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**Sequential electrodialytic recovery of phosphorus from low-temperature gasification ashes of
chemically precipitated sewage sludge**

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Abstract

Phosphorus recycling from secondary materials like sewage sludge ashes offers an alternative to mining of phosphates from primary resources and a mean to counteract the current phosphorous rock depletion concern. A separation of P from the bulk ash is normally required, due to its low plant availability and the presence of heavy metals. Previously, more than 80% of P was recovered from incineration sewage sludge ashes using a two-compartment electrodialytic cell. In contrast, the recovery was below 30% for ashes from low-temperature gasification using the same setup. The low recovery was due to a high presence of Al- and Fe(III)-P bindings. In the present study, an electrodialytic process combining sequentially a pair of two-compartment cells allowed a recovery of up to 70% of phosphorus from these ashes. The use of a second cell, where the ash was

23 suspended in an alkaline solution, allowed the P solubilisation from aluminium and ferric
24 phosphates. In addition, P was separated from most metals as they became insoluble under the
25 prevailing chemical environment. The obtained ratio of Al, Fe, Mg and most heavy metals to P was
26 comparable to wet process phosphoric acid. Therefore, this sequential process was found to be
27 suitable to recycle P and potentially use it in the production of common fertilizers like diammonium
28 phosphate.

29

30 **Keywords:** Electrodialysis, Heavy metals, Iron phosphates, Low-temperature gasification,
31 Phosphorus, Sewage sludge ash

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1. Introduction

Europe is dependent on phosphate rock imports [1], the reserves of which are estimated to be exhausted within 50-400 years [1-3]. The European Commission included this mineral in the list of 20 critical raw materials in 2014. Moreover, mineral P-fertilizers are the main contributors of toxic elements accumulation such as cadmium [4] and uranium [5] in agricultural soils. For these reasons, P recycling from secondary resources, like sewage sludge, has gained increased attention among researchers, private companies and public institutions over the last decade [6-9]. Around 16% of phosphate rock import can be potentially substituted with unrecycled P from sewage sludge in Europe [1]. In order to promote P recycling, some countries e.g. Denmark have set goals for P recovery [10], and others e.g. Germany, Switzerland and Sweden currently have proposals to make it obligatory. The content of heavy metals as well as potential unwanted organic pollutants and pathogens are of major concerns in respect to sewage sludge's direct use on agricultural fields [8, 11]. Another difficulty is the limited plant-availability of P when sewage sludge is precipitated with Al and Fe salts in the wastewater treatment plant to avoid eutrophication of natural water system recipients, a practice which is common in many countries [7, 12-15].

Thermal processes such as incineration [16] and low-temperature gasification [17] can lead to the removal of organic contaminants from sewage sludge, but additional treatments of the resulting sewage sludge ashes (SSA) are required to separate P from heavy metals and ensure its bioavailability [7, 8, 18, 19]. Electrodialysis (ED) has been studied as a technique to extract P from different SSA using 2-compartment cells [19, 20]. In this setup, SSA is suspended in water in the anode compartment, which is separated from the cathode compartment by a cation exchange membrane. When applying the electric field the cations are transported from the anolyte to the catholyte through the membrane. Protons are concurrently produced from water electrolysis at the anode, which increases the solubilisation of the different elements present in the SSA [19, 20].

Thus, the applied electric field results in acidic leaching combined with cation migration into the cathode compartment. Large recoveries of P (higher than 80%) have been achieved for incineration SSA [20] and biologically precipitated SSA from low-temperature gasification [19]. On the contrary, less than 26% of P was recovered from chemically precipitated SSA from the same gasification unit. The reason for the low recovery was found to be the influence of Fe(III) on P-solubility and the formation of positively charged Fe-P complexes in acidic medium [19].

Other processes than ED have been investigated for the recovery of P from SSA and the majority can be grouped into either:

- a) Acid extraction of P from SSA with H_2SO_4 , HCl , HNO_3 and/or H_3PO_4 , followed by further steps to separate P from the leached impurities like heavy metals by means of sulphide precipitation [18], solvent extraction [21] and/or ion exchange columns [13, 18, 22, 23], as well as through the chemical precipitation of P as Ca-phosphates [9, 22, 24, 25]. The biggest industrial agreement to recycle P from SSA until now was signed in the beginning of 2015 between the Belgian company Ecophos and the Dutch companies HVC and SNB, which includes the construction of a plant to treat 50-60,000 tonnes of incineration SSA yearly using a method belonging to this group.
- b) Thermal removal of heavy metals at high temperatures (above 1400°C) [9, 26], which also allows the separation of the main metals like Fe; or at around 1000°C in combination with chemicals like calcium or magnesium chloride [27], Na- and K- salts and bases [9, 28, 29], which at the same time increases the plant availability of P in the ashes.

