

## Phosphorus cycle — possibilities for its rebuilding\*

Katarzyna Gorazda<sup>1</sup>✉, Zbigniew Wzorek<sup>1</sup>, Barbara Tarko<sup>1</sup>, Anna K. Nowak<sup>1</sup>, Joanna Kulczycka<sup>2</sup> and Anna Henclik<sup>3</sup>

<sup>1</sup>Cracow University of Technology, Kraków, Poland; Institute of Chemistry and Inorganic Technology; <sup>2</sup>AGH University of Science and Technology, Kraków, Poland; <sup>3</sup>The Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Kraków, Poland

The rebuilding of the phosphorus cycle can be performed with the use of both biotechnology and chemical technology. This paper presents a review of the phosphorus cycle and the different approaches that can be taken to the recovery of phosphorus from phosphate-rich waste. Critical issues in the phosphorus cycle are also discussed. Methods for the recovery of phosphorus from sewage sludge ash are widely explored and divided into two groups: wet extraction methods and thermochemical methods. Laboratory-scale methods are described, as well as proposed industrial technologies, with particular regard to the possibilities for their implementation in Poland. Phosphorus recovery methods from SSA (sewage sludge ash) in our country seems to be promising due to the increasing number of sewage sludge incineration plants, which could easily supply ash to future recovery installations. For the effective recovery of P from sewage sludge ash, it is essential to make the right choice in determining the appropriate method to use with respect to the particular properties of the ash composition available. A patented method of phosphorus recovery by acid extraction methods, developed by Cracow University of Technology, results in an efficiency of 80–96% for phosphorus recovery. 3000 to 4000 tons of phosphorus per year can be recycled and introduced back into the environment, that covers around 7% of the total amount of phosphorus ore imported into Poland between 2008 and 2009.

**Key words:** phosphorus cycle, phosphorus recovery, sewage sludge ash, acidic extraction of phosphorus, sewage sludge incineration

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### INTRODUCTION

The reports all over the world unanimously state that further global development will be dependent on the restoration of equilibrium between economic progress and the protection of natural resources (Morsee *et al.*, 1993; Jasinski, 2010). Phosphorus is an essential element of life and is fundamental to the modern agricultural system. The importance of this element in affecting ecological dynamics comes not only from its predominance in cells but also from its relative abundance in the environment (Blank, 2012). P is considered a potentially critical resource because its reserves are limited. Phosphorus limitation often arises because much soil-based P is actually unavailable to most plant life. According to Li & Brett (2013), analysis of Soluble Reactive Phosphorus (SRP) showed that it provides a poor index of dissolved phosphorus bioavailability in natural systems.

Within 21 inorganic and organic phosphorous-containing compounds, 81% did not fit the classic assumption that SRP approximately equals bioavailable P. From inorganic compounds, all of the P that was bioavailable for algal growth was only in the form of  $\text{CaHPO}_4$ .

Phosphorus compounds are mostly used in modern agriculture for both crop farming and animal husbandry. From a total production of 24.87 Mt of phosphorus, fertilizers accounted for 82% of the total phosphate rock consumption in 2012 (Scholz *et al.*, 2013; Scholz & Wellmer, 2013). The main reserves of phosphate rock are found in relatively few countries. 65% of global raw material production belonged to 3 countries: China, United States and Morocco & Western Sahara (IFDC, 2010; Jasinski, 2012). Annually, Poland imports approximately 460 000 tons (2008) of raw phosphorus material in the form of concentrates, mainly from Morocco, Tunisia and Syria (GSMiE PAN, 2011). The current state of global P reserves and resources is extremely complex and depends heavily on the cost-efficiency of the mining and extraction processes used. According to forecasts, world phosphorite and apatite reserves will become exhausted during the next 60–400 years, depending on a potential trend in the phosphate industry moving increasingly towards improved recovery rates and the mining of lower-grade phosphate rock (Heffer *et al.*, 2006; IFDC, 2010; Jasinski, 2012).

