Fly ash as a raw material for geopolymerisation–
mineralogical composition and morphology

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Abstract. The article discusses the main features fly ashes (FAs) as a raw material for geopolymerisation taking into consideration mineralogical composition and morphology. It is continuation the previous research connected with chemical composition and physical properties. This article is focused on the examination of a FA from the CHP plant in Skawina (Poland) and assessment it as a main component for geopolymers production. The characteristic of the FA is presented, including the morphology and mineralogical structure. The morphology was examined using Scanning Electron Microscopy (SEM). The structure of the FA was monitored also by Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray diffraction (XRD).

1. Introduction
A lot of mineral deposits in Europe are mostly depleted, reuse of waste and so called by-products is one of the main principles of sustainable development and circular economy [1, 2]. Additionally, growing environmental awareness and importance of development the sustainable construction materials with decreasing environmental impact for construction industry are main motivators to research works on possibility to use secondary raw material such as fly ash (FA) [3, 4].

Nowadays, the using of FA as so called secondary raw material becomes more and more popular, but still most FAs are deposited in open dumps without any pre-treatment. It involves a high risk of ecosystem pollution with danger to both human health and the environment [4, 5]. While the FA based geoplymer is an emerging alternative to conventional cement-based materials in civil engineering applications [1]. The particular motivation to implementation in the construction sector is planned eco-friendly effect. Currently, the building material production appears to be closer to traditional production models, characterized by high energy demand and high Green House Gases emissions, than other industries [2, 6]. These models should be turned into a green, circular and low-carbon economy [2, 7]. New solution such as using FAs and other wastes streams, including waste materials form construction and demolish industry and mine tailings as raw materials for geopolymerisation process help in contribution this sector in circular economy [1, 6, 8].

For the effective using waste materials such as FAs in geopolymerisation their quality is important [9, 10] as well as their safety for human health and the environment [11, 12]. The previous studies show that the chemical composition as well as the physical properties of the FA from the CHP plant in
Skawina (Poland) are proper for using this material for geopolymer synthesis. The chemical composition of this FA is fulfill the requirements for a class F according to ASTM678 standards (ASTM-C618-2). This FA contains less than 5% of unburned material, less than 10% of iron compounds and a low amount calcium content [13, 14]. The amount of the reactive silica is about 36% - it is under optimal value: 40 to 50%. The limits for content of heavy metals and toxic elements for this FA is much below standards [12]. It has also good physical parameters -the content of particle under the size 45 μm is about 88%.

But not only the physical and chemical properties influenced on the behaviour of fresh and hardened geopolymer also the crystallographic and morphology of the FA play important role [15, 16]. This paper analyses the mineralogical and morphology of the FA from the coal power plant ‘Skawina’ as a raw material for geopolymer production.

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. 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 a combustion by product with the no. 10 01 02 (Fly ash from coal).

2.2. Research methods
The mineralogy composition was determined using powder X-ray diffraction Debye-Scherrer Hull method. Diffractograms of samples were recorded with the use of a Rigaku SmartLab X-ray diffractometer. The following parameters were applied: CuKα radiation, a graphite reflection monochromator, tube voltage 45 kV, tube current 200, step scan mode: step size = 0.05°2θ, count time per 1 step = 1 s. The identification of phases based on data contained in the ICDD Catalogue (International Centre for Diffraction Data 2014) and XRAYAN software. The structure of the FA was determined by Fourier Transformed Infrared Spectroscopy (FT-IR). The samples induced by infra range electromagnetic waves was detected by JASCO FT-IR 4200 type Fourier Transformed Infrared Spectrometer in reflection mode, diamond ATR was used. The morphology of the samples was examined by means of the scanning electron microscopy (SEM) type JEOL JSM 820 with EDS. The FA had been properly prepared before i.e. dried to the constant mass, put on the coal base to carry the electric charge of the sample away, and covered with thin layer of gold with the JEOL JEE-4X vacuum sputter. The observations were made at various magnifications (between 20 and 1000 times).

3. Results and discussion

3.1. Mineralogical characterization of FA (FT-IR, XRD)
The mineralogical composition is partly connected with the chemical composition and physical properties of the FA, especially content of reactive silica. The provided tests allow to observe non-crystalline phases in the FA. In the literature, this kind of phases are differently called by different authors: amorphous phase, vitreous phase or glassy phase [19-21]. However, there is some differences according chemical point of view between these terminologies [22] in the article there will be use appellation - amorphous phase.

The results of X-ray diffraction analysis of the FA from coal power plant ‘Skawina’ are presented in figure 1.
Figure 1. XRD pattern of the FA from the CHP plant in Skawina (Poland).

The identified phases were fitted to the diffractogram of the examined FA - table 1.

