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New Generation of  
Construction Materials

Edited by  
**Marijana Serdar  
Nina Štirmer  
John Provis**

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Materials, Systems and Structures  
(SMSS 2019)**  
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## **IMPROVING MECHANICAL CHARACTERISTICS OF LIGHTWEIGHT GEOPOLYMERS THROUGH MECHANICAL ACTIVATION OF FLY ASH**

**Tijana G. Ivanović (1), Miroslav M. Komljenović (1), Nataša M. Džunuzović (1), Violeta M. Nikolić (1) and Gordana G. Tanasijević (1)**

(1) Institute for Multidisciplinary Research, University of Belgrade, Serbia

### **Abstract**

The present paper investigated the influence of mechanical activation of fly ash and various parameters, such as curing temperature and concentration of foaming agent (Al powder), on physical-mechanical characteristics of lightweight geopolymers. Prior to alkali activation, fly ash was mechanically activated in a high energy planetary ball mill. Lightweight geopolymers were obtained by mixing the mechanically activated fly ash with various amounts of Al powder and sodium silicate solution ( $\text{SiO}_2/\text{Na}_2\text{O}$  mass ratio of 1.5). Geopolymer paste samples were cured covered in plastic either at room temperature for 28 days or at elevated temperature (95 °C) for 4 hours. It was observed that the mechanical activation of fly ash resulted in a drastic increase of geopolymer compressive strength regardless of curing conditions, preserving the lightweight properties at the same time. The lightweight geopolymers based on mechanically activated fly ash might be used both in constructive and insulating applications.

**Key words:** mechanical activation, lightweight geopolymers, compressive strength, aluminum powder

### **1. INTRODUCTION**

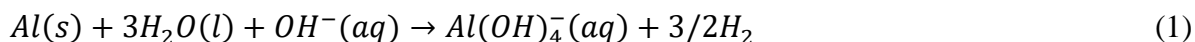
Alkali activated materials (AAMs) represent a group of inorganic binding materials, formed by chemical (alkali) activation of aluminosilicate and calcium silicate material with concentrated alkali activator solution. Research in the field of AAMs has shown that binding materials based on alkali-activated industrial waste materials and/or by products, such as fly ash (FA) from thermal power plants and blast furnace slag from pig iron production, have great potential especially in terms of valorization of different types of industrial waste materials and/or by product [1-3]. It is well known that these binding materials show properties comparable with the properties of commercial binders based on Ordinary Portland Cement (OPC) including good flexural and compressive strength, good durability in aggressive environments, high temperature resistance, etc. Therefore, the main application of

AAMs is in the industry of building materials, as an alternative for concrete and binders based on OPC. Depending on the selection of the initial materials and synthesis conditions, AAMs can show improved properties compared to binders based on OPC.

Lightweight geopolymers represent relatively new research field within research of alkali activated materials. For creating porosity during their synthesis various chemical (pore forming or foaming) agents such as aluminum (Al) powder [4-8] or hydrogen peroxide [9-14] can be used. Chemical agents react in an alkaline environment releasing the gases generating bubbles i.e. creating porous structure, whereby the materials with low density, low thermal conductivity and good high-temperature resistance are obtained. The advantage of lightweight geopolymers over conventional thermal insulating materials based on OPC primarily is in less detrimental environmental impact, i.e. industrial waste recycling and lower carbon dioxide emission. Reducing carbon dioxide emissions by using appropriately-selected materials is of critical importance. Besides that, according to some recently published research data [15, 16], lightweight geopolymers could show better properties comparing to conventional thermal insulating and high-temperature resistant materials.

Fly ash (FA) is generated as an industrial by product in the process of coal combustion in thermal power plants. The mechanical activation was proved to be quite successful method for FA reactivity improvement [17], as well as for enhancing the adsorptive properties of FA [18], the improvement of thermal stability of FA based geopolymers [19], and for the stabilization/solidification of hazardous waste [20]. The changes induced in material during the mechanical activation process include not only the obvious reduction of particle size, but also the changes in particle morphology, increase in specific surface area, structural defects, as well as the decrease in crystallinity degree, implying significant structural rearrangement [21, 22]. This paper investigated the influence of mechanical activation of fly ash and various synthesis parameters on physical-mechanical characteristics of lightweight geopolymers. The most important outcome of the use of mechanically activated fly ash for the geopolymer synthesis was the increase of FA reactivity and consequently the improvement of mechanical strength of ensuing geopolymers [17].

