

Original Research

**GREEN METAKAOLIN GEOPOLYMERS:  
SYNTHESIS AND CHARACTERIZATION DURING AGEING**

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**Abstract**

*Metakaolin-based geopolymers represent a significant advancement in sustainable development and the green economy, particularly within the construction industry, by providing a high-performance alternative to traditional Ordinary Portland Cement (OPC). By using metakaolin, a highly reactive aluminosilicate material derived from thermal treatment of kaolin clay, these binders significantly reduce carbon emissions and enable the immobilization of industrial wastes. This paper outlines the production of geopolymer using a metakaolin as an environmentally friendly, energy saving, clean technology to conserve natural environment and resources. The paper examines the influence of NaOH concentration on the physico-chemical properties of geopolymers during the aging process. Two samples with different concentrations were synthesized. Analyzes were performed using XRF, XRD, FTIR and SEM methods.*

**Keywords:** metakaoloin, geopolymer, green materials, ageing time, characterisation.

**INTRODUCTION**

In recent decades, there has been increased attention to environmental issues and the need to reduce CO<sub>2</sub> emissions in order to combat climate change. In addition to the high greenhouse gas emissions associated with the ordinary Portland cement (OPC) production process, the huge environmental impact of the cement industry is also associated with the massive consumption of raw materials (lime, aggregates, water) and the high demand for energy [1,2]. There is growing interest in developing new binders with a reduced carbon footprint, high performance and durability, which could be used as green alternatives to OPC [3,4]. Geopolymers are innovative class of ceramic materials that possess advanced technological features, such as low energy consumption of production for construction

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purposes. Geopolymers are usually obtained through inexpensive and ecofriendly synthetic procedures with low waste gas emission [5,6], which is one of the reasons why they are called the green materials [7]. Geopolymers have attracted global attention as an environmentally friendly alternative to OPC for the production of mortar and concrete [8] synthesized by the reaction between an aluminosilicate precursor, which can be obtained from natural minerals and/or from industrial waste (metakaolin, ash, mining-furnace slag, etc.) and alkaline activators. Synthesis of geopolymers can be made by mixing a reactive aluminosilicate material as precursor with high alkaline solutions. NaOH or KOH are the most commonly used components of activator solutions. The concentration of hydroxide in the solution of activator plays an important role in the process of geopolymerization [9]. Most of the research and knowledge [10] concerning a mechanism of geopolymerization are based on the use of metakaolin as a precursor. Metakaolin is a good source of silicon and aluminum which are highly reactive and react with alkaline activator.

The presented study aims at analyzing the effect of different concentrations of sodium hydroxide (NaOH) on the structure of obtained inorganic polymer during the geopolymerization reaction. The physical and chemical properties from the starting material to the final geopolymers have been monitored to understand the geopolymerization mechanism.

## MATERIALS AND METHODS

In this work, natural white clay (kaolin) was used as the starting material. Kaolin is a soft, earthy, natural mineral powder rich in the mineral kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). Kaolin was obtained from Rudovci (Lazarevac Serbia). Further calcination of kaolin at 750 °C yielded metakaolin, which we used for the synthesis of geopolymer (GP).

For the synthesis of GP, in addition to MK, we also need an alkaline activator. The alkaline activator solution was prepared from a solution of  $\text{Na}_2\text{SiO}_3$  and different molar concentrations of NaOH (2M and 8M). The geopolymer (GP) samples were formed from metakaolin and the different alkaline solutions, which were mixed for 10 min and then left at room temperature for one day. After that, the sample mixture was kept in a drying oven for 2 days at 60 °C. The curing and in the same time aging, of geopolymer samples has been followed for 7, 14, 21 and 28 days in covered molds at opened chamber and room relative humidity of 95. Based on different concentrations of NaOH, 2 samples were synthesized, namely GP2M and GP8M. The molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  of obtained geopolymer samples is shown in Table 1.

