Sustainable use of sewage sludge ash in fertilisers production-PolFerAsh technology

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Abstract

The main raw materials having industrial importance in phosphorus compounds manufacture are phosphorite and apatite. Mineral raw materials are non-renewable sources of this element, and their resources are limited and gradually depleted. Sewage sludge – waste containing phosphorus compounds concentrated at cellular matter or in the form of insoluble phosphates, after thermal processing could be potentially used as a source of concentrated phosphorus and as a substitute for natural ore. In this paper phosphorus recovery technology from Polish industrial Sewage Sludge Ashes was investigated (PolFerAsh – Polish Fertilizers form Ash). Research was conducted on ashes from eight thermal treatment stations located in Poland. Experiments of phosphorus recovery from SSA with mineral acid were carried out to obtain monoammonium phosphate (MAP). The mass balances of the conducted processes, the composition of the obtained extracts and remaining sediments allowed to nominate ashes for further recovery of phosphorus and mineral fertilizers production. Phosphorus leaching experiments were carried out in the laboratory and technical scale to obtain repeatability of the process. The obtained extracts were neutralized with the use of ammonium compounds to produce fertilizers containing primary (N, P) and secondary (Ca and Mg) nutrients with the addition of micronutrients (Fe, Zn, and Cu). The obtained products were characterized by high purity and phosphorus availability compatible with the EU standards.

Keywords

sewage sludge ash, phosphorus recovery, PolFerAsh, fertilizers, leaching, phosphorus extraction, mineral acids, circular economy, sustainable development, alternative raw materials, phosphorus industry, secondary raw materials, MAP, monoammonium phosphate.

1. Introduction

The Critical minerals are the raw materials with a risk of interruption of the supply liquidity, limited resources with no possibility to introduce their replacements. In May 2014 the European Commission published an updated list of critical raw materials, which are crucial for the global economy. Among six new materials attached to the list from 2011, there were phosphorus ores [1]. This step provides increasing awareness among policy makers, who began to see the role of phosphorus as an element conditioning existence of life. On the other hand the problem of intensive unsustainable exploitation of phosphorus ores and impossibility of closing phosphorus cycle was highlighted [2-4].

The demand for food production is directly proportional to the population growth and need efficient agriculture, seeking to obtain the maximum yield per unit of arable land. Demand for fertilizers continues to grow, and presumably their production will be increased for about another century. Thus, intensifying concerns about the depletion of non-renewable phosphorus deposits, which is the only industrial raw material, and growing interest in the possibility of phosphorus recovery from alternative sources [5,6,3,7-9].

The search for alternatives for phosphorus raw materials is therefore justified not only because of the principle of sustainable development or circular economy, but mostly for safety reasons due to rapidly changing geopolitical situation in the world. About 75% of world reserves of phosphorus deposits is located in Morocco, while Europe is strongly dependent on imported raw materials and the prices dictated by the world's leading mining industry [9-11].

Circular economy (CE) is sustainable development strategy characterized in closed loop flows of materials in production, distribution and consumption created for a better balance between environment and society [12-14]. Nowadays China is pioneering in realization of CE concept by “promotion law” and detail governmental plans for economic development, which allows to control materials inputs and environment pollution on national level [15]. The concept of CE was also presented in European communication “Towards a circular economy: A zero waste programme for Europe” in 2014. In line with CE model the value of products should be maintained as long as possible, it offers possibility to reduce costs and dependence on natural resources, stimulates economic growth and eliminates waste and harmful effects on environment [16]. In December 2015 the European Commission adopted a package for the economy in the closed cycle, which covers the entire product life cycle, waste management and recyclable materials. One of the activities towards implementation of such a model is a proposal to amend the Regulation on fertilizers, especially organic and derived from waste, because so far these products could not compete with conventional fertilizers produced from raw materials [17,18].

Also, the analysis of the phosphorus flows shows that the largest losses bring the waste streams. The development of methods for the recovery of phosphorus from waste is therefore a key measure aimed at improving the balance of phosphorus, both globally and locally [19].

The promising alternative sources of phosphorus are by-products of wastewater treatment like sewage sludge and ashes after its combustion, as well as sewage side-streams. Many European countries develop technology in this area, with an emphasis on local solutions [20-25]. Sewage sludge ash seems to be promising alternative as phosphorus source with maximum efficiency of phosphorus recovery between 80-90% [26-28]. During the thermal conversion phosphorus concentration in mineral fraction takes place and its content in ashes is more favourable (7-11% P) and can be compared with poorer natural ore [23,29,30].

2. Phosphorus recovery methods– PolFerAsh technology

Numerous technologies have been developed to recover phosphorus from waste water, sewage sludge, sewage sludge ash (Figure 1), or other wastes (bones, meat-bone meal) to close broken phosphorus cycle [27,31,32,28,33,34].

