

The influence of thermal processing of sewage sludge on the usage properties of the formed ash

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The influence of sewage sludge incineration temperature on the formed ash constitution was examined. The comparative extraction tests of two differently prepared ashes (laboratory and industrial) were carried out in order to verify if the parameters of sewage sludge incineration influence the extraction selectivity of phosphorus compounds. The laboratory ash (A_{lab}) were prepared from sewage sludge incinerated at 950°C on a laboratory scale while the industrial ash (A_{ind}) comes from thermal utilization system of the sewage sludge at the Gdynia Sewage Treatment Plant, which uses fluid-bed furnace incineration at 850 – 900°C. It was found that the temperature and the conditions of the sewage sludge incineration process have an effect on the usage properties of the formed ash. Despite the twofold lower Fe content in the industrial ash than that of the laboratory one, its content in extracts after phosphoric acid leaching is 4.7 times higher. The lower values of PO_4^{3-} leaching degree from the industrial ash than the laboratory ash were observed, as well as a decrease of extraction productivity.

Keywords: phosphorus recovery, ash properties, ash extraction, industrial ash.

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INTRODUCTION

The sewage sludge, waste after municipal sewage treatment processes, are the source of mineral and organic elements including a series of valuable fertilizing components, which make them a potential substitute for natural phosphorus ore.

The sewage sludge causes significant problems in the global system of waste management because of its complicated composition and properties^{1,2}. Currently the prevailing method of management in Poland, is storage. The thermal utilization methods are applied only for 2% of generated sewage sludge but the importance systematically increases because they allow a significant mass reduction, concentration of the inorganic fraction as ash and remove the bacteriological menace thoroughly³.

The driving force for the development of thermal utilization methods are high storage costs of sewage sludge as well as the plans for the modification of EU Directive 86/278 in the direction of a more restrictive approach to its agricultural utilization⁴⁻⁶.

Presently there are several systems for phosphorus recovery from sewage sludge – Cambi/KreproTM and Bio-Con created in the Netherlands, but only a few that propose ash treatment⁷⁻⁹. EBRP – the Japanese process – should be mentioned here as it proposes intensive ash washing with demineralized water at 53°C⁸. A further solution, investigated on a laboratory scale, is phosphorus extraction from ash with the use of sulfuric acid⁹. The phosphate was precipitated from the solution by the addition of aluminum sulfate and sodium bicarbonate addition (pH~4). The acquired product might be used as a binding or refractory material and a raw material for glass production. Nevertheless, the authors claim that so far there has been no industrial technology in which such a product could be used. Japan Sewage Works and Sanki Engineering Co. Ltd.^{10, 11} developed a fertilizer produc-

tion technology, melted calcium-magnesium phosphate, on the basis of ash from sewage sludge combustion. This method consists in ash melting with an addition of calcium and magnesium at the temperature of 1350 – 1500°C. Then the alloy is water-cooled and steered to fertilizer production, which fulfills the requirements of Japanese fertilizers standards. In the year 2000 the Japanese technology of phosphorus recovery from ash or sewage sludge in the form of white phosphorus or phosphoric acid was patented¹².

Our earlier investigations, to the influence of sewage sludge combustion temperature on the obtained ash composition, reveal that ash extraction selectivity depends significantly on the parameters of its thermal processing¹³⁻¹⁵. In the instance when the sewage treatment plant uses chemical precipitation for phosphorus removal in the form of iron phosphate, the sewage sludge, as well as the obtained ash, contain unwanted iron ions, which have an unfavorable impact on phosphorus availability in fertilizers or feed products.

The conducted investigations allowed a selection of the best parameters of phosphorus compounds extraction from ash (prepared at 950°C) with nitric and phosphoric acid¹⁶. In the case of nitric acid, application of 0.45 [g/g] acid to ash mass ratio and acid concentration 2.71 [mol/dm³] resulted in 94.89% of PO_4^{3-} ions recovery and high extraction productivity – 0.423 [mol PO_4^{3-} /mol HNO_3]. The most favorable conditions for ash extraction with phosphoric acid were: acid to ash mass ratio – 0.45 [g/g] and acid concentration – 2.68 [mol/dm³]. The leaching degree of phosphate ions reached was 96.1% and extraction productivity – 0.35 [mol PO_4^{3-} /mol HNO_3].

In order to confirm the influence of sewage sludge combustion conditions on phosphorus extraction selectivity further research was conducted. The main goal was the comparison of extraction results of ashes obtained

after sewage sludge combustion on a laboratory scale and from the industrial sewage sludge combustion plant.

