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**Electrodialytic extraction of phosphorus from ash of low-temperature gasification of sewage  
sludge**

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## **Abstract**

Low-temperature gasification allows the production of energy from biomass with high contents of low melting point compounds, like sewage sludge, and the recycling of the nutrients as P from the resulting ashes as renewable fertiliser. Major drawbacks are, however, the presence of heavy metals and the low plant-availability of Al- and Fe- phosphate compounds in the gasification ashes. In the present research, the feasibility of a 2-compartment electrodialytic (ED) setup for P separation from Al, Fe and heavy metals in two different low-temperature gasification ashes was investigated. One ash was from gasification of sewage sludge where P was precipitated with Fe and Al salts, from which it was possible to extract up to 26% of the P. The other ash was from co-gasification of a mixture of biologically precipitated sewage sludge and wheat straw pellets. More promising results were obtained with this ash, as up to 90% of the P was extracted from the ashes. For both ashes, P was extracted by ED in acidic aqueous solutions with ratios of Fe, Al and each heavy metal to P considerably below the values found in the initial ashes. Therefore, the 2-compartment ED cell technology was proved as possible method to separate Al, Fe and heavy metals from P for low-temperature gasification ashes.

**Keywords:** Phosphorus; Low-temperature gasification; Sewage sludge ash; Electrodialysis; Heavy metals

## 1. Introduction

Phosphorus is an essential element for life which has no biological or technological substitutes [1]. Current P supply for agriculture is dominated by phosphate rock (P-rock) fertilisers. However, the reserves of this mineral are estimated to be depleted in a period ranging from 50 to 400 years, depending on the study [2, 3] and both the production and reserves are concentrated in Morocco, China and USA [4]. Thus, scarcity is likely to increase phosphate production costs by factor 3 to 5 in this century [5] and geopolitical issues might also influence both the cost and availability. In 2013, the European Union countries imported around 86% of the consumed P-rock, a dynamic observed at least over the last decade [6]. Today, only about one fourth of the P applied to agricultural fields is actually recycled [1]. Moreover, P-rock fertilisers have been a major contributor to the addition of heavy metals like Cd to soils over the last decades [7, 8]. For all these reasons, innovative recycling and re-use technologies need to be developed and implemented.

Paradoxically, while the global reserves of P-rock rapidly decline, urban and industrial regions generate increasing amounts of waste rich in organic phosphate that is currently not appropriately recycled and utilised [1]: P is usually immobilised and precipitated in sewage sludge during wastewater treatment by phosphate accumulating organisms [9] and/or by Fe/Al salts addition [10].

Low-temperature gasification allows an energy production from biomass resources like sewage sludge with high contents of low melting point ash compounds [11] – which are often shown to be a source of boiler operational problems in more traditional incineration [12]. The resulting sewage sludge ashes (SSA), with a high P content, could potentially be recycled back to agricultural soils after this thermal gasification process securing a safe renewable P fertiliser without the risk of applying organic contaminants like pharmaceuticals, detergent metabolites and others. Major drawbacks of using gasified SSA directly as fertiliser, however, are its heavy metal content and the

presence of low plant available Al- and Fe- phosphates [13-15]. Hence, a mobilisation of P from the bulk gasification ashes and a simultaneous separation from heavy metals would be beneficial.

P separation from incinerated SSA can be achieved by acid leaching; but, heavy metals are also released [16-18]. Electrodialysis (ED) has been investigated as a technology to recover P from incineration SSA, from Al- and Fe- precipitation, and separate it from heavy metals, with a 3-cell compartment (Figure 1.a) [19, 20]. In this set up, the ashes are placed in the middle compartment together with an acid solution and stirred constantly, so as to extract both P and heavy metals from incinerated SSA [19, 20]. Released heavy metals are expected to be found as positively charged species and therefore migrating towards the catholyte during the ED treatment. In contrast, solubilised P is likely to be found in negatively charged or neutral species at acidic pH ( $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^{2-}$ ), except for Al-P and Fe-P complexes formation, so P ions would stay in the middle compartment and/or migrate towards the anolyte. In one of the studies, P separation into the middle compartment liquid and the anode compartment ranged around 15-85% for Al-precipitated incinerated SSA, a lower recovery than for Fe-precipitated ones which was around 45-95% [19]. In the other research, up to 70% of the P was recovered in the anode compartment [20].

Recently, a patent has been applied for a new set-up developed at the Technical University of Denmark, consisting of 2 compartments (Figure 1.a), which simplifies the experimental procedures in relation to the 3-compartment cell (Figure 1.b). The principle idea is that there is an acidification of the ash suspension by protons generated from electrolysis at the anode, and thus no acid addition is needed. The P remains in the filtrate of the ash suspension, instead of potentially dividing it between the anolyte and the middle compartment liquid. A study compared the performance of the two setups used in the P-recovery from incinerated SSA, and observed a lower voltage in the 2-compartment than in the 3-compartment ED cells by several orders of magnitude, when the ash was stirred only with water [21]. This can be due to a higher presence of ions in the suspension in the

former than in the latter, as well as the use of one membrane and one electrolyte liquid instead of two. Thus, there is a potential saving on electricity and chemical costs with this new setup.

Furthermore, with the 2-compartment setup it was possible to mobilise up to 90% of the P in the anode compartment [21]. No investigation has been made to recover P from gasification SSA by either acid or ED extraction, although the viability of low-temperature sewage sludge gasification depends partly on nutrient recycling. The aim of the present study was to test the technical feasibility of the 2-compartment ED cell to extract P, and separate it from Al, Fe and heavy metals, from SSA produced by low-temperature gasification of dried sewage sludge from two different plants.