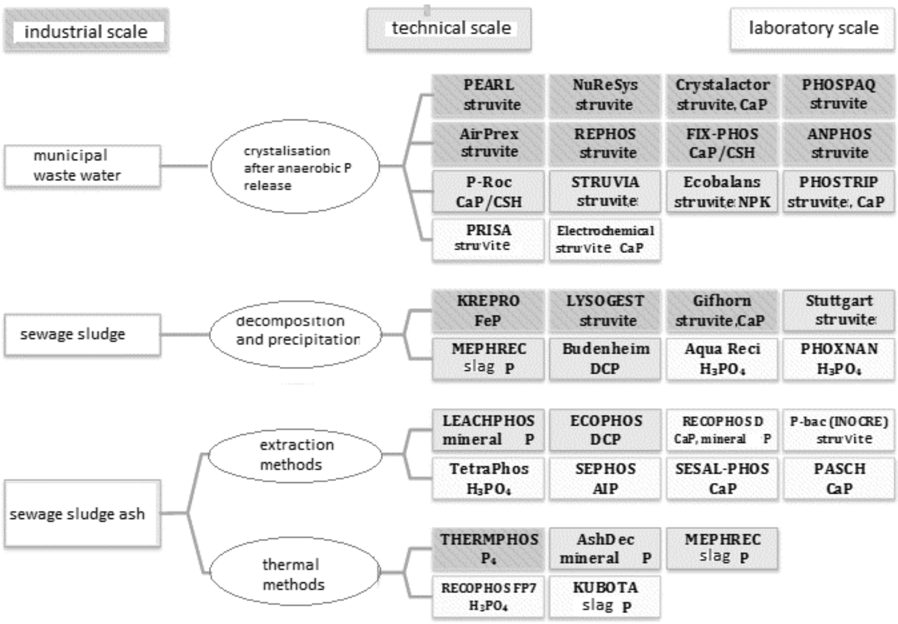


Fig. 1. Methods of phosphorus recovery [35].

Basically, two ways of dealing with ash from incineration of sewage sludge may be distinguished: wet chemical extraction methods and thermochemical methods.

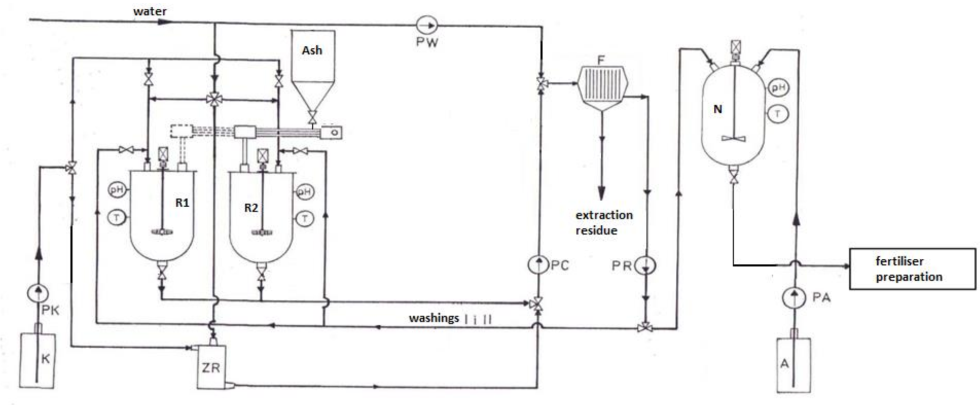
Thermochemical methods, which include the process of phosphorus production in an electric furnace and ash calcination with a chlorine donor, require a low content of iron in ash. Hence, the solutions suggested in the literature in the case of Polish ashes will have a limited application. In the thermochemical method, which consists in ash calcination with a chlorine donor, heavy metals constituting volatile forms are removed, however iron and aluminium compounds still remain in the solid phase. The process is energy-consuming since ash requires additional heating to a temperature of approximately 1000°C. Moreover, it is necessary to implement a system of treatment of waste gases that contain volatile chlorides of heavy metals. The content of available phosphates in obtained products at the level of 82% means that approximately 18% of phosphorus contained in fertilizer still remains in the form unavailable for plants.

The main idea behind extraction methods is carrying out the extraction of ash with the application of solutions of acids, alkalis or their sequence, or water in its supercritical state, as leaching agent [36-39,26,40,29]. The most frequently encountered solution is the extraction of ash with the application of the following acid solutions: H_2SO_4, HCl, HNO_3, H_3PO_4 with pH below 2 (table 1). The extraction of ash with the application of hydrochloric acid and sulphuric acid is connected with generating additional waste in the form of calcium chloride or phosphogypsum (apart from the remains left after ash extraction). Moreover, calcium, which is a secondary component in fertilizers, is lost together with the waste. Therefore, it was confirmed that the application of leaching ash with nitric acid and phosphoric acid, still remains the most favorable solution for the reason of producing extracts rich in nitrogen and phosphorus compounds, without generating additional waste. *Tetra-Phos (Remondis)* [41], *Leachphos* BSH Umweltservice [42], *Ecophos® or SESAL-Phos* were scaled up and are available at pilot or industrial scale [26,28].

Table 1. Selection of the extraction agents used in the SSA leaching

Extraction agents	Conducted research
Acids	
H_2SO_4	(Donatello et al. 2010)[38],(Franz 2008)[43] , (Tan & Lagerkvist 2011)[32], (Biswas et al. 2009)[36], (Montag 2007)[44]
HCl	(Donatello et al. 2010)[38],(Franz 2008)[43] , (Tan & Lagerkvist 2011)[32], (Biswas et al. 2009)[36], (Montag 2007)[44], (Schaum et al. 2007)[45]
HNO_3	(Gorazda et al.)[29,46] (Tetra-Phos Remondis n.d.) (Montag 2007)[44]
H_3PO_4	(Gorazda et al.)[29,46,30] (Tetra-Phos Remondis n.d.), (Montag 2007)[44]
$C_2H_2O_4$	(Biswas et al. 2009)[36] (Atienza-Martínez et al. 2014)[47]
$C_6H_8O_7$	(Biswas et al. 2009)[36]
Base	
NaOH	(Stark et al. 2006)[48] , (Biswas et al. 2009)[36], (Montag 2007)[44]
Combination of acid and base	
	(Stark et al. 2006)[48] , (Schaum et al. 2007) [55], (Levlin & Hultman 2012) [61]
Bioextraction and others	
Acidithiobacillus Ferrooxidans	(Tan & Lagerkvist 2011) [52]
Extraction of ashes after *SCWO – supercritical water oxidation*	(Stark et al. 2006) [46]

