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Parameters Affecting the Mechanical Properties of Fly Ash-Based Geopolymer Binders – Experimental Results

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Abstract. As the demand for concrete and the needs to satisfy development of infrastructure facilities increase, it is essential to find alternatives to create environment-friendly concrete. The particular procedure of alkaline activation of fly ash - in which ash resulting from a power plant is combined with a specific alkaline activator in order to create a solid material, then dried at a certain temperature - opened new opportunities for this new material to get attention worldwide. In order to obtain a material with similar properties of ordinary Portland cement concrete and to obtain desirable compressive strengths, the parameters that affect this type of binders should be fully understood. The aim of this paper is to study the main parameters affecting the mechanical strength of the fly ash-based geopolymer paste and their interactions. Parameters such as molarity of sodium hydroxide (from 8M to 12M) and alkaline activators ratio (from 0,5 to 2,5) were analysed to observe how they affect the mechanical properties of the geopolymer paste. Experimental results show that the compressive strength of the fly ash-based geopolymer paste produced using Romanian local raw materials increases with the increase of the concentration of sodium hydroxide and higher ratios of Na_2SiO_3/NaOH solution.

1. Introduction

Large amounts of fly ash, resulting from burning coal power-plants, in Romania, can create new opportunities to use this type of waste as a total substitute for Portland cement in the production of new types of materials. When partially used in the production of concrete, mixed with Portland cement, fly ash helps obtaining concrete with improved performances. The concept of alkali-activated materials (AAM) has been known since the early 20th century, but more recently, since the 1990s, research in the field of AAM and geopolymer materials (which are a subclass of the AAM) have experienced an impressive progress. The vast majority of the research is focused on the microstructure of these materials and much less on establishing or verifying their implementation process, service life, sustainability or advanced engineering properties. This type of materials are seen more as niche applications and not necessarily as ordinary Portland concrete (OPC) substitutes [1].

The substantial progress made in the field of alkali-activated materials and geopolymer materials is particularly highlighted by the growing interest in the environmental problems, particularly regarding the carbon dioxide emissions into the atmosphere. More and more countries are aligning themselves to the international standards on environmental issues, this creating an important niche for civil engineering research and beyond.

A geopolymer binder is generally formed by the interaction of an alkaline solution (activating solution or activator) with a highly reactive aluminosilicate “powder” [2]. In the usual practice, the production of geopolymer materials is based on a mixture between fly ash and the alkaline-activator. When in contact with the alkaline liquid, the fly ash partially dissolves and its components are rearranged, forming an alumino-silicate gel, which hardens in the presence of heat forming the geopolymer matrix (or binder). By adding sand and aggregates it is possible to obtain a concrete with similar or even better properties than conventional Portland cement concrete.

The microstructure of the geopolymer binder depends mainly on the chemical composition of the constituent materials, their specific ratios in the proposed mixtures and the thermal curing of the obtained material [3]. A suitable heat curing is essential for geopolymeric materials, as without it the obtained material develops a porous microstructure and, as consequence, low mechanical performances [4]. Addition of rich silicon-containing materials into the alkaline liquid can lead to the formation of a homogeneous and uniform microstructure of the geopolymer [5], which can also determine improved mechanical performances.

Mechanical behavior represents basic property of a material used in the construction industry, making it suitable for specific applications. Compressive strength is crucial, especially for a concrete type material. The early 1950 geopolymeric mixes proved good compressive strength results, reliable workability and durability even superior to those of OPC concrete. However, the compression behavior of the geopolymer materials strongly varies depending on the raw materials used, namely their chemical properties, and also on the used production methods [7]. In order to obtain good compressive strength properties, one must take into account the type and molar ratios of the oxides in the source material rich in Al-Si, the type, the pH and the molar properties of the alkaline solution and also the solubility of the source material in the activating alkaline-solution [8, 9].

Regarding the importance of the dissolution of the Al-Si-rich materials in the alkaline solution and the actual geopolymerisation process, it was proved that the mechanical properties of the material are directly affected by the reorganization of the source material at the time of the chemical reaction. Flexural strength, compressive strength and apparent density of the material increase with the increase in the NaOH solution concentration [10], and the amorphous content of the product has also increased [11].

