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1 **Sequential electro dialytic recovery of phosphorus from low-temperature gasification ashes of**
2 **chemically precipitated sewage sludge**

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12
13 **Abstract**

14 Phosphorus recycling from secondary materials like sewage sludge ashes offers an alternative to
15 mining of phosphates from primary resources and a mean to counteract the current phosphorus
16 rock depletion concern. A separation of P from the bulk ash is normally required, due to its low
17 plant availability and the presence of heavy metals. Previously, more than 80% of P was recovered
18 from incineration sewage sludge ashes using a two-compartment electro dialytic cell. In contrast, the
19 recovery was below 30% for ashes from low-temperature gasification using the same setup. The
20 low recovery was due to a high presence of Al- and Fe(III)-P bindings. In the present study, an
21 electro dialytic process combining sequentially a pair of two-compartment cells allowed a recovery
22 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

32

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34

35 **1. Introduction**

36 Europe is dependent on phosphate rock imports [1], the reserves of which are estimated to be
37 exhausted within 50-400 years [1-3]. The European Commission included this mineral in the list of
38 20 critical raw materials in 2014. Moreover, mineral P-fertilizers are the main contributors of toxic
39 elements accumulation such as cadmium [4] and uranium [5] in agricultural soils. For these reasons,
40 P recycling from secondary resources, like sewage sludge, has gained increased attention among
41 researchers, private companies and public institutions over the last decade [6-9]. Around 16% of
42 phosphate rock import can be potentially substituted with unrecycled P from sewage sludge in
43 Europe [1]. In order to promote P recycling, some countries e.g. Denmark have set goals for P
44 recovery [10], and others e.g. Germany, Switzerland and Sweden currently have proposals to make
45 it obligatory. The content of heavy metals as well as potential unwanted organic pollutants and
46 pathogens are of major concerns in respect to sewage sludge's direct use on agricultural fields [8,
47 11]. Another difficulty is the limited plant-availability of P when sewage sludge is precipitated with
48 Al and Fe salts in the wastewater treatment plant to avoid eutrophication of natural water system
49 recipients, a practice which is common in many countries [7, 12-15].

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

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

65 Other processes than ED has been investigation for the recovery of P from SSA and the majority
66 can be grouped into either:

67 a) Acid extraction of P from SSA with H_2SO_4 , HCl, HNO_3 and/or H_3PO_4 , followed by further
68 steps to separate P from the leached impurities like heavy metals by means of sulphide
69 precipitation [18], solvent extraction [21] and/or ion exchange columns [13, 18, 22, 23], as
70 well as through the chemical precipitation of P as Ca-phosphates [9, 22, 24, 25]. The biggest
71 industrial agreement to recycle P from SSA until now was signed in the beginning of 2015
72 between the Belgian company Ecophos and the Dutch companies HVC and SNB, which
73 includes the construction of a plant to treat 50-60,000 tonnes of incineration SSA yearly
74 using a method belonging to this group.

