Geopolymers based on plasma incineration waste as a material for circular economy

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Abstract. Plasma waste treatment technology is one of the promising methods of reducing problematic waste, but the technology itself create other kind of waste that must be effectively used to recognize this technology as a suitable for circular economy. The aim of the article is to show the possibility of using waste materials from a plasma incineration plant as a raw material for the production of geopolymeric materials. The samples were made based on waste from plasma incineration plant in Liberec (Czech Republic), fly ash from thermal power plants in Skawina (Poland) and sand mixed with an aqueous chemical solution. Next they mechanical properties, microstructure and mineralogical composition have been investigated. The results show the combination of these raw materials can increase the strength of the material and, consequently find applications in the utilization of plasma incineration waste. The article show the geopolymerization could be effective process for using waste materials from a plasma incineration plant as a raw material for creating the products for construction industry.

1. Introduction

The circular economy and its aspect of reusing waste as a substitute for natural resources is a current research topic all over the world. Various types of waste from various market sector can be used to invent new types of materials, the use of which will correspond to the current needs of the market, mainly in the construction and transport industries. The production of more and more waste forces the development of new technologies combined with the recovery of energy and materials [1].

Plasma waste treatment technology is one of the promising methods to reduce waste generated in industrial plants, research institutes, hospitals and even nuclear reactors [2,3]. It is a safe and cost-effective method for the disposal of the most troublesome wastes with a high degree of harmfulness. In addition, the action of temperatures above 1400°C (which occur in plasma combustion) reduces the
volume of waste treated [2]. Research shows higher efficiency of plasma technology compared to commonly used waste incineration technologies, especially due to the ability to treat different types of waste [4,5]. This technology can be used also for immobilization of hazardous slags, however in practice it just reduces it volume, but not eliminate whole problem. Nevertheless it is commonly used for hazardous wastes processes in EU [6]. The use of high temperature plasma stream, low content of atmospheric oxygen and the speed of the process are likely to neutralize the toxic substances contained in hazardous class waste [3]. Temperatures of several hundred thousand degrees allow the processing of any type of waste (solid, liquid, gaseous), where a high Energy decomposition of substances takes place [7]. Plasma gasification technology is a modern method of utilizing waste and, as a result, obtaining electricity or fuels [8]. This modern technology can replace non-renewable fossil fuels with clean energy recovery [8,9].

Fly ash from municipal waste incineration plants is a major environmental problem. They pose a threat to human life and health due to heavy metals and other toxic pollutants. The solution to this problem and stabilization of the fly ashes is their vitrification as a result of plasma combustion. This method is environmentally friendly and has a sustainable effect of treating waste from municipal incineration plants [10]. A reasonable method of neutralizing the mentioned waste resulting from the incineration of municipal waste is also the use of fly ash for geopolymer mortars [11].

Geopolymers are inorganic polymers made from the synthesis of silicon and aluminum geologically obtained from minerals, fly as or slags [12,13]. The production temperature of geopolymeric materials does not exceed 100°C (most often 75°C) [14,15]. The most popular material used for the synthesis of geopolymers is metakaolin, which, due to its high price, limits the development of these materials [16]. Therefore, there is a need to replace natural resources with materials from secondary processing, such as by-products of coal mining, or material from various types of incineration plants [17]. The materials obtained in the geopolymerization process are not only characterized by high mechanical properties, but also a number of features, such as bonding of heavy metal elements or refractoriness [18,19]. In the context of current research geopolymers are especially interesting because of their properties connected with immobilization of hazardous materials [20]. Anastasiadou et al. described in their paper the possibility of managing bottom ash and fly ash from medical incinerators. By storing them in a safe manner (not in hazardous waste landfills), it is possible to sink them into a matrix using Portland cement [21].

