Fly ash as a raw material for geopolymerisation - chemical composition and physical properties

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Abstract. The article discuss the main features of fly ashes as raw material for geopolymerisation. This article is focused on the examination of the fly ash (FA) from the CHP plant in Skawina (Poland) and assessment it as a main component of geopolymers. The article is focused on chemical and physical properties. The characteristic of the FA is presented, including particle size distribution, density, and chemical composition. The all parameters are discussed according to advantages and disadvantages using this FA to geopolymerisation process, including possibilities to achieve better results through proper preparation of the raw material.

1. Introduction

Producing and using coal affects the environment, especially air quality, including emissions from coal combustion such as: carbon dioxide (CO₂), sulphur dioxide (SO₂), nitrogen oxides (NOₓ), particulates, mercury and other heavy metals as well as residues created when power plants burn coal - fly ash (FA) and bottom ash. The estimations show that coal is responsible for 45% of energy-related carbon emission[1, 2]. Notwithstanding this, coal is the main energy source to produce electricity[3, 4]. Contemporary it is the second largest-energy source worldwide, covering almost 30% of global primary energy consumption. Hard coal together with lignite (brown coal) is the leading the world's non-renewable primary energy source with about 40% of globally generated power[2, 5]. Despite the forecasts that shows the percentage of the coal participation in the word energy sources will be quite rapidly decline, it hold their position. The coal consumption forelectricity generation is almost growing at the same rate as the electricity consumption (2.8% per year versus 3% per year between 2000 and 2017). It is driven primarily by Asian countries such as China and India[6, 7].

The amount of FA growth with the amount of burned coal. The estimations show that solid products of coal combustion such as coarse bottom ash and fine FA are 5–20 wt% of feed coal[1, 8]. For example, a thermal power plant with a capacity of about 1000 MW and with an operation 6600 equivalent hours per year, generates about 69000 tons of a slag and 383 000 tons of a FA [3]. The first one is composed of the residual coal ash that settles on the bottom of the boiler. The second - it is that floats into the exhaust stacks and it is collected by electrostatic precipitators during the coal burning process [1]. Usually, the FA is produced at a temperature between 1200-1700° C from feed coal. In this temperature the minerals in the coal melt to become fluid and on cooling form an amorphous
spherical FA particles. The percentage and quality of solid by-products are dependent on various factors, including: type of coal (bituminous, sub bituminous, lignite or anthracite), chemical and mineralogical composition (i.e. containing organic and inorganic materials), percentage of ash in coal, coal particle fineness, combustion technique used, boiler operating conditions such as air/fuel ratio, burners used, type of boiler and process undergone before combustion [6, 8]. As a result a FA characteristic is highly variable from source to source or even in different batches from the same source [9, 10].

The FA is a fine, spherical shape, heterogeneous glass-like particles - glassy spheres such as: precipitators, cenospheres and plerospheres. They generally have bumpy surfaces. Moreover, the FV contains glassy fragments, carbon blocks as well as small and spongyeous grains [1, 4]. The FA has various colour from tan to grey to black. The colour depends mainly on the amount of unburned carbon and presence of iron compounds [4, 7]. The size of particle is usually between 0.01 and 200 μm. Generally, 10% to 30% of particles are larger than 45μm [4, 7]. Specific gravity is from 1.9 to 3.0 [4, 9] and the bulk density is between: 1 - 2.5 g/cm³ [4, 7] and specific surface area is between 2,000 to 6,800 cm²/g [7].

Taking into consideration mineral composition, the FA is a powdery material, consisting primarily of silicon dioxide (SiO₂) (both amorphous and crystalline), aluminium oxide (Al₂O₃) and iron (III) oxide (Fe₂O₃) and calcium oxide (CaO) [7, 9]. The FA typically contains 90 - 99% inorganic material, 1-9% organic material, and up to 0.5% fluid components [1, 11]. The inorganic material is composed of 34 - 80% amorphous materials and 17% - 63% crystalline phases. The crystalline phases are usually: quartz, mullite, and various iron rich phases such as: hematite, goethite and calcite. The FA organic component is characterized by unburned carbon [1, 9].