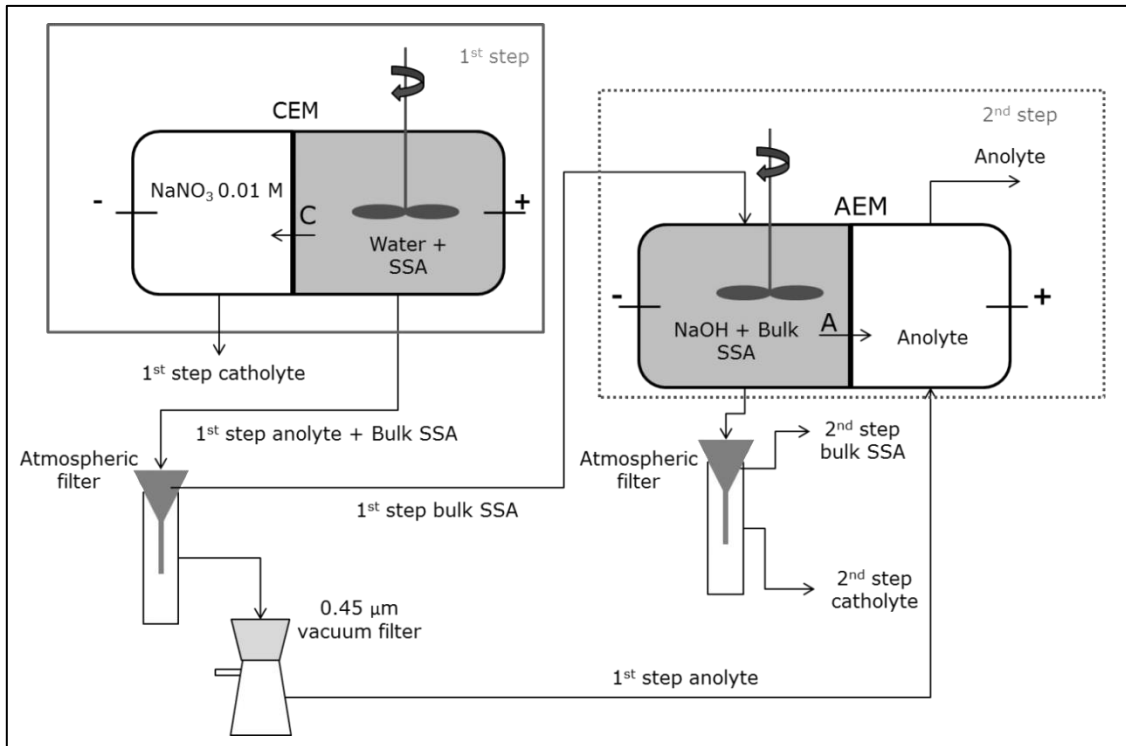
75 b) Thermal removal of heavy metals at high temperatures (above $1400^\circ C$) [9, 26], which also
76 allows the separation of the main metals like Fe; or at around $1000^\circ C$ in combination with
77 chemicals like calcium or magnesium chloride [27], Na- and K- salts and bases [9, 28, 29],
78 which at the same time increases the plant availability of P in the ashes.

79 However, these researches have focused on chemically precipitated incineration SSA, where Fe(III)
80 is not controlling P solubility [30, 31], which is on the contrary to gasification SSA. An alkaline
81 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



103

104

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

105 2. Experimental

106 2.1 Experimental SSA

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

113 2.2 Analytical methods and sampling

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

120 The concentrations of elements were measured for each batch: in triplicates for the alkaline
121 extraction as well as for the sequential extraction, and in eight samples for the ED experiments. It
122 was also measured in triplicates after each step of the sequential extraction and the ED experiments.
123 The targeted elements were: Al, As, Ca, Cd, Cu, Cr, Fe, K, Mg, Ni, P, Pb and Zn. Na was analysed
124 only for the initial samples of the ED experiments. Their content was measured by Varian 720-ES
125 inductively coupled plasma optical emission spectrometry (ICP-OES) after pre-treatment by Danish
126 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

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

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

153 Where V_{acid} and $V_{alkaline}$ were the volumes of filtrates recovered after each extraction, C_{P-acid} and $C_{P-alkaline}$
 154 the concentration of P in these filtrates, $C_{P-ash-alkaline}$ the P-concentration in the dry ash after the
 155 alkaline extraction, whereas $m_{ash-start}$, $m_{ash-acid}$ and $m_{ash-alkaline}$ were the mass of dry ash at the
 156 beginning and at the end of each extraction. The reason for the inclusion of the ratio between m_{ash-}
 157 $acid$ and $m_{ash-start}$, multiplying the second term in the dividend and the divisor, was to extrapolate the
 158 result of the alkaline extraction step to all the bulk dry ash mass after the acid extraction. The same
 159 equation was used to calculate Ca, Al and Fe extraction.

160 2.5 ED experimental setup

161 An illustration of the ED sequential process used is shown in Fig. 1. Both cells consisted of two
 162 compartments made of cylindrical Plexiglas® with an internal diameter of 8 cm. The compartment
 163 with the ash suspension was 10 cm long and the other compartment 5 cm. The anode compartment
 164 contained 35 g ash and 350 ml DI water. In the second step, the cathode compartment contained 25
 165 g of the bulk ash resulting from the first step and 300 ml DI water, as well as 8 mL of NaOH 1 M
 166 added at the beginning of the experiment. A plastic strip attached to a glass-stick connected to an
 167 overhead stirrer (IKA RW11) was used to stir the ash suspensions during the experiments. In the
 168 cathode compartment of the first step, 500 mL electrolyte solution (0.01 M NaNO₃, pH < 2 adjusted
 169 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

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

194 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

195

196 Catholyte (in the first step) and anolyte (in the second step) samples were taken in 20 mL vials
197 before applying the electrical current and after 5 minutes of electrolyte circulation; at the end of the
198 experiments, catholyte and anolyte volumes were measured and sampled in 20 mL vials. 16 mL of
199 the samples from the catholyte in the 2nd step was mixed with 4 mL HNO₃ 68%, and heated at 200
200 kPa (120°C) for 30 min. The element content was measured in the ICP-OES for all electrolytes after
201 filtration through a 0.45 μm syringe filter. Na content in the catholyte of the second step was also
202 measured by ICP-OES.