The production of geopolymer paste for the current study this research is carried out using specific, state-of-the-art methods and it is based on the reaction between the silicon and aluminum in the fly ash (FA) and the alkaline liquid (sodium silicate solution and sodium hydroxide solution). In this paper, various factors which influence the compressive strength of the alkali-activated fly ash-based geopolymer paste have been studied and the results are discussed by means of graphical representation corresponding to the compressive strength of the batches. Therefore, the actual goal was developing various geopolymer paste mixes, with 100% OPC replacement by processed FA resulted from Romanian local sources and to evaluate the influence of different parameters affecting the mechanical properties of the material. Hence the effect of various parameters affecting the compressive strength of the alkali-activated fly ash-based geopolymer paste (i.e. ratio of sodium silicate solution to sodium hydroxide solution, concentration of sodium hydroxide solution, curing temperature) should be carefully controlled for optimizing and improving the overall performances of this materials developed by using Romanian local raw materials.

2. Materials and methods

Similar to the OPC traditional concrete mixes, the basic constituents of the fly ash-based geopolymer concrete are the cement paste (in this case geopolymer paste) and the aggregates. In case of the geopolymer concrete, the geopolymer paste (or binder) results from combining the fly ash and the alkaline liquid (a mixture of sodium hydroxide solution and sodium silicate solution).

2.1. Fly ash (FA)

Ashes from power-plants (fly ash, FA) can be defined as fine powders of spherical vitreous particles, derived from the combustion of pulverized coal [12, 13]. According to the classification of the

American Society for Testing and Materials (ASTM) [14], there are identified various FA types that can be used in the production of fly ash-based geopolymer binders. The present research used a typical Class F FA powder with good pozzolanic properties and characterized by SiO_2+Al_2O_3+Fe_2O_3 > 70%, SO_3 < 5% and lost on ignition (L.O.I.) < 6%.

The mineral composition of the FA sample used in the production of the alkali-activated fly ash-based geopolymer paste with Romanian local raw materials was determined by X-Ray fluorescence analysis (XRF) and it is presented bellow (Table 1).

Table 1. XRF analysis data for the fly ash batch.

Oxides	%
SiO_2	53.61
Al_2O_3	26.16
Fe_2O_3	7.58
CaO	2.42
MgO	1.49
SO_3	0.26
Na_2O	0.59
K_2O	2.60
P_2O_5	0.12
TiO_2	1.04
Mn_2O_3	0.08
L.O.I.	3.57

2.2. Alkaline liquid

The used alkaline solution is a mix between sodium silicate solution (Na_2SiO_3 solution) and sodium hydroxide solution (NaOH solution). The sodium silicate solution was purchased from the market and its chemical oxide composition is SiO_2=30%, Na_2O=14% and H_2O=56%. The sodium hydroxide solution is prepared dissolving NaOH, 98% purity, flakes in water to obtain the desired concentration of the final solution. The NaOH solution concentration for the mixes in this study is set to 8M, 10M and 12M. To obtain 8M NaOH solution, 320g of NaOH flakes were dissolved in one liter of solution (40g x 8M = 320g NaOH/ liter of solution, where 40g is the molecular weight of NaOH). It was measured that for one kilogram of NaOH solution, the mass of the NaOH was 262g (1 kg of NaOH solution, 8M = 26,2% NaOH and 73,8% water). Similarly, the mass of NaOH flakes per kg of solution for the other concentrations were: for 10M: 314 grams (31,4% NaOH and 68,6% water) and for 12M: 361 grams (36,1% NaOH and 63,9% water). It is very important to note that the mass of the NaOH solids is only a fraction of the mass of the NaOH solution, water being the major component that affects the water to geopolymer solids influence.

