
INFLUENCE OF THE HEAT TREATMENT PROCEDURE ON THE GEOPOLYMER MATERIALS PROPERTIES – A REVIEW

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ABSTRACT

The term “geopolymer” was originally introduced by the French chemist Davidovits, representing a wide range of anorganic materials. According to him, among the nine different classes of geopolymers, geopolymer concrete is of particular interest, consisting of materials containing aluminosilicates that could be used to completely replace the amount of Portland cement in ordinary concrete. The aim of this study is to present relevant data in the field of alkali-activated geopolymer materials regarding the production of this type of materials using both ambient and heat curing and studying the differences between the two procedures.

Keywords: geopolymers; fly ash; curing treatment.

REZUMAT

Termenul geopolimer a fost introdus inițial de chimistul francez Davidovits, reprezentând o gamă largă de materiale organice. Potrivit acestuia, printre cele nouă clase diferite de geopolimeri, betonul geopolimer reprezintă un interes special, realizat din materiale care conțin aluminosilicați care ar putea fi folosite pentru a înlocui complet cantitatea de ciment Portland din betonul obișnuit. Scopul acestui studiu este de a prezenta date relevante în domeniul materialelor geopolimerice activate alcalin în ceea ce privește producția de acest tip de materiale, folosind ambele metode de tratament termic și studiind diferențele dintre acestea.

Cuvinte cheie: geopolimeri; cenușă zburătoare; tratament termic.

1. INTRODUCTION

In the early 1940s, a combination of several zeolite materials and alkaline solutions were used to produce alkali-activated cements with heat treatment, such as a mixture of blast furnace slag with sodium hydroxide, but also with fly ash as raw material. The multitude of raw materials with which alkali-activated materials can be obtained is quite high. These can be made from minerals of natural origin, such as kaolin or metakaolin (burnt kaolin), diatomite or from industrial by-products such as granulated blast furnace slag from the steel industry and fly ash obtained by burning coal, which makes heat treatment an essential parameter in the development of such alternative materials.

The heat treatment procedures used to produce alkali-activated geopolymer materials

vary both in temperatures and durations and can be summarized as follows (Roy, 1999):

- Curing in ambient temperature - geopolymers can be designed to harden at an ambient temperature by an appropriate choice of binder and reagent. Any procedures that increase the temperature of the fresh or hardened mixture will obviously compensate for the effects of low ambient temperatures;
- Accelerated hardening - geopolymer concrete quickly gains strength if Steam hardening is done or encapsulated and dried at high temperatures;
- Wet hardening - hardening methods that allow excessive amounts of free water in contact with the surface of the geopolymer concrete are not

recommended, since water produces the dilution of the alkaline solution.

It can be stated that the two methods of making Geopolymer Concrete with heat treatment, at certain temperatures and duration of exposure and without heat treatment, the best procedure is represented by ambient temperature treatment. This procedure is optimal for the development of such materials by generating increased mechanical properties of the hardened material.

2. RESULTS AND DISCUSSIONS

Geopolymer cement has been reported as having very good mechanical properties with heat treatments at different temperatures and certain heat treatment durations. Some researchers, taking advantage of the high temperatures in their countries, studied the behavior of geopolymer concrete without heat treatment, only at ambient temperature.

Although the treatment of geopolymers is normally carried out in electric furnaces, many alternative methods of heat treating the geopolymer have been observed to achieve good results on the mechanical properties of the material. Some researchers have shown that using microwave ovens reduce the duration of heat treatment (Chatveera and Makul, 2012), as well as a preheating of the alkaline solution before mixing would increase the strength of the geopolymer concrete (Dutta et al., 2012). However, heat treatment in furnaces is usually the most used method for the production of alkali-activated geopolymer materials.