**Table 1** The molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  of GP2M and GP8M

| Samples                                     | GP2M | GP8M |
|---------------------------------------------|------|------|
| $\text{SiO}_2/\text{Na}_2\text{O}$          | 3.50 | 2.45 |
| $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ | 1.98 | 1.46 |

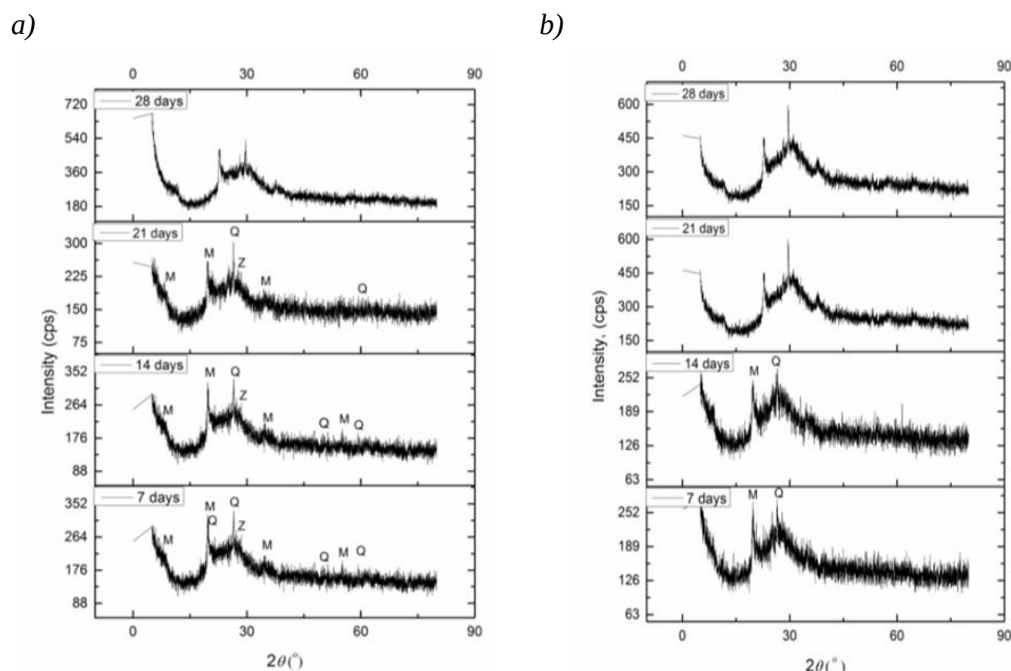
After the synthesis was completed, the physicochemical characteristics of the samples were examined and measured every 7 days during the aging process. The samples were characterized by X-ray diffractometry (XRD). FTIR (Fourier Transform Infrared

Spectroscopy) was used to identify and analyze the chemical composition of the materials. The samples were finely and homogeneously dispersed in anhydrous potassium bromide (KBr) pellets (1.5/150 mg KBr). Spectral data of the samples were collected in the region from 4000–400  $\text{cm}^{-1}$ . The surface morphology of the samples was studied using field emission scanning electron microscopy (FESEM, Tescan MIRA 3 XMU) at 20 kV. The samples were sputtered with Au/Pd alloy before analysis.

## RESULTS AND DISCUSSION

As previously mentioned, the structural changes that occur during geopolymerization of alkali-activated materials were monitored depending on the NaOH concentration (2M and 8M) and time (7, 14, 21 and 28 days) using FTIR and XRD methods.

