The Effect of Alkaline Activator Ratio on the Compressive Strength of Fly Ash-Based Geopolymer Paste

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Abstract. Alkaline activation of fly ash is a particular procedure in which ash resulting from a power plant combined with a specific alkaline activator creates a solid material when dried at a certain temperature. In order to obtain desirable compressive strengths, the mix design of fly ash based geopolymer pastes should be explored comprehensively. To determine the preliminary compressive strength for fly ash based geopolymer paste using Romanian material source, various ratios of Na₂SiO₃ solution/NaOH solution were produced, keeping the fly ash/alkaline activator ratio constant. All the mixes were then cured at 70°C for 24 hours and tested at 2 and 7 days, respectively. The aim of this paper is to present the preliminary compressive strength results for producing fly ash based geopolymer paste using Romanian material sources, the effect of alkaline activators ratio on the compressive strength and studying the directions for future research.

1. Introduction
Concrete is the most versatile, durable and trustworthy construction material and also the most used material in the construction industry. Because of this, huge quantities of Portland cement are needed and it is very well known that the cement industry is considered to be the second carbon dioxide generator. Environmental problems associated with the production of ordinary Portland cement are very well known and are closely monitored in terms of carbon dioxide amount released into the atmosphere during its production. Since industry is growing at an accelerated pace, the involvement of new, alternative, modern building materials in the industry is more than necessary.

New materials, known as geopolymers, were introduced in 1987 by Davidovits to describe a group of mineral binders. This binders could be produced by the alkali-activation of source materials of geological origin or by-product materials rich in silicon (Si) and aluminium (Al) [1,2]. The microstructure of the geopolymer materials is amorphous although the chemical composition is similar to natural zeolitic materials [3].

An alkali-activated material (or a geopolymer material) is mainly composed from one or several mineral components and one or more activators [4]. In this case, fly ash, which is a solid aluminosilicate material is used as source material in order to produce alkali-activated fly ash-based geopolymer paste. As an industrial waste, in Romania, fly ash is mainly stored, this representing one of the most common method of waste disposal and leads to land, atmosphere and ground pollution, only few quantities of it being used in different industries. The huge available amount of fly ash
unused in Romania creates new perspectives on the global existing research about the production of the fly ash-based geopolymer materials.

The most common alkaline solution used to produce geopolymer concrete is a mixture of sodium silicate solution (Na$_2$SiO$_3$ solution or also known as waterglass) and sodium hydroxide solution (NaOH solution) [5]. Mixing the fly ash with the alkaline activator creates a binder that is generally known as alkali-activated fly ash-based geopolymer paste. Sand can be added to the mixture for producing geopolymer mortars and also aggregates in order to produce geopolymer concrete.

In order to obtain a material with good mechanical properties the source materials used in the production of fly ash-based geopolymer paste need to be carefully analyzed and it is necessary to fully understand the mix design of the geopolymer paste [6]. One of the most important parameters affecting the mechanical strength of the geopolymer materials is the Na$_2$SiO$_3$ solution / NaOH solution ratio [7]. Usually, researchers that investigate the production and development of alkali-activated fly ash-based geopolymers propose Na$_2$SiO$_3$/NaOH solution ratios in the range of 0.4 to 2.5 [8] with ratios of fly ash/alkaline activator between 0.5 to 3.0 [5]. Another important parameter affecting the mechanical strength of the geopolymer material is the NaOH solution concentration, and in order to produce a good geopolymer material this should be between 8M and 16M [9].

Based on the previous studies in the literature, the parameters affecting the production of alkali-activated fly ash-based geopolymer paste are the concentration of the sodium hydroxide solution, the curing temperature, the Na$_2$SiO$_3$/NaOH ratio and the fly ash/alkaline activator ratio [10,11]. The chemical composition of the source material is also an important parameter affecting the mechanical properties of the geopolymer material [12]. Previous studies also shown that using an alkaline activator composed of sodium hydroxide solution (NaOH solution) and sodium silicate solution (Na$_2$SiO$_3$ solution) leads to better mechanical properties (including compressive strengths) than using only NaOH solution as an activator [13,14]. The Na$_2$SiO$_3$ solution percentage in the alkaline activator also has an important effect since the solution favors the polymerization process adding more silicon (Si) atoms to the product and thus resulting better mechanical strength [15].

