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Phosphorous recovery from sewage sludge ash suspended in water in a two-compartment electrodialytic cell

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ABSTRACT

Phosphorus (P) is indispensable for all forms of life on Earth and as P is a finite resource, it is highly important to increase recovery of P from secondary resources. This investigation is focused on P recovery from sewage sludge ash (SSA) by a two-compartment electrodialytic separation (EDS) technique. Two SSA are included in the investigation and they contained slightly less P than phosphate rock used in commercial fertilizer production and more heavy metals. The two-compartment electrodialytic technique enabled simultaneous recovery of P and separation of heavy metals. During EDS the SSA was suspended in water in the anolyte, which was separated from the catholyte by a cation exchange membrane. Electrolysis at the anode acidified the SSA suspension, and hereby P, Cu, Pb, Cd and Zn were extracted. The heavy metal ions electromigrated into the catholyte and were thus separated from the filtrate with P.

21 More than 95% P was extracted from both SSAs. The charge transfer to obtain this varied when treating
22 the two SSAs, and for one ash it was about 30% higher than for the other as result of a higher buffering
23 capacity against acidification. The repeatability of EDS results between experiments with the same SSA
24 and the same experimental conditions was good, which shows that the process is easy to control at the
25 studied laboratory conditions. About 80% P and 10% of the heavy metals remained in the filtrate from
26 the anolyte after treatment of both SSAs. The heavy metal content relative to P in the filtrate by far meet
27 the limiting values for use of industrial wastes as fertilizers, thus the filtrate is ready for direct processing
28 into P-fertilizer.

29

30 **1. INTRODUCTION**

31 By the human perspective, resources are non-renewable when their rate of consumption exceeds the rate
32 of recovery. Depletion of P from primary sources is a result of non-sustainable use. It is time to
33 acknowledge the reality of the finite limit and develop methods for recovery of P from secondary sources.
34 One such source is ash from incineration of sewage sludge (SSA). Sewage sludge incineration is a well
35 proven technology with hundreds of plants worldwide (Werther and Ogada, 1999); 1.7 million tonnes of
36 SSA are produced annually world-wide, and the production is likely to increase in the future (Donatello
37 & Cheeseman 2013). The concentration of P in SSA is generally 5-10% (Cyr et al. 2007), thus
38 approaching the content in virgin phosphorite, which indicates that SSA is a significant potential
39 secondary P resource. There is limited gain in crop yield if SSA is spread directly at agricultural land as
40 P is not in a plant available form in the ash. In addition, heavy metals are concentrated in the SSA during
41 incineration, which prohibits use of SSA in agriculture.

42

43 Different techniques are under development for recovery of P from SSA. The techniques can be grouped
44 in two: thermochemical treatment or chemical extraction. These methods are reviewed in (Donatello &
45 Cheeseman 2013). Current practice for handling the SSA from the two Danish plants, from where ash
46 was sampled for the present investigation, is landfilled in special landfills with only SSA. The purpose
47 is to recover the P from the landfilled ashes, when proper and economical methods have been developed.
48 This work updates the technology where the P is extracted in acid. A major problem with acid extraction
49 is the simultaneous extraction of heavy metals and P (Donatello et al. 2010a; Ottosen et al. 2013). In
50 order to obtain a clean P product, various processes for separation of P and heavy metals have been
51 suggested: pH adjustment (Franz 2008, Takahashi 2001), sulfide precipitation (Franz, 2008), cation
52 exchange (Franz, 2008; Donatello et al. 2010b) and electrodialytic separation (Ottosen et al. 2014,
53 Guedes et al. 2014, Ebbers et al. 2014a). The first three separation techniques require a two-step
54 treatment, first P extraction and subsequent separation. In electrodialytic separation the P extraction and
55 heavy metal separation occur simultaneously. The present paper focus on electrodialytic separation and
56 reports laboratory tests with two-compartment electrodialytic P recovery from sewage sludge ash from
57 incineration of municipal wastewater sludge. A major focus is on describing the major elements and
58 heavy metal content of the recovered P and comparing it to commercial P-fertilizers. The ashes originate
59 from the two (out of three) largest sewage sludge incineration plants in Denmark as it is interesting to
60 investigate the robustness of EDS method for ashes from both plants.

