

Article

Thermochemical Treatment of Sewage Sludge Ash (SSA)—Potential and Perspective in Poland

Marzena Smol ^{1,*} , Christian Adam ² and Stefan Anton Kugler ²

¹ Mineral and Energy Economy Research Institute, Polish Academy of Sciences, Wybickiego 7A str., 31-261 Cracow, Poland

² Bundesanstalt für Materialforschung und -prüfung (BAM), Zweiggelände Adlershof, Richard-Willstätter-Straße 11, 12489 Berlin, Germany; christian.adam@bam.de (C.A.); stefan-anton.kugler@bam.de (S.A.K.)

* Correspondence: smol@meeri.pl; Tel.: +48-12-617-16-60

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Abstract: Phosphorus (P) recovery from sewage sludge ash (SSA) is one of the most promising approaches of phosphate rock substitution in mineral fertilizers and might be a sustainable way to secure supply of this raw material in the future. In the current investigation, the process of thermochemical treatment of SSA was applied to SSA coming from selected mono-incineration plants of municipal sewage sludge in Poland (Cracow, Gdansk, Gdynia, Lodz, Kielce and Szczecin). The Polish SSA was thermochemically converted in the presence of sodium (Na) additives and a reducing agent (dried sewage sludge) to obtain secondary raw materials for the production of marketable P fertilizers. The process had a positive impact on the bioavailability of phosphorus and reduced the content of heavy metals in the obtained products. The P solubility in neutral ammonium citrate, an indicator of its bioavailability, was significantly raised from 19.7–45.7% in the raw ashes and 76.5–100% in the thermochemically treated SSA. The content of nutrients in the recycles was in the range of 15.7–19.2% P₂O₅, 10.8–14.2% CaO, 3.5–5.4% Na₂O, 2.6–3.6% MgO and 0.9–1.3% K₂O. The produced fertilizer raw materials meet the Polish norms for trace elements covered by the legislation: the content of lead was in the range 10.2–73.1 mg/kg, arsenic 4.8–22.7 mg/kg, cadmium 0.9–2.8 mg/kg and mercury <0.05 mg/kg. Thus, these products could be potentially directly used for fertilizer production. This work also includes an analysis of the possibilities of using ashes for fertilizer purposes in Poland, based on the assumptions indicated in the adopted strategic and planning documents regarding waste management and fertilizer production.

Keywords: sewage sludge (SS); sewage sludge ash (SSA); critical raw materials (CRMs); phosphorus (P); fertilizer

1. Introduction

Phosphorus (P) is one of the primary nutrients for plant growth (next to nitrogen and potassium). It is a non-renewable [1], but a fundamental element for all living organisms as P is an important component of nucleic acids and lipids and plays a strategic role in energy transfer at the cell level [2]. P is involved in many of the life processes of plants; it participates in the process of photosynthesis, as well as the synthesis of carbohydrates, proteins and fats. It affects the rapid growth of roots and stimulates tillering. Moreover, it increases the uptake of other nutrients and improves plant resistance to environmental stresses, such as low temperatures or fungal diseases [3]. As P is an essential nutrient for photosynthetic carbon assimilation, and the most common nutrient, its sustainable and circular management is of particular interest to researchers and practitioners operating in the fertilizer sector [4].

Primarily, P is extracted from mined ores, in the form of phosphate rock formed from fossilized marine animal remains (sedimentary phosphate rock), which contains approx. 6.5–17.9% P [5]. In 2014, phosphate rock was indicated as one of the most valuable critical raw materials (CRMs) for the European economy and it was placed on the CRMs list [6]. The CRMs list contains those raw materials that show economic and strategic importance for the European Union (EU) economy [7], but also show a high risk resulting from their supply. Currently, approx. 90% of phosphate rock is used in the production of fertilizers, as mineral fertilizers, animal fodder and feed phosphates [8]. In 2017, the CRMs list has been revised and expanded to include white P, which is a vital element in the chemical sector [9]. The newest CRMs list published in September 2020 also includes phosphate rock and P [10]. More than 90% of white P is used in the manufacturing of detergents and other chemicals as polymer additives, pharmaceuticals, lubricants, agrochemicals or catalysts [11]. P resources cannot be replaced by any other element [12]; therefore, the substitution index of phosphate rock is 1.0 (where 1 being the least substitutable), and there is low possibility of white P substitution, reaching 0.91. Moreover, the demand for these materials in the EU is almost completely covered by imports (88% of phosphate rock and 100% of white P), mainly from countries located outside the EU, such as Kazakhstan, Morocco, China or Russia, which negatively affects the security of the EU supply [9]. A similar situation occurs in the production of P raw materials, as the main centers are located outside the EU, in China, Russia and the United States.

To maintain the security of P fertilizer materials, the European Commission (EC) emphasized the role of P for the European economy in several official documents related to sustainable [13] and circular [14–16] management of P raw materials from both primary and secondary sources. Improvements in the management of nutrients is an important objective of the newest European Green Deal strategy, which was proposed by the EC in late 2019 [17]. A strategic role in the transformation to a Green Deal should be the Farm-to-Fork strategy, which aims to reduce nutrient losses by at least 50%, while ensuring no deterioration in soil fertility and reduce fertilizer use by at least 20% by 2030. Moreover, the inclusion of P resources onto the CRMs list should have stimulated development of methods and technologies for P recovery from internal waste resources [9]. The most promising secondary sources of P are wastes produced in the municipal wastewater treatment plants (WWTPs) [18], wherein the P recovery potential appears at various stages of waste processing [19], as effluent from the treatment station, leachate (sedimentary liquid) [20,21], sewage sludge (SS) [22–28] and sewage sludge ash (SSA) [29,30]. In each of the subsequent waste treatment processes, the volume of substrate used for the P recovery is getting smaller, but the concentration of this element per unit volume is increasing [31]. Consequently, the highest P recovery potential is given for SSA (>90%), whereas recovery technologies based on side stream processing in the WWTP are limited to <40% [32].

