A Study on the Physicochemical Properties of Different Post-Process Wastes from Thermal Processes

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Abstract. The main aim of the article is to determine the safety for use the anthropogenic raw materials such as ashes and slags produced in waste incineration plants and possibilities of their using for manufacturing building materials. The article presents the results of research on physicochemical properties of ashes and slags produced in waste incineration plants. The research methods used were: water leaching, radioactivity, dioxins and furans content, oxide and phase composition. The major treatment for investigated waste is a high level of leaching of harmful substances and the content of dioxins and furans. It is necessary to take appropriate measures to develop procedures for safe processing and storage of this type of materials. As shown in the research, ashes from the two investigated waste incinerators do not meet the requirements for leaching levels for hazardous waste landfills. These wastes must undergo processing to reduce to an appropriate level of leaching. Referring to the sum of dioxins in soils in urban areas, which is from 5 to 10 ng/kg, it can be stated that the waste tested contains very high dioxin contents and is hazardous waste. Working with this kind of waste requires special precautions. The ashes from waste incineration plants exceed this limit several dozen times (e.g. 221 ng I-TEQ/kg). Due to very high values of leaching and dioxin content in the raw materials, even the rinsing process does not guarantee the possibility of obtaining waste that could be stored in hazardous waste landfills. The article suggests the further way of safety processing this kind of materials.

1. Introduction

Every year, the expenditure for the planned and implemented investments related to the construction of municipal waste incineration plants keeps on increasing throughout the world. This procedure enables a significant reduction in the volume of the waste generated in the extent from 80 to 95%. However, also as a result of the combustion process, various post-process materials are created – ashes and slags that contain heavy metals and other dangerous substances; these materials should be properly solidified or processed in such a way that enables their safe economic use [1].

As a result of municipal waste incineration, per each ton of burnt waste approximately 0.25 ton of slags are generated and approx. 0.075 ton of fly ash, as well as dust from dust removal, filter cakes and gypsum from exhaust gas cleaning processes [2]. At present, intensive research is being carried out all over the world, focusing on improving the existing technologies and developing new ones, which will
enable the safe use or storage of waste generated as a result of the incineration of municipal and other waste.

Among the most popular immobilisation processes, we can distinguish the following ones [2]:

- cementation
- bituminisation
- vitrification
- other technologies, i.e. Synrock or Geodur – based on mixes dedicated to a given type of waste
- geopolymerisation

According to literature data regarding the currently used methods of stabilisation, it is not possible to carry out an effective stabilisation process of fly ash generated from municipal waste incineration without proper pre-treatment – e.g. rinsing [1,3]. It is widely known that the stabilisation of this type of waste in cement matrices without its pre-treatment does not make it possible to reduce leaching of chlorides and sulphates to the levels that are permitted by law. In addition, chlorides and sulphates have a negative impact on the durability of cement matrices. Serving as an alternative solution may be a matrix based on geopolymers. The use of individual solutions, including geopolymers, requires comprehensive testing of processed waste. As already mentioned, there are many technologies for processing hazardous materials generated in thermal processes, while post-process residues generated in the energy industry are valuable secondary raw materials that have many different applications. It is important, however, to accurately identify the properties of such by-products, as they can significantly differ in chemical composition and properties. Research by means of SEM, XRD, DTG, pycnometry, etc. allows for a comprehensive definition of the properties of post-process waste which may be the basis for making decisions regarding their practical implementation [4].

In identifying the composition and properties of by-products of thermal waste treatment, among the methods that serve to be particularly useful there is, for example, the conjugated heat transfer analysis [5,6].

Understanding the properties of waste is of particular importance when it comes to eluviation (leaching) of certain elements. In the case of bottom ashes, the stability of such leaching is established, but the impurities exceed the legal limits for e.g. copper, antimony, chloride and sulphate. Therefore, research should focus on the reduction of these specific pollutants in the examined bottom ash [7]. Also with regards to leaching, bottom ashes should be used as aggregates on roads, since metal leaching is less significant than in the case of aggregates used in concretes [8].

Knowledge of the characteristics of waste originating from thermal processes, including the recognition of its leachability, or the content of metallic elements, facilitates not only the selection of the right technologies for their processing, but it also allows for an optimisation of their composition in order to reduce their harmfulness to the environment. As shown by studies [9], the addition of the metallic Fe decreases Pb (among others) elution.

The conducted research presented in this paper was aimed at determining the basic physicochemical properties of waste in view of choosing their processing technology in the future. A further goal of the conducted research was to obtain information on the possibilities of safe application and processing of waste in technological processes.