Research conducted on geopolymer concrete showed that the most used thermal hardening is adopted for temperatures between 30 and 90°C in the first 24 hours after casting, and leads to a rapid development of compressive strength of the material. The compressive strength at 6 hours is almost directly proportional to the curing temperature (from 50°C to 90°C) and there is a large, sharp exothermic peak after about 0.5-1 hours after curing.

According to the literature, it has been observed that alkali-activated low calcium fly

ash-based geopolymer concrete does not exhibit an exothermic reaction within the first 25 hours after casting at room temperature, while metakaolin-based geopolymer material exhibits a direct relationship between exothermic reaction and increased compressive strength. Opinions are divided on the temperature and duration of heat treatment on the properties of reinforced geopolymer concrete.

It has been reported (Sindhunata et al., 2006; Lăzărescu et al., 2018a) that hardening at temperatures between 30°C and 75°C helps to expand the total volume of pores and surface in the geopolymer matrix, that accelerates the dissolution of the precursor. They also noted that for lower temperatures (below 30°C), the binder is formed with the precipitation of dissolved species instead of poly-condensation of silicon and aluminum.

Also treatment in coated molds is more beneficial than dry treatment and steam treatment for the development of the mechanical performances of the geopolymer material. Coated molds stop the evaporation of water from the geopolymer binder, providing a water environment for the exchange of silicon and aluminum ions in synthesis (Kovalchuk et al., 2007, Lăzărescu et al., 2017). In the above study, the specimen preserved in sealed bags reached a maximum compressive strength of 102.1 MPa, while the dry specimen and the steam-cured specimen recorded 31.8 MPa and 71 MPa, respectively.

Previous research has shown several types of heat treatment for the production of alkali-activated geopolymer materials. This should be maintained between 40°C and 60°C to avoid cracks (Perera et al., 2007). In addition, it was found that the combination between a heat treatment temperature of 60°C and 48 hour heat treatment duration provides optimal strength for the binder (Swanepoel et al., 2002). Memon et al. (2011) showed that samples preserved at a temperature of 70°C have the maximum strength and stated that longer heat treatment (more than 48 hours) is not beneficial for the alkali-activated geopolymer material.

Thakur and Ghosh (2009) claimed that the maximum compressive strength was obtained for their geopolymer samples which were heat treated at 85°C for 48 hours. Hou et al. (2009) reported as effective a curing at 65°C temperatures. Bakharev (2005) found that for alkali-activated fly ash-based geopolymer materials, it is significantly beneficial to store the samples at 23°C, 24 hours before heat treatment and the heat treatment temperatures should be between 75°C and 95°C.

A rest period of 24 hours increased the compressive strength, being equivalent to that of a sample continuously exposed to a high temperature. Even if heat treatment is essential for establishing a pure alumino-silicate geopolymer (Class F fly ash or metakaolin based geopolymers), calcium-rich alumino-silicate source materials can be activated at room temperature (ambient treatment). Gao et al. (2015) showed that the compressive strength the alkali-activated geopolymer material heat cured at room temperature increased by adding slag in the mixture.

The properties of the alkali-activated geopolymer materials are influenced not only by the duration of the heat treatment and the temperature of the heat treatment, but also by the quantities of alkali activators, the ratio between them, the molarity of the hydroxides used, as well as the content of Si and Al that the mineral additives used in the mixtures have.

2.1. Effects of heat treatment on alkali-activated geopolymer properties

Research conducted on alkali-activated geopolymer paste and mortars with a heat treatment between 30°C and 90°C showed an increase in the chemical reaction, leading to an increase in the compressive strength of the samples from an early age. (Van Jaarsveld et al., 2002). Other researchers (Rovnaník, 2010) claim that too high heat treatment temperature (e.g. above 90°C) would lead to a geopolymer with a porous structure due to the rapid loss of water, causing a negative effect on the final mechanical properties of the geopolymer material.

The optimum temperature of the heat treatment was found to be around 60-75°C, which could properly improve the process of geopolymerization and adequate microstructural development (Chindaprasirt et al., 2010).