However, these researches have focused on chemically precipitated incineration SSA, where Fe(III) is not controlling P solubility [30, 31], which is on the contrary to gasification SSA. An alkaline extraction step could potentially dissolve Fe(III)-phosphates [32, 33] existing in gasification SSA,

82 with the advantage of preventing the formation of complexes like $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$ or $\text{Fe}(\text{HPO}_4)^+$ which
83 complicate P separation in ion exchange processes and ED [19, 34]. By such treatment, alkaline-
84 insoluble Ca-phosphates [35] would, however, not be dissolved. Instead, a common strategy to
85 leach P from materials containing both Ca-P and Al/Fe(III)-P bonds, previously used for Al-
86 precipitated SSA [36, 37], soils [38], sediments [39], and municipal solid waste fly ashes [40], is to
87 solubilize the different Ca-bearing phases in an acidic step, and the Al/Fe(III)-P bindings in an
88 alkaline step. Nevertheless, the order of execution requires an investigation. Starting with an acidic
89 extraction can lead to P re-precipitation as Al-P [36, 37], and probably Fe(III)-P, which increases
90 the hydroxide demand for their dissolution in the subsequent alkaline step. Starting with an alkaline
91 extraction, P could re-precipitate as Ca-P or adsorb to Ca compounds [37, 38, 41], which increases
92 the proton demand for P dissolution in the following acidic step. In order to assess which
93 combination is best to recover P, both possible two-stage chemical processes are compared in the
94 present study.

95 Recently, a patent concerning an innovative sequential ED process (Fig. 1) has been filed with the
96 European Patent application number 15187370.0. The new method combines two existing 2-
97 compartment cell configurations, one with a cation exchange membrane [19, 20] and another one
98 with an anion exchange membrane [42], into a sequential process. The present research focuses on
99 achieving a higher recovery of P from low-temperature gasification SSA, which has been
100 chemically precipitated, using a sequential ED process in comparison to a single step with a 2-
101 compartment cell with a cation exchange membrane.

102

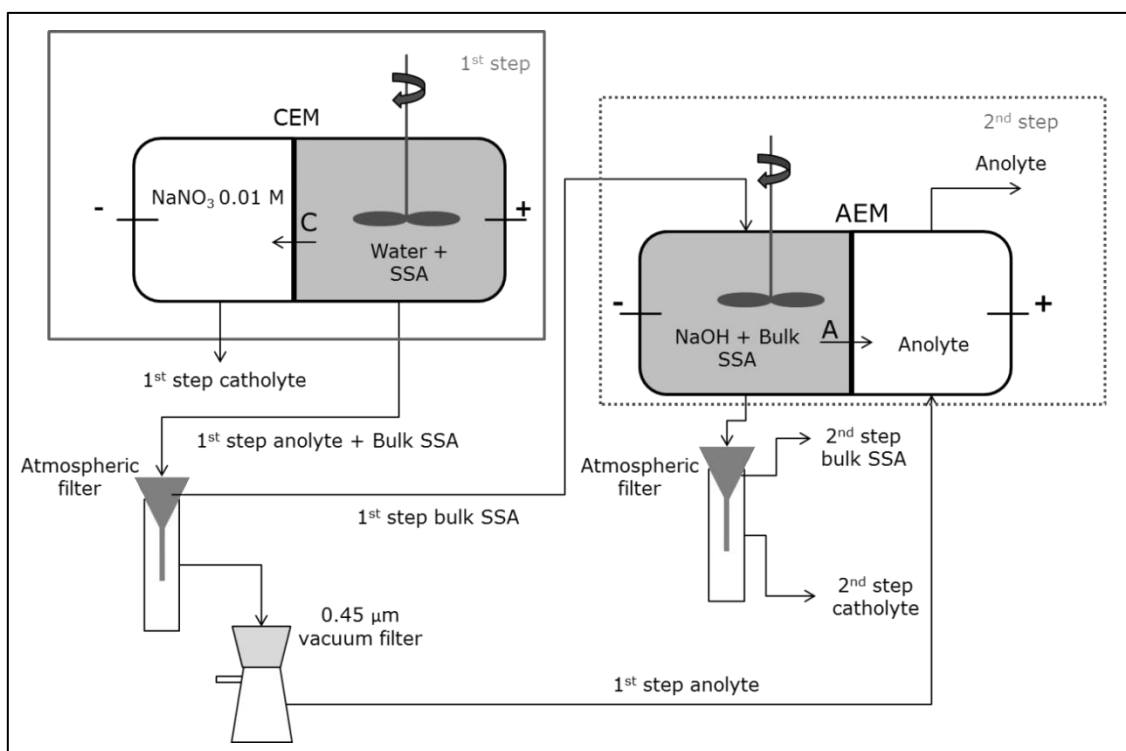


Fig. 1. Schematic view of the sequential ED process. C: cations, A: anions.

2. Experimental

2.1 Experimental SSA

The investigated SSA were the same as in previous published work [19], where the ashes were collected from the second cyclone of a 100 kW experimental Low Temperature Circulating Fluid Bed gasifier [43] at the Department of Chemical and Biochemical Engineering in the Technical University of Denmark. The original feedstock was dried sludge collected at the wastewater treatment plant in the Randers Municipality, Denmark, where P was captured approximately 50:50 by biological and chemical means. The chemical precipitation was based on Fe and Al chlorides.