The action of the plasma jet on the waste material results in a transition to a glassy state, otherwise known as the glass transition point [22]. Under the influence of high temperature (about 1400°C), the incinerated waste is transformed into a liquid phase and then in the cooling phase into a solid phase, which has the structure of glass [23]. Vitrification applies to inorganic materials that contain oxides of silicon, aluminum and other glass-forming elements. Due to its composition, vitrified material after appropriate mechanical treatment (crushing, grinding) can potentially be used as a raw material for the production of geopolymers. Until now, research on this solution has been carried out on waste residues from air pollution control [24]. This waste is generated during the treatment of gas emissions in municipal waste Energy processing plants. The research showed the possibility of forming geopolymeric materials from the presented raw materials, and the produced samples showed high compressive strength [22,25].

The article examines the possibility of using waste from plasma incineration plants for the production of geopolymeric materials. This method of managing hazardous class waste is ecologically effective and allows for the disposal of toxic residues [26].

2. Materials and sample preparation
The waste from the plasma incinerator in Liberec (Figure 1), due to the different particle sizes (even above 30 mm), was mechanically crushed to obtain increasingly smaller fractions. Finally, an electric mill with a mesh size of 0.75 mm was used, yielding grain fractions in the range of 0.00 - 0.74 mm after grinding (Figure 2).
Conventional fly ash of F class was obtained from Skawina Heat and Power Plant (Skawina, Poland), while river sand came from Świętochłowice site (Poland).

Analysis by EDS X-ray detector showed that the chemical composition of the studied waste material from the plasma incinerator in Liberec contains mostly oxygen – 52%, silicon – 21%, aluminum 15%, calcium – 6%, iron – 4.5%. A significant amount of oxygen, silicon and aluminum allows the formation of compounds, that promote the activation of the alkaline material and the formation of characteristic phase for geopolymer materials, which was confirmed in the X-ray diffractometry XRD.

The chemical composition of the fly ash used is typical for class F. Lach et al. also used the same type of fly ash from the same source for their research [27]. It contains less than 5% unburned carbon, less than 10% iron compounds and little calcium. The amount of reactive silica is about 36%. Fly ash has good physical parameters, contains a lot of spherical particles, has good workability [28] and a large amount of amorphous phase [27].

The alkaline activator was a solution of 10 mol/dm$^3$ sodium hydroxide and R-145 sodium water glass with a molar modulus of 2.5 and a density of about 1.45 g/cm$^3$. The solution was prepared according to the scheme: flakes of technical hydroxide were dissolved in water, and then an aqueous solution of sodium silicate was added. The ingredients were mixed and allowed to reach a constant concentration.

To prepare the geopolymer mixture, precursors were mixed with activator for about 10 minutes. The obtained plastic paste was used to fill sets of prismatic forms with dimensions 50 mm x 50 mm x 200 mm and cubic 50 mm x 50 mm x 50 mm, and then placed on the vibrating table. The molds were placed on a vibrating table to remove air bubbles. After preparing the masses, the samples were covered with foil and placed in a laboratory dryer (SLW 750 STD, Pol-Eko-Aparatura, Wodzisław Śląski, Poland) for 24 hours at 75 °C. The samples were removed from the mold and cured under laboratory conditions (temperature about 20 °C, relative humidity about 50%) for 28 days.
After this period of time, mechanical properties were tested and microstructure was observed by SEM. Table 1 shows the composition of the prepared samples and their mass proportions. For flexural strength testing, 4 specimens of each type of geopolymer were prepared. For compressive strength testing, 6 specimens of each type of material were prepared.

Table 1. The composition of the prepared samples.

| Sample | Solution (mol/dm$^3$) | Composition                        |
|--------|------------------------|------------------------------------|
| FA-S   | 10                     | fly ash + sand (1:1) - reference sample |
| FA-SL  | 10                     | fly ash + sand + glass from plasma incineration plant (1:1:1) |
| FA-L   | 10                     | fly ash + glass from plasma incineration plant (1:1) |

3. Methods

The density of the produced geopolymers was determined using the geometric method, which consists in precisely dimensioning the sample with a caliper (to the accuracy of 0.01 mm) and weighing in with an analytical balance with an accuracy of 0.001 g.