## 2. Experimental

### 2.1 Gasification ashes

Two gasification ashes were collected from the second cyclone of a 100 kW experimental Low Temperature Circulating Fluid Bed gasifier (Figure 2) at the Department of Chemical and Biochemical Engineering, Roskilde campus of the Technical University of Denmark [11]. The process is based on separate pyrolysis and gasification fluid bed reactors with a suitable circulating heating medium to transfer the heat from the gasification process to the pyrolysis. The temperature is kept below the melting point of the ash components (700 - 750°C) avoiding sintering of the ash and subsequent fouling (from e.g. potassium) or corrosion (from e.g. chlorine) of the plant unit operations. The char conversion in the experimental Low Temperature Circulating Fluid Bed gasifier is a combination of sub stoichiometric oxidation of the char and steam gasification [22]. The ash particles are circulated in the process until they are too small/light to be separated by the primary cyclone. Most of the ashes are separated out of the hot gas by the secondary cyclone [11], where they were sampled for this research. The original feedstocks of the two gasification ashes were:

- Randers ash: Dried sludge collected at the wastewater treatment plant in the municipality of Randers, Denmark, where P was captured 50% biologically and 50% chemically (with Fe and Al chlorides), approximately. The gasification took place in July 2013.
- Stegholdt ash: Wheat straw pellets (70% in weight) and dewatered sewage sludge (30% in weight) from Stegholdt wastewater treatment plant, Denmark, where P was mainly removed biologically with a minor amount of Fe salts. The co-gasification of both materials took place in June 2013.

## *2.2 Analytical methods and sampling*

For both gasification ashes, small batches of around 200 grams were sampled from the total mass collected. Each ash was thereafter dried at 105°C overnight, cooled in the fume hood, homogenised with a steel spatula and immediately stored in plastic bags and under dry conditions.

The concentration of elements was investigated for all untreated and treated gasification ashes. The targeted elements were: Al, Ca, Cd, Cu, Cr, Fe, K, Ni, P, Pb and Zn. The element content was measured by Varian 720-ES inductively coupled plasma optical emission spectrometry (ICP-OES) in six samples for the untreated ashes and in triplicates for the ED treated ashes after pre-treatment by Danish Standard DS259 [23]: 1 g ash and 20mL 7.3 M HNO<sub>3</sub> were heated at 200 kPa (120°C) for 30 min. The liquid was thereafter separated by vacuum filtration through a 0.45 µm filter and diluted to 100 mL with deionised (DI) water.

Additionally, for the untreated gasification ashes, C and Si contents were measured. C concentration was determined using LECO induction furnace CS-200 Analyzer in triplicates, whereas Si content was measured by Varian MPX axial viewed ICP-OES in triplicates after digestion based on the Danish Standard EN 13656 [24]: 6mL 35-37% HCl, 2mL 65-70% HNO<sub>3</sub> and 2 mL 40-45% HF were added separately to 0.25 g of each ash, and heated in the microwave until the sample was completely dissolved. Hereafter 12 mL of 10% H<sub>3</sub>BO<sub>3</sub> was added and the mixture was heated in the microwave for 20 min. The mineralogy of both untreated ashes was examined using X-ray powder diffraction (XRPD) with a PANalytical X'Pert PRO, and the results were analysed using X'Pert HighScore Plus with ICDD PDF 2 database.



### *2.3 Acid extraction*

In order to assess the dependence of solubility of the target elements to acidic solutions, 5 g of ash was shaken at 150 rpm for 1 week with 25 mL of HNO<sub>3</sub> at 1M, 0.5 M, 0.3 M, 0.1 M and 0.01M respectively. Additionally, the same procedure was repeated for Randers ash with HNO<sub>3</sub> 0.8 M. The pH of the leachate was measured by a Radiometer Analytical pH electrode. Element content in the leachate was measured by the Varian 720-ES ICP-OES after filtration through a 0.45 µm syringe filter.

### *2.4 ED experimental setup*

The ED cell used is shown in Figure 1b. It consisted of two compartments made of cylindrical Plexiglas® with an internal diameter of 8 cm. The anode compartment was 10 cm long and contained 35 g ash and 350 ml deionised water. A plastic strip attached to a glass-stick connected to an overhead stirrer (IKA RW11) was used to stir the ash suspension during the experiments. In the cathode compartment 500 mL electrolyte solution (0.01 M NaNO<sub>3</sub>, pH < 2 adjusted with HNO<sub>3</sub>) was circulated by a Totton Pump NDP 10/2. The electrodes were made of platinum coated titanium wire (diameter 3 mm) obtained from Permascand®. An Agilent E3612A DC power supply was used to maintain a constant DC current. The cation exchange membranes used were from Ionics (model CR67).

### *2.5 ED experiments*

The durations of the ED experiments were 1, 3 and 7 days at 50 mA for both gasification ashes. The intensity was chosen following the findings from previous researches using ED for P extraction from incinerated SSA [19-21]. Voltage between the two electrodes was monitored during the whole experiment. The pH in both compartments and the conductivity of the ash suspension were measured daily during the ED experiments. The pH of the catholyte was adjusted to <2 with HNO<sub>3</sub>

5M, to avoid precipitations due to the production of  $\text{OH}^-$  by the electrode reaction at the inert cathode.

At the end of the experiments, the ash suspension was filtered at atmospheric pressure. The resulting liquid volume was measured and the ash was dried during 48 hours at 50 °C. The amount of liquid evaporated was measured by weight difference before and after drying. The dried ash was loosened by hand in a mortar and stored in plastic bags and under dry conditions. The volume of the catholyte was measured; the electrodes were rinsed in 5 M  $\text{HNO}_3$ , the membrane and the stirrer in 1 M  $\text{HNO}_3$ , and the concentrations of metals were measured in all of the liquids by ICP-OES after filtration through a 0.45  $\mu\text{m}$  syringe filter.

Catholyte samples were taken in 20 mL vials before applying the electrical current and after 5 minutes of electrolyte circulation; at the end of the experiments, catholyte and anolyte samples were also taken in 20 mL vials. The element content was measured in the ICP-OES after filtration through a 0.45  $\mu\text{m}$  syringe filter. The element content in the ashes before and after the experiments was measured as described in section 2.2.

### 3. Results and discussion

#### 3.1 Characteristics of the untreated gasification ashes

The element content and the ratio of heavy metals and P (HM/P) of the gasification ashes are shown in Table 1. Most elements presented a considerable variability, which is due to the inherent inhomogeneity of the gasification ashes and it should be considered in further discussions.

