Properties of ashes formed after the combustion of sewage sludge

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Abstract. The objective of the research presented in the paper was to analyze the ash formed in the process of incineration in the thermal sewage sludge treatment facility being a part of Sitkówka-Nowiny wastewater treatment plant, located in the vicinity of Kielce. The research involved the investigation of heavy metal and total phosphorus content , leachability of certain ions and X-ray phase analysis. The comparison of the obtained results with those available in literature revealed similarities in the crystallographic structure of ashes from different treatment plants. Then, the differences observed in the content of heavy metals in particular ashes are related to the composition of sewage flowing into treatment plants. Attention was also paid to a significant sulphate content revealed in the leachability analysis, found both in the ash from Sitkówka-Nowiny treatment plant and in the ash analyses results available in the literature sources. High sulphate concentration can limit the use of ash for construction purposes.

1 Introduction

The amount of municipal sewage sludge obtained in Poland in wastewater treatment plants at the end of 2015 was estimated at 754 thousand tonnes of dry matter of sewage/year [1]. Then, it is estimated that in Europe it is about 11.6 million tonnes of dry matter of sewage sludge per year [2]. There is also a tendency of an annual increase in the amount of sewage sludge. Legal regulations [3] issued in recent years aim to reduce the storage of sewage sludge. Regulation of the Minister of Economy of January 8, 2013 [3] on the criteria and procedures for the acceptance of waste for landfill disposal indicates that from January 1, 2016, depositing sewage sludge in landfills is not allowed if these sediments contain more than 5% of the total organic carbon. Therefore, the main methods of their utilization should involve: reclamation of landfills, incineration, composting, growing plants that are not intended for consumption and animal feed production.

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Due to energy recovery and the elimination of potentially pathogenic microorganisms in thermal processes, they have become a prime solution for sludge utilization. In Europe, over 27% [2] of sewage sludge is thermally processed. Thermal treatment of sewage sludge can take the form of: combustion (in shelf furnaces, rotary furnaces, fluidized-bed furnaces), co-combustion (in municipal waste incineration plants, in cement plants, power plants) and by alternative processes (wet oxidation, gasification, pyrolysis). Fluidized-bed furnaces are definitely the most popular solution. Combustion of sewage sludge in a fluidized-bed is fully compliant with the European Directive IPPC 96/61/EC and recognized as the Best Available Technique for the disposal of sewage sludge. The main advantage of combustion in a fluidized-bed furnace is the possibility of neutralizing all waste generated at sewage treatment plants: travelling screens, contaminated sand from sand separators, grease, primary sludge and excess biological sludge.

Although combustion reduces the volume of municipal sewage sludge and provides energy [4], this is not an ultimate solution because it produces fly ash, which must then be utilized. The ash formed in the combustion of sewage sludge consists of fine particles that contain i.a. leachable heavy metals and, if their concentration is high enough, may be classified as hazardous waste. Ash management is thus becoming one of the most important environmental problems associated with the combustion of sewage sludge.

Due to a high content of elements such as Si, Ca, Al, Fe and Mg in the ash formed as a result of sewage sludge combustion, following the thermal treatment fly ash can be used to prepare concrete mixes for construction purposes [5] e.g. for the needs of civil engineering (road bases or sewage networks), excluding buildings intended for permanent residence of people or animals and for the production or storage of food. Ash can also replace sand in cement-stabilized embankments in road structures [6].

Due to a high content of magnesium, calcium and phosphorus in the ash this waste became the feed for the production of phosphate fertilizers. This issue is particularly important due to the depletion of economically viable phosphorus resources. Therefore, in Europe, thermochemical technologies of phosphorus recovery with simultaneous removal of heavy metals have begun to be developed. The best-known phosphorus recovery technologies include: ASH DEC, Sephos, PASH or BioCon [7].

2 Methodology of research

The research involved the application of ashes from anaerobically stabilized sewage sludge from the wastewater treatment plant in Sitkówka-Nowiny (sediments incinerated in a fluidized-bed furnace).

The ash samples were analyzed with regard to the following:

- Heavy metal content.

  Mineralization of the sample was performed using aqua regia.

  The content of heavy metals in the obtained extracts was analyzed on a Perkin-Elmer Optima 8000 ICP-OES excited plasma spectrophotometer.
- Total phosphorus content.

  The measurement was carried out in accordance with the orthophosphate determination procedure using phosphate-molybdenum blue [8] after prior sample mineralization with aqua regia.