2. Methodology
This article only presents selected studies of waste from several selected thermal installations. Dioxin measurements were performed in the Track Tests Laboratory at the Cracow University of Technology. The morphology of the samples shown below was examined using a JEOL JSM-820 scanning microscope. The samples were properly prepared in advance. A small amount of ash was dried into a solid mass and then placed on a carbon substrate ensuring the discharge of the load from the sample. The materials were sprayed with a thin layer of gold using the JEOL JEE-4X sprayer. Natural
radioactivity tests were carried out using a PI-MAZAR 01 device. The sample weight in each case amounted to 2400 g. Measurement time: 30 cycles of 2000 seconds each.

Leaching tests were performed in accordance with PN-EN 12457-4: 2006. The pH value of the obtained water extract was determined as per PN-EN ISO 10523: 2012 using the accredited method.

The designations and description of the test samples have been shown in Table 1 below.

| Symbol   | Description of the waste                                                                 |
|----------|------------------------------------------------------------------------------------------|
| WASTE1   | The fly ash proceeding from a waste incineration plant in the city of Klaipeda in Lithuania, |
| WASTE2   | The fly ash from a combined heat and power plant in Jedlicze (steam boilers fired with fuel oil, natural gas and culm), |
| WASTE3   | The fly ash proceeding from a waste incineration plant in Katowice (Poland) MPGK Sp. z o.o.; 19 01 07 * Solid wastes from treatment |
| WASTE4   | The slag proceeding from a waste incineration plant in Katowice (Poland) MPGK Sp. z o.o.; 19 01 11 * Slags and bottom ash containing hazardous substances |

Four different types of samples were tested whereby the waste materials came from 3 different installations, and, whereas in the case of the incineration plant in Katowice, it was the slag and ash that were tested (WASTE 3 and 4).

3. Results

Table 1 presents the results of the investigation of the oxide composition of the examined waste. Samples were characterised by the highest content of calcium oxide CaO ranging from 5% for WASTE2 waste to more than 40% for WASTE4 waste. The content of Na₂O, K₂O, MgO, TiO₂ in the examined waste groups ranged from 0.09-5.88%. These contents (due to low values) should not affect the course of processing this waste). Roasting losses ranged from 13% to 58%.

| Symbol | SiO₂ | Al₂O₃ | Fe₂O₃ | Na₂O | K₂O | CaO | MgO | TiO₂ | SO₃ | LOI |
|--------|------|-------|-------|------|-----|-----|-----|------|-----|-----|
| WASTE1 | 1.39 | 0.57  | 0.64  | 0.70 | 3.34| 35.23| 0.16| 0.34 | 9.65| 30.92|
| WASTE2 | 13.16| 6.08  | 10.14 | 0.21 | 1.71| 5.07 | 0.66| 0.95 | 1.90| 58.55|
| WASTE3 | 0.71 | 0.23  | 0.05  | 1.47 | 0.53| 34.72| 0.09| 0.27 | 1.53| 35.07|
| WASTE4 | 17.58| 4.34  | 3.83  | 1.01 | 0.38| 40.30| 0.84| 5.88 | 7.58| 13.03|

The figures 1-4 below show the morphology of the particles of the examined waste materials. The samples differed significantly in shape, degree of fragmentation and surface development. A significant porosity of the WASTE2 material was noted. These are probably particles of unburnt carbon, which is also confirmed in the LOI amounting to 58.55%. The WASTE1 material occurs as a very fine particle agglomerate, similarly to WASTE3. The degree of fragmentation of the WASTE3 material is larger (it has smaller particles).
Figure 1. Morphology of the sample WASTE1.

Figure 2. Morphology of the sample WASTE2.

Figure 3. Morphology of the sample WASTE3.
Figure 4. Morphology of the sample WASTE4.

In order to obtain information on the possibilities of safe application and treatment of waste obtained from incinerators in technological processes, the content of dioxins and furans present in the materials in question was examined. The results have been shown in Table 3. Upon referring these obtained contents to the level of the sum of dioxins measured in soils in urbanised areas, which amounts to 5 to 10 ng/kg, it can be stated that the examined waste has a very high dioxin content and must therefore be considered hazardous waste. Working with this kind of waste requires special precautions.