2.3. Mix design, moulding and curing treatment

In order to study the effect of different parameters affect the mechanical properties of fly ash-based geopolymer paste using Romanian local raw materials, the alkaline activator/fly ash ratio was set to 0,5 because, based on the preliminary results obtained on geopolymer paste, it proved good workability, [15]. The sodium silicate solution to sodium hydroxide solution ratio (Na_2SiO_3/NaOH) was varied between 0.5 and 2.5, according to the literature specifications, in order to study the effect of the alkaline activator ratio on the compressive strength of the alkali-activated fly ash-based geopolymer paste.

The effect of the concentration of the sodium hydroxide solution (NaOH solution) was studied by increasing the molar concentration of the solution, from 8M to 12M, for all the proposed Na_2SiO_3/NaOH solution ratio. For all the studied mixtures, their molar constituents ratios were calculated to obtain the water to geopolymer solids ratio and to evaluate this effect on the paste fresh properties. Details of the alkali-activated fly ash-based geopolymer paste are presented in Table 2.

The preparation of the alkaline activator by combining the sodium silicate solution with the sodium hydroxide solution took place 24 hours prior mixing. The fly ash and the activator were mixed together for 5 minutes, until a homogeneous paste was obtained. The alkali-activated geopolymer paste was then placed in 40mm x 40mm x 160mm moulds and exposed for 24 hours to 70°C heat curing. The effect of heat curing temperature over geopolymer pastes. Namely compressive strength variation, was studied by varying from 60°C to 70°C, the heat regime curing. During the heat curing a glass film was applied on top of the molds to prevent the water quick release from the pastes. After samples removing from the molds, 24 h after casting, the prismatic specimens were kept in the climatic chamber, at (20±1)°C and (60±5)% humidity, until the 7 days compressive strength tests.

Table 2. Mixture details of the geopolymer paste.

Alkaline liquid / Fly ash	Na_2SiO_3 / NaOH ratio	NaOH solution concentration
0.5	0.5	8M 10M 12M
	1.0	
	1.5	
	2.0	
	2.5	

2.4. Testing methods

The compressive strength of the studied mixtures, for all the alkali-activated fly ash-based geopolymer paste prepared using Romanian local raw materials, was determined using three specimens for each mixing batch and the corresponding average value was considered as relevant. Tests were conducted according to SR EN 196-1:2006 standard method for evaluation of mechanical performances of OPC paste and standard type mortar. The testing was performed at the age of 7 days.

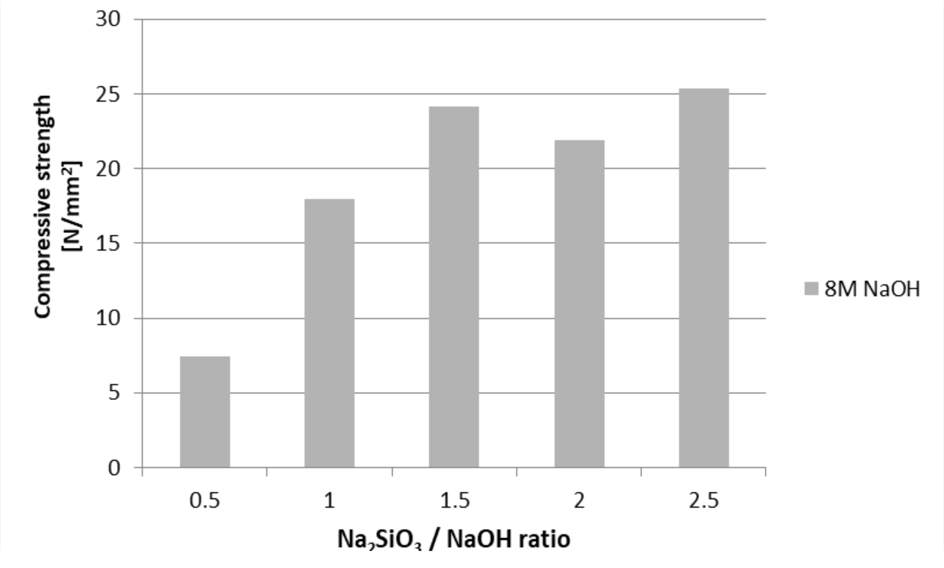

Figure 1. Influence of the Na_2SiO_3/NaOH ratio on the compressive strength (8M concentration NaOH solution).