Alkali-activated geopolymer concrete has also been studied under different conservation conditions. Demie et al. (2011) and Reddy et al. (2012) have found that good compressive strength of the material was achieved when the heat treatment temperature was in the range of 60°C to 70°C, while additional heat treatment at temperatures of 80°C to 90°C led to a decrease in the compressive strength of the geopolymer material.

However, the Australian Standard (CA 3600:2009) and the American Concrete Institute Building Code (ACI 318-11: 2011) adopt the minimum standard structural design for a reinforced alkali-activated geopolymer concrete column with heat treatment at 60°C for 24 hours (Sumajouw et al., 2007).

It can be summarized that the conservation temperature (heat treatment) is one of the important factors influencing the mechanical properties of the alkali-activated geopolymer materials. Although higher temperatures (above room temperature) give a higher resistance of the material, too high curing temperatures could cause cracks, which lead to a decrease in the mechanical performances. Rapid loss of moisture could also lead to the formation of micro-cavities. The temperature range from 40°C to 80°C clearly improves mechanical properties, but the optimal one varies from 40°C to 60°C (Hounsli et al., 2013; Lăzărescu et al., 2018a).

Curing temperature effect – Compressive strength at early ages is almost directly proportional to the curing temperature up to 90°C. For example, an ordinary mixture with a steam hardening for 6 hours at 55°C had a compressive strength of 12 MPa, and a hardening at 90°C for 6 hours had a strength of 90 MPa;

- Curing time effect – At any curing temperature, the compressive strength increases with the curing time so that in the end all will have a similar resistance, independent of the curing temperature. Geopolymer concrete continues to create strength with age in the first weeks after accelerated hardening, but remains constant after that;
- Heat hardening - Geopolymer concrete can be thermally hardened dry, but the samples must be encapsulated or at least coated to minimize surface drying.

2.2. Compression strength of geopolymers with heat treatment at certain temperatures

Compressive strength of the alkali-activated geopolymer materials is influenced by the time and temperature of the heat treatment as well as the raw materials used for their production. Omar et al. (2015) presented the results obtained on compressive strength of some geopolymer materials at different time intervals, after having previously undergone a heat treatment at a temperature of 60°C for 24 hours (Figure 1). The geopolymers produced contain fly ash, crushed stone (D) and steel slag (s), sodium silicate solution and sodium hydroxide solution.

As can be seen from Figure 1, the compressive strength increased with the molarity from 10-16 as well as the amount of fly ash in the mixture increased from 350 kg / mc to 450 kg / mc, although previously all geopolymers had a heat treatment for 24 hours at a temperature of 60°C.

Following the research, different compressive strength values were obtained, having the same heat treatment duration with a duration of 24 hours and a temperature of 60°C, but at different test ages (Figure 2) for alkali-activated fly ash-based geopolymer concrete with NaOH-2M solution and Na₂SiO₃ solution (Hardjito and Rangan, 2005).

Also, the results obtained for the compressive strength of the alkali-activated geopolymers obtained from fly ash, NaOH -

2M solution, Na₂SiO₃ solution and fine sand, tested at 7 days, after having undergone a heat treatment of 4,8,12,24,48,72,96 hours, at a temperature of 60°C are presented in Figure 3.

It can be seen from Figure 3, that due to the period of heat treatment, compressive strength of the samples increased when adopting the same mixture. Thus, the compressive strength increased 3 times, from 25 MPa with a heat treatment of 60°C for 4 hours to 82 MPa at the same temperature but for 96 hours. Therefore, it can be concluded that compressive strength increases with the duration of heat treatment.

Following the studies conducted, Mustafa al Bakri et al. (2011) obtained the best compressive strength of 67 MPa, using fly ash (Malaysian power plant) and NaOH 12 M and a heat treatment temperature of 60°C for 24 hours. For heat treatment temperatures above 60°C, the compressive strength has decreased. (70°C-35.41 MPa, 80°C-27.87) (Figure 4).

