Strength and leachability of geopolymers with the addition of municipal solid waste ashes

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Abstract. The paper presents the results of the study concerning the possibility of immobilization of secondary waste from municipal waste incineration plants in geopolymers. The study was conducted for 2 different sources of ash from Poland and Lithuania. Three different types of waste were tested. Geopolymers were made with 70% added waste from incineration plants. The samples were made in many variants: geopolymers were made on the basis of fly ash and metakoline and waste was added untreated and after washing with water in a ratio of 1:5 (solid/liquid). Compressive strength and water leaching tests were carried out. As a result of the study, geopolymers as a material for immobilization of secondary waste from waste incineration plants were found to be useful. Water leaching tests proved that all the tested wastes stabilized in geopolymers are characterized by very low leachability values of metals such as: copper, zinc, lead, etc.

1. Introduction
One of the methods of disposal of post-processing waste from incineration plants is geopolymerization, which has been increasingly used in many industrial sectors in recent years [1-4]. Geopolymers are a group of materials defining inorganic aluminosilicate polymers with specific composition and properties. They are hard, mechanically resistant materials which also have extraordinary resistance to chemically aggressive environments. The term "geopolymer" was first used by the French scientist Professor Joseph Davidovits in 1970. These materials were initially developed as a fire-resistant alternative to organic thermosetting polymers. Since then, however, the main applications for geopolymer binders have been in the construction industry [1, 2].

Geopolymeric materials are a family of modern construction materials with a number of properties that enable them to replace popular engineering materials such as traditional concrete or building composites. In the future, they may also become an ideal material for the disposal of hazardous materials, including ashes from waste incineration plants [11-12]. Scientific research shows that in comparison to Portland cement technology, solutions for the containment of hazardous waste in geopolymers and alkaline-activated binders offer much greater possibilities for immobilization of heavy metals. Studies on the possibility of metals immobilization in alkali activated binders [5] have shown that alkali activated slags can be used as a means of immobilizing heavy metals. The
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microstructure of alkaline-activated slags shows a higher number of gel pores compared to Portland cement-based slags and at the same time a much lower number of capillary pores. The use of MSWI bottom ash may also increase the density and homogeneity of geopolymer and cement matrix [6].

The results showed that metal leaching in a geopolymer matrix based on fly ash from incineration plants and volcanic ash was significantly reduced. The leaching levels were much lower than the limit set by the United States Environmental Protection Agency (USEPA) [7]. Although geopolymer technology is more effective for leaching pollution compared to other technologies, the study [8] has shown that the values obtained for e.g. chlorides are still higher than the restrictions imposed by e.g. Italian regulations for the disposal of stabilized waste in landfills for non-hazardous waste. As regards the release of chlorine, the values detected in waste stabilized in geopolymers indicate that pre-treatment of waste is required.

The available scientific literature increasingly describes the need for pre-treatment by waste washing. It is not possible to carry out an effective process of stabilizing fly ash from municipal waste incineration without appropriate pre-treatment [6,9,10]. The pre-washing process is most often used to remove chlorides that have a negative effect on the stabilization of a solidified cement-based matrix [13]. The conducted study [14] allows to state that the preliminary treatment of waste consisting in rinsing with water increases the final strength of geopolymers with waste compared to unwashed ashes. IR spectra also suggest that geopolymers with water-washable ashes can provide a more chemically stable heavy metal capsule.

This article presents the results of the study of compressive strength and water leaching for geopolymers with introduced waste from municipal waste incineration plants. The focus was on the comparison of the leaching values for untreated waste and waste after the rinsing process.

2. Material and methods

2.1. Material

Geopolymers were made in two variants: based on 30% of fly ashes from the Skawina CHP Plant and based on 30% of metakaoline. 70% of processed waste (after washing processes) and unprocessed waste was used as additives/fillers from waste. To produce geopolymers flakes of technical sodium hydroxide were used and an aqueous solution of sodium silicate (R-145) whose molar ratio was 2.5 and density was about 1.45 g/cm³. The tap water was used instead of the distilled one. The alkaline solution was prepared by means of pouring the aqueous solution of sodium silicate over the solid sodium hydroxide. The solution was thoroughly mixed for 15 minutes in a low-speed mixer and allowed to equilibrate until a constant concentration and temperature. Next, the obtained paste was poured into cubic molds 100x100x100 mm. The solidification was conducted on the vibratory table. Then the molds were heated for 24 hours at 75°, cooled to the ambient temperature, taken out of the molds and stored for 28 days.