Cadmium concentration in the liquid from the ash sample digestion (as explained in section 2.2) was, in most cases, below the lowest standards used in the ICP measurements (0.02 mg/L). For this element, a range was given instead of the average together with the standard deviation of the six replicates. Furthermore, Cd results are not further discussed in the present work, as it is not possible to determine an accurate value and thereby whether Cd is effectively separated from P. As expected, Randers ash had a higher concentration of Fe and Al than Stegholdt ash; this is due to the usage of Fe and Al salts to precipitate P in Randers wastewater treatment plant, in contrast to its minor use in Stegholdt plant.

The P concentration in the ashes was around 3.2% and 1.9% respectively, which was below the range 3.9%-10.9% found in Fe-rich incinerated SSA [16-18, 25] and gasified SSA resulting from steam gasification at 700 °C [13]. For Randers ash, this is due to a considerably higher concentration in Si. The source of this high Si content is probably the sand used during the Pyroener process. Indeed, the only mineral phase identified in the XRPD for this bio ash was quartz (SiO<sub>2</sub>). Thus, Randers ash in fact consists of SSA diluted with sand.

For Stegholdt ash, the Si content was not as high as for Randers ash. Nonetheless, the Si content in the ashes was in the higher range of the previously reported in literature for incineration SSA [16-18, 25] and similar to the concentration found in other wheat straw ashes from low-temperature gasification (180 mg per kg of dry sample [26]). For these ashes, there is most likely a parallel

dilution of the P from Stegholdt sewage sludge with wheat straw (which normally has a lower P-content [26] than sewage sludge on a dry matter basis) and sand, which explains the lower content of P, compared to incineration SSA, gasification SSA and Randers ash (Table 1). Because of the feedstock proportion, these ashes had K content substantially higher than incinerated and gasified SSA (Table 1), but slightly lower than gasified wheat straw ashes (120 mg per kg of dry sample [26]). Accordingly, the mineral phases identified in the XRPD for Stegholdt ashes were  $\text{SiO}_2$  and sylvite (KCl).

Unburned C content in both untreated ashes seemed not to be a major cause of P dilution: for Randers ash, C was around 4%, close to the maximum loss of ignition (3%) typically found in incinerated SSA [27] and well below the 22% found in other gasified SSA [13]. For Stegholdt ash, C content was around 30%, which is slightly higher than the concentration previously reported in gasified SSA (22.3%, table 1).

Both ashes presented a black colour. Yet, the reason can be different for each SSA: in Randers ash it is probably due to the presence of magnetite ( $\text{Fe}_3\text{O}_4$ ) [28], which was previously identified in gasification SSA [14], whereas in Stegholdt ash it is most likely due to the higher content of unburned C.

The heavy metal concentrations were compared to Danish sewage sludge regulation limits for application in agriculture [29]. Only Ni limits were exceeded on average for Stegholdt ash. HM/P values found in commercial fertilisers [7] are included in Table 1, as a reference of the heavy metal content in the most common P-sources applied to agricultural soils. HM/P values were clearly higher in both Pyroneer ashes compared to commercial fertilisers for Cu, Ni, Pb and Zn. Cr/P was generally higher in the Pyroneer ashes, although the higher range found in commercial fertilisers had the same order of magnitude as both gasification ashes. In contrast, Cd/P ratio was in the range

of commercial fertilisers for Randers ash and in the lower or below the range for Stegholdt ash. If applied in agricultural land on a basis of P dose without treatment, Pyroneer ashes would potentially increase heavy metal content in agricultural soils.

### *3.2 Acid extraction*

As it can be seen in the acid extraction diagrams (Figure 3), the lower the pH the higher the release of P and heavy metals. This makes an acidic extraction ineffective to produce a P-fertiliser with low content in heavy metals, which has similarly been observed from acid leaching on incinerated SSA [16-18]. Consequently, an additional step would be needed to separate P from heavy metals, if acid leaching was used.

Randers ash release of P (1%) at pH 2.1 (Figure 3.a) correspond to concentrations of  $2.6 \cdot 10^{-3}$  M, which is above or close to the solubilities of  $\text{FePO}_4$  ( $10^{-4}$ - $10^{-3}$  M) and  $\text{AlPO}_4$  ( $10^{-3}$ - $10^{-2}$  M) at pH 2 [30], and below the ones of calcium phosphates like  $\beta\text{-Ca}_3(\text{PO}_4)_2$  (between  $10^{-2}$  [31] and 1 M [32]) and for Fe(II)-phosphates like vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) (0.1 M [33]) at pH 3. Molar ratios, calculated from average concentrations (Table 1), are 0.34 for Al/P, 0.88 for Ca/P and 0.99 for Fe/P. Previous works indicated the presence of Al-, Ca- and Fe- phosphates in gasification SSA [13, 14]. Consequently, P-solubility for Randers ash at acid pH are probably controlled by Fe(III), with some influence of Al- and Ca- bindings, although it requires further study for appropriate confirmation. The P solubility results (Figure 3.a) are considerably below the values observed for pH-desorption experiments for Fe-rich incinerated SSA, where 40-67% of the P solubilise at pH around 2 with the same liquid-to-solid ratio (L/S) [18]: Fe(III)-P compounds are not commonly present in Fe-rich incinerated SSA, as the trivalent iron phosphate bonds originally existing in sewage sludge are broken during incineration, resulting in the formation of more acid-soluble Ca-phosphates [19, 34, 35] as well as acid-insoluble Fe-oxides [34-36]. The low solubility of P in Randers SSA implies a

low plant-availability [15], which is a hindrance for its direct fertilizer application in agricultural soils.

In the Stegholdt ash around 60% of the P was released at pH 2.2 (Figure 3.b), corresponding to a concentration  $7.9 \cdot 10^{-2}$  M, which is more than one order of magnitude higher than Randers SSA value at pH 2.1. This is probably due to the lower influence of Fe(III) and Al in P-solubility in these ashes. Indeed, molar ratios of Al/P and Fe/P, calculated from average concentrations (Table 1), are 0.18, well below stoichiometric ratios of Al- and Fe- phosphates, in contrast with Ca/P ratio (1.5). These facts, together with the high leaching of Ca (80%), indicate the high presence of Ca-P bindings.