EXPERIMENTAL SECTION

The industrial ash A_{ind} comes from the sewage sludge thermal utilization plant at Municipal Sewage Treatment Plant in Gdynia. The installation with a capacity near 80 Mg/day combusts sewage sludge with the 70% moisture¹⁷. The combustion process is carried out in a fluid-bed furnace at the temperature of 850 – 900°C, where sand with 0.2 – 1.5 mm grain-size is used as a fluid bed. The sand grains, as a result of movement and polymorphous transformation, undergo a size reduction, then, as a solid phase, are separated from combustion gasses at cyclone and with other incombustible components formed ash. Yearly 2 000 Mg of ash is formed from ~20 000 Mg of sewage sludge, which is then stored in a dry state at a separate stockyard.

The laboratory ash A_{lab} was acquired from sewage sludge combustion at 950°C for 3h. The sewage sludge was taken out from the Municipal Sewage Treatment Plant „Kujawy” in Kraków-Pleszów, which uses a three-stages cleaning technology with the activated sludge and the chemical precipitation of phosphorus with iron sulfate. The sewage sludge after methane fermentation and gravity thickening is stored in the quantities of 55 Mg/day.

Table 1. The chemical constitution and the physical parameters of the laboratory ash A_{lab} and the industrial ash A_{ind}

COMPONENT	ASHES	
	A_{lab}	A_{ind}
PO ₄ ³⁻ [%]	22.86	33.7
Fe [%]	16.63	8.95
Ca [%]	11.26	11.97
Mg [%]	1.120	3.40
Zn [%]	0.54	1.136
Pb [%]	0.012	0.0137
Cu [%]	0.054	0.0709
Ni [%]	0.017	0.0113
Cr [%]	0.070	0.0844
Cd [%]	0.0020	0.00398
Co [%]	0.00510	0.00465
SiO ₂ [%]	–	19.5

Table 2. The conditions of the ash extraction process with nitric and phosphoric acid

Experimentno.	Ash amount [g]	Ash/acid mass ratio[g/g]	PO ₄ ³⁻ introduced with ash [g]	Acid	Acid concentration [mol/dm ³]
1a	35.00 A_{lab}	0.447	8.00	Nitric acid	2.71
1b	23.60 A_{ind}	0.302	8.00		2.71
2a	30.00 A_{lab}	0.370	6.86	Phosphoric acid	2.68
2b	20.23 A_{ind}	0.250	6.86		2.68

Table 3. A compilation of extraction degree and extraction productivity for the experiments of ash extraction with nitric and phosphoric acid

Experiment No	Ash/acid mass ratio [g/g]	PO ₄ ³⁻ extraction degree [%]	Extraction productivity
Experiment 1a A_{lab} extraction	0.447	94.85	0.423 [mol PO ₄ ³⁻ /mol HNO ₃]
Experiment 1b A_{ind} extraction	0.302	86.33	0.383 [mol PO ₄ ³⁻ /mol HNO ₃]
experiment 2a A_{lab} extraction	0.370	96.10	0.355 [mol PO ₄ ³⁻ /mol H ₃ PO ₄]
Experiment 2b A_{ind} extraction	0.250	81.07	0.308 [mol PO ₄ ³⁻ /mol H ₃ PO ₄]

The chemical constitution and the physical parameters of the industrial ash from the Municipal Sewage Treatment Plant in Gdynia (A_{ind}) and the laboratory ash from the Municipal Sewage Treatment Plant „Kujawy” in Kraków-Pleszów (A_{lab}) are presented in Table 1.

The results of Thermal and X-Ray Analysis of both ashes are shown in Figures 1,2.

The X-Ray Analysis reveal that the main phases of laboratory ash were quartz and hematite and that the additional crystalline phases (variety of γ -Fe₂O₃, maghemite-C and Ca₉FeH(PO₄)₇) were present in the case of the industrial ash.

The ashes were extracted both with nitric (experiment 1a and 1b) and phosphoric acid (experiment 2a and 2b). The extraction was carried out for 29h in a tight polypropylene reactor and the conditions of the process are shown in Table 2.

RESULTS AND DISCUSSION

The most important parameters of the conducted experiments: PO₄³⁻ extraction degree and extraction productivity (counted on phosphoric and nitric acid) are shown in Table 3.

The difference in PO₄³⁻ extraction degree between both ashes prepared under different conditions is clearly marked. The laboratory ash extraction with phosphoric acid results in higher PO₄³⁻ extraction degree by 10% than the industrial ash extraction, in spite of introducing the same quantities of phosphate ions (8.0g) with both ashes. In the case of nitric acid extraction, the PO₄³⁻ extraction degree for the laboratory ash is higher than that of the industrial ash extraction even by 19%.

In order to get better acquainted with the differences between the conducted experiments the concentration of PO₄³⁻, Ca²⁺, Mg²⁺ and Fe²⁺ ions in the extracts after ash extraction with phosphoric acid (Figure 3) and nitric acid (Figure 4) were compared.

The higher extraction degree of phosphate ions from the laboratory ash results in obtaining the extracts with higher phosphate content, 103.9 g/dm³, respectively, when nitric acid was used and 91.9 g/dm³ for the phosphoric acid extraction (347.5 g/dm³, including phosphate ions introduced with the acid). These concentrations in the extracts after the industrial ash extraction amounts are 93.9 g/dm³ and 78.8 g/dm³ (330.7 g/dm³), respectively.