From the chemical point of view the FA major qualitative compositions are similar to the natural earthy materials [4]. Usually, 95-99% of the FA consists of oxides of Si, Al, Fe, Ca and Ti and about 0.5% to 3.5% consists of Na, P, K, Mg, Mn and S. The rest of the FA is composed of trace elements such as As, B, Ba, Br, Cd, Cl, Co, Cu, Cr, Fe, Ga, Hg, I, In, Mo, Ni, Pb, Po, Pb, Pb, Sb, Se, Sr, Ti, W, V and Zn [4, 12]. It is worth to notice that the FA among these elements also consists of toxic elements, especially Cr, Pb, Hg, Ni, V, As, and Ba. The concentrations of the toxic trace elements in the FA is from 4 to 10 times higher than in origin coal [1, 4, 7]. Moreover, it may include dioxins and polycyclic aromatic hydrocarbon compounds [4, 13]. The pH of the FA is ranging from 4.5 to 12.0. It mainly depends on particle size and subsequent concentration of trace metals [4].

The most popular classification of the FAs based on ASTM678 standards (ASTM-C618-2). Depending on the chemical and mineralogical composition, there are two types of FAs, namely class F and class C – table 1 [7, 14].

**Table 1. Requirements for the chemical composition of class C and F ashes [15, 16].**

| Type of FA | SiO₂ + Al₂O₃ + Fe₂O₃ | SO₂ | Loss of ignition | Moisture |
|-----------|----------------------|-----|-----------------|---------|
| Class C   | min. 50              | max. 5 | max. 6             | max. 3  |
| Class F   | min. 70              | max. 5 | max. 6             | max. 3  |

The class F is characterised by a high percentage of silica (SiO₂), alumina (Al₂O₃), and iron oxide (Fe₂O₃) - min. 70% and additionally, low percentage of calcium oxide (CaO) – max. 4%, while class C has a high lime percentage (usually contains more than 20%), and constitutes at least 50% of silica (SiO₂), alumina (Al₂O₃), and iron oxide (Fe₂O₃) [7, 8]. When the FA is used with reactive aggregate for both types of FAs, the so-called alkali content - Na₂O eq. (as equivalent Na₂O), which means Na₂O eq. = Na₂O + 0.658 K₂O should be max. 1.5% [15].

The FAs-use become more and more popular, but still most FAs are deposited in open dumps without any pre-treatment, which involves a high risk of ecosystem pollution with danger to both human health and the environment [7]. Contemporary, the main directions of the FAs-use are:
construction industry, especially as admixture to concrete and concrete products, groutblended cement and feed for clinker, road base/sub-base, ceramic industry, mining application, catalysis, soil modification and stabilization, soil amendment and agricultural use, environmental remediation (against water pollutions), flowable fills, structural fills and embankments, blastind crit and roofing granules, wastestabilization and solidification, oil field services and miscellaneous [1, 13]. The literature also shows the possibility of using the FAs for the production of geopolymers, but the quality of received material is strongly depend on the chemical composition and physical properties used FA.

2. Material and methods

2.1. Material
The FA was delivered from the coal power plant ‘Skawina’ (located in: Skawina, Lesser Poland, Poland). The base material is bituminous coal. The power plant generates electricity and heat in its combined production. It has a generating capacity of 492 MW. The plant supplies heat and hot water to the Skawina city and the Western part of Cracow.

This FA is obtained by electrostatic precipitation of fine particles from the exhaust gases from coal-fired furnaces. According to the Polish law [17, 18], the FA is classified as combustion by-product with the no. 10 01 02 (Fly ash from coal).

2.2. Research methods
Physical and chemical characteristic of the FA was given by the supplier. Additional tests have been conducted, including determined particle size distribution of the FA by laser diffraction - Horiba PARTICA LA950 V2 type laser particle size analyser. During the measurement processes to achieve the appropriate dispersity state the distillate water was applied.

3. Results and discussion

3.1. Chemical composition
The table 2 shows chemical composition (oxides) of the FA given by the supplier.

| No | Oxide            | Value          |
|----|------------------|----------------|
| 1  | loss on ignition | 2.84 ± 0.14    |
| 2  | SO$_3$           | 0.95 ± 0.24    |
| 3  | chloride (Cl)    | 0.034 ± 0.010  |
| 4  | CaO              | 0.02 ± 0.01    |
| 5  | SiO$_2$ (reactive)| 35.86 ± 0.64   |
| 6  | SiO$_2$          | 47.81          |
| 7  | Al$_2$O$_3$      | 22.80          |
| 8  | Fe$_2$O$_3$      | 7.60           |
| 9  | SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ | 78.21 ± 1.28 |
| 10 | MgO              | 3.06 ± 0.23    |
| 11 | P$_2$O$_5$       | 0.0008 (8 ± 1 mg/kg) |
| 12 | Na$_2$O          | 1.72           |
| 13 | K$_2$O           | 4.62           |
| 14 | Na$_2$O$_{eq}$   | 4.76 ± 0.47    |