In the last years, there has been a significant increase in the amount of research works devoted to the possibility of P recovery from various wastes generated in WWTPs. They have been summarized in the “Global Compendium on Phosphorus Recovery from Sewage/Sludge/Ash” [33]. Many national, European and global projects have been focusing on the development of new techniques of P recovery from waste, while others have been verifying already existing technologies to achieve the highest efficiency in terms of both recovery level and economic viability. One of the European projects that focused on the development of a circular, sustainable P recovery method from SS and SSA was the “Sustainable and safe re-use of municipal sewage sludge for nutrient recovery” (SUSAN) project, funded under the EU 6th Framework Research and Development Programme [34]. The main achievement of the project was an integrated technology for the thermal treatment of SS (energy recovery and destruction of organic pollutants) and subsequent thermochemical treatment of SSA (heavy metals removal and increasing the phosphorus bioavailability). In the last years, the so called AshDec technology had been improved and tested for SS and SSA coming from various WWTPs in different countries [29,35–37]. In the current paper, the core of the AshDec process, which is the thermochemical treatment of SSA for P recovery, was evaluated for ashes coming from mono-incineration plants in Poland. Until now, the thermochemical treatment has not been used to recover P from this waste stream

in Poland. Despite the relatively high content of P in SSA [38], it is chemically bound and is not readily available to plants; therefore, additional conversion methods (including chemical or thermochemical) should be used to increase the availability of P to plants. In the current work, the SSA samples were thermochemically treated together with sodium (Na) additives and a reducing agent (dried sewage sludge) to transform the insoluble phosphates present in the SSA into highly plant-available phosphates (CaNaPO_4) and to remove the heavy metals. The laboratory experiments are supported by a discussion on the potential of and perspectives on usage of these products in agriculture under Polish conditions.

2. Materials and Methods

The section provides a description of the materials and methods used in the current study. A scheme of the research framework adopted in the study is shown in Figure 1.

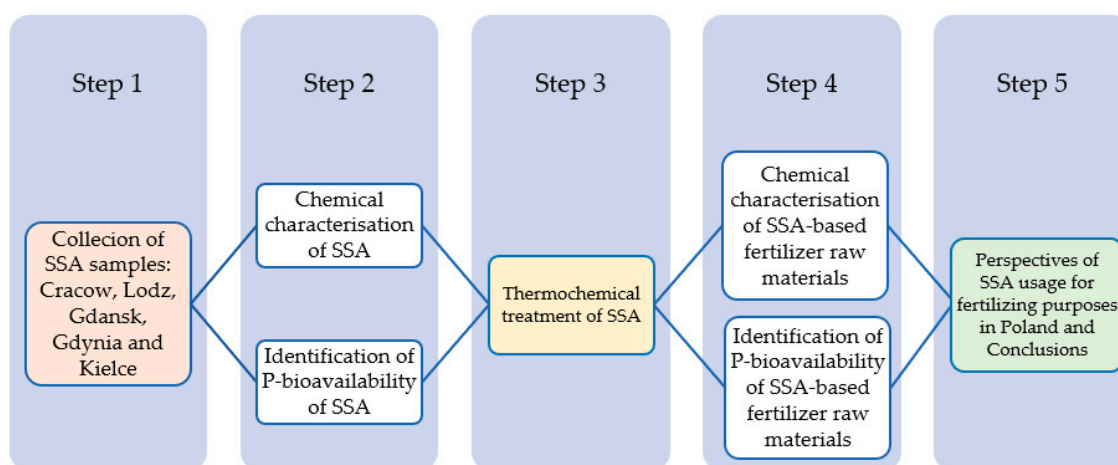


Figure 1. Research framework.

2.1. Materials

Samples of ashes were taken from selected facilities for the thermal transformation of municipal sewage sludge in Poland: Cracow, Gdansk, Gdynia, Lodz, Kielce and Szczecin. These plants incinerate sewage sludges that were produced in municipal WWTPs equipped with mechanical and biological wastewater treatment installations, based on activated sludge units. The detailed information about the methods used for P removal at the selected WWTPs and the characteristics of the mono-incinerations (combustion method, annual capacity of the plant and amount of ashes generated) are shown in Table 1. In most of the facilities, the fluidized bed technology is used for combustion (Cracow, Gdansk, Gdynia, Lodz and Kielce), while in one facility a grate stoker is operated (Szczecin).

Approx. 0.5 kg of SSA was sampled from the mono-incineration plants by the operators, which have been instructed how to proceed with the sampling to acquire representative samples. Then, the samples were transported in plastic containers to the laboratory for further analysis. Samples of dried SS, which were used as a reducing agent in the thermochemical experiments [29], were collected from a WWTP in Bavaria, Germany.

Table 1. Basic information about the analyzed Polish mono-incineration plants [39–41].