Table 1. The marked phases.

| Name          | Chemical formula | [%] | Ref. Code     |
|---------------|------------------|-----|---------------|
| Quartz        | SiO₂             | 43,0| 01-070-3755   |
| Mullite       | Al₆Si₂O₁₃        | 52,8| 00-015-0776   |
| Hematite      | Fe₂O₃            | 0,6 | 01-084-9870   |
| Magnetite     | Fe₃O₄            | 0,6 | 04-006-6550   |
| Anhydrite     | CaSO₄            | 2,4 | 01-085-6133   |
| Rutile        | TiO₂             | 0,4 | 00-034-0180   |

The results show the presence of crystalline phases typical for FAs such as: quartz (related with silicon dioxide), mullite and anhydrite. The curves indicated also on presence amorphous phase (indicated by diffuse halo / curves has a broad hump). The presented composition is typical for FAs. Usually, the most frequent crystalline phases are: quartz, feldspar, mullite, anhydrite and hematite [19]. In case of application in geopolymer manufacturing the most important is large amount of amorphous phase. During the reaction, the reactive components undergo geopolymerisation and create binders whereas the un-reactive components behave like aggregate in traditional concretes [20].

To confirm of presence the aluminosilicates in the FA, especially amorphous phases the FT-IR measurements has been done. The FT-IR was made for the FA from the CHP plant in Skawina (Poland) - bituminous coal and compared with two coals form Hungarian: form brown coal and lignite [23, 24]. The results are shown in figure 2.
Figure 2. The FT-IR for the FA from the CHP plant in Skawina (Poland) with comparison to Hungarian FAs.

FT-IR clearly shows the presence of aluminium silicates and/or aluminosilicates in all FAs. The results show the domination of bands associated with the silica dominated in the all spectra. These are: the most intense band at about 1100 cm\(^{-1}\) which is connected with asymmetric stretching vibrations and also Si-O(Si) bound at about 460 cm\(^{-1}\) connected with bending vibrations O-Si-O presented in silicate tetrahedra [25, 26]. The doublet about 800 cm\(^{-1}\) is associated with the symmetric stretching vibrations of Si-O-Si bridges. It is probably connected with low temperature quartz appearance that is lower in the FA form CHP plant ‘Skawina’ then for other FAs. A high full width at half maximum (FWHM) indicates on significant amount of amorphous phase which structure is silicate and/or aluminosilicate [25, 26].

Moreover, the band at around 1000 cm\(^{-1}\) appear in the analysed spectra. It may be connected with asymmetric stretching vibration of Si-O (Al) presented in aluminosilicates structures. Substitution of aluminium atoms in tetrahedral positions in these structures results in a change the position of the band: from the position about 1100 cm\(^{-1}\), in the case of ‘pure’ silica structure, to lower and lower wavenumbers with increasing Al/Si ratio [25, 27]. The Al/Si ratio increases with the decreasing values of wavenumbers due to the substitution of aluminium atoms for Si at the tetrahedral position [25, 28, 29].

The bound at about 915 cm\(^{-1}\) confirms the presence of aluminium in the octahedral position, confirming - the existence of mullite [27, 29]. Additionally, it is worth to notice presence the bounds associated with calcite (at about 1450 and 875 cm\(^{-1}\)) and other bounds appearing at around 3400 cm\(^{-1}\) and 1625 cm\(^{-1}\) are attributed to the stretching vibration and bending vibration of OH in H\(_2\)O molecules. The second one indicates a small amount of molecular water [25].

Taking into consideration geopolymerisation process one of the most important parameters in amount of amorphous phase. The amount of amorphous phase is connected with content of reactive material in the FA. The ‘reactivity’ does not only refer to the amorphous phase, but to the FA as a whole [19, 30]. However, the amorphous SiO\(_2\) content, amorphous Al\(_2\)O\(_3\) and the median particle size of the FA can be used as reactivity index of FA used for geopolymers [21]. That means the increasing amount of amorphous content is reflected in a high proportion of so-called reactive silica [25, 26]. Usually, the FAs form coal has between 46 and 50% reactive silica [31] and amount of amorphous phase could be between 30 and 80% [32].

The FA reactivity and solubility in an alkaline solution also depends on the composition and content of the amorphous phase [19, 33]. The higher amount of amorphous phase is connected with lower Si/Al ratio and higher amount of soluble aluminium [19,34]. For the geopolymerisation process
FAs with different reactivity are expected to produce diverse reaction products, resulting in different compressive strengths [35, 36]. Especially, low reactivity of FA results in slow binding and early strength development. It caused delayed setting and lack of development full 3D network in material structure - the dissolution of the FA does not complete before the final hardened structure is formed [20, 28, 37]. In case of FAs that have high amount of reactive content, when there are mixed with the alkaline dissolution, the amorphous component is quickly dissolved. In such a situation, main reaction product is an amorphous or semi-crystalline material. The higher the amount of amorphous phase in the FA, the faster the activation process and the higher the degree of reaction in geopolymers is. It significantly influence on the mechanical strength of the final products [38, 39].

