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Control of geopolymer properties by grinding of land filled fly ash

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ABSTRACT

This paper is focused on the investigation of a land filled Hungarian fly ash (Tiszaújváros dumpsite) as a main component of geopolymer. After determination of the fly ash properties such as particle size distribution, moisture content, real and bulk density and specific surface area, mechanical activation by fine grinding of the fly ash sample was performed in laboratory scale ball mill, vibratory mill and stirred media mill in order to improve its reactivity. Grinding kinetics was determined in each mill. The geopolymer cylindrical specimens were prepared and their uniaxial compressive strength was measured. The structure of the fly ash and the geopolymer was monitored by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD); furthermore, the morphology was examined using optical microscopy and Scanning Electron Microscopy (SEM). Finally, Isothermal Conduction Calorimetry (ICC) measurements were carried out in order to determine the reactivity of the mechanically activated fly ash samples. As a result of the investigation, the relationship between the grinding process, the ground material properties and the geopolymer characteristics was established. It was found that the strength of the specimen strongly depends on the grinding conditions, i.e. type of mill, residence time.

1. Introduction

Geopolymers are amorphous alumino silicates which can be produced by the reaction between silica and alumino silicate in alkaline medium (NaOH and/or KOH) at ambient or elevated (30–100 °C) temperature. Due to its simple, energy efficient and eco-friendly production method, excellent durability and good mechanical property geopolymers can replace conventional materials from low tech application (building industry, waste immobilization) to high tech industry (ceramics with special properties, composites). Every material is suitable for geopolymer production which contains silica and alumina bearing phases, like primary (kaolinite, illite, …) (Xu and Van Deventer, 2000) or secondary (fly ash, steel slag, red mud, etc) raw materials (Komintsas and Zaharaki, 2007; Phair and Van Deventer, 2002).

At the beginning in the 1950s Glukhovsky (1959) developed an alkali activated system in Ukraine. The system contains calcium silicate hydrated (CSH) and alumino silicate phases which had been used for the construction of a high building in Russia. Glukhovsky was the first who assumed that geological process of some volcanic rock transformation to zeolites occurs during formation of sedimentary rocks at low temperature and pressure. This process can be used for modeling cementitious systems. By the controlled synthesis of alkali alumino silicate minerals an artificial rock phase composited material with long durability can be produced. These alkali aluminosilicate cementitious systems were first called soil silicates (Komintsas and Zaharaki, 2007).

Davidovits in 1972 coined the term geopolymers for three dimensional aluminosilicates formed from naturally occurring aluminosilicates in short time at low pressure and temperature (Komintsas and Zaharaki, 2007; Davidovits, 1999).

Fly ash is a potential raw material for geopolymers, thanks to the presence of SiO_2 and Al_2O_3 as the main components (Davidovits, 2011). The limiting factor which obstructs the use of fly ash for geopolymerisation is its low reactivity. The reactivity of fly ash depends on its particle size distribution and the amount and composition of glassy phase (Kumar and Kumar, 2011; R. Kumar et al., 2007; S. Kumar et al., 2007; Temuujin et al., 2009; Mucsi et al., 2010, 2013c). Low reactivity of fly ash results in slow binding and early strength development. Many times the dissolution of fly ash did not finish before the final hardened structure was formed. It has been proven that calcined materials like granulated blast furnace slag, fly ash and metakaolin (which are mainly amorphous) has higher reactivity during geopolymerisation reaction unlike uncalcined materials (Komintsas and Zaharaki, 2007). It can be explained that calcination activates materials from crystalline to amorphous structure and extra energy stored in them (Komintsas and Zaharaki, 2007).

Additionally, the activation of fly ash can be realized by grinding in several types of mills. Mechanical activation through ultrafine milling

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is an effective procedure where an improvement in technological processes can be attained via a combination of several bulk and surface effects, which influence the properties of applied minerals (Baláž, 2000; Juhász and Opoczky, 1990). The primary effect of mechanical activation is changes in a great number of physicochemical properties of a particular system. During mechanical activation, the crystal structure of a mineral usually becomes disordered and the generation of defects or other metastable forms can be registered (Baláž and Achimovicová, 2006; Baláz et al., 2010).

Mechanical activation provides an opportunity to alter the bulk and surface reactivity of solid materials without altering the chemical composition of material (Juhász and Opoczky, 1990). Kumar et al. (2005) proved that addition the mechanical activated slag to clinker and replacing clinker by ground slag can reach better compressive strength and better hydration reaction, or the complete self hydration of activated slag can be reached. Several research groups are dealing with the mechanical activation effect of raw materials on the geopolymerisation worldwide.

Investigations carried out by Kumar and Kumar (2011) used mainly high energy density mills, such as vibratory and stirred media mill. It was revealed that beside the particle size distribution or the specific surface area the reactivity depended on the mill type used for the mechanical activation of the raw material. Material with the same fineness activated in different type of mill resulted in different mechanical and structural properties of geopolymer. The effect of mechanical activation of fly ash on geopolymers was investigated also by Temuujin et al. (2003, 2009), MacKenzie et al. (2007, 2008), Hounsi et al. (2013), Mucsi et al. (2010, 2013b, 2013c).

