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Extracting phosphorous from incinerated sewage sludge ash rich in iron or aluminum

Lisbeth M. Ottosen *, Gunvor M. Kirkelund, Pernille E. Jensen

Department of Civil Engineering, Building 118, Technical University of Denmark, 2800 Lyngby, Denmark

HIGHLIGHTS

- Two sewage sludge ashes rich in Fe or Al are characterized and acid washed.
- Fe for P-precipitation during waste water treatment ease P recovery from the ash.
- Heavy metals are extracted simultaneous to P.
- Extraction in H_2SO_4 result in significant formation of gypsum crystals.

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ABSTRACT

Ashes from mono-incineration of sewage sludge (ISSA) generally contain high concentrations of phosphorous (P) and can be regarded as secondary P resources. ISSA has no direct value as fertilizer as P is not plant available. The present paper experimentally compares P extraction in acid from two different ISSAs; one rich in Al (67 g/kg) and the other in Fe (58 g/kg). The difference related to P precipitation at the waste water treatment facilities. Another major difference between the ashes was that flue gas purification products were mixed into the first ash and it contained about 5% activated carbon. The Al rich ash had a significantly higher buffering capacity and required more acid for extraction of P. When acid extraction of P from ISSA is the method for recovery, it is thus beneficial to go back to the waste water treatment facility and e.g. choose Fe for P precipitation rather than Al.

Formation of a high amount of gypsum crystals in both ashes after extraction in H_2SO_4 was seen by SEM–EDX. H_2SO_4 is the cheapest mineral ash, but the gypsum formation must be taken into account when either finding possibility for using the remaining ash in e.g. construction materials or if the choice is deposition, as the gypsum increases the volume significantly.

1. Introduction

Phosphorus is an essential and irreplaceable, yet limited resource. This is why efforts increase to recycle phosphorous contained in wastewater (Cornel and Schaum, 2009). Sewage sludge from waste water treatment generally contains appreciable amounts of N and P, but during water and sludge treatment, N may escape as gaseous compounds whereas the P is entirely retained in the sludge (Huang and Shenker, 2004). Sewage sludge has been widely applied to agricultural land, but limit values for pollutants in both EU (Council Directive 86/278/EEC) and at national levels e.g. in Denmark (BEK 1650, 2006) restrict this direct use.

Sewage sludge incineration is a well proven technology with hundreds of plants worldwide (Werther and Ogada, 1999). Incineration results in a mass reduction, but also in a concentration of heavy metals. On a dry matter basis the heavy metal content in the ash following incineration increase considerably compared to the feed sludge (Lapa et al., 2007; Donatello et al., 2010c). The concentration of P in ISSA is generally 5–10% per weight (Cyr et al., 2007). ISSA is thus a potential secondary resource for P, and this paper focus on P recovery. Considerable literature is published on the use of ISSA in construction materials (e.g. in cementitious material, bricks or lightweight aggregates) (see Donatello, 2009 for review), but none of these applications make use of the valuable P resource in the ISSA.

The P in ISSA is not plant available. The gain in crop yield when spreading the ash directly is consequently limited. Development of different techniques for P recovery from ISSA is ongoing. Recovery by particle separation is not possible (Franz, 2008), and dissolution from ash particles is necessary. The techniques for this are either thermal separation or wet chemical treatment followed by a separation step (Cornel and Schaum, 2009).

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* Corresponding author. Tel.: +45 45252260; fax: +45 45883282.
E-mail address: lo@byg.dtu.dk (L.M. Ottosen).

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The present paper deals with acid extraction for P recovery. The characteristics of ISSA vary depending on the socio-economic nature of the catchment area, type of sludge incinerated and sludge pretreatment process (Donatello, 2009). During waste water treatment different precipitating agents are used to retain P to avoid eutrophication of surface waters. These precipitating agents are often Al-, Fe or Ca-rich compounds, reacting with P to precipitate stable phosphates in the sludge. This paper focuses on the influence of Al and Fe used in the waste water treatment process on the characteristics of the ISSA and on extraction of P by acid. Experimental work is conducted with two ashes. The obtained knowledge may be used when operating waste water treatment plants in order to produce ISSA from which the P recovery consumes least acid, thus benefitting the recovery.

2. Experimental

2.1. Sewage sludge ashes for experiments

ISSAs from two Danish mono-incineration plants were used. In both the sludge was incinerated in a fluidized bed combustor at about 850 °C. The sewage sludge incinerated was from urban wastewater in both cases. The two ashes differ in the chemicals originally used for P precipitation during waste water treatment and in the ash collection systems at the incineration plants.