In the investigated PolFerAsh technology (Polish Fertilizers from Ash), sewage sludge ash is leached with the use of phosphoric and nitric acid or its mixture to dissolve phosphorus compounds from SSA and achieve high phosphorus recovery rate (ca. 70-99%), without additional purification of leachates. Such agents were proposed because of a high phosphorus concentration and no additional by-product in the form of $CaSO_4$ or $CaCl_2$ formed during the extraction with sulfuric or hydrochloric acid [46,49,39,30]. In the second stage after filtration, extracts are neutralized with the use of hydrated CaO or ammonia to produce solid fertilizers in the form of calcium phosphates, ammonium phosphates or mixture of both [50,51]. The process is illustrated in figure 2.



PK – acid pump, PA – alcali pump, PC – filter pump, PR – solution pump, PW – water pump, R1,2 – phosphorus extraction reactors, N – neutralisator, ZR – diluted acids tank, K – concentrated acid tank, A – neutralising agent tank, F – filtration, pH – pehameter, T – termometer

Fig. 2. PolFerAsh technology for phosphorus recovery

The same acids or its combination is used in process RecoPhos and Tetra-Phos [27]. However, due to the lack of a decontamination step, RecoPhos process can be apply for high quality ash with low heavy metal content, therefore excluding Polish sewage sludge ash. In Tetra-Phos process diluted phosphoric acid, nitric acid or its mixture (70%H_2O,15%HNO_3 and 15%H_3PO_4) is used to produce RePacid® - phosphoric acid, gypsum as well as iron and aluminium salts. Newertheles calcium removal at the first stage with gypsum and calcium addition at the third one, as well as aluminium compounds utilization as they are produced in the form unsuitable for sewage treatment plants or gypsum generation are the main disadvantages of this process [41].

However, a new issue appeared, i.e. the verification of extraction process parameters depending on the characteristics of ash and additional components introduced together with phosphorus, both in fertilizers and as interfering agents, which are standardized later in obtained products. In order to achieve that goal, it was necessary to obtain the complete physicochemical characteristics of residues generated in sewage sludge combustion installations.

This paper examines the phosphorus recovery in the form of monoammonium phosphates (MAP) from SSA using wet chemical treatment with phosphoric acid and neutralization. To find out the Polish perspective for using proposed technology, ashes obtained through combustion of municipal sewage sludge in fluidized bed (6 installations) and a grate furnace (1 installation) were examined. Monoincinerators are of a local character; they are situated in Gdynia, Gdańsk, Łódź, Kielce, Bydgoszcz, Kraków, Warszawa, Szczecin, Łomża, Olsztyn, Zielona Góra and utilize sludge generated directly in a given sewage treatment plant or in the immediate vicinity. Research was focused on influence of parameters of sewage sludge ash on the efficiency of phosphorus recovery. Ashes with the best characteristic were introduced to extraction and precipitation process in the semi-technical scale. NP fertilizers were produced from the obtained leachates and their characteristics were compared with the limits given in the Polish and EU regulations.

3. Material characteristics and experimental procedures

3.1. Identification methods

The chemical composition of SSA and fertilizers, as well as the composition of the extracts were determined with the use of Atomic Absorption Spectroscopy (AAnalyst 300 Perkin Elmer) and ICP-OES (Plasm 40 Perkin Elmer) after digestion in H_2SO_4 or microwave-assisted digestion (Magnum II Ertec) in HNO_3 (30 min, 480W) in the case of Ca and Pb determination.

The phosphorus content of the SSA and the extracts was determined with the use of a spectrophotometric method according to the polish standard PN-85/C-84092 for phosphorus raw materials, while total and soluble phosphorus in fertilizers were determined according to the fertilizers standards WE 2003/2003.

The phase composition of the SSA was determined with the use of XRD Analysis using X'Pert Pro MD PANalytical.

Nitrogen analysis were carried out according to the fertilizers standards WE 2003/2003 (distillation with steam).

3.2. Phosphorus extraction method and MAP production

The extraction process was conducted in a closed-vessel reactor under continuous pH and temperature control. The leaching agent was phosphoric acid at a concentration of ca. 2.7 M. The amounts of the ash and acid were calculated on the basis of previous research according to the phosphorus content in the ash as follows: for each gram of phosphate ions present in the ash 11.8 g of acid solution were used [46,39]. The neutralization of the obtained extracts was carried out with 25% ammonia solution (experiments 1-5) or gaseous ammonia (experiment 6 and 7) at a pH range of 5-7. After the extraction and precipitation, samples of both the solution and the sediment were analyzed for Fe, P, Al, Mg, Ca, Zn, Pb, Cu, Ni, Cr, Cd, and Co. The fertilizers products were dried and analyzed according to the EU decree WE 2003/2003.