2.2 Analytical methods and sampling

Small batches of around 200 grams were sampled from the total mass collected. Each batch was dried at 105°C overnight, cooled in the fume hood, homogenised with a steel spatula and immediately stored in plastic bags under dry conditions. A different batch was used for each experiment: alkaline extraction (Batch 1), two-stage chemical extraction (Batch 2) and ED experiments (Batch 3). The CaCO₃ content in another separate batch from the same overall sample was measured following the German standard DIN 18 129 [44].

The concentrations of elements were measured for each batch: in triplicates for the alkaline extraction as well as for the sequential extraction, and in eight samples for the ED experiments. It was also measured in triplicates after each step of the sequential extraction and the ED experiments. The targeted elements were: Al, As, Ca, Cd, Cu, Cr, Fe, K, Mg, Ni, P, Pb and Zn. Na was analysed only for the initial samples of the ED experiments. Their content was measured by Varian 720-ES inductively coupled plasma optical emission spectrometry (ICP-OES) after pre-treatment by Danish Standard DS259 [45]: 1 g ash and 20mL 7.3 M HNO₃ were heated at 200 kPa (120°C) for 30 min.

127 The liquid was thereafter separated by vacuum filtration through a 0.45 μm filter and diluted to 100
128 mL with deionised (DI) water.

129 Element concentrations among the batches were compared through a one-way analysis of variances
130 (ANOVA).

131 2.3 Alkaline extraction

132 In order to assess the dependence of solubility of the target elements to alkaline solutions, 5 g of ash
133 was shaken at 150 rpm for 1 week with 25 mL of NaOH at 1, 0.5, 0.1, 0.05 and 0.01 M
134 respectively. The pH of the leachate was measured by a Radiometer Analytical pH electrode. The
135 concentrations of the targeted elements in the leachate were measured by the Varian 720-ES ICP-
136 OES after filtration through a 0.45 μm syringe filter.

137 2.4 Two-stage chemical extractions

138 Two different two-stage chemical extraction procedures were compared in order to investigate the
139 most suitable order of the sequential P-extraction: alkaline-acid or acid-alkaline. The combined acid
140 and base load (H^+ and OH^- moles per kg of dry ash) was equal to 5; this value was equivalent to the
141 acid load in which almost all P could be mobilised in a previous research with the same ash [19]. In
142 the alkaline-acid extraction, 10 g of ash were shaken at 150 rpm for 24 hours with 50 mL of NaOH
143 at 0.5 M; the ash suspension was filtered at atmospheric pressure, the filtrate volume and pH were
144 measured and sampled with a 0.45 μm syringe filter, and the ash was dried during 48 hours at
145 50 °C. The dried ash was weighted, loosened by hand in a mortar, sampled and 5 g of it were
146 shaken at 150 rpm for 24 hours with 25 mL of HNO_3 at 0.5 M. In the acid-alkaline extraction, the
147 same procedure was repeated starting with a step with 0.5 M HNO_3 followed by 0.5 M NaOH. All
148 targeted elements were measured by the Varian 720-ES ICP-OES in the liquid phases at the end of

each step. The amount of P, Ca, Al and Fe found in the filtrate of each step was considered to be extracted. The overall % of P extraction was calculated as:

$$\begin{aligned} \%P \text{ extraction} &= \frac{P \text{ extracted in filtrates}}{\text{Total P at the end of the experiment}} \\ &= \frac{V_{acid} \cdot C_{P-acid} + V_{alkaline} \cdot C_{P-alkaline} \cdot \frac{m_{ash-acid}}{m_{ash-start}}}{V_{acid} \cdot C_{P-acid} + (V_{alkaline} \cdot C_{P-alkaline} + C_{P-ash-alkaline} \cdot m_{ash-alkaline}) \cdot \frac{m_{ash-acid}}{m_{ash-start}}} \end{aligned}$$

Where V_{acid} and $V_{alkaline}$ were the volumes of filtrates recovered after each extraction, C_{P-acid} and $C_{P-alkaline}$ the concentration of P in these filtrates, $C_{P-ash-alkaline}$ the P-concentration in the dry ash after the alkaline extraction, whereas $m_{ash-start}$, $m_{ash-acid}$ and $m_{ash-alkaline}$ were the mass of dry ash at the beginning and at the end of each extraction. The reason for the inclusion of the ratio between $m_{ash-acid}$ and $m_{ash-start}$, multiplying the second term in the dividend and the divisor, was to extrapolate the result of the alkaline extraction step to all the bulk dry ash mass after the acid extraction. The same equation was used to calculate Ca, Al and Fe extraction.

2.5 ED experimental setup

An illustration of the ED sequential process used is shown in Fig. 1. Both cells consisted of two compartments made of cylindrical Plexiglas® with an internal diameter of 8 cm. The compartment with the ash suspension was 10 cm long and the other compartment 5 cm. The anode compartment contained 35 g ash and 350 ml DI water. In the second step, the cathode compartment contained 25 g of the bulk ash resulting from the first step and 300 ml DI water, as well as 8 mL of NaOH 1 M added at the beginning of the experiment. A plastic strip attached to a glass-stick connected to an overhead stirrer (IKA RW11) was used to stir the ash suspensions during the experiments. In the cathode compartment of the first step, 500 mL electrolyte solution (0.01 M NaNO₃, pH < 2 adjusted with HNO₃) was circulated by a Plastomec pump model P05. In the anode compartment of the

170 second step, the anolyte resulting from the first step was circulated using the same pump model
171 after vacuum filtration through a 0.45 μm filter. The electrodes were made of platinum coated
172 titanium wire (diameter 3 mm) obtained from Permascand®. An Agilent E3612A DC power supply
173 was used to maintain a constant DC current. The cation and anion exchange membranes used were
174 from Ionics (model CR67 and AR204SZRA respectively).

