
EXPERIMENTAL RESEARCH ON THE DEVELOPMENT OF GEOPOLYMER MATERIALS USING ROMANIAN LOCAL MATERIALS

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ABSTRACT

The demand for concrete and also for the current infrastructure facilities development is experiencing worldwide exponential growth. Environmental issues associated with the production of Portland cement are very well known and therefore they are carefully monitored, especially in terms of CO₂ emissions released into the atmosphere. Therefore, it is essential to find alternatives namely creating environmental-friendly materials. The particular procedure of alkali-activating the fly ash, combined with a specific alkaline activator, offers possibilities for the development of a material with cementitious-like properties. Large quantities of fly ash, resulting from electricity production in Romania, open new opportunities for studying and developing Geopolymer composites with local materials.

Keywords: development; alkali-activation; geopolymer.

REZUMAT

Cererea de beton și nevoia de a satisface dezvoltarea facilităților de infrastructură pe întreg globul sunt în continuă creștere. Problemele de mediu asociate producerii cimentului Portland sunt foarte bine cunoscute și sunt atent monitorizate, mai ales în ceea ce privește emisiile de CO₂ eliberate în atmosferă. Astfel, devine esențială găsirea unor alternative pentru crearea de materiale "prietenoase" cu mediul. Procedura particulară de activare alcalină a cenușii de termocentrală, prin care aceasta este combinată cu un activator alcalin specific, oferă posibilități pentru dezvoltarea unui material cu proprietăți asemănătoare materialelor cementoase. Cănițările mari de cenușă de termocentrală rezultate în urma producerii energiei electrice în România deschid noi oportunități de studiere și dezvoltare a compozitelor de tip geopolimer cu materiale locale.

Cuvinte cheie: dezvoltare; activare alcalină; geopolimer.

1. INTRODUCTION

Environmental problems associated with ordinary Portland cement production are extremely well known and they represent a problem which is carefully monitored, in terms of carbon dioxide amount released into the atmosphere during its production, lime calcination and burning of fossil fuels. The industry is constantly growing, therefore, the involvement of modern building materials in the economic world is more than necessary. New materials, known as "geopolymers", were introduced in 1987 by Davidovits to describe a mineral group with a chemical composition

similar to natural zeolite materials, but with an amorphous microstructure (Davidovits, 1991).

Alkali-activated fly ash-based geopolymer composites are under constant development, research growing rapidly, mostly based on the global need to reduce CO₂ emissions.

The development of these types of composites with similar properties to cementitious composites, but without using cement in the composition, can be an extraordinary opportunity for the environment and for the construction industry, constituting itself as an alternative to traditional technology, both due to mechanical properties

and high resistance in aggressive environments (Palomo et al., 1999; Duxon et al., 2007).

A geopolymer is a cementitious-like alumino-silicate amorphous material, which can be synthesized by the polycondensation reaction between a geopolymeric material and alkaline polysilicates. This process is called geopolymerization (Davidovits, 1979). This innovative technology allows the conversion of alumino-silicate materials into products called geopolymers or inorganic-polymers. In a simplified method, it can be stated that geopolymers can be synthesized by an alkaline activation of materials that are rich in SiO_2 and Al_2O_3 .

Since the 90s, research in the field of alkali-activated materials has grown dramatically across the globe. Most of them focus on developing materials with acceptable performances, made with local materials available in the area. Any new and unconventional technology is difficult to translate into ordinary practice, since existing standards for concrete do not specify the directions for producing geopolymer materials (Hooton, 2008). Standards regulate products that are already accepted on the market, ensuring that they comply with certain rules and have certain characteristics and qualities (Bilodeau and Malhotra, 2000).

The large amount of fly ash resulting from the energy industry in Romania can create new opportunities to use this waste as a substitute for Portland cement in the production of new materials. The purpose of this paper is to study the possibility of developing alkali-activated fly ash-based geopolymer composites using the available local materials and to present the preliminary experimental results obtained in the laboratory.

