Environmental Research 154 (2017) 171–180

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Fertilisers production from ashes after sewage sludge combustion – A strategy towards sustainable development

Katarzyna Gorazda[a,*], Barbara Tarko[a], Zbigniew Wzorek[a], Halyna Kominko[a], Anna K. Nowak[a], Joanna Kulczycka[b], Anna Henclik[c], Marzena Smol[c]

[a] *Institute of Inorganic Chemistry and Technology, Cracow University of Technology, Ul. Warszawska 24, Kraków, Poland*
[b] *Cracow University of Science and Technology, Ul. Gramatyka 10, Kraków, Poland*
[c] *The Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Ul. Wybickiego 7, Kraków, Poland*

ARTICLE INFO

Keywords:
Sewage sludge ash
Phosphorus recovery as fertilizers
Circular economy
Sustainable development
Alternative raw materials

ABSTRACT

Sustainable development and circular economy rules force the global fertilizer industry to develop new phosphorous recovery methods from alternative sources. In this paper a phosphorus recovery technology from Polish industrial Sewage Sludge Ashes was investigated (PolFerAsh – Polish Fertilizers form Ash). A wet method with the use of mineral acid and neutralization was proposed. Detailed characteristic of SSA from largest mono-combustion plans were given and compared to raw materials used on the market. The technological factors associated with such materials were discussed. The composition of the extracts was compared to typical industrial phosphoric acid and standard values characterizing suspension fertilizers. The most favorable conditions for selective precipitation of phosphorus compounds were revealed. The fertilizers obtained also meet EU regulations in the case of the newly discussed Cd content. The process was scaled up and a flow mass diagram was defined.

1. Introduction

Phosphorus as an essential element of life is of crucial importance for the modern agricultural system and food security. Sustainability of phosphorus is a two-sided challenge: pollution on the one hand, scarcity on the other. It is estimated that there are 67 billion tons of phosphate ore in the world with phosphorus concentrations ranging from 28% to 39% P_2O_5. However during the next 60–70 years more than a half of all phosphate ore deposits will be depleted (Gorazda et al., 2013b; IFDC, 2010; Jasiński, 2015). Phosphate rock is unevenly distributed across the globe, which results in only a small number of countries controlling the world's remaining reserves. According to the US Geological Survey in 2015, Morocco, China, Algeria, Syria & South Africa together control 88% of the world's reserves. Morocco alone controls 75% of the world's high-quality reserves. By contrast, the European Union (EU) is almost entirely dependent on imports of phosphate rock from the rest of the world. In addition to these politico-economic challenges, the pollution of phosphate with heavy metals like cadmium and uranium is leading to shortages of the right quality of phosphate rock (Marjolein de Ridder et al., 2012). Low-grade primary resources are not easily processed into high-analysis fertilizers. Moreover, the European Commission is currently reviewing fertilizer regulation aiming at access to the primary and secondary resources, as well as limiting the pollutant concentration in fertilizers. If the proposed limits are enforced, a lot of feedstock material will need to be additionally processed by thermo- or wet chemical metal separation processes. Secondary resources could compensate for the limited supply of rock phosphates, especially those derived from waste (Scholz et al., 2013, 2014).

Recently provided global P flows estimate the largest two flows of lost P in the environment: agricultural runoff and erosion (quantity equivalent to 46% of P mined globally) and animal wastes (40%) (Rittmann et al., 2011). The P discharged into human sewage and sewage-treatment sludge is also significant. About one-half of that phosphorus after treatment in municipal wastewater treatment plants directly enters waterways, increasing eutrophication (8% of mined P), while the majority of the remainder (7% of mined P) is disposed of in landfills (Clift and Shaw, 2012; Cordell et al., 2009; Gorazda et al., 2013b; Rittmann et al., 2011; Schröder et al., 2010). One of the sustainable development strategies, which should be implemented in phosphorus recovery, is circular economy (CE), characterized by closed loop flows of materials in production, distribution and consumption.

---

[*] Corresponding author.