175 2.6 ED experiments

176 Three set of sequential ED experiments were performed; the first step ran until the pH in the anolyte
177 reached 1.5 , 1.7 or 2, whereas the second step ran equally for 3 days in each experiment. The time
178 and final pH of the SSA suspension in each ED experiment are shown in Table 1. The pH values in
179 the first step were similar to the results of previous ED experiments with the same ash [19], and the
180 aim was to investigate their influence in the recovery of P. The intensity was 50 mA, chosen
181 following the findings from previous researches using ED for P extraction from incinerated and
182 gasification SSA [19, 20, 34, 46]. Voltage between the two electrodes was monitored during the
183 whole experiment. The pH in both compartments and the conductivity of the ash suspension were
184 measured twice a day during the ED experiments. The pH of the catholyte of the first step was
185 adjusted to <2 with HNO_3 5M, to avoid precipitations due to the production of OH^- by the
186 electrode reaction at the inert cathode.

187 At the end of each step, the ash suspension was filtered at atmospheric pressure, and after the first
188 step the ash was flushed with 200 mL of DI water in order to displace the elements in solution
189 retained in the humidified ash. The resulting liquid volume was measured, and the ash was dried
190 during 48 hours at 50 °C. The dried ash was loosened by hand in a mortar and stored in plastic bags
191 under dry conditions. The electrodes were rinsed in 5 M HNO_3 , the membranes in 1 M HNO_3 , and

the concentrations of the elements were measured in all of the liquids by ICP-OES after filtration through a 0.45 μm syringe filter.

Table 1. Final pH in the SSA suspensions and duration of each step in the ED experiments.

Experiment	ED step	Final pH	Duration [hours]
A	1 st	1.5	125
	2 nd	11.6	72
B	1 st	1.7	52.5
	2 nd	12.2	72
C	1 st	2.0	27.5
	2 nd	12.2	72

Catholyte (in the first step) and anolyte (in the second step) 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 volumes were measured and sampled in 20 mL vials. 16 mL of the samples from the catholyte in the 2nd step was mixed with 4 mL HNO₃ 68%, and heated at 200 kPa (120°C) for 30 min. The element content was measured in the ICP-OES for all electrolytes after filtration through a 0.45 μm syringe filter. Na content in the catholyte of the second step was also measured by ICP-OES.

2.7 Experimental ED parameters

The ED experiments were evaluated in terms of rates of P recovery and the impurity level of the obtained product.

206 The amounts of P found in the anolyte of the 1st and 2nd steps were considered as recovered, since
 207 they were expected to be solutions rich in this element and depleted of impurities like metallic
 208 cations. The overall % of P recovered was calculated as:

$$210 \quad \%P \text{ recovery} = \frac{P \text{ in anolytes}}{\text{Total P at the end of the experiment}}$$

211 And the amount of P in the anolytes was calculated as:

$$212 \quad V_{1^{st} \text{ step}} \cdot C_{P-1^{st} \text{ step}} + V_{2^{nd} \text{ step}} \cdot C_{P-2^{nd} \text{ step}} \cdot \frac{m_{ash-1^{st} \text{ step}}}{m_{ash-2^{nd} \text{ step-start}}}$$

213 Where $V_{1^{st} \text{ step}}$ and $V_{2^{nd} \text{ step}}$ were the volumes of anolyte at the end of each step, $C_{P-1^{st} \text{ step}}$ and $C_{P-2^{nd} \text{ step}}$
 214 $C_{P-1^{st} \text{ step}}$ the concentration of P in the anolytes for each ED step, whereas $m_{ash-1^{st} \text{ step}}$ and $m_{ash-2^{nd} \text{ step-start}}$
 215 were the mass of dry ash at the end of the 1st step and at the beginning of the 2nd step, respectively.
 216 The inclusion of the ratio between $m_{ash-1^{st} \text{ step}}$ and $m_{ash-2^{nd} \text{ step-start}}$ multiplying the second term was
 217 used to extrapolate the result of the 2nd ED step to all the bulk dry ash mass after the 1st step.

218 In order to assess the amount of impurities in the recovered P, it was compared to wet process
 219 phosphoric acid (WPA), the product of leaching phosphate rock with sulfuric acid [47] which is
 220 applied to over 70% of mined phosphates [48]. A common parameter to evaluate the suitability of
 221 WPA in the fertilizer industry is the minor element ratios (MER), defined as:

$$222 \quad MER = \frac{Fe_2O_3 + Al_2O_3 + MgO}{P_2O_5}$$

223 Additionally, the amount of P bound to Ca and Al/Fe(III) in the bulk SSA at the beginning and at
 224 the end of the 2nd step were estimated by:

- Considering all remaining Ca to be bound to P according to the stoichiometry of $\text{Ca}_3(\text{PO}_4)_2$. This implied an overestimation of these bindings, since there could be other Ca compounds not containing P, but it gave an overview of the effectiveness of the sequential ED method.
- Considering all P not bound to Ca, in the previous point, to be bound to Al or Fe(III).
- In both cases, average concentrations of Ca and P in the bulk SSA were used.