4. Results and discussion

4.1. Influence of physicochemical characteristics of Polish SSA on extraction processes

Analyses were conducted for representative industial ash obtained from working stations of thermal utilization of sewage sludge in: Kraków, Kielce, Łódź, Warszawa, Szczecin, Bydgoszcz and Gdynia. Results of the analyses together with the information obtained from technological installations demonstrated high variation of the composition and structure of particular ash depending on a conducted process of sewage treatment, thermal utilization and exhaust treatment.

The analyzed ashes were characterized by bulk density within the range of 0.64-1.2 kg/dm^3, specific surface area within the range of 1.7-12.8 m^2/g, low humidity content of less than 1.5% and alkaline pH of the water extract at 1%. The identification of ash components, both qualitative (XRF) and quantitative (F-AAS, ICP-OES) demonstrated the presence of SiO_2 (30-55%), P (3.5-12.2%), Ca (9.9-20.7%), Mg (1.4-2.8%), K (0.19-1.4%), Al (1.1-8.7%), Fe (2.0-11.3%) as well as Cu, Zn, Na, Cr, As, B, Ba, Cd, Co, Hg, Li, Mo, Ni, Pb, Sb, Sn, Sr, Ti, V, W or Zr. Among the main components analyzed, the highest variation determined with the help of the coefficient of variation (CV) was demonstrated by Al (70%) and Fe (40.8%), which results from varying applications in treatment plants of coagulants in the form of Al and/or Fe salts for the processes of phosphorus chemical precipitation as well as enhancement of sludge sedimentation through a reduction in the development of filamentous microorganisms in activated sludge.

The identified elements are present in ash in different crystalline configurations. Phosphorus compounds were identified mainly as calcium-iron phosphates, calcium-magnesium phosphates or iron phosphates. Iron is present as iron phosphate and hematite as well as in mixed configurations in the form of calcium-iron phosphates. Ca forms configurations in the form of calcium phosphates, aluminium-calcium phosphates or calcium-magnesium phosphates. In the case of ash from Bydgoszcz it is also present as anhydrite and in the forms of CaO and $Ca(OH)_2$ – it is identified in the dust fraction, which is related to the treatment of exhaust gases through addition of limestone to the fluidized-bed furnace. Al is present in phosphate configurations with calcium and as $AlPO_4$. Phases which were identified in all the ashes were $Ca_9Fe(PO_4)_7$ and SiO_2. SEM micrographs point to differences in the surface morphology between ashes [30,29]. The surface of ash constitutes a system composed of crystallites of different sizes and composition. Single spheres of aluminosilicates (fine fraction of Szczecin ash, Warszawa ash) as well as tiny crystals of calcium-iron phosphates can be noticed. In the case of ashes from Szczecin and Bydgoszcz in the form of slag, large clusters in the form of glaze with tiny crystallite inclusions were identified, which correlates with the studies into specific surface area, which in the case of these ashes was the lowest and amounted to 1.8m^2/g.

On the basis of the conducted characteristics it was concluded that ash resulting from the incineration of sewage sludge constitutes a source of phosphorus compounds comparable to phosphate rocks, however it contains higher amounts of Al, Fe, Cd, As, Cr, Hg, Pb, Co, Zn and Cu. Taking into account further utilization, one should be prepared for the necessity of minimizing the contents of standardized elements in final products, i.e. Cd, As, Hg, Pb, whereas Fe, Cu, Zn, Mn or B should be treated as beneficial microelements in fertilizer products. Ash in the form of slag (Szczecin, Bydgoszcz) and ash from Bydgoszcz containing the highest amount of calcium compounds will demonstrate the lowest potential for the recovery of phosphorus compounds. The lowest content of phosphorus compounds (3.49% P) as well as the smallest specific surface area disqualify the ash from Bydgoszcz in the form of slag from further applications in the extraction process.

A high content of Al in ash reduces the utilization of ash in extraction processes of phosphorus recovery. The mass ratio of Al/P in ash applied as feedstock not higher than 0.7 was accepted as the limit value. Ash from Warszawa, originating from the incineration of sewage sludge obtained from Warszawa-Południe and Warszawa-Czajka treatment plants, where simultaneous treatment of sewage with biological and chemical methods with the use of iron and aluminium coagulants in largest amounts is applied, is characterized by the mass ratio of Al/P equal to 0.97 and the Al content at the level of 7.14%. It cannot be used as an alternative phosphorus raw material in the suggested extraction methods since the resulting extracts transform into a gel form, which renders further stages of processing impossible. A high content of aluminium in Warszawa ash contributes to an increased concentration of Al in the liquid phase, which is followed by the precipitation of $AlPO_4$ and $Al(OH)_3$ (the final pH value of the reaction system amounts to approximately 2, and at this value the precipitation of both these compounds is possible). Aluminium hydroxide or other aluminium compounds present in the solution lead to the formation of a gel structure of the extract. This assumption is confirmed by relatively low aluminium content in the extract, which equals approximately 0.6 g/l. The extracts underwent solidification after a few days of storage. Moreover, a low degree of leaching phosphorus, operational difficulties with the division of phases after the extraction process as well as the precipitation and loss of the phosphorus compounds introduced into the system in the case of extraction with the acid H_3PO_4 disqualify Warszawa ash as a material suitable to undergo the analyzed extraction procedures. The utilization of ash from the largest Polish station of thermal utilization of sewage sludge would be possible after abandoning the use of the aluminium coagulant for the chemical precipitation of phosphorus, which would considerably increase the amount of ash that could be processed.