  Phosphorus determination was performed by spectrophotometric method using a PERKIN ELMER UV-VIS Lambda 25 spectrophotometer.
- Leachability of selected anions

  The leaching of heavy metals from sewage sludge ashes was performed in accordance with PN-EN 12457-2 [9].

- X-ray phase analysis

  The analysis was carried out with the counter method on the Empyrean diffractometer from PANalytical, CuKα radiation in the range of 5-60°2θ, recording speed 0.05°2θ/s. The ICDD database (International Center for Diffraction Data) was used to analyze the registered diffractogram.

At the same time, the article cites literature data on the properties of ashes after the combustion of sewage sludge from other treatment plants, i.e.

• "Kujawy" treatment plant - the sludge from this treatment plant was dried and then combusted in a chamber furnace at 600°C [10].

• "Beckton" treatment plant - the sludge from this treatment plant was combusted in a fluidized-bed furnace at temperatures in the range of 850-950°C [11].

• "G2" treatment plant - sewage sludge combustion took place in fluidized-bed boilers [12].

• "K1" treatment plant - combustion of sewage sludge took place in fluidized-bed boilers [12].

3 Discussion of results

The percentage contents of heavy metals in the ash from "Sitkówka-Nowiny" treatment plant are presented in Table 1. At the same time, the table presents literature data showing the content of certain heavy metals in ashes from other wastewater treatment plants ("Kujawy" [10], "Beckton" [11]).

Table 1. The content of heavy metals in the ash.

Element	The content of heavy metals in the ash [%]		
	"Sitkówka-Nowiny"	"Kujawy" [10]	"Beckton" [11]
Zn	0.5164	0.570	0.2562
Pb	0.0187	0.011	0.0419
Ni	0.0098	0.015	0.0085
Cd	0.0001	0.002	0.0003
Cr	0.0166	0.043	0.0084
Cu	0.1018	0.049	0.1256

The figures of the percentage contents of heavy metals in the ash (Table 1) indicate a high variability in the amount of these elements. This variability can be related to different temperatures used in the combustion process and the composition of sewage sludge subjected to thermal processing. In the case of sewage sludge, the variable inflow of pollution loads from industrial sewage plays a significant role. The amounts of individual heavy metals in the analyzed ash varied, but their content did not exceed 1%. Analyzing the properties of ashes, attention should be paid to the important issue of phosphorus recovery. In view of the constantly growing world population, the demand for phosphate fertilizers is increasing [13,14]. However, phosphates, which are the primary source of raw material for the production of fertilizers, are a non-renewable resource. Therefore, in the world there are now a number of technologies for recovering phosphorus from sewage sludge and ashes after combustion. The results of investigating total phosphorus content indicate a high percentage of this element in the ashes. In the case of the analyzed ash from "Sitkówka-Nowiny" treatment plant, this content was high and amounted to about 10%, which indicates the possibility of using ash from this thermal processing plant in phosphorus recovery technologies. In order to assess the potential use of ashes in the phosphorus recovery processes, an X-ray phase analysis of ash from "Sitkówka-Nowiny" treatment plant was performed (Figure 1).