For Görhan and Kürklü the optimum heat treatment temperature for an geopolymer binder based on fly ash, alkaline activated (Turkey thermocentral ash) was 85°C.

Patil et al. (2014) obtained compressive strength of 26.16 MPa at 7 days and 36.2 MPa at 28 days for a geopolymer based on fly ash, with a heat treatment at a temperature of 60°C.

Each researcher applied different temperatures and heat treatment durations, different types of alkaline solutions, as well as certain raw materials with different characteristics. Figure 5 shows the compressive strength values obtained for different alkali-activated geopolymer materials, reported by various researchers, depending on the heat treatment procedure and the age of testing the samples.

2.3. Compressive strength of geopolymers without heat treatment

Some researchers studied the compressive strength of some geopolymer materials, without heat treatment, but with different raw materials, at different test ages. Hu et al. (2008) obtained a compressive strength of 45 MPa, using metakaolin as raw material, at the age of 28 days and Anuar et al. (2011)

obtained a compressive strength of 18 MPa, using as raw material waste paper – sludge, also at the test age of 28 days (Figure 6).

It can be seen that the compressive strength, performed at an ambient temperature, using the same NaOH and Na₂SiO₃ alkaline solutions, at the same test age of 28 days, is different, being influenced by the raw materials used in the mix design of the alkali-activated geopolymer materials.

Nematollahi (2017) studied the compressive strength with or without heat

treatment and the density of three types of ash-based geopolymers. Compressive strength with curing in the environment at 7 days was equivalent to 70-90 % of the strength at 28 days-from 33.9 MPa at 7 days to 36.9 MPa at 28 days (Table 1).

Pati et al. (2014) achieved compressive strength of 3.94 MPa at 7 days and 17.5 MPa at 28 days for a geopolymer based on fly ash, without heat treatment.

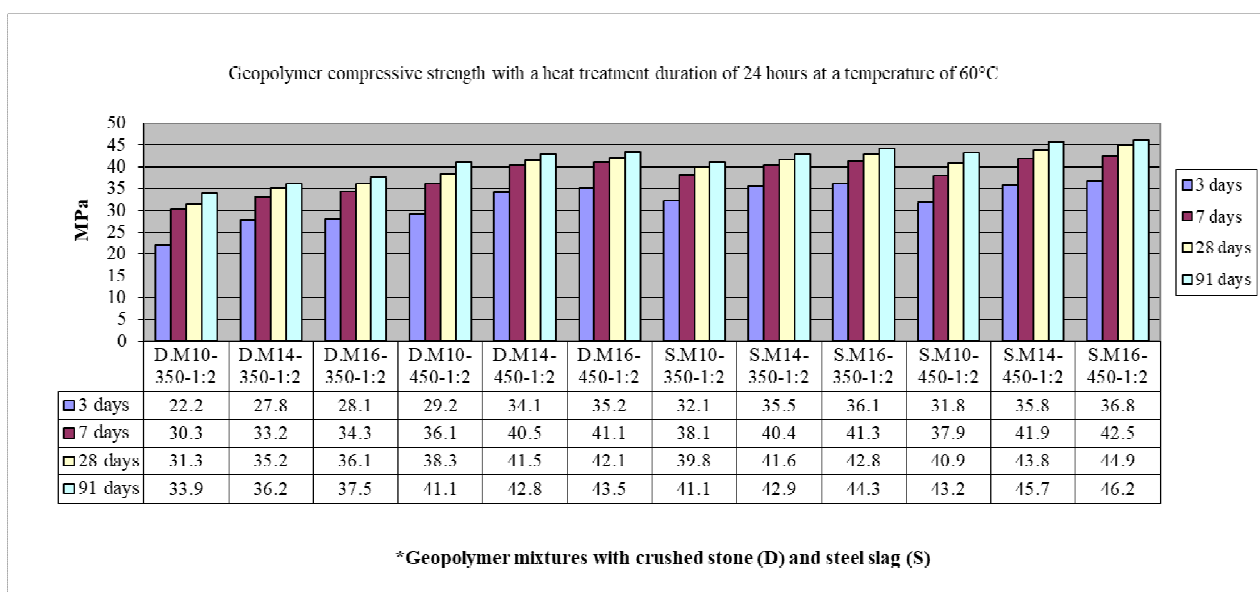


Fig.1. Geopolymer compressive strength with a heat treatment duration of 24 hours and a temperature of 60°C (Omar et al., 2015)