Location of Mono-Incineration Plant	Phosphorus Removal Method in WWTP	Type of Combustion Furnace	Rated Capacity (Mg d.w./year)	Annual Production of SSA (in 2018) (Mg)
Cracow	3-stage Bardenpho, biological phosphorus removal	fluidized bed	23,000	4885
Lodz	MUCT-activated sludge technology with biological denitrification and dephosphatation followed by secondary sedimentation, biological phosphorus removal with periodical chemical precipitation with iron salts	fluidized bed	21,000	3824
Gdansk	Anaerobic/anoxic/oxic (A ₂ O) process	fluidized bed	14,000	3279
Gdynia	Biological phosphorus removal, chemical precipitation with aluminum salts (PAX) and iron salts (PIX)	fluidized bed	9000	1676
Szczecin	Aeration ditch, biological phosphorus removal, chemical precipitation with iron salts (PIX)	grate stoker	6000	1426
Kielce	Biological phosphorus removal, chemical precipitation with iron salts (PIX)	fluidized bed	6200	719

2.2. Analysis of Chemical Composition

The samples of the raw SSA, SS and thermochemically treated products were analyzed for selected elements, such as the main elements (P, Mg, Ca, S, K, Na, Fe, Al and Si) and trace elements (Cd, Cu, Cr, Zn, Pb, Ni, As, Co, Mn, Mo and Sn). All samples were completely digested in a microwave before analysis. Preparation of the samples included the following stages [29,42,43]:

- drying, grinding and homogenization of the sample with a rotary disc mill;
- preparation of mix of 0.1 g ± 0.1 mg of sample with 4 cm³ of concentrated nitric acid (HNO₃), 1.5 cm³ perchloric acid (HClO₄) and 0.5 cm³ hydrofluoric acid (HF);
- digestion of samples at 240 °C for 15 min in a microwave (mikroPrepA, MLS GmbH, produced in Leutkirch, Germany);
- cooling of samples;
- complexation of excess HF with 2.5 cm³ of cold-saturated boric acid (HBO₃);
- filtration of the solution (neoLab round filter paper, type 388) and topping up to 50 cm³ with distilled water.

Then, all samples were directed towards determination of the abovementioned elements with the use of inductively coupled plasma optical emission spectroscopy (ICP-OES) and, specifically for the trace elements, inductively coupled plasma mass spectrometry (ICP-MS). Moreover, the content of Si was determined by the X-ray fluorescence (XRF) method (MagiX Pro from PANalytical) equipped with a water-cooled 4 kW Rh tube. The data quantification was conducted with the use of the semi-quantitative, standardless analysis package “Omnian”, PANalytical).

The amounts of SSA, SS and NaHCO₃ mixed in the individual experiments are provided in Table 2. The results presenting the chemical composition of the SSA and SS are presented in Table 3.

Table 2. The amounts of the SSA, SS and NaHCO₃ mixed in the individual experiments.

No.	Location of the Mono-Incineration Plant	Amount of SSA	Amount of SS	Amount of NaHCO ₃
		(g)	(g)	(g)
1	Cracow	30.0	7.5	12.8
2	Lodz	30.0	7.5	19.8
3	Gdansk	30.0	7.5	21.9
4	Gdynia	30.0	7.5	17.7
5	Szczecin	30.0	7.5	18.7
6	Kielce	30.0	7.5	19.9

Table 3. Elemental composition of the SSA from the mono-incineration plants and the SS used in the experiments.

Component	SSA					
	Cracow	Lodz	Gdansk	Gdynia	Szczecin	Kielce
P (%)	6.90	11.37	12.74	11.31	10.83	11.24
Mg (%)	1.56	2.60	3.07	2.41	2.36	2.31
Ca (%)	7.52	10.51	9.80	11.46	9.81	13.97
K (%)	0.79	1.12	1.41	0.91	0.92	0.87
Na (%)	0.09	0.16	0.16	0.10	0.14	0.11
Fe (%)	15.23	6.64	6.16	6.07	11.60	10.14
Al (%)	2.38	3.49	4.75	11.31	10.83	2.86
Co (mg/kg)	39	40	25	21	74	37
Sn (mg/kg)	248	309	97	57	7	56
Mn (mg/kg)	1085	607	669	725	520	1103
Mo (mg/kg)	50	15	16	4	11	11
Si (%)	8.60	11.01	9.94	8.04	9.25	8.52
Cu (mg/kg)	739	691	730	772	695	899
Cr (mg/kg)	560	703	122	106	100	134
Cd (mg/kg)	9	8	4	4	1	6
Zn (mg/kg)	3750	3205	2625	2768	1209	2993
Pb (mg/kg)	94	77	67	62	16	78
Ni (mg/kg)	222	260	112	135	91	802
As (mg/kg)	57	9	12	10	6	13
Hg (mg/kg)	<0.05	0.11	0.12	<0.05	<0.05	<0.05

2.3. Thermochemical Treatment of SSA

The SSA samples were thermochemically treated to convert the low plant available P compounds in the SSA to the highly plant available P forms while reducing the heavy metal content. The core of the process was an addition of sodium compounds (Na additives) and a reducing agent (dry sewage sludge) to the SSA samples and placing the samples thus prepared in a muffle furnace where they were treated at high temperatures (1000 °C) for a defined retention time [29].

In total, 6 experiments were carried out for all analyzed SSA samples. Dosing of the sodium additive had to be adapted to the P and Si contents of each SSA as it reacts with the phosphates and SiO₂ (quartz) of which the reaction with quartz is an unwanted side reaction. As the additive dry sewage sludge also contains P and Si, it must be taken into account. The required amounts of sodium compounds ($m_{(d)}$) were thus calculated based on the contents of P and Si in the given mixture of SSA and SS (based on the results of HF/HClO₄-digestion and ICP-OES analyses), according to the equation provided below [1]:

$$\frac{n_{Na}}{n_P + n_{Si}} = \frac{\frac{c_{Na(SSA)} * m_{(SSA)} + c_{Na(SS)} * m_{(SS)} + c_{Na(d)} * m_{(d)}}{M_{Na}}}{\frac{c_P(SSA) * m_{(SSA)} + c_P(SS) * m_{(SS)}}{M_P} + \frac{c_{Si(SSA)} * m_{(SSA)} + c_{Si(SS)} * m_{(SS)}}{M_{Si}}} \quad (1)$$

where: *SSA*—sewage sludge ash; *SS*—sewage sludge; *d*—donor (NaHCO_3); *c*—molar concentration of the given component; *m*—mass of the component; and *M*—molar mass of the given component, number of moles of the component.

