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Characteristic of wet method of phosphorus recovery from polish sewage sludge ash with nitric acid

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Abstract: Sewage Sludge Ash (SSA) is a concentrated source of phosphorus and can be successfully recycled via a number of different routes. This paper presents research results on phosphorus recovery from differently combusted sewage sludge with the use of nitric acid extraction. Different SSA forms from Polish thermal utilization stations were compared. It was revealed that sewage treatment technology as well as combustion technology influence many physical and chemical parameters of ashes that are crucial for further phosphorus recovery from such waste according to the proposed method. Presented research defines extraction efficiency, characterized extracts composition and verifies the possibility of using SSA as cheaper and alternative sources of phosphorus compounds. Gdynia, Kielce and Kraków SSA have the best properties for the proposed technology of phosphorus recovery with high extraction efficiency greater than 86%. Unsuitable results were obtained for Bydgoszcz, Szczecin Slag and Warszawa SSA. Extraction process for Łódź and Szczecin Dust SSA need to be improved for a higher phosphorus extraction efficiency greater than 80%.

Phosphorus content in extracts varies from 1.6 to 103.4 g PO_4^{3-} per 1 dm^3 , nitrogen content was 167.4 g per 1 dm^3 while the K content reached 0.2 to 2.37 g per 1 dm^3 . The lowest content of Fe, Ni, Cr, Cd is noted in extracts after phosphorus recovery from Gdynia SSA, where the phosphorus content is also at the highest level.

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The proposed solution can be considered as waste minimization technology by the rational recycling of phosphorus and could be used in industry to produce fertilizers.

Keywords: sewage sludge ash, phosphorus recovery, alternative raw materials, wet extraction, incineration technology

1 Introduction

P is considered as a potentially critical resource because its reserves are limited and may become exhausted within the next 60–400 years, depending on factors such as phosphate industry trends to improve recovery rates and the mining of lower grade phosphate rock [1-3]. Only 10% of the mined phosphorus is currently consumed, while the rest is lost as waste streams (food, animal waste, sewage, sewage sludge, production waste), soil erosion and runoff [4-9]. In the EU, 10–21% of sewage sludge is incinerated, constituting nearly 0.6 million tons of sewage sludge ash (SSA) per year; this amount will continue to increase. Forecasts predict that Old Member States will continue to lead these technologies. It is estimated that by 2020, thermal treatment with energy recovery could make up 37%, which is more than double compared to EU-12. Incineration procedures have undergone significant improvements during the last few years, mainly in the areas of technology, cost reduction and environmental protection. However, topics such as the cost of treatment of flue gases and ashes, dioxin and furan emission, the release of heavy metals and the handling of solid residues are still of significant importance to thermal processes [10-13].

Thermal methods of sewage sludge utilization in Poland have not been very popular in recent years, though Poland is the greatest sludge producer in the EU-12 countries. Today 11 incineration plants operate in

our country with nominal capacity covering only 20% of sewage sludge produced annually in Poland. [14,17,29].

For the utilization of SSA as a potential source of phosphorus, several parameters of the ash have to be taken into consideration. The P in SSA is not readily available as it appears mostly in the form of calcium phosphate, stanfieldite, whitlockite and berlinite. The gain in crop yield when spreading the ash directly is consequently limited due to its insolubility within the soil environment [7,15,16].

The chemical composition of the ash depends on the treatment method (either biological or chemical) used in wastewater treatment plants. The type of the precipitating agent is also significant: iron or aluminium salts used for phosphorus compound precipitation cause a higher concentration of Fe or Al in ash. The presence of heavy metals (HM) like lead, zinc, cadmium and nickel disqualify SSA from direct usage as a fertilizer (despite a high phosphorus concentration) [15,16].

The characteristics of the ash differ according to the type of thermal utilization. The most popular method is incineration in a fluidized bed, which is considered to be the best available technique (BAT) for sewage sludge disposal and is also implemented in Poland. The main drawback of this method is the relatively low incineration temperature usually used in fluidized bed furnaces. The temperature that is high enough to achieve stabilization of the waste and to remove pathogens and organic compounds is around 750–900°C is frequently [16].

But there are also other techniques for sewage sludge treatment. Combustion installations with a grate furnace are most commonly used in municipal waste incineration systems rather than in sewage sludge incineration. Initially, such solutions were used exclusively to heat power plants. However, after suitable equipping of such an installation, especially in exhaust gases treatments, it became possible to adapt this technology for co-firing and the combustion of dried sewage sludge [18]. Mono-incineration of sewage sludge in grate furnace technology are used in 3 Polish incineration plants.