3. Results and discussions

3.1. Influence of sodium silicate solution to sodium silicate solution ratio on the compressive strength

The effect of the sodium silicate solution to sodium hydroxide solution ratio effect was evaluated considering all mixes developed in the current experimental study. The results are graphically presented in Figure 1, Figure 2 and Figure 3. It has been noticed that, as the ratio value increases, the compressive strength of the alkali-activated fly ash-based geopolymer paste increases as well. The increasing values of the compressive strength of the samples is considered to mainly depend on the chemical process governing the geopolymerization. Increasing this ratio leads to more SiO_2 species, therefore more Si-O-Si bonds are formed, creating a stronger material [16]. Some mixes presenting a decreased compressive strength may happen because the geopolymerisation rate of them was lower, therefore, the compressive strength of the batches was lower.

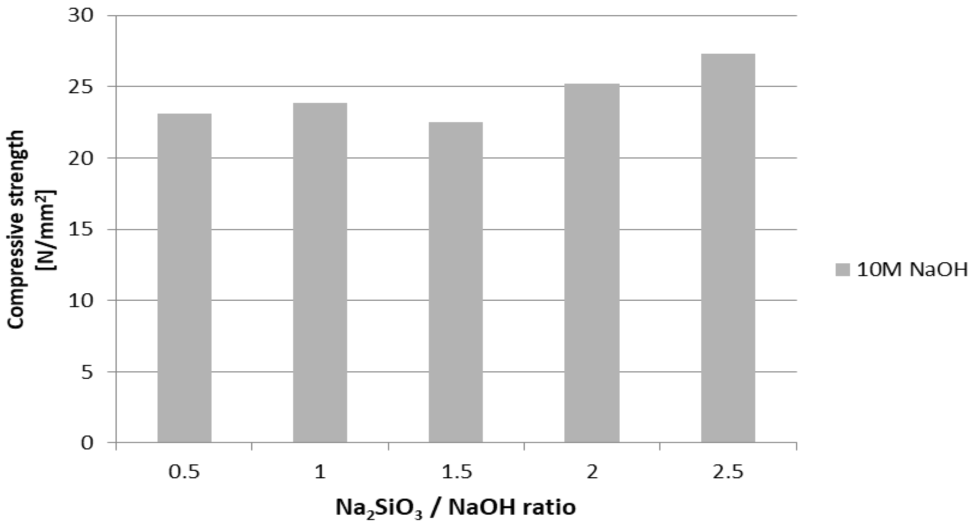

Figure 2. Influence of the Na_2SiO_3/NaOH ratio on the compressive strength (10M concentration NaOH solution).

