A Review on Fly Ash as a Raw Cementitious Material for Geopolymer Concrete

AISSA BOUAISSI¹*, LONG YUAN LI¹, LIGIA MIHAELA MOGA², IOAN GABRIEL SANDU^{3,4}, MOHD MUSTAFA AL BAKRI ABDULLAH⁵, ANDREI VICTOR SANDU^{3,4*}

¹School of Marine Science and Engineering, University of Plymouth, PL4 8AA, UK

² Technical University of Cluj-Napoca, Faculty of Civil Engineering, Department of Buildings and Management,Baritiu 25 St., Cluj-Napoca, Romania

³ Gheorghe Asachi Technical University of Iasi, Faculty of Materials Science and Engineering, 64 D. Mangeron St., 700050 Iasi, Romania

⁴ Romanian Inventors Forum, Iasi, 3 Sf. Petru Movila St., Bloc L11, Sc. A. III/3, 700089 Iasi, Romania

⁵ Center of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Kangar, Perlis Malaysia.

This paper presents a review on fly ash as prime materials used for geopolymer. Due to its advantages of abundant resources, less in cost, great workability and high physical properties which lead to achieve high mechanical properties. Fly ash is considered as one of the largest generated industrial solid wastes or so-called industrial by products, around the world particularly in China, India and USA. The characteristics of fly ash allow it to be a geotechnical material to produce geopolymer cement or concrete as an alternative of Ordinary Portland cement. Many efforts are made in this direction to formulate a suitable mix design of fly ash based-geopolymer by focusing on fly ash as the main prime material. The physical properties, chemical compositions and chemical activation of fly ash are analysed and evaluated in this review paper. Reference has been made to different ASTM, ACI standards and other researches work in geopolymer area.

Keywords: Fly Ash, Physical characteristics, Specific gravity, Particle shape, Chemical activation, workability

The production of Ordinary Portland cement (OPC) contributes approximately 7% to the total of global greenhouse gas emissions, this is considered as a serious problem for the environment [1, 2]. Recently, much research has been done to explore an alternative product which could replace OPC. Geopolymer was firstly proposed by Davidovits [3] as an alternative binder to OPC. Geopolymer is defined as a chemical reaction of aluminosilicate compounds, which have geological origins, such as clay and metakaolin or from industrial by-products for example, Fly Ash (FA) and ground granulated blast furnace slag (GGBFS) [3-6].

The collection of FA from the coal-fired power plants is based on different equipment and filtration processes. The source and the structure of burned coal significantly impacted on FA compounds. But, generally, all types of FÅ contain a huge amount of silicon dioxide (SiO₂) (both amorphous and crystalline), aluminium oxide (Al^LO₃) and calcium oxide (CaO) [7]. The typical chemical composition of FA which is obtained from Manjung power plant at Perak in Malaysia is presented in Table (1). It is classified as class F fly ash, which will be detailed in the next section. FA with high percentage of silica (SiO_2) and alumina (Al_2O_3) (more than 80%) could be appropriate in the production of geopolymer as a raw material. According to Davidovits [3] geopolymers are classified as binder materials, which could be formed by the activation of aluminosilicate with alkaline solutions. The term 'Geopolymer' was first introduced by Davidovits and also well known as inorganic polymers or alkaline activated binder material [7]. This review paper evaluates the significant characteristics of FA and its advantages as raw materials in geopolymer cement and concrete.

Classification

ASTM C618 classified FA into two main classes based on the source of mineral coal, these categories are appropriately considered as important classes in the uses of concrete [9]. The named class F and class C of FA have many similarities in terms of physical characteristics. However, a chemical composition analysis is required to distinguish between both classes. The total amount of silica (SiO_{2}) , alumina $(Al_{2}O_{2})$, and iron oxide $(Fe_{2}O_{2})$ as the constituents of FA will determine the type of class. Fly ash is therefore classified as class F if the silica, alumina and iron oxide content is at least 70% of the total mass, and has a limited percentage of calcium oxide (CaO) (content no more than 10%). Class C FA constitutes at least 50% of silica (SiO₃), alumina (Al₂O₃), and iron oxide (Fe₂O₃) of the total mass and the calcium oxide (CaO) content is high (from 10 to 30%), with a high reactivity of almost all constituents [10].

Recently, many studies have been attempted in analysis and synthesis of geopolymer. Some challenges have been faced in researching geopolymer process conditions and trying to identify the main aspects that limit and determine the reactivity of FA and geopolymers structure and its characteristics. FA based geopolymer could be affected by many parameters, these parameters are significantly related to the primary materials and their characteristics, such as size and distribution of particles, the glassy phase

Composition	SiO ₂	A12O3	Fe2O3	CaO	MgO	SO3	K ₂ O	Na2O	Table 1
Concentration %	43.73	27.8	12.37	8,01	3.75	1.45	1.96	0.93	CHEMICAL COMPOSITIONS OF FA [8]

^{*} email: aissa.bouaissi@plymouth.ac.uk; sav@tuiasi.ro

in the content, the reactivity of both silicon and aluminium, constituent of iron, calcium and inert particles, and also the type of activator solution and its concentration [11–43].

