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Sewage sludge ash – A promising secondary phosphorus source for fertilizer production

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HIGHLIGHTS

- Direct use of sewage sludge ashes (SSA) as fertilizer often not possible
- New approach of SSA treatment aiming at P-fertilizers with high P-bioavailability
- Comparison of different Na- and K-bearing additives for the thermochemical process
- Evaporation of As, Cd, Hg, Pb and Zn at 950 °C under reducing conditions
- Results of a demonstration trial for fertilizer production from SSA

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ABSTRACT

Sewage sludge incineration is extensively practiced in some European countries such as the Netherlands, Switzerland, Austria and Germany. A survey of German sewage sludge ash showed that the recovery potential is high, approx. 19,000 t of phosphorus per year. However, the survey also discovered that the bioavailability of phosphorus in the sewage sludge ash is poor and that more than half of the ashes cannot be used as fertilizers due to high heavy metal content. A new thermochemical process for sewage sludge ash treatment was developed that transforms the ash into marketable fertilizer products. Sewage sludge ash was thermochemically treated with sodium and potassium additives under reducing conditions, whereby the phosphate-bearing mineral phases were transformed into plant available phosphates. High P-bioavailability was achieved with a molar Na/P ratio > 1.75 in the starting materials. Sodium sulfate, carbonate and hydroxide performed comparably as additives for this calcination process. Potassium carbonate and -hydroxide have to be added in a molar K/P ratio > 2.5 to achieve comparable P-solubility. The findings of the laboratory scale investigations were confirmed by an industrial demonstration trial for an ash treatment with sodium sulfate. Simultaneously, the volatile transition metal arsenic (61% removal) as well as volatile heavy metals such as cadmium (80%), mercury (68%), lead (39%) and zinc (9%) were removed via the off-gas treatment system. The product of the demonstration trial is characterized by high bioavailability and a toxic trace element mass fraction below the limit values of the German fertilizer ordinance, thus fulfilling the quality parameters for a P-fertilizer.

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1. Introduction

More than 30 million tons of sewage sludge are produced annually in the world's developed countries, with an increasing trend (UN-Habitat, 2008). The main disposal routes include applications in agriculture or landscaping, incineration and landfilling (Kelessidis and Stasinakis, 2012). The utilization of different disposal pathways for sewage sludge differs strongly from country to country in the EU (Milieu Ltd., 2010). The direct use in agriculture is controversial because sewage

sludge as a sink for pollutants in waste water treatment plants is often contaminated with heavy metals and organic contaminants (e.g., pharmaceuticals and personal care products), which are a focus of discussion (Zuloaga et al., 2012). Eliminating the organic pollutants present in sewage sludge is possible by incineration, either by mono-incineration or co-incineration (e.g., the cement industry, municipal waste incineration and power plants). The Netherlands and Switzerland incinerate their total amount of sewage sludge (Binder et al., 2009; CBS Statistics Netherlands, 2015). Germany is one of the countries with a relatively high proportion of incineration with 55% (Destatis, 2013). Nearly half of the incineration takes place in 26 mono-incineration facilities that solely incinerate sewage sludge

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(Lehrmann, 2013). In this case, sewage sludge ash (SSA) is produced. It has a concentrated mineral fraction and has gained interest as a secondary resource for phosphorus. The utilization of phosphorus from SSA could replace phosphate rock-based products and reduce EU dependence on phosphorus imports. Until now the EU completely depends on imports because there are no significant phosphate rock deposits in Europe (USGS, 2014). Furthermore, phosphate rock and rock-based P-fertilizers are in many cases contaminated with heavy metals that may pollute farmlands, such as Cd and U (Dissanayake and Chandrajith, 2009; Römer et al., 2010).

To determine the resource potential of SSA, a complete survey (2011/2012) of German sewage sludge ash was conducted with the focus on phosphorus (P) and other critical raw materials (EU Commission, 2014; Krüger et al., 2014). In Germany, approx. 300,000 t/a SSA accrues, containing 19,000 t/a of phosphorus, which is equivalent to approx. 13% of P applied in the form of mineral fertilizer in German agriculture (Krüger and Adam, 2015). If SSA is to be used for fertilizer production, it has to comply with the limit values stipulated by the German fertilizer ordinance and with the high bioavailability of P in conventional mineral fertilizers such as triple superphosphate (TSP). The bioavailability of P can be estimated by the solubility of P in neutral ammonium citrate (P_{NAC}), mostly given as a fraction of the total P-content (P_{NAC} -solubility). TSP is completely soluble in neutral ammonium citrate (Severin et al., 2014). The mean P_{NAC} -solubility of German SSA is very low (31% of total P), indicating that untreated SSA is not suitable as a fertilizer (Krüger and Adam, 2015). Furthermore, the mass fraction of heavy metals partly exceeds the limit values of the German fertilizer ordinance. For example, the mean values of all samples in the German survey of Pb (151 mg/kg) and Ni (106 mg/kg) are above the respective limit values (150 mg/kg for Pb and 80 mg/kg for Ni) of the German fertilizer ordinance (Düngemittelverordnung, 2012; Krüger et al., 2014). For this reason, the variation of the heavy metal mass fractions of different incineration facilities over the monitoring time period are discussed in this article to identify the real need for heavy metal removal. It is important to determine whether SSA has to be treated prior to fertilizer production to decrease these element mass fractions.