The amounts of *SSA*, *SS* and NaHCO_3 mixed in the individual experiments are provided in Table 2. The amounts of *SSA* and *SS* were kept constant while the amount of NaHCO_3 was calculated according to Equation (1).

In each experiment, 10 g of the prepared mixture was placed in crucibles and closed with a loose lid, to ensure non oxidative atmospheric conditions. Then, the crucibles were put in a pre-heated muffle furnace and were treated at a temperature of 1000 °C for a retention time of 30 min. After this time, the crucibles were removed from the furnace and allowed to cool under ambient conditions. The corundum lid remained on the crucible during cooling to ensure reducing conditions. The crucibles filled with the samples were weighed before and after the experiment. The thermochemically treated samples (fertilizer raw materials) were thoroughly ground using a rotary disc mill and directed towards chemical characterization, as described in Section 2.2.

2.4. Phosphorus Bioavailability

Samples of *SSA* before and after thermochemical treatment were directed towards identification of the P bioavailability. One of the criteria to evaluate P bioavailability is the determination of the P-solubility in a neutral ammonium citrate solution (P_{NAC}), mostly given as a fraction of the total P content (P_{NAC} -solubility). According to the procedure provided in [42,43], an amount of 1 g of each *SSA* sample before and after thermochemical treatment was placed in a volumetric flask (250 cm³) with addition of 100 cm³ of pre-heated (65 °C) neutral ammonium citrate solution and shaken in a heated water bath for 1 h at 65 °C. After 1 h, the volumetric flask with solution was topped up to 250 cm³ with cool milli-Q water. The obtained solution was filtered of which the first 50 cm³ of the extract were discarded. For ICP-OES analysis, 0.1 cm³ of the extract (P_{NAC}) was diluted with an acid solution (15 cm³ 65% HNO_3 to 500 cm³ milli-Q water).

3. Results

3.1. Chemical Composition of Raw SSA

The results of the chemical composition of *SSA* samples are presented in Table 3.

The *SSA* from six Polish plants of municipal sewage sludge combustion are characterized by a high content of selected nutrients. High P concentrations were determined for almost all analyzed samples, reaching 12.74% in the *SSA* from the plant in Gdansk. This highest P mass fraction determined in this study is significantly higher compared to a previous study that determined 9.59% P in *SSA* from the plant in Gdansk [44]. The P contents in ashes from Gdynia, Lodz, Kielce and Szczecin were around 11%. In the available literature, the P content in *SSA* from the facility in Lodz was lower, with 8.7%, while the P contents in other *SSA* were in a comparable range of 11.3–12.2% in the *SSA* from Gdynia [40,45], 8.29–10.80% from Kielce [45,46] and 9.93–9.77% from Szczecin [40,45]. The lowest P concentration in the analyzed samples was detected in the *SSA* coming from the plant in Cracow (6.9%). Previous research showed similar data; the ashes from Cracow had the lowest P content (7.8% to 9.98%) compared to samples taken from other installations in Poland, in the same period of time [45,47]. The results confirm that the analyzed ashes are suitable secondary raw materials, which can be used as a substitute of rock phosphates in the production of P fertilizers.

Special interest in the current study is paid to the values of the P contents but also other elements were of interest. The Si contents were comparable for all analyzed ashes. The Si mass fractions of the individual samples were equal to 8.04% (Gdynia), 8.52% (Kielce), 8.60% (Cracow), 9.25% (Szczecin), 9.94% (Gdansk) and 11.01% (Lodz). Similar results were obtained for the *SSA* from facilities located in Germany (12.1%) [43] and Switzerland (11.6%) [29]. In the available literature, the Si content in the *SSA* from the Polish mono-incinerations was not commonly marked. The fragmentary data showed

that the Si contents in the ashes coming from a small compact installation for the thermal conversion of municipal SS in Wielkopolskie Voivodship (Poland) was higher compared to the data from this study, 11.45% compared to 23.76% [48]. In previous research, the Si content varied depending on the place of collection of the SSA, reaching 17.5% for samples from Kielce; 16.4%–18.2%—Cracow; 20.8%—Szczecin; 21.6%—Gdynia; and 24.7%—Lodz [45]. It was proven that the SSA with a low Si content might be a preferred raw material for the AshDec process [29] as SiO₂ (quartz) causes undesired side reactions consuming the Na donor. As the reaction of the Na with quartz to different silicates is thermodynamically preferential over the reaction with phosphates the Na donor has to be dosed in excess [29]. The observed differences in the Si content arise from the residual sand coming from the sludge and fluidized bed [45].

The analyzed samples of the SSA are characterized by a relatively high Fe content (up to 15.23% in SSA from the plant in Cracow). The reported values of Fe in the ash from Cracow were the highest (11.34–16.8%) compared to the other Polish SSA [40,47], which might be due to simultaneous P precipitation with iron salts to complement biological P removal. There were also high Fe contents in samples from Kielce (10.14%) and Szczecin (11.6%). As a result of the transformation during combustion of the iron compounds present in the sludge, Fe appears in SSA in the form of hematite, which is poorly soluble in mineral acids. So, it ensures the immobilization of iron in the ash, and thus improves the selectivity of the extraction of the P compounds in relation to Fe [47].

The samples of SSA are also rich in Ca, Mg and S, which are secondary micronutrients [49]. The Ca content was the lowest in samples from Cracow (7.52%). The Ca content in samples from Gdansk and Szczecin was around 9.8%, and the rest of the samples were above 10%, reaching the maximum value 13.97% in the SSA from the plant in Kielce. The previous works showed similar results in most of the Polish SSA, except for samples from Cracow, in which higher Ca levels were reported, ranging from 10% to 12% [40,47]. The contents of Mg in the analyzed samples were in the range of 1.56% (SSA from plant in Cracow) to 3.07% (SSA from plant in Gdansk). Concentration of Al ranged from 2.38% in the SSA from Cracow (bio-P removal probably with simultaneous dosing of Fe-salts) to 11.31% in samples of the SSA from plant in Gdynia, which is due to the utilization of Al salts for P precipitation in the WWTP.