For lightweight geopolymers synthesis aluminum powder was used as a foaming agent. Chemical foaming agents react in an alkaline environment releasing the gases generating bubbles i.e. creating porous structure, whereby the materials with low density and low thermal conductivity were obtained. Regarding the reactive metal powders, these react with water and hydroxide in an alkaline environment, liberating bubbles of hydrogen and forming hydrolyzed metal complexes [23]. This reaction takes place according to the following equation:



The  $H_2$  gas produced leads to expansion of the paste, provided the latter possesses a suitable consistency to entrap it.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Fly ash from Serbian thermal power plant “Nikola Tesla”, Unit B, Obrenovac, was used as a solid precursor (as-received FA). FA sample used in this study belongs to the ASTM

Class F [24]. Sodium silicate solution (so-called water glass) was used as an alkaline activator (“Galenika-Magmasil”, Serbia: 26.25 % SiO<sub>2</sub>, 13.60 % Na<sub>2</sub>O, 60.15 % H<sub>2</sub>O). Modulus (n) of sodium silicate solution (SiO<sub>2</sub>/Na<sub>2</sub>O mass ratio) was modified by adding NaOH (VWR, Germany, p.a. 99 %).

### **2.1.1 Mechanical activation of fly ash**

Mechanical activation of fly ash was carried out in planetary ball mill (Fritch Pulverisette type 05 102, Germany). The diameter size of stainless steel balls was 13 mm, while the FA to ball mass ratio was 1:20, according to the previously optimized procedure [25]. FA samples were mechanically activated in an air atmosphere for 15 min, at maximum speed of 380 rpm.

### **2.1.2 Lightweight geopolymer synthesis**

Lightweight geopolymer pastes were prepared by adding the activator solution to water and then mixing the solution with FA or MFA and aluminum powder for 2 minutes. Modulus of sodium silicate solution used as alkaline activator in this study was 1.5, while the concentration of the activator was 10% of Na<sub>2</sub>O with respect to the dry FA or MFA mass. These values of modulus and concentration were selected as optimum values for alkali activation reaction, based on our previous research [26]. Various amount of Al powder was used (0.1 % or 0.5 % with respect to the FA or MFA mass). Dimensions of the paste samples were approximately 160×40×40 mm and the samples were cured covered in plastic either at room temperature for 28 days or at elevated temperature (95 °C) for 4 hours.

## **2.2 Methods**

The compressive and flexural strength of the geopolymer pastes were tested according to the SRPS EN 196–1 standard, using “Controls-Advantest 9” (Italy).

The water absorption test was also carried out in this study. Principally, the test consists of two major steps. First, the geopolymers specimens are immersed in water until the change in mass during 24 hours is less than 0.1 %. The obtained saturated mass is called M<sub>s</sub>. Afterwards; the specimens are dried in a ventilated oven at a temperature of 105 °C until the difference in mass during 24 hours is less than 0.1 %. The dry mass is called M<sub>D</sub>. The water absorption by immersion (W) is expressed as the water uptake relative to the dry mass:

$$W = [(M_s - M_D)/M_D] * 100 \quad (2)$$

## **3. RESULTS**

### **3.1 The influence of mechanical activation of FA and concentration of foaming agent on mechanical strength and density of geopolymers**

The mechanical activation can drastically enhance the FA reactivity in the process of geopolymerization, which was previously established by the exceptional increase of compressive strength of geopolymers based on mechanically activated FA [17]. The results presented here are confirming the previous findings.