Too high content of Ca reduces the use of ash in the extraction processes of phosphorus recovery, which was demonstrated in the publication[29]. The mass ratio of Ca/P in ash applied as feedstock, which is not higher than 1.4, was accepted as the limit value. The ash from Bydgoszcz has the highest concentration of Ca (20.71%), which results from adding calcium compounds to the treatment process of flue gases, in the form of limestone (fluidized-bed furnace), milk of lime (semi-dry reactor) as well as lime (dry reactor). This results in a considerable change of the extraction process conditions: an increase in the temperature of the system to 60.3°C, the pH of the initial stage of extraction (pH=4) and of the final stage of extraction (pH up to 8). The process yield reaches slightly more than 1%, hence it may be concluded that extraction is inefficient with the applied procedure, so the ash from Bydgoszcz was excluded as an independent raw material.

The application of a grate furnace for the incineration of sewage sludge reduces the utilization of ash in extraction processes of phosphorus recovery. This issue was analyzed for ash Szczecin slag, where satisfactory extraction yields (62% H_3PO_4) were not achieved. Parameters of the extraction of ash from Szczecin obtained in a grate furnace were compared with the parameters of ash from Kielce, which was obtained with the use of the technology of a fluidized-bed furnace. It was proved that the temperature of the combustion process and the retention time in the furnace play a crucial role in the later character of the obtained ash. The main reasons for low degrees of leaching are a different microstructure, in particular a small specific surface area of ash in the form of slag (1.7 m^2/g) as well as the smallest total volume of pores, which significantly changes the kinetics of the extraction process. Moreover, preparation of the material for extraction requires an initial process of fragmentation, thus imposing additional energy expenditure. Szczecin fine fraction, however, is characterized by better parameters (the degree of phosphorus leaching amounted to 80% for nitric acid and 71% for phosphoric acid); nevertheless, it constitutes only a small part of the whole material obtained from the grate furnace.

It was confirmed that differences in the composition of ashes obtained at different periods of sewage treatment plant operation remain without a significant impact on the extraction parameters [30]. Ash from Gdynia dating from various periods (spring and winter) differs in the contents of some metals (Ca, Zn, Fe, Al) and phosphorus. A higher content of iron in winter time results from the application of biological enhancement while treating sewage with an iron coagulant during the period of a lowered activity of activated sludge, whereas in spring time with an Al coagulant, which also exerts an influence on the appropriate development of microorganisms in activated sludge, thus facilitating further processing of excessive sludge. Very high yields of the leaching process were achieved, both for the winter time ash and spring time ash (yield of 95%). Low iron contents in the extracts from leaching both ashes ('Spring' – lower concentrations) suggest a possibility of further utilization of these extracts without the necessity of treatment.

The complete characteristics of the process of phosphorus recovery from obtained ash on a laboratory scale made it possible to select a material of a considerable potential for the technology of phosphate fertilizers production (figure 3).

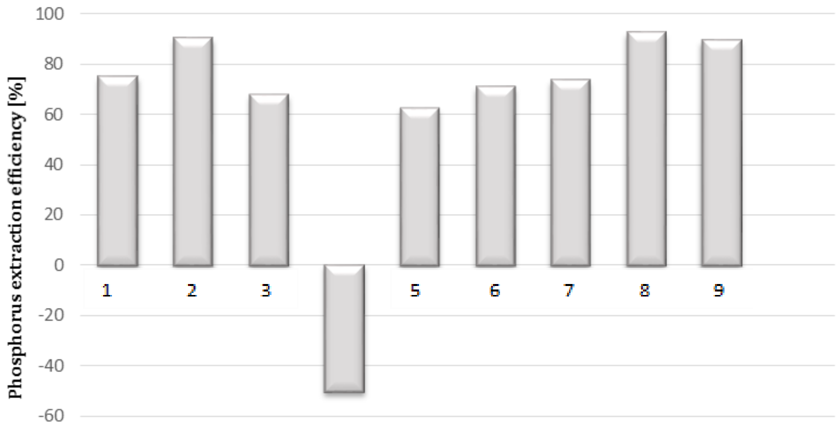


Fig.3. Phosphorus extraction efficiency for analyzed SSA:
1-Kraków, 2-Kielce, 3-Łódź, 4-Warszawa, 5-Szczecin slag, 6-Szczecin dust, 7- Gliwice, 8-Gdynia Spring, 9-Gdynia Winter

The ashes ”Kraków”, ”Łódź”, ”Kielce” and ”Gdynia” were selected for the research into an increase in the process scale, as they constitute an invaluable raw material from which it is possible to recover phosphorus with phosphoric acids at the yield exceeding 70%. In the case of a large laboratory scale, in a glass reactor Syrris Globe (fig. 4A) of a capacity of 5 litres, the best yields were obtained for the ashes from Gdynia and Kielce (77-92% for H_3PO_4), hence these materials were used as a raw material for a micro-technical scale (50l reactors, fig. 4B).