- *MAl*: Mølleåværket Renseanlæg Lundtofte incinerates sludge from wastewater treatment from 1,35,000 PE. P was precipitated with Al. The ash was a mixture of ash from a multicyklon and flue gas purification products. The flue gas purification system was treatment with sodiumbicarbonate and activated carbon.
- *AFe*: Spildevandscenter Avedøre, Hvidovre, incinerates wastewater sludge from about 3,30,000 PE. P was precipitated with Fe. The ash from electrofilters was mixed with flue gas neutralization products (lime) from bag filters.

After sampling, the ashes were stored in closed plastic containers at room temperature.

2.2. Ash characterization

Characterization and extraction experiments were made with dried ash (105 °C, 24 h). Concentrations of P, Al, Fe, Na, Cu, Cd, Ni, Pb and Zn were measured after pre-treatment of the ash in accordance to DS259; 1.0 g ash and 20.0 ml (1:1) HNO_3 was heated at 200 kPa (120 °C) for 30 min. Filtration through 0.45 μm filter and the concentrations were measured with ICP–OES. Ash pH was measured by suspending 10.0 g ash in 25 ml distilled water. After 1 h agitation pH was measured directly in the suspension. Loss on ignition (LoI) was found after 30 min at 550 °C. Water content was measured as weight loss after 24 h at 105 °C (calculated as weight loss over the weight of the wet sample). Five duplicates of each of these analyses were made. Grain size distribution was determined with laser diffractometry. Solubility in water was evaluated: 50.0 g ash suspended in 500 ml distilled water and agitated for 1 min. After settling the water was decanted. New 500 ml distilled water added. This was repeated so the ash was washed three times. Finally the suspension was filtered and the ash dried and weighed. The gas production after suspension in 10% HNO_3 was measured with a volumetric calcimeter method.

Morphology and element distribution analysis was performed by SEM–EDX. No pre-treatment of the samples was made. The accelerating voltage of the SEM was 20–25 kV with large field detector and X-ray cone. Major element content was determined by X-ray fluorescence (XRF).

2.3. Acid extraction

Extractions were made in HNO_3 and H_2SO_4 with different aims. Extractions in HNO_3 show the direct pH dependent extraction. H_2SO_4 is cheapest mineral ash and thus relevant for P extraction in industrial scale. In H_2SO_4 extractions, however, there is a risk for precipitation of different sulfates and the actual extraction as a result of lowering pH of the elements forming sulfates cannot be evaluated.

2.3.1. pH dependent extraction in HNO_3 of various elements

To examine the pH dependent extraction of P, Al, Fe, Na, Cu, Ni, Pb and Zn from the ashes, the following procedure was used: 10.0 g dry ash and 50 ml HNO_3 in various concentrations (from 0.01 M to 1.5 M) were suspended for 1 week. The suspensions were filtered (0.45 μm). The concentrations were measured in the liquid phase with ICP–OES. Each extraction was made in duplicate. Extractions in distilled water were made as reference.

2.3.2. Extraction in H_2SO_4 for P recovery

Extractions were made in different acid concentrations and L:S ratios to create a range of different pH environments in which the solubility of P and other elements can be monitored. Extractions in H_2SO_4 were made for 2 h or 1 week (all as double determinations) in 0.19 M H_2SO_4 at liquid to solid ratios (L:S) of 2, 5, 10 and 20. Extractions were also made in H_2SO_4 for 2 h in 0.08 M H_2SO_4 and 0.28 M H_2SO_4 at L:S of 2, 5, 10 and 20. Conductivity and pH were measured in the suspensions. The suspensions were filtered (0.45 μm) and the filtrate saved for ICP–OES analysis (Cu and P). The ash at the filter paper was flushed with distilled water under vacuum. The water was discharged and the ash dried and saved for SEM–EDX analyses.

3. Results and discussion

3.1. Chemical characterization of ashes

Results from the ash characterization are shown in Table 1. Both ashes are secondary resources for P as they contain 7% and 10% per weight. A much higher Fe concentration was found in AFe than in MAl whereas the Al concentration was highest in MAl. The mutual distribution underlines the use of chemicals during waste water treatment. The Na concentration was much higher in MAl than in AFe, which was related to use of sodium bicarbonate to neutralization the flue gas.

The LoI was very low in AFe (0.2%) revealing good incineration. This LoI was lower than in seven English ISSA (between 0.9% and 2.1%), which were characterized in (Donatello, 2009). The LoI in MAl (5.7%) was on the contrary higher than in these ashes. During extraction experiments with MAl small, black particles were floating. These contributed to about 6% of the total weight, corresponding well to the LoI. These black particles may be activated carbon from the flue gas purification process.

Both ashes were alkaline (pH about 10). Apart from this, they were reacting differently when suspended in water or acid. MAl was most reactive. The solubility in water of MAl was almost 10 times higher. The conductivity measured in an ash suspension in water was likewise higher (about 20 times). Further the production of gas when reacting with acid was about 10 times higher from MAl than AFe.