Phosphorus Recovery from Sewage Sludge Ash – A Wet Chemical Approach

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Abstract: In laboratory-scale experiments with ashes from different full-scale sludge incineration plants the elution behaviour of phosphorus and metals at different pH-values were examined. The elution of ashes with water alone did not cause any significant release of phosphorus, while depending on the ash origin and formation, a phosphorus release of maximum 30% was measured when using sodium hydroxide solution. With sulphuric acid, it was possible to release phosphorus and (heavy) metals quantitatively at pH-values less than 1.5. In addition to the elution experiments, precipitation and nanofiltration were investigated as methods for the separation of phosphorus and metals from the liquid phase. Sequential precipitation of phosphorus (SEPHOS Process) seems to be promising. The generated product, an "aluminium phosphate", is a valuable raw material for the phosphorus industry. After alkaline treatment of the "aluminium phosphate", it is possible to precipitate phosphorus as calcium phosphate (advanced SEPHOS Process). Following acidic elution of the ash, nanofiltration can also be used to separate phosphorus.

Keywords: Nutrient Recovery, Phosphorus, Sewage Sludge Ash

INTRODUCTION

In view of the limited resources of phosphorus and the rising concern about the sustainability of wastewater and sludge treatment, the recovery of phosphorus from wastewater, sewage sludge and sludge ash is a promising approach.

The phosphorus load into German municipal wastewater treatment plants (WWTP) has been decreasing continuously, mainly because of the use of phosphate-free detergents. At present, the phosphorus load amounts to between 1.6 and 2.0 g P/(PE × d), resulting in phosphorus influent concentration of 8 to 10 mg/l at 200 l per person and day. The effluent limits are 1 - 2 mg/l for most plants, depending on their size. This amounts to 0.2 - 0.4 g P/(PE × d). Thus, about 90% of the phosphorus must be eliminated in the WWTP.
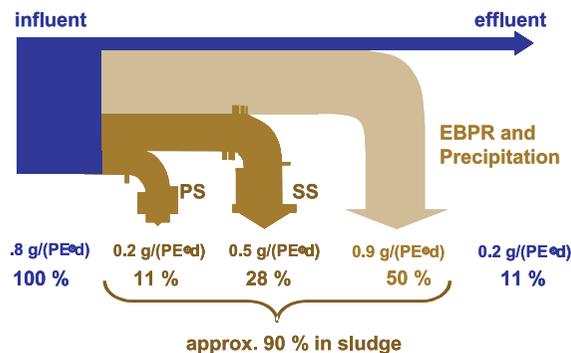

Figure 1. Phosphorus balance for a typical WWTP in Germany (PS: Primary Sludge; SS: Secondary Sludge (surplus sludge); PE: Population Equivalent)

Figure 1 shows the phosphorus balance for a typical wastewater treatment plant in Germany. Approximately 11 % of the phosphorus is separated by the primary sludge (PS) and 28% by the secondary (surplus) sludge (SS) without any specific phosphorus removal. Thus, approximately 50% of the phosphorus has to be eliminated by means of enhanced biological phosphorus removal (EBPR), precipitation, or other phosphorus-removal techniques. With the generally applied EBPR and/or precipitation techniques, 90% of the incoming phosphorus ends in the sewage sludge. It seems worthwhile to develop methods for the separation of phosphorus from sludge, or, taking into account the future development towards sludge incineration, for extracting phosphorus from the ash (Jardin, 2002; Schaum et al., 2004).

MATERIAL AND METHODS

Origin and Composition of the Sewage Sludge Ashes

15 samples of sewage sludge ash were selected from mono incineration plants in Germany and European countries. All investigated samples were random samples, made anonymous as ash #A to #O.