2. MATERIALS AND METHODS

In case of alkali-activated fly ash-based geopolymer materials the dissolution process of Al (Al) and Silicon (Si) from the fly ash (the geopolymerization reaction) begins when the fly ash comes in contact with the alkaline solution. Larger molecules will condense and form a gel which, under the alkaline attack on

their surface, will lead to their expansion, covering the remaining voids to form a matrix similar to that of the cement paste (Pacheco-Torgal et al., 2008).

The microstructure of the geopolymer composite depends largely on the chemical structure of the ash, the alkaline solution and the conditions in which the obtained material is heat treated. A suitable heat treatment is essential for geopolymeric materials, because if this does not happen, the material will have a porous microstructure, resulting in low mechanical performance. Addition of silicon-containing materials into the alkaline liquid mixture can lead to a homogeneous and uniform microstructure of the material (Mehta, 2002), which can also lead to improved mechanical performance.

In the absence of clinker, when using the fly ash, the basic material in the mixtures, a careful analysis and choice of the component materials is required. They must have certain chemical properties so that the geopolymerization reaction can occur (Bilodeau and Malhotra, 2000). Most of the alkali-activated geopolymer's components, which are essential in their production, are often described in the literature as Type II additions in cementitious systems using Portland cement. In the case of alkali-activated systems, neither the solid part of the mixtures (alumino-silicate elements) nor the liquid part (alkaline activator) should be considered additions - they are the basic materials for the production of geopolymer composites (Mehta and Burrows, 2001).

Regarding the dissolution of Al-Si-rich materials in the alkaline solution and the proper geopolymerization process, it can be said that the mechanical properties of the product are directly affected by the microstructural reorganization of the source material at the time of the chemical reactions finish. It has been shown that flexural strength, compressive strength and apparent density of the geopolymer concrete increased with increasing NaOH solution concentration (Wang et al., 2005) and also the amorphous content of the product increased (Luz Granizo et al., 2007).

This section summarizes both the current state of the art literature regarding the materials used to produce alkali-activated fly ash-based geopolymers, the methods used in the experimental research, the design of the geopolymer binder mixture, the casting methods, the heat treatment needed and test methods to obtain the results of the mechanical resistance characteristics.

2.1. Fly ash

Fly ash is one of the most used pozzolanic materials and has played an extremely important role in the production and development of high strength concrete. It can be defined as the fine powder, consisting mainly of spherical vitreous particles, derived from the combustion of pulverized coal (Xu and van Deventer, 2000; Anuradha et al., 2012).

Since in the case of high strength concrete the optimum quantity of fly ash in the mixture is determined only by laboratory tests (Ionescu et al., 1999), for the production of geopolymer concrete the literature recommends the same. Most power plants produce fly ash with a loss of L.O.I. (Loss on Ignition) less than 5%. Although certain characteristics may be common, due to the type of burned coal, the process to which it was subjected, and certain operating conditions, fly ash may have different characteristics. Their composition and behavior change from one case to another, their standardization being a very difficult process (Palacios and Puertas, 2011). Loss on ignition of fly ash differs from one lot to another because the carbon content is different from one ash type to another.

Literature shows that the best fly ash used for the production of alkali-activated geopolymer materials are those included in class F. These have good pozzolanic properties for their use in the production of fly ash-based geopolymer. Although each chemical characteristic of the fly ash is important and must be known, in order to be class F, fly ash must have the following characteristics: $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$, $\text{SO}_3 < 5\%$ and $\text{L.O.I.} < 6\%$ (Davidovits, 1994).

For the preliminary laboratory research and for preparing the preliminary mixes of alkali-activated geopolymer paste, the ash was obtained from a power plant in Romania, having the chemical characteristics within the limits established in the literature (Figure 1).