61

62 **1.1 Two-compartment EDS**

63 The principle of the two-compartment EDS setup used in this paper is illustrated in figure 1. The major
64 objective with this setup is a simultaneous extraction of P and removal of heavy metals from the liquid
65 with P. When the electrical DC current is applied to the electrodes, the SSA suspension will gradually be

66 acidified due to electrolysis at the anode ($\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^-$). During the acidification heavy
67 metals and P are extracted from the ash. The heavy metals are transported by electromigration over the
68 cation exchange membrane (CEM) and concentrate in the cathode compartment. The extracted P remains
69 in the filtrate of the ash suspension. Hereby simultaneous extraction and separation is obtained.

70

71 A two-compartment electro-dialytic setup has previously been tested for purification of wet industrial
72 phosphoric acid (Touaibia et al. 1996), but this setup was opposite to the one of this paper. In (Touaibia
73 et al. 1996) the two compartments were separated by an anion exchange membrane (AEM) and the
74 phosphoric acid to be treated was placed in the cathode compartment. Here the impurities were retained
75 in the catholyte and P electromigrated to the anolyte where phosphoric acid was formed with protons
76 produced by the anodic electrolysis. The concentration of the phosphoric acid produced by this method
77 was, however, limited by proton leakage through the AEM (Touaibia et al. 1996). The two compartment
78 system with the cathode placed in reject water from a WWWT plant and separation of P into the anolyte
79 was tested in (Ebbens et al. 2015b), however, the increase in pH caused P precipitation and limited the
80 recovery. A three compartment EDS system based on the idea of recovering phosphoric acid in the
81 anolyte and heavy metals in the catholyte was tested by Ottosen et al. (2014) and by Guedes et al (2014).
82 These works, however, showed that the transport of P into the anolyte was inefficient. Phosphorous has
83 four speciation steps: H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} and the corresponding acid constants (pK_a , 298
84 K) are 2.12; 7.2 and 12. Thus at pH less than 2, P is present as phosphoric acid without any charge and
85 thus not mobile for electromigration. But at the same time pH needs to be less than 2 to fully extract P
86 from SSA (Ottosen et al. 2013). Contrarily, the heavy metal transport into the catholyte progressed well
87 in the three compartment electro-dialytic cell, as heavy metals are present in ionic form as released from
88 the SSA by acid (Ottosen et al 2014). The insufficient P recovery in the anode compartment using the

89 three compartment EDS cell formed basis for the idea of a simpler setup; the two compartment EDS cell.
90 The overall idea of the two-compartment EDS is to keep the P in the filtrate to which it is extracted and
91 transport the heavy metals out from this filtrate in the applied electric field. By placing the anode directly
92 in the suspension a faster acidification and subsequent release of P and heavy metals is obtained
93 compared to the three compartment cell.