Figure 2 shows the percentage distribution of the main components of the tested ashes in a box-plot diagram. The length of the boxes defines the range, to which 50% of all values belong. The average phosphorus content is about 16% P_2O_5. The comparison indicates that iron oxide and calcium oxide show a larger range within the 25 to 75 percentile than aluminium oxide.
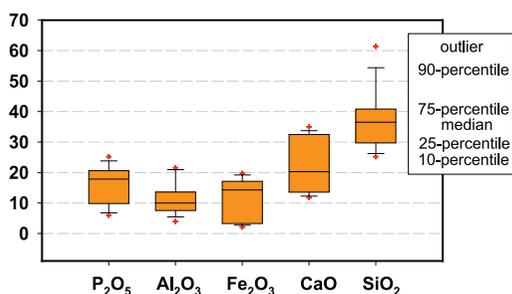

Figure 2. Distribution of the main components of sewage sludge ash as box-plot diagram

Figure 3 presents a three-phase diagram of calcium oxide, iron oxide and aluminium oxide. The diagram shows the percentage distribution of these components in the ash samples, i.e. the sum of calcium oxide, iron oxide and aluminium oxide is 100% for each sample. Following the diagram, two types of ashes can be identified with reference to aluminium and iron concentrations:

- *"**aluminium ash**"* - This ash is defined by its high aluminium content ($Al_2O_3 > 35\%$) combined with a low iron content ($Fe_2O_3 < 10\%$), as can also be seen in the greyish ash colour.

- *"**iron ash**"* - This ash is defined by its high iron content ($Fe_2O_3 > 25\%$), as can also be seen in the reddish brown ash colour.

In all ash samples, the content of calcium oxide (CaO) is between 30% and 70%, whereby iron oxide as well as aluminium oxide vary across this range.
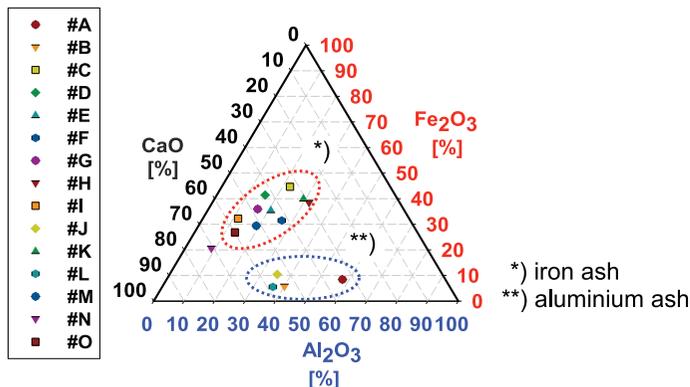
Figure 3. Three-phase diagram of calcium oxide, iron oxide and aluminium oxide in samples of sewage sludge ash, and their characteristic colouring

Thermal Treatment of Mixtures of Pure Substances

In order to investigate the transfer of aluminium, phosphorus and calcium, the following mixtures of pure substances were heated in a muffle furnace at T_{max} = 500, 700 and 900 °C:

- **"mixture A"** 10 g aluminium phosphate, 5 g calcium carbonate and 20 g silicon dioxide
- **"mixture B"** 10 g aluminium phosphate, 10 g calcium carbonate and 20 g silicon dioxide

By varying the calcium content, the influence of calcium on the transfer of phosphorus was to be determined. The reaction time at T_{max} was 2 h each. Following the thermal treatment, elution with hydrochloric acid and analyses of the dissolved substances were carried out.

Elution Tests

In order to maximize the stability of the pH-value, elution tests with hydrochloric acid, cf. DIN 38414-4 1984, were carried out. The concentrations of the hydrochloric acid were 0 - 0.031 - 0.063 - 0.125 - 0.25 - 0.5 - 0.75 - 1.0 - 1.5 - 2.0 mol HCl/l, whereby deionised water was used for "zero concentration".

The ratio of ash to elution solvent was 1:10 (cf. DIN 38414-4 1984). In order to achieve a constant pH-value, the samples - transferred to plastic bottles - were treated in an overhead stirrer at room temperature overnight. Following sedimentation and filtration (0.45 m Schleicher & Schuell ME 25), the pH-value was measured (Mettler Toledo Inlab 1003 electrode and WTW pH 197), and the dissolved substances were analysed via ICP-OES (DIN EN ISO 11855, 1998). In addition to the acidic elution, an alkaline elution was carried out, using a 1 mol/l sodium hydroxide solution.