Table 4 presents the results of the natural radioactivity test. These tests were conducted only for two of the four waste type examined. The results showed that the materials meet the requirements regarding the content of natural radioactive isotopes in relation to raw materials and building materials used in buildings intended as shelter for humans and livestock (f1 <1.2, f2<240 Bq/kg).

\[
f1 = \frac{C_K}{300 \text{Bq/kg}} + \frac{C_{Ra}}{300 \text{Bq/kg}} + \frac{C_{Th}}{200 \text{Bq/kg}}; f2 = C_{Ra}; C_K, C_{Ra}, C_{Th}\ - \text{isotope concentrations}
\]

Table 3. Total content of dioxins in the tested wastes.

| WASTE1 | WASTE2 | WASTE3 | WASTE4 |
|--------|--------|--------|--------|
| The sum of dioxin (I-PCDD/F-TEQ) | 221±57 | 124 ± 32 | 5518±1435 | 14±3.7 |

Table 4. Results of the study of natural radioactivity of waste using the Gamma Spectrometry method

| Parameter      | WASTE1      | WASTE4      |
|----------------|-------------|-------------|
| Potassium Sk   | 926.92 ± 56.66 | 100.71 ± 13.39 |
| Radium SRa    | 12.93 ± 3.91  | 10.34 ± 2.86 |
| Thorium STh   | 3.94 ± 2.15   | 8.72 ± 1.78 |
| Indicators    | f₁ = 0.37 ± 0.03 | 0.11 ± 0.02 |
|               | f₂ = 12.93 ± 3.91 | 10.34 ± 2.86 |

Table 5 presents the results of the leachability test. The waste from the WASTE1 and WASTE3 groups does not meet the requirements for leaching levels for hazardous waste landfills. This waste must undergo processing to adapt it to an appropriate level of leaching. The waste from the WASTE2 group is allowed to be stored in a hazardous waste landfill in view of its exceeded selenium leaching (Se) (exceeded for landfills other than hazardous and inert waste). Similarly, the WASTE4 slag is permitted to be stored in a hazardous waste landfill in view of its exceeded Bar (Ba) leaching for landfills other than hazardous and inert waste.
Table 5. Comparison of the results of leaching waste water studied

|          | WASTE1 | WASTE2 | WASTE3 | WASTE4 |
|----------|--------|--------|--------|--------|
|          | mg/kg  | mg/kg  | mg/kg  | mg/kg  |
| Arsenic (As) | <0.50  | 0.2    | <1.0   | <0.10  |
| Bar (Ba)    | 76.5   | 1.7    | 113    | 120    |
| Cadmium (Cd)| 0.25   | <0.010 | <0.050 | <0.010 |
| Total chrome (Cr)| 0.26 | 0.17 | 0.27 | <0.050 |
| Copper (Cu)| 225    | <0.050 | <0.25  | 0.1    |
| Mercury (Hg)| <0.010 | <0.010 | <0.010 | <0.010 |
| Molybdenum (Mo)| 1.5 | 0.25   | 0.33   | 0.19   |
| Nickel (Ni)| <0.050 | <0.050 | <0.10  | <0.050 |
| Lead (Pb)| 365    | <0.050 | 33.4   | <0.050 |
| Antimony (Sb)| <0.50 | 0.13 | <1.0   | <0.10  |
| Selenium (Se)| <0.10 | 0.58 | <0.50  | <0.10  |
| Zinc (Zn)| 44.5   | <0.50  | 160    | <0.50  |
| Chlorides (Cl-)| 162 000 | <50 | 304 000 | 2 000 |
| Fluorides (F-) | 44    | 37    | 28     | 1.4    |
| Sulphates (SO42-) | 27 800 | 441 | 11 700 | 41     |
| Dissolved organic carbon (DOC) | 24    | 19    | 740    | 70     |
| Solid dissolved compounds (TDS) | 360 000 | 1 460 | 544 000 | 20 300 |
| Chrome 6+ | <1.0 | <0.20 | <1.0 | <0.10 |
| pH       | >12.0 | 8.8   | >12.0  | >12.0  |

The waste examined is characterised by significant leaching values of TDS and chlorides. In view of the very high leaching values of these substances in the starting material, probably even the rinsing process does not guarantee the possibility of obtaining waste that can be stored in inert waste landfills. This process can only support further processing.

Conclusions
Thermal processes of waste treatment allow for a reduction of significant amounts of waste, but they generate considerable volumes of post-process waste containing hazardous substances. Such materials should be properly disposed of using the best possible technologies and simultaneously maintaining economic efficiency. To make this possible, post-process waste must be thoroughly examined with regards to its physicochemical properties and its harmfulness to humans and the environment. It is only on the basis of comprehensive research that it is possible to apply the appropriate method of waste treatment and to select subsequent stages of the procedure. Post-process waste generated in thermal waste treatment processes differs significantly depending on the type of waste incinerated, installations and many other variables.

As shown in the studies described in this paper, waste originating from thermal processes contains very high dioxin volumes and is therefore considered hazardous waste. Working with this kind of waste requires special precautions. Due to substance leaching, the majority of waste can be stored only on landfills for hazardous waste, or due to exceeding the permissible values, some of them should be processed to obtain an appropriate leaching level.
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