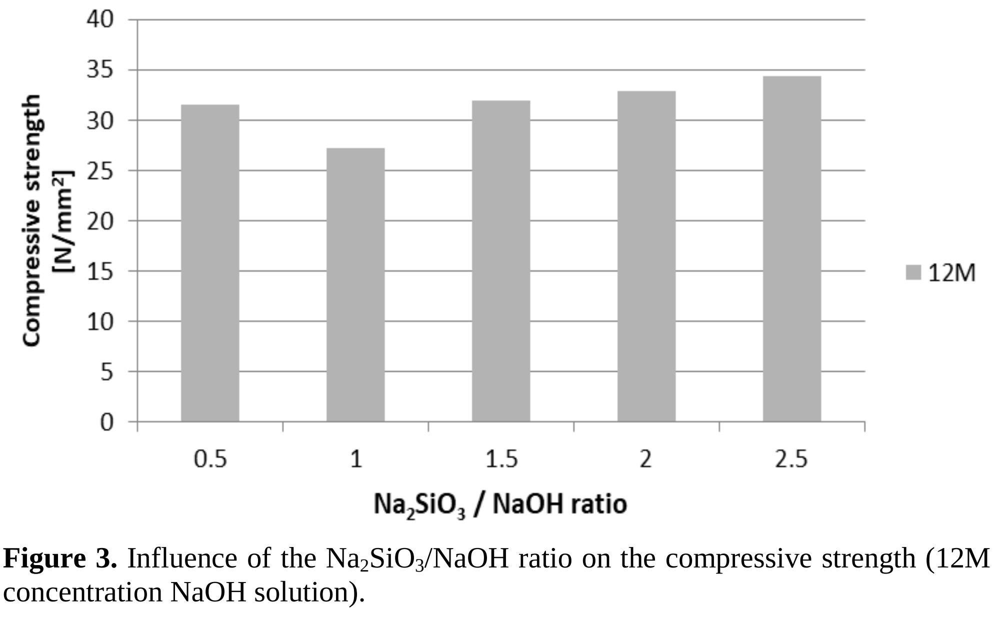

Figure 3. Influence of the Na_2SiO_3/NaOH ratio on the compressive strength (12M concentration NaOH solution).

3.2. Effect of sodium hydroxide solution on the compressive strength

The effect of the sodium hydroxide concentration on the alkali-activated fly ash-based geopolymer paste samples is analysed on all the developed mixtures and the testing results are presented in Figure 4. It has been noticed that higher concentration of the sodium hydroxide solution induces better compressive strengths, when the alkaline activator to fly ash and alkaline activator ratio is kept constant.

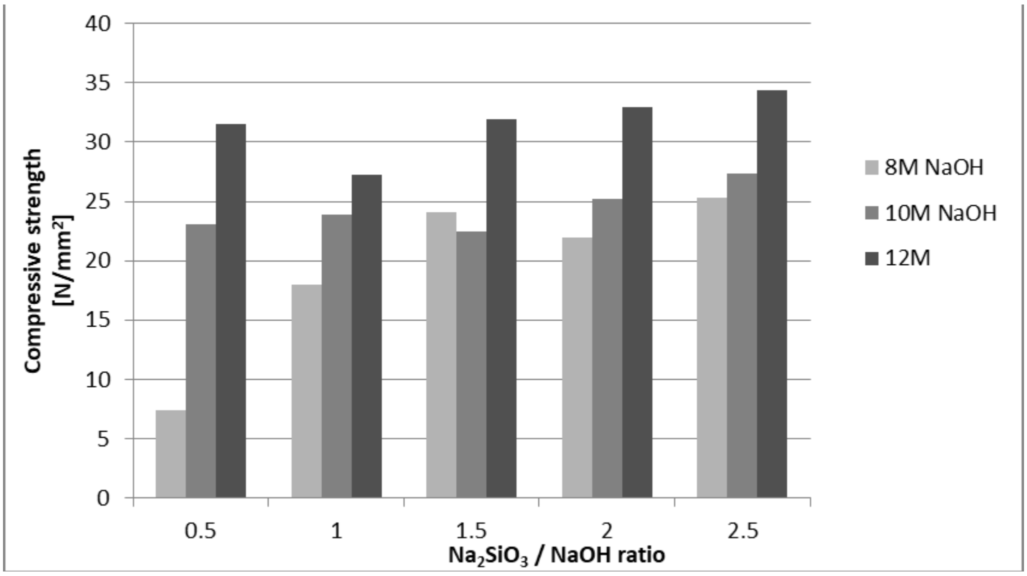

Figure 4. Influence of the NaOH solution concentration on the compressive strength for all the studied mixtures of fly ash-based geopolymer paste.

4. Conclusions

All the desirable properties of geopolymer paste developed by using fly ash combined with alkaline solution, mainly mechanical performances, can be enhanced only by carefully monitoring and controlling the relative quantities of used reactants and also by controlling the overall conditions where the geopolymerisation process takes place. The chemical composition of the used raw materials is one of the most important, influencing parameters of the the geopolymerization process, therefore, it is considered that before conducting any experimental study regarding geopolymer materials, these properties should be well evaluated and known.