Compressive strength tests were carried out on a testing machine MATEST 3000 kN with a speed 0.05 MPa/s, according to the standard [29]. The tests were carried out on cubic samples with dimensions of 50mm x 50mm x 50mm.

The flexural strength tests were carried out similarly to the compressive strength tests, according to the standard [30] on the MATEST 3000 kN testing machine with a speed of 0.05 MPa/s. These tests were carried out on samples of dimensions 50 mm x 50 mm x 200 mm. The distance between the support points in the testing machine was 150 mm.

In order to identify the mineral composition of individual types of geopolymeric materials, created on the basis of waste from the plasma incineration plant in Liberec, an analysis was carried out using XRD diffractometer. By using HIGH Score Plus software and crystalline materials database (PDF4+), a phase type was assigned for each sample.

The observation of the microstructure of the geopolymers was made using the scanning electron microscope (SEM) of the JEOL JSM 820 type with EDS on the breakthroughs of the samples after the compressive strength tests. Preparation of samples for the observation was to their previous sputtering a thin layer of gold by vacuum sprayer JEOL – JEE-4X. The samples were observed at different magnifications.

4. Results and discussion

4.1. Density

The true density of the produced FA-S, FA-SL, and FA-L geopolymers was determined using the geometric method. The density was determined as the average of measurements for 3 samples of each type of geopolymer material.

Table 2. Density result.

| Sample | Density [g/cm$^3$] |
|--------|-------------------|
| FA-S   | 2.0 ± 0.06        |
| FA-SL  | 2.2 ± 0.07        |
| FA-L   | 2.5 ± 0.1         |

The density of the produced geopolymers is in the range of 2.0 and 2.5 g/cm$^3$. The density should be correlated with the result obtained in the bending and compression tests. Geopolymer samples made of fly ash and waste from a plasma incineration plant are characterized by the highest density – 2.5 g/cm$^3$. The samples based on fly ash and sand have the lowest density 2.0 g/cm$^3$. This means that the material from the plasma incineration plant in Liberec has a high density.
4.2. Compressive strength

The results from compressive strength tests are presented in table 3.

| Sample | Compressive strength [MPa] |
|--------|---------------------------|
| FA-S   | 23.9 ± 2.45               |
| FA-SL  | 39.6 ± 9.22               |
| FA-L   | 14.9 ± 4.32               |

The best results were achieved for the samples made with fly ash, sand and plasma incineration plant waste ~ 39.6 MPa. Samples based on fly ash and waste form the incineration plant in Liberec had a lower result by more than half ~ 14.9 MPa. Reference samples (fly ash and sand) were achieved 23.9 MPa. The results for individual samples had significantly different values. The reason for such large differences in the values obtained could be the different material composition of the types of geopolymers.

4.3. Flexural strength

The results from flexural strength tests are presented in table 4.

| Sample | Flexural strength [MPa] |
|--------|-------------------------|
| FA-S   | 6.3 ± 1.29              |
| FA-SL  | 7.4 ± 2.69              |
| FA-L   | 3.6 ± 2.28              |

The flexural strength tests give similar results as compressive strength tests. The best results were achieved for the samples made with fly ash, sand and plasma incineration plant waste 7.4 MPa. The second best result was obtained for the reference samples 6.3 MPa, which is not significantly different from the former. Clearly worse values were obtained for the geopolymers based on fly ash and plasma incineration waste. The results for these samples were only 3.6 MPa. The reason for such low crushing strength results for the last type of geopolymer may be due to the lack of presence of additional aggregate in the form of sand grains, which were present in the first and second type of geopolymer material.