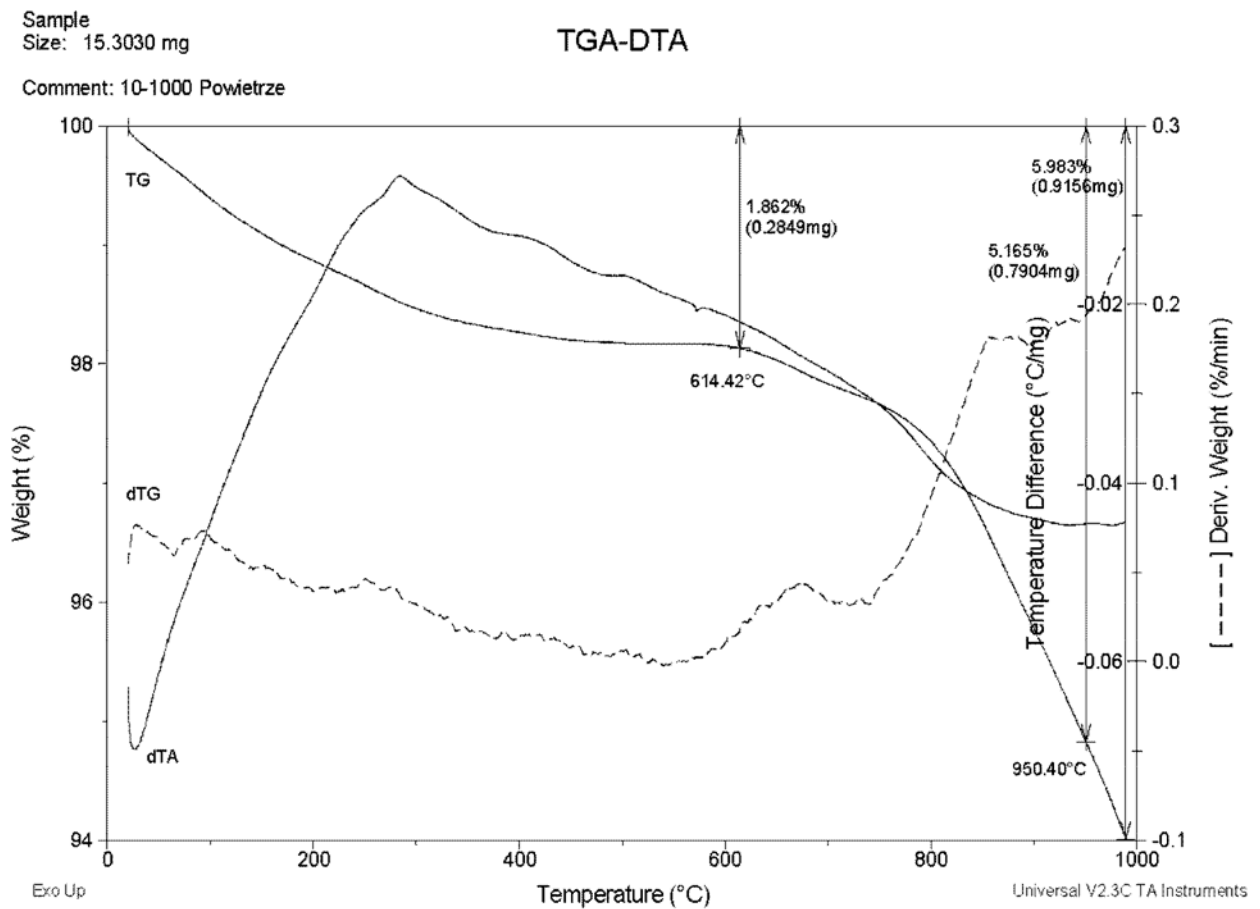
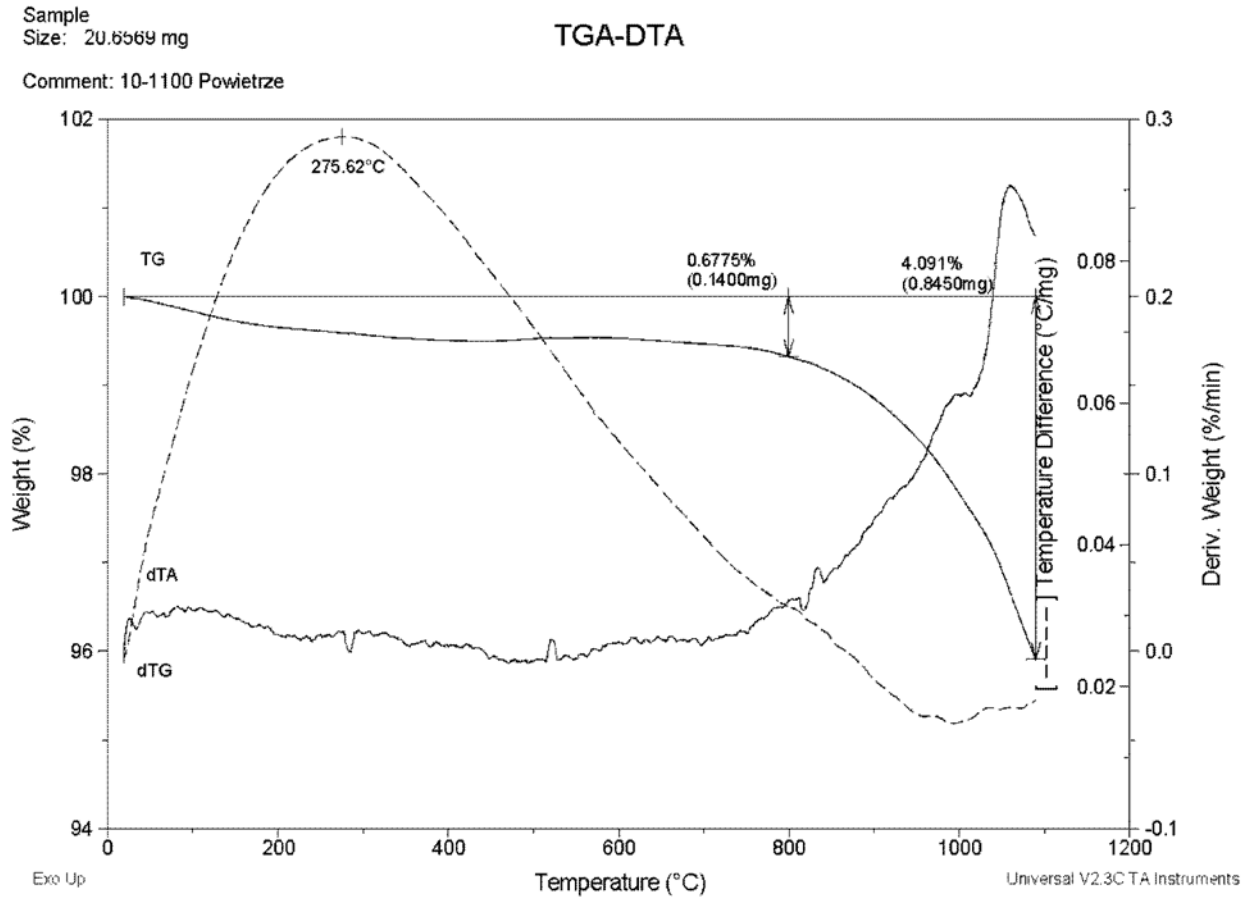