Separation of Phosphorus and Metals via Sequential Increase of the pH-value

Following the acidic elution with 1 mol/l sulphuric acid, the pH-value is gradually increased by means of a 10 mol/l sodium hydroxide solution. The results are precipitation reactions. A fully-automatic, computer-controlled titration unit (Metrohm, Type MPT-Titrino 798 with a Profitrode) was used to adjust the pH-value. After precipitate separation and filtration (0.45 m Schleicher & Schuell ME 25) the dissolved substances were analysed via ICP-OES (DIN EN ISO 11855, 1998).

Separation of Phosphorus and Metals via Nanofiltration

The separation of phosphorus from ash eluate was tested in a stirred cell, using a phosphorus selective solution-diffusion membrane (Membrane Desal 5 DK made by Osmonics). Sulphuric as well as nitric acid were used to produce the ash eluate. At regular intervals, permeate samples were taken, which were tested for dissolved substances via ICP-OES (DIN EN ISO 11855, 1998).

RESULTS AND DISCUSSION

Thermal Treatment of Mixtures of Pure Substances

Figure 4 shows the release rates of aluminium, calcium and phosphorus, with different incineration temperatures and different ratios of phosphorus to calcium (mixture A and B). By increasing the incineration temperature, the release of aluminium decreased, using acidic as well as alkaline elution. The release of phosphorus by temperature increase changed significantly only in case of alkaline elution. An increase of the percentage of calcium (mixture B) in combination with alkaline elution results in decreasing release rates of phosphorus, dropping to < 1% at 900°C. In contrast, with acidic elution the release of phosphorus is almost 100%, irrespective of temperature and calcium content.
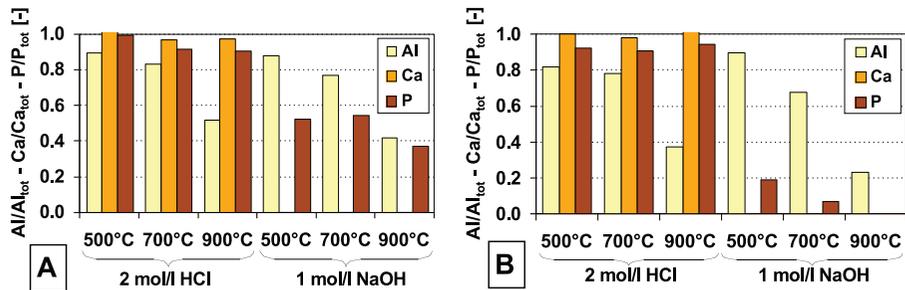

Figure 4. Release of aluminium, calcium, and phosphorus in mixtures of pure substances (aluminium phosphate, calcium carbonate, silicon dioxide), after thermal treatment at 500, 700, and 900 °C; mixture A: $P_{tot}/Ca_{tot} \approx 1\,½$ [mol/mol]; mixture B: $P_{tot}/Ca_{tot} \approx ¾$ [mol/mol]

Investigations of sewage sludge ashes by Schirmer (1998) using x-ray diffractometry showed, that through incineration the crystalline structures quartz, hematite (Fe_2O_3), whitlockite ($Ca_3(PO_4)_2$) and anorthite ($CaAl_2Si_2O_8$) dominate. The results of incineration tests with pure substances by Schirmer (1998), using a mixture of aluminium phosphate, calcium carbonate and quartz, confirmed the formation of calcium phosphate and anorthite. Through the incineration of a mixture of iron phosphate and calcium carbonate, he could also prove evidence of the formation of calcium phosphate and hematite. He identified whitlockite as well as hydroxylapatite ($Ca_5(PO_4)_3OH$) and assumed that incineration conditions affects the formation.

The change in solubility behaviour, which was shown in the experiments, confirmed the investigations by Schirmer (1998). Aluminium oxides hardly soluble in acids are formed during the thermal treatment of mixtures of aluminium phosphate, calcium carbonate and silicon dioxide. At the same time, the dissolution behaviour of phosphorus and calcium suggests that transfer of phosphorus occurs and calcium phosphate is formed. This phenomenon is affected by the incineration temperature and the ratio of phosphorus to calcium. It is important to note that calcium phosphate is soluble only in acids, cf. Stumm und Morgan (1996).