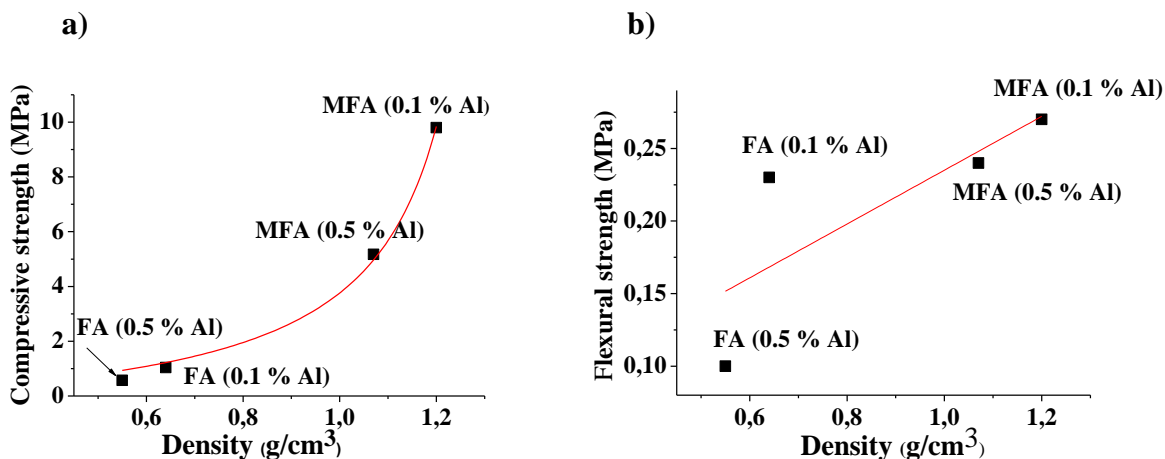


Figure 1: Correlation of FA and MFA-based lightweight geopolymers strength and density: a) compressive strength and b) flexural strength.

The mechanical strength of lightweight geopolymers based on as-received FA after curing at 95 °C for 4 h, was very low in all cases (Figures 1a and b). In sharp contrast to that, the compressive strength of geopolymers based on MFA (developed under the same curing conditions), increased 8 fold when the content of Al powder was 0.1 %. In the case of 0.5 % of Al powder added, the MFA-based geopolymer samples showed both higher density and compressive strength (increased 5 fold), compared to the lightweight geopolymers based on as-received FA.

### 3.2 The influence of mechanical activation of FA and concentration of foaming agent on water absorption of geopolymers

The results of water absorption by immersion of FA and MFA-based lightweight geopolymers are shown in Figure 3. The lowest water absorption by immersion (8.3 %) was noticed for the sample FA (0.1% Al), while the highest water absorption (47.7 %) was for the sample MFA (0.5% Al). As it can be seen in Figure 2, the mechanical activation had a significant influence both on density and water absorption of lightweight FA-based geopolymers. On the other hand, the concentration of Al powder added also had an effect on the water absorption of lightweight geopolymers i.e. the higher concentration of Al powder added is connected with the higher water absorption of lightweight geopolymers, which is in an agreement with the published data [4 - 8]. This effect was more pronounced in the case of MFA.

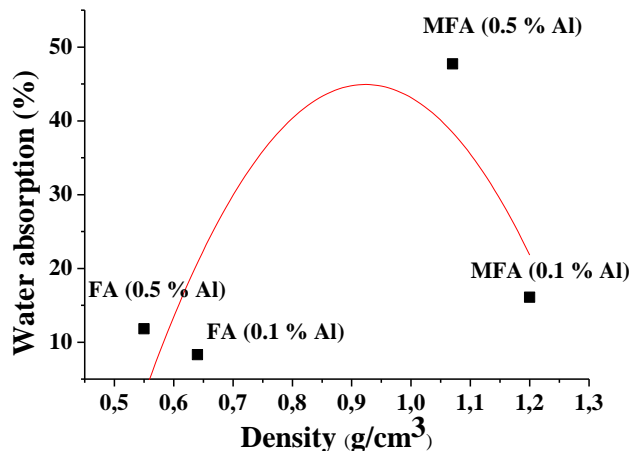


Figure 2: Water absorption of FA and MFA-based lightweight geopolymers versus density.

### 3.3. Prediction of thermal conductivity of mechanically activated geopolymers

As it can be seen from the literature data given in Figure 3, the thermal conductivity of AAMs can be correlated with the materials' density [12, 13, 16, 27 - 30].