Factors such as content of useful elements in SSA (including phosphorus, calcium, potassium and magnesium), the presence of heavy metals and crystalline phases of ash components, determine the possibility of using SSA as a potential raw material for the recovery of phosphorus compounds in the form of fertilizers. It was revealed that phosphorus recovery by particle separation is not possible. Its dissolution from ash particles either by thermal separation or wet chemical treatment is necessary [14-16,18,19].

This paper presents research on the phosphorus recovery from SSA using wet chemical treatment with nitric acid. Different types of SSA were compared (1) ashes from fluidized bed combustion (6 industrial installation) and, (2) ash from the grate furnace (1 industrial installation). The influence of various parameters of sewage sludge on the possibility of phosphorus recovery was investigated.

2 Materials and methods

2.1 Identification methods

The XRD Analysis of SSA was conducted using X'Pert Pro MD PANalytical. Scanning Electron Microscope Jeol JSM-7500F with EDS-INCA PentaFETX3 used for the analysis of surface morphology of the SSA.

After preparing the sample using wet microwave mineralization, the chemical composition of SSA, was determined using Atomic Absorption Spectroscopy on AAnalyst 300 Perkin Elmer and ICP-OES method on Plasm 40 Perkin Elmer.

The phosphorus content in SSA and the extracts were determined using the spectrophotometric method according to Polish standards for phosphorus raw materials PN-85/C-84092.

The chemical composition of extracts obtained after phosphorus recovery from SSA was determined using the Atomic Absorption Spectroscopy on AAnalyst 300 Perkin Elmer and ICP-OES method on Plasm 40 Perkin Elmer.

2.2 Sewage Sludge Ash (SSA) characteristics

Differently combusted SSA were used during the experiments for phosphorus recovery:

(1) sewage sludge ash in the form of slag and dust from the Thermal Utilization Station at the Municipal Sewage Treatment Plant Szczecin Pomorzany. The combustion process was carried out in the furnace with a mechanical grate and a nominal capacity of 9000 Mg of d.s. per year, at a temperature of 850–1000°C. SSA was introduced to the extraction experiments as a very fine fraction with grain-size under 0.25 mm, after vibration milling.

(2) sewage sludge ash, in the form of dust, from the Thermal Utilization Stations at Municipal Sewage Treatment Plant Sitkówka near Kielce, Kraków, Warszawa,

Table 1: The characteristic of the phosphorus removal method from sewage and combustion technology of sewage sludge (technological data from each plant, 2012).

Location	Phosphorus removal method	Combustion Technology [29]
Szczecin	aeration ditch, biological phosphorus removal, chemical precipitation with iron salts (PIX)	belt dryer, grate furnace , bag filter
Kielce	biological phosphorus removal, chemical precipitation with iron salts (PIX)	disc dryer, fluidized bed , cyclone and bag filter
Kraków	3-stage Bardenpho, biological phosphorus removal	disc dryer, fluidized bed , multicyclone and electrofilter and bag filter
Warszawa	biological phosphorus removal, chemical precipitation with Aluminum salts (PAX) and iron salts (PIX)	disc dryer, fluidized bed , multicyclone and bag filter and selective catalytic reduction (SCR)
Łódź	MUCT- activated sludge technology with biological denitrification and dephosphatation followed by secondary sedimentation, biological phosphorus removal with periodical chemical precipitation with iron salts	disc dryer, fluidized bed , multicyclone and bag filter
Bydgoszcz	5-stage Bardenpho, biological phosphorus removal with periodical chemical precipitation with iron salts (PIX)	disc dryer, fluidized bed , semi-dry reactor and bag filter and selective catalytic reduction (SCR)
Gdynia	biological phosphorus removal, chemical precipitation with aluminum salts (PAX) and iron salts (PIX)	drum dryer, fluidized bed , bag filter and scrubber

Table 2: The chemical composition of SSA.