Several processes targeting P-recovery from SSA were developed in the past. Extraction of P by acids is one of the extensively investigated approaches. The major challenge is the separation of metals that are also leached by acids and the precipitation of P in desired bioavailable chemical forms. High amounts of acids are required for leaching and the amount of wet solid residues for disposal is higher than the amount of SSA that was treated. An excellent review about the wet chemical approaches was published by Petzet et al. (2012). Furthermore, phosphorus can be recovered by high temperature metallurgical processes. Processes were developed that transfer phosphorus into a metallurgical slag by reductive smelting at temperatures above 1450 °C in a shaft furnace (Scheidig, 2009) or that reduce phosphorus to elemental phosphorus that is separated via the gas phase in an inductively heated shaft furnace at similar temperatures (Schönberg et al., 2014). In both cases, volatile heavy metals such as Zn, Pb, Cd and Hg are separated from the product via the gas phase, and heavy metals with high boiling points such as Fe, Cu, Ni and Cr are separated in the form of an alloy.

Another approach for SSA treatment targeting P-recovery is thermochemical treatment below the melting point of SSA. This approach is the focus of this article. In contrast to the wet chemical approaches that extract P from the ash, thermochemical processes target metal removal from SSA and transformation of the P-bearing mineral phases into plant available forms. A P-recovery process was developed within the framework of the European FP6-project SUSAN (www.susan.bam.de, 2005–2008), which separates heavy metals in the form of the respective chlorides via the gaseous phase at temperatures of approx. 1000 °C in a rotary kiln (Adam et al., 2009). Simultaneously, new phosphates such as magnesium and magnesium calcium phosphates are formed. The process was already successfully tested on an industrial scale in Leoben, Austria (Mattenberger et al., 2008, 2010). However, the fertilizing

performance of the product was not satisfying for all types of soils. The fertilizing effect was comparable to that of TSP on acidic soil, but it was less efficient on alkaline soil. This result was consistent with the relatively low P_{NAC} -solubility of only 30–40% (Nanzer et al., 2014). The limited bioavailability of this fertilizer raw material was the reason for further research activities that focused on new P-bearing mineral phases with high P-efficiency regardless of the pH of the soil. Sodium calcium phosphate ($NaCaPO_4$) is well known from the Rhenania process. This process was applied for P-fertilizer production mainly in the first half of the 20th century (Werner, 1967). The basis of the Rhenania phosphate process was calcination of phosphate rock with sodium carbonate. Analogous to this process, a thermochemical treatment for SSA was developed that produces bioavailable phosphates and reduces the content of heavy metals (Stemann et al., in press).

In this article the contamination of German SSA with heavy metals is discussed in the context that SSA could be used to substitute or complement phosphate rock based mineral fertilizers. SSA or fertilizers based on SSA must comply with the respective fertilizer ordinances and with market requirements. The newly developed thermochemical process presented in this article targets products that meet these requirements. The applicability of the process was demonstrated in an industrial scale trial.

2. Material and methods

2.1. Materials

A total of 24 of 26 German mono-incineration facilities took part in the survey, altogether providing 252 SSA samples. In most cases, a period of one year was covered with 12 samples. The facilities were numbered from 1 to 26 according to an internal system for anonymization. Facilities 10 and 24 did not take part in the survey. Only one sample was available from facilities 18 and 21, respectively. Thus, variations in mass fractions over time could not be evaluated for SSAs from these facilities. Detailed information about the samples from each facility is in Krüger and Adam (2014) and Krüger et al. (2014).

The SSA for laboratory scale calcination experiments and the demonstration trial was taken from mono-incineration facility 14. This SSA originated from the incineration of municipal sewage sludge and can be classified as suitable for P-recovery due to its relatively high P content of 9.4%. Dried sewage sludge (SS) was pulverized to a particle size of <500 µm for muffle furnace experiments. Elemental compositions of SSA and SS are displayed in Table 1. Sodium sulfate technical reagent grade for the demonstration trial was acquired from Cordenka GmbH & Co KG Obernburg, Germany. For laboratory scale experiments, sodium carbonate (Na_2CO_3) was acquired from Merck, potassium sulfate (K_2SO_4) from Sigma-Aldrich, potassium hydroxide (KOH) and sodium hydroxide (NaOH) from AppliChem, sodium sulfate (Na_2SO_4) and potassium carbonate (K_2CO_3) from Fischer Scientific.

2.2. Analysis

All samples in the survey were dried, ground and homogenized before analysis. 0.1 g ± 0.1 mg of SSA or thermochemically treated ash was weighed, mixed with 4 mL of concentrated nitric acid (HNO_3), 1.5 mL perchloric acid ($HClO_4$), and 0.5 mL hydrofluoric acid (HF) and digested in a microwave (mikroPrepA, MLS GmbH, Leutkirch, Germany). Excess HF was complexed with 2.5 mL of cold saturated boric acid (HBO_3). Independent digestions were prepared for ICP-OES (inductively coupled plasma optical emission spectroscopy) and ICP-MS (inductively coupled plasma mass spectrometry). Additional information on the analysis, quality assurance, and the results of the survey can be found in Krüger et al. (2014) and Krüger and Adam (2015).

The total digestion was developed during the monitoring survey for SSA. The survey was aimed to determine the composition of German SSA as accurately as possible. Thus perchlorid/hydrofluoric acid digestion was used to achieve a complete dissolution of the SSA samples. It

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