4.4. Microstructural investigation

Figure 4 shows three randomly selected points on the sample FA-S, from which the elements present in the material were determined by means of X-rays. Figures 5(a, b, c) show the spectra obtained, on the basis of which the respective characteristics of the elements were adjusted.

![Figure 4](image1.jpg)

**Figure 4.** SEM image of sample FA-S.

![Figure 5a](image2.jpg)

**Figure 5a.** EDS analysis of point 1 of the sample FA-S.
The composition of the investigated type of geopolymer (Fa-S) contains elements such as O, Na, Mg, Al, Si, K, Ca and Fe. Their percentage varies depending on the point determined for EDS analysis.

The surface of the FA-SL sample (Fig.6) was analyzed at three random points. The obtained spectra allowed for the characterization of individual elements present on the surface of the tested material.

![Figure 5c. EDS analysis of point 3 of the sample FA-S.](image)

**Figure 5c.** EDS analysis of point 3 of the sample FA-S.

![Figure 5b. EDS analysis of point 2 of the FA-S sample.](image)

**Figure 5b.** EDS analysis of point 2 of the FA-S sample.

![Figure 6. SEM image of sample FA-SL.](image)

**Figure 6.** SEM image of sample FA-SL.

![Figure 7a. EDS analysis of point 1 of the sample FA-SL.](image)

**Figure 7a.** EDS analysis of point 1 of the sample FA-SL.

![Figure 7b. EDS analysis of point 2 of the sample FA-SL.](image)

**Figure 7b.** EDS analysis of point 2 of the sample FA-SL.

![Figure 7c. EDS analysis of point 3 of the sample FA-SL.](image)

**Figure 7c.** EDS analysis of point 3 of the sample FA-SL.
In all three cases of EDS analysis (Figure 7a, b, c) for the FA-SL geopolymer, a high content of elements such as O, Al, Si and Na was obtained. These are the basic elements present in fly ash based geopolymers. The additional metals present in the sample (Ni, Zn, Fe, Cr or Mg) may be components of the plasma combustion wastes that were used as an additional aggregate during the preparation of the FA-SL sample.

The surface of the geopolymer material based on fly ash and waste from the plasma incineration plant in Liberec was tested using the EDS system (Fig. 8).

The analyzed point 1, 2, 3 in Fig. 8 and the obtained spectra (Fig. 9a, b, c) correspond to the characteristics of elements such as O, Na, Al, Si, Ca, Fe. The second element in terms of intensity is Nb. Its presence may be due to the admixture of ash from the burning of waste from the Liberec plasma incinerator.

4.5. Mineralogical composition

Figure 10 shows XRD measurements registered for the FA-S sample, along with the symbols of the identified phases. Table 5 presents a summary of the different phases along with a description of the chemical composition of each phase.
Figure 10. XRD diffractogram of FA-S geopolymer.

Table 5. Identified phases and their chemical formulas of the FA-S geopolymer.

| Sample ID       | Identified phases | Chemical formula |
|-----------------|-------------------|-----------------|
| FA-S Reference sample | Quartz           | SiO₂            |
|                 | Sillimanite       | Al₂(SiO₄)O      |
|                 | Arcanite          | K₂(SO₄)         |
|                 | Hematite          | Fe₂O₃           |
|                 | Aluminum Phosphate| AlPO₄           |
|                 | Brookite          | TiO₂            |

Based on the diffractometric analysis performed, it was found that the reference sample is characterized by a high content of quartz and aluminum phosphate. In addition, phases such as Sillimanite, Arcanite, Hematite and Brookite were identified.

The XRD diffractogram presented in Figure 11 was obtained for a geopolymer based on sand, fly ash and waste from plasma incineration plant in Liberec. Table 6 gives the chemical composition of the individual compounds present in the above material.