Component	Szczecin Slag	Szczecin Dust	Kielce	Kraków	Warszawa	Łódź	Bydgoszcz	Gdynia
	A	B	C	D	E	F	G	H
P [%]	9.93	9.77	10.8	7.80	7.34	8.70	8.03	11.3
Ca [%]	11.2	12.0	11.7	10.50	10.90	12.37	20.71	12.21
Mg [%]	2.67	2.78	1.17	1.93	1.44	2.24	2.18	2.41
K [%]	1.25	1.37	1.30	0.528	0.632	0.845	0.665	0.759
Al [%]	4.67	5.83	2.26	2.34	7.14	1.37	2.94	2.32
Fe [%]	6.01	6.76	8.69	11.34	3.76	7.22	4.19	9.01
Zn [%]	0.061	0.099	0.280	0.610	0.265	0.324	0.281	0.329
Pb [mg kg ⁻¹]	3.47	14.15	78.8	135	80.1	71.3	112	103
Cu [mg kg ⁻¹]	1015	942	849	625	712	900	505	864
Ni [mg kg ⁻¹]	120	134	95	168	77.3	83.3	-	92
Cr [mg kg ⁻¹]	148	137	165	917	390	1336	532.7	92.2
Cd [mg kg ⁻¹]	13	14	20	26	4	16	< 0.03	0.571
Co [mg kg ⁻¹]	10.7	12.7	14.6	47.8	9.2	13.9	10.9	9.96
Sr [mg kg ⁻¹]	552	760	319	366	424	457	573	517
As [mg kg ⁻¹]	0.404	< 0.110	8.89	3.29	9.79	4.81	< 0.095	< 0.100
Hg [mg kg ⁻¹]	0.081	< 0.01	0.098	0.094	0.093	0.069	< 0.01	< 0.01

Łódź, Bydgoszcz, Gdynia. The installations, with a nominal capacity of 6000–70000 Mg of d.s. per year, combusts sewage sludge in a fluidized bed furnace at a temperature of 850–900°C, where sand is used as a fluid bed. SSA was introduced to the extraction experiments as a very fine fraction with grain-size under 0.25 mm.

The characteristic of thermal utilization stations and the sewage treatment method used at municipal treatment plants is shown in Table 1, while the chemical composition of SSA, used in the experiments, is presented in Table 2.

The XRD analysis of SSA reveal that phosphorus appears in the form of calcium phosphate- $\text{Ca}_{62.58}\text{P}_{42.00}\text{O}_{168.00}$ (32.5–46.8%) and stanfieldite- $\text{Ca}_4(\text{Mg}, \text{Fe}^{2+}, \text{Mn})_5(\text{PO}_4)_6$ (6.2–10.2%), iron as hematite – Fe_2O_3 (1.7–16.1%) and magnesioferrite- Fe_2MgO_4 (1.6–8.6%) and aluminum in the form of anorthite- $\text{CaAl}_2\text{Si}_2\text{O}_8$ (4.9–21.8%) and Berlinite- AlPO_4 (1.8–11.6%). Quartz – SiO_2 (21.6–32.6%), Anatase- TiO_2 and Tridymite- SiO_2 was also identified.

SEM analysis showed differences in the surface morphology of the selected SSA (Fig. 1).

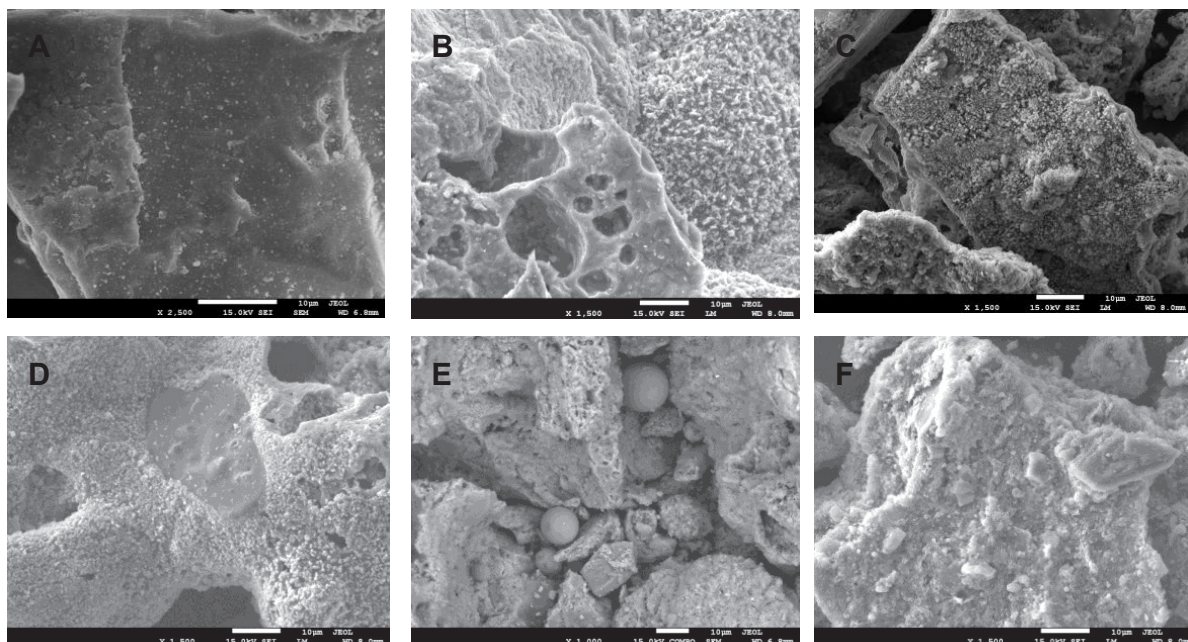


Figure 1: Scanning electron micrographs of SSA: A-Szczecin Slag, B-Szczecin Dust, C-Kielce, D-Kraków, E- Warszawa, F-Łódź.