Diaz et al. [21] supposed that the mechanical strength of geopolymer could be affected by many parameters of the mix design, for example the ratio of NaOH to Na₂SiO₃ and activator solution to FA ratio. In addition, other factors could have significant impact on the behaviour of fresh and hardened geopolymer, such as the physical and chemical properties and also the crystallographic of FA.

Particles size of FA could have a significant impact on the strength development in two ways. Firstly, when the particles are up of 45 μ m, this has an influence on the water requirement in an adverse way. Particles sizes have an important effect on the reaction rate of FA at early stages. Secondly, once diffusion and dissolution of materials occur in concentrated pastes, surface area of the particles might play a considerable role in determining the kinetics of different processes [10]. Salloum [22] concluded that, form a study of 36 different concrete mixtures, there was a relationship linked to the fineness of FA and strength development in concrete. Due to the fineness of ash particles the reactivity level increases, this could appear in the case of low-calcium ashes compared to those of higher in calcium content.

Physical characteristics

The performance of concrete is significantly impacted by the physical characteristics of FA, these characteristics could be the volume, rheology and water content in the slurry, pore distribution and also the reactivity of constituents. Table 2 presents different standards of pulverized FA (PFA) and its uses in concrete [10].

Brahammaji et Muthyalu [44] claimed that, the production of optimal properties of a geopolymer binder, class F fly ash should contain less than 5% of unburned material, no high than 10% of Fe₂O₃ and lower in CaO content. Also the reactive silica amount should be between 40 to 50%, and 80 to 90% of particles should be smaller or in the range of 45µm. A high amount of CaO leads to produce higher compressive strength, due to the formation of calcium-aluminate-hydrate (C-A-H) at the early age. The other characteristics which could influence the suitability of FA as a source material for geopolymers are, amorphous content, this means the amount of SiO₂, Al₂O₃ and Fe₂O₃ and also the morphology of FA. Other researchers [39] have reported that the amount of CaO+MgO could controls the characteristics of surface and the degree of progress

SI	Particulars	ASTM	BS 3892	IS 3812]
No		C618Type F	Part 1		
i	Particle density (kg/m3, min)	Not specified	2000	Not specified	
ii	Blaine fineness (m2/kg)	Not specified	Not	320	
			specified		
iii	Retention on 45 µm (325 mesh) sieve (%, max)	34.0	12.0	34.0	
iv	Loss on ignition (%, max)	6.0	7.0	5.0	
v	Water requirement (% of PC, max)	105	95	Not specified	
vi	Moisture content (%, max)	3.0	0.5	2.0	
vii	Soundness (autoclave, max)	0.8%	10 mm	0.8%	
viii	Strength activity index (%) ^b	75	80	80	
ix	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ (%, min)	70	Not	70	Table 9
			specified		COMPARISON OF SOMI
x	SiO ₂ (%, min)	Not specified	Not	35.0	STANDARDS ON PFA
			specified		CONCRETE ^a [10]
xi	Reactive silica (%, min)	Not specified	Not	20.0	
			specified		
xii	CaO (%, max)	Not specified ^c	10.0	Not specified	
xiii	MgO (%, max)	Not specified	Not	5.0	
			specified		
xiv	SO3 (%, max)	5.0	2.0	3.0	
xv	Alkalis as Na ₂ O (%, max) ^d	1.5	Not	1.5	
			specified		
xvi	Total chlorides (%, max)	Not specified	0.10	0.05	1

^a The individual standards may be referred for more details.

^b The 28 day compressive strength (N/mm²) of blended cement mortar is expressed as the percent of that of the control Portland cement (PC) mortar. The ASTM standard for the purpose: ASTM C311: Standard test methods for sampling and testing fly ash or natural pozzolans for use in Portland-cement concrete.

^c Not specified but generally below 10% when FA is produced from burning of anthracite or bituminous coal. ^d The equivalent alkali content, expressed as Na_2O , is obtained as: $Na_2O + 0.658$ K₂O.



Fig. 1. Scanning electron microscope of FA: (a) cenospheres and (b) plerospheres particles [10]

of mortar and concrete carbonation. This occurs by providing anions and controls dosage requirements of water-reducing agents.

Particle shape and form

Particle distribution and their size are considered the main physical factor for the geopolymerization process [23, 25]. Komljenovic *et al.* [26] stated that, the reactivity of FA increases with increasing its fineness, which leads to an improvement of geopolymer properties. Basically, the formation of ash particles occurs during the condensation and liquefaction process of incombustible inorganic matter, which is remained after coal combustion [27-29]. The shapes of FA particles depend on the combustion conditions and condensation process. In general, there are two major combustion processes. The first process occurs when the temperature ranges from 1204 to 1727°C, this process is called the pulverized coal firing system. The second process is known as fluidized bed combustion which could be peaked at temperature ranged between 827 and 927°C. Typically, the first process is the most common used one in the large thermal plants [20].