The aim of this current research is to produce alkali-activated fly ash-based geopolymer paste using Romanian local raw materials and to investigate the effect of the Na$_2$SiO$_3$/NaOH solution ratio on the compressive strength of the geopolymer paste. Preliminary results will be presented in this study, further research on alkali-activated fly ash-based geopolymer paste produced using source materials from Romania still being conducted and will open new perspectives on the global existing research.

2. Materials and Methods – Experimental method

In this chapter will be presented the materials and the methods used for producing alkali-activated fly ash-based geopolymer paste using Romanian local raw materials, the mix design, the molding methods, the curing treatment proposed and the testing methods for obtaining the compressive strength results for the geopolymer paste.

2.1. Materials

The low-calcium fly ash that was used in this study is obtained from the Mintia power plant, Hunedoara county, Romania and the chemical composition was established through X-ray fluorescence analysis (XRF analysis) and it is given in table 1. Since the CaO content of the fly ash was less than 10% [16] and SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ > 70%, SO$_3$ < 5% and L.O.I. < 6% [17], the fly ash used in this study complies with the ASTM requirements, classifying it as Class F fly ash.

| Oxides   | %   |
|----------|-----|
| SiO$_2$  | 53.61 |
| Al$_2$O$_3$ | 26.16 |
| Fe$_2$O$_3$ | 7.58  |
| CaO      | 2.42  |
The alkaline activator used in this study was a combination between sodium silicate solution (Na$_2$SiO$_3$ solution) and sodium hydroxide solution (NaOH solution). The chemical composition of the sodium silicate solution is SiO$_2$=30%, Na$_2$O=14% and H$_2$O=56%. The sodium hydroxide solution was prepared dissolving the NaOH flakes, 98% purity, into water in order to obtain the desired concentration of the solution. For all the mixes in this study the NaOH solution concentration was set to 8M. To obtain a 8M NaOH solution, 320g of NaOH flakes were dissolved in water, for one liter of solution (40g x 8 = 320g NaOH/liter, where 40g is the molecular weight of NaOH). It was measured that for one kilogram of solution, the mass of NaOH was 262g (1 kg of NaOH solution, 8M = 26.2% NaOH + 73.8% water).

2.2. Mix design, moulding and curing treatment

Preliminary results obtained on geopolymer paste using Romanian local raw materials led to a fly ash/alkaline activator ratio of 2.0, because it has shown good workability of the alkali-activated fly ash-based geopolymer paste. The Na$_2$SiO$_3$/NaOH solutions ratio was set between 0.5 and 2.5, also according to the literature, in order to study the effect of the alkaline activator ratio on the compressive strength of the geopolymer paste. details of the mixtures of alkali-activated fly ash based geopolymer paste are given in table 2. In order to study the effect of the percentage of Na$_2$SiO$_3$ solution content of the alkaline activator on the compressive strength of alkali-activated fly ash-based geopolymer paste, for every Na$_2$SiO$_3$/NaOH ratio the percentage of waterglass was obtained.

After the preparation of the alkaline activator, 24 hours prior to mixing (by combining the sodium silicate solution with the sodium hydroxide solution), the fly ash and the activator were mixed together for ten minutes, until a homogeneous mixture was obtained. The alkali-activated geopolymer paste was then placed in 40mm x 40mm x 160mm molds and heat cured at 70°C for 24 hours. During the heat treatment a glass was put on top of the molds in order to prevent the quick release of the water from the mixtures. After demolding, the samples were kept in the climatic chamber at (20±1)°C and (60±5)% humidity until the day of the compressive strength tests (2, respectively 7 days age).