2.3 Phosphorus extraction method

SSA was subjected to the phosphorus recovery process by the wet extraction method within 2h with the use of $2.7 \text{ mol dm}^{-3} \text{ HNO}_3$. Experiments were conducted using the same amount of phosphorus introduced with each ash to the solution. Such extractants and conditions were considered the most favourable on the basis of earlier research and patents [20-24]. The mixture was continuously mixed in the reactor with constant velocity and continuous pH and temperature as well as periodical phosphorus determination. After the extraction, samples of the solution and sediment (rinsed and dried) were analyzed for Fe, P, Al, Mg, Ca, Zn, Pb, Cu, Ni, Cr, Cd, Co content. Phosphorus concentration was determined spectrophotometrically, while the remaining metals were determined by the AAS and ICP method.

3 Results and discussion

The concentration of phosphorus compounds leached from ash to the solution during nitric acid extraction, varies according to the examined SSA, despite the same amount of P introduced with each SSA to the process (Fig. 2). The highest concentration of phosphorus compounds was reached for ashes samples from Kraków,

Kielce, Szczecin Dust, Łódź and Gdynia after an initial 30 minutes of leaching. A much lower increase of phosphate concentration in the solution was observed for Warszawa, Szczecin Slag and Bydgoszcz SSA. During the extraction process, after 30 minutes, a maximum concentration of phosphorus compounds was reached, and a slow reduction occurred for Szczecin Slag and Bydgoszcz samples. The reason might be the saturation of the solution, resulting in precipitation of calcium phosphate and a lower concentration of the phosphate ions in the liquid phase. Unsuitable results were obtained for the Bydgoszcz SSA with the highest Ca concentration (20.71%), for Szczecin Slag introduced to the process after milling (grate furnace technology), and the Warszawa SSA with the highest concentration of Al in ash. Moreover, in extracts after phosphorus leaching from the Warszawa SSA a gelation effect occurred precluding a phase separation and further calculation of extraction efficiency.

Conducted experiments showed that ashes act differently during extraction processes resulting in different physical and chemical properties of extracts (Table 3) and composition (Table 4). As the most important parameter of the conducted experiments, PO_4^{3-} extraction degree was counted and shown in Table 3. The difference of phosphorus compounds extraction from SSA is clearly marked, with a varied composition and production under different conditions. In spite of introducing the same quantities of

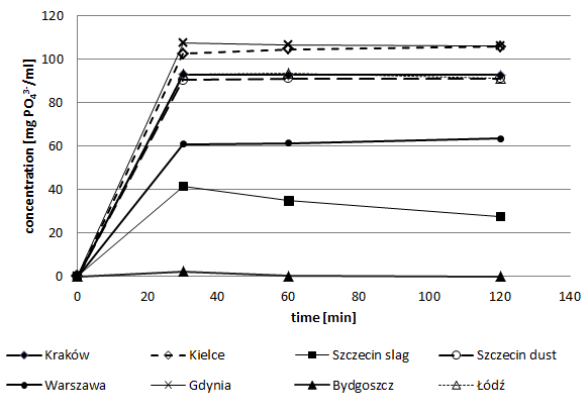


Figure 2: PO₄³⁻ concentration in extracts during SSA leaching with 2.7 mol dm⁻³ HNO₃.

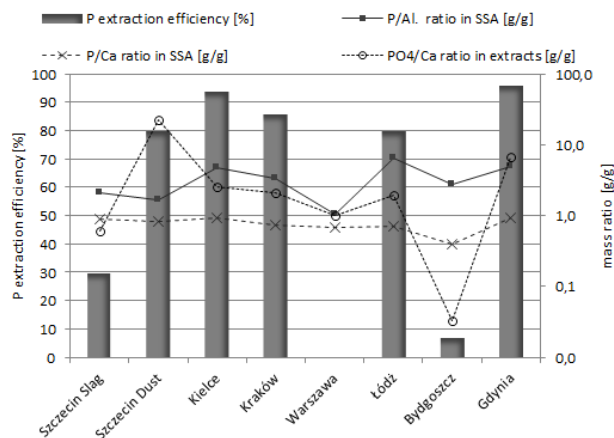


Figure 3: Comparison of P extraction efficiency with main components ratio in SSA and obtained extracts.

phosphorus with SSA, its extraction from the Gdynia SSA (fluidized bed technology) is 3 times more efficient than from the Szczecin Slag SSA (grate furnace technology). Such low extraction efficiency disqualifies SSA as ground slag for further industrial phosphorus recovery.