94
95 Phosphorous extraction in two-compartment EDS was experimentally compared to three-compartment
96 EDS (Ebbers et al. 2014a) where experiments were made with ash suspended in distilled water or H₂SO₄.
97 The fastest recovery of P was obtained in the two-compartment cell when the SSA was suspended in
98 H₂SO₄. However, when suspending the ash in H₂SO₄ gypsum was formed by Ca²⁺ released from the ash
99 and the SO₄²⁻ from the acid (Ottosen et al. 2014). The formation of gypsum increases the volume of
100 particulate matter to be landfilled. Environmentally as well as economically it would be beneficial to use
101 the remaining ash in e.g. construction materials rather than landfilling. SSA has been suggested to be
102 used in different construction materials. Donatello & Chesemann (2013) reviewed the use in: sintered
103 ceramics (bricks and lightweight aggregates) and in concrete as cement replacement or in the production
104 of the cement. The gypsum formation may hamper such use. Also other anions, such as Cl⁻ or NO₃⁻ added
105 by use of other mineral acids for P dissolution may impede the use of the residual ash in construction
106 materials and they will be impurities in the phosphoric acid. This problem is completely avoided by the
107 use of EDS and acidification thorough electrolysis at the anode. For use in concrete, milling of SSA
108 showed very beneficial due to improved pozzolanic activity (Donatello et al. 2010a). For this reason and
109 because the finer particle size after milling eased keeping the ash suspended during EDS, the SSA was
110 milled prior to treatment in the present work. Experiments were conducted with SSA's from two different
111 incineration plants. We investigated and compared the recovery of P from the two SSAs and the

112 separation of heavy metals from the filtrate into the catholyte. Finally the purity of a phosphorous salt
113 produced from evaporation the water from the filtrate was evaluated.

114

115 **2. MATERIALS AND METHODS**

116 **2.1 Experimental ashes**

117 SSAs from the two major Danish mono-incineration plants were used. The sludge incinerated at both
118 plants originated from municipal wastewater treatment. Iron was used in both waste water facilities to
119 precipitate P, and the sewage sludge was incinerated in a fluidized bed combustor at about 850°C. Ash
120 A was sampled at Spildevandscenter Avedøre and ash B was from Lynettefællesskabet. Both ashes were
121 sampled directly from ash silos when the ash was filled in trucks for transportation away from the plants.
122 Ash A was sampled as a mix of electrofilter ash and bag filter ash (2%), whereas ash B was sampled
123 directly after the electrofilter. After sampling, the ashes were stored in closed plastic containers at room
124 temperature. Before use, the ashes were milled for 30 seconds in a Vibrating Cup Mill PULVERISETTE
125 9.

126

127 **2.2 Analytical and ash characterization**

128 Characterization was made with dried ash (105°C, 24 hours). Concentrations of P, Cu, Pb, Zn and Cd
129 were measured in all samples with a Varian 720-ES ICP-OES (Inductively Coupled Plasma - Optical
130 Emission Spectrometry). SSA samples were pre-treated in accordance to Danish Standard DS259: 1.0 g
131 ash and 20.0 ml (1:1) HNO₃ was heated at 200 kPa (120°C) for 30 minutes and filtered through a 0.45
132 µm filter prior to the analysis by ICP-OES. Ash pH and conductivity were measured after suspending
133 10.0 g ash in 25 ml distilled water. After 1 hour agitation pH and conductivity were measured directly in

134 the suspension with Radiometer electrodes. Water content was measured as weight loss after 24 hours at
135 105°C (calculated as weight loss over the weight of the wet sample). Loss on ignition (LoI) was found
136 after 30 minutes at 550°C. Five duplicates of each of these analyses were made. Solubility in water was
137 evaluated: 50.0 g ash suspended in 500 ml distilled water and agitated for 1 min. After settling the water
138 was decanted. New 500 ml distilled water added. This was repeated so the ash was washed three times.
139 Finally the suspension was filtered and the ash dried and weighed.