Surface tension of the melt plays a significant role in the formation of spheroidization of pulverized FA particles. Two types of particles could be formed, cenospheres form which are ash particles hollow from the inside, and plerospheres which are hollow ash particles but including smaller particles inside as is shown in figure 1. Brouwers and Eijk [30] suggested that, the formation of plerospheres is as a result of the cracking or puncturing of the primarily hollow particles during handling work, but not related to the melting process. Jayant [10] reported that the shape and surface characterization of FA particles have an impact on concrete in terms of water domend in particular at the concrete in terms of water demand, in particular at the desired slump stage. The spherical forms of FA particles minimize inter-particle friction and leads to the creation of a dynamic system between particles in a concrete. This process improves the flow properties of the concrete. An experimental study was carried out by Atis et al. [31] on the properties of different types of FA. Their results showed that there is many similarities between the chemical and mineralogical composition of all types of FA and also the physical properties such as specific surface area, particles shape and their distribution. To explain the performance of concrete from the strength and workability point of view, some authors proposed a new parameter called 'Shape factor' which is mainly based on the specific surface area of FA particles [10].

Another study shows that, around 90 % of tested FA could reduce water requirement of mortar mixtures. A correlation has been proposed to show the relationship between water demand and fineness and also water requirement and loss on ignition. Further, the addition of FA has a significant effect on the rheological properties of cement paste and workability of concrete, due to the small spherical particles of FA. Givi et al. [32], believed that, the proportion of coarse

material in the ash usually (up to 45 μ m) is mostly the main parameter affecting the workability of concrete. A study carried out by Feng and Clark [33], confirmed that the water requirement has been effected by both sieved residue and loss on ignition (LOI), where the LOI has impacted on water demand, due to the absorption of water molecules by porous carbon particles.

Particle specific gravity According to ASTM C188 the specific gravity of FA particles can be determined by the same method that is used for hydraulic cement [34]. If there is a water-soluble molecule in FA, it is recommended to use non-aqueous solvent as a replacement for water. ASTM C188 classified the specific gravity of various and common mineral admixtures such as FA, PC and GGBFS as follows; 2.0 -2.7, 3.0 - 3.20 and 2.9 - 3.0 respectively [10]. Sabat [35] assumed that FA could be the most suitable geotechnical material, due to its resistivity in terms of high shear strength, low specific gravity, less compressibility and good physicochemical properties. FA mainly contains silica, alumina, iron and calcium, with less quantity of magnesium, sulphur, sodium, potassium and carbon. The density or specific gravity of FA depends on its chemical compounds and typically ranges between 1.9 and 2.8 [36].

Size and fineness of particle

As mentioned before, FA particles have spherical solid forms with hollowing inside as cenospheres or plerospheres form. FA particle sizes vary from 1µm to more than 100 μ m. In general, 10% to 30% of particles are larger than 45µm, with 300 to 500 m²/kg of surface area. However, some types of FA have low or high surface area between 200 m²/kg and 700 m²/kg respectively [36-54]. There are two ways to measure the particle size and fineness of FA:

-Specific surface area by Blaine apparatus: This method is based on the time passing through a bed of FA and correlated with its specific surface area in m²/kg.

ASTM does not exaggerate any specific requirement for the surface area of FA, which could be used in concrete. Whereas, the Indian Standard IS 3812 Part 1 [37] specifies 320 m²/kg of FA as a minimum Blaine area for use in concrete.

-Residue on 45 µm sieve by wet-sieve analysis: This method is used to measure the percentage of particles in FA bigger than 45 μ m as is referred to in ASTM430 [38]. Many countries follow this method for their national standards [10].



Fig. 2. Scanning electron microscope (SEM) micrographs of fly ash particles [48]

Some research showed that, particles of raw FA mostly range from 1 to 100 μm in figure 2. The particles less than 10 μ m are the ones that react and contribute in the formation of early strength (7 and 28 days). Whereas, the particles between 10 and 45 µm react slowly and lead to the formation of a late strength (up to 1 year). The particles higher than $45 \,\mu m$ could be considered as inert and largely act as fine sand (filler) [10, 36].

Colour

FA from bituminous coal has a darker grey colour which comes from lignite or sub-bituminous coal and also can be buff to tan in colour. It is thought that the grey colour could be explained by the presence of unburned carbon (UBC). If the percentage of carbon is low or absent in ash, then the colour might be brown, due to the presence of iron (+3) compounds. The colour changes to bluish grey to grey if the iron compounds are (+2) [10].

Tanosaki, Yu and Nagataki (2011) have reported that the use of colorimetric methods or as is known as the Munsell system to identify colours by following the next three dimensions, Hue, Value (lightness), and Chroma (colour purity). In 1905, Professor Albert H. Munsell created the Munsell system [39]. According to Malacara [40] figure 3, describes the colour circle system. The system is divided into five principle hues: Red, Yellow, Green, Blue, and Purple, along with five intermediate hues halfway between adjacent principle hues. Each of these ten categories is used to divide into other ten sub-categories, so that 100



Unburned carbon

Unburned carbon (UBC) is mostly the significant affecting particles on the loss on ignition (LOI). During hydration process the carbon particles do not have any part in the chemical reactions. However, they have an impact on the water requirement in concrete. Carbon particles have a very strong affinity and attraction to the organic chemical admixtures. For example, air-entraining agents (AEA), this chemical agent has absorbed on the carbon and negatively effects the hardened concrete. In general, the absorption degree depends on many factors, such as surface area, and type of carbon in terms of its polarity and particles size. An experimental study showed that FA with less than 3 to 4% of carbon not have a greater effect on the performance of organic chemical admixtures [10]. On the other hand, Ha et al. [41] reported that the use of FA as raw material, which contains around 8% of UBC could accelerate the corrosion of reinforcement steel.