Gdynia and Kielce SSA showed the best results as the P extraction degree was higher than 90%. The extracts that were obtained had a phosphate content level of 103.4 and 101.0 g dm⁻³ respectively. The ash to acid mass ratio during the extraction process also had the lowest value of 0.27 and 0.31 [g g⁻¹]. Together with the ash composition it produced the lowest pH for the final solutions (0.13 and 0.97). In contrast, the final extracts after the phosphorus recovery from Bydgoszcz SSA showed very low efficiency (P extraction degree 7%) with a pH of 7.9. It was caused by a high Ca content in ash and a rapid dissolution of its compounds in the solution resulting in Ca/PO₄³⁻ molar ratio of extracts greater than 72 [mol mol⁻¹].

Table 3: Extraction characteristic: P extraction degree, pH and density of extracts and ash to acid solution mass ratio used during leaching process.

SSA	P extraction degree [%]	Extracts pH	Extract density [g cm ⁻³]	Ash/acid mass ratio [g g ⁻¹]
Szczecin Slag	30	1.64	1.18	0.34
Szczecin Dust	80	1.07	1.22	0.34
Kielce	94	0.97	1.23	0.31
Kraków	86	0.73	1.21	0.43
Warszawa	-	1.97	1.23	0.46
Łódź	80	1.1	1.22	0.39
Bydgoszcz	7	7.9	1.15	0.42
Gdynia	96	0.13	1.22	0.27

Considering further use of extracts for fertilizer production, a high content of macronutrients was recommended while Cd, As, Pb and Hg were limited in extracts. Nitrogen was introduced to the extraction process with 2.7 mol dm⁻³ nitric acid and its content in each extract was 37.83 g L⁻¹ (1675 g NO₃⁻ per 1 L). Phosphorus content, depending on extraction efficiency, varied from 0.52 g L⁻¹ (Bydgoszcz SSA) to 33.74 g L⁻¹ (Gdynia SSA). The lowest content of As and Hg was noted in the extracts after phosphorus extraction with the highest efficiency by Gdynia SSA, where phosphorus content was also at the highest level.

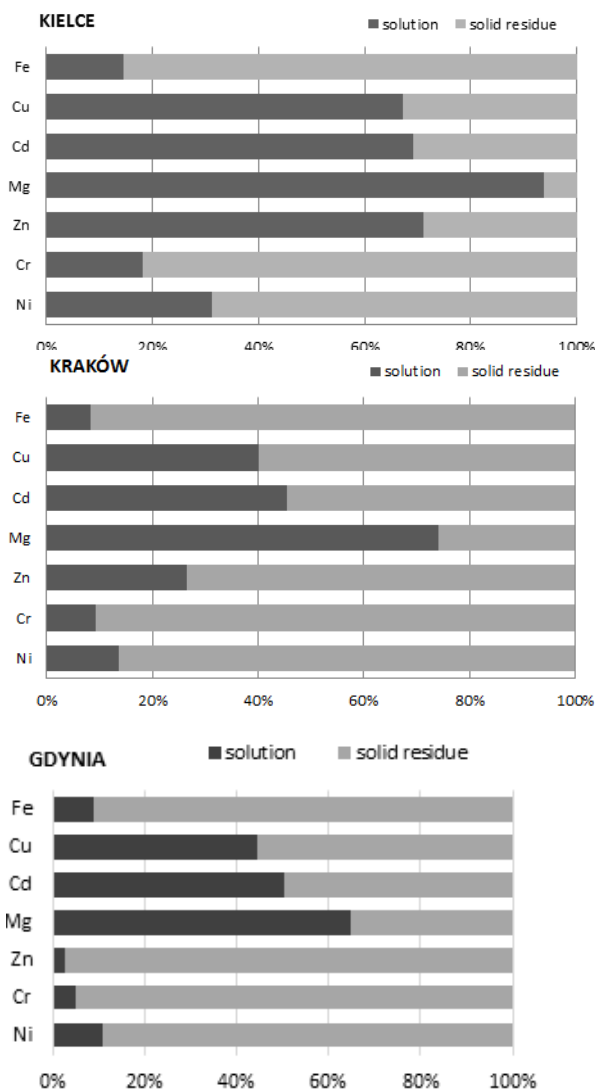
The comparison of P extraction efficiency with the composition of ash, shows that the best results correspond with high P/Ca mass ratio in the SSA (0.74–0.92 [g g⁻¹]), as well as high ratio of P to Al (higher than 3.3 [g g⁻¹]). This is exhibited in Fig. 3. Consequently, extracts with the lowest mass ratio of phosphate ions to calcium correspond with the lowest phosphorus extraction efficiency from ash (Szczecin Slag, Bydgoszcz, Warszawa).