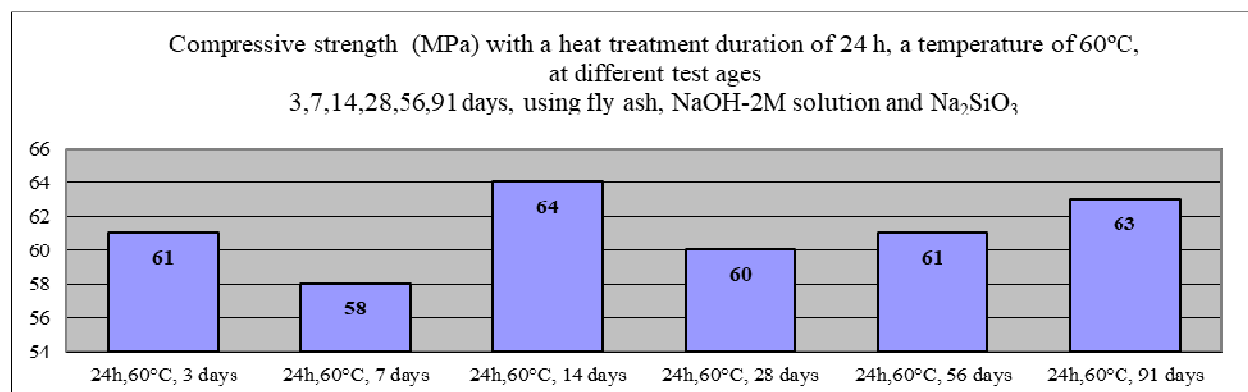


Fig.2. Geopolymer compressive strength with a heat treatment of 24 hours at a temperature of 60°C at different test ages

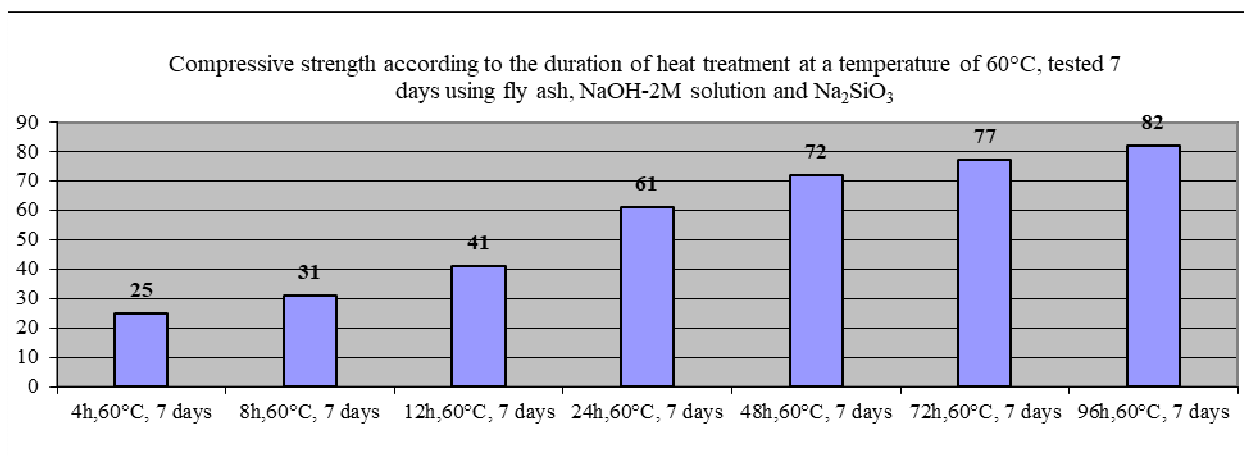


Fig.3. Geopolymer compressive strength with a heat treatment at a temperature of 60°C, with different heat treatment durations, at the age of 7 days