A critical issue in the phosphorus cycle is the low efficiency and losses associated with the production and use of phosphate fertilizers. Only about 10% of mined phosphorus is currently consumed, according to Cordell *et al.* (2009). The two largest causes of P loss globally have been identified as erosion and runoff of mined P (estimated at 46%) and animal waste (40%). Nearly all of the P consumed by humans is transported as sewage to municipal wastewater treatment plants. About one-half of that phosphorus is discharged after treatment and directly enters waterways, increasing eutrophication (8% of mined P), while the majority of the remainder (7% of mined P) is disposed of in landfills as sludge (Rittmann *et al.*, 2011; Liu *et al.*, 2008; Cordell *et al.*, 2009; Schröder *et al.*, 2010; Clift & Show, 2012). Therefore the impending scarcity of phosphorus in the coming centuries is not a physical problem, but economic, technical and political one.

Phosphorus sustainability is defined as a two-sided challenge: pollution on the one hand, scarcity on the other. This predicament creates a broad field of oppor-

✉ e-mail: gorazda@chemia.pk.edu.pl

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tunity, calling for the improvement of technologies and practices that 'complete the phosphorus cycle'. The key areas for action according to the European Union are the balancing of consumption, improving the processing and utilization of phosphorus, the recycling and reuse of phosphorus from sewage sludge and bio-waste and reducing organic phosphorus losses in the food chain. EU recommendations were echoed in the activities of the European fertilizer industry, which intends to replace natural phosphorus materials in phosphorus-rich waste (Schroder *et al.*, 2009; EEA, 2011).

#### POSSIBILITIES FOR REPAIRING THE PHOSPHORUS CYCLE

The rebuilding of the phosphorus cycle can be performed with the use of both biotechnology and chemical technology. Aspects of biotechnology reviewed by Blank (2012) include phosphate solubilisation (from the soil), phosphate recovery and uptake, phosphate storage, and phosphate mobilisation. Enhanced biological phosphorus removal (EBPR) reactors with phosphate-recovery technologies in combination with low pressure wet oxidation and nanofiltration to recover phosphate as diluted phosphoric acid or phosphate-based fertiliser should be mentioned (Yan *et al.*, 2013; Raj *et al.*, 2013; Blöcher *et al.*, 2012; Wong *et al.*, 2013). As an example, a full-scale EBPR plant operating in Fukuyama City, Japan recovered phosphorus in the form of calcium phosphate using an additional step of heating the sludge, followed by clarification and  $\text{CaCl}_2$  precipitation (Blank, 2012). Other examples are the use of microbes for phosphate mobilisation in soil to improve phosphate efficiency on fertilized fields, the development of crop variants with altered root morphology enabling improved P acquisition and the use of Phytate as an alternate P source (Tian *et al.*, 2012; Adeola & Cowieson, 2011; Ridoutt *et al.*, 2013).

Chemical technology is useful for recovery of phosphorus from waste water streams (Bradford-Hartke *et al.*, 2012; Petzet *et al.*, 2012; Sengupta *et al.*, 2011; Kodera *et al.*, 2013), sewage sludge (Sano *et al.*, 2012), animal waste (Schröder & Verloop, 2010), industrial waste and other industrial emissions (Hutnik *et al.*, 2013; Gorazda *et al.*, 2010).

Sewage sludge — waste containing phosphorus compounds concentrated at cellular matter or in the form of insoluble phosphates, after thermal processing could potentially be used as a source of concentrated phosphorus and as a substitute for natural ore. In the EU, 10–21%

of the whole amount of sewage sludge is incinerated, constituting nearly 0.6 million tons of sewage sludge ash (SSA) per year and this amount will continue to increase. 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 (Nowak *et al.*, 2012), dioxin and furan emission (Tyagi & Lo, 2013), the release of heavy metals (Nzihou *et al.*, 2013; Li *et al.*, 2012) and the handling of solid residues are all still of significant importance to thermal processes (Fytli *et al.*, 2008). According to forecasts, Old Member States will continue to lead on these technologies and probably by 2020, thermal treatment with energy recovery could make up 37%, more than double compared to EU-12.

Although Poland is the greatest sludge producer (regarding EU-12 countries, 42% of total sludge amounts is produced in Poland), thermal methods of sewage sludge utilisation have not been very popular in recent years (Kelessidis *et al.*, 2012). Nowadays, a different tendency is observed, due to the EU regulation implemented on 1<sup>st</sup> January 2013, banning deposition of this waste in landfills. Presently, 11 incineration plants are operating in our country, bringing about a significant reduction in the volume of sewage sludge and resulting in full stability and biological safety of this waste (Table 1). Phosphorus concentration in the ash can be compared to the poorest natural raw phosphate materials with average P concentration in European ashes being around 7%. Table 2 shows the content of selected elements in SSA from 25 different European and 6 Polish sewage sludge incineration plants.