Considering the possibility of using waste as an alternative source of raw materials (including CRMs) in the fertilizer sector, it is important to identify the content of the contaminants indicated in the regulations authorizing fertilizers to be marketed and applied to the soil. In the investigated SSA samples, the following levels of heavy metal concentrations were detected: Pb in the range of 16 to 94 mg/kg; Cr in the range of 100 to 703 mg/kg; Ni in the range of 91 to 802 mg/kg; As in the range of 6 to 57 mg/kg; and Hg in the range of <0.05 to 0.12 mg/kg (Table 2). Comparing to the German or the Austrian Fertilizer Ordinances [50], which allow the use of SSA as fertilizers (under certain conditions), in Poland, such a practice is not possible because national legal acts forbid the application of SSA directly to the soil [51–53]. There is the possibility to direct the sewage sludge for fertilizer purposes, based on the Regulation of the Minister of the Environment on the R10 recovery process “Land treatment resulting in benefit to agriculture or ecological improvement” [52]. This regulation specifies the requirements for waste treatment on the land surface bringing benefits for agriculture or improving the environment and defines the types of waste allowed for such recovery. The ashes coming from the mono-incineration plants are not included in the list of wastes that could be used in R10 recovery process. However, SSA can be treated and then used for fertilizer purposes [54,55]. Therefore, in the current study, the samples of SSA were directed to thermochemical treatment. The results are described in the next section.

3.2. Chemical Composition of Thermochemically Treated SSA—Secondary Raw Materials for Fertilizer Production

The results of the experiments showed that the thermochemical treatment can transform SSA into valuable raw materials for fertilizer production. The obtained results are presented in Tables 4

and 5. As the content of nutrients in fertilizers is generally indicated as its respective oxides (except for nitrogen), the results of the elemental analysis of the treated ashes are also expressed as oxides. According to the Polish Regulation of the Minister of Agriculture and Rural Development regarding the implementation of certain provisions of the Act on fertilizers and fertilization [54], it is stated that solid mineral fertilizers, in which P, N or K (or their sum) is declared, the content of individual components may not be less than 2% total nitrogen, 2% phosphorus as P_2O_5 and 2% potassium as K_2O . The content of P_2O_5 in the obtained products were in the range 15.7% to 19.2%. The lowest value (analogous to raw SSA) was reported in samples from Cracow. The highest P_2O_5 content was observed in SSA from Gdynia. According to the mentioned regulation, the produced fertilizers meet the conditions for placing products on the market in the criteria of required P_2O_5 content. In the previous research, P_2O_5 content in thermochemically treated ashes was approx. 21.4% [55], 20% [50], 16% [29] and 13–18% [36]. It should be noted that even in single superphosphates (SSP) the P_2O_5 concentration may vary, depending on the manufacturing process, P concentration in the phosphate rock and other factors. According to other studies, the available P_2O_5 content values in the SSP ranged from 16% to 23% [56], while multi-nutrient fertilizers like PK and NPK fertilizers contain around 5–12% P_2O_5 [50]. Therefore, it can be concluded that the obtained recyclates have a full fertilizing value (taking into account the P_2O_5 content and the bioavailability of the phosphates), comparable to commercial fertilizers currently used in agriculture. Moreover, according to European law [16], inorganic macronutrient fertilizers intend to provide plants with at least one of the basic macronutrients, such as P, N or K, and secondary macronutrients Ca, Mg, Na or S. The obtained recyclates meet these conditions and can be classified in this fertilizer category. The contents of the oxides of these components are also shown in Table 4.

Table 4. Mass fractions of main elements (expressed as oxides) of the thermochemically treated SSA.

Parameter	Cracow	Lodz	Gdansk	Gdynia	Szczecin	Kielce
	%					
P_2O_5	15.7	17.0	18.0	19.2	18.4	16.5
CaO	10.8	11.4	10.7	13.9	12.0	14.2
K_2O	1.1	1.1	1.3	1.1	1.1	0.9
MgO	2.6	3.1	3.6	3.4	3.2	2.8
Na_2O	3.5	4.6	5.4	4.5	3.5	4.5
SiO_2	15.2	21.5	23.7	19.6	21.0	19.5
Al_2O_3	5.0	5.4	7.3	6.1	4.6	4.5
Fe_2O_3	21.1	7.4	7.0	7.8	13.5	10.5
CaO/ P_2O_5	0.69	0.67	0.6	0.72	0.65	0.87

There was significant growth in the content of Na due to the dosing of $NaHCO_3$ as an additive for thermochemical treatment of the SSA. In the raw SSA, the Na_2O mass fraction was approx. 0.1%, while in the fertilizer products it was equal to 3.5% in the samples from Cracow and Szczecin, in the range of 4.5–4.6% in samples from Lodz, Gdynia and Kielce, and 5.4% in samples from Gdansk. The concentration of CaO was in the range of 10.8% in products based on the SSA from Cracow to 14.2% in products from Kielce. Similar results (14%) were found for ashes from Switzerland [29]. The share of K_2O was around 1% in the obtained recyclates, while the content of MgO was in the range of 2.6–3.6%. For those components, comparable results were obtained in previous studies [57]. The concentrations of iron vary depending on the origin of the SSA samples. Thus, the highest concentration of Fe_2O_3 was recorded in recyclates from Cracow (21.1%), while the lowest in products from Lodz (7.4%), Gdansk (7.0%) and Gdynia (7.8%). The recyclates contain 15.2–23.7% of SiO_2 . Those high Si contents were also reported in works [29,57]. The aluminum content, expressed as Al_2O_3 , was approx. 4.5–7.3%.

