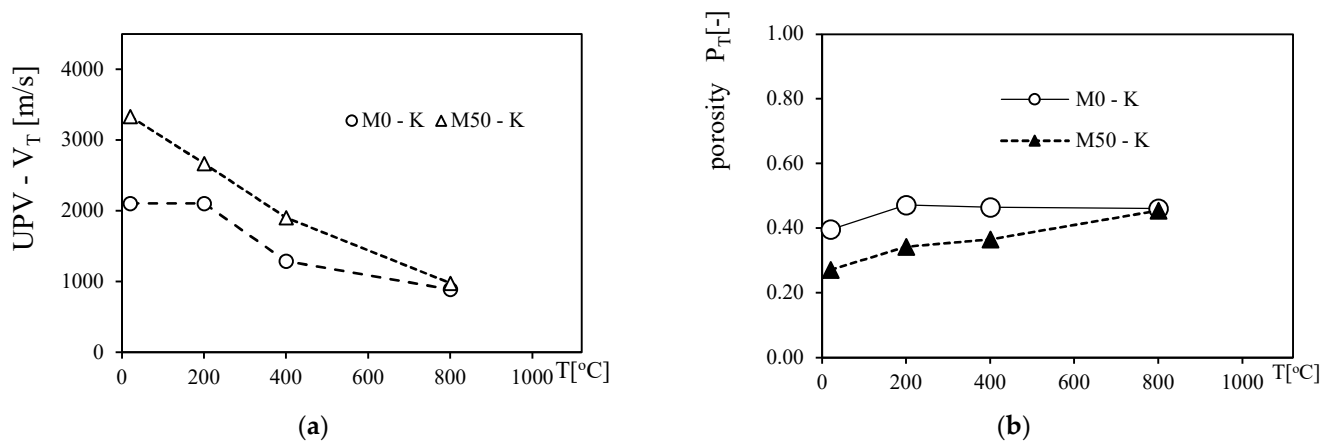


Figure 5. (a) Ultrasound Pulse Velocity (UPV— V_T) and (b) porosity (P) with temperature.

After high temperature exposure, the apparent density of the samples slightly decreased due to the drying process and changes in the matrix. Once exposed to high temperatures, the components of the samples, such as aggregate, became dry. The moisture contained in the material was gradually removed through heating. Furthermore, heating did not significantly affect the change in density. The physically bound water was entirely evaporated, and the hydroxyl groups were removed at high temperatures. Some sources showed that the dihydroxylation process begins at 250 °C and continues up to 600 °C [10], which causes the geopolymer binder to shrink.

For the M0-K, an increase in density after exposure to 200 °C was observed, while for the M50-K, density increased to 400 °C. This is related to the continuous geopolymerization process under elevated temperature; the mortar behaves similarly to an autoclaving mortar, with binder connections developing and strengthening. This was confirmed by the increase in tensile strength and applies more to a matrix without GGBSF. Another insignificant drop in density over 400 °C was related to the cracking of the matrix.

The density (ρ) and the apparent density (ρ_0) values enabled the total porosity (P) to be determined. The variation in total porosity P with increasing temperature is presented in Figure 5. The M0-K presents an increase in porosity between 20 °C and 200 °C. In this temperature range, the porosity remained stable (47%) from 200 °C up to 800 °C. On the other hand, for the M50-K, a slight increase in porosity from 20 °C (27%) to 800 °C (45%) was observed. The stable porosity level in the entire range of tested temperatures ensured constant thermal insulation parameters with increasing temperature, which is extremely important in cases of fire protection or fire-resistant material. Therefore, the M0-K, independently from its lower initial mechanical properties, can be developed in the direction of fire protection applications.

The UPV values decreased in the entire temperature range (20–800 °C), Figure 5a. However, in M0-K, a stable velocity was measured between 20 °C and 200 °C. The stable UPV up to 200 °C confirms the development of the M0-K matrix at elevated temperatures, as the UPC reflects the amount of air pores in the material. Moreover, the final UPV after exposure to 800 °C reached similar values for both the M0-K and M50-K. The same quality was confirmed for both the mechanical and physical properties of the tested materials when exposed to 800 °C.

5. Conclusions

The effect of elevated temperature ranging from 200 °C to 800 °C on samples with 100% fly ash and 50% fly ash, and ground granulated blast furnace slag blended geopolymer mortar was investigated in the presented research by evaluating compressive strength, tensile strength, apparent density, specific density, porosity, and the ultrasound pulse velocity. Based on the results, the following conclusions are drawn:

- The initial mechanical properties (compressive and tensile strengths) of a geopolymer mortar containing 50% fly ash and ground-granulated blast furnace Slag (M50-K) are greater than those of a geopolymer mortar containing 100% fly ash (M0-K). This is probably due to the presence of two precursors (fly ash and metakaolin) in the mixture. Previous research has shown that the geopolymer materials based on FA can be improved with the addition of other wastes or precursors.
- After exposure to a high temperature, the M50-K specimens continue to present higher values of compressive and tensile strengths through the temperature range of 200–600 °C, while the rate of decrease with temperature is more significant than for the M0-K.
- The M0-K, despite having lower mechanical properties than the M50-K, presents a developing bond at elevated temperatures (up to 200 °C), remaining more stable until 800 °C than the M50-K. Therefore, the M0-K can be considered a valuable solution to develop in the direction of fire protection applications.
- The physical properties have also been evaluated. The high temperature exposure contributes to the damage of the material's cross section, resulting in a decrease in density, apparent density, and Ultrasound Pulse Velocity. The M50-K is slightly higher than the M0-K in terms of apparent density, but we had the opposite principle in terms of true densities after exposure to high temperatures. The M0-K porosity remains quasi-stable across the entire temperature range, whereas the M50-K porosity increases until 800 °C.
- It should be noted that the tested samples exhibited a high temperature a relatively short time after production. In the case of the geopolymer mortars with a fly ash precursor, curing in ambient conditions, the matrix properties developed much slower. Previous team research results show that after 3 months, the FA-based geopolymer matrix is much more resistant to high temperatures.

According to the obtained results, both materials can be used as the basis for developing fire insulation materials or thermal barriers. They remain stable in terms of integrity under high-temperature conditions, presenting porosity at an affordable level. Despite the drop in mechanical properties, compressive strength, even after exposure to 800 °C, remained at a satisfactory level in terms of the structural application.

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