Elution Tests

The results of elution tests with sewage sludge ash indicate that with pH-values < 1.5, it is possible to release phosphorus almost completely, irrespective of the type of ash (aluminium ash or iron ash) and despite the fact of limited release of aluminium and iron (cf. Figure 5). Thereby, the limited release rates of aluminium and iron confirm the assumption that oxides of low solubility are formed as well as calcium phosphate during sewage sludge incineration.
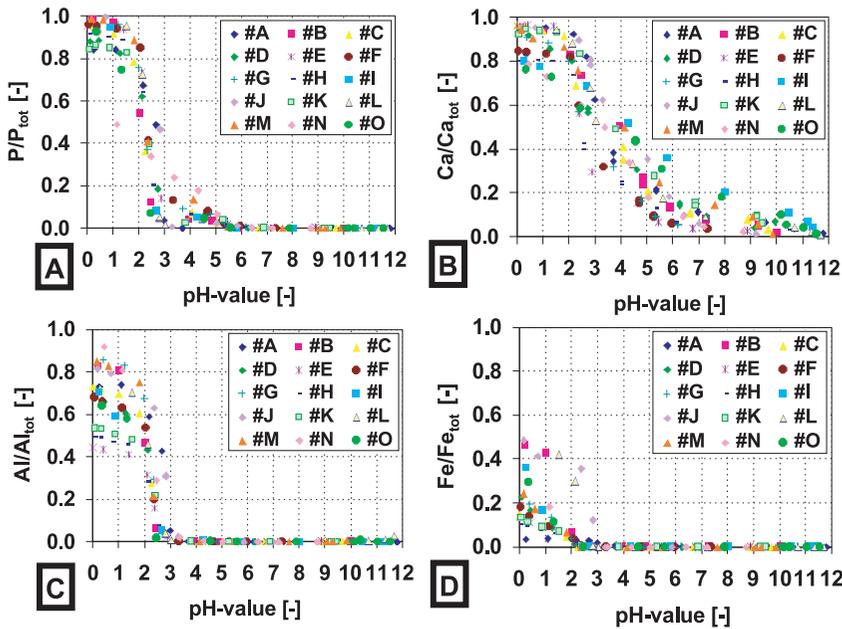
Figue 5. Release of phosphorus, calcium, aluminium and iron from sewage sludge ash at different pH-values; elution of the ashes #A - #O with HCl
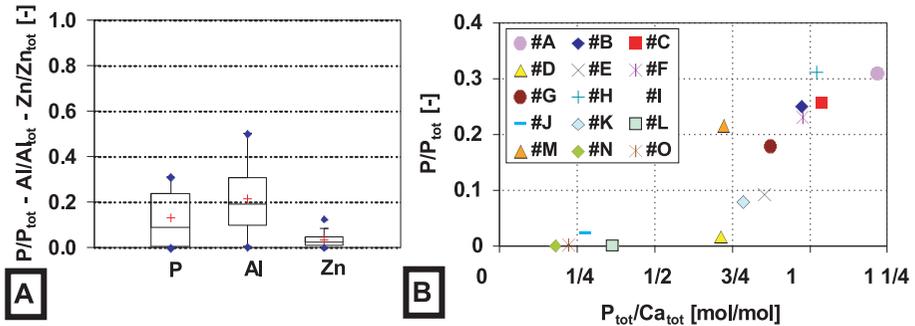

Figure 6. A: Release of phosphorus, aluminium and zinc after elution of sewage sludge ash (ashes #A - #O) with 1 mol/l sodium hydroxide solution, presentation as box-plot diagram; B: release of phosphorus as a function of the calcium content of the ash

Figure 6 shows that with alkaline elution the release of phosphorus is limited. An average release rate of merely about 10% (P_{tot} based) was observed, ranging from < 1 minimum to 30% maximum. Furthermore, ashes with low calcium concentrations, i.e. large ratio of P_{tot} to Ca_{tot}, lead to a higher release rate of phosphorus (cf. Figure 6). Analogue to the tests with pure substances, the results of alkaline elution of sewage sludge ashes show a higher release of phosphorus in those ashes with low calcium concentrations.