Fig. 1. Romanian fly ash

2.2. Alkaline liquid

When the alkaline liquid comes into contact with the reactive solids and the geopolymerization process takes place, a hard, water-resistant material is formed by forming an aluminosilicate network (Duxon et al., 2007). Regarding the alkali-activated fly ash-based geopolymer mixes, the geopolymerization process begins when the fly ash is mixed with the alkaline activator, resulting in the dissolution of the silicon and aluminum atoms of the fly ash forming a homogeneous matrix (Provis and van Deventer, 2007). By using an alkaline hydroxide activating solution and a silicate, the $\text{SiO}_2 / \text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O} / \text{SiO}_2$ ratios in the mixture are optimized to obtain higher mechanical performances (Rangan, 2008; Malhotra, 2002).

The most commonly used combination for the production of the alkaline liquid is sodium hydroxide (NaOH) or potassium hydroxide (KOH) together with a sodium silicate solution ($\text{nSiO}_2\text{Na}_2\text{O}$) or potassium silicate solution ($\text{nSiO}_2\text{K}_2\text{O}$) (Barbosa et al., 2000). Waterglas adds silicon atoms and mixed liquid, both of which play an important role in producing the geopolymerization process.

The main parameter of the sodium hydroxide solution is the concentration, which differs from one solution to the other, and is the most important feature to be taken into account in the design of geopolymer materials

as it influences the final mechanical characteristics of the composite. In general, sodium hydroxide is commercially available and can be purchased in solid form (transported on pallets) or can be purchased in the form of flakes or pearls.

Cementitious materials are homogeneous materials, and the main purpose of using sodium hydroxide is to interact with the sodium silicate solution and to activate the fly ash. It is recommended to use sodium hydroxide of purity between 94 and 99%. Regarding the sodium hydroxide solution, it should be prepared 24 hours before use, but not longer than 36 hours because it loses its properties as an activator (Anuradha et al., 2012). The NaOH solids (Figure 2a) must be dissolved in water in order to obtain a solution with the required concentration that may vary between 8M and 12M. Sodium hydroxide concentration has an important influence on the final mechanical properties of the alkali-activated fly ash-based geopolymer material (Rangan, 2014; Sofi, et al., 2007).

In order to produce preliminary alkali-activated fly ash-based geopolymer pastes using local materials, a combination of sodium hydroxide solution (NaOH) and sodium silicate solution (Na_2SiO_3) was chosen (Figure 2b)



Fig. 2. a. NaOH Flakes b. Alkaline solution

2.3. Mix design of alkali-activated geopolymers

Most of the existing studies on alkali-activated geopolymer materials are focused on studying the properties of the fresh geopolymer paste and mortar. All the characteristics of this type of material are measured only by making small specimens, the research being limited. Moreover, the full

details of the compositions of the paste mixtures have not been reported in detail.

To begin with, alkali-activated fly ash-based geopolymer pastes were performed using the trial-and-error method. The material ratios used in the compositions are shown in Table 1. The workability and mechanical properties of the geopolymer materials are highly influenced by the properties of the materials themselves and the ratios in which they are used in the mixes.

Table 1. Mix design ratios

	Alkaline liquid / Fly ash ratio	Na_2SiO_3 / NaOH ratio	NaOH
1	0,5	0,5	8M 10M and 12M
2		1,0	
3		1,5	
4		2,0	
5		2,5	

3. RESULTS AND DISCUSSIONS

The most important objectives of the preliminary laboratory work were to familiarize with the process of producing alkali-activated fly ash-based geopolymer pastes with the available local materials and, also, a complex understanding of the sequence of combining the alkaline liquid with the solid constituents of the mixtures (the fly ash) for the geopolymerization process to take place.

The behavior of the fresh geopolymer paste (Figure 3) was studied and, depending on the experimental results obtained, a mixing process was developed, with a specified heat treatment, therefore understanding the basic proportions of the constituent materials in the mix design.