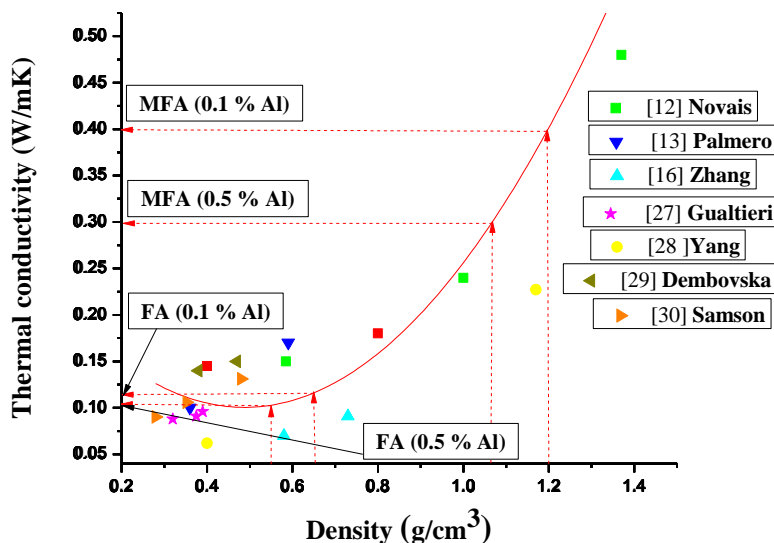


Figure 3: Thermal conductivity versus density of lightweight geopolymers (literature data).

According to the literature data given in Figure 3 and in agreement with the low densities reached, the as-received FA-based lightweight geopolymers produced most probably possess low thermal conductivity (0.10-0.12 W/mK). On the other hand, it is estimated that the values of thermal conductivity of mechanically activated FA-based lightweight geopolymers might be approximately 0.40 W/mK for MFA (0.1 % Al) and 0.30 W/mK for MFA (0.5 % Al) samples. It is also possible to further optimize the thermal conductivity of FA-based lightweight geopolymers, for example by mixing the MFA and as-received FA. This mixing



will lead to density and strength reduction of geopolymers in comparison to the MFA-based lightweight geopolymers, as well as to lower thermal conductivity.

### 3.4. The influence of concentration of foaming agent and curing conditions on physical-mechanical characteristics of MFA-based geopolymers

Both mechanical strength and density are crucial properties for application of lightweight building materials in constructions, either as porous building blocks or insulating materials. The mechanical strength of lightweight geopolymers was directly affected by the amount of foaming agent. The compressive strength of samples cured for 4 h at 95 °C decreased from 9.80 MPa down to 5.16 MPa when Al content increased from 0.1 to 0.5 mass %. The compressive strength of samples cured for 28 days at 20 °C decreased from 6.14 MPa down to 5.45 MPa when Al content increased from 0.1 to 0.5 mass%. This trend could be directly translated into a relation between density and compressive strength, as presented in Figure 4.

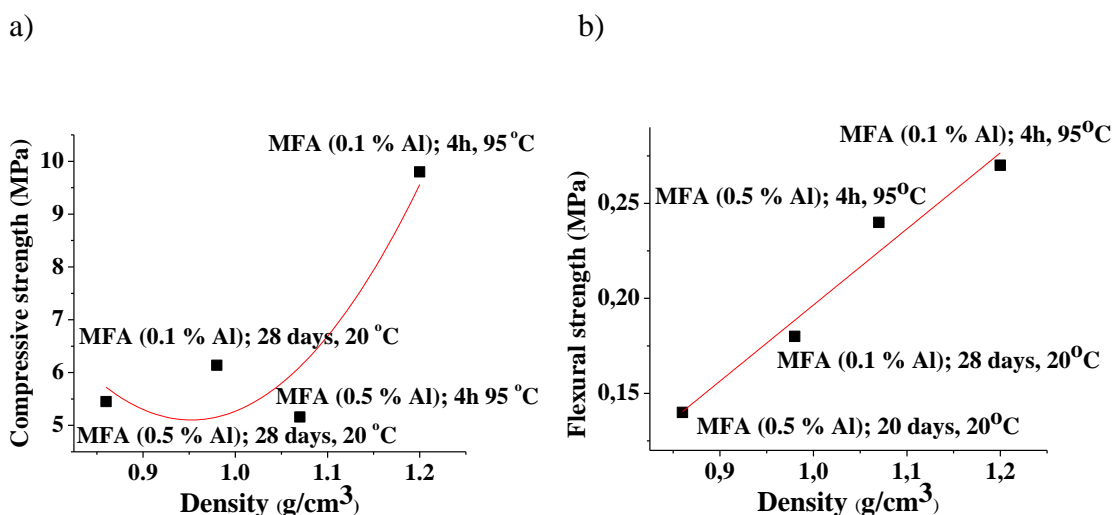


Figure 4: Strength of MFA-based lightweight geopolymers versus density for different curing conditions and Al concentrations: a) compressive strength and b) flexural strength.