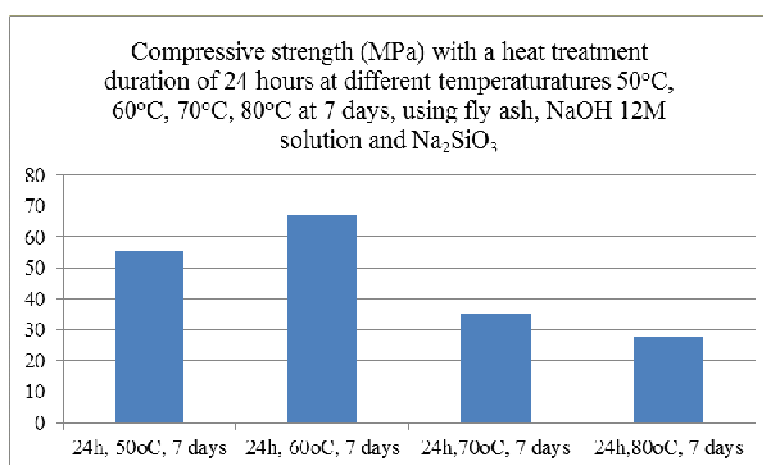


Fig.4. Geopolymer compressive strength with a heat treatment duration of 24 hours, at different temperatures 50°C, 60°C, 70°C, 80°C at the age of 7 days

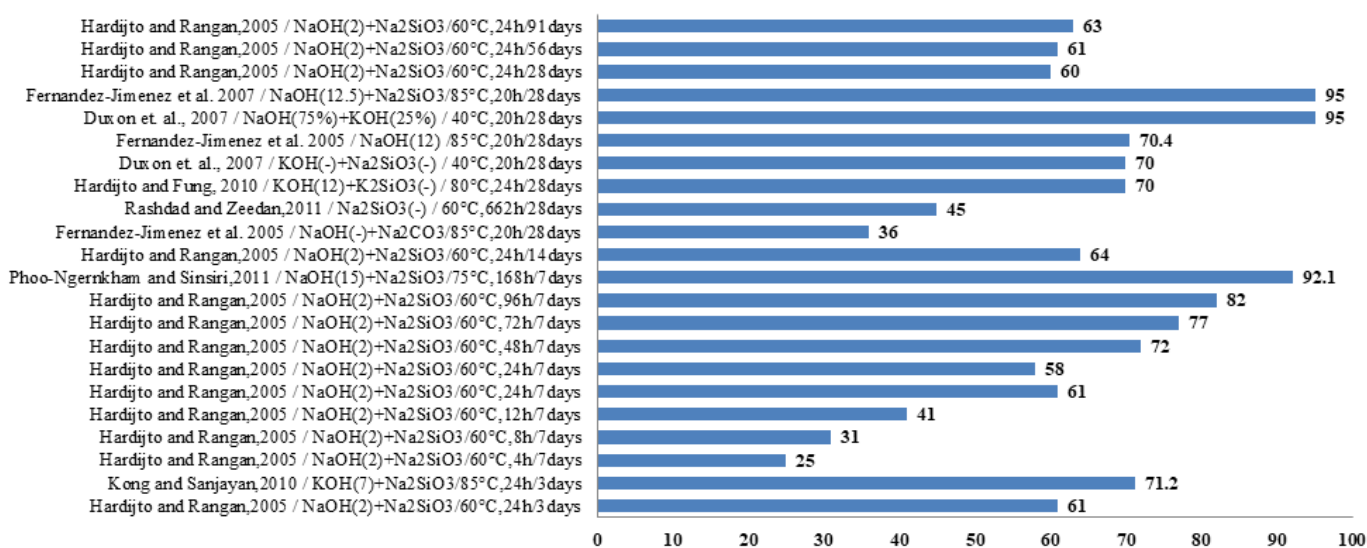


Fig.5. The compressive strength of geopolymers, reported by various researchers, depending on the heat treatment and the test age