### *3.3 ED experiments*

#### *3.3.1 Element distribution at the end of the ED experiments*

The distribution of the elements in the cell at the end of the remediation for each ED experiment was determined, considering that:

- Since the resulting ash retained some P-rich liquid from the anolyte during the filtration, a subtraction of the mass of each element found in the anolyte was made to the direct measurement of element content in the treated ashes. The resulting amount was considered as the element found in the bulk ash. The element mass subtracted was found by means of multiplying the concentrations found in the ICP-OES for the P-rich solution and the volume of liquid dried (section 2.5), assuming a liquid density equal to water.
- The mass of each element subtracted from the treated ashes, explained in the previous point, was added to each element mass found in the filtrate of the ash suspension since it is potentially mobile through water washing, and the sum was considered to be separated in the anolyte,.

- The catholyte, the cathode and the cationic membrane were grouped as the cathode compartment.
- The total mobilisation of each element, including P, was the sum of the masses found in anolyte solution, the anode, the stir and in cathode compartment.

The element contents found precipitated at the stirrer and the anode were always below 0.1% of the initial content in the untreated ash. Therefore, their results are not shown in detail in the present study.

### *3.3.2 Mass balances and ash inhomogeneity*

Mass balances for each element, defined as the relation between the sum of mass found in the different ED cell compartments at the end of the experiments and the amount initially found in the mass of untreated ash placed in the ED cell, were made to control the quality of the experiments (Table 2). Results between 90 and 110% were considered acceptable. Elements were in this range for Randers ash in five out of six cases, whereas it was only six out of ten for Stegholdt ash. The most noticeable results are Cr and Pb for Stegholdt ashes, which can be due to the inherent inhomogeneity of elements found in trace levels, and indicate that a better homogenization before sampling from small batches (see section 2.2) might be needed. Concentration measurements which were below the lowest standard used in the ICP analyses (0.02 mg/L), only affecting Cr and Pb concentrations in the anolyte for some cases, were considered as 0.02 mg/L for the mass balances and for further calculations in the present work like the ratio HM/P. The overall impact of this approximation was small as the element mass were below 2% of the total final amount found at the end of the ED experiments.

### 3.3.3 P-separation results

ED applied to Randers ash gave a separation of P in the anolyte ranging 13-26%, depending on the remediation time (Figure 4.a): the longer the experiment, the higher the extraction of P. The pH of the anolyte was reduced in parallel to the increase in remediation time, due to the production of H<sup>+</sup> at the anode through electrolysis of water:



As seen in section 3.2, acidification of the ash suspension favoured P and other elements release. However, the P-extraction after ED was visibly higher than the acid extraction results at similar pH. The total mobilisation of P (Figure 4.a) was 13 % after 1 day (pH 2.2), 28% after 3 days (pH 1.7) and 34% after 7 days (pH 1.6). In the acid extraction experiments, 1% P was released at pH around 2.1, and 25% at pH 1.5 (Figure 3.a). The reason for a higher release of P in ED experiments can be a combination of an increased solubilisation of P compounds, due to equilibrium displacement by Al, Ca and Fe cations migration into the catholyte, together with a higher liquid-to-solid ratio (L/S) in the ED remediation (L/S=10) than in the acid extraction experiments (L/S=5). Moreover, the longer reaction time in the acid extractions could imply a lower P-extraction, as observed in a previous work when comparing acid P-extraction from incineration SSA for 2 hours and 1 week at different L/S, probably due to re-precipitation or adsorption of P over the time [18]. Further research is required to compare the ED with the acid extraction of P, from SSA similar to Randers ash, at the same pH and L/S, as well as the influence of the reaction time.

It should be noted that the difference of P separation to the anolyte between 3 (23%) and 7 (26%) days was not remarkable, and that these rates were considerably lower than previously reported from 2-compartment ED experiments with Fe-rich incinerated SSA for 7 days (around 80% [21]) also at 50 mA. The poor separation of P from Randers ashes in comparison to incineration SSA is



rather due to the ash characteristics than the ED setup. The reason is most likely to be the Fe(III) role in P-solubility at acid pH in Randers ashes, as discussed in the section 3.2. At the end of experiments, less than 5% Al and Fe was found in the anolyte; the rest of these two elements mostly remained in the bulk ashes (above 80%) and, to a minor extent, migrated to the cathode compartment. The resulting mass ratio in the anolyte ranged 50-100 for P/Al and 10-150 for P/Fe, depending on the remediation time, whereas in the untreated ash they were 3.4 for P/Al and 0.6 for P/Fe using average values (Table 1). Thus P was effectively separated from Al and Fe for Randers ash with the present ED setup.

An increase in ED duration could imply a higher P extraction due to a pH decrease; however, higher amounts of Fe and Al were also released in more acidic conditions as seen in Figure 3.a. This fact could lead to the formation of positively charged Fe-P and/or Al-P complexes. Calculations with MINTEQA6, using the concentrations found in the anolyte for P, Al, Fe (Fe (II) or Fe (III)) and Ca at the end of the 7-day ED experiment and a pH of 1.6, showed a major formation of positively charged Fe-P complexes like  $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$  and  $\text{Fe}(\text{HPO}_4)^+$  or  $\text{Fe}(\text{H}_2\text{PO}_4)^+$  (Table 3). If higher proportions of Fe are released, such complexes are likely to form in higher percentages. As these complexes are positively charged, P would migrate towards the cathode during ED, which jeopardises the separation to the anolyte. Indeed, the difference between the P found in the anolyte and the total mobilisation increased with increased ED duration and following decrease in pH: 0.5%, 5% and 8% after 1, 3 and 7 days of ED, respectively. This is likely due to a higher proportion of the abovementioned positively charged Fe-P complexes at longer duration, and consequent migration to the cathode compartment. Therefore even at prolonged treatment times, P and heavy metals cannot be sufficiently separated by the investigated technique when high amounts of Fe are simultaneously dissolved.