From the mineralogical point of view, together with increasing the content of amorphous phase, the capacity of activation for the FA is higher [38]. The content of amorphous phase is related with thermodynamic and kinetics of the activation process and affects the amount of aluminosilicates which is dissolved in the alkaline medium as well as to its rate of dissolution [38]. Finally, the reactivity of the material is connected with coal burning. The high temperature caused that the process the calcination has a place and the calcined materials such as the FA are mainly amorphous and has higher reactivity during geopolymerisation than uncalcined materials [37]. It is caused that calcination activates materials from crystalline to amorphous structure and extra energy stored in them [36, 37]. The amount of amorphous phase is also connected with the quick cooling of the FA from sintered state. It makes the FA to be basically amorphous with small amounts of crystalline components [38]. That mean the reactivity depends strongly on the burning parameters for the coal in CHP plant.

3.2. Morphology

Moreover, is worth to notice that for the reactivity of the FA could influence not only the amount of the amorphous phase, but also the physical properties of the FA such as: the particles size - the best up of 45 μm (an important effect on the reaction rate of FA at early stages) [5, 40] and the surface area of the particles (considerable role in determining the kinetics of different processes) [5, 40]. Due to the fineness of FA particles the reactivity level increases [19, 41], with the surface area of the particles the issue is a little bit more complicates, because the process depends not only on measured value but also on the particles morphology [5].

The morphology of the particles of fly ash was typical of such by-products of coal combustion and suitable for the process of alkali-activation [16]. Observations of the morphology of the FA from the CHP plant in Skawina (Poland) particles have shown that they have regular shapes, mostly spherical (figure 3). From the point of view of the geopolymerisation process, the presence of spherical particles is beneficial and improves the rheological properties of the mixture, in particular, improves its workability and reduces the need for liquid substances [40], which in turn has a positive effect on seasoning and ensures the receipt of geopolymer materials with good mechanical properties. Additionally, EDS analyses confirmed the high content of key elements for the geopolymerisation process – silica and aluminium and the low calcium content (figure 4andfigure 5).

EDS analyse was performed for the selected approximation in point (figure 4) and in a selected area (figure 5). They were carried out on selected particles of the FA visible on the SEM image (figure 3). The main element is oxygen due to the composition of the FA, which is composed of oxides of various elements. Analyses show a large amount of silicon and aluminium in the ash and low calcium content. In addition, in point 1 (figure 4), the analysis showed a significant amount of iron, suggesting that it is visible in figure 4 on the "raid" sphere, iron oxides are present in the FA. Analyse in the area 3 (figure 5) show a small amount of this element. It is coherent with results of investigation for mineralogical composition - XRD. The FA also contains admixtures of other elements, i.e. magnesium in small amounts.
Figure 3. SEM image – the FA from the CHP plant in Skawina (Poland) [16].

The properties of the FA based geopolymer could be affected by many parameters. A lot of them is significantly related to the primary materials and their characteristics. The particular parameters are often related each other, exemplary size and distribution of particles, the amorphous phase in the content and the reactivity of both silicon and aluminium are very often related with burning process [5, 28]. Other parameters such as: curing temperature and pressure, duration of curing, type of curing (conventional heating or microwave heating), type and concentration of alkalis or alkaline liquid-to-raw material ratio, are connected with geopolymerisation process. All of them must be properly combined to receive required properties of the final product [43, 44]. Usually, the manufacturer do not have influence on the quality of the raw materials, but it could implement some modifications for increasing their usefulness for geopolymerisation process trough pre-treatment or selection the process’ parameters. Because of that it is very important to have a knowledge about the raw materials for proper design the geopolymerisation reaction.

4. Conclusions
The reactivity of the FA (defined as the ability of the FA to react with alkali solution and form geopolymers) is the combined effect of particle size and content as well as amorphous phase composition. The analyses confirm the usefulness of FA from the CHP plant in Skawina (Poland) for geopolymerisation.

The morphology examined by Scanning Electron Microscopy (SEM) shows that it is suitable for the process of geopolymerisation. The FA contains a lot of spherical particles and should have good workability and reasonable requirements on liquid substances. At the same time the mineralogical structure was investigated by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). The research shows the composition typical form FAs with large amount of amorphous phase, what is required in geopolymers bounding creation. The article do not presented the mechanical and physical properties of the FA that have been studied in other manuscript.

It can be concluded that the use of the FA from the CHP plant in Skawina (Poland) as a raw material in the production of geopolymers is highly recommended. It has required properties for this process and utilization this by-products, without down-cycling, for a production of construction materials. The quality of this secondary raw materials is comparable or in some case even better than
compared to primary mining products such as metakaolin. Because of that it could have a significant contribution to circular economy and environmental protection development as well as possible energy savings and CO$_2$ emission reductions.

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