203 2.7 Experimental ED parameters

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

206 The amounts of P found in the analyte 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:

209

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

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

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

213 Where $V_{1^{st} \text{ step}}$ and $V_{2^{nd} \text{ step}}$ were the volumes of analyte 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 analytes for each ED step, whereas $m_{\text{ash}-1^{st} \text{ step}}$ and $m_{\text{ash}-2^{nd} \text{ step-start}}$
 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 $m_{\text{ash}-1^{st} \text{ step}}$ and $m_{\text{ash}-2^{nd} \text{ step-start}}$ 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:

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

230

231 **3. Results**

232 3.1 Element content in untreated SSA

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

242

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

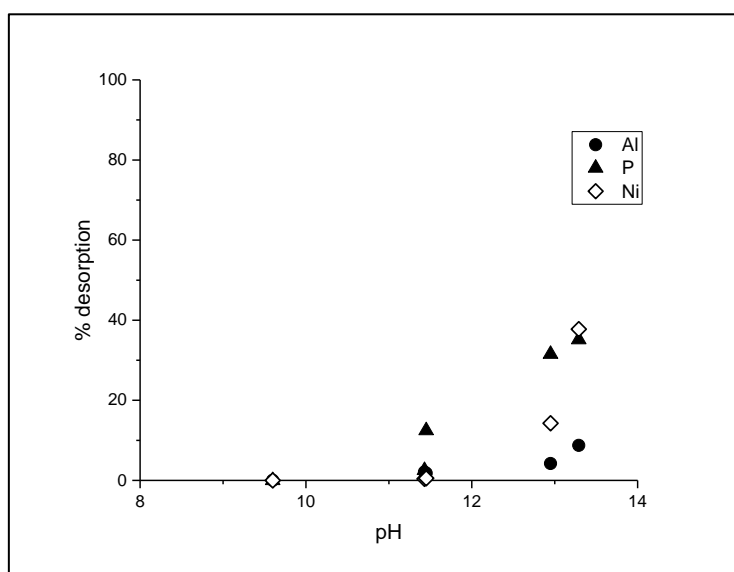
Element	Previous research [19]	Batch 1 - Alkaline extraction	Batch 2 – Two-stage chemical extraction		Batch 3 - ED	Units
			per kg of dry ash	per kg of P		
Al	9.5±1.3	11.6±0.5	14.9±3.9	10.5±1.2	-	g/kg
Ca	36.7±5.1	40.4±0.6	51.9±10.7	34.3±4.4	-	g/kg
Fe	57.6±8.3	58.3±2.9	82.6±21.1	58.3±6.7	-	g/kg
Mg	-	3.0±0.6	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.



255

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

257

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

265 highly acidic and alkaline conditions [35]. Second, P can simultaneously be adsorbed or re-
266 precipitate in the presence of calcium compounds e.g. CaCO₃ (these SSA contained 1.14±0.14%
267 CaCO₃), CaO and CaSO₄ at alkaline pH [37, 38, 41]. As a consequence, it is not possible to
268 determine accurately the predominance of each bond (Ca-, Fe(III)- and/or Al- phosphate). The
269 reason for the low solubility of Fe in the alkaline extraction ($4.4 \cdot 10^{-5}$ M at pH 13.0) is most likely
270 due to re-precipitation of the solubilized Fe(III), previously bound to P, to hydroxides, for which the
271 solubility are around 10^{-4} M at pH 13 [47].

272 An acidic step followed by an alkaline extraction allowed an extraction of up to 81% of P (Table 3).
273 This high percentage is possibly due to the removal of over 90% of Ca in the acidic step (Table 3),
274 so that most Ca-P bindings are dissolved and Al/Fe(III)-P bindings (more soluble at pH~11-12 than
275 at pH~1.5 [35]) are broken in the subsequent alkaline step without Ca compounds interference. In
276 contrast, only 36% of P was extracted following the opposite order (Table 3). Since most Ca was
277 removed in the acidic step (Table 3), this poor result can be due to the formation of acid-soluble
278 Fe(III) and/or Al solids in the alkaline step (i.e. hydroxides) and subsequent re-precipitation of P
279 with Al and/or Fe(III) in the acidic step. Then, the ideal order for P recovery from these SSA is to
280 use an acidic step followed by an alkaline step, as previously found for incineration SSA, where P
281 has been precipitated with Al salts during the waste water treatment [36, 37]. In the alkaline step of
282 this sequence, most P was extracted whereas all metals leached at low rate (Table 3, <1% for the
283 rest), except for As leaching, which was equivalent to 2.2 mg/kg of dry SSA, representing at least a
284 50% of As content in Batch 3 (Table 2). Thus, this combination can also potentially separate P from
285 most metals. Since results in Table 3 are obtained without running two or more replicates, they are
286 used as an orientation and not for numerical comparisons in the next sections.