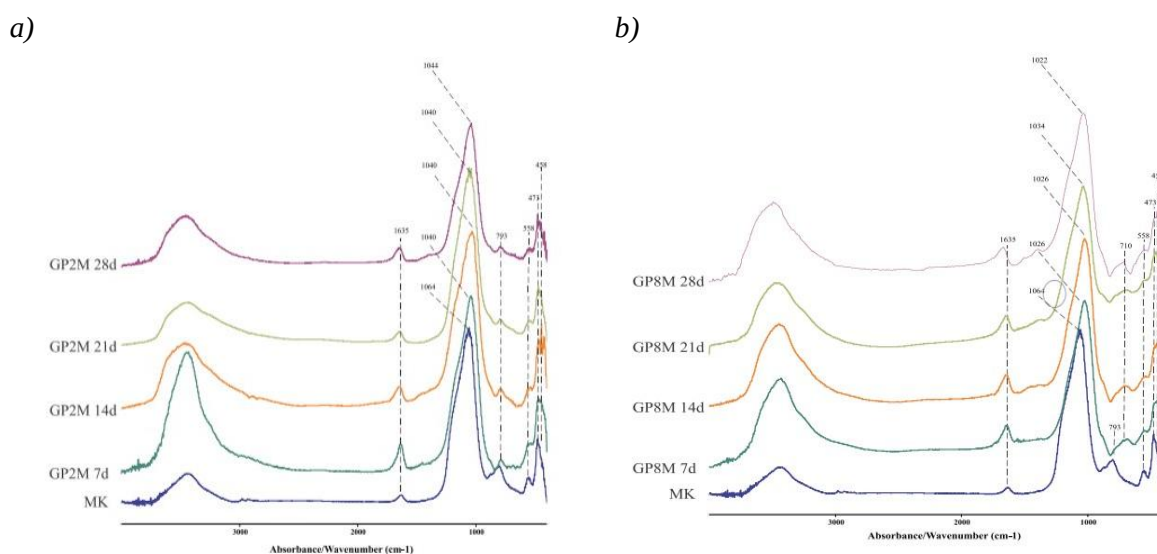
Figure 1 shows the results of the XRD patterns of the synthesized geopolymer samples, GP2M (a) and GP8M (b). One way to monitor the changes in the crystal structure during the geopolymerization reaction is to monitor the changes in the XRD patterns of the samples cured at different times at room temperature. It is also important to compare the XRD patterns of the samples cured at room temperature and with different concentrations of NaOH. XRD analysis of almost all geopolymer samples revealed their amorphous structure with the position of the amorphous halo in the range of  $18^\circ$ – $32^\circ$   $2\theta$ , indicating a short-range ordering of the reference sample with a crystalline addition of  $\text{SiO}_2$  ( $\alpha$ -quartz). The presence of muscovite was also observed. The lines characteristic of quartz (Q), muscovite (M), and zeolite (Z) are shown in Figure 1.



**Figure 1** X-ray diffractograms of a) GP2M sample; and b) GP8M sample every 7 days, up to 28<sup>th</sup> day

When comparing the XRD patterns of GP2M and GP8M samples aged at room temperature for 7, 14, 21 and 28 days, it is observed that the intensity of the main peaks of quartz and muscovite decreases after 28 days. It is characteristic that the amorphous halo is somewhat narrow and shifted to a higher angle for GP8M aged 21 and 28 days. Zhang *et al.* [11] found that the proportion of the crystalline phase gradually increases with longer curing times.

FTIR spectra of geopolymers after aging time at room temperature are shown in Figure 2. Spectras show a broad band with a maximum at  $\sim 3450\text{ cm}^{-1}$  and a small band at  $1635\text{ cm}^{-1}$ , which are attributed to stretching and deformation vibrations of physically adsorbed water molecules (O-H) on the surface, respectively. The FTIR absorption spectra of these samples were compared with known absorption lines in the literature.



**Figure 2** FTIR of GP2M (a); and GP8M (b) samples after 7, 14, 21 and 28 days

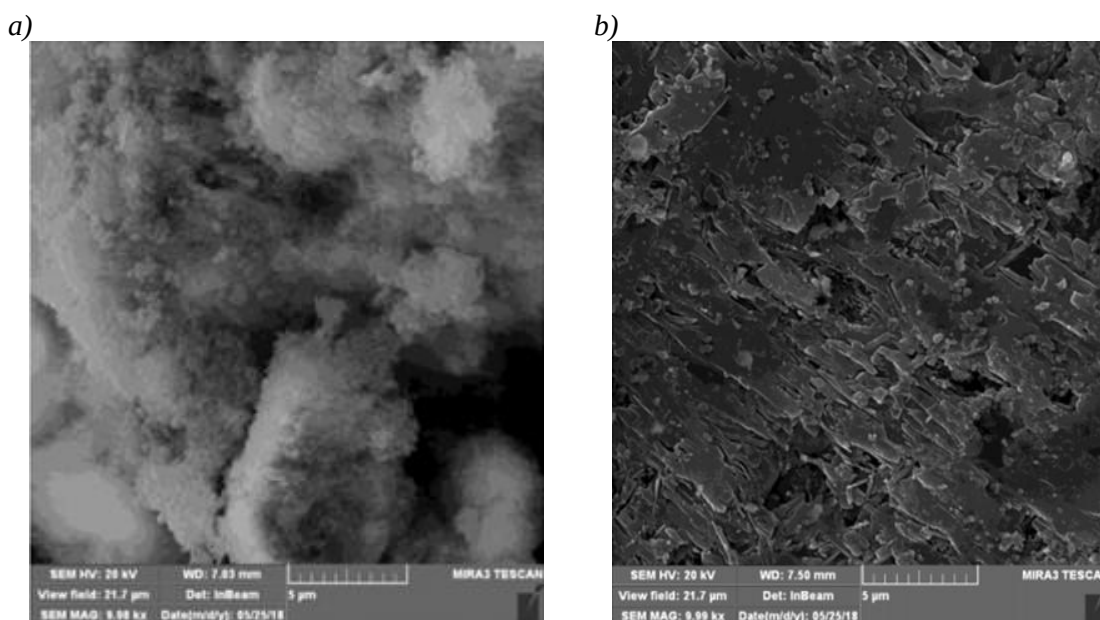
The FTIR spectra of the samples show a strong peak at  $\sim 1000\text{ cm}^{-1}$ , which is associated with the asymmetric Si-O-Si stretching vibrations and is an imprint of geopolymerization [12]. In the spectral range of  $1200\text{--}1000\text{ cm}^{-1}$ , there are two broad bands, (Si-O-Si stretching vibration) and another (Si-O and Si(Al)-O stretching vibration) [13]. The influence of NaOH concentration on the changes in chemical structure that occur during geopolymerization can be seen by comparing the given spectra. The bands located at  $1100$  and  $1000\text{ cm}^{-1}$ , which belong to the stretching of Si-O bonds [14], shift to the right, and the shape of these bands changes due to the structural rearrangements of the geopolymer during 7-28 days of aging, and due to the influence of different NaOH concentrations in the activator solutions. The broadening of these bands is more pronounced when using 8M NaOH concentration.