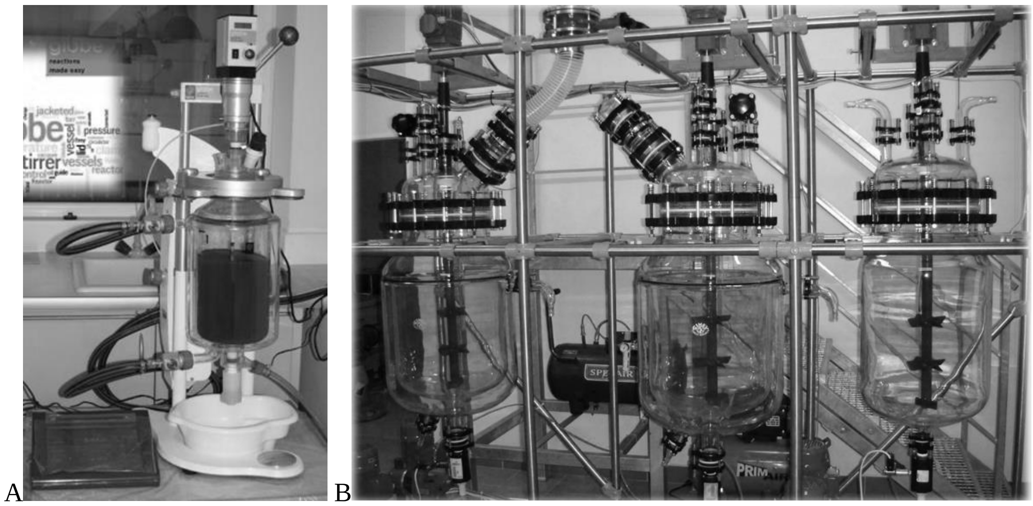


Fig.4. Reactors used for scaling up PolFerAsh Technology:
A- large laboratory scale 5l, B-micro-technical scale 50l

4.2. MAP production experiments

A solution of ammonia water or ammonia gas was added to extracts after SSA Kielce and Gdynia treated with phosphoric acid, until the pH value of the system reaches between 5 and 7. The process was carried out at continuous stirring, with batch- or single-dosing of the ammonia solution or ammonia gas until the desired pH value is reached.

Industrial technologies are characterized by using relatively pure phosphoric acid, whereby the presence of impurities contributes to lowering the molar ratio of the products (especially for MAP production)[52]. In this experiments, extracts containing a number of impurities are used. The presence of elements such as calcium, magnesium or iron can affect the production of compounds different than those resulting from the N/P molar ratio. In the MAP production technology, the appropriate N/P molar ratio is obtained by maintaining the pH of the mother liquor at pH = 5 [53]. Therefore the trials in which the decisive parameter of the process was to obtain a suitable pH value of the system were also conducted. In the experiments 1-5, ammonia water (about 25% by weight) was added to pH 5, using different conditions for the separation of the reaction mixture and drying parameters of the product (Table 2). In experiment 6, an attempt was made to neutralize the extract with gaseous ammonia (up to pH = 5), while in the experiment 7 ammonia gas was added in a molar ratio of N/P = 2.

In the experiment 1, cooling of the reaction system was additionally used, as well as washing of the separated precipitate with water and product drying. Further experiments 2-5 were carried out using evaporation of the reaction mixture rather than phase separation by filtration. Then dried under given conditions. While experiments 6-7 were conducted by dispensing ammonia gas into the extract. The obtained products were characterized by high density and were subjected to drying without evaporation of excess water.

Table 2. Characteristic of the MAP production experiments

Exp. No.	**Extract**	**Ammonia form**	**pH**	**Assumed N/P ratio**	**Final N/P ratio**	**Phase separation**
1	Kielce SSA treated with H_3PO_4	25% liquid solution	5.0	0.64	0.64	Pressure filtration
2			5.0	0.64	0.64	Evaporation
3			5.0	0.64	0.64	
4			5.0	0.64	0.64	
5	Gdynia SSA treated with industrial H_3PO_4	25% liquid solution	5.0	0.64	0.64	
6		gas	5.0	1.0	0.7	Not applied
7			7.1	2.0	0.9	Not applied

Mass balance of main components (nitrogen and phosphorus) was prepared for experiments 2, 5, 6 and 7. As it is shown in Figure 5, the neutralization process is very efficient for phosphorus (94-98% for all experiments). The nitrogen efficiency is slightly lower, as a result of carrying out the process under atmospheric pressure, where ammonia losses are inevitable, especially in open systems. Much lower yields of nitrogen were obtained in experiments with gaseous ammonia (65% in response to the assumed

N/P ratio of 1 and 42% in the case of assumed N/P = 2). The cause may be the non-quantitative separation of ammonia in NH_3 gas production apparatus, as well as slow dosing of this reagent.