Chemical and mineralogical composition of FA

FA has varieties of chemical compositions, the averages of the main elements of FA in some European countries (France, UK, Germany), USA and far Asian countries (Japan, China, India) are given as follow 53.05 %, 27,24 %, 5.50 % for SiO₂, Al₂O₃ and Fe₂O₃ respectively [10]. However, another study reported that FA consisted of a heterogeneous mixture of complex aluminosilicate glasses and other crystalline elements [42]. The structure of aluminosilicate glass is an amorphous form, but it could be modified due to the addition of alkaline and metal oxides such as Na₂O, K₂O, MgO, CaO, and FeO. A study carried out by Das and Yudhbir [43] showed that a strong correlation exists between the glass content and the ratio of potassium to aluminium oxides (K_2O/Al_2O_3). ASTM classification shows that, the composition of glass in class F fly ash is different from that in class C. A high polymerized glass network is observed in class F FA, but the glass matrix depolymerizes when the CaO increases in comparison with Al_2O_3 content [10, 30, 44].

Setting time

The addition of FA or other raw material such as GGBFS generally delays the setting time of concrete. The initial and final setting time averages of class F and class C FA are 4:50, 4:40 and 6:45, 6:15 (h:min) respectively. Setting time could be affected by different factors, for example the amount of Portland cement, water demand, the reactivity of the pozzolan dosage or FA and the temperature of concrete. Hot weather plays a positive effect on setting times and is considered as an advantage, by giving enough time for placing and finishing the handled work. On the other hand, if the weather is cold, setting time could be controlled by additives, which delay the finish operation. Some of accelerating admixtures and calcined shale or clay could be used to decrease setting time [36].

FA might have an influence on the rate of hardening of cement [46, 48] for the following reasons:

-FA is considered as cementitious and contains high calcium (class C FA).

-FA could containing sulphates which leads to a reaction with cement in the same way as when gypsum added to Portland cement.

-The fly ash cement mortar might contain less water and this has a significant effect on the rate of stiffening.

-The surface-active agent which could be added to modify the rheology (water reducers) of concrete, could be absorbed by FA and this leads to an influence on the stiffness of mortar.

-FA particles could act as nuclei for crystallization of cement hydration products [45-48].

Physical treatment

A study carried out by Barry [49] shows that the CSA (Canadian Standards Association) standard A23.5-M1982 on plant scale gets an advantage by improving the quality of use FA with high finer size of particles. The results showed an improvement in terms of reactivity and activity of FA, reducing water requirement and resulting in an enhanced the ability to control alkali-aggregate reaction. It is observed that the particle size (or the particle surface area) and the size distribution have a significant role in determining the activity of FA. Therefore, FA with finer particles size could replace a high proportion of cement without affecting the strength [10].

However, Adam [59] and Ramezanianpour [48], have performed more than 340 tests of 14 sources of FA [48-64]. Their results showed that there is no correlation between fineness and compressive strength at the ages of 7 and 28 days for mortars, but a minor correlation was found at 90 days. Joshi [63] and Ravina [64] have exploited a new phenomenon which is called 'particle-size segregation phenomenon'. Electrostatic precipitators' method was used to obtain FA fractions of different fineness from a particular source. Another experiment was carried out by Joshi [63] by investigating the proportion of particles of four types of FA, which are up to 45µm from a modern power plant. The retained percentages of 45 µm sieve for each type of FA are 5, 16, 32 and 38%. The results indicated that replacing 10 and 20% of finer FA in concrete leads to develop a significant strength. These results have been supported by those found by Ravina [64], when the pozzolanic activity index of low calcium FA from the same precipitator, was used for testing.

Effect of FA on workability and water requirement

In general, rheological properties of cement pastes could be impacted by the morphology and the small size of the spherical particles of FA. The amount of calcium in FA particles (low calcium) has a significant influence on the rheology of pastes by reducing the amount of water demand and increasing workability. According to Davis et al. [50], FA is considered as a particular material comparing with



Fig. 4. Influence of coarse-particulate content of FA on water requirement for equal workability in concrete [51]

other pozzolans by leading to the increased water requirement of concrete mixtures. Owens [51] believed that the main characteristic of FA, which has a significant effect on workability of concrete, is the proportion of coarse material (up to $45 \ \mu$ m) which could exist in FA. The effect of coarse particles on the water requirement is shown in figure 4.

Much research has been carried out by Lloyd and Rangan [52] on the use of FA in geopolymer concrete. It is investigated that not only compressive strength could be affected by the characteristics of initial materials, but also workability of geopolymer concrete. However, other studies have shown that workability might be related to; the ratio of alkaline activator solution (AAS) to binder, and composition and nature of the chemical admixture which has been used [57].

Sathia, Babu Ganesh and Santhanam [68] have reported that the ratio of H_2O to Na_2O of 10-14 is only used when FA content is about 408 Kg/m³ in a designed concrete, this ratio could be changed depend on FA content [64-73]. Thus, Siddique and Iqbal Khan [73] stated that for an equal w/c ratio and depending to the spherical shape and glassy phase on the FA particles surface a greater workability could be achieved.