140

141 **2.3 Experiments with two-compartment electrolysytic P recovery**

142 The experiments were conducted in a cylindrical cell as shown in figure 1. The length of the anode
143 compartment with ash suspension was 10 cm and the length of the cathode compartment 5 cm. The
144 internal diameter of both compartments was 8 cm. The cation exchange membrane was from Ionics
145 (CR67 HUY N12116B). The electrodes were made of platinum coated titanium wire (diameter 3 mm)
146 obtained from Permascand®) and the length of the electrode in the catolyte was approximately 4 cm. A
147 power supply (Hewlett Packard E3612A) was used to maintain a constant current of 50 mA. The SSA
148 was kept suspended in the anode compartment by an overhead stirrer (RW11 basic from IKA). In the
149 cathode compartment 500 mL 0.01 M NaNO₃ adjusted to pH 2 with HNO₃ was circulated. The circulation
150 of the catolyte ensures a continuous flow in this compartment and prevents build-up of high concentration
151 gradients at the surface of the cation exchange membrane and it flushes the produced H₂ gas from
152 electrolysis out of the compartment. During experiments, pH was adjusted manually in the cathode
153 compartment to between 1 and 2 daily with 1 M HNO₃. Conductivity and pH in the ash suspension and
154 voltage between electrodes were also measured daily.

155

156 Totally 12 EDS experiments were made with duration and type of SSA as the two varying parameters
157 (see table 1). In every experiment 25 g SSA was suspended in 350 ml distilled water (corresponding to
158 a liquid to solid ratio L:S = 14). Three identical experiments A4-A6 were conducted to investigate the
159 repeatability of the results.

160

161 At the end of the EDS experiments the suspension was filtered at atmospheric pressure. Contents of P,
162 Cu, Zn, Pb and Cd were measured in the ash, solutions, cation exchange membrane and on the cathode.
163 The ash was dried before measurement of the same chemical elements (triplicate measurements). The
164 contents in the cation exchange membrane were measured after extraction in 1.0 M HNO₃ and rinsing of
165 the electrodes prior to measurement was done in 5.0 M HNO₃. For further investigating the purity of the
166 P produced, the filtrate from experiment A6 was placed in an oven at 50°C in order to evaporate the
167 water and produce a salt. As shown later the P extraction had reached maximum in experiment A6 and
168 this was the reason for choosing it. The purpose was twofold: to analyze the concentration of heavy
169 metals in relation to P and to evaluate the quality of the produced salt as basis for P fertilizer. The
170 produced salt was stored in a desiccator to hinder hygroscopic uptake of moisture from the air. The salt
171 was characterized by the total content of macro elements (P, Ca, Fe and Al), heavy metals (Cu, Pb, Zn
172 and Cd) after DS259 (described above). It was checked that the macro elements analyzed were those
173 present in the salt by elemental mapping of the salt crystals using Scanning Electron Microscopy with
174 Energy Dispersive X-Ray Analysis (SEM-EDX). The water soluble fraction in the salt of the same
175 elements extracted in distilled water at liquid to solid ratio (L:S) 2.5 was measured as well.

176 **3. RESULTS AND DISCUSSION**

177 **3.1 The SSAs as secondary P resource**

178 Characteristics of the SSAs are shown in table 2. Both ashes were alkaline, but Ash A had lower pH (pH
179 9.5) than Ash B (pH 12.4). Ash B contained a larger water soluble fraction than ash A, seen from both
180 the higher water soluble fraction and the higher conductivity when suspended in water.

181

182 It is interesting to compare the SSAs as being secondary resources for P to the primary resource being
183 the phosphate rock. Phosphorus pentoxide (P_2O_5) is the commonly reported constituent of the phosphate
184 rock. The economic grade of phosphate rock varies from 25% to 37% P_2O_5 (Gupta et al 2014). This
185 concentration range corresponds to 110-160 g P/kg phosphate rock and thus the P concentration in SSA-
186 A (110 g/kg) is exactly at the lower end of this range, but the concentration in SSA-B (73 g/kg) is lower.
187 The concentrations in the SSAs are though high enough to be considered as secondary P resources. Ores
188 of the phosphorous rock contain various toxic metals and radionuclides which later are transferred to
189 phosphate fertilizers (Gupta et al. 2014). The concentrations Cu, Zn and Pb in different phosphate rock
190 for production of fertilizer were compiled by (Aydin et al 2010), and the ranges reported were 6-130 mg
191 Cu/kg, 6-515 mg Zn/kg and 4-455, 93-2060 mg Pb/kg, 0.1 – 60 mg Cd/kg. The heavy metal
192 concentrations reported in literature in different SSAs were collected in (Cyr et al 2007): 200-5400 mg
193 Cu/kg; 1080-10,000 mg Zn/kg, 93-2060 mg Pb/kg and 4-94 mg Cd/kg. In general Zn and Cu
194 concentrations in SSAs are thus higher than in phosphate rock, Pb concentrations are overlapping in the
195 high range of phosphate rocks and low range of SSA. The concentration ranges are overlapping in the
196 case of Cd, though higher Cd concentrations were found in the SSAs. The ashes of the present
197 investigation follow this general trend, yet the heavy metal concentration is low. The concentrations in
198 the two SSAs of the present investigation fall within the lower ends of these ranges for heavy metals in
199 SSA except for Pb in SSA-B and Cd in both ashes, which are even lower than the lowest concentration
200 previously reported. In summary, the SSAs contained slightly less P than phosphate rock used in