3. Results

3.1 Element content in untreated SSA

The element concentrations in the three batches used are shown in Table 2, together with the results for a batch from a previous research on ED treatment of the same SSA [19]. After performing an ANOVA with a P-value >0.05 , average values were the same for the batches used in the ED treatment (Batch 3 and from [19]) for Al, Ca, Fe, P, Cr, Cu, Ni, Pb and Zn. In contrast, Ca, P, Pb and Zn average contents were different between Batches 1 and 3. Mean concentrations for Al, Fe, P, Cr, Ni and Zn were also different between Batches 2 and 3. These differences, together with the standard deviation in elements like Ca, Fe and P in Batches 2 and 3, show a relatively high degree of the inhomogeneity of these SSA and demand a rather qualitative comparison of the results of the different experiments.

243 Table 2. Element concentration (average±standard deviation) of untreated SSA from different
 244 batches analysed by ICP, after digestion following Danish Standard DS259 [44]. *Below ICP LOD

Element	Previous	Batch 1 -	Batch 2 –		Batch 3 - ED	Units
	research	Alkaline	Two-stage			
	[19]	extraction	chemical	extraction		
	per kg of dry ash			per kg of P		
Al	9.5±1.3	11.6±0.5	14.9±3.9	10.5±1.2	-	g/kg
Ca	36.7±5.1	40.4±0.6	51.9±10.7	34.3±4.4	-	g/kg
Fe	57.6±8.3	58.3±2.9	82.6±21.1	58.3±6.7	-	g/kg
Mg	-	3.0±0.6	3.7±0.9	3.4±0.4	-	g/kg
P	32.4±4.6	38.7±2.3	49.3±11.8	30.0±3.6	-	g/kg
As	-	<2*	<2*-4	<2*-4.4	<67*-133	mg/kg
Cd	<2*-3.14	3.7±0.3	<2*	<2*	<67*	mg/kg
Cr	34±3.8	36.8±2.3	42.3±9.8	34.8±3.3	1,160	mg/kg
Cu	160±21	180±14	200±54.7	165±16.2	5,490	mg/kg
Ni	28±1.6	33.3±1.0	36.7±4.7	30.1±3.1	1,000	mg/kg
Pb	37±6.7	47.7±5.2	52.1±17.9	40.5±4.2	1,350	mg/kg
Zn	1,000±130	1,630±88	1,680±41	1,000±109	33,400	mg/kg

245

246 3.2 Alkaline and two-stage chemical extractions

247 The solubility of all studied elements increased with the increase of pH except for Ca. Desorption of
 248 Fe, Cr, Cu, Zn was generally below 0.05%, and the highest desorbed percentage of these being

249 0.5% for Zn at pH 13.3. The concentrations of Cd and Pb were below the limit of detection (LOD),
 250 0.02 mg/L, in all alkaline leaching experiments. Solubilised percentages of As are not included due
 251 to the inhomogeneity of its concentration in the ashes, with some results below LOD (Table 2);
 252 however, the results show a high degree of solubilisation, equivalent to 0.6, 1.6 and 3.0 mg/kg of
 253 drySSA at pH 11.5, 13.0 and 13.3, respectively. Fig. 2 shows the results for Al, P and Ni, as the
 254 most remarkable results, as they are well above 5% in at least one of the alkaline extractions.

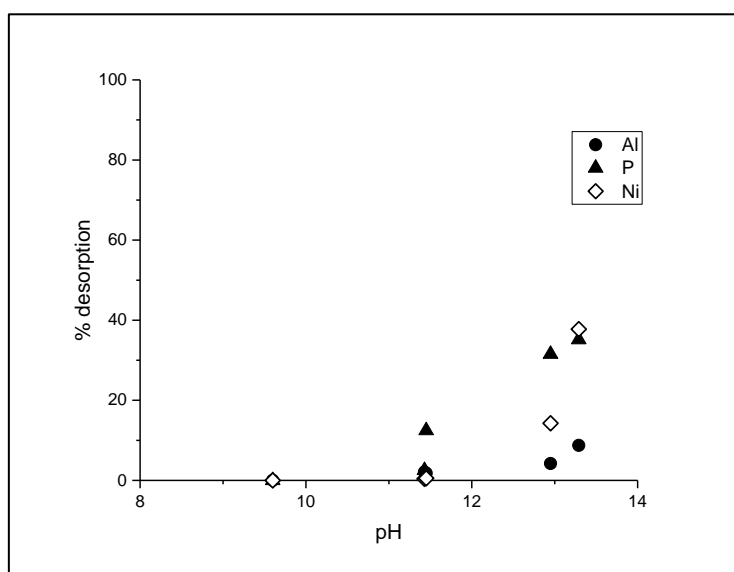


Fig. 2. Alkaline extraction of Al, Ni P in the SSA.