In summary, Gdynia, Kielce and Kraków SSA have the most favorable parameters considering the wet extraction method with nitric acid for phosphorus recovery. The distribution of the selected SSA components between the liquid and solid phase during phosphorus recovery process is shown in Fig. 4.

The concentration of Fe in extracts strongly depends on the mineral composition of SSA; this in turn is related to the chemical and thermal treatment of sewage sludge (Table 1) [15,23,24]. The highest concentration of iron in extracts was obtained for Szczecin Slag SSA while the lowest was for Gdynia SSA. Such results confirm our previous observation during phosphorus recovery from laboratory combusted sewage sludge [24]. When iron is

Table 4: Chemical composition of extracts after phosphorus recovery form SSA.

SSA	PO_4^{3-} g L^{-1}	Fe g L^{-1}	Ca g L^{-1}	K g L^{-1}	Mg g L^{-1}	Ni mg L^{-1}	Cu mg L^{-1}	Cr mg L^{-1}	Cd mg L^{-1}	Zn mg L^{-1}	As mg L^{-1}	Pb mg L^{-1}	Hg mg L^{-1}
Szczecin Slag	27.4	8.7	39.98	1.29	7.3	12	-	4	1	104	< 0.001	< 0.001	< 0.001
Szczecin Dust	88.5	5.1	4.02	0.214	7.0	-	-	12	2	160	< 0.001	0.042	< 0.001
Kielce	101.0	4.1	39.66	2.37	7.9	9	107	8	3	662	2.71	8.13	< 0.001
Kraków	92.2	3.5	43.23	1.02	6.1	15	142	46	4	630	1.53	19.89	< 0.001
Warszawa	39.9	1.8	39.40	1.47	5.0	25	147	9	3	215	< 0.001	3.75	< 0.001
Łódź	89.7	2.4	46.60	1.18	7.2	6	148	78	3	390	2.59	2.25	< 0.001
Bydgoszcz	1.6	0.089	48.68	0.711	4.3	227	35	27	6	6	< 0.001	0.001	< 0.001
Gdynia	103.4	1.59	37.01	1.36	4.3	3	143	2	2	65	< 0.001	4.08	< 0.001

**Figure 4:** Distribution of SSA components between the liquid and solid phase for Kielce, Kraków and Gdynia SSA.

immobilized in the hematite phase, slightly insoluble even in the strong acids, extraction is more selective towards phosphorus compounds. That fact is confirmed by XRD analysis of SSA and solid residue after extraction of Kraków SSA, with the highest content of Fe in ash. Distribution of Fe between solid and liquid phase is most favorable (Fig. 4). Kraków SSA contained iron in the form of hematite (11.6%), and magnesioferrite (8.6%), while in the Szczecin Slag SSA, the highest percentage share of iron compounds belongs to stanfieldite (10.2%) and the rest to hematite (4.3%) and magnesioferrite (2.7%). During the phosphorus recovery via extraction with nitric acid, stanfieldite dissolved completely, releasing iron into solution, while insoluble hematite and magnesioferrite remains in solid residue after extraction. 16.5% of hematite was determined in solid residue after Kraków SSA extraction while in Szczecin Slag SSA only 5% is notice. Taking into account further usage properties of obtained extracts it is a very advantageous effect, because the presence of iron ions influence unfavorably the phosphorus compounds availability especially in fertilizers.

The extraction with nitric acid results in high phosphorus compounds dissolving, and the remaining solid residue consisting of quartz (51–64%), hematite (5–30.5%), magnesioferrite (0.9–12.9), Berlinite (5–12%). Calcium phosphates are determined only for Szczecin Slag SSA, Bydgoszcz SSA and Łódź SSA).

According to proposed non-waste and ecological technology of phosphorus compounds recovery, solid residue can be used for building materials such as primary or secondary components of cement, aggregates and micro-filers, special blends (lean concrete and substructures) as mentioned in literature [16,25–28]. Such an utilization that is currently being investigated is possible only when the phosphorus content in residue after the extraction

Table 5: Minimum concentration of the micronutrients declared in suspension fertilizers according to the Regulation of Minister of Economy with respect to the extract composition.