Table 2. Mixture details of alkali-activated fly ash-based geopolymer paste

| Mix | Fly ash/Alkaline liquid | Fly ash [g] | Alkaline liquid [g] | Na$_2$SiO$_3$/NaOH | Na$_2$SiO$_3$ [g] | NaOH 8M [g] |
|-----|-------------------------|-------------|---------------------|-------------------|-------------------|-------------|
| Mix 1 | 2                       | 1000        | 500                 | 0.5               | 166.6            | 334.4       |
| Mix 2 |                          |             |                     | 1.0               | 250              | 250         |
| Mix 3 |                          |             |                     | 1.5               | 300              | 200         |
| Mix 4 |                          |             |                     | 2.0               | 333.3            | 166.7       |
| Mix 5 |                          |             |                     | 2.5               | 357.15           | 142.85      |

2.3. Testing method

To obtain the compressive strength results, for all the alkali-activated fly ash based geopolymer pastes, minimum three samples were tested to determine the average value of the compressive strength.
Tests were conducted according to SR EN 196-1:2006, the standard for ordinary Portland cement concrete. The samples were tested at 2, respectively 7 days age.

3. Results and discussions
The influence of the Na$_2$SiO$_3$/NaOH solution ratio on the compressive strength of the alkali-activated fly ash-based geopolymer paste, measured at 7 days age of the batches, is shown in figure 1. It can be easily seen that the compressive strength of the geopolymer paste increased from 7.40 MPa, for the mixes with the Na$_2$SiO$_3$/NaOH solution ratio 0.5, to a maximum of 25.30 MPa, for the geopolymer paste samples with the ratio 2.5. The increasing values of the compressive strength of the samples depend mainly on the chemical process in which the geopolymerization takes place. Increasing the Na$_2$SiO$_3$/NaOH solution ratio leads to more SiO$_2$ species therefore more Si-O-Si bond are formed, creating a stronger material [7].

![Figure 1. Influence of the Na2SiO3/NaOH solution ratio on the compressive strength of the geopolymer paste.](image)

In order to obtain a good geopolymerization process the molar constituents of the mixtures have to be well known (table 3). Previous research have indicated that the effect of the Na$_2$O/SiO$_2$, SiO$_2$/Al$_2$O$_3$ and H$_2$O/Na$_2$O ratios have an important effect on the compressive strength of the alkali-activated fly ash-based geopolymer pastes [14].

| Mix/ Ratio | Na$_2$O/ SiO$_2$ | SiO$_2$/ Al$_2$O$_3$ | H$_2$O/ Na$_2$O |
|------------|-----------------|----------------------|----------------|
| Mix 1 Ratio 0.5 | 0.16 | 3.801 | 12.742 |
| Mix 2 Ratio 1.0 | 0.146 | 3.964 | 12.734 |
| Mix 3 Ratio 1.5 | 0.137 | 4.061 | 12.729 |
| Mix 4 Ratio 2.0 | 0.132 | 4.126 | 12.725 |
| Mix 5 Ratio 2.5 | 0.128 | 4.172 | 12.722 |

Table 3. Molar constituents of the mixtures.
Studies indicate that the mechanical strength of the alkali-activated fly ash-based geopolymer paste increases with the decrease of the Na$_2$O/SiO$_2$ ratio [18]. Compressive strength results obtained on geopolymer paste produced using Romanian local raw materials (figure 2) are agreed with the results held in the literature [9]. Water also has an important influence on the mechanical strength of the geopolymer paste because it helps both the destruction of the solid particles in fly ash and to achieve the necessary workability. Despite previous research [7] where the compressive strength of the alkali-activated fly ash-based geopolymer paste increased as the H$_2$O/Na$_2$O ratio increased, for the present study it can be seen (table 3) that although the ratio slightly decreased there was an important increase in the compressive strength of the samples.