258 P solubilisation results in Fig. 2 confirms the existence of alkaline-soluble Fe(III)-P (and/or Al-P)
 259 bonds in these ashes, as previously suggested for the sameSSA [19]. P extraction using 1 M NaOH
 260 was 35%, considerably lower than the result of using 1 M HNO₃, which was 96% in the previous
 261 work with the same material [19]. This unsymmetrical leaching behaviour of an individual acid and
 262 alkaline extraction step was previously reported for chemically precipitated incineration SSA [36,
 263 49]. There are mainly two explanations for this asymmetry. First, the presence of Ca-phosphates,
 264 which are acid-soluble but alkaline-insoluble; in contrast, Fe- or Al- phosphates are soluble at both

highly acidic and alkaline conditions [35]. Second, P can simultaneously be adsorbed or re-precipitate in the presence of calcium compounds e.g. CaCO_3 (these SSA contained $1.14 \pm 0.14\%$ CaCO_3), CaO and CaSO_4 at alkaline pH [37, 38, 41]. As a consequence, it is not possible to determine accurately the predominance of each bond (Ca-, Fe(III)- and/or Al- phosphate). The reason for the low solubility of Fe in the alkaline extraction ($4.4 \cdot 10^{-5}$ M at pH 13.0) is most likely due to re-precipitation of the solubilized Fe(III), previously bound to P, to hydroxides, for which the solubility are around 10^{-4} M at pH 13 [47].

An acidic step followed by an alkaline extraction allowed an extraction of up to 81% of P (Table 3). This high percentage is possibly due to the removal of over 90% of Ca in the acidic step (Table 3), so that most Ca-P bindings are dissolved and Al/Fe(III)-P bindings (more soluble at pH~11-12 than at pH~1.5 [35]) are broken in the subsequent alkaline step without Ca compounds interference. In contrast, only 36% of P was extracted following the opposite order (Table 3). Since most Ca was removed in the acidic step (Table 3), this poor result can be due to the formation of acid-soluble Fe(III) and/or Al solids in the alkaline step (i.e. hydroxides) and subsequent re-precipitation of P with Al and/or Fe(III) in the acidic step. Then, the ideal order for P recovery from these SSA is to use an acidic step followed by an alkaline step, as previously found for incineration SSA, where P has been precipitated with Al salts during the waste water treatment [36, 37]. In the alkaline step of this sequence, most P was extracted whereas all metals leached at low rate (Table 3, <1% for the rest), except for As leaching, which was equivalent to 2.2 mg/kg of dry SSA, representing at least a 50% of As content in Batch 3 (Table 2). Thus, this combination can also potentially separate P from most metals. Since results in Table 3 are obtained without running two or more replicates, they are used as an orientation and not for numerical comparisons in the next sections.

287

Table 3. Final pH and percentage of element extracted to the filtrates in the two-stage chemical extractions.

Element	Alkaline-Acid extraction			Acid-Alkaline extraction		
	Alkaline step	Acid step	Overall extraction	Acid step	Alkaline step	Overall extraction
P	26%	15%	36%	30%	73%	81%
Ca	0%	91%	91%	92%	0%	91%
Al	6%	16%	21%	17%	0%	18%
Fe	0%	1%	1%	16%	0%	17%
Final pH	13.2	1.7	-	1.5	11.7	-

3.3 ED experiments

In a two-compartment ED cell, pH of the water and SSA suspension decreased when placed in the anode compartment, or increased if placed in the cathode compartment due to water electrolysis at the electrodes. Thus, an acid-alkaline sequential extraction can be adapted in an ED process connecting a couple of 2-compartment ED cells (Fig. 1).

3.3.1 Element distribution and mass balances

The element distribution in the different compartments at the end of the experiments was determined, considering that:

- The catholyte, the cathode and the cation exchange membrane were grouped as the cathode compartment in the 1st step.
- The total mobilisation or desorption of each element, including P, was the sum of the masses found in all electrolyte solutions, membranes and electrodes at the end of the experiments.
- The amount of each element migrated to the catholyte in the 1st step, and to the anolyte in the 2nd step was defined as the difference in each element amount in the electrolyte solution at the end minus at the start of the step.
- The amounts of each element found at the anode in all ED experiments were always below 0.2% of the initial content in the untreated SSA. In consequence, their results are not shown in detail in the present work.

Mass balances for each element (except Cd and As), defined as the division of the amount found at the end of the experiments by the mass initially found in the initial SSA placed in the ED cell, were made to control the quality of each step of the experiments. Most mass balances varied between 80 and 120%, which is probably due to the inherent inhomogeneity of the SSA (Table 2 and Section 3.1). Concentration measurements which were below the LOD used in the ICP analyses (0.02 mg/L), were considered to have this value, except for the anodes and the 1st step catholyte prior to applying the electrical current which were considered to be zero. This arrangement affected several measurements in the cathode compartments for Cr, Cu, Ni and Pb and, together with Cd, in the anolytes. The reason was to be able to calculate the mass balances and the worst-case value for other important parameters in the present work like the heavy metal to P ratio in the anolytes. The

320 overall impact of these approximations was small: below 2.5% of the total final element mass found
321 at the end of the ED experiments.