In order to summarise the results of phosphorus, calcium, aluminium and iron release, the process is described mathematically. The release process of phosphorus and calcium against the pH-value can be described by the general formula for the release of metal hydroxides according to Sposito (1984):

According to Sposito (1984): $$\frac{P}{P_{tot}}; \ \frac{Ca}{Ca_{tot}} = \frac{1}{1 + e^{a + b \cdot pH}} \qquad \text{(Eq. 1)}$$

The non-linear regression showed that, using a correlation coefficient of $R^2 > 0.9$, Eq. 1 is a good approach to describe the release behaviour of phosphorus and calcium. In order to map the significant increase in aluminium release between pH-values 3 and 2, Eq.1 was modified:

$$\text{Adaptation for the release of aluminium:} \quad \frac{Al}{Al_{tot}} = c \cdot \frac{1}{1 + e^{a + b \cdot pH}} \qquad \text{(Eq. 2)}$$

In case of iron, no adaptation was possible neither with Eq. 1 nor Eq. 2 using a correlation coefficient of $R^2 > 0.9$. In both cases the correlation coefficient $R^2 = 0.5$. Figure 7 shows the release of phosphorus, calcium, aluminium and iron from sewage sludge ash against the pH-value. Thereby, the ash type (aluminium or iron ash) has hardly any influence on the release behaviour.
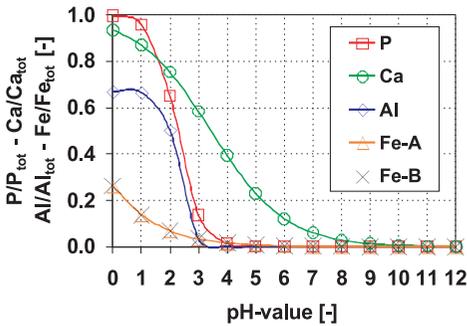

Figure 7. Release of phosphorus (Eq. 1), calcium (Eq. 1), aluminium (Eq. 2) and iron (Fe-A: Eq. 1, Fe-B: Eq. 2) from sewage sludge ash against the pH-value after non-linear regression

Separation of Phosphorus and Metals via Sequential Increase of the pH-value

Following the acidic ash treatment (pH-value 1.5), the pH-value of the filtrate was increased step-wise by adding sodium hydroxide solution. Figure 8-A shows the concentration of aluminium, iron and phosphorus against the pH-value. Both aluminium and phosphorus dissolve in acidic as well as alkaline environment. Thereby, the run of the curves is very similar. It is assumed that by increasing the pH-value an amorphous aluminium phosphate precipitates at pH-values 3 - 4, which releases in alkaline environments.
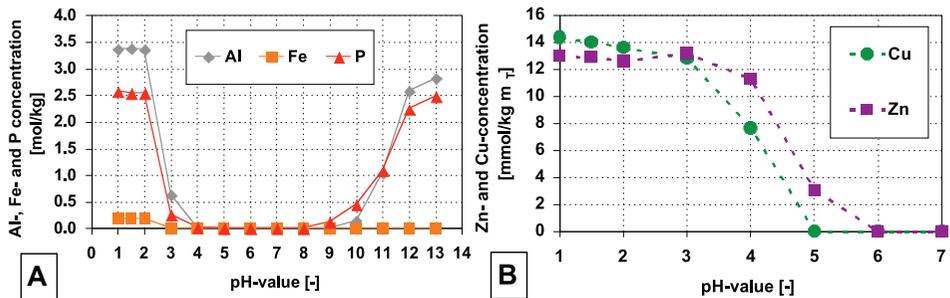

Figure 8. Sequential precipitation by increasing the pH-value (following the elution with 1 mol/l H_2SO_4), ash #A, A: aluminium, iron and phosphorus concentrations against pH-value, B: copper and zinc concentrations against pH-value

Analogous to Figure 8-A, in Figure 8-B the concentrations of zinc and copper against the pH-value are illustrated. The run of the curves shows that the heavy metals remain mainly in solution at pH-values between 2 and 3. Due to this phenomenon, it is possible to produce a heavy-metal depleted precipitate by keeping the pH-value below 3.5.

