Mechanical activation of two different types of fly ash and their effect on alkali activation.

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Abstract. The article aim is to analyze the influence of mechanical activation of a fly ash, with different proportion of mechanically activated and not mechanically activated material on alkali activation. The paper describes fly ash based geopolymers and their mechanical properties. Fly ashes were mixed in four different ratios with mechanically activated fly ash. Activation solution was constant in all specimens. Compressive and flexural strengths of the hardened product were tested after 7 and 28 days of the storage in laboratory conditions and samples were cured after activation in hot air chamber for 6 hours in 80°C temperature. The results show how mechanical activation of materials affects their strengths with highest amount achieved was 44 MPa.

1. Introduction
Fly ash is a by-product derived from coal combustion in thermal power plants and heating plants. Fly ash is a fine powder containing predominantly spherical vitreous particles originated from the combustion of finely ground coal. It is considered as a material that predominantly contains SiO₂ and Al₂O₃. These properties make it an attractive raw material for secondary industrial processing [1]. Fly ash as an excellent source of aluminosilicate material is a raw material for production of alkali-activated binders known as geopolymers. Geopolymers exhibit many excellent properties, such as high compressive strength, good acid resistance, low shrinkage, low creep and fire resistance [2]. They are generally synthesized by mixing aluminosilicate-reactive material with strong alkali solutions. Alkali activating solution is important for the dissolution of Si and Al to form geopolymer precursors and finally aluminosilicate material [3]. Geopolymers are obtained from the chemical reaction of aluminosilicate oxides with sodium silicate solutions in a highly alkaline environment. As an alkaliactivating solution, a strongly alkaline aqueous solution of sodium or potassium hydroxide is most commonly used [3, 4]. Under a strong alkali solution, aluminosilicate-reactive materials dissolve and form free SiO₄ and AlO₄ tetrahedral units. With the progress of reaction, water is gradually removed, and the SiO₄ and AlO₄ tetrahedral clusters are linked to yield polymeric precursors through the sharing of all oxygen atoms between two tetrahedral units, thereby forming amorphous geopolymers [5].

The most commonly used fly ash for geopolymer production is Class F fly ash with low content of calcium. However, more and more researches are found, in which fluidized bed combustion fly ashes with high content of calcium are used for geopolymer production. Our research is focused on fly ashes without industrial utilization, deposited in landfills. The main reason why these fly ashes have no industrial applications is their high loss on ignition (LOI) that in some types of fly ash is almost 25%.
However, based on previous research [6], it was shown that high content of loss on ignition is no limitation for utilization of fly ashes in alkali activation. The geopolymers now represent a new group of inorganic substances, because they have a significant environmental and energy potential. They belong to a group of the inorganic polymer covalently bound macromolecules with the chain consisting of -Si-O-Al-O-.

The geopolymers find a broad range of applications in the field of transportation, emergency repairs, metallurgy, coating, membrane materials, and nuclear waste disposal. Despite a significant commercial and technological potential geopolymers’ easy-brittle character limits their extensive applications where great efforts are made to overcome such a disadvantage. Numerous studies are dedicated to optimize the strength of geopolymer products and to understand the mechanism of the geopolymerization [7–10]. Recently, there have been many studies on the mechanical activation (MA) of solids for new materials or processes. The purpose of MA is to change the reactivity or physical-chemical properties of a solid. In particular, solid reactivity is induced by mechanical energy or a combination of mechanical and chemical effects through shearing, compression, extension, bending, and impact. Kumar et al. showed that mechanically activated slag could achieve complete hydration without any chemical addition, and MA had a positive effect on the early strength development of the cement [11, 12].

In the last years, different studies have investigated the possibility of using different types of wastes mixed with fly ash or slag as raw materials. The selection of the materials to create the geopolymers depends on several factors such as availability, disposal urgency, difficulty for recycling and final applications [13].

The aim of presented contribution is to point out to possibility of utilization of seemingly no utilisable by-products of coal combustion for production of alkali-activated materials – geopolymers.

2. Materials and methods

The materials used for the alkali activation were two types of fly ash (TO, TF). Fly ash TO is derived from combustion of black coal in pulverized coal boilers obtained from an upper layer of the coal-ash sludge bed. Fly ash TF is derived from the same combustion process as fly ash TO, except that it is obtained from a fly ash hopper.

Chemical composition of the fly ashes determined by X-ray fluorescence (XRF) spectrometer Spektro X-lab 2000 is shown in table 1. Phase composition of fly ashes performed using the X-ray diffractometer D8 Bruker 2 theta / 2 theta using CuKα radiation is shown in figure 1. Figure 2 shows morphology of fly ash particles performed by scanning electron microscopy (SEM) using the device MIRA 3 FE-SEM microscope (TESCAN, Czech Republic) equipped with a high-resolution cathode (Schottky field emitter) and with three-lens Wide Field Optics™ design.

| Table 1. Chemical composition of fly ashes used in alkali activation. |
|---------------------------------------------------------------|
| Type of fly ash | Al₂O₃ | SiO₂ | CaO | Fe₂O₃ | Na₂O | LOI   |
| TO              | 14.55 | 32.01| 1.75| 7.55  | 0.23 | 24.80 |
| TF              | 24.01 | 44.27| 2.36| 9.67  | 0.90 | 19.81 |
Based on results from performed analysis of fly ashes it can be concluded that morphology and phase composition of fly ashes are affected by combustion method, at which the fly ash is produced. The combustion of coal in pulverized coal boilers taking place at combustion temperature 1400–1700°C results in a melting of particles of combusted coal. Therefore, particles of fly ash have spherical shape and fly ash contains high content of vitreous phase (halo indicated between 2-Theta = 20°–35°).