Figure 11. XRD diffractogram of the FA-SL geopolymer.
Table 6. Identified phases and their chemical formulas of the FA-SL geopolymer.

| Sample ID | Identified phases | Chemical formula |
|-----------|-------------------|------------------|
| FA-SL     | Anorthite         | CaAl$_2$Si$_2$O$_8$ |
|           | Microcline        | KAlSi$_3$O$_8$   |
|           | Mullite           | (AlO$_3$)$_2$(SiO$_4$)O |
|           | Quartz            | SiO$_2$          |

The sample based on sand, fly ash and waste from plasma incineration plant in Liberec was characterized by a high content of Quartz and Microcline. Additionally, the recorded peaks indicated the presence of Mullite and Anorthite.

Figure 12 shows the diffraction pattern obtained for the material based on fly ash and waste from the plasma incineration plant in Liberec (sample FA-L).

Table 7 identifies the chemical formulas of the various phases present in the FA-S geopolymer.

Table 7. Identified phases and their chemical formulas for FA-L geopolymer.

| Sample ID | Identified phases | Chemical formula |
|-----------|-------------------|------------------|
| FA-L      | Tridymite         | SiO$_2$          |
|           | Attakolite        | CaMnAl$_8$(HSiO$_4$)(PO$_4$)$_4$(OH)$_4$ |
|           | Cornetite         | CuPO$_4$(OH)$_3$ |
|           | Aluminum Phosphate| AlPO$_4$        |
|           | Chopinite         | Mg$_3$(PO$_4$)$_2$ |
|           | Kieserite         | MgSO$_4$(H$_2$O) |

Through XRD analysis, the FA-SL geopolymer was found to have high peaks, corresponding to compounds such as aluminum phosphate, concretite or tridymite. In addition, additional phases were found to be present: Attakolite, Chopinite and Kieserite.

Figures 13, 14 and 15 show the microstructure of all types of geopolymer materials analyzed in the above article. Figure 13 shows images of the FA-S geopolymer.

Figure 12. XRD diffractogram for the FA-L geopolymer.
FA-S geopolymer is characterized by a compact, amorphous structure with visible pores with a maximum size of about 50 µm. Undecomposed fly ash particles in spherical form are also visible. This material structure is typical for fly ash based geopolymer materials. In the literature, the microstructure of geopolymer mortars is described as a heterogeneous porous mixture, in which some of the fly ash grains did not dissolve or reacted only in a certain volume [28].

Figure 14 shows the geopolymer surfaces of the FA-SL.

Observation of the microstructure of the FA-SL geopolymer (Figure 14) indicates a compact material structure, with pore sizes oscillating between 20 µm and 50 µm. In addition, like the reference sample material, undiluted fly ash particles can be observed. The irregular, pointed grains with a size of 100 - 200 µm represent aggregate material in the form of waste from the plasma evaporation plant, which did not react with other components during the geopolymerization process. In this case, alkali gel ash and sand provide the matrix for the above particles.

Figure 15 shows the surfaces of the geopolymer based on fly ash and waste from plasma incineration plant in Liberec (sample FA-S).
Figure 15. SEM image of FA-L geopolymer.

FA-L geopolymer is characterized by a cohesive structure with no apparent pores. Under higher magnification also, no undecomposed fly ash particles were observed. A characteristic feature of the studied geopolymer is the presence of sharp-edged and irregular fragments associated with the geopolymer matrix. Most likely, these are fragments from the plasma incinerator that did not react during the geopolymerization process. The size of these structures ranges from 25 µm to 100 µm.

5. Conclusions
The results obtained from the compressive strength and flexural strength tests are closely related. The highest results were obtained for samples based on three components: fly ash, sand and waste from the plasma incineration plant in Liberec (FA-SL geopolymer). This shows that the combination of these raw materials can increase the strength of the material and, consequently find applications in the utilization of plasma incineration waste. The received values are proper for application in many construction application such as pavements, bricks or slabs, however the future leaching and radiological investigation is necessary to confirm the safety of this material [20]. Plasma waste incineration technology is still a new technique that requires research and improvement.

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