Figure 1. The Thermal Analysis results: a) industrial ash A_{ind} b). laboratory ash A_{lab}

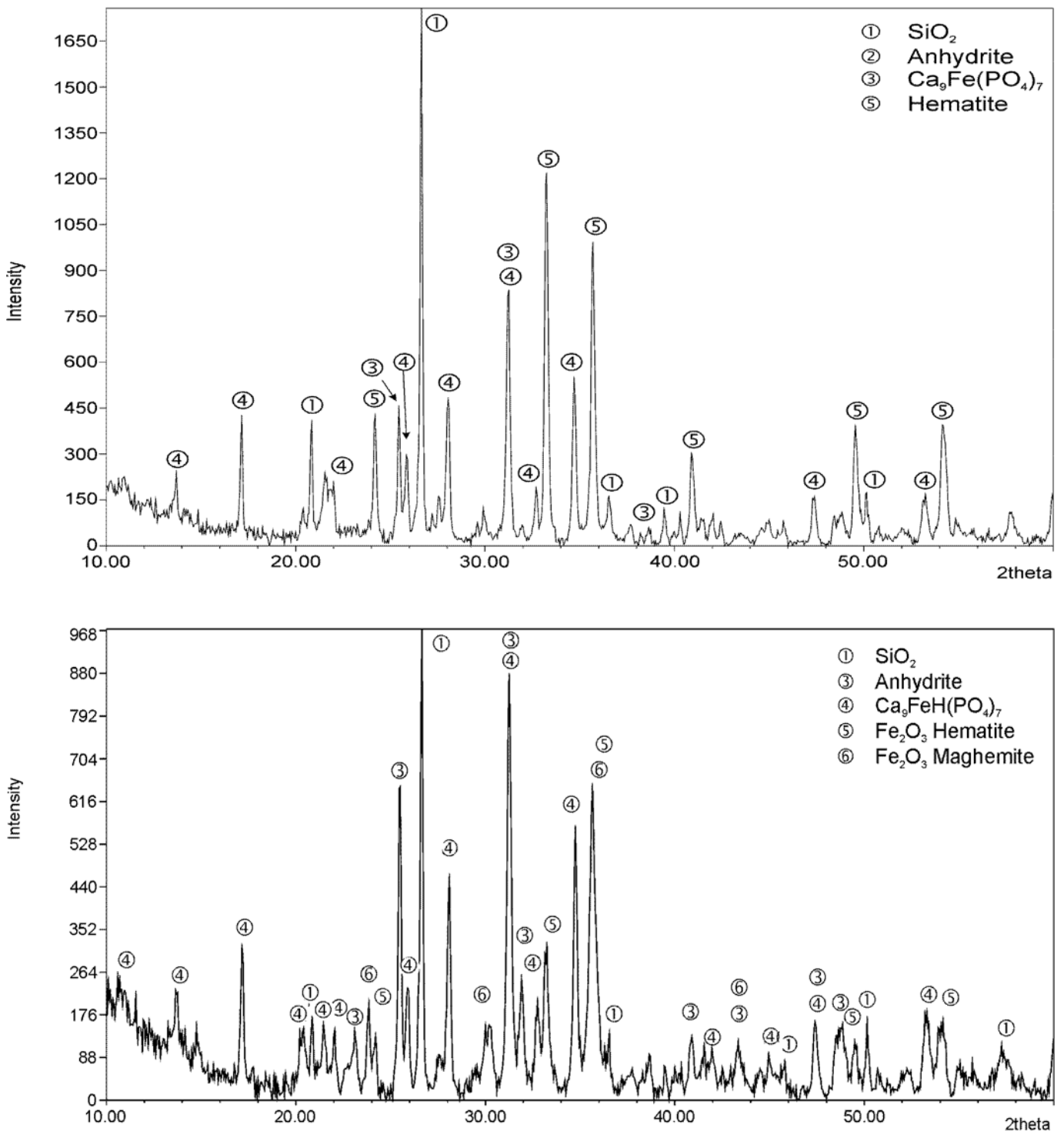


Figure 2. X-Ray Analysis : a) laboratory ash A_{lab} b). industrial ash A_{ind}

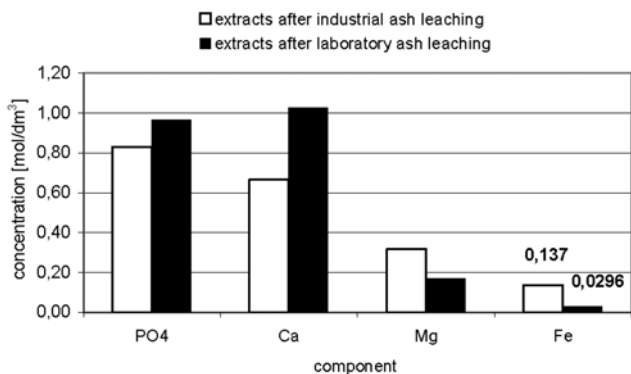


Figure 3. A comparison of PO_4^{3-} , Ca^{2+} , Mg^{2+} , Fe^{2+} concentrations in the extracts after the laboratory (A_{lab}) and the industrial (A_{ind}) ash leaching with phosphoric acid

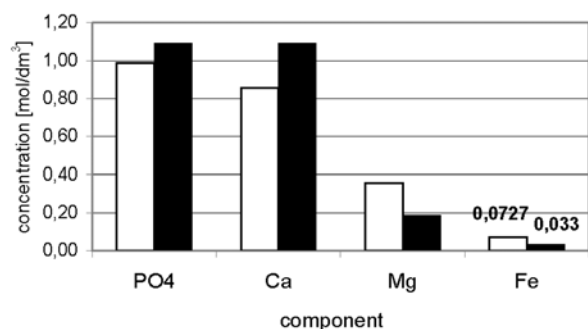


Figure 4. Comparison of PO_4^{3-} , Ca^{2+} , Mg^{2+} , Fe^{2+} concentrations in extracts after laboratory (A_{lab}) and industrial (A_{ind}) ash leaching with nitric acid

The concentration of Fe^{2+} ions in the extracts after the leaching process strongly depends on the temperature and the way of thermal ash treatment. In the case of laboratory ash, when higher temperature of ash thermal processing was used as well as a longer time of retention in the furnace, the iron concentrations amounts were: 1.85g/l for nitric acid extraction and 1.67 g/l for phosphoric acid extraction. These concentrations are considerably lower than in the extracts after the industrial ash extraction – 4.07g/l and 7.67 g/l, respectively. It should be mentioned that iron quantities introduced into the extraction processes with the laboratory ash was almost three times lower than that of which was introduced with the industrial ash.

The $\text{Fe}^{2+}/\text{PO}_4^{3-}$ mass ratio in the extracts, which indicates the selectivity of phosphorus compounds extraction towards iron, also decreases in the case of using a higher temperature of ash thermal processing in the case of laboratory ash. This parameter is two times lower for the laboratory ash extraction with nitric acid (0.017g/g) than that for the industrial ash (0.036g/g). In the case of the extraction with the use of phosphoric acid the $\text{Fe}^{2+}/\text{PO}_4^{3-}$ mass ratio is even five times lower for the laboratory ash (0.0181g/g) than that of industrial ash (0.091g/g).