Pre-treatment of waste - the washing process - was carried out in the following way - the waste was rinsed with running water in the ratio of 1:5, then the excess water was filtered and dried in a dryer to a constant mass. The rinsing time was 15 minutes. The rinsing was carried out in a slow-running laboratory mixer.

The study was carried out using 3 types of waste from municipal waste incineration plants. Description and marking of waste used are presented in Table 1.
Table 1. Symbols and descriptions of the materials tested.

| Symbol | Description of the waste |
|--------|--------------------------|
| FY1    | The fly ash proceeding from a waste incineration plant in the city of Klaipeda in Lithuania, |
| FY2    | The fly ash from a waste incineration plant in Konin (Poland) 19 01 13* |
| FY3    | The fly ash from a waste incineration plant in Konin (Poland) 19 01 15* |

Table 2 presents variants of prepared samples and their determinations. For example, a sample labeled FFY1W is a fly ash based geopolymer with the addition of FY1 waste from the rinsing process. Geopolymers were prepared in 6 composition variants and for each variant rinsed and untreated wastes were used. In total, 12 different compositions were prepared and subjected to further examination.

Table 2. Labels and descriptions of samples.

| Symbol | Geopolymer based on: | Type of waste | Washing |
|--------|----------------------|---------------|---------|
| MFY1   | Metakaoline          | FY1           | *NW; **W |
| MFY2   | Metakaoline          | FY2           | *NW; **W |
| MFY3   | Metakaoline          | FY3           | *NW; **W |
| FFY1   | Fly ash              | FY1           | *NW; **W |
| FFY2   | Fly ash              | FY2           | *NW; **W |
| FFY3   | Fly ash              | FY3           | *NW; **W |

*NW – not washed
**W- washed

2.2. Research methods

Compressive strength tests according to EN 12390-3, using Matest 3000 kN, were conducted on cubic samples 100x100x100 mm conditioned at room temperature for 28 days. Five repetitions were carried out for each type of sample.

Leaching tests were conducted according to the PN-EN 12457-4:2006 standard. The samples were prepared according to the PN-EN ISO 15587-2:2005 standard. Depending on the type of analyzed substance, one of the following methods was used: gravimetry, spectrophotometry, ion chromatography and inductively coupled plasma atomic emission spectroscopy (ICP-OES). The mass of each sample was approximately 2.5 kg.

3. Results and discussion

Table 3 present a summary of compressive strength results for geopolymers with untreated and treated wastes. The highest values of compressive strength are characteristic for geopolymers containing 70% FY1 ash, both based on fly ash (12.3 MPa) and metakaoline (8.9 MPa). It should be noted that high compressive strength values were obtained in this case only for geopolymers containing rinsed waste. In the case where no previous treatment has been carried out, the geopolymers with waste FY1 have a compressive strength below 1.

Geopolymers containing waste from the Konin incineration plant with code 190113* are characterized by compressive strength - 2.9 MPa for waste rinsed with water, based on fly ash, 5.4 MPa for waste rinsed with water, based on metakaoline.
Table 3. Results of compressive strength tests of geopolymers made with the addition of waste from municipal waste incineration plants.

| Symbol | Compressive strength |
|--------|----------------------|
|        | Not processed | After washing H2O |
| FFY1   | <1            | 12.3             |
| FFY3   | 4.2           | 2.1              |
| FFY2   | <1            | 2.9              |
| MFY1   | <1            | 8.9              |
| MFY3   | 2.4           | 2.5              |
| MFY2   | <1            | 5.4              |

Figure 1. Minor efflorescences and discolorations on the surface of a geopolymer with FFY1 and FFY2 waste.