287

288 Table 3. Final pH and percentage of element extracted to the filtrates in the two-stage chemical
 289 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	-

290

291 3.3 ED experiments

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

296

297 3.3.1 Element distribution and mass balances

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

- 300 • The catholyte, the cathode and the cation exchange membrane were grouped as the cathode
301 compartment in the 1st step.
- 302 • The total mobilisation or desorption of each element, including P, was the sum of the masses
303 found in all electrolyte solutions, membranes and electrodes at the end of the experiments.
- 304 • The amount of each element migrated to the catholyte in the 1st step, and to the anolyte in
305 the 2nd step was defined as the difference in each element amount in the electrolyte solution
306 at the end minus at the start of the step.
- 307 • The amounts of each element found at the anode in all ED experiments were always below
308 0.2% of the initial content in the untreated SSA. In consequence, their results are not shown
309 in detail in the present work.

310 Mass balances for each element (except Cd and As), defined as the division of the amount found at
311 the end of the experiments by the mass initially found in the initial SSA placed in the ED cell, were
312 made to control the quality of each step of the experiments. Most mass balances varied between 80
313 and 120%, which is probably due to the inherent inhomogeneity of the SSA (Table 2 and Section
314 3.1). Concentration measurements which were below the LOD used in the ICP analyses (0.02
315 mg/L), were considered to have this value, except for the anodes and the 1st step catholyte prior to
316 applying the electrical current which were considered to be zero. This arrangement affected several
317 measurements in the cathode compartments for Cr, Cu, Ni and Pb and, together with Cd, in the
318 anolytes. The reason was to be able to calculate the mass balances and the worst-case value for
319 other important parameters in the present work like the heavy metal to P ratio in the anolytes. The

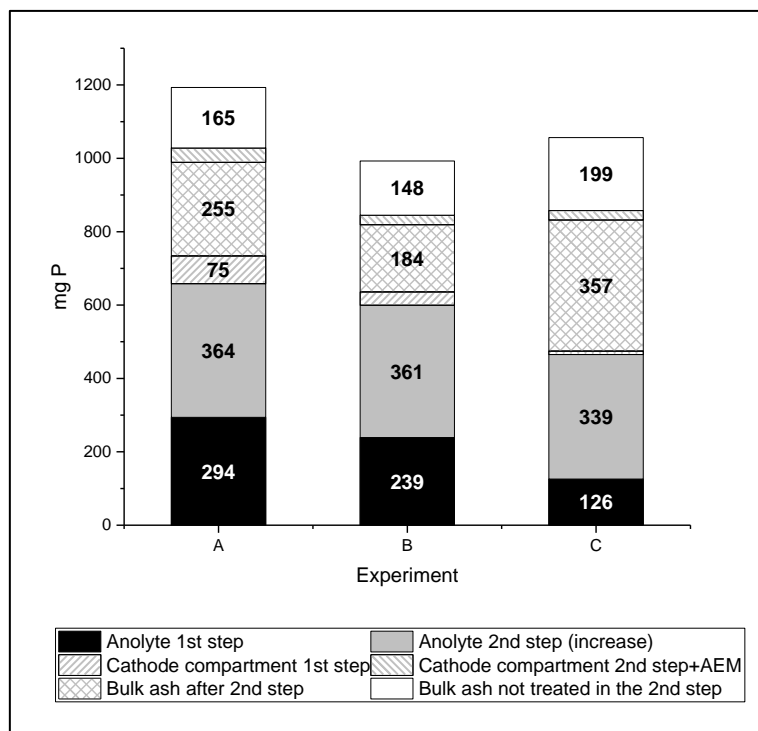
320 overall impact of these approximations was small: below 2.5% of the total final element mass found
321 at the end of the ED experiments.

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.