322 3.3.2 Evolution of ED cell voltage, ash suspension pH and conductivity

323 The voltage between the two electrodes decreased during both steps of the three sets of ED
324 experiments, which corresponded to an increase in electrical conductivity, as well as the pH
325 decrease (1st step) or increase (2nd step) of the SSA suspension. This is due to the increase of ionic
326 concentration in all electrolyte solutions by the generation of either protons (1st step) or hydroxides
327 (2nd step) at the electrodes, as well as the desorption of the elements from the SSA with the changes
328 in pH. Moreover, the rise in conductivity discards possible fouling in the ion exchange membranes
329 [50]. The final pH values of each step are seen in Table 1.

330 3.3.3 P-recovery: 1st and 2nd step

331 Fig. 3 shows the distribution of P at the end of the sequential ED experiments. The amount of P in
332 the 1st step anolyte increased with the time of remediation: 126, 239 and 294 mg P (Fig. 3) after
333 27.5, 52.5 and 125 hours (Table 1). This is consistent with the previous results with the same SSA
334 [19], where the recovered amounts are calculated to be 147, 261 and 295 mg of P after 24, 72 and
335 168 hours, respectively. Therefore, no big differences were observed above 72 hours of ED
336 experiments in terms of P recovery (below 15%), despite the much longer treatment. This can be
337 explained by the low solubility of Fe(III)-phosphates at acidic pH [35], and the higher P migration
338 towards the cathode with longer treatments (Fig. 3, and [19]), due to the formation of positively
339 charged Fe-P and Al-P complexes. Therefore, a higher recovery cannot be expected with a longer
340 duration of a single ED stage using the configuration of the 1st step.

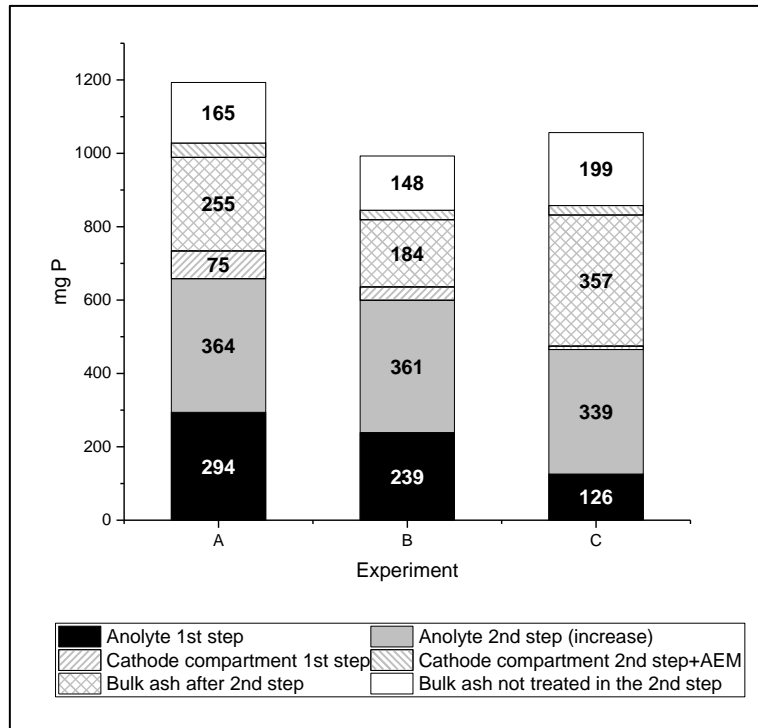


Fig. 3. P distribution at the end of ED experiments.

Around 6-8 grams of the bulk SSA resulting from the first step were not treated in the second step, because a part of it (3 grams) was used for sampling and the rest could not be recovered from the filter paper. The corresponding amounts of P are shown in Fig. 3 as “Bulk ash not treated in the 2nd step”. Despite that, a higher amount of P was recovered to the anolyte in the 2nd step compared to the 1st step for all three experiments (Fig. 3), which is consistent with the results of the second step of the acid-alkaline extraction (Table 3).

As seen, a lower pH in the first step (Table 1) implied a higher recovery of P mass in the anolytes (Fig. 3). The amounts of P recovered in the 2nd step (Fig. 3) were similar (~350 mg) for the three experiments, and below the estimated amount of P bound to Fe(III)/Al in the bulk SSA at the beginning of this step (Table 4). In fact, Fe(III)- or Al-P bindings would still be predominant in the

bulk ash at the end of experiments A and B (Table 4). Considering a valence of three, 350 mg of P represent a transport number of around 0.25 in the 2nd step. A reason for this low migration can be a low solubilisation in the cathode compartment, as a higher amount of P was bound to Fe(III) or Al in the ashes (Table 4) than found in the cathode compartment at the end of the 2nd step (Fig. 3). In order to increase P mobilisation from these SSA, longer remediation times or higher initial NaOH concentrations could be used, although it requires further study.