Ramezanianpour [48], stated that, due to the necessity of mixing and placing concrete in a reinforced fromwork, it is necessary to maintain its workability. This could be determined by the rheological properties of the system, which are in turn impacted by all the components. Thus, it is important to understand the rheological behavour and the main role of FA in the fresh concrete, which leads to exploit the potential role of FA for improving concrete [48].

The impact of FA on durability of concrete exposed to elevated temperatures

Recently, the requirement of infrastructure and its development such as in nuclear reactor containment structures exaggerates the use of concrete, which could withstand high temperatures. Many researchers have studied the effect of elevated temperature on FA concrete in the range of 230°C [54-57]. Another study was carried out by Carette et al. [57] which showed the influence of a temperature 600°C on concrete with a mix of Portland cement, slag and FA, as is illustrated in Figure 5. Under a high temperature, the addition of FA has no effect on the behaviour of the concrete, however the changes in concrete properties or decreasing of strength could be observed at the same range of temperatures [46].



Fig. 5. Compressive strength of concretes after 1 month of exposure to various elevated temperatures [58]

In addition, degradation of concrete structures is strongly affected by the chemicals attack. For example, the penetration of chloride ions into the concrete lead to chemical reactions which could help in the formation of corrosion around reinforcement. This could be the reason of early end to a structure's life cycle. Other studies have carried out by Thomas et al., [66], Uddin and Shaikh, [67] have reported that resistance of concrete to the immigration of chloride ions is mainly controlled by porosity and inter-connectivity of pores system and also depends to the chemical binding capacity of cement.

FA requirements for geopolymer

In order to achieve an efficient geopolymer synthesis, it is required that silica (SiO₂), alumina (Al₂O₂) and iron (Fe₂O₃) should be in high proportions [69]. Further, the activity of FA or the formation of aluminosilicate gel is related to the nature of environment, which could be acidic or basic [70] and also high concentration of calcium has an important effect on the reaction, by accelerating its rate. Komljenovic, Basc and Marjanovic [26] reported that, the reactivity of FA could be influenced by many factors which inturn effects the characteristics of FA-based geopolymer, such as glassy phase, particle size distribution, the presence of iron, calcium, and inert elements. However, the reactivity of FA is not depending only to the glassy phase, but to the whole FA, this means that the glassy phase has a limitation degree. Therefore, the reactivity of FA is usually depends on the dissolution level of FA in the alkaline activator [20]. As aforementioned, Loss on ignition (LOI) is defined as the unburned carbon presents in FA and how that affects the quality of paste or concrete by increasing the water requirement and reducing the reactivity of pozzolanic constituents. ASTM C618 (2008) has reported that, the required percentage of LOI is limited to 6% maximum [59]. Another study showed that a high proportion of SO₃ in concrete could lead to instability in volume, which in turn has an impact on durability. However, it is reported that, about 5% of SO₃ of FA could be used as a concrete binder [76-84].

Chemical activation

Blanco et al. [71] have proposed a procedure of using of wet milling and leaching with sulphuric acid to activate FA. One of the main applications to use the activated FA is to substitute silica fume in concrete, which could lead to achieve a high strength, due to the decrease of pore size in the hardened concrete. The addition of a limit amount of sodium sulfate or potassium sulfate $(Na_2SO_4 \text{ or } K_2SO_4)$ mixed with calcium hydroxide $(Ca(OH)_2)$ has a substantial effect on acceleration of hydration and compressive strength. A study carried out by Görhan and Kürklü [65] investigated that the activation of mortar samples by using NaOH of 6M leads to increase in compressive strength values by 21.3 MPa and 22 MPa, compared to those samples which activated by 9M NaOH. Therefore, it has reported by other authors [60, 72] that, to achieve a great reactivity of FA particles within the activator solution, the liquide phase plays a significant role as a transport meduim and a less smoothly gel is formed, due to the faster reaction of NaOH.

Addition of FA to cement and concrete

FA is classified into two classes by ASTM C618. Class F FA is as pozzolanic, with minimum or no cementing value, whereas class C FA has cementitious as the same as pozzolanic properties [9]. The main parameter to formulate a concrete mix design with addition of FA is the proportion of the mix under consideration of the variation of watercementitious ratio. This could lead to achieve the requirements for compressive strength at different ages, air content and workability. ACI 211.1 or 211.2 has determined the procedures for the mix design in details, in terms of proportioning of water, cement (or cement plus FA), and aggregate materials [71].

However, the specific gravity of FA is lower than PC, which needs to be taken into consideration in the mix proportioning process. Other standards such as the European standard BS EN206 provides some requirements for the use FA in concrete [10, 36, 62]. Further study has been carried out by Horpibulsuk, Rachan and Raksachon [74], reported that FA could consider as a dispersing material, when it is mixed with cement. This in contrast when FA is used in concrete as a pozzolanic material. Due to the pozzolanic reaction which lead to consum of Ca(OH)₂ during the hydration process.