341

342

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

343

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

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

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

360

361 Table 4. Estimation of mg of average P bound to Ca or Al/Fe(III) in the bulk SSA at the end of the
 362 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

364 The total mass of P recovered in experiment B was 600 mg (Fig. 3), with a total remediation time of
 365 124.5 h. This amount doubled the results of running only the 1st ED step for 125 (1st step of
 366 experiment A) and 168 hours (see the beginning of this section), even though not all bulk SSA was
 367 used in the 2nd step, and confirms its potential to treat these SSA. P-recoveries in experiments A, B
 368 and C were 62, 70 and 54%, respectively. The reason for the lower % P-recovery in experiment A
 369 than B, despite a higher amount of P recovered, is primarily due to the higher content of P in the
 370 initial ash (Fig. 3).

371

372 3.3.4 Characterisation of the recovered P-rich liquid

373 The P concentrations in the analyte after the 2nd step were 1.7, 1.3 and 1.0 g/L for A, B and C
374 respectively (Table 5), higher than the results previously achieved with a single ED step of the
375 same SSA (0.5-0.9 g P/L [19]). Nevertheless, these values are far below concentrations of
376 commercial phosphoric acid or liquid fertilisers (around 450 g P/L [19]) or WPA (above 340 g P/L
377 [47]), which needs to be addressed in future studies. For the three experiments, MER were lower in
378 the analyte after the 2nd than after the 1st step (Table 5): 0.05, 0.04 and 0.04 at the end of
379 experiments A, B and C respectively. These values were below the limit for WPA (0.085) to be
380 used in the production of diammonium phosphate (DAP [47]), the most commonly traded fertilizer
381 in the world according to the International Fertilizer Industry Association. Moreover, individual Al,
382 Fe and Mg ratios to P were below or in the range of WPA values for all experiments, except for
383 Fe/P in experiment A (Table 5).

384

385 Table 5. Chemical composition of the analyte 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 analyte at the end of each experiment decreased in comparison to the analyte in the 1st
 392 step for some of the elements: Cu, Zn in all experiments, Ni in experiments A and C, Cr in

393 experiment A and As in experiment C; As/P increased in experiments A and B, whereas Pb/P
394 increased in experiment B. The rest of heavy metals concentrations were below LOD after the 2nd
395 step, and therefore it cannot be concluded if they were decreased or increased in relation to the 1st
396 step. The values eventually achieved in all experiments for Cr, Cu, Ni, Pb and Zn were at least an
397 order of magnitude below the initial SSA (calculated from Table 2) and, except for Pb (which were
398 below LOD), in the range or below the values found in WPA [47]. The arsenic ratio in the solutions
399 was in the range 108-139 mg As/kg P, similar to the highest value in the range of the untreated SSA
400 (133 mg As/kg P, calculated from Table 2). This can be explained by its similar ionic form to PO₄³⁻
401 once extracted from the bulk SSA in the 2nd ED step: MINTEQ calculations with the concentrations
402 and pH of the catholyte at the end of each 2nd step indicate a high predominance of arsenate
403 (AsO₄³⁻). This must be taken into account in future research addressing ED recovery of P from SSA
404 with higher concentration in As.

405 **4. Conclusions**

406 In the present work, up to 70% of P was recovered from low-temperature gasification SSA using an
407 innovative ED sequential process. The SSA had a high proportion of Fe(III)-P bindings . The result
408 is a considerable improvement for extraction of P from these SSA compared to treatment in a single
409 2-compartment ED cell, where the recovery was less than 30%.

410 Phosphorus was effectively separated from Al, Ca, Fe, Mg and most heavy metals. This was
411 partially due to the alkaline pH of the ash suspension in one of the steps of the ED treatment, where
412 P bound to Fe(III) and/or Al was extracted and most metals were insoluble. The final product was
413 an acidic P-solution with a metal content comparable to WPA, and a combined impurity level of Al,
414 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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422

423

424 **References**

425 [1] K. C. van Dijk, J. P. Lesschen, and O. Oenema, "Phosphorus flows and balances of the
426 European Union Member States," *Science of the Total Environment*, vol. 542, pp. 1078-
427 1093, 2016.

428 [2] D. Cordell, J. O. Drangert, and S. White, "The story of phosphorus: Global food security
429 and food for thought," *Global Environmental Change-Human and Policy Dimensions*,
430 Review vol. 19, no. 2, pp. 292-305, May 2009.

431 [3] C. J. Dawson and J. Hilton, "Fertiliser availability in a resource-limited world: Production
432 and recycling of nitrogen and phosphorus," *Food Policy*, Article vol. 36, pp. S14-S22, Jan
433 2011.