For the utilization of SSA as a potential source of phosphorus, several parameters of the ash have to be taken into consideration. It is also important to choose the most appropriate recovery method. The chemical composition of the ash depends on the treatment method (either biological or chemical) that is used in wastewater treatment plants. The type of precipitant agent used is also significant: iron or aluminium salts that are used for phosphorus compound precipitation cause a higher concentration of Fe or Al respectively. It is also possible to observe a high concentration of iron in the ash that originates from the biological treatment due to a significant amount of this element present in the water in certain regions. The presence of heavy metals (HM) like lead, zinc, cadmium and nickel in the ash disqualify this waste from direct usage as fertilizer (despite a

**Table 1. Characteristic of the Polish mono-incineration plants (technological data from each plant, 2012)**

Location	Starting year	Quantity of incinerated sewage sludge (T d.S./Day)	Technology	Ash production (T/day)
Gdynia	1997	25	Fluidised bed	10
Łódź	2010	46	2 Fluidised bed Pyrofluid R-43	15
Kielce	2011	19	Fluidised bed	3.1
Bydgoszcz	2012	19	Fluidised bed	2.3
Kraków	2011	55	Fluidised bed Pyrofluid	19.5
Warszawa	2013	Max. 613	Fluidised bed Pyrofluid R-67	73
Szczecin	2010	40	Grate furnace	12

**Table 2. Content of selected elements in Polish and European Sewage Sludge Ash (SSA) (Donatello *et al.*, 2010; Franz, 2008; Stark *et al.*, 2006; Lapa *et al.*, 2007; Adam *et al.*, 2009)**

		P (%)	Fe (%)	Cd (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
SSA from 25 European incineration plants	Min	3.6	1.5	0	40	417	910
	Max	11.2	17.0	14	621	2,483	46 000
	Average	7.3	8.8	5	121	956	921
SSA from 6 Polish incineration plants	Min	8.7	3.8	4	59	483	799
	Max	11.2	11.3	71	300	979	7 200
	Average	10.1	8.1	25.2	139.8	758	3 903

high phosphorus concentration). Recovery methods have to take into account a significant amount of these elements in the ash while HM removal seems to be an absolute prerequisite in considerations regarding methods of phosphorus recovery from SSA.

The characteristics of the ash differ according to the type of thermal utilization employed. 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 (Table 1). The main drawback of this method is the relatively low incineration temperature usually used in fluidized bed furnaces. It is often 850°C that is the temperature high enough to achieve total stabilization of the waste and to remove pathogens and organic compounds. However, it is also at this temperature that iron present in the sludge occurs in the form of calcium-iron phosphate, which causes handling problems during extraction and recovery processes. It has been proven that at a temperature of 950°C, iron contained in the ash is converted into a hematite form, which is insoluble in mineral acids. As a result, it is possible to recover phosphorus selectively (Gorazda *et al.*, 2012). Additional treatment options have to be taken into consideration in the case of sewage sludge ash containing iron that will be in soluble form during extraction process.

#### METHODS OF PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE ASH

Essentially, the methods of phosphorus recovery from SSA can be divided into two groups: wet extraction methods and thermochemical methods.

The principle behind the wet extraction method is the leaching of sewage sludge ash with acids or bases. The efficiency of the process depends on; the type and concentration of the extractant, the pH value, the extraction time and the incineration temperature of sewage sludge. The extraction methods could be divided into following groups:

— Acidic leaching with H<sub>2</sub>SO<sub>4</sub> (Donatello *et al.*, 2010; Franz, 2008; Tan & Lagerkvist, 2011; Biswas *et al.*, 2009; Dittrich *et al.*, 2009), HCl (Donatello *et al.*, 2010; Tan & Lagerkvist, 2011; Biswas *et al.*, 2009; Dittrich *et al.*, 2009; Schaum *et al.*, 2013), HNO<sub>3</sub> (Tan & Lagerkvist, 2011; Biswas *et al.*, 2009; Gorazda *et al.*, 2012), H<sub>3</sub>PO<sub>4</sub> (Dittrich *et al.*, 2009; Gorazda *et al.*, 2012), citric and oxalic acid (Biswas *et al.*, 2009);

— Basic leaching with NaOH (Biswas *et al.*, 2009; Dittrich *et al.*, 2009; Schaum *et al.*, 2013; Stark *et al.*, 2006);

— Bioextraction with acidithiobacillus ferrooxidans bacteria (Tan & Lagerkvist, 2011);

— Supercritical fluid extraction or wet oxidation of ashes from supercritical water oxidation (Stark *et al.*, 2006; Tyagi & Lo, 2013).