ED was also applied to the Stegholdt ash, showing more encouraging results than Randers ash. The P found in the anolyte was around 54%, 87% and 90% after 1, 3 and 7 days respectively (Figure 4.b). These results should be taken with care, as mass balances were within the range 70-77% (see Table 3). However, they clearly indicate a high rate of P-separation for Stegholdt ash. As in the case of the Randers ash, the % P in the anolyte was not much higher at 7 than at 3 days. The high P-extraction results are possibly due to the high content in Ca-P compounds, which are more acid-soluble than Al- and Fe- phosphates (see section 3.2). Similarly to Randers ash results, P/Al and P/Fe mass ratios in the anolyte at the end of the ED experiments were higher than in the initial ash: in the range of 15-100 for P/Al and 50-250 for P/Fe, whereas in the untreated ash these ratios were 6 and 3 using average values (Table 1), respectively.

The final concentration of P in the anolyte varied from 0.5 to 0.9 g P/L for Randers ash leachates, and from 0.6 to 1.4 g P/L for the Stegholdt ash leachates. These values were well below the concentration found in commercial phosphoric acid (450 g P/L approximately) as well as in liquid fertilisers, examples of which vary approximately from 11 to 230 g P/L [37]. A higher P-concentration could possibly be reached by reducing the L/S in the experiments. The Stegholdt ash contained a high concentration of K from the straw. This is another important nutrient (however not scarce) and in the future the process could be extended also to recover K. In the present setup though, around 80% of the total K migrated to the catholyte together with the heavy metals so a separation step is needed (e.g. increasing pH so the heavy metals precipitate and K remains in solution).

#### *3.3.4 Heavy metal reduction results*

At the end of the ED treatment, at least 80% (and in most of the cases above 95%) of the mass of heavy metals was found either in the bulk ash or in the cathode compartment. Consequently, for both ashes, HM/P in the anolyte was considerably lower than in the original material in most cases, showing an efficient heavy metal load reduction (Figures 5 and 6) in the P-solution of the anolyte. Such reduction was observed when treating incineration SSA with both the 2- and 3-compartment ED cell [19, 20]. The HM/P in the anolyte for Cr and Pb were below or in the usual values found for commercial fertilisers for all treatment times (Figures 5, 6 and Table1). For the rest of heavy metals (Cu, Ni and Zn) there was a promising approach to fertiliser values (Figures 5, 6 and Table1), but more research is needed in order to achieve them.

#### *3.3.5 ED cell voltage and ash suspension conductivity*

The voltage between the two electrodes decreased continuously during the ED experiments for both SSA, in parallel to the increase in conductivity of the ash suspension. This was similarly observed in a previous work on electrodialytic remediation of incinerated SSA with the two-cell compartment [21]. The rise in conductivity in the suspension is due to the higher presence of protons, generated by electrolysis at the anode, and other ions released from the ashes as the suspension pH drops. Furthermore, the decrease in electrical resistivity in the ED cell during the experiments indicates the absence of significant fouling or deposit formation on the cationic exchange membrane, usually caused by calcium hydroxides and carbonates in ED processes [38].

#### **4. Conclusion**

The 2-compartment electro dialytic (ED) cell technology is an effective method to separate P from Al, Fe and heavy metals for gasified sewage sludge ashes (SSA). However, further work is required to achieve a higher ED extraction of P from chemically precipitated sewage sludge gasification ashes. It was possible to extract up to 26% of the P in the anolyte from chemically precipitated sewage sludge gasification ash, and up to 90% of the P from co-gasified wheat straw and biologically precipitated SSA. The presence of Fe-P bindings and the formation of positively charged Fe-P complexes in the ash from chemically precipitated sewage sludge were hampering the optimal ED separation. The ratios of Al, Fe, most heavy metals and P in the anolyte solutions were considerably below the one in the initial ashes; noticeably, for Cr and Pb they were below or in the range of commercial fertilisers. This is because most of the studied metals either remained in the ashes or migrate to the catholyte in case of solubilisation.

## 5. Acknowledgements

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Table 1. The concentration (average± standard deviation) of elements in the two studied gasification ashes. HM/P was calculated using average values. Values exceeding on average the Danish legislation for agricultural use are shown in bold. The results are compared with the element concentrations found in incineration SSA, gasification SSA and commercial fertilisers (CF).

Element	per kg dry weight of sample				per kg P in sample (average values)			per kg P in CF [7]	Unit	
	Randers ash	Stegholdt ash	Fe-rich SSA (literature values)		Danish limits for agricultural use [25]	Randers ash	Stegholdt ash			Danish limits for agricultural use [25]
			Incineration [16-18, 26]	Gasification [13]						
Al	9.5±1.3	3.1±0.1	20-166	23	-	-	-	-	g/kg	
Ca	36.7±5.1	35.3±3.7	54-163	110	-	-	-	-	g/kg	
Fe	57.6±8.3	6.2±0.7	47-170	88	-	-	-	-	g/kg	
P	32.4±4.6	18.6±1.8	39-109	102	-	-	-	-	g/kg	
K	1.7±0.3	83.3±4.3	4-23	8	-	-	-	-	g/kg	
Si	266±10.6	162±5.4	85-203	44	-	-	-	-	g/kg	
C	38.8±1.3	301±2.1	-	223	-	-	-	-	g/kg	
Cd	<2.0*-3.14	<2.0*	<0.4*-5	**	0.80	<61.7*-96.9	<107.5*	100	12-60	mg/kg
Cr	34±3.8	19±1.6	88-130	98	100	1,050	1,010	-	125-794	mg/kg
Cu	160±21	32±1.8	417-1,270	1,159	1,000	4,880	1,710	-	10-80	mg/kg
Ni	28±1.6	<b>60±4.4</b>	40-98	122	30	866	<b>3,230</b>	2,500	42-168	mg/kg
Pb	37±6.7	4.6±0.7	90-264	88	120	1,150	245	10,000	9-53	mg/kg
Zn	1,000±130	140±8.1	910-2,740	753	4,000	31,000	7,700	-	291-1,080	mg/kg
*Below ICP standards/**Below limit of detection										

Table 2. Mass balances (%) for the ED experiments. Values outside 90-110% range are shown in bold.