434 [4] M. B. McBride and G. Spiers, "Trace element content of selected fertilizers and dairy
435 manures as determined by ICP-MS," *Communications in Soil Science and Plant Analysis*,
436 Article vol. 32, no. 1-2, pp. 139-156, 2001.

- 437 [5] M. D. Taylor, "Accumulation of uranium in soils from impurities in phosphate fertilisers,"
438 *LANDBAUFORSCHUNG VOLKENRODE*, vol. 57, no. 2, pp. 133-139, 2007.
- 439 [6] C. Sartorius, J. von Horn, and F. Tettenborn, "Phosphorus Recovery from Wastewater-
440 Expert Survey on Present Use and Future Potential," *Water Environment Research*, Article
441 vol. 84, no. 4, pp. 313-322, Apr 2012.
- 442 [7] K. Gorazda, Z. Wzorek, B. Tarko, A. K. Nowak, J. Kulczycka, and A. Henclik, "Phosphorus
443 cycle - possibilities for its rebuilding," *Acta Biochimica Polonica*, vol. 60, no. 4, pp. 725-
444 730, 2013.
- 445 [8] O. F. Schoumans, F. Bouraoui, C. Kabbe, O. Oenema, and K. C. van Dijk, "Phosphorus
446 management in Europe in a changing world," *Ambio*, Article vol. 44, pp. S180-S192, Mar
447 2015.
- 448 [9] H. Herzel, "Technical comparison on the design, operation and performances of ash
449 processes - Deliverable D 4.1 of the P-REX project," BAM, 2015.
- 450 [10] "Denmark without waste," The Danish Government, 2013.
- 451 [11] P. J. A. Withers *et al.*, "Stewardship to tackle global phosphorus inefficiency: The case of
452 Europe," *Ambio*, Article vol. 44, pp. S193-S206, Mar 2015.
- 453 [12] E. Paul, M. L. Laval, and M. Sperandio, "Excess sludge production and costs due to
454 phosphorus removal," *ENVIRONMENTAL TECHNOLOGY*, vol. 22, no. 11, pp. 1363-1371,
455 2001.
- 456 [13] S. Donatello, D. Tong, and C. R. Cheeseman, "Production of technical grade phosphoric
457 acid from incinerator sewage sludge ash (ISSA)," *Waste Management*, Article vol. 30, no. 8-
458 9, pp. 1634-1642, Aug-Sep 2010.

- 459 [14] G. Rodriguez-Garcia, M. Molinos-Senante, A. Hospido, F. Hernandez-Sancho, M. T.
460 Moreira, and G. Feijoo, "Environmental and economic profile of six typologies of
461 wastewater treatment plants," *WATER RESEARCH*, vol. 45, no. 18, pp. 5997-6010, 2011.
- 462 [15] O. Kruger, A. Grabner, and C. Adam, "Complete Survey of German Sewage Sludge Ash,"
463 *Environmental Science & Technology*, Article vol. 48, no. 20, pp. 11811-11818, Oct 2014.
- 464 [16] S. Donatello and C. R. Cheeseman, "Recycling and recovery routes for incinerated sewage
465 sludge ash (ISSA): A review," *Waste Management*, Review vol. 33, no. 11, pp. 2328-2340,
466 Nov 2013.
- 467 [17] T. P. Thomsen, G. Ravenni, J. K. Holm, J. Ahrenfeldt, H. Hauggaard-Nielsen, and U. B.
468 Henriksen, "Screening of various low-grade biomass materials for low temperature
469 gasification: Method development and application," *Biomass and Bioenergy*, vol. 79, pp.
470 128-144, 8// 2015.
- 471 [18] M. Franz, "Phosphate fertilizer from sewage sludge ash (SSA)," *Waste Management*, Article
472 vol. 28, no. 10, pp. 1809-1818, 2008.
- 473 [19] R. Parés Viader, P. E. Jensen, L. M. Ottosen, J. Ahrenfeldt, and H. Hauggaard-Nielsen,
474 "Electrodialytic extraction of phosphorus from ash of low-temperature gasification of
475 sewage sludge," *Electrochimica Acta*, vol. 181, pp. 100-108, 2015.
- 476 [20] B. Ebbbers, L. M. Ottosen, and P. E. Jensen, "Comparison of two different electro-dialytic
477 cells for separation of phosphorus and heavy metals from sewage sludge ash,"
478 *Chemosphere*, 2015.
- 479 [21] C. Dittrich, W. Rath, D. Montag, and J. Pinnekamp, "Phosphorus recovery from sewage
480 sludge ash by a wet-chemical process," presented at the *International Conference on*
481 *Nutrient Recovery from Wastewater Streams*, 2009.