Significant quantities of heavy metals in the ash require an additional treatment step. It is possible to remove HM via the precipitation method (metals removed in the form of sulphides), liquid-liquid extraction, ion-exchange, as well as nanofiltration (Donatello *et al.*, 2010). The most popular extractants are sulphuric acid and hydrochloric acid due to their relatively low price and a high recovery level of up to 99% P (Donatello *et al.*, 2010; Franz M, 2008; Biswas *et al.*, 2009). Nevertheless, during the process some problematic by-products are formed: gypsum or CaCl<sub>2</sub>. Other studies have shown that leaching efficiency drops to 30% in the case of a base being used as an extractant (Dittrich *et al.*, 2009).

The second group of methods of phosphorus recovery from SSA is the thermochemical treatment of ash. In this process sewage sludge ash is mixed with a chloride donor and subsequently heated within a temperature range of 900–1050°C, leading to the transformation of phosphate compounds into a bioavailable form. Meanwhile, heavy metals present in the ash react with the chloride donor resulting in the formation of volatile chlorides, which evaporate and hence the heavy metal-free ash is obtained. The investigations proved that the HM removal efficacy is related to the chloride donor type, the temperature of the process, the reaction time, the reactor type and the form of the ash eg. pellets or briquettes (Nowak *et al.*, 2012; Mattenberger *et al.*, 2010).

It is also possible to classify metallurgical methods into the thermochemical group. The ash is used as a substitute for raw phosphate rock present in the conventional technologies of phosphorus production (Schipper *et al.*, 2001).

Table 3 summarizes the characteristics of the extraction and thermochemical methods, which have recently been studied in Europe.

The technologies for recovery from ash must take into account the industrial procedures of sewage treatment plants in Poland, where the maximum phosphorus content in the treated wastewater is related to the use of biological or chemical methods of phosphorus removal with iron or aluminium salts. The significant amount of iron present in Polish ash disqualifies it from its possible utilisation in the thermochemical methods (iron does not form volatile chlorides) and also in the metallurgical method, where the maximum acceptable iron concentration must not exceed 1% according to Mattenberger *et al.* (2010). Thus the proper means of SSA disposal would