As presented above, the sample MFA with 0.1 % of Al powder cured for 4 h at 95 °C showed a higher density (22.4 %), but also 60 % higher compressive strength compared to the sample MFA with 0.1 % of Al powder cured for 28 days at 20 °C. Curing conditions had a significantly lower impact for the samples with higher content of Al powder (0.5 %). In that case the sample MFA cured 4 h at 95 °C showed a higher density (24.4 %), and slightly higher compressive strength (5.62 %) compared to the sample MFA cured 28 days at 20 °C.

## 4. CONCLUSION

Lightweight geopolymers were synthesized by alkali activation of as-received fly ash (FA) and mechanically activated fly ash (MFA), with addition of various amounts of foaming agent (Al powder), and under different curing conditions (at room and at elevated temperature).

Mechanical activation of fly ash resulted in a significant improvement of mechanical properties of synthesized geopolymers. Presented results demonstrated that the mechanical

activation of fly ash had a major effect on the compressive strength and density of synthesized lightweight geopolymers, whereby their flexural strength was less influenced. It can be concluded that mechanical activation significantly enhanced FA reactivity in the process of geopolymerization.

On the other hand, the density of the lightweight geopolymers, and consequently the thermal conductivity, is strongly influenced by the dosage of Al powder in all cases. The effects of Al powder strongly depended on the curing conditions. The amount of Al powder had a major effect on the compressive strength of lightweight geopolymers when they were cured at elevated temperature (4h at 90 °C) and minor effect when they were cured at room temperature (28 days at 20 °C).

## ACKNOWLEDGEMENT

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## **PRELIMINARY STUDIES ON BROWN COAL FLY ASH AS A CEMENT REPLACEMENT FOR GEOPOLYMER BRICK APPLICATIONS**

**Muhamed Khodr (1), David Law (1), Chamila Gunasekara (1) and Sujeeva Setunge (1)**

(1) School of Engineering, RMIT University, Australia

### **Abstract**

The continued use of Portland Cement (PC) as the main binder in concrete has raised economic and environmental concerns due to PC production being a pivotal contributor to the growing CO<sub>2</sub> emissions. Thus, research into alternatives using industrial by-products has become well established in recent years, with much attention being focussed on Ground Granulated Blast Furnace (GGBS) and Fly Ash (FA). The studies have shown that 100% Class F FA concrete can produce similar strengths to that achieved by from PC concrete, but unlike Class F FA, Brown Coal Fly Ash (BC FA) has high Sulphur and Calcium content and low aluminosilicate content which are detrimental to the strength that can be achieved. However, the opportunity may exist to use BC FA as a geopolymeric material for low strength application such as geopolymer concrete bricks. This paper reports a preliminary study conducted to investigate the feasibility of using Yallourn BC FA for geopolymer concrete brick production. The physical and chemical characteristics of the BC FA have been identified, and an optimum mix design has been generated by varying both the activator modulus (AM) and the Na<sub>2</sub>O dosage. Compressive strength results were obtained at 7, 14 and 28 day intervals. Moreover, a standard flow table test was conducted for each mix design to understand the impact of flowability of this new material, which is essential in concrete casting.

**Keywords:** Brick, Brown-Coal-Fly-Ash, Compressive-strength. Flowability, Environmental-friendly-material, Geopolymer, Mix-design optimisation

### **1. INTRODUCTION**

Cement production is linked to environmental issues such as high carbon emissions and substantial energy consumption. It had been forecast that cement production worldwide was expected to increase from 2.54 to 4.38 billion tonnes annually from 2006 to 2050, but according to Schneider et al. [1] the projected levels have already been surpassed with current production reaching 4.6 billion tonnes of cement. An alternative to cement are alkali activated materials