Remediation time	Gasification ash	Al	Ca	Fe	P	K	Cr	Cu	Ni	Pb	Zn
1 day	Randers	101	101	99	98	101	106	96	104	101	107
	Stegholdt	110	93	100	<b>70</b>	94	<b>176</b>	<b>123</b>	100	<b>223</b>	104
3 days	Randers	<b>88</b>	101	<b>86</b>	90	97	<b>89</b>	<b>77</b>	93	<b>86</b>	92
	Stegholdt	99	90	102	<b>77</b>	<b>84</b>	<b>157</b>	107	94	<b>195</b>	90
7 days	Randers	104	105	101	103	<b>112</b>	106	110	107	108	105
	Stegholdt	<b>122</b>	100	<b>119</b>	<b>77</b>	107	103	<b>77</b>	98	108	98

Table 3. MINTEQ calculation of major speciation of Al, Ca, Fe(II)/Fe(III) and phosphate ions for the analyte concentrations of Randers ash 7-day ED treatment at pH=1.6.

Element	Total ion concentration (mg/L)	Major species distribution (Fe as Fe <sup>2+</sup> )	Major species distribution (Fe as Fe <sup>3+</sup> )
Al	24 (as Al <sup>3+</sup> )	86.7% Al <sup>3+</sup> , 13.2% Al(HPO <sub>4</sub> ) <sup>+</sup>	87.8% Al <sup>3+</sup> , 12.2% Al(HPO <sub>4</sub> ) <sup>+</sup>
Ca	187 (as Ca <sup>2+</sup> )	93.0% Ca <sup>2+</sup> , 7.0% Ca(H <sub>2</sub> PO <sub>4</sub> ) <sup>+</sup>	96.1% Ca <sup>2+</sup> , 3.9% Ca(H <sub>2</sub> PO <sub>4</sub> ) <sup>+</sup>
Fe	276 (as Fe <sup>2+</sup> or Fe <sup>3+</sup> )	37.3% Fe <sup>2+</sup> , 62.7% Fe(H <sub>2</sub> PO <sub>4</sub> ) <sup>+</sup>	1.5% Fe <sup>3+</sup> , 60.1% Fe(H <sub>2</sub> PO <sub>4</sub> ) <sup>2+</sup> , 38.2% Fe(HPO <sub>4</sub> ) <sup>+</sup>
P	2864 (as PO <sub>4</sub> <sup>3-</sup> )	22.4% H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , 65.9% H <sub>3</sub> PO <sub>4</sub> , 0.4% Al(HPO <sub>4</sub> ) <sup>+</sup> , 1.1% Ca(H <sub>2</sub> PO <sub>4</sub> ) <sup>+</sup> , 10.3% Fe(H <sub>2</sub> PO <sub>4</sub> ) <sup>+</sup>	21.0% H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , 61.5% H <sub>3</sub> PO <sub>4</sub> , 0.4% Al(HPO <sub>4</sub> ) <sup>+</sup> , 1.0% Ca(H <sub>2</sub> PO <sub>4</sub> ) <sup>+</sup> , 9.9% Fe(H <sub>2</sub> PO <sub>4</sub> ) <sup>2+</sup> , 6.3% Fe(HPO <sub>4</sub> ) <sup>+</sup>

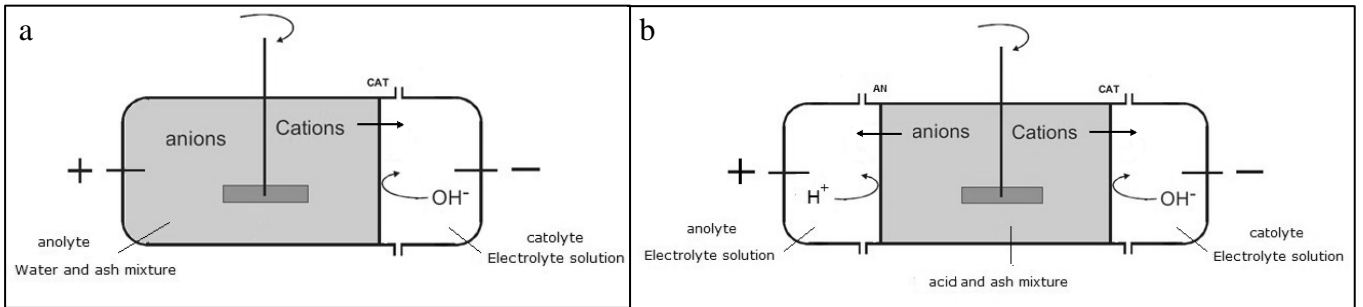


Figure 1: Schematic view of a 2-compartment (a) and a 3-compartment (b) ED cell. CAT: cation-exchange membrane. AN: anion-exchange membrane

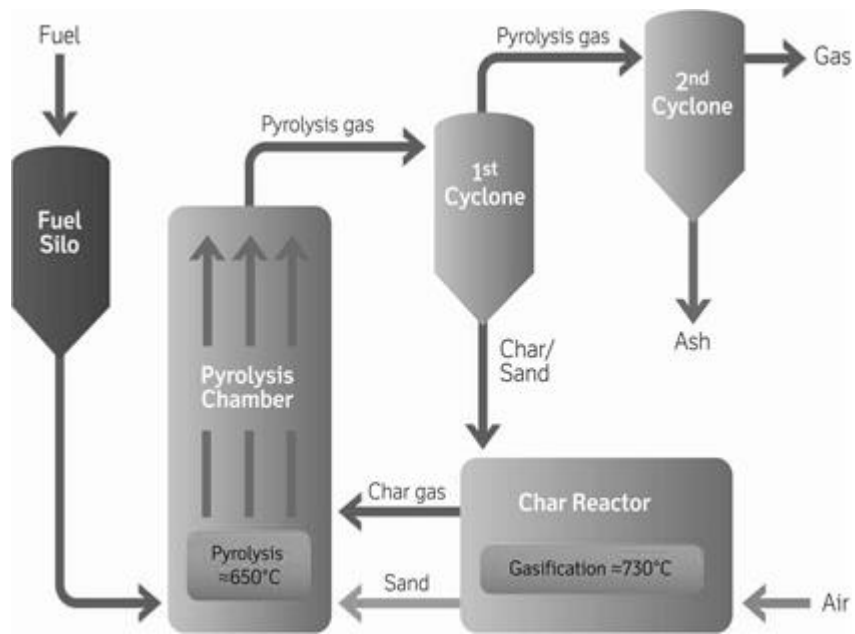


Figure 2: Schematic of experimental Low Temperature Circulating Fluid Bed gasifier [11]