- 482 [22] J. Lehmkuhl and M. Lebek, "Purifying crude phosphoric acid, comprises reacting crude
483 phosphoric acid with ash, calcium hydroxide and at least one sulfide, and depositing the
484 acid-insoluble portion of the solids to obtain a filtrate or eluate," Patent DE102014006278-
485 B3; WO2015165481-A1.
- 486 [23] M. Takhim, "Method for recovering ash from waste incineration used in e.g. agricultural
487 field, involves digesting ash by leaching liquor containing phosphate ions and separating
488 liquid phase comprising phosphate ions from solid phase," Patent WO2015091946-A1.
- 489 [24] J. Lehmkuhl and M. Lebek, "Extracting precipitates of calcium nitrate, calcium phosphate,
490 calcium sulfate or aluminum hydroxophosphate from phosphate-containing ash from waste
491 incineration plants, comprises extracting e.g. calcium phosphate and calcium nitrate," Patent
492 DE102013018650-B3; WO2015067328-A1.
- 493 [25] J. Lehmkuhl and M. Lebek, "Recovering precipitates including e.g. calcium nitrate from
494 phosphate-containing solids, comprises e.g. reacting solids with e.g. nitric acid or
495 phosphoric acid, and adding calcium oxide or calcium carbonate to filtrate or supernatant,"
496 Patent DE102013018652-A1.
- 497 [26] A. Schönberg, K. Samiei, H. Kern, and H. Raupenstrauch, "Der RecoPhos-Prozess –
498 Rückgewinnung von Phosphor aus Klärschlammmasche, The recophos process: recovering
499 phosphorus from sewage," *Osterreichische Wasser- Und Abfallwirtschaft*, vol. 66, no. 11-
500 12, pp. 403-407, 2014.
- 501 [27] C. Adam, B. Peplinski, M. Michaelis, G. Kley, and F. G. Simon, "Thermochemical
502 treatment of sewage sludge ashes for phosphorus recovery," *Waste Management*, Article
503 vol. 29, no. 3, pp. 1122-1128, Mar 2009.

- 504 [28] O. Krüger, C. Adam, L. Hermann, and H. Herzel, "Sewage sludge ash - A promising
505 secondary phosphorus source for fertilizer production," *Science of the Total Environment*,
506 vol. 542, pp. 1136-1143, 2016.
- 507 [29] J. Stemann, C. Adam, and B. Peplinski, "Thermochemical treatment of sewage sludge ash
508 with sodium salt additives for phosphorus fertilizer production - Analysis of underlying
509 chemical reactions," *Waste Management*, vol. 45, 2015.
- 510 [30] Y. Cohen, "Phosphorus dissolution from ash of incinerated sewage sludge and animal
511 carcasses using sulphuric acid," *Environmental Technology*, Article vol. 30, no. 11, pp.
512 1215-1226, 2009.
- 513 [31] K. Gorazda, Z. Kowalski, and Z. Wzorek, "From sewage sludge ash to calcium phosphate
514 fertilizers," *Polish Journal of Chemical Technology*, Article vol. 14, no. 3, pp. 54-58, 2012.
- 515 [32] A. Sano, M. Kanomata, H. Inoue, N. Sugiura, K.-Q. Xu, and Y. Inamori, "Extraction of raw
516 sewage sludge containing iron phosphate for phosphorus recovery," *Chemosphere*, vol. 89,
517 no. 10, pp. 1243-1247, 2012.
- 518 [33] P. Wilfert, P. S. Kumar, L. Korving, G.-J. Witkamp, and M. C. M. van Loosdrecht, "The
519 Relevance of Phosphorus and Iron Chemistry to the Recovery of Phosphorus from
520 Wastewater: A Review," *Environmental Science and Technology*, vol. 49, no. 16, pp. 9400-
521 9414, 2015.
- 522 [34] L. M. Ottosen, P. E. Jensen, and G. M. Kirkelund, "Electrodialytic Separation of Phosphorus
523 and Heavy Metals from Two Types of Sewage Sludge Ash," *Separation Science and
524 Technology*, vol. 49, no. 12, pp. 1910-1920, 2014.
- 525 [35] W. Stumm and J. J. Morgan, *Aquatic chemistry : Chemical equilibria and rates in natural
526 waters*. Wiley, 1996.