360

Table 4. Estimation of mg of average P bound to Ca or Al/Fe(III) in the bulk SSA at the end of the 1st and the 2nd ED step.

mg P bound to	At the end of the 1 st step			At the end of the 2 nd step		
	A	B	C	A	B	C
Ca	78	119	197	74	84	213
Al/Fe(III)	658	468	436	180	99	144

363

The total mass of P recovered in experiment B was 600 mg (Fig. 3), with a total remediation time of 124.5 h. This amount doubled the results of running only the 1st ED step for 125 (1st step of experiment A) and 168 hours (see the beginning of this section), even though not all bulk SSA was used in the 2nd step, and confirms its potential to treat these SSA. P-recoveries in experiments A, B and C were 62, 70 and 54%, respectively. The reason for the lower % P-recovery in experiment A than B, despite a higher amount of P recovered, is primarily due to the higher content of P in the initial ash (Fig. 3).

371

3.3.4 Characterisation of the recovered P-rich liquid

The P concentrations in the anolyte after the 2nd step were 1.7, 1.3 and 1.0 g/L for A, B and C respectively (Table 5), higher than the results previously achieved with a single ED step of the same SSA (0.5-0.9 g P/L [19]). Nevertheless, these values are far below concentrations of commercial phosphoric acid or liquid fertilisers (around 450 g P/L [19]) or WPA (above 340 g P/L [47]), which needs to be addressed in future studies. For the three experiments, MER were lower in the anolyte after the 2nd than after the 1st step (Table 5): 0.05, 0.04 and 0.04 at the end of experiments A, B and C respectively. These values were below the limit for WPA (0.085) to be used in the production of diammonium phosphate (DAP [47]), the most commonly traded fertilizer in the world according to the International Fertilizer Industry Association. Moreover, individual Al, Fe and Mg ratios to P were below or in the range of WPA values for all experiments, except for Fe/P in experiment A (Table 5).

385 Table 5. Chemical composition of the anolyte solutions in each step of the ED experiments. MER
386 values exceeding 0.085, and metal to P ratios exceeding the values in WPA [47] are shown in bold.

387 * below LOD in ICP-OES.

Parameter	Experiment						WPA [47]	Units
	A		B		C			
	1 st step	2 nd step	1 st step	2 nd step	1 st step	2 nd step		
P content	0.03	0.02	0.50	1.32	0.25	1.01	~340-450	g P/L
Al/P	0.15	0.05	0.02	0.02	0.02	0.03	<0.03	
Fe/P	0.02	0.01	0.06	0.02	0.02	0.01	<0.04	kg/kg P
Mg/P	0.07	0.04	0.02	0.01	0.05	0.01	0.01-0.03	
MER	0.13	0.05	0.06	0.04	0.07	0.04	-	-
As/P	94	108	<40*	139	159	117	20-70	
Cd/P	<31*	<11*	<40*	<15*	<80*	<20*	120-500	
Cr/P	<31*	14	<40*	<15*	<80*	<20*	100-3,000	
Cu/P	683	250	491	150	627	42	10-400	mg/kg P
Ni/P	64	22	<40*	<15*	93	21	100-700	
Pb/P	<31*	<11*	<40*	48	<80*	<20*	<4	
Zn/P	2,200	746	1,970	834	4,270	1,070	100-10,000	

388

389 Similarly to the acid-alkaline extraction (section 3.2), the high pH in the 2nd step enabled an
390 effective separation of P and most heavy metals .As it can be seen in Table 5, the heavy metal to P
391 ratio in the anolyte at the end of each experiment decreased in comparison to the anolyte in the 1st
392 step for some of the elements: Cu, Zn in all experiments, Ni in experiments A and C, Cr in

experiment A and As in experiment C; As/P increased in experiments A and B, whereas Pb/P increased in experiment B. The rest of heavy metals concentrations were below LOD after the 2nd step, and therefore it cannot be concluded if they were decreased or increased in relation to the 1st step. The values eventually achieved in all experiments for Cr, Cu, Ni, Pb and Zn were at least an order of magnitude below the initial SSA (calculated from Table 2) and, except for Pb (which were below LOD), in the range or below the values found in WPA [47]. The arsenic ratio in the solutions was in the range 108-139 mg As/kg P, similar to the highest value in the range of the untreated SSA (133 mg As/kg P, calculated from Table 2). This can be explained by its similar ionic form to PO_4^{3-} once extracted from the bulk SSA in the 2nd ED step: MINTEQ calculations with the concentrations and pH of the catholyte at the end of each 2nd step indicate a high predominance of arsenate (AsO_4^{3-}). This must be taken into account in future research addressing ED recovery of P from SSA with higher concentration in As.

4. Conclusions

In the present work, up to 70% of P was recovered from low-temperature gasification SSA using an innovative ED sequential process. The SSA had a high proportion of Fe(III)-P bindings. The result is a considerable improvement for extraction of P from these SSA compared to treatment in a single 2-compartment ED cell, where the recovery was less than 30%.

Phosphorus was effectively separated from Al, Ca, Fe, Mg and most heavy metals. This was partially due to the alkaline pH of the ash suspension in one of the steps of the ED treatment, where P bound to Fe(III) and/or Al was extracted and most metals were insoluble. The final product was an acidic P-solution with a metal content comparable to WPA, and a combined impurity level of Al, Fe and Mg suitable for the manufacturing of DAP, the most commonly trade mineral fertilizer.

415 Future studies need to investigate different alternatives to remove arsenic as well as to increase the
416 concentration in the final P-product.

417

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