The susceptibility to efflorescence was evaluated visually by observing the surface of samples soaked in water. Sample observations are presented in Fig. 2. Only small efflorescences visible on the surface of geopolymers were observed in the tested samples. It was observed that geopolymers containing waste from washing processes are less prone to efflorescence. It should be emphasized that even if no efflorescence was observed in the conducted study, there is a risk of its occurrence at a later date, e.g. during the use of geopolymer products containing waste.

Table 4 presents the results of water leaching tests of the tested wastes and geopolymers made with the addition of these wastes. For each waste, the leachability of raw waste, the leachability values after the washing process and the leachability values of waste immobilized in geopolymer matrices are presented.
Table 4. Leaching of the examined samples

| Analyzed substance | Criteria for admittance of hazardous waste | FY1 | MFY1W | FY2 | FY2W | MFY2W | FFY2W | FY3 | FY3W | FFY3W | MFY3W |
|--------------------|-------------------------------------------|-----|-------|-----|------|-------|-------|-----|------|-------|-------|
|                    | mg/kg                                     | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg |
| Arsenic (As)       | 25                                         | <0.5 | 3.2   | <1.0 | <0.5 | 6.1   | 1.5   | 1.4  | <0.2 | <0.1  | 11.8  | 17.5  | 3.8   |
| Barium (Ba)        | 300                                        | 76.5 | <0.3  | 82   | 9.3  | <0.3  | 0.33  | 0.58 | 3    | 1.2   | 0.16  | 0.22  | <0.3  |
| Cadmium (Cd)       | 5                                          | 0.25 | <0.03 | <0.05 | <0.02 | <0.02 | <0.03 | <0.03 | <0.01 | <0.01 | <0.05 | <0.05 | <0.03 |
| Chromium (total amount (Cr)) | 70                               | 0.26 | 3.2   | 0.5  | 0.35 | 2.7   | 0.85  | 1.2  | 2.1  | 1.8   | 4.2   | 2.3   | 1.3   |
| Copper (Cu)        | 100                                        | 225  | <0.1  | <0.2 | <0.05 | 0.061 | <0.1  | <0.1 | <0.05 | <0.05 | <0.10 | <0.3  | <0.1  |
| Mercury (Hg)       | 2                                           | <0.01 | <0.02 | <0.01 | <0.01 | <0.02 | <0.02 | <0.01 | <0.01 | <0.01 | <0.01 | <0.02 | <0.02 |
| Molybdenum (Mo)    | 30                                         | 1.5  | 2.5   | 1.6  | 0.68 | 1.8   | 4.9   | 4.4  | 1.8  | 0.89  | 5.3   | 4.4   | 2.1   |
| Nickel (Ni)        | 40                                         | <0.05 | <0.1  | <0.05 | <0.05 | <0.10 | <0.05 | <0.10 | <0.05 | <0.05 | <0.3  | <0.2  | <0.1  |
| Lead (Pb)          | 50                                         | 365  | 18.8  | 125  | 4    | <0.05 | 0.19  | <0.20 | 2.1  | <0.05 | <0.05 | <0.1  | <0.05 |
| Antimony (Sb)      | 5                                          | <0.5 | 0.79  | <0.5 | <0.3 | 3.1   | 1.7   | 2.6  | <0.2 | <0.10 | 3.2   | 5.6   | 8     |
| Selen (Se)         | 7                                          | <0.1 | 0.79  | <0.5 | <0.3 | 1.6   | 2.7   | <1.0 | <0.2 | <0.10 | 1.9   | 2.4   | 2.1   |
| Cynk (Zn)          | 200                                        | 44.5 | <0.5  | 58   | 8.8  | <0.5  | 1.8   | <0.5 | 18.5 | <0.5  | 7.6   | <0.5  | 0.5   |
| Chlorides (Cl−)    | 25 000                                     | 162 000 | 18 200 | 177 000 | 55 300 | 1 160 | 27 000 | 78 700 | 15 000 | 1 050 | 9 930 | 1 290 | 25 200 |
| Fluorides (F)      | 500                                        | 44   | 56    | 51   | 21.5 | 57    | 62    | 51   | 34   | 8.4   | 100   | 94    | 600   |
| Sulfates (SO4^2−)  | 50 000                                     | 27 800 | 68 200 | 8 880 | 10 200 | 23 200 | 50 200 | 41 800 | 14 200 | 10 200 | 31 600 | 25 700 | 47 100 |
| Dissolved organic carbon (DOC) | 1 000         | 24   | 400   | 60   | 65   | 400   | 160   | 71   | 26   | 25    | 140   | 350   | 430   |
| Total dissolved solids (TDS) | 100 000                  | 360 000 | 150 000 | 448 000 | 146 000 | 101 000 | 152 000 | 21 900 | 69    | 20    | 84    | 107   | 143 000 |
| Chromium (VI)      | 25 000                                     | <1.0 | <4.0  | <1.0 | <4.0 | <1.0  | <4.0  | <4.0 | <4.0 | <5.0  | <4.0  | <2.0  |