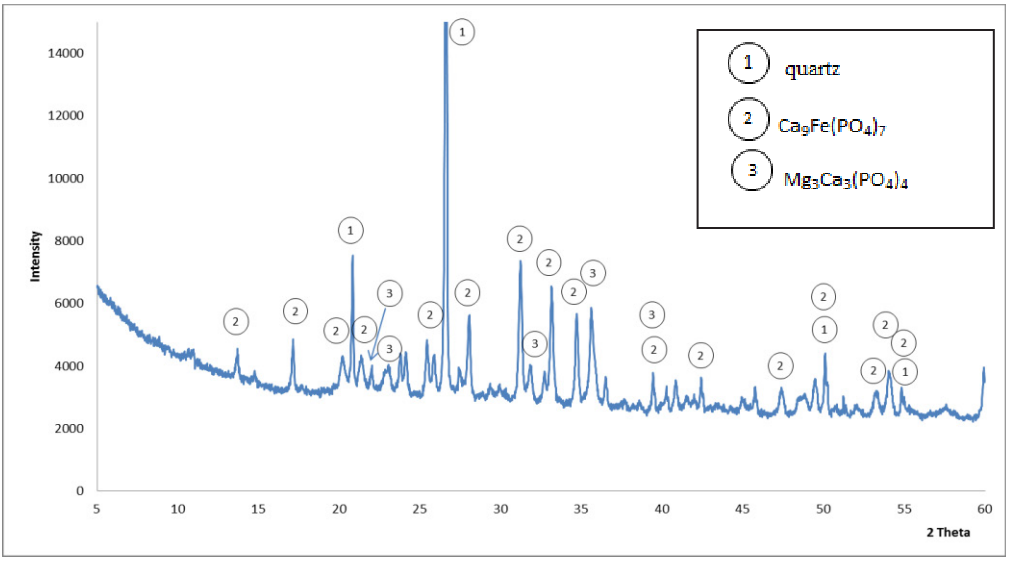

Fig.1. Diffractogram of ash obtained from the incinerated excess sludge from"Sitkówka-Nowiny" treatment plant.

X-ray analysis of ash from "Sitkówka-Nowiny" sewage treatment plant revealed that the basic crystalline phases are quartz (SiO_2) and calcium-iron phosphate ($Ca_9Fe(PO_4)_7$) as well as magnesium-calcium phosphate ($Mg_3Ca_3(PO_4)_4$). In the case of ash coming from "Kujawy" sewage treatment plant, quartz and calcium-iron phosphate represented also the basic crystalline phases, however, the analysis of this ash indicated the presence of i.a. calcite, anhydrite and hematite as well[10]. Analyzing the results of X-ray analysis of ash from "Beckton" plant [11], it was found that quartz and calcium phosphate are also the main crystalline phases, called whitlockite with the molecular formula: $Ca_9X(PO_4)_7$ (where X is most commonly Fe but may also be Cu, H, Al, Mg, Sr, or Ni). The research carried out by Doantello et al. [15] suggests that whitlockite is highly soluble in acids, which is particularly important in technologies for recovering phosphorus from ashes.

Ashes generated as a result of sewage sludge incineration can be used in construction industry, e.g. to prepare concrete mixes (excluding buildings intended for permanent residence of people or animals and for the production or storage of food), ash may also replace sand in cement-stabilized embankments in road structures. However, it must have appropriate chemical properties to be made use of. Table 2 presents the results of the leachability analysis of certain ions from "Sitkówka-Nowiny" treatment plant ashes and juxtaposed literature data concerning ashes from other treatment plants. Analyzing the leachability of individual ions, one can notice similarity in their concentrations in extracts from various ashes. Particularly important - especially when using ashes in construction industry - is the concentration of ions that can corrode building materials. The leachability analysis presented in Table 2 indicates a high concentration of sulphates (VI). In the case of ashes from "Sitkówka-Nowiny" sewage treatment plant, it amounts to 1521.3 mg / dm^3. The limit value for mixing water that can be used for construction purposes is 2000 mg SO_4^{2-}/dm^3. However, taking into account the ratio of ash to distilled water in leachability analysis, which was 1:10, it can be assumed that if the ratio of ashes to water during cement production is changed, the sulphate value can significantly exceed the limit value.

Tab.2. Analysis of the leachability of selected ions from ashes.

Ion	The leachability of ions from ashes coming from different treatment plants [mg/dm^3]		
	„Sitkówka- Nowiny"	„G2" [12]	„K1" [12]
F^-	3.61	4.93	1.27
Cl^-	49.3	6.70	53.5
SO_4^{2-}	1521.3	924.6	857.9
K^+	26.1	62.80	74.72
Ca^{2+}	114	227.30	379.2
Mg^{2+}	35.8	91.17	0.15

Concentration of sulphates and chlorides is also an important aspect when using ashes for fertilizing purposes, because their introduction into the soil can cause saline stress in plants and negatively affect their development.

4 Conclusions

The performed investigation analyzing the ash formed during the combustion of sewage sludge in "Sitkówka-Nowiny" treatment plant indicates that this ash contains significant amounts of phosphorus (about 10%), including that in the crystalline form, which is easily soluble in acids. Similar results were obtained by other researchers [10,11]. It can therefore be assumed that ashes from sewage sludge will be well extracted with acids, which is of particular importance in the recovery processes of this element. However, the analysis of heavy metals showed significant variability of heavy metal content in ashes from different treatment plants, which may result from the variable composition of sewage sludge subjected to thermal processing. Also the high sulphate concentration obtained in the leachability test may result in limited use of ashes for construction purposes.

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