Table 5. Content of heavy metals in the thermochemically treated SSA compared with the heavy metal limiting values that apply to mineral fertilizers.

Element	SSA Sample						Maximum Levels	
	Cracow	Lodz	Gdansk	Gdynia	Szczecin	Kielce	Polish Fertilizer Regulation [54]	EU Fertilizer Regulation [49]—Mineral Fertilizer
mg/kg Dry Matter of Sample								
Pb	73.1	29.6	32.8	19.4	10.2	43.3	140	120
As	22.7	8.8	4.8	5.5	10.0	5.8	50	40
Cd	2.8	0.9	1.1	1.0	1.7	1.4	50	60 mg/kg of P ₂ O ₅ ⁽¹⁾
Hg	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	2.0	1.0
Ni	180.4	491.4	235.5	57.7	59.5	48.9	ns.	100
Cu	49.6	35.5	31.3	42.1	35.0	32.8	ns.	ns.
Zn	4459.9	2483.2	2115.3	2357.7	1072.8	2461.0	ns.	ns.
Cr	547.4	497.5	113.5	103.4	99.0	130.9	ns.	ns.
Mn	1112.6	558.8	593.4	707.2	548.1	924.3	ns.	ns.
Co	39.5	935.8	439.1	39.0	41.5	27.6	ns.	ns.

ns.—not standardized. ⁽¹⁾ In case the total phosphorus content in the inorganic macronutrient fertilizer is equal to or greater than 5%, calculated as phosphorus pentoxide (P₂O₅) (“phosphoric fertilizer”).

The Polish Regulation [54] specifies the permissible values of contaminations in mineral fertilizers. The regulation provides limited values for four elements—arsenic (50 mg/kg d.w.), cadmium (50 mg/kg d.w.), lead (140 mg/kg d.w. of fertilizer) and mercury (2 mg/kg d.w.). As it can be seen from Table 4, the produced fertilizer meet the polish norms for all indicated trace elements covered by the regulation. The content of lead was in the range of 10.2 to 73.1 mg/kg d.w.; arsenic—from 4.8 to 22.7 mg/kg d.w.; cadmium—from 0.9 to 2.8 mg/kg d.w.; and mercury below <0.05 mg/kg d.w. As all produced materials meet the Polish limited values for the trace elements, these materials could potentially be used as raw materials in fertilizer manufacturing.

The obtained raw materials for fertilizer production were also analyzed in order to compare their compliance with EU regulations. In 2019, the EC has published the new EU fertilizer regulation laying down provisions on the making available on the market of EU fertilizer products [49]. This regulation indicates that there is a demand on the market for the use of certain recovered waste as fertilizer products within the meaning of Directive 2008/98/EC as ash-based products. It is pointed out that the inorganic macronutrient fertilizers are to be produced for supplying plants with at least one of primary macronutrients (N, P and K) and secondary macronutrients (Ca, Mg, Na or S). Certain requirements for the waste used as input in the recovery process, requirements for the processing processes and techniques as well as the requirements for the fertilizer products obtained in the recovery process, to ensure that the use of these fertilizer products does not lead to overall adverse environmental or human health effects, must be defined. For EU fertilizing products, these requirements are laid down in this Regulation. The limit values of the selected heavy metals are presented in Table 5.

The obtained products meet the requirements for contents of lead (<120 mg/kg d.w.), arsenic (<40 mg/kg d.w.) and cadmium (<3.0 mg/kg d.w.). The content of Ni was exceeded in samples from Cracow, Lodz and Gdansk. For the rest of the samples, the Ni values were below the limit (100.0 mg/kg d.w.). The contents of Hg were below the limited value, which is 1.0 mg/kg d.w. in the EU fertilizer regulation. In previous research, the thermochemical treatment allowed for separation of Hg bound to carbon material. Moreover, even after treatment at temperatures of 1000 °C, inorganic Hg compounds remained in the SSA [58]. It should be pointed out that, according to the Polish regulation, the content of Hg was not exceeded, while the content of Ni is not limited.

3.3. Phosphorus Bioavailability

Bioavailable P is defined as the sum of the immediately available forms of P. The possible use of waste and waste-based products in the fertilizer sector has to be supported by the sufficient amount of nutrients that will be available to plants. Therefore, an assessment of P bioavailability should be conducted to correctly identify the fertilizing values of a given material [59]. In the current research, both the SSA and recyclates were examined to determine the P bioavailability. The results of the P bioavailability of the SSA produced in selected mono-incineration facilities and the respective fertilizer raw materials after thermochemical treatment are presented in Figure 2. The P-solubility in ammonium citrate of the untreated SSA was in the range 19.7% to 45.7%. The individual values reached 19.7% in SSA from Kielce; 26%—Gdynia; 32.3%—Szczecin; 35.9%—Lodz; 42.4%—Cracow; and 45.7%—Gdansk. These results indicate that the P in the untreated SSA is at least partially bioavailable. In German studies, the average values of the P bioavailability of raw SSA were 31.2% [42] and 35% [60]. It has to be pointed that these values are not sufficient for fertilizers, which ideally exhibit complete solubility of P in neutral ammonium citrate solutions [42]. The main P-bearing phosphate phase in SSA is poorly soluble tricalcium phosphates [29]. Therefore, a treatment to enhance the bioavailability of P in SSA is strongly recommended to obtain fully applicable products [61]. Previous research showed a high efficiency of the thermochemical process in increasing the P bioavailability of the SSA, reaching 82% [62] and 97% [50]. In the current study, the process of thermochemical treatment allowed to increase the values of the P bioavailability of the fertilizer products, reaching 76.5% for samples from Gdynia; 83.7%—Szczecin; 94%—Kielce; 98.3%—Cracow; 99.6%—Lodz; and 101%—Gdansk. These results are indicated in Figure 2. The obtained fertilizer products contain P forms (CaNaPO_4 —buchwaldite) that are highly available for plants [29], which confirms the further possibility of the usage of thermochemical treatment in the production of secondary mineral P fertilizers. The reason for the relatively low P_{NAC} solubilities in the cases of Gdynia and Szczecin are not clear yet. It should be further investigated if the P-bioavailability of these two plants could be increased towards 100%, e.g., by higher Na-additive dosing.