Consequently, more iron is stopped in the form of insoluble compounds in the solid residue after the laboratory ash extraction processes. In the case of the laboratory ash extraction with nitric acid the iron concentration in

the solid residue amounts to 23.9% while with phosphoric acid 26.1% and in the case of the industrial ash 18.2% when nitric acid was used, while with phosphoric acid 14.6%.

Taking into account further usage properties of the obtained extracts it is a very advantageous effect, because the presence of iron ions influence the phosphorus compounds availability, especially in fertilizers, unfavourably.

The X-Ray Analysis of the solid residue after extraction has shown that its main crystalline phases are SiO_2 , hematite and anhydrite (Figure 5 and 6).

The research results confirm that the selective extraction of phosphorus compounds from ash is possible because of the insoluble hematite phase appearance (Fe_2O_3). Due to the higher incineration temperature of the sewage sludge, more iron compounds are transformed into the hematite phase and, as a consequence, the concentration of iron extracted simultaneously with phosphorus into solution, is much lower.

The Zn, Cu, Ni, Cr, Cd, Co and Pb concentrations in extracts are shown in Table 4.

CONCLUSION

The conducted investigations confirm the influence of sewage sludge thermal processing on the usage properties of the obtained ash. In spite of the three times lower Fe

Table 4. The Zn, Cu, Ni, Cr, Cd, Co and Pb concentrations in extracts after the laboratory A_{lab} and industrial ash A_{ind} extraction

Experiment no		Zn	Cu	Ni	Cr	Cd	Co	Pb
1	A_{lab}	0.82	0.113	0.0061	0.0056	0.0022	0.0023	0.019
	A_{ind}	2.05	0.119	0.0098	0.058	0.011	0.0026	0.0086
2	A_{lab}	0.73	0.109	0.0052	0.074	0.0037	0.0039	0.026
	A_{ind}	2.04	0.111	0.015	0.081	0.0065	0.0049	0.0061