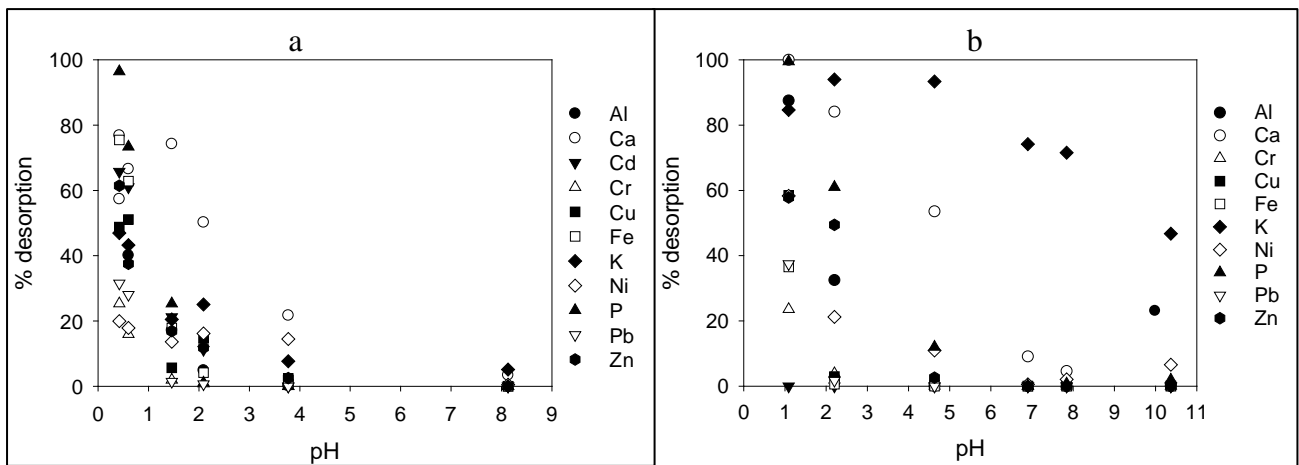


Figure 3: acid extraction of Al, Ca, Fe, K, P and heavy metals in a) Randers ash, b) Stegholdt ash