Conclusions

This paper reviews FA as basic raw materials for geopolymer concrete and its properties in terms of microstructure, reaction mechanism and characterization. From the review, it can be concluded that many studies have been done on the use of FA as a prime material in the production of geopolymers. Substantial results show that including FA in geopolymerization provides a greater performance and acid resistance, due to its physical characteristics compared to that given by OPC. These findings make the use of FA of particular interest to researchers. As a result of the excellent properties, geopolymers based FA have been successfully applied in various traditional and new applications. Other applications are yet to be discovered in future.

List of notation

FA is the Fly AshPFA is the Pulverized Fly AshGGBFS is the ground granulated blast furnace slagOPC is the Ordinary Portland cementPC is the Portland cementCSA is the Canadian Standards Association

AEA is the air-entraining agents

UBC is the unburned carbon

LOI is the loss on ignition

Acknowledgements: The authors would like to acknowledge the Faculty of Engineering Technology, Center of Excellence Geopolymer & Green Technology (CeGeoGTech), Universiti Malaysia Perlis (UniMAP) to provide us this research opportunity and supporting us with all the necessary facilities.

References

1.NEUPANE, K., Mechanics of Materials, 103, 2016, p. 110.

2.MUSTAFA AL BAKRI, A.M., KAMARUDIN, H., KHAIRUL NIZAR, I., SANDU A.V., BINHUSSAIN, M, ZARINA, Y., RAFIZA, A, R., Rev. Chim. (Bucharest), **64**, no. 4, 2013, p. 382.

3.DAVIDOVITS, J., Journal of Thermal Analysis, **37**, no. 8, 1991, p. 1633.

4.FARIS, M.A., ABDULLAH, M.M.A., SANDU, A.V., ISMAIL, K.N., MOGA, L.M., NECULAI, O., MUNIANDY, R., Mat. Plast., **54**, no. 1, 2017, p. 145. 5.JAFFAR, M.I., BADARUZZAMAN, W.H.W., ABDULLAH, M.M.A., BAHAROM, S., MOGA, L.M., SANDU, A.V., Mat. Plast., **52**, no. 2, 2015, p. 243.

6.SHAHEDAN, N.F., ABDULLAH, M.M.A., HUSSIN, K., SANDU, I., GHAZALI, C.M.R., BINHUSSAIN, M., YAHYA, Z., SANDU, A.V., Mat. Plast., **51**, no. 3, 2014, p. 258.

7.PAVITHRA, P., SRINIVASULA REDDY, M., DINAKAR, P., HANUMANTHA RAO, B., SATPATHY, B.K., MOHANTY A.N., Journal of Cleaner Production, **133**, 2016, p. 117.

8.HAMIDI, R.M., MAN, Z., AZIZLI, K.A., Procedia Engineering, 148, 2016, p. 189.

9.*** Standard, A.S.T.M., 2008. C618-08a: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. Annual Book of ASTM Standards.

10.JAYANT, D., Mineral Admixtures in Cement and Concrete, Taylor & Francis Group, LLC, 2013.

11.FERNANDEZ-JIMENEZ, A., PALOMO, A., CRIADO, M., Cement and Concrete Research, **35, no.** 6, 2005, p. 1204.

12.DEVENTER, V. J. S. J., PROVIS, J.L., DUXSON, P., LUKEY, G.C., Journal of Hazardous Materials, **A139**, 2007, p. 506.

13.REES, C.A., PROVIS, J.L., LUKEY, G.C., VAN DEVENTER, J.S., Physicochemical and Engineering Aspects, **318**, no. 1, 2008, p. 97.

14.HAJIMOHAMMADI, A., PROVIS, J.L., VAN DEVENTER, J.S., Chemistry of Materials, 22, no. 18, 2010, p. 5199.

15.HAJIMOHAMMADI, A., PROVIS, J. L., VAN DEVENTER, J. S. J., Cement and Concrete Research, **41**, no. 3, 2011, p. 210.

16.SHI, C., JIMENEZ, A.F., PALOMO, A., Cement and concrete research, 41, no. 7, 2011, p. 750.

17.PACHECO-TORGAL, F., CASTRO-GOMES, J., JALALI, S., Construction and Building Materials, **22**, no. 7, 2008, p. 1315.

18.KHALE, D., CHAUDHARY, R., Journal of Materials Science, **42**, no. 3, 2007, p. 729.

19.KOMLJENOVLÆ, M., Handbook of Alkali-Activated Cements, Mortars and Concretes, 2015, 171–215.

20.NIKOLIC, V., KOMLJENOVIC, M., BASEAREVIC, Z., MARJANOVIC, N., MILADINOVIC, Z., PETROVIC, R., Construction and Building Materials, **94**, 2015, p. 361.

21.DIAZ, E.I., ALLOUCHE, E.N., EKLUND, S., Fuel, 89, 2009, p. 992.

22.SALLOUM, T., Effect of fly ash replacement on alkali and sulphate resistance of mortars, Master's Thesis, 2007, Concordia University, Canada.

23.YAHYA, Z. MUSTAFA AL BAKRI A,M., KAMARUDIN, H., KHAIRUL NIZAR, I., SANDU, A, V., PETRICA, V, RAFIZA, A.R., Rev. Chim. (Bucharest), **12**, no. 1, 2013, p. 32.