The results of the analysis of the FA according to supplier's declaration show useful the FA for the production of geopolymer materials. The FA is rich in oxides such as SiO$_2$ and Al$_2$O$_3$ and contains low amount of CaO. According to ASTM-C618-2, it belongs to class F.

The chemical composition of the FA as a raw material is very important for the formation of bonds characteristic for geopolymers. In the literature, the terms geopolymers and alkaline activated
materials are very often used as a synonyms. However, this approach is not correct due to the differences in the structure of these materials [20, 21].

Geopolymers consist of co-polymers of silicon and aluminium, which are stabilized by metal cations (M⁺), most often sodium, potassium, lithium or calcium, and bound water [20, 22]. In addition to these chains, the material usually contains other phases, i.e. silicon oxide, unreacted aluminosilicate substrate and zeolites [20, 23]. The geopolymer is characterized by the presence of SiO₄ and AlO₄ tetrahedrons in a three-dimensional structure. They are alternately bound by oxygen atoms. Binding usually occurs in strongly alkaline aqueous solutions, but the reaction can also be carried out in acids [20, 24]. The reactive aluminosilicates are dissolved, and next in the polycondensation process the tetrahedral structures [SiO₄]₄⁺, [AlO₄]₅⁻ combine together with the corners, forming amorphous or sub-crystalline spatial aluminosilicate structures [21, 25]. The presence of monovalent Na⁺, K⁺ or other metal cations balances the negative charge of this structure [20, 21]. Considering the entire geopolymerization process, alkaline activation is only the first step in creating geopolymer materials [20, 25]. In particular, differences in structure are visible in NMR microstructural studies, but it is possible to predict the structure of the material based on the composition of the raw material used for production [21].

Alkaline activated materials do not form 3D networks, but only a 2D structure. This affects their properties. The different structures mean that geopolymer and alkaline activated materials have different physico-chemical and functional properties, especially resistance to chemical agents, functional properties such as fire resistance and long-term properties - durability [20]. Wherein, the mechanical properties of alkaline activated materials could be even higher than that of geopolymers, especially in the short term [20].

In this case, the change in Si:Al ratio and distribution of essential oxides for geopolymerisation (SiO₂ and Al₂O₃) are important. It significantly influences on the position of most intensive band and finally affects final strength of geopolymers[26, 27].Moreover, weight ratios such as: SiO₂/Al₂O₃, CaO/Al₂O₃, CaO/SiO₂, SiO₂/Na₂O and Al₂O₃/Na₂O had very scattered effect on mechanical properties [27, 28]. For example, previous studies [9] have demonstrated that the FA with a high reactive Si:Al ratio (≥5) was sodium aluminate activated and produced geopolymers with low to moderate “as cured” compressive strengths. Despite the low mechanical properties, final material had excellent dimensional stability during heating and greater compressive strengths after heating. In contrast, the FA with a low reactive Si:Al ratio had high “as cured” compressive strengths but poor dimensional stability during heating and reduced compressive strengths after heating [9]. It is hard to specify exactly amount/ values of individual elements or their oxides in the base material, because it is one of the many factors that could influence on the whole process.

The chemical composition of the raw materials is particularly important for material structure forming. The high aluminium content and low calcium content promote the formation of geopolymer materials – 3D structure. Too high CaO content means that the binding process is too fast and thus the geopolymerisation process is not carried out properly. The polycondensation, that is main binding mechanism in geopolymers, needs time. Quick binding may cause insufficient dissolution of active ingredients in the mass and then an alkali activated material with a slightly different structure than geopolymers is created[24, 29].