When keeping the alkaline liquid to fly ash mixing ratio constant and varying the Na_2SiO_3 to NaOH solution ratio and also the NaOH solution concentration, it was possible to study the effect of the two main parameters on the compressive strength of the alkali-activated fly ash-based geopolimer binder. Results show that by increasing the sodium silicate solution content in the mixtures, a significant increase in the compressive strength of the materials was induced. This effect was considered to happen because the solution provides extra silicon (Si) species, which play an important role in the geopolymerization process, thus creating a much performed, well packed matrix of the material. Also, by increasing the concentration of the NaOH solution in the current study, increased compressive strength values were obtained, therefore, increasing the concentration of the solution from 8M to 12M increased the mechanical properties of the material.

As the “green” building materials started to become more desirable in comparison to traditional OPC, and they also became more and more present, both technologically and commercially, in the construction industry, a need for standard methods for material testing and general evaluation becomes more than necessary. The initial and long-term properties of these materials must be well understood, so they could be properly designed and controlled from the initial step at their best. Large scale acceptance of the geopolymer cement and concrete could reduce Portland cement demands and represent a green solution for worldwide maintaining concrete the most used building material.

The above results obtained on alkali-activated fly ash-based geopolymer paste using Romanian local source materials have shown not only the possibility of producing this type of material, but also the opportunities for further research in this topic. The aim of this research was both to produce alkali-activated fly ash-based geopolymer paste using Romanian local source materials and to study the influence of two main parameters on the compressive strength of the material.

5. References

[1] Provis J L, van Deventer Alkali J S J *Activated Material*, State-of-the-Art Report RILEM TC 224-AAM
[2] Duxon P, Fernandez-Jimenez A, Provis J L, Lukeym G C, Palomo A, van Deventer J S J 2007 *Journal of Materials Science* **42**(9) 2917-2933
[3] Hardjito D, Rangan B V 2005 Development and properties of low calcium fly ash-based geopolymer concrete *Curtin University of Technology, Research Report GC1*, Curtin University, Australia
[4] Davidovits J 1988 Geopolymers of the first generation: SILFACE-Process *Geopolymer '88, First European Conference on Soft Mineralogy* Compiegne, France, p. 49-67
[5] Duxon P, Provis J L, Lukey G C, Mallicoar S W, Kriven W M, van Deventer J S J 2005 *Colloids and Surfaces: A – Physicochemical and Engineering Aspects* **269**(1-3) 47-58
[6] Davidovits J 1999 Chemistry of geopolymeric systems, terminology *Geopolymer '99 International Conference, France 9-44*
[7] Mhidi B 2009 *Materials Technology* **24**(2) 79-87
[8] Xu H *Geopolymerisation of aluminosilicate minerals*, PhD. Thesis Department of Chemical Engineering, University of Melbourne, Australia
[9] Mustafa Al Bakri Abdullah A M, Kamarudin H, Binhussain M, Nizar K, Mastura W I W 2011 Mechanism and Chemical Reaction of Fly Ash Geopolymer Cement – A Review *Article in Asian Journal of Scientific Research*
[10] Wang H, Li H, Yan F 2005 *Colloids Surf. A: Physicochem. Eng. Aspects* **268** 1-6
[11] Luz Granizo M, Blanco-Varela M T, Martinez-Ramirez S 2007 *J. Mater. Sci* **42** 2934-2943
[12] EN 450-1 Fly ash for concrete. Part 1: Definition, specifications and conformity criteria
[13] EN 197-1 Cement. Part 1: Composition, specifications and conformity criteria for common cements
[14] Davidovits J 1994 Properties of geopolymer cements, *Alkaline Cements and Concretes*, Kiew, Ukraine, p. 131-149
[15] Lăzărescu A V, Szilagyi H, Baeră C, Ioani A 2017 The Effect of Alkaline Activator Ratio on the Compressive Strength of Fly Ash-Based Geopolymer Paste *International Conference on Innovative Research – ICIR EUROINVENT 2017, IOP Conf. Series: Materials Science and Engineering,* 209 012064
[16] Mustafa al Bakri Abdullah A M, Omar A K A, Kareem A, Myint S 2009 Study On The Effect Of Alkaline Activators Ratio In Preparation Of Fly Ash-Based Geopolymer *RAAM & ASMP 2009* Conference Paper