24.FERNANDEZ-JIMENEZ, A., PALOMO, A., Fuel, **82**, no. 18, 2003, p. 2259.

25.VAN JAARSVELD, J.G.S., VAN DEVENTER, J.S.J., LUKEY, G.C., Materials Letters, **57**, no. 7, 2003, p. 1272.

26.KOMLJENOVIC, M., BAAREVIC, Z., BRADIC, V., Journal of Hazardous Materials, **181**, no. 1-3, 2010, p. 35.

27.VAN RIESSEN, A., CHEN-TAN, N., Fuel, 106, 2013, p. 569.

28.MARJANOVIC, N., KOMLJENOVIC, M., BASEAREVIC, Z., NIKOLIC, V., Construction and Building Materials, **57**, 2014, p. 151.

29.NIKOLIC, V., KOMLJENOVIC, M., MARJANOVIC, N., BASEAREVIC, Z., PETROVIC, R., Ceramics International, **40**, no. 6, 2014, p. 8479. 30.BROUWERS, H.J.H., EIJK, R.J.V., Chemical Reaction Of Fly Ash, Proceedings of the 11th International Congress on the Chemistry of Cement, 11-16, 2003. Durban, South Africa.

31.ATIS, C.D., SEVIM,U.K., ZCAN, F.O., BILIM, C., KARAHAN, O., TANRIKULU, A.H., EKS, A., Civil Materials Letters, **58**, no. 9, 2004, p. 1446.

32.GIVI, A.N., SURAYA, A.R., FARAH NORA, A.A., MOHAMAD AMRAN, M.S, Construction and Building Materials, **24**, no. 11, 2010, p. 2145.

33.FENG, X., CLARK, B., Evaluation of the Physical and Chemical Properties of Fly Ash Products for Use in Portland Cement Concrete, World of Coal Ash (WOCA) Conference, 2011, Denver, CO, USA. p. 1–8.

34.FERDOUS, M.W., KAYALI, O., KHENNANE, A., A Detailed Procedure Of Mix Design For Fly Ash Based Geopolymer Concrete, Fourth Asia-Pacific Conference on FRP in Structures, 2013, Melbourne, Australia. 35.SABAT, A. K., EJGE, **20**, 2015, p. 155–166.

36.MALVAR, L.J., CLINE, G.D., BURKE, D.F., ROLLINGS, R., GREENE, J., SHERMAN, T.W., Alkali-Silica reaction mitigation: State-of-theart (No. NFESC-TR-2195-SHR). Naval Facilities Engineering Command Port Hueneme Ca Engineering Service Center, 2001.

37.*** IS 3812: Part I., (Second revision), Pulverised fuel ash Specification Part I. For use as pozzolana in cement, cement mortar and concrete. Bureau of Indian Standards, 2003. New Delhi, India.

38.*** Standard, A.S.T.M., C430. Standard Test Method for Fineness of Hydraulic Cement by the 45-Ìm (No. 325) Sieve. ed: West Conshohocken, PA: ASTM International, 2003.

39.TANOSAKI, T., YU, Q., NAGATAKI, S., Are Fly Ashes Green/?, World of Coal Ash (WOCA) Conference 2011, in Denver, CO, USA. p. 1–5.

40.MALACARA, D., Color vision and colorimetry: Theory and Applications, 2011, Washington: SPIE.

41.HA, T.H., MURALIDHARAN, S., BAE, J.H., HA, Y.C., LEE, H.G., PARK, K.W., KIM, D.K., Construction and Building Materials, **19**, no. 7, 2005, p. 509.

42.BAPAT, J.D., Advances in Cement Research, **13**, no. 4, 2001, p. 139. 43.DAS, S.K., Cement and concrete research, **36**, no. 10, 2006, p. 1827.

44.BRAHAMMAJI, S.V., MUTHYALU P.V., International Journal of Advances in Engineering & Technology, **8**, no. 4, 2015, p. 574.

45.MALHOTRA, V.M., RAMEZANIANPOUR, A.A., Springer Geochemistry/ Mineralogy, 1994. p.307.

46.MALHOTRA, V.M., Investigation of High-Volume Fly Ash concrete Systems. EPR1TR-10315 Project 3176-66, Final Report, Oct, 1993.

47.CHINDAPRASIRT, P., JATURAPITAKKUL, C., SINSIRI, T., Construction and Building Materials, **21**, no. 7, 2007, p. 1534.

48.RAMEZANIANPOUR, A. A., Fly Ash, Springer, 2014.

49.BARRY, E.E., Special Publication, **114**, 1989, p. 241.

50.DAVIS, R.E., CARLSON, R.W., KELLY, J.W., DAVIS, H.E., In Journal Proceedings, **33**, no. 5, 1937, p. 577.

51.OWENS, PL., The Concrete Society, 13, no. 7, 1979, p. 21.

52.LLOYD, N.A., RANGAN, B.V., Geopolymer concrete: A review of development and opportunities, In 35th Conference on Our World in Concrete and Structures, 2010, Singapore.

53.SABITHA, D., DATTATREYA, J.K., SAKTHIVEL, N., BHUVANESHWARI, M., JAFFER SATHIk, S.A., Current Science, **103**, no. 11, 2012, p. 1320. 54.NASSER, K.W., MARZOUK, H.M., American concrete institute (ACI), Special Publication, **79**, 1983, p. 383.