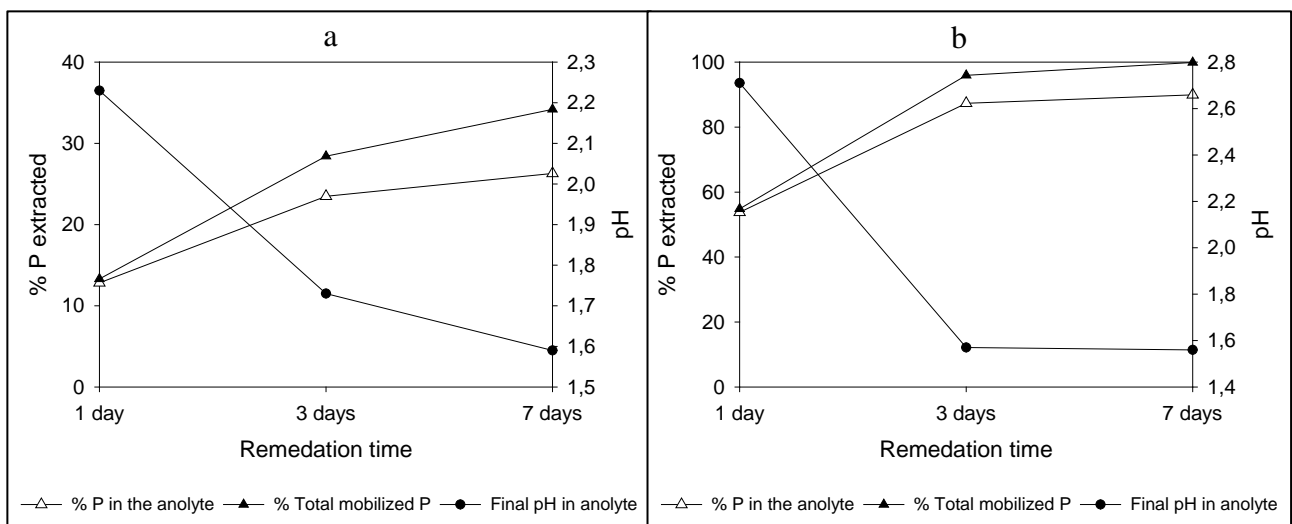
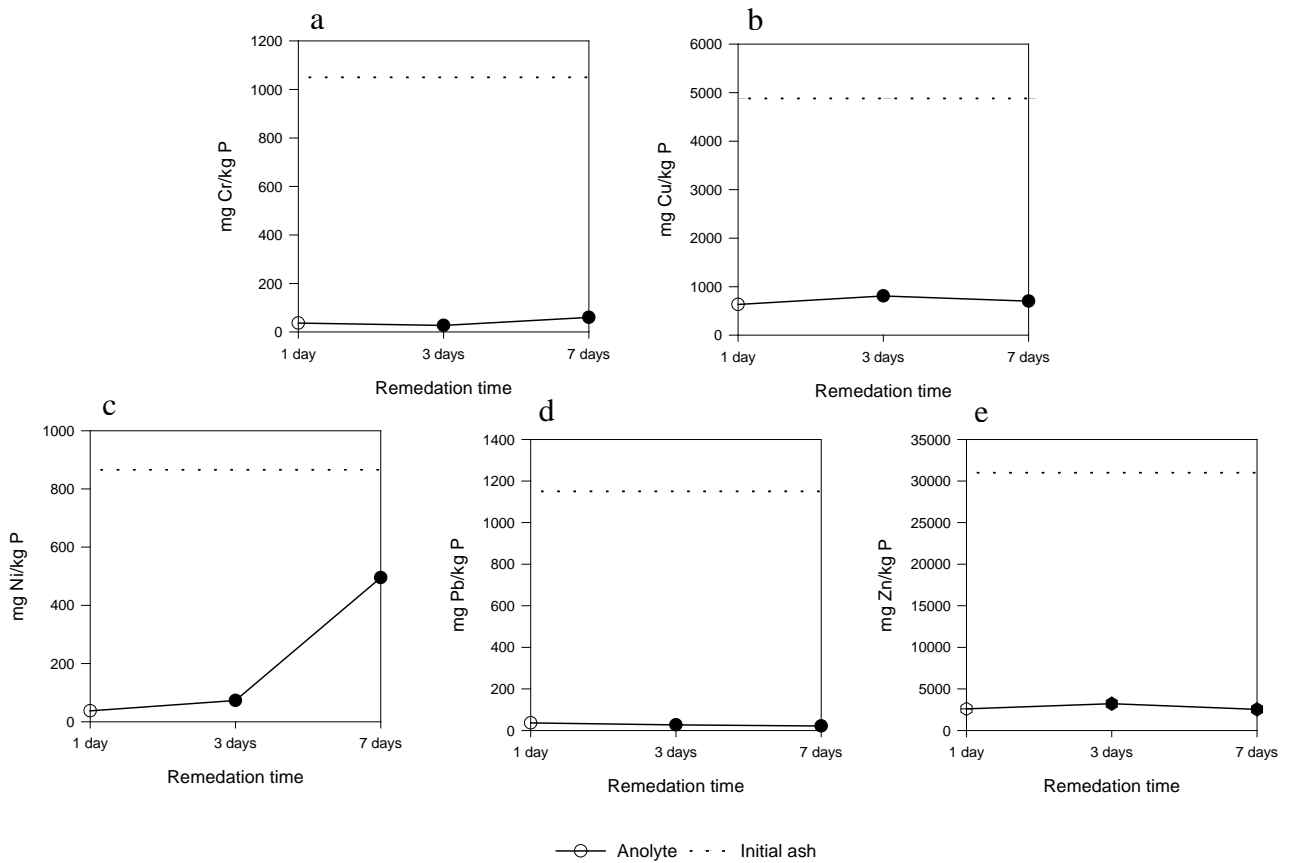
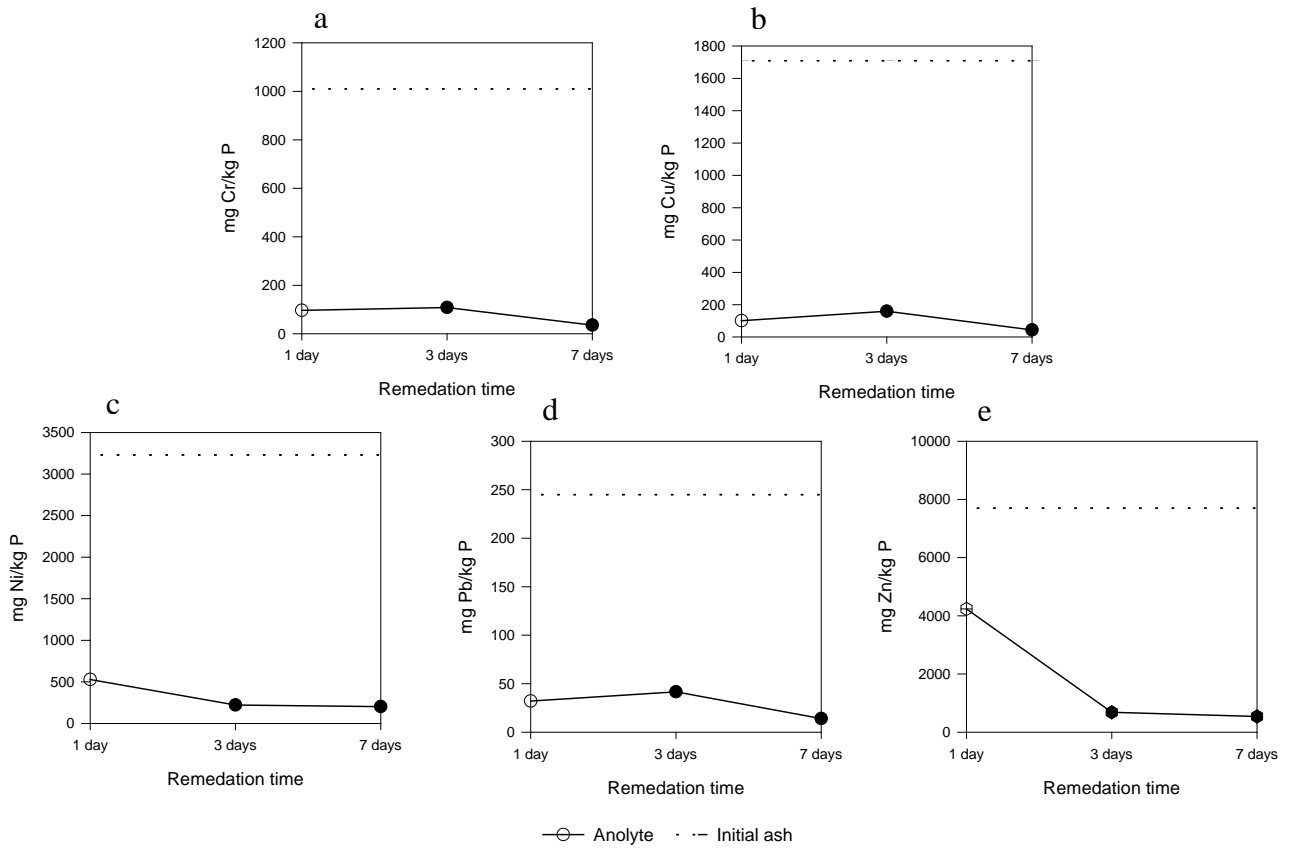


Figure 4: P separated in the anolyte after ED treatment at different remediation times from a) Randers ash, b) Stegholdt ash



**Figures 5.a-e:** Ratio of heavy metals and P in the initial ash and in the analyte at the end of the ED treatment at different remediation times for Randers ash



**Figures 6.a-e:** Ratio of heavy metals and P in the initial ash and in the anolyte at the end of the ED treatment at different remediation times for Stegholdt ash