- 527 [36] S. Petzet, B. Peplinski, and P. Cornel, "On wet chemical phosphorus recovery from sewage
528 sludge ash by acidic or alkaline leaching and an optimized combination of both," *Water*
529 *Research*, Article vol. 46, no. 12, pp. 3769-3780, Aug 2012.
- 530 [37] S. Petzet, B. Peplinski, S. Y. Bodkhe, and P. Cornel, "Recovery of phosphorus and
531 aluminium from sewage sludge ash by a new wet chemical elution process (SESAL-Phos-
532 recovery process)," *Water Science and Technology*, Article vol. 64, no. 3, pp. 693-699,
533 2011.
- 534 [38] P. Benzing and C. J. Rickardson, "CaCO₃ causes underestimation of NaOH extractable
535 phosphorus in sequential fractionations," *Soil Science*, Article vol. 170, no. 10, pp. 802-809,
536 Oct 2005.
- 537 [39] D. C. Ribeiro, G. Martins, R. Nogueira, J. V. Cruz, and A. G. Brito, "Phosphorus
538 fractionation in volcanic lake sediments (Azores, Portugal)," *Chemosphere, Chemosphere,*
539 *Chemosphere*, vol. 70, no. 7, pp. 1256-1263, 2008.
- 540 [40] Y. Kalmykova and K. K. Fedje, "Phosphorus recovery from municipal solid waste
541 incineration fly ash," *Waste Management*, vol. 33, no. 6, pp. 1403-1410, 2013.
- 542 [41] J. Chen, H. Kong, D. Wu, X. Chen, D. Zhang, and Z. Sun, "Phosphate immobilization from
543 aqueous solution by fly ashes in relation to their composition," *Journal of Hazardous*
544 *Materials*, vol. 139, no. 2, pp. 293-300, 2007.
- 545 [42] D. Touaibia, H. Kerdjoudj, and A. T. Cherif, "Concentration and purification of wet
546 industrial phosphoric acid by electro-electrodialysis," *JOURNAL OF APPLIED*
547 *ELECTROCHEMISTRY*, vol. 26, no. 10, pp. 1071-1073, 1996.
- 548 [43] J. Ahrenfeldt, T. Thomsen, U. B. Henriksen, and L. R. Clausen, "Biomass gasification
549 cogeneration – A review of state of the art technology and near future perspectives," *Applied*
550 *Thermal Engineering*, vol. 50, no. 2, pp. 1407-1417, 2013.

- 551 [44] P. Rothenhofer, A. Huber, B. Kainzmaier, S. Wohnlich, and S. Peiffer, "Ein Vergleich von
552 vier Methoden zur Bestimmung des Karbonatgehaltes, A comparison of four methods for
553 determining carbonate contents," (in German), *Wasser Und Boden, Wasser Boden, Wasser
554 Und Boden Zeitschrift Fuer Die Gesamte Wasserwirtschaft*, vol. 52, no. 10, pp. 37-42, 2000.
- 555 [45] Danish standard, "DS259: Determination of metals in water, sludge and sediments - General
556 guidelines for determination by atomic absorption spectrophotometry in flame," 2003.
- 557 [46] P. Guedes, N. Couto, L. M. Ottosen, and A. B. Ribeiro, "Phosphorus recovery from sewage
558 sludge ash through an electrodialytic process," *WASTE MANAGEMENT*, vol. 34, no. 5, pp.
559 886-892, 2014.
- 560 [47] R. Gilmour, "*Phosphoric Acid Purification, Uses, Technology, and Economics*," *CRC Press
561 (Taylor & Francis Group)*, 2014.
- 562 [48] Scholz, R. W., Roy, A. H., & Hellums, D. T. *Sustainable Phosphorus Management: a
563 Global Transdisciplinary Roadmap*," Springer, 2014.
- 564 [49] B. K. Biswas, K. Inoue, H. Harada, K. Ohto, and H. Kawakita, "Leaching of phosphorus
565 from incinerated sewage sludge ash by means of acid extraction followed by adsorption on
566 orange waste gel," *Journal of Environmental Sciences*, vol. 21, no. 12, pp. 1753-1760, //
567 2009.
- 568 [50] M. Araya-Farias and L. Bazinet, "Effect of calcium and carbonate concentrations on anionic
569 membrane fouling during electrodialysis," *Journal of Colloid and Interface Science*, vol.
570 296, no. 1, pp. 242-247, 2006.

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