Table 3. A comparison of recovery methods of phosphorus from sewage sludge ash

Method name	Scale	Principles	Obtained product
SEPHOS/ Advanced SEPHOS (Schaum <i>et al.</i> , 2013)	Lab.	SSA leaching with H <sub>2</sub> SO <sub>4</sub> added up to pH value 1.5. Neutralization of the system with NaOH (pH=3.5) and AlPO <sub>4</sub> precipitation. Advanced method: dissolution of AlPO <sub>4</sub> in NaOH and heavy metals separation.	AlPO <sub>4</sub> / Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>
PASH (Dittrich <i>et al.</i> , 2009)	Pilot	SSA leaching with 8% HCl, liquid-liquid extraction using tri-(C <sub>8</sub> C <sub>10</sub> )-alkilamine (Alamine® 336) and tri-n-butyl phosphate (TBP) to obtain high phosphorus against iron recovery selectivity. Final step: phosphates precipitation.	Magnesium or calcium phosphate/MAP
BIOCON (Donatello <i>et al.</i> , 2010)	Pilot	SSA leaching with sulphuric acid. The step of treating extract on ion exchange columns.	H <sub>3</sub> PO <sub>4</sub>
AquaReCi (Stark <i>et al.</i> , 2006)	Pilot	SSA from supercritical water oxidation process (374°C, 220 bar), subsequently leaching with base. Phosphate compounds precipitation with lime milk.	Calcium phosphate
SESAL-Phos (Petzet <i>et al.</i> , 2012)	Lab.	Acidic leaching due to phosphorus transformation into Al-P form, afterwards precipitate dissolution in basic extractant, selectively among HM. Phosphorus compounds obtained <i>via</i> CaO addition.	Calcium phosphate
Zero sludge discharge technology (SPIRIT 21, 2007)	Project	SSA basic leaching with KOH or NaOH, an intermediate for liquid fertilizers is obtained. Final step: precipitation with lime milk.	liquid K <sub>3</sub> PO <sub>4</sub> / calcium phosphate
ECOPHOS (PL) (Gorazda <i>et al.</i> , 2012)	Micro-technical	Thermic pre-treatment of the ash at 950°C (iron transferred into hematite form that is insoluble in acids), acidic leaching with HNO <sub>3</sub> or H <sub>3</sub> PO <sub>4</sub> , phosphate precipitation with CaO.	Calcium phosphate
AshDEC (Nowak <i>et al.</i> , 2012)	Pilot	Thermochemical treatment of the ash mixed with MgCl <sub>2</sub> or CaCl <sub>2</sub> at 1000°C, volatile chlorides formation, transformation of the phosphorus compounds into bioavailable form.	Ash as fertilizer
Mephrec (Nieminen, 2010)	Pilot	SSA briquettes sintering in a shaft furnace with dolomite and lime as a fluxing material and coke as a reducer and an energy carrier. Temperature of the process: 2000°C, silica phosphate from metals separation at 1450°C	Ash with high calcium and phosphorus concentration
Termphos (Schipper <i>et al.</i> , 2001)	Industrial	SSA used as a raw phosphate rock substitute. P <sub>4</sub> is produced in an electric furnace at 1500°C.	P <sub>4</sub> /FePO <sub>4</sub>

be iron immobilization while carrying-out the wet extraction process with acidic extractants, which is in fact the goal of the Ecophos project being conducted at Cracow University of Technology, in accordance with patented technological solutions (Gorazda *et al.*, 2010; Gorazda *et al.*, 2012). Phosphoric and nitric acid usage will minimize the generation of undesirable waste. The proposed solution can be used industrially for the production of chemical phosphate fertilizers and can be used in the construction industry as well as for municipal waste minimization technology through the beneficial recycling of phosphorus.

## CONCLUSIONS

Rebuilding the global and local phosphorus cycles will only be possible with the use of sustainable development rules and adequate phosphate-rich waste management. Sewage Sludge Ash is a concentrated source of phosphorus and can be successfully recycled via a number of different routes. Unfortunately there are only a handful of industrial scale examples of such recycling currently in existence, which does not encourage its wide-scale adoption. It is however likely that the technologies that have been presented here will become more attractive as both phosphate prices and ash disposal costs continue to rise. Sewage sludge ash generated by Polish incineration plants tend to contain considerable amounts of phosphorus, but the significant amount of iron present

in the ash eliminates the possibility for its utilisation in thermochemical methods. A patented method of phosphorus recovery by acid extraction methods, developed by Cracow University of Technology, results in an efficiency of 80–96% for phosphorus recovery (Gorazda *et al.*, 2012; Gorazda & Wzorek, 2006). The amount of waste generated from the thermal treatment of sewage sludge in eight Polish incineration plants is approximately 43000 tons per year. The average phosphorus content in Polish ash is around 9.7%, though 3000 to 4000 tons of phosphorus per year can be recycled and introduced back into the environment. That amount is equivalent to 30770 tons of phosphorus ore with an average phosphorus content level of 13% (Morocco, Tunisia phosphates) and covers around 7% of the total amount of phosphorus ore imported into Poland between 2008 and 2009. According to forecasts for Poland, in 2020 about 95000 tons of dry mass of sewage sludge will be utilised thermally, which will undoubtedly increase the potential for phosphorus recycling (GUS, 2012).

Moreover, analytics for the European Union and the Polish Market clearly indicate that growing demand for phosphate fertilizers worldwide is expected and the establishment of export duties will be a significant obstacle to furthering the development of existing technology based on phosphate fertilizers and compound fertilizers (Technological Foresight, 2011). From published reports, it is also clear that to ensure food security in Poland, all the basic mineral fertilizers must be produced in our

country. Developing technologies that take into account local conditions and that result in fertilizer production is fundamental. Even more important than this is to establish the possibilities for obtaining cheaper or alternative sources of phosphorus for individual industries.

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