Minority crystalline phase of used fly ashes is mainly composed of quartz, mullite, hematite, magnetite, maghemite and graphite.

Fly ashes TF and TO contain different phase composition, even though they are derived from the same process combustion. Fly ash TF contains despite of quartz also graphite and iron in the form of calcium iron oxide. Fly ash TO contains no graphite content and iron in three different forms as hematite, magnetite, and maghemite. Fluidized bed combustion fly ashes contain calcium compounds.
**Figure 2.** SEM patterns of fly ashes used in alkali activation (upper row TF, bottom row TO).

**Figure 3.** Particle size distribution of fly ashes before (TF, TO) and after milling (TFM, TOM).
Grain size analysis revealed that about 55% particles of fly ash TF, 70% of TO is passing through a sieve size of 45 microns. After mechanical activation (MA) it is about 75% particles of fly ash TF and 95% of TO, is passing through a sieve size of 45 microns. Particle size distribution before and after MA is shown in figure 3.

Milling was performed in laboratory ball mill with steel balls with different diameters. The laboratory mill used for mechanical activation had volume 30 dm$^3$ and was filled with steel ball with diameters ranging from 2 to 10 cm. Material for mechanical activation with steel balls formed 60% of mill volume. Revolution was adjusted to 90 per minute. The material was homogenised before alkali activation. No other treatment was applied to the material.

The activation solution was prepared by mixing solid NaOH pellets with sodium water glass and water. The sodium water glass from the Kittfort Praha Co. with the density of 1.328–1.378 g/cm$^3$ was used. It contains 36–38% Na$_2$SiO$_3$ and the molar ratio of SiO$_2$/Na$_2$O is 3.2–3.5. The solid NaOH with the density of 2.13 g/cm$^3$ was obtained from Kittfort Praha Co. containing at least 97–99.5% of NaOH.

The fly ash mixture samples with different amount of mechanically activated FA were prepared. Activation solution used has 8% of Na$_2$O, 1.25 SiO$_2$/Na$_2$O ratio and water-to-fly ash ratio was adjusted to 0.3. Material for alkali activation was created by mixing pure FA with 0, 50, 75 and 100% addition of mechanically activated FA.

FA and MAFA mixture were stirred with the activation solution for 10 minutes, until a creation of a homogenous mixture. The mixture was then filled into prismatic molds with the dimensions 40 x 40 x 160 mm and compacted on the vibration table VSB-40. The pastes were cured in a hot air drying chamber at 80°C for 6 hours. Thereafter, the samples were removed from the molds, marked, and stored in laboratory conditions till the moment of the strength test. The values of compressive and flexural strengths were determined after 7 and 28 days according to the Slovak Standard STN EN 12390-3.

3. Results and discussion

Properties and a composition of material play an important role in the alkali activation. The samples were synthetized from two different types of FA with an addition of MAFA by several proportions. The effect of mechanical activation on final compressive strength and flexural strengths as examined. The resulting strengths from TF fly ash are shown in figures 4 and 5.

![Figure 4. Flexural strengths of TF fly ash mixtures.](image-url)
Figure 5. Compressive strengths of TF fly ash mixtures.

The flexural strength results show that maximum strength of all samples is not achieved in the mixture prepared with 100% mechanically activated fly ash, but with only 75% of mechanically activated FA. In all samples after 28 days the flexural strengths were lower from their first flexural strengths. In contrary compressive strengths results show that geopolymer mortar created only by mechanically activated fly ash has the highest strength 44 MPa after 28 days. All samples have the highest compressive strength values after 28 days.

TO based geopolymers mortar showed a little different result. These results are depicted in figures 6 and 7.

Figure 6. Flexural strengths of TO fly ash mixtures.
Flexural strengths were downgrading with higher amount of the mechanically activated fly ash used in geopolymer mortar. Common thing in these two fly ashes was that both have lower strengths after 28 days. Compressive strengths were also lower in comparison with TF mixtures. In this case the results were similar in all mixtures so we can conclude that the amount of the mechanically activated fly ash in this case is not that relevant and is not suitable or needed with TO fly ash.

Results of the previous work [6] found that increase in content of particles higher than 45 µm by grinding results in increase of mechanical strength alkali-activated fly ashes. Higher mechanical strength is result of improved dissolution of fly ash into alkaline liquid following a decrease particle size (an increase surface area); leading to improved polymerization and hardening of the geopolymer phase, therefore higher compressive strength is achieved [14]. Comparing strength of alkali-activated fly ashes TF and TO obtained by the same combustion process is found higher compressive strength of alkali-activated fly ash TF and higher flexural strength of alkali-activated fly ash TO. Compared to fly ash TO, fly ash TF contains higher content of aluminosilicate component and higher content of soluble phase that can explain its higher compressive strength. Content of aluminosilicate component in sources material is important factor because the silica and alumina are the main precursors for the geopolymeric reaction. Aluminosilicate materials with the higher extent of dissolution developed higher compressive strength after geopolymerization [3].

4. Conclusions
Fly ash from coal combustion is a valuable by-product that has still no complete industrial utilization. Therefore, it is necessary to find further possibilities of its utilization. Fly ash contains the high content of aluminosilicate component; therefore, alkali activation is seen to be an applicable method for its utilization.

In this experimental programme, fly ash based geopolymer mortar samples were casted by varying the proportion of the mechanically activated fly ash such as 0%, 50%, 75% and 100% by weight of fly ash.

Mechanical activation in these types of fly ash had different effect on final strengths. In the first type strengths were little bit enhanced after the mechanical activation. The second type of geopolymers mortars showed that mechanical activation is not necessary and all samples had approximately same strengths.

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