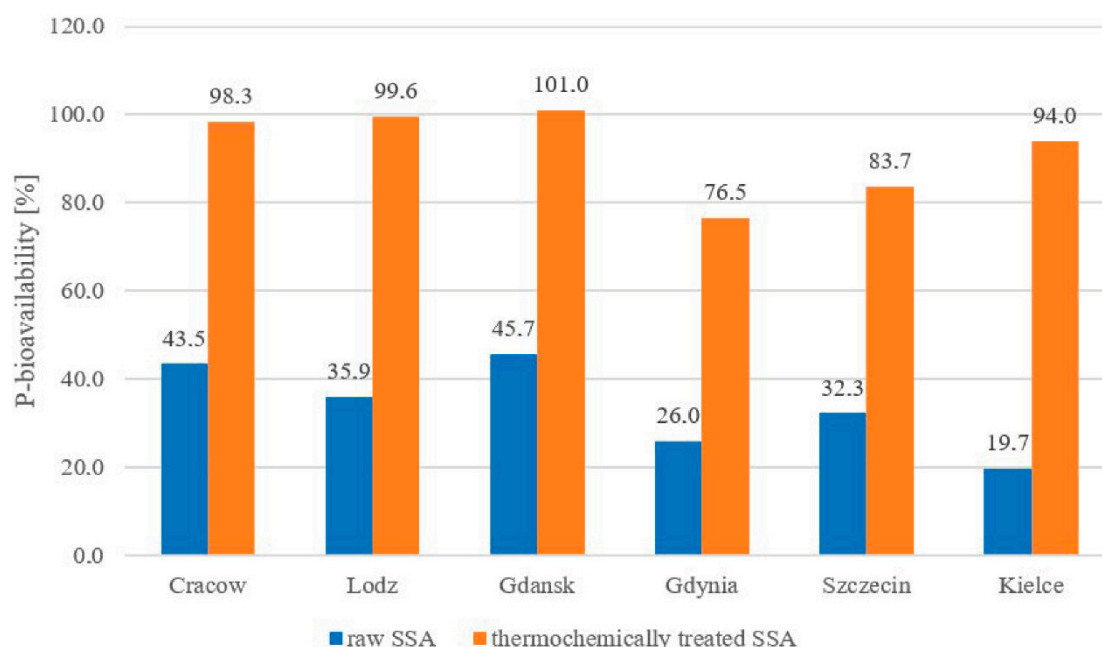


Figure 2. Phosphorus bioavailability (stated as solubility in neutral ammonium citrate P_{NAC}) of the SSA generated in selected Polish mono-incineration plants—before and after thermochemical treatment.

4. SSA for Fertilizing Purposes in Poland

Nowadays, the fertilizer industry, which is one of the key branches of the chemical industry in Poland, is facing challenges in the implementation of the circular economy (CE), which is indicated as a priority of the EU's economic policy [15]. The CE assumes more rational practices in the production of fertilizers from primary sources, but also more sustainable methods and stimulation of the production of fertilizers from secondary sources [14]. To maintain the current position of the fertilizer sector and ensure its continuous development, it is recommended to intensify activities aimed at the production of fertilizers from secondary materials [16], including waste produced in various branches of industry. The current research showed that one of the possibilities of the CE implementation in the fertilizer sector is the management of waste generated in municipal WWTPs as a source of P in the fertilizer products. This gives the opportunity to reduce the demand for the import of the P raw materials and raise the security of P resources in the country.

In the recent years, the Polish government initiated the necessity of nutrients recovery in official documents related to the circular economy [63], waste management [64], municipal sewage sludge [65] and fertilizers [66]. The recovery of resources from waste substances is the basis of the bioeconomy, which is one of the key areas for implementing CE in Poland indicated in the national roadmap towards CE [67]. The further development of the bioeconomy could contribute to the reduction in pressure on the natural environment, including by reducing the demand for non-renewable resources, such as P. Sustainable and circular nutrient management is recommended in the National Waste Management Plan (NWMP), which is a part of the strategy papers adopted at the European and national levels [68]. It underlines the importance of P recovery from waste as municipal sewage sludge, and the products of its treatment. In the context of P recovery from SSA, it emphasizes that ashes have to be collected selectively to be able to use different P recovery methods, now or in the future. The storage of ashes in a way that enables phosphorus recovery is strongly recommended. The importance of P recovery from waste generated in municipal WWTPs was mentioned in the assumptions [69] for the strategy for treatment of municipal sewage sludge [65]. It pointed out the need for an estimation of SSA mass flow generated in domestic mono-incineration plants, selection of the location of P recovery installation and selection of the most effective technology in terms of technical, financial and economic factors. Detailed analysis of the mass streams of waste generated in Polish mono-incineration plants for municipal sewage sludge was a part of the current project "Towards circular economy in wastewater sector. Knowledge transfer and identification of the recovery potential for phosphorus in Poland" (CEPhosPOL), founded by the National Exchange Agency Academic (NAWA). There is a clear increasing trend in the amount of SSA generated in mono-incineration of municipal sewage sludge in recent years, from 10,023 Mg in 2011 to 26,756 Mg in 2018, which also affects the growth in the amount of potential secondary raw material for the production of mineral fertilizers based on SSA in Poland [41,70]. The analysis concerned the largest 9 of 11 mono-incineration plants for municipal sewage sludge, in Warsaw, Cracow, Lodz, Gdansk, Gdynia, Olsztyn, Bydgoszcz, Szczecin and Kielce, without Lomza and Zielona Gora. The theoretical P recovery potential from the SSA was estimated for samples taken from plants in Cracow, Lodz, Gdansk, Gdynia, Szczecin and Kielce, and it was equal to 1613.8 Mg per year, of which 33.9% was bioavailable [70]. The P recovery potential from the small WWTPs cannot be estimated because the incineration of sewage sludge is not currently used on a large scale in smaller facilities. However, in the context of the lack of the possibility of storing waste with a combustion heat above 6 MJ/kg DM, small WWTPs are looking for and testing various methods of sludge management. From the point of view of the possibility of P recovery the products of thermal sludge treatment, such as pyrolysis, gasification and plasma processing, it is a future-proof solution for such facilities. Considering investments in installations for the thermal treatment of municipal sewage sludge, it is necessary to take into account environmental, technological, social and economic aspects. To date, the analyzed method of SSA treatment has been implemented in a large-scale pilot plant in Leoben (Austria) in 2009, and in Weimar (Germany) in 2014. Currently, the BAM conducts the further process optimizations at the technical scale in their