![Figure 2. Effect of the molar Na$_2$O/SiO$_2$ ratio on the compressive strength of geopolymer paste.](image)

4. Conclusions
By keeping the fly ash/alkaline liquid mixing ratio constant and changing the Na$_2$SiO$_3$/NaOH solution ratio it was possible to study the effect of the alkaline activator ratio influence on the compressive strength of the alkali-activated fly ash-based geopolymer paste produced using Romanian local source materials and to investigate the geopolymerization process. Preliminary results show that increasing the sodium silicate solution content in the alkaline activator significantly increases the compressive strength of the geopolymer paste. The sodium silicate solution provides extra silicon (Si) species, which play an important role in the geopolymerization process.

Based on the presented results, it can be seen that the mix design of the alkali-activated fly ash-based geopolymer paste is an important factor in obtaining the proposed mechanical properties of the material. Different parameters affecting the compressive strength of the geopolymer paste need to be understood and carefully studied. The effect of alkaline activator ratio on the compressive strength is one of the most important factors affecting the material.

Results obtained on alkali-activated fly ash-based geopolymer paste produced using Romanian local source materials create opportunities for further research to continue. The aim of this research was both to produce alkali-activated fly ash-based geopolymer paste using Romanian source materials and to study the effect of the alkaline activator ratio on the compressive strength. Further research is still in progress and the directions are to produce more alkali-activated fly ash-based geopolymer pastes, geopolymer mortars and geopolymer concrete and study the influence of different parameters on the compressive strength of this material.
References

[1] Davidovits J 1994 High-Alkali Cements for 21st Century Concretes. In Concrete Technology, Past, Present and Future Proceeding of V. Mohan Malhotra Symposium, Editor: P. Kumar Metha ACI SP-144 383-397

[2] Davidovits J 1988 Geopolymer chemistry and properties. In: Proceeding of 1988 geopolymer conference I 25-48

[3] Rangan B V 2008 Fly Ash-Based Geopolymer Concrete Your Building Administrator 2

[4] Silverstrim T, Martin J and Rostami H 1988 Geopolymeric Fly Ash Cement. In: Proceeding of 1988 geopolymer conference I 107-108

[5] Abdullah M, Kamarudin H, Nizar I K, Sandu A V, Binhussain M, Zarina Y and Rafiza A R 2013 In: Rev. Chim 64(4) 382-387

[6] Lăzărescu A V 2017 Proiectarea și testarea rețetelor de beton geopolimer cu cenușă de termocentrală PhD. Research Report Technical University of Cluj-Napoca

[7] Mustafa A M B, Omar A K A, Kareem A and Myint S 2009 Study On The Effect Of Alkaline Activators Ratio In Preparation Of Fly Ash-Based Geopolymer RAMM & ASMP 2009 Conference Paper

[8] Hardjito D, Wallah S E, Sumajouw D M J and Rangan B V 2004 ACI Material Journal 101 467-472

[9] Hardjito D and Rangan B V 2005 Development and properties of low-calcium fly ash-based geopolymers concrete. Research report GC1, Faculty of Engineering Curtin University of Technology, Perth, Australia

[10] Davidovits J 1999 Chemistry of geopolymeric system, terminology Geopolymer '99 International Conference, France 9-44

[11] Gokhale C 2001 The immobilization of inorganic waste through geopolymerization University of Stellenbosch

[12] Lloyd R R and Van Deventer J S J 2005 The microstructure of geopolymers synthesized from industrial waste 1st International Conference on Engineering for Waste Treatment (WastEng), Albi, France

[13] Palomo A, Grutzek M W and Blanco M T 1999 Cem Concr Res 29 1323-1329

[14] Fernandez-Jimenez A and Palomo A 2003 Fuel 82 2259-2265

[15] Criado M, Palomo A and Fernandez-Jimenez A 2005 Fuel 84 2048-205.

[16] Davidovits J 2008 Hand book of Geopolymer Chemistry and Applications 2 277-278

[17] Davidovits J 1994 Properties of geopolymer cements Alkaline Cements and Concretes, Kiev, Ukraine 131-149.

[18] Kirschner A and Harmuth H 2004 Cerma Silic 48 117-120

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