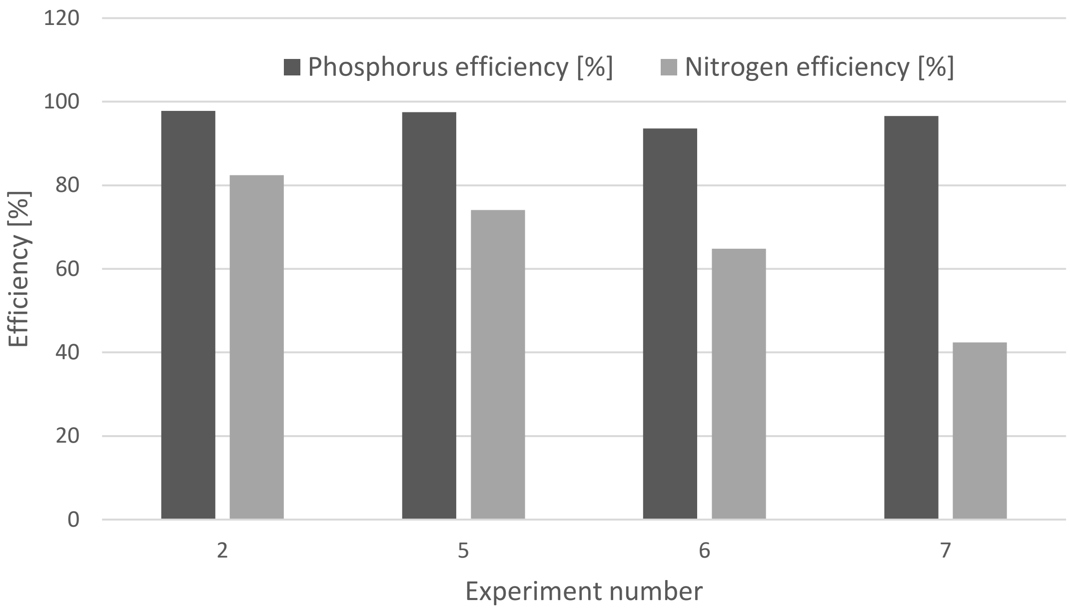


Fig. 5. Efficiency for phosphorus and nitrogen usage during MAP production experiments

4.3. MAP products characteristic

The Regulation EC 2003/2003 defines NP fertilizers as products obtained by chemical treatment or by mixing, without the addition of organic substances of plant or animal origin, with a minimum nutrient content of 18% (N + P_2O_5). At the same time the content of the individual nutrients must reach a minimum level of 3% N and 5% P_2O_5. At least 75% of the declared phosphate content should be soluble in 2% citric acid solution, phosphorus soluble only in mineral acids should not exceed 2%. Declarations referring to secondary components cover Ca, Mg, Na and S, their content must be declared accordingly above 1.4% Ca, 1.2% Mg, 2.2% Na and 2%S. The Regulation EC defines ‘nutrient microcomponents’ as elements: boron, cobalt, copper, iron, manganese, molybdenum and zinc, necessary for the growth of plants in small amounts when compared to basic and secondary nutrients. The minimum contents of nutrient microcomponents in fertilizers EC containing basic or secondary nutrients, applied to the soil in agricultural farming and on grassland, amount to, respectively: 0.5% for Fe, 0.01% for Zn and 0.01% for Cu. However, when it comes to gardening these are: 0.02% for Fe, 0.002% for Zn and 0.002% for Cu.

The Regulation EC does not specify the allowable content of Cd, Hg, Pb and As in fertilizers. In accordance with Polish regulations, these limits are included in the Regulation of the Minister of Economy concerning ‘the way of packaging mineral fertilizers, placing labels containing information about fertilizer components on these packages, methods of examining mineral fertilizers and types of agricultural lime', and they are as follows - Cd: 50 mg/kg of dry matter; Pb: 140mg/kg of dry matter; Hg 2 mg/kg of dry matter; As: 50 mg/kg of dry matter.

Thickening the resulting pulps by evaporation in experiments 2-7 resulted in the desired product - ammonium dihydrogen phosphate (MAP), marked on the XRD diagrams (fig. 6) as mineral bifosphamite. Prolonged drying of the product has a positive effect on the increase in sample crystallinity. The use of cooling at the neutralization stage does not significantly affect the form of the resulting product. In experiment 7 diammonium phosphate (DAP) was expected. Obtaining a different phase is probably related to the previously described ammonia dosing and phase equilibrium. Low concentration of phosphate ions is preferable to produce MAP, despite the high N/P ratio.

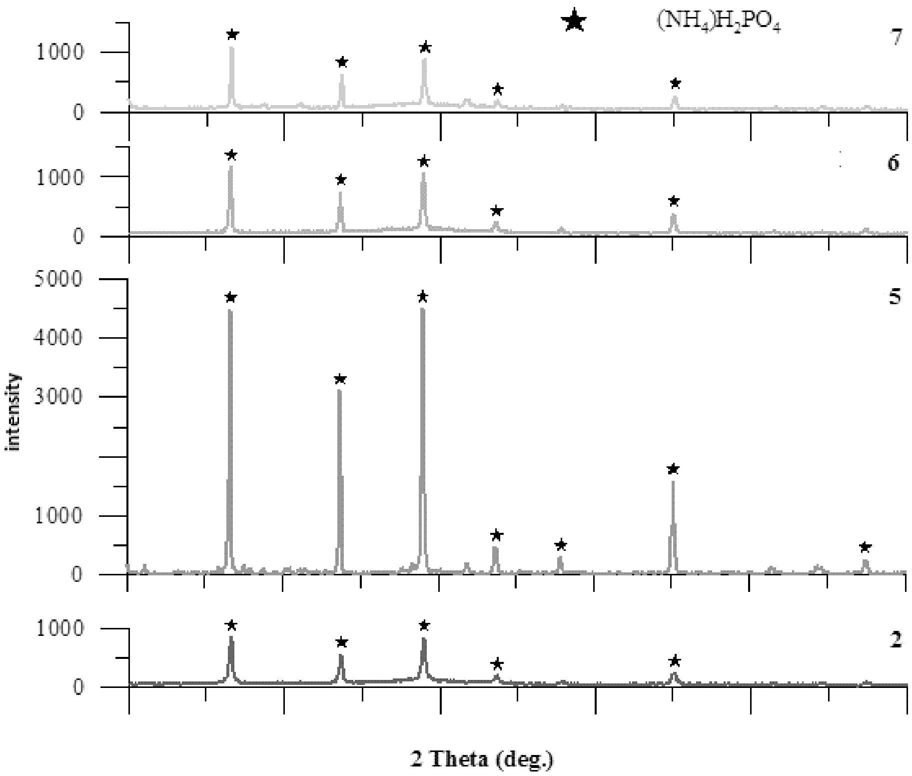


Fig. 6. XRD analysis of products obtained after MAP production experiments (exp. no. 2,5,6 and 7).

