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Improving reactivity of fly ash and properties of ensuing geopolymers through mechanical activation

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HIGHLIGHTS

- Effects of mechanical activation of fly ash on properties of fly ash and geopolymers were studied.
- Mechanical activation was conducted in ball mill.
- Mechanical activation resulted in exceptional increase of compressive strength.
- Strength increase was related to the physical and structural changes of fly ash.

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ABSTRACT

This paper investigated the effects of mechanical activation of fly ash (FA) from thermal power plants on physical–mechanical properties and structure of geopolymers. FA from different power plants in Serbia was mechanically activated in planetary ball mill. Geopolymerization was conducted by use of sodium silicate (water glass) at elevated temperature (95 °C) for 4 h. It was observed that mechanical activation of FA for 15 min resulted in drastic increase of geopolymer compressive strength (in all cases >1000%). High strength values were associated with improved FA reactivity obtained mainly by the reduction in particle size and reduced water/binder ratio.

1. Introduction

Fly ash is generated as an industrial waste material in the process of coal combustion in thermal power plants. Relatively small quantities of this material are recycled, while the rest is usually landfilled. The negative impact that continuous disposal of huge amounts of FA has on the environment is well known and thoroughly discussed [1–5]. In recent years, there is an ongoing demand worldwide for the use of large quantities of FA as an aluminosilicate raw material and not just waste. The number of intensive research on the characterization, processing and various aspects of the implementation of FA is just indicative enough for the global interest that exists to this material. The possibility of utilization of large quantities of FA is the most conspicuous in the area of cement and concrete, where FA (along with other industrial waste) is being consumed as a supplementary cementitious material for many years [6–9]. Over the last few decades, a new group of binding materials, geopolymers, has emerged as a result of alkaline activation of aluminosilicate materials such as metakaoline and FA. Besides enabling the utilization of large amounts of FA, geopolymers based on this material represent quite attractive binding material, given the high mechanical strength they can develope. Moreover, geopolymer binders based on FA are known of having good resistance to the impact of aggressive environment, good fire resistance, low density and porosity, low shrinkage and low thermal conductivity [10–14]. For the geopolymer synthesis, the presence of amorphous component in FA is of utmost importance. The amorphous component of FA has a binding potential that can be "activated" by alkaline solution, resulting in hardened structure of geopolymer binder. The binding potential of FA amorphous component can also be triggered and "activated" by mechanical activation, which unfolds new possibilities of FA utilization. Mechanical activation is usually carried on by high-energy milling devices. Changes induced in material during the mechanical activation process include reduction in particle size, changes in particle morphology, increase in specific surface area, structural defects, decrease in crystallinity degree, implying structural rearrangement [15–19].

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The most important consequence of transformations that occur in material during the mechanical activation is its enhanced reactivity.

Mechanical activation, as a method which can improve FA reactivity, is often applied for different applications of this material. Improved reactivity is primarily the result of increased particle fineness. Finer particles of FA represent more reactive material even without extra mechanical impulse. It is known that particles below 45 μm, obtained through various methods of separation, tend to improve mechanical strength of mortar when used as a supplementary cementitious material [20–23]. Utilization of mechanically activated FA as a supplementary cementitious material is also well discussed [24–33], and there are reports that, for the same application, FA can be modified also by combination of mechanical and chemical impact [34,35]. In addition to this, mechanical activation of FA is used with the purpose of enhancing the adsorptive properties of FA [36], for the stabilization/solidification of hazardous waste [31], and for the improvement of thermal stability of FA for metal matrix nano composites production [37]. There are reports on synthesis of composite binding materials based on mechanical activation of FA from different industrial sources [38], as well as based on mechanically activated blends of FA and cement kiln dust [39].

Although there are numerous data relating to the mechanical activation of FA, the literature concerning the application of mechanically activated FA for the geopolymer synthesis is rather scarce. The main advantage of using mechanically activated FA in synthesis of geopolymers is the possibility of in-bulk utilization of FA, and not only its specific (finer) fraction. The most prominent work on this subject is conducted by Kumar et al. [24,40–43]. The most important outcome of the use of mechanically activated FA for the geopolymer synthesis is the improvement of mechanical strength. Thereby the experimental parameters may vary in terms of mechanical activation of FA (selection of milling device, the material to media ratio, the duration of mechanical activation) and in terms of alkali activation (nature and concentration of alkali activator and curing conditions of synthesized geopolymers). The selection of milling device proved to be the key parameter for the development of high strength. Kumar et al. managed to obtain higher strength of geopolymer synthesized from FA mechanically activated by a vibration mill, compared to both, the strength of geopolymer synthesized from FA of similar fineness mechanically activated using attrition mill, and strength of geopolymer synthesized from FA of better fineness, but obtained without mechanical activation (air classification of fine fraction) [24,40–43].