It was observed that due to immobilization in geopolymers and rinsing processes the amount of leachability of such metals as barium, lead, zinc, chlorides was significantly reduced. It was also noted that in some cases the leaching values of e.g. sulfates or dissolved organic carbon increased. This is related to the process of leaching the components of the geopolymer matrix (metakaoline and fly ash). The conducted study confirmed the validity of the processes of preliminary washing of waste and neutralization of waste in the geopolymer technology.

4. Conclusions
The aim of the study was to determine the basic properties of waste solidified in the geopolymer technology. The most important conclusions, which were formulated on the basis of the conducted study, are described below:
In case of geopolymers containing waste from Klaipeda, only after rinsing treatment it is possible to produce geopolymers of high strength - 12.3 MPa for fly-ash geopolymers and 8.9 MPa for metakaoline-based geopolymers. Geopolymers based on fly-ash containing 70% by weight of waste from the Konin incineration plant (code 190113*) are characterized by compressive strength - 2.9 MPa for waste rinsed with water and 5.4 MPa for waste rinsed with water for geopolymers based on metakaoline. In case of waste from the Konin incineration plant, the water flushing process is
necessary to obtain geopolymers with strength above 2 MPa. The stabilization and solidification of waste in geopolymers should be carried out using metakaoline (less frequently fly ash). In order to make it profitable, it is possible to use metakaoline obtained e.g. from calcined coal shales. Water leaching tests proved that all the studied waste stabilized in geopolymers is characterized by very low leaching values of metals such as: copper, zinc, lead, etc.

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References
[1] Davidovits J 2015 Geopolymer Chemistry and Applications (Saint-Quentin, France: Geopolymer Institute)
[2] Provis L and Jannie S. J. van Deventer 2009 Geopolymers: structure, processing, properties and industrial applications, Woodhead Publishing
[3] Łach M, Korniejenko K and Mikula J 2016 Procedia Engineer. 151 410
[4] Davidovits J 30 Years of Successes and Failures in Geopolymer Applications. Market Trends and Potential Breakthroughs; Geopolymer 2002 Conference, October 28-29
[5] Deja J 2002 Cement and Concrete Research 32 1971–79
[6] Wongsa A, Boonserm K, Waisurasingha Ch, Sata V and Chindaprasirt P 2017 Journal of Cleaner Production 148 49-59
[7] Tome S, Etoh M A, Etame J and Sanjay K 2018 Recycling 3 (4) 50
[8] Ferone C et al 2013 Materials 6 3420-37
[9] Wang X, Li A and Zhang Z 2016 Procedia Environmental Sciences 31 440-446
[10] Hui-Sheng Shi, Li-Li Kan, 2009 J. Hazard. Mater. 164 750–754
[11] Łach M, Mierziński D, Korniejenko K, Mikula J and Hebd M 2018 Journal of the Air and Waste Management Association 68 (11) 1190-97
[12] Mierziński D, Lach M, Mikula J and Goly M 2018 E3S Web of Conferences 44 3
[13] Zheng L, Wang Ch, Wang W, Shi Y and Gao X 2011 Waste Management 31 2 311-317
[14] Yakubua Y et al 2018 International Journal of Scientific & Engineering Research 9 (6)