labs in Berlin (Germany). Moreover, a full-scale installation is planned to be constructed in Southern Germany in the coming years. The most important barrier in the technology implementation is the economic efficiency. The operator of the installation must take into account not only the investment, but also the maintenance and service costs that are often higher than the revenues from the sale of the recyclates obtained. So far, the recyclates are only exceptionally sold and usually they are distributed for free or at more or less just symbolic prices. Therefore, such technologies' implementation should have law-enforced P recovery, as it was already implemented in Switzerland and Germany [33].

The rational management of wastes produced in the water and wastewater sector is an important topic of interest of the Environment Committee at the Polish Senate, which in recent years has presented several of its opinions on the circular management of municipal sewage sludge [4]. In 2016, an opinion on the innovative use of wastewater as a source of energy and resources underlined the importance of further development of research on the P recovery from waste generated in WWTPs. In 2017, the Environment Committee also emphasized inclusion of the sewage sludge management in the area of nutrients (phosphorus and nitrogen) and energy recovery from sludges in the works aimed at the implementation of the CE in Poland. Moreover, the recirculation of nutrients (especially P) from sewage sludge to use their valuable properties and energy potential is recommended in an opinion regarding the position of the Helsinki Commission on sewage sludge (so-called HELCOM recommendations). Finally, in 2018, an opinion on the management of by-products of combustion from the energy sector promotes the use of materials from energy facilities (as mono-incineration plants) as a replacement of natural resources, reducing the need for their extraction and related emissions processes. It is also emphasized that the use of wastes generated in combustion processes is an important and justified step in striving to reduce the emissions of the economy and implement the CE principles.

As it was mentioned before, despite the good fertilizer properties, according to the Polish restrictions the raw SSA is waste [53] that cannot be directly used in agriculture [52]. It is also underlined that fertilizers (granulated) obtained from ashes from biomass combustion and municipal sewage sludge have not been used for agriculture in the country so far, and they should be considered as substances "unknown in fertilization". Therefore, the potential direct use of SSA as a fertilizer is not currently considered. It is also indicated that the chemical composition of the SSA needs to be investigated and monitored, because it is a variable material that contains significant amounts of P but also heavy metals and other contaminants (depending on the source of the sludge). Further studies are needed in this field to specify the instructions for its use and determining the size of the doses. Therefore, for now, the uncontrolled introduction to soils of granulated fertilizers obtained from SSA is prohibited. It is recommended to produce fertilizers in the processes of P extraction from SSA due to the obtained mineral fertilizers that may be placed on the market, according to the legal restrictions [51].

Taking into account the recommendations of the Polish government, in previous studies, an analysis of chemical P extraction by leaching with mineral acid and neutralization was conducted. The recyclates (extracts) obtained from leaching of SSA with phosphoric acid were valuable products, which may be utilized in the production of commercial fertilizers. Moreover, it was confirmed that the SSA composition did not change significantly during the year. Therefore, it is possible to produce recyclates with a nearly constant elemental content for a long time [45]. In turn, in the current study, the thermochemical transformation process was evaluated for the ashes coming from Polish installations for municipal sewage sludge combustion. The obtained results showed that the fertilizers produced based on the Polish SSA in the process of thermochemical transformation are stable, with a high content of P and a low content of heavy metals, making these products potentially possible for further agricultural use. The final selection of P recovery technology for a specific facility is a very complex task where all the elements of sustainability—economic, environmental and social—have to be considered. Based on the available analyses, the SSA as the input for P recovery is the preferable solution in terms of the independence of sludge incineration plants, their recovery efficiency [18] and the location of the WWTP [71].

5. Conclusions

Wastes generated in municipal WWTPs are valuable sources of P that can be successfully used as substitutes for the production of mineral fertilizers. Special attention should be paid to ashes generated in Polish facilities, due to the dynamic increase in their quantity, which is the result of an increase in the amount of municipal sludge sent to the combustion processes in these facilities. Although SSA may contain significant amounts of fertilizer raw materials, such as phosphorus, calcium or potassium, the bioavailability of these compounds for plants may be limited. Moreover, SSA contains significant amounts of heavy metals, which limits the possibility of their use for the production of granulated fertilizers. In order to increase the availability of nutrients for plants and reduce the amount of pollutants, ashes should be directed to nutrient recovery processes. As a result of chemical and thermochemical transformation, it is possible to obtain recyclates that meet the requirements for mineral fertilizers. Further research aimed at the development of P recovery technology, as well as an assessment of the digestibility of the nutrients and the impact of fertilizers from ashes on soil properties and plant yield in Polish conditions, is recommended in national strategic documents.

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