The other compounds included in FAs, which may also have a negative effect on the geopolymerisation process, are: high content of sulphur compounds, unburned coal or some iron compounds [25]. The sulphur compounds (SO₃) could lead to instability in volume, which in turn has an impact on durability of final material [7]. Other sulphur compounds could also accelerate activation [7, 30]. The high content of unburned carbon increases the water requirement. Additionally, carbon particles have a very strong affinity and attraction to the organic chemical admixtures, these also influence on final properties, including the hardening process. In this case not only amount of it has significance, but also surface area, and type of carbon in terms of its polarity and particles size [7, 31]. With an increase in the content of loss on ignition (LOI), the content of other components (especially SiO₂) decreases. It affects for the activity of the FA - reducing the reactivity of pozzolanic
Additionally, as the quantity of unburned carbon particles increases, the mechanical properties of geopolymers decrease, in particular a compressive strength \[7, 25\]. A large amount of iron (on the order of several percent) in the form of hematite or magnetite could negatively affect the dissolving process of ash grains, which makes the geopolymer formation difficult. These compounds usually form on the surface of ash grains the layer and hinder the access of the liquid phase to its vitreous \[25, 32\]. However, some research shows that even high content iron oxide (Fe₂O₃) should positively influence on 3D structure \[7, 33\] and could be important in the high temperature applications \[34\].

Taking into consideration chemical composition, the best for the production of the geopolymer that has optimal properties, seems to be the FA class F that contains: less than 5% of unburned material, max. 10% of Fe₂O₃ and lower amount of CaO content \[7, 35\]. This kind of characteristic has the FA from the coal power plant ‘Skawina’. However, it should be emphasized that the chemical composition of the FA could be changeable. Other requirements is the high value of reactive silica. According to the literature the best will be reactive silica amount between 40 to 50% \[35, 36\]. The FA from ‘Skawina’ has smaller amount than optimal. However, there are some possibilities for increasing the reactive level of the FA, exemplary by milling \[37\] or supplementation by proper admixtures \[38\].

The other important factor, taking into consideration potential applications, is the content of heavy metals and toxic elements \[39, 40\]. The FA from the coal power plant ‘Skawina’ has limits for this kind of elements much below standard.

3.2. Physical properties

The physical properties also are important for the final material's properties. The FA from the coal power plant ‘Skawina’ has following physical properties: fineness of 16.7%, density 2.22 g /cm³ and an index of pozzulan activity after 28 days at level 92.0%, and after 90 days at 108.8% \[41\]. The size of particles was investigated. The median size was 14.54 μm. The mean size was 23.88 μm. About 88% of all particles were below 45 μm. The detailed results are presented in figure 1.

![Figure 1. The particle size distribution of the FA.](image)

The particle size distribution of the FA plays an essential role in the development of the mechanical strength of the obtained materials and it is connected with the reactivity of the FA \[32, 42\]. Contemporary, according to the literature sources, the most important are two mechanisms. Firstly, when the particles are up of 45 μm, this fact has a negative influence on the water requirement.
Particles sizes have also an important effect on the reaction rate of the FA at early stages. Secondly, once diffusion and dissolution of materials occur in concentrated pastes, surface the area of the particles could play an important role in determining the kinetics of different processes [7, 27]. The research shows when the particle fraction sized higher than 45 μm is removed, the mechanical strengths increase, reaching even 70 MPa compressive strength after 1 day [32, 34, 43].

Other important role plays fineness and specific surface area. The mechanical properties of geopolymers increase together with increase the specific gravity, decrease offineness and increase specific surface area [34].

The FA from the coal power plant ‘Skawina’ has good physical parameters for geopolymerisation process. The content of particle smaller than 45 μm is about 88%. According to the literature, the good FA should have between 80 to 90% of particles smaller or in the range of 45 μm [7].

4. Conclusions
The analyses confirm the usefulness of the FA from the CHP plant in Skawina (Poland) for geopolimerisation process. The chemical composition of this FA is typically for class F. It contains less than 5% of unburned material and less than 10% of iron compounds. Additionally, it has lower amount calcium content. The amount of the reactive silica in investigated material is reasonable – ca. 36%, however a little bit under optimal value (40 to 50%). This FA has also good physical parameters for the geopolymerisation process. The content of particle under the size 45 μm is ca. 88%. According to the literature, it is optimal value, also fineness declared by supplier shows that it could be useful material for application in geopolymers production.

This paper analyses only chemical and physical properties. To receive full information additional mineralogical and morphology analysis are required. The further characteristic of the FA from the CHP plant in Skawina (Poland), including the morphology examined by Scanning Electron Microscopy (SEM), the structure investigated by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD) is a topic of the second article.

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