55.NASSER, K.W., LOHTIA, R.P., Journal Proceedings, **68**, no. 3, 1971, p. 180.

56.NASSER, K.W., LOHTIA, R.P., Journal Proceedings, 68, No. 4, 1971, p. 276.

57.NASSER, K.W., MARZOUK, H.M., In Journal Proceedings, **76**, No. 4, 1979, p. 537.

58.PAINTER, G.C.K., Concrete International, 4, no. 7, 1982. p.16.

59.ADAM, A. A., Strength and Durability Properties of Alkali Activated Slag and Fly Ash-Based Geopolymer Concrete, PhD Thesis, 2009, University of Melbourne, Australia.

60.MUSTAFA AL BAKRI, A.M., HUSSIN, K., BNHUSSAIN, M., ISMAIL, K. N., IBRAHIM, W. M. W., Int. J. Pure Appl. Sci. Technol, **6**, no. 1, 2011, p. 35.

61.*** Standard, A.C.I., Standard practice for selecting proportions for normal, heavyweight, and mass concrete. ACI Manual of Concrete Practice, Part, 1, 211-1, 1996.

62.*** EN, B., 2000 Concrete. Specification, performance, production and conformity, 206-1, 2001. p.22.

63.JOSHI, R.C., In Proceedings of 6th International Symposium on Fly Ash Utilization, 1982. 82-52.

64.RAVINA, D., Proceedings of the symposium of fly ash incorporation in hydrated cement systems, 1981, Boston. 2-11.

65.GORHAN, G., KURKLU, G., Composites Part B: Engineering, 58, 2014, p. 371.

66.THOMAS, C., SETIEN, J., POLANCO, J.A., ALAEJOS, P., SÁNCHEZ DE JUAN, M., Construction and Building Materials, **40**, 2013, p. 1054. 67.UDDIN, F., SHAIKH, A., International Journal of Sustainable Built Environment, **5**, no. 2, 2016, p. 277.

68.SATHIA, R., BABU GANESH, K., SANTHANAM, M., Durability Study of Low Calcium Fly Ash, The 3rd ACF International Conference-ACF/ VCA, 2008, D.21.

69.KEN, P. W., RAMLI, M., BAN, C. C., Construction and Building Materials, 77, 2015, p. 370.

70.DUXSON, P., FERNANDEZ-JIMENEZ, A., PROVIS, J.L., LUKEY, G.C., PALOMO, A., van DEVENTERN, J.S.J., Journal of Material Science, **42**, no. 9, 2007, p. 2917.

71.BLANCO, F., GARCIA, M.P., AYALA, J., MAYORAL, G., GARCIA, M.A., Fuel, **85**, no. 14–15, 2006, p. 2018.

72.DUCHESNE, J., DUONG, L., BOSTROM, T., FROST, R., Waste and Biomass Valorization, 1, no. 3, 2010, p. 367.

73.SIDDIQUE, R., KHAN, M.I., Supplementary Cementing Materials, Engineering Materials, Verlag Berlin Heidelberg, 2011, 1-66.

74.HORPIBULSUK, S., RACHAN, R., RAKSACHON, Y., Soils and Foundations, **49**, no. 1, 2009, p. 85.

75.TOMA, S.L., Surface & Coatings Technology, 220, 2013, p. 261.

76.CALIN, M.A., CURTEZA, A., TOMA, S., AGOP, M., Metalurgia International, **18**, no. 1, 2013, p. 19.

77.TOMA, S.L., BEJINARIU, C., BACIU, R., RADU, S., Surface & Coatings Technology, **220**, 2013, p. 266.

78.VIZUREANU, P., Metalurgia International, 14, no. 5, 2009, p. 5.

79.IOANNOU, P.D., NICA, P., PAUN, V., VIZUREANU, P., AGOP, M., Physica Scripta, **78**, no. 6, 2008, art. 065101

80.JUN, N.H., MINCIUNA, M.G., ABDULLAH, M.M.A., JIN, T.S., SANDU, A.V., MING, L.Y., Rev. Chim. (Bucharest), **68**, no. 10, 2017, p. 2367.

81.SZILAGYI, H., BAERA, C., CORBU, O., PUSKAS, A., Nano, Bio And Green - Technologies for A Sustainable Future Conference Proceedings, (16th International Multidisciplinary Scientific Geoconference SGEM 2016), vol **II**, 2016, p. 197-202.

82.CORBU, O., POPOVICI, A., POPITA, G.E., RUSU, T., ROSU, C., PUSKAS, A., Geoconference on Nano, Bio and Green - Technologies For A Sustainable Future, Vol **II** (14th International Multidisciplinary Scientific Geoconference SGEM 2014), 2014, p. 81-88.

83.IONESCU, D., MATASARU, D., RADU, V., University Politehnica of Bucharest Scientific Bulletin-Series A-Applied Mathematics and Physics, **75**, no. 4, 2013, p. 265.

84.PUSKAS, A., MOGA, L., Procedia Technology, **22**, 2015, p. 304-311. (DOI: 10.1016/j.protcy.2016.01.102)

Manuscript received: 16.01.2018