According to available literature, the work of Kumar et al. is of special interest in the area of applying mechanical activation in geopolymer technology. However, Kumar et al. conducted mechanical activation of fly ash collected from only one thermal power plant, by using attrition and vibration mills. Furthermore, Kumar et al. mainly used NaOH as an activator solution and the compressive strength was determined only on geopolymer paste samples. To the best of our knowledge, there are no data regarding the strength of mortar of geopolymer based on mechanically activated FA.

The objective of this paper was to expand the existing research and to synthesize the geopolymer mortar based on different conditions of mechanical and alkali activation of fly ash. In this study, four different fly ash samples (from four thermal power plants) were subjected to mechanical activation in the planetary ball mill. The rationale for using planetary ball mill for mechanical activation of fly ash is that up to date, there have been no published data dealing with the synthesis of geopolymer based on FA mechanically activated in planetary ball mill although it is rather accepted technique for valorization of this material [31,32,36,44,45] and has the advantages of being simple, relatively inexpensive, applicable to any class of materials and easily scaled up to large quantities [45]. Alkali activation was carried out by using water glass as an activator and the compressive strength was determined on geopolymer mortar samples. Additionally, the influence of mechanical activation on both, properties of FA utilized and synthesized geopolymers was studied.

2. Materials and methods

2.1. Materials

In this study, FA samples from four thermal power plants (TPPs) from Serbia were used:

1. FA TENT A, TPP "Nikola Tesla", Unit A, Obrenovac.
2. FA TENT B, TPP "Nikola Tesla", Unit B, Obrenovac.
3. FA Kolubara, TPP Kolubara, Veliki Crljani.
4. FA Kostolac, TPP Kostolac B_1, Kostolac.

The results of chemical analysis of FA samples are given in Table 1. All FA samples used in this study belong to class F [46].

Sodium silicate solution (water glass) was used as alkaline activator ("Galenika-Magmasil", Serbia, 26.25% SiO_2, 13.60% Na_2O, 60.15% H_2O). Modulus (n) of sodium silicate solution (SiO_2/Na_2O ratio) was modified by adding NaOH (VWR, Germany, p.a. 99%).

2.2. Experiment design

Experimental research was based on simultaneous investigation of raw FA samples (RFA) and mechanically activated FA samples (MFA) and geopolymers based on RFA/MFA, synthesized under same conditions of alkali activation.

2.2.1. Mechanical activation of FA

Mechanical activation of FA was carried out in planetary ball mill (Fritch Pulverisette type 05 102, Germany). The diameter size of stainless steel balls was 13 mm. FA to ball mass ratio was 1:20. Described milling parameters have been established according to previous experience in the work with the particular equipment used [47].

FA samples were mechanically activated in an air atmosphere for 15, 30, 45 and 60 min, at maximum speed of 380 rev/min. The milling scheme was established in such manner that for each of the milling times specified, a new amount of material was loaded to the mill.

2.2.2. Geopolymer synthesis

2.2.2.1. Geopolymer mortars. Modulus of sodium silicate solution used as alkaline activator in this study was 1.5, while the concentration of the activator was 10% Na_2O content with respect to the FA mass. These values of modulus and concentration were selected as optimum values for alkali activation reaction, based on previous report [48]. Geopolymer mortars were prepared by adding the activator solution to water and then mixing the solution with RFA/MFA and standard sand. FA: sand ratio was 1:3.

Each raw FA required different amount of water to obtain similar mortar consistency. Optimum amount of water for each RFA sample was determined by flow table test (the mortar flow, measured on a flow table was 125 ± 5 mm). Therefore, the water/binder ratio (Table 2) was different for each mortar. Water in water/binder ratio represents the total amount of water in the system (the water from the activator solution + the water added for obtaining the proper consistency), while binder represents the total fly ash mass and the solid part of the activator solution. Relatively high w/b ratio of RFA geopolymer paste and mortar samples is also demonstrated in our previous papers [14,48].

Prior to the synthesis of geopolymer mortars based on MFA, it was taken into consideration that the time interval between mechanical activation and the geopolymer synthesis should not exceed 24 h. Geopolymer mortars based on MFA were all prepared with the same water/binder ratio (Table 2). The water demand was strikingly lower than in the case of mortars prepared from RFA samples. This can be explained by the destruction of unburned carbon particles in FA samples by mechanical activation. It is known that, when FA is used as a substitution for cement, the presence of porous unburned carbon particles influence the higher water demand for standard consistency of mortars [49]. In this study, all the MFA based mortars, after mixing of reactive components, were extremely flowable (as if they had excess of water), but then almost in a matter of minutes showed fast hardening, making the workability of the mixture extremely low. It was possible to determine the optimum water amount by the flow table test only for the mortar based on MFA TENT B. The amount of water determined for MFA TENT B mortar was then kept constant for all other MFA mortars, which eventually highlighted the influence of mechanical activation on the strength development. Additionally, mortar based on RFA TENT B with the same water/binder ratio as in the MFA TENT B mortar