E-mail addresses: gorazda@chemia.pk.edu.pl (K. Gorazda), btarko@indy.chemia.pk.edu.pl (B. Tarko), wzor@chemia.pk.edu.pl (Z. Wzorek), halyna.kominko@gmail.com (H. Kominko), akn@indy.chemia.pk.edu.pl (A.K. Nowak), kulczycka@meeri.pl (J. Kulczycka), a.henclik@meeri.pl (A. Henclik).

http://dx.doi.org/10.1016/j.envres.2017.01.002
Received 27 July 2016; Received in revised form 24 December 2016; Accepted 3 January 2017

The implementation of the CE concept at macro-level needs redesign in industrial, infrastructure, cultural and social systems. Circular economy is a new model that helps to optimize natural resource use through closed flows of materials and energy, minimizing waste production and preventing environment pollution. In last decades this concept became very popular. Nevertheless, the implementation of the CE concept is still on the initial stage. Besides opportunities, which CE gives, like reducing pressure on environment, increasing competitiveness, innovations and economic growth, there are also challenges, that need to be considered. One of the major barriers is cost of "green" innovation. It is a lack of pricing system encouraging resource reuse and collaboration between producers and recyclers (Ghisellini et al., 2015; Stahel, 2016). Moreover, due to large volume demand, secondary resources must be collected from a number of widespread livestock and wastewater treatment facilities. Thus, according to Scholz et al. (2013), facilities using secondary resources will be decentralized, regional and considerably smaller.

Sewage sludge ash (SSA) rich in phosphorus compounds can be used as substitute of natural raw materials according to sustainable development rules (Gorazda et al., 2013a; Herzel et al., 2016; Krüger and Adam, 2015). Methods based on thermal drying and incineration are considered the optimum solution for sewage sludge disposal, as they are more economically justified due to possible autothermal process, possibility of mass reduction, elimination of organic pollutants, microorganisms and pathogens as well as phosphorus recovery from the final form of mineral ash (Bień, J.D. and Bień, B. 2015; Kelessidis and Stasinakis, 2012; Pająk, 2013). The low heating value of sewage sludge can be compensated by the addition of a supplementary fuel, especially biomass. Biomass is a carbon-neutral fuel, its co-combustion with sewage sludge may produce lower CO_2 emissions decreasing technological costs (Kijo-Kleczkowska et al., 2016). During the combustion of sewage sludge both P and heavy metals are concentrated in the ash. In order to transfer phosphorus into a water-soluble form and reduce heavy metals concentration in the final product several methods were developed: thermo-chemical treatment or wet extraction.

A high temperature of up to 1005 °C and the addition of chloride additives ($MgCl_2$, KCl_2, $CaCl_2$, $NaCl_2$) to SSA in the AshDec® method lead to heavy metals decontamination higher than 90% in the case of Cd, Cu, Pb and Zn, and better bioavailability of P (Adam et al., 2009; Biswas et al., 2009). Treated ash can be mixed with additional nutrients (N, P, K) to produce commercial fertiliser PhosKraft® under SUSAN-project (Nanzer et al., 2014). Temperatures above the melting point of ash (1500 °C) are used in thermo-electric processes (Thermophos®) or thermo-reductive reactors (InduCarb, RecoPhos) where white phosphorus or pure phosphorus is produced (Schipper et al., 2001; Schönberg et al., 2014). The advantages of such solutions are 98% of phosphorus recovery potential and low consumption of chemicals; on the other hand investment costs (rotary kiln, electric arc-furnace, flue gas treatment facilities), energy costs and proper composition of ash in some solutions need to be considered and compensate by the installation size.

The more flexible methods of phosphorus recovery are the wet methods, using acidic solutions for SSA leaching. The extraction methods can be divided into following groups: acidic leaching with H_2SO_4 (Biswas et al., 2009; Dittrich et al., 2009; Donatello et al., 2010; Franz, 2008; Petzet et al., 2012; Tan and Lagerkvist, 2011), HCl (Biswas et al., 2009; Dittrich et al., 2009; Donatello et al., 2010; Schaum et al., 2013; Tan and Lagerkvist, 2011), HNO_3 (Biswas et al., 2009; Gorazda et al., 2012; Gorazda, 2010; Sano et al., 2012; Tan and Lagerkvist, 2011), H_3PO_4 (Dittrich et al., 2009; Gorazda and Wzorek, 2006), citric and oxalic acid (Biswas et al., 2009).