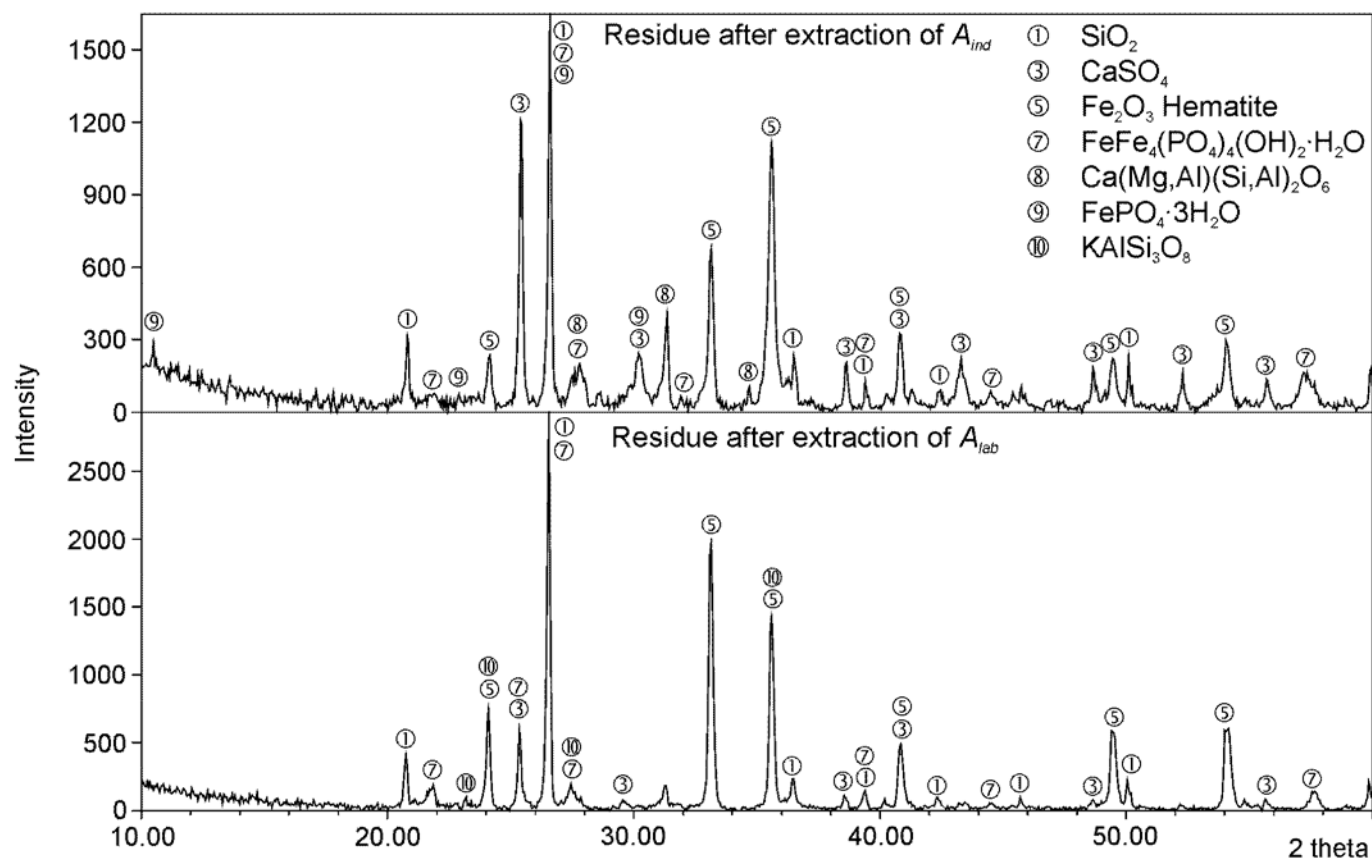


Figure 5. The X-Ray Analysis of the solid residues after an extraction of the industrial A_{ind} and the laboratory A_{lab} ash with phosphoric acid

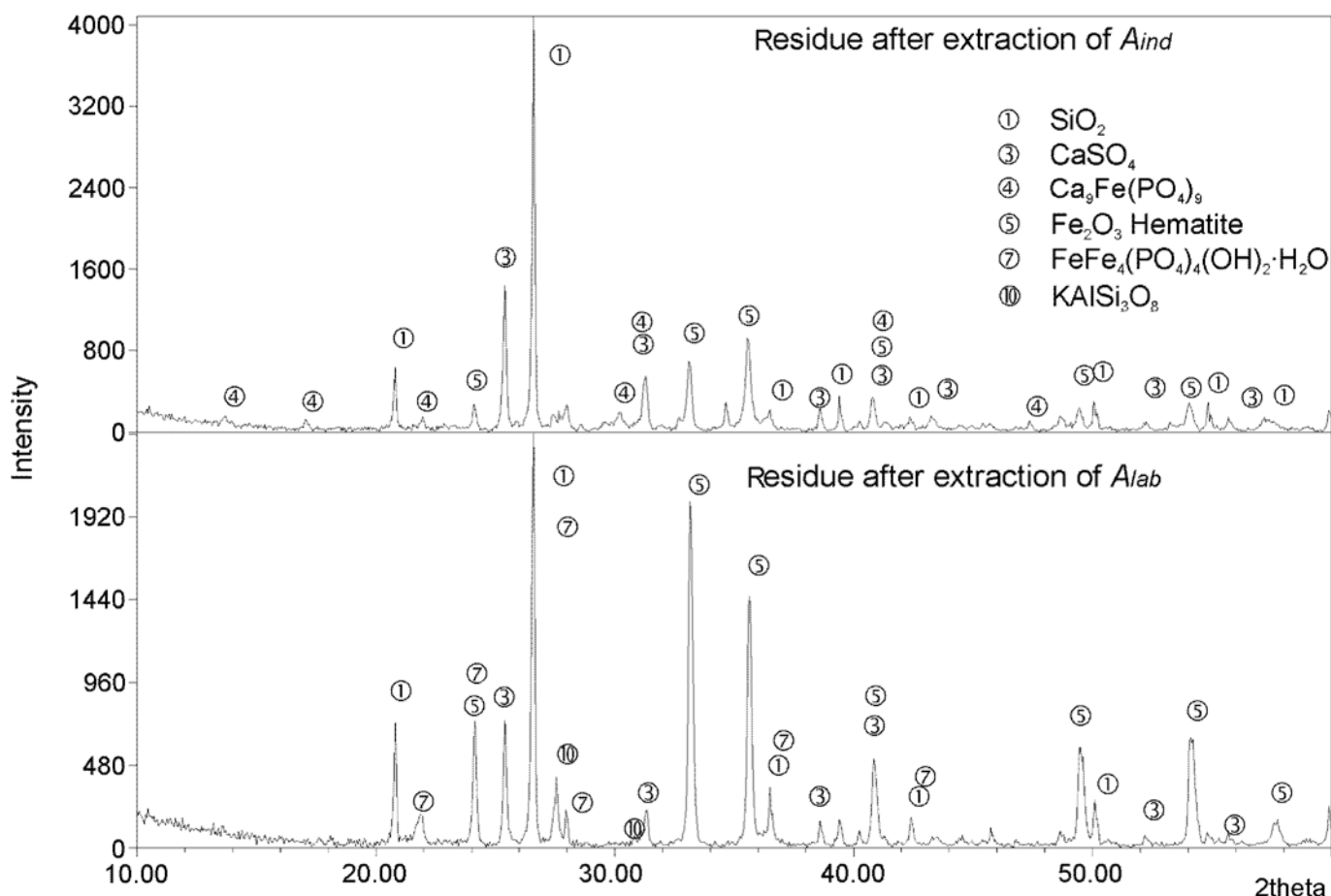


Figure 6. The X-Ray Analysis of the solid residues after an extraction of the industrial A_{ind} and laboratory A_{lab} ash with nitric acid

content in the industrial ash A_{ind} , its concentration in the extracts after phosphoric acid extraction was 4.7 times higher than in the extracts following the laboratory ash extraction. In the case of nitric acid extraction the Fe concentration was 2.2 times higher.