SSA	Fe [mg kg ⁻¹]	Cu [mg kg ⁻¹]	Zn [mg kg ⁻¹]	Mn [mg kg ⁻¹]	B [mg kg ⁻¹]
Kielce	3333	87	538	149	29.96
Kraków	2893	117	520	149	9.95
Gdynia	1303	117	53	157	35.1
Minimum values of micronutrient according to [30]	200	20	20	100	100

is very low. That requirement disqualifies Szczecin Slag SSA, Warszawa SSA and Bydgoszcz SSA for phosphorus recovery and forces the improvement of the extraction process towards even a better phosphorus transfer to the liquid phase.

Connecting all the data from the extraction processes of SSA with surface morphology (Fig.1.) and combustion technology the following conclusions can be drawn. Combustion technology influences the mineral composition and surface morphology of SSA. If a fluidized bed is used, dewatered sewage sludge (28–45% d.s.) and hot compressed air with temperature 500–600°C are fed to the combustion chamber where the sand bed temperature reaches 750°C while the overhead freeboard zone is 800–900°C. The sand bed stabilizes the temperature fluctuation in the incinerator. Particles are in the combustion chamber for only about 1–2 s. The remaining inorganic material, the fine particles, is removed from the exhaust gas by filters, cyclones or electrostatic precipitators [16].

When the furnace with the mechanical grate is used, dried sewage sludge (90% d.s.) is introduced to the incinerator. The combustion chamber has three points of air supply and a mechanical grate cooled with water. The residence time is counted in minutes with a temperature exceeding 850°C. Such technological differences definitely influence the form of SSA, fine and powdery after fluidal combustion and the mixture of slag and powder after grate combustion. Moreover, a longer residence time and a higher temperature in the grate furnace effect a glassy appearance shown in Fig. 1. Such a structure is more resistant on the extraction due to a lower surface of interphase contact; therefore more components stay in a solid residue.

Comparing the composition of extracts with the highest extraction efficiency (Kielce Kraków and Gdynia SSA) with minimum values of micronutrient declared in suspension fertilizers (Table 5), extracts do not exceed these values for the concentration of boron (100 mg kg⁻¹), molybdenum (10 mg kg⁻¹) and cobalt (20 mg kg⁻¹). This

information is according to the Regulation of Minister of Economy. The rest of the listed elements like Fe, Cu, Mn are present in the extract after Gdynia, Kraków and Kielce SSA leaching at a greater amount [30].

According to Regulation (EC) No 2003/2003 of the European Parliament and to the Council of 13 October 2003 relating to fertilizers [31] with the further changes, fluid fertilizer is defined as fertilizer in suspension or solution:

- ‘Solution fertilizer’ – fluid fertilizer that is free of solid particles.
- ‘Suspension fertilizer’ – a two-phase fertilizer in which solid particles are maintained in suspension in the liquid phase.

If we consider extracts as NP fluid fertilizers, a minimum total content of nutrients (percentage by weight) should be 18 %, (N + P₂O₅). At the same time, the minimum content for each of the nutrients should exceed 3 % N and 5 % P₂O₅. The total content of nutrients in the analysed extracts varies between 8.81–9.43% and is below minimal levels (Table 6). The Ca content exceeds the level required for secondary nutrients.

Micro-nutrients were defined as elements boron, cobalt, copper, iron, manganese, molybdenum and zinc, and which are essential for plant growth in small quantities compared to those of primary and secondary nutrients. The micro-nutrient content for mixtures of fertilizers containing at least two different micro-nutrients, shall be declared by indicating:

- the total content, expressed as a percentage of the fertilizer by mass,
- the water-soluble content, expressed as a percentage of the fertilizer by mass, where the soluble content is at least half of the total content [31].

Fluid fertilizers with micro-nutrients were divided into three groups:

- fluid mixtures of micro-nutrient fertilizers, where the micro-nutrient was present in a form that was exclusively mineral or chelated or complexed,

Table 6: Minimum concentration of the nutrients and secondary nutrients in fluid fertilizers according to the Regulation (EC) No 2003/2003 of the European Parliament and to the Council relating to fertilizers with respect to the extract composition.

SSA	N [%]	P ₂ O ₅ [%]	N+ P ₂ O ₅ [%]	Ca [%]
Kielce	3.07	6.14	9.21	3.22
Kraków	3.12	5.69	8.81	3.57
Gdynia	3.10	6.33	9.43	3.03
Minimum values of nutrients and secondary nutrients [31]	3	5	18	1.4

Table 7: Minimum concentration of the micro-nutrients in fluid fertilizers according to Regulation (EC) No 2003/2003 of the European Parliament and to the Council relating to fertilizers with respect to the extract composition.