Based on the investigations presented above, the so-called **SEPHOS Process - *Sequential Precipitation of Phosphorus*** was developed, cf. Cornel et al. (2004, 2006), Schaum et al. (2005). First, sewage sludge ash is eluted with sulphuric acid. After removing the undissolved residues, the ph-value of the filtrate is increased, thus inducing precipitation reactions. Finally, the phosphate-rich and heavy-metal depleted precipitate can be reused elsewhere.
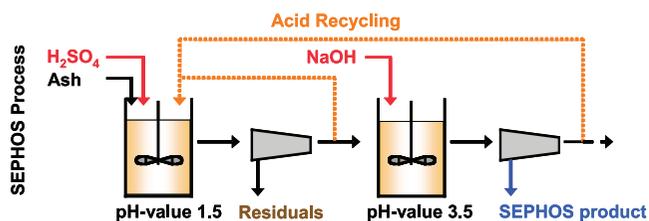

Figure 9. **Flow diagram of the *SEPHOS Process* (Schaum et al., 2005)**

Through alkaline treatment of the precipitate, phosphorus can be separated as calcium phosphate, and aluminium can be reused as precipitant, cf. ***Advanced SEPHOS Process*** (Schaum et al., 2005).

Separation of Phosphorus and Metals via Nanofiltration

The investigations using a stirred cell indicated that nanofiltration is a suitable method for phosphorus separation (Niewersch et al., 2007). In case of ash #C, about 50% of the phosphorus passed the membrane. Thereby, sulphuric acid as well as nitric acid were used for elution. With polyvalent ions, such as aluminium, iron, calcium and zinc more than 98% were retained by the membrane, cf. Table 1. Only sodium, i.e. as monovalent ion, passed the membrane. For charge balance, the anions chloride, sulphate, and nitrate, for the most part, could pass the membrane.

The results of the stirred-cell tests show, that it is possible to separate phosphorus selectively by nanofiltration. Thereby, it can be expected that advancements in membrane technology will increase the membrane permeability for phosphorus. In order to allow the implementation of nanofiltration as a suitable method for phosphorus recovery, it is necessary to remove the solids from the ash eluate, e.g. by pre-stage microsieving. An operational pressure of 60 - 70 bar was necessary to achieve permeate fluxes, thus leading to a high energy demand. As the phosphorus concentration of the permeate is relatively low and further anions, such as nitrate, sulphate and chloride are present (depending on the type of acid used for ash elution), direct reuse as phosphoric acid seems improbable. Thus, further treatment steps are necessary, e.g. precipitation as calcium phosphate or magnesium ammonium phosphate.

Table 1. Concentration of various components in feed and permeate, ash #C

CONCLUSIONS

The mono incineration of sewage sludge leads to a transfer of phosphorus and thus to the formation of calcium phosphate and aluminium and iron oxides. By acidic elution at pH-values < 1.5, phosphorus is released, as well as a large percentage of the metals. Due to the formation of calcium phosphate, a release in alkaline environments is limited and mainly dependent on the ash composition. The investigation of 15 sewage sludge ashes presented a maximum release rate of about 30% for phosphorus.

After removing the insoluble solids, sand in particular, phosphorus has to be separated from the metals. Hereby, two different processes were presented, i.e. sequential precipitation and nanofiltration.

Following the acidic elution of the ash, sequential precipitation of phosphorus (SEPHOS Process) is induced by increasing the pH-value systematically to approximately 3.5, thus leading to the precipitation of aluminium phosphate. As copper and zinc only precipitate at ph-values > 3.5, separation of phosphorus from the heavy metals is possible. Aluminium phosphate can then be used in the electro-thermal phosphorus industry. Rough estimations show that the costs for chemicals needed to produce the precipitate "aluminium phosphate" via the

SEPHOS Process are approximately 3 - 3 times higher than the current world price of raw phosphate. By optimizing elution and precipitation processes, the consumption of chemicals needed and thus the costs can be reduced. Furthermore, the prices of raw phosphate are expected to increase, following its decreasing quality and quantities.

Through alkaline treatment of the aluminium phosphate (Advanced SEPHOS Process), phosphorus as well as aluminium dissolves. By adding calcium, calcium phosphate precipitates, while aluminium stays in solution and can be recycled as precipitant.

The results of phosphorus separation by nanofiltration confirmed the general feasibility of this method for phosphorus recovery. It can be expected that advancements in membrane technology will increase the membrane permeability for phosphorus.

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