The solid residue after the industrial ash extraction contains more PO_4^{3-} ions than after the laboratory ash extraction. The content of the PO_4^{3-} ions amounts to 19% in the case of phosphoric acid extraction and 14% after nitric acid extraction.

The values of the extraction degrees are also lower in the case of the industrial ash extraction and reach 86.33% for nitric acid extraction and 81.07% for phosphoric acid.

The extraction productivity also insignificantly decreases.

The research results confirm that the thermal processing of sewage sludge is significant for further ash utilization and phosphorus compounds recovery. A higher temperature and a longer combustion process result in better ash parameters in the case of phosphorus compounds extraction with a limited transfer of ferrous ion into solution.

On the grounds of the conducted research, thermal utilization technologies should be selected on the basis of sewage sludge composition, control the combustion process such as to result in proper physicochemical characteristics of the ash produced with the view to further phosphorus compound recovery by means of selective extraction methods

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LITERATURE CITED

- (1) Bożym M., Waclawek W.: Problem zagospodarowania Osadów Ściekowych w Polsce, Krajach Unii Europejskiej i USA. *Chemia Dydaktyka Ekologia Metrologia* (Polish). **2000**, 5, 105.
- (2) Bień J., Kempa E.: Gospodarka osadami z oczyszczalni ścieków, inżynieria środowiska stan obecny i perspektywy rozwoju. *Monografie Komitetu Ochrony Środowiska PAN* (Polish). **2002**, 10, 323.
- (3) Data of Główny Urząd statystyczny (Polish), **2002**. / unpublished/
- (4) Steen I.: Phosphorus availability in the 21st century: Management of a non-renewable resources, *Phosphorus Potassium*. **1998**, 217, 25.
- (5) Driver J., Lijmbach D., Steen I.: Why recover phosphorus for recycling, and how?. *Environ. Technol.* **1999**, 20, 651.
- (6) EU considers tighter sludge spreading rules, *CEEP Scope Newsletter*. **2000**, 37, 2.
- (7) Duley B.: Recycling phosphorus by recovery from sewage. *Second International Conference on the recovery of phosphorus from sewage and animal wastes*, 12 – 13 march **2001**. <http://www.nhm.ac.uk/mineralogy/phos/Duley.doc>
- (8) Andersen A.: „Disposal and recycling routes for sewage sludge” report for the UE Commission-DG-Environment-B/2,SEDES. http://europa.eu.int/comm/environment/waste/sludge/sludge_disposal.htm
- (9) Takahashi M., Kato S., Shima H., Sarai E., Ichioka T., Hatykawa S., Miyajiri H.: Technology for recovering phos-

phorus from incinerated wastewater treatment sludge. *Chemosphere*. **2001**, 44, 23.

(10) Jozuka T.: P-recovery from sewage sludge incineration ash. *CEEP Scope Newsletter*. **2001**, 43, 7.

(11) Suzuki Y.: P-recovery from sewage-sludge incineration ash. *CEEP Scope Newsletter*. **2003**, 52, 4

(12) Nakahara: et al. Method for recovering phosphorus from organic sludge. US Patent 6,022,514. **2000**.

(13) Wzorek Z., Jodko M., Gorazda K., Rzepecki T.: Extraction of phosphorus compounds from ashes from thermal processing of sewage sludge. *J. Loss. Prevent. Proc.* **2006**, 19, 39.

(14) Gorazda K., Kowalski Z., Wzorek Z., Jodko M., Rzepecki T., Kulczycka J., Przewrocki P.: Possibilities of phosphorus recovering from municipal sewage sludge. *Pol. J. Appl. Chem.* **2003**, 2, 51.

(15) Kowalski Z., Wzorek Z., Jodko M., Gorazda K., Przewrocki P., Kulczycka J.: Thermal utilization of sewage sludge in Poland. *Miner. Energ.* **2003**, 2, 34.

(16) Gorazda K., Kowalski Z., Wzorek Z., Jodko M.: Phosphorus compound extraction from ash after the sewage sludge combustion. *Pol. J. Chem. Technol.* **2005**, 7, 24.

(17) Rzechuła J., Hupka J.: Charakterystyka i możliwości zagospodarowania popiołów i żużli ze spalania odpadów. *Paliwa z Odpadów (Polish)*. **2003**, 5, 243.