Somna et al. (2011) studied NaOH-activated ground fly ash geopolymers, cured at room temperature. Ground fly ash with a median particle size of 10.5 μm, was used as raw material mixed with NaOH as an alkali activator. Results indicated that ground fly ash gave higher strength geopolymer paste compared to original fly ash. The compressive strengths at 28 days of 20.0–23.0 MPa were obtained.

Aydın et al. (2010) showed that grinding process of fly ash improved the mechanical properties of cement/fly ash mortar significantly. Furthermore the incorporation of fly ash with different fineness and ratios also decreased the expansions to harmless levels of cement mortars due to alkali–silica reaction.

Paul et al. (2007) carried out high energy ball milling of class F fly ash (which has lower CaO content and higher SiO_2 content than class C one, according to the standard ASTM C618) in order to convert it into nanostructured material. They found that the surface of the produced nano size fly ash has become more active as it was observed from Fourier Transform Infrared Spectroscopy (FTIR) studies. Morphological studies revealed that the surface of the nano structured fly ash is more uneven and rough and shape is irregular, as compared to fresh fly ash which are mostly spherical in shape. They achieved significant reduction in crystallinity in high energy milled fly ash after 60 h residence time.

Fu et al. (2008) investigated the physical–chemical characteristics of mechanically-treated circulating fluidized bed combustion (CFBC) fly ash. It was found that the grinding process can be divided into three stages. The increase in fineness of ground CFBC fly ash is very sharp in the first stage, then it slows down in the second stage, and in the last stage it remains almost fixed. The water requirement decreases with prolonged grinding time, and slightly increases during the last stage of grinding. The pH of ground CFBC fly ash is greater than that of the original CFBC fly ash, indicating that ground samples react more rapidly with water. The intensity of the crystalline phases of ground CFBC fly ash decreases, while the half peak width of ground CFBC fly ash increases with prolonged grinding time, which means that ground fly ash has a higher reactivity than the original fly ash.

Hounsi et al. (2013) investigated the influence of mechanical activation of raw kaolin on the final compressive strength of geopolymers. Mechanical activation was performed by dry planetary ball-milling of kaolin at 250 rpm for various residence times. Mechanical activation was performed to improve mechanical properties of the resulted geopolymer. Results showed that without mechanical activation, the optimal curing condition was 24 h at 70 °C and the compressive strength was 15 MPa after 28 days of aging. Under mechanical activation, improvement of the compressive strength was obtained with a curing time of 24 h at 100 °C (76% improvement). Authors explained their findings with the following phenomena: milling affects the crystallinity degree of the raw kaolin and promotes the reaction of geopolymerization. Namely, the geopolymerization of KBip kaolin results in a relative decrease in intensity of the kaolinite peaks. This decrease is more important for the milled kaolin based-geopolymers. It can be explained by the partial amorphization caused by the milling. They found that the formation of alkaline aluminosilicate gels and new crystalline hydrated phases controlled the strength development of geopolymers while the occurrence of carbonated species was responsible for the degradation of mechanical properties.

More than 80% of coal used in the world in thermal generation is currently black coal (Heidrich et al., 2013). Therefore, the investigation of black coal utilization is a more frequent question than that of brown coal or lignite. However, there are enormous brown coal and lignite resources and power stations firing the above coal types worldwide producing huge amount of fly ash which are today mostly land filled due to its low reactivity. For instance, in Hungary the coal based power stations are operating using the above mentioned low rank lignite and brown coal. However, their reactivity can be improved by mechanical activation.

Regarding this problem, the investigation of land filled brown coal fly ash based geopolymer preparation from mechanically activated fly ash using high and low energy density mills is not reported in the literature. Therefore, the aim of the present research is to study the grinding kinetics of fly ash in three different laboratory scale mills, namely tumbling ball mill, vibratory mill and stirred media mill, and to follow the material characteristics of the resulted fly ash and the ground fly ash based geopolymer. The above research was carried out in order to control the geopolymer physical properties.

2. Materials and methods

2.1. Materials

The deposited brown coal fly ash sample used for laboratory experiments is originated from Tiszaújváros dumpsite which chemical composition can be found in Table 1. The alkaline activator used for the preparation of geopolymer was caustic liquor (180 g/l Na_2O) from MAL PLC. Ajka, Hungary. The main physical and chemical properties are as follows. Characteristic particle size values of the raw fly ash were $x_{50} = 97.14$ μm and $x_{80} = 167.34$ μm. The specific surface area (SSA) of the raw fly ash was found to be 580.37 cm^2/g. Additionally, the bulk, the particle and the material density were found to be 0.85 g/cm^3, 1.65 g/cm^3 and 2.13 g/cm^3 respectively. Moisture content was 17.3%. From the XRF analysis, the SiO_2/Al_2O_3 ratio was found to be 2.3. The combined SiO_2, Al_2O_3 and Fe_2O_3 content of the fly ash was

Table 1
Chemical composition of deposited brown coal F-type fly ash originated from Tiszaújváros.

Composition	Fly ash, wt.%
L.O.I.	1.92
SiO_2	61.32
Fe_2O_3	4.27
Al_2O_3	26.71
CaO	1.50
MgO	0.89
Na_2O	1.06
K_2O	1.72
SO_3	0.25