Fig.3. Fresh geopolymer paste

Given the limited information and characteristics of producing this type of material, a rigorous trial-and-error study was initiated to determine the possibility of developing such composites and to determine the parameters that influence both the fresh properties of the material and the long-term ones.

The workability and mechanical properties of the geopolymer materials are highly influenced by the properties of the materials and by the proportions in which they are used in making the compositions. With respect to the alkaline liquid, it is preferable that the two constituent solutions (NaOH solution and Na_2SiO_3 solution) should be mixed at least 24 hours prior to mixing.

Some mixes of the alkali-activated fly ash-based geopolymer paste became very rigid and dry for certain mixes. This has happened both because of the increased rate of addition of the alkaline liquid to the fly ash, but sometimes also due to the increased mixing time of the components.

In order to determine the long-term properties of the geopolymer samples, it is necessary to perform many tests over a long period of time. The methods proposed by the researchers are the same as those for testing ordinary Portland cement concrete. In terms of compressive strength, it is necessary to manufacture numerous samples of geopolymer mixes, in order to study the effect of age on compressive strength. Studies have shown that curing temperature has an important effect on the mechanical properties of the mixes. Together with the heat treatment time and the type of alkaline liquid, the temperature is an accelerator of the geopolymerization reaction. A higher curing temperature and a longer curing time resulted in a higher compressive strength for the samples.

Preliminary results obtained in the laboratory for the compressive strength of the alkali-activated fly ash-based geopolymer paste have shown both the possibility of realizing this type of material using local materials in Romania, as well as an opening for new opportunities for continuing research in this domain (Lăzărescu et al., 2017, 2018).

When producing geopolymer paste with the selected materials presented above, with an alkaline-liquid to fly ash ratio of 1,0, at a constant NaOH solution concentration set at 8M, with a $\text{Na}_2\text{SiO}_3/\text{NaOH}$ solution ratio varying from 0.5 to 2.5 and a heat treatment of 70°C for 24 hours, the samples showed compressive strength values varying from 11 MPa to 20 MPa (Figure 4) at 7 days of age.

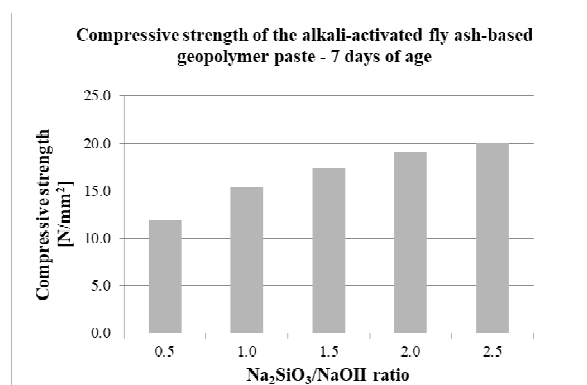


Fig. 4. Compressive strength values, at 7 days of age

Based on the preliminary results obtained, it was considered appropriate to continue the studies on the development of alkali-activated fly ash-based geopolymer composites by improving the parameters of the alkaline liquid and analyzing the obtained results. Future studies also focus on experimental research on the production of geopolymer mortars and concretes by adding aggregates to already optimized geopolymer pastes and studying all the parameters that influence these types of materials.

4. CONCLUSIONS

Preliminary results obtained in INCERC laboratory at NIRD URBAN-INCERC, Cluj-Napoca Branch on alkali-activated fly ash-based geopolymer pastes, show not only the possibility of producing this type of material with local materials, but is also opening new opportunities for further research to continue by optimizing the current compositions, studying all parameters that affect the mechanical properties of the material, as well as durability characteristics. The ongoing research project includes investigations

dedicated to the specified areas by establishing stable compositions of alkali-activated geopolymers and on adding sand and aggregates in these compositions (producing mortars and geopolymer concrete) and to study all the parameters affects this type of material.

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