SSA	Fe [%]	Cu [%]	Zn [%]	Mn [%]	B [%]
Kielce	0.33	0.0087	0.054	0.015	0.002
Kraków	0.29	0.012	0.052	0.015	0.0008
Gdynia	0.13	0.012	0.0053	0.016	0.003
mixtures of micro-nutrient fertilisers, where the micro-nutrient is present in a mineral form	2.0	0.5	0.5	0.5	0.2
fertilisers containing primary and/or secondary nutrient(s) with micro-nutrient(s) applied to the soil,	0.02	0.002	0.002	0.01	0.01
- for horticultural use	0.5	0.01	0.01	0.1	0.01
-for crops or grassland					
fertilisers containing primary and/or secondary nutrient(s) with micro-nutrient(s) applied for the leaf sprays	0.020	0.002	0.002	0.010	0.010

- fertilizers containing primary and/or secondary nutrient(s) with micro-nutrient(s) applied to the soil,
- fertilizers containing primary and/or secondary nutrient(s) with micro-nutrient(s) for leaf sprays.

Analysed extracts can be considered as fluid fertilizers applied to the soil containing secondary nutrients with Fe, Cu, Zn, and Mn as micro-nutrients for horticultural application (Table 7).

There are changes proposed by EU legislation in reference to cadmium content in fertilizers. The main anthropogenic sources of Cd in cultivated soils are phosphorus-fertilizers. The Regulation (EC) No.

2003/2003 did not impose limits for Cd content. With the Commission Decisions 2006/347/WE, 2006/348/WE and 2006/349/EC, Sweden, Finland and Austria prohibit placing phosphorous mineral fertilizers (containing 5% P₂O₅ or more) on the market with a cadmium content exceeding 100 g/tP, 50 and 75 mg kg⁻¹ P₂O₅ respectively. Also the Czech Republic limited cadmium content to 50 mg kg⁻¹ P₂O₅. In Poland this limit is 50 mg kg⁻¹ of dry weight of mineral fertilizer [30]. A new limit of 60mg kg⁻¹ P₂O₅ is being discussed that would gradually change to a level of 20 mg Cd per 1 kg P₂O₅ within 15 years [32]. The Cd content in analysed extracts Kielce, Kraków and Gdynia is 40, 58 and 26 mg per 1 kg of P₂O₅ respectively and has fulfilled new limits.

4 Conclusions

Gdynia, Kielce and Kraków SSA after fluidal combustion of sewage sludge has the best properties for the proposed technology of phosphorus recovery by extraction with nitric acids with high extraction efficiency greater than 86%.

Unsuitable results were obtained for Bydgoszcz SSA with the highest Ca concentration (20.71%), for Szczecin slag introduced to the process after milling (grate furnace technology), and Warszawa SSA with the highest concentration of Al in ash. Moreover, in extracts after phosphorus leaching from the Warszawa SSA a gelation effect occurred precluding phase separation.

The extraction process for Łódź and Szczecin Dust SSA need to be improved for a higher phosphorus extraction efficiency greater than 80%.

Thermal utilization of sewage sludge and ash origin play a key role for final ash properties introduced to the recovery process. The technologies for phosphorus recovery from SSA must take into account the industrial procedures of sewage treatment plants in Poland, where phosphorus is removed during biological or chemical treatment with iron or aluminium salts. The research result confirms that the selective extraction of phosphorus compounds from ash is possible because of insoluble hematite phase appearance (Fe₂O₃).

Comparing SSA from different industrial technology of sewage sludge combustion, SSA after grate furnace in the form of grinded slag showed significantly poorer properties for phosphorus recovery. Moreover, the purification method of exhausted gases is important, especially when calcium salts are added for sulphur compounds reduction as in the Bydgoszcz Plant. Low extraction efficiency, high

phosphorus content in solid residue disqualifies such waste for further industrial phosphorus recovery.

Presently, conducted research confirmed that extracts could be used for NPK fertilizer production in the form of solid or suspension fertilizers by a further neutralization method. Conducting these processes with the use of ammonium and solid waste reach in phosphorus and potassium will provide proper composition of nutrients. During that operation, the elemental composition of the fertilizer could be modified and adjusted to the individual needs. It is an opportunity to utilize different extracts or blend them, as well as conduct extractions with ash mixtures, depending on specific metal content. Such a procedure eliminates the purification stage depending on the heavy metal content.

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