Less popular is using base as an extractant (Schaum et al., 2013; Stark et al., 2006), bioextraction (Tan and Lagerkvist, 2011) or supercritical fluid extraction and wet oxidation of ashes from supercritical water oxidation (Tyagi and Lo, 2013).

The investigation into phosphorus recovery from ashes after co-combustion of wood and sewage sludge (15%) with sulfuric acid, revealed 50–95% of phosphorus yield depending on the used sewage sludge. Ashes from combustion of sewage sludge that was formed using aluminum sulphate as flocculating agent released nearly all the phosphorus at a pH value of 1. When iron sulphate was used as flocculating agent, this affected the chemistry of the resulting ashes, making phosphorus recovery more difficult (Pettersson et al., 2008). Such results are opposite to sewage sludge ash behavior during extraction with nitric acid. When iron is immobilised in the hematite phase, slightly insoluble even in strong acids, extraction is more selective towards phosphorus compounds (Gorazda et al., 2016; Ottosen et al., 2013).

The above technologies were tested and scaled up only for sewage sludge ash, some of them are available at a larger scale: P Tetra-Phos (Remondis) (Lehmkuhl, 2015), Leachphos, Ecophos® or SESAL-Phos (Egle et al., 2015; Petzet et al., 2012).

Advantages of the presented solutions are their high recovery potential, flexibility (ash composition and adjustable leaching parameters) as well as simpler devices for extraction and phase separation. No heavy metal removal or specific heavy metal removal steps, operating with mixture of different liquid streams and a high consumption of chemicals are factors that need to be taken into consideration.

In the investigated PolFerAsh technology, phosphoric and nitric acid or its mixture was proposed as a leaching agent because of a high phosphorus recovery rate (ca. 70–99%) and no additional by-product. On the other hand, the extraction with sulfuric or hydrochloric acid, leads to the formation of $CaSO_4$ and $CaCl_2$ (Gorazda et al., 2012; Wzorek et al., 2006). Another advantage of using phosphoric acid is obtaining extracts with high phosphorus concentration. As a result, these products can be suitable for phosphate fertilizer production.

The same acids or their combination are used in RecoPhos and Tetra-Phos processes (Egle et al., 2016). The RecoPhos technology uses industrial grade phosphoric acid (52%H_3PO_4) to produce a product similar to triplesuperphosphate, with water-soluble calcium or magnesium phosphate (RecoPhos® P38 product) and 16.6% of P. However, this process is only applicable for high quality ash with low heavy metal content due to the lack of a decontamination step. In Tetra-Phos process developed by Remondis, working in pilot-scale in Hamburg, diluted phosphoric acid, nitric acid or their mixture (70% H_2O, 15% HNO_3 and 15% H_3PO_4) is used for phosphorus recovery. The solution is enriched with the phosphate from the ash and after-filtration step is treated in four different stages. At the first stage after addition of sulfuric acid, gypsum is separated. At the second stage the filtrate can be recycled to the first stage or neutralized with CaO to produce $Al(OH)_3AlPO_4$, separated by filtration. The filtrate rich in phosphoric and nitric acid can be recycled to the first step or concentrated by evaporation. Following addition of CaO and evaporation leads to calcium phosphate precipitation and crystallization of calcium nitrate (Lehmkuhl, 2015). Various products are available at the end of the process including phosphoric acid (RePacid®) used to produce phosphates for manufacturing of fertilizers, gypsum, as well as iron and aluminum salts. There are some questionable aspects of Tetra-Phos process like calcium removal at the first stage and calcium addition at the third one, as well as aluminum compounds utilization since they are produced in the form which is unsuitable for sewage treatment plants or gypsum generation. Therefore in the investigated PolFerAsh technology only phosphoric acid or nitric acid was used as a leaching solution to dissolve phosphorus compounds from SSA and achieve high phosphorus recovery rate without additional purification of leachates. It can be achieved by operating in the low concentrated acids solutions and proper solid to liquid phase composition.

Moreover, the leachates contain metals such as Fe, Cr, Mo, Mn or Cu, which are valuable micronutrients and are required for proper plant growth (Gorazda et al., 2012; Nanzer et al., 2014). However,