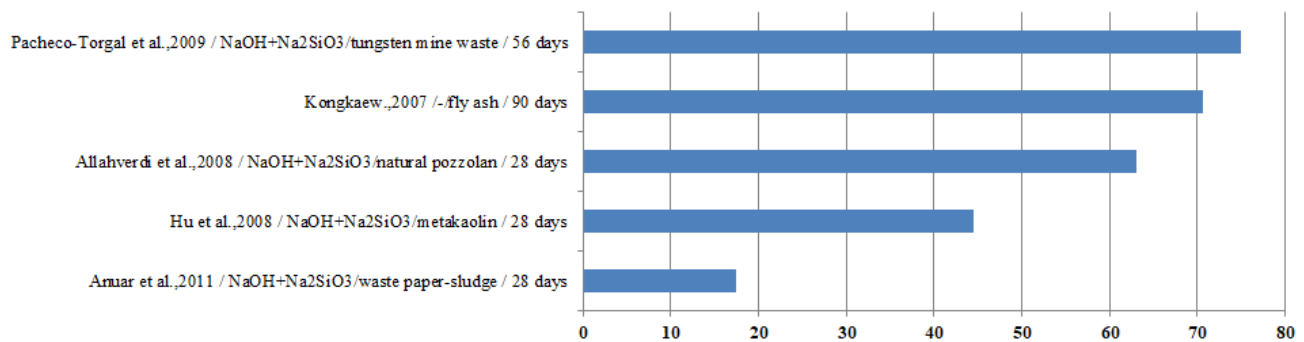


Fig.6. Geopolymers compressive strength at ambient temperature, reported by various researchers

Table 1. Compressive strength values for different types of geopolymer material hardening

Mixture	Density (g/cm ³)			Compressive strength (MPa)		
	Ambiental temperature		Heat	Ambiental temperature		Heat
	7 days	28 days	-	7 days	28 days	-
M4	1.89	1.87	1.72	10.4	14.2	14.9
M8	1.88	1.92	1.93	33.9	36.9	37.3
M11	1.86	1.9	1.88	42.1	48.6	44.7

3. CONCLUSIONS

There are two types of producing alkali-activated geopolymer materials with heat treatment, at certain temperatures and duration of exposure and without heat treatment, at ambient temperature. Most of the reports in the literature refer to a limited range of heat treatments at certain temperatures and different heat treatment durations, due to the specifics of each research and due to the multitude of raw materials used for the production of the geopolymer material.

Research conducted on alkali-activated geopolymer concrete showed that thermal hardening adopted for temperatures between 30°C and 90°C in the first 24 hours after casting, led to a rapid development of compressive strength.

In order to give up long-term heat treatment at certain temperatures, which means additional energy consumption, geopolymers can be designed to strengthen at an ambient temperature by an appropriate choice of binder and reagent. Any procedures that increase the temperature of the fresh or hardened mixture

will obviously compensate for the effects of low ambient temperatures.

The properties of the alkali-activated geopolymer materials are influenced not only by the duration of heat treatment and temperature, but also by the quantities of alkali activators, the ratio between them, the molarity used in the study, as well as the content of Si and Al of mineral additions used in the mix-design.

To date, there are many controversies about the influence of each factor, so a generally valid manufacturing technology is not available. Further research will be focused on producing alkali-activated geopolymer materials using different raw materials and mineral additions from Romania, therefore studying the possibility of producing these types of materials with local raw materials available.

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