According to the literature [15], wide strip at  $710\text{ cm}^{-1}$  could be attributed to asymmetric stretching Si-O-Al. On the other hand, the band of the Al-O bond at  $793\text{ cm}^{-1}$  is also shifted to the right. The intensity of the Si-O-Al (Si) bond band at  $710\text{ cm}^{-1}$  increases with concentration of NaOH. These shifts indicate that there are fine changes of the aluminosilicates structure as the geopolymer synthesis progresses. The intensity of the peaks at  $558\text{ cm}^{-1}$  for the GP8M sample increases with the time. This type of addition has not been observed to sample

GP2M. If we look at the end of the process, we can see clear influence of molarity. Peak that occurs on  $1044\text{ cm}^{-1}$  for sample GP2M is moving on  $1022\text{ cm}^{-1}$  for sample GP8M. It also shows a wide strip on  $710\text{ cm}^{-1}$  for GP8M sample, while on GP2M sample is not noticed. With increasing molarity of NaOH, intensity of strip on  $793\text{ cm}^{-1}$  is decreasing on the value of the strip on  $710\text{ cm}^{-1}$ .

Both methods XRD and FTIR, revealed that the concentration of NaOH has higher effect on structural changes in geopolymer than aging time.

Various types of morphologies were formed during the geopolymerization process. The surfaces of geopolymers GP2M and GP8M aged for 28 days are shown in Figure 3. Figure 3a shows micrographs of GP2M. We can see the foam structure, probably the incomplete dissolution process of metakaolin and incomplete geopolymerization. The layered gel porous structure of GP8M is shown in Figure 3b. There are also a number of individual particles. The samples show a porous microstructure formed by unreacted micron-sized particles and the geopolymer matrix formed during polycondensation.



**Figure 3** SEM of GP2M (a); and GP8M (b)

Based on the micrographs, it can be observed that increasing the NaOH concentration results in significant differences in the microstructure of the GP2M and GP8M samples. The surface morphology of the GP2M sample indicates an incomplete geopolymerization process, whereas the surface of the GP8M sample consists of dense plate-like formations generated through the geopolymerization of metakaolin, which most likely represent the strongest constituents of the newly formed geopolymeric material.

## CONCLUSION

Metakaolin-based geopolymers represent a significant advancement in sustainable development and the green economy. Results presented in this paper reveal a diverse

influence that the concentration of NaOH and aging time have on a process of polymerization of a metakaolin. More compact structure of the geopolymer, which correlates to the degree of polymerization is obtained with increasing concentration of NaOH, but also with the time of aging. On the other hand, no significant changes in its crystallinity have been observed with the increase of NaOH concentration in the activation solution. The most important outcome of this study is that is possible to control the properties of a geopolymer, with respect to its application, by avoiding the investment of the energy and solely by the process that is completely eco-friendly.

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