Table 3 lists the content of total and accessible phosphates and nitrogen. The products obtained as a result of the conducted experiments contained 50.0-55.6% m/m P_2O_5, 6.7 – 11.0% m/m N_{NH3}. Compared to the stoichiometric content of phosphorus and nitrogen in MAP (61.8% P_2O_5, 12% N), the products are characterized by lower content of these components, but nevertheless meet the requirements for fertilizer products (sum of N + P_2O_5> 18%). They are characterized by high content of accessible forms of phosphates (87% to 100%) soluble in neutral ammonium citrate or citric acid. Fertilizer from experiment 5 is the best material in terms of the content of accessible forms of phosphate and nitrogen. The nitrogen content of this fertilizer is 11.6%, which is approximately the stoichiometric amount of nitrogen in pure MAP (12%). The fertilizer contains slightly less phosphorus (55.6% P_2O_5) than pure

MAP (61.8% P_2O_5), but this is related to the presence of other ingredients from an extract such as magnesium or iron.

The lead content for all products is below the allowable concentration. Cadmium concentration is slightly exceeded in the case of experiments 6 and 7, which may be related to the raw material used during the micro-technical scale – industrial wet process phosphoric acid (WPPA). WPPA also contains chromium, which results in an increase of this element in products. Nickel in all products does not exceed 50 mg/kg.

The fertilizers contain additionally calcium (about 2%), magnesium (0.7-1.1%) and iron (0.76-1.1%), Zinc is up to 0.17% and copper is 360 mg/kg, so these ingredients concentration is to low to be declared as micronutrients in the product.

Table 3. Characteristic of the MAP products

Experiment no.		2	4	5	6	7
Total phosphates, $\%P_2O_5$		54.7	54.2	55.6	50.0	51.0
Phosphates soluble in neutral ammonium citrate, $\%P_2O_5$		47.5		55.9	49.9	50.3
Phosphates soluble in 2% citric acid, $\%P_2O_5$		-	53.7	55.4	47.3	48.1
Phosphates soluble in water, $\%P_2O_5$		36.2	36.4	53.4	35.6	35.0
Nitrogen, $\%N_{NH3}$		7.2	7.2	11.6	6.7	9.2
Ni	mg/kg	20	23	49	41	41
Cr		11	13	391	328	327
Zn		1596	1700	384	1758	1757
Cd		25	11	45	55	57
Cu		235	245	24	360	360
Pb		22	26	11	13	13
Fe	%	1.07	1.10	0.76	1.08	1.09
Ca		2.04	2.48	-	2.01	2.03
Mg		0.74	0.71	0.50	1.10	1.11

Conclusions

Ash after the incineration of sewage sludge, due to the removal of organic matter and pathogens as well as phosphorus concentration in mineral remnant after the process, constitute a precious source of phosphorus, whose content fluctuates between around 7% and over 11%, which may be compared to poorer phosphorus ores. Due to a low pool of phosphorus available to plants, which constitutes only 30% of its total content, this material does not find its application as a fertilizer. At the same time during the thermal process a concentration of metals, among others of iron, aluminium and metals standardized in soils takes place.

Experiments have yielded fertilizer products that meet the requirements for mineral fertilizers containing phosphorus and nitrogen and secondary ingredients and micronutrients.

Neutralization should be carried out by adding ammonia water or gaseous ammonia, and then concentration and drying the resulting reaction pulp at 100-120 ° C. The use of ammonia gas allows the energy expenditure to be reduced as the evaporation stage can be omitted due to a sufficiently thick reaction pulp which, when mixed with the solid dry product, can be granulated.

The obtained fertilizer pulps have a considerably higher content of nitrogen and microelements, such as iron, zinc and copper, in comparison to the conventional method of the production of ammonia phosphate fertilizers, or the extraction methods of phosphorus recovery from solutions after leaching ash, which were described in the literature, and whose final products are calcium phosphates. In this way it is possible to obtain enriched phosphorus-nitrogen mineral fertilizers without the necessity of introducing additional substances containing iron, zinc and copper. The verified method of conducting the neutralization of extracts is advantageous due to a reduction of the mass ratio of heavy metals content to primary fertilizer components (nitrogen and phosphorus) in a final product in comparison to fertilizer products obtained as a result of the neutralization with a calcium agent of extracts after leaching ash with nitric acid, where the final product contains only phosphorus component.

The high phosphorus yield indicates precipitation of the phosphorus compounds contained in the extract.

The pulp obtained after the reaction can be directed to the production process of mineral fertilizers as a raw material serving as the basis on which NP mineral fertilizers enriched with microelements are produced.

If all the sludge generated in Poland in 2014 be subjected to a thermal utilization, the amount of mineral residues amount to approx. 61 thousand. tonnes (assuming that they constitute 11% of the total weight of sediment), which corresponds to approx. 5.5 thousand. tones of phosphorus (average phosphorus content in the ash order of 9%). The recovery of this element from the ash would replace 42 thousand. tons of phosphorus ore containing 13% P. With the current levels of raw material prices ($115/t), it would be possible to save more than 18 million PLN. In addition, the creation in our country, a recovery of phosphorus from the ashes after combustion of sewage sludge would be a step in the direction of the economy with a closed circuit, which is the future of the European Union.

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