201 commercial fertilizer production and more heavy metals. The heavy metals in P fertilizer are taken up by
202 the crops (Gupta et al. 2014) and if the P related heavy metal concentration in SSA is not reduced, this
203 issue causes concern in the use of SSA as resource for P fertilizer. Thus separation of P and heavy metals
204 from SSA is important.

205

206 **3.2 EDS process repeatability**

207 Acceptable mass balances (defined as mass of an element in the different parts at the end of the
208 experiment over the mass of the element initially in the ash) were obtained for P, Cu, Zn and Pb in every
209 experiment (90-110%), whereas for Cd, the mass balances were not this good due to a low initial
210 concentration. Subsequently only the distributions for Cu, Zn and Pb from the EDS experiments are
211 given. The content of Cd in the final P product is discussed on basis of the produced salt later.

212

213 The repeatability of EDS experiments can be evaluated by comparing the three identical experiments
214 with SSA-A and the duration 10 days (A4 to A6). In each of these three experiments about 54% ash was
215 dissolved during the treatment and final pH of the suspension was 1.1 (table 1). The distribution of P,
216 Cu, Pb and Zn in ash, filtrate and cathode compartment (cation exchange membrane, catholyte and at the
217 cathode) are shown in figure 2. The average values are given with error bars showing minimum and
218 maximum values. The separation results were very similar for the three experiments and the deviation
219 from the average value was 5% or less. Almost all P was extracted, and only 2-3% remained in the ash
220 at the end of the experiments. Around 80% P was found in the filtrate of the suspension. Also for each
221 of the heavy metals the distributions are the same. For Cu and Zn the major parts are found in the cathode
222 compartment (>70%) whereas 60% Pb remained in the ash. On the basis of the very similar result

223 obtained in these experiments A4-A6 it was decided to make the remaining experiments of the
224 investigation as single experiments.

225

226 **3.3 Optimal duration of EDS for P recovery**

227 The development in distribution of P, Zn, Pb and Cu as result of the EDS duration is seen in figure 3
228 (SSA-A) and figure 4 (SSA-B). The general trend between the two ashes is a slower extraction of all four
229 elements from SSA-B. During the first 5 days less than 10% of each element was released from SSA-B,
230 whereas about 80% P; 65% Zn and Cu; and 10% Pb were released from SSA-A. This corresponds to the
231 faster acidification of the suspension with SSA-A and faster ash dissolution (table 1). This is in
232 accordance with previous findings, as release of both P and heavy metals from SSA was shown to
233 increase with decreasing pH (Ottosen et al. 2013, Donatello et al. 2010). It was also previously shown
234 that different SSAs have different buffering capacities and require different amounts of acid for P
235 extraction (Ottosen et al. 2013) and this was also the case for the two present ashes even if they are both
236 from fluidized bed incineration of Fe rich ash at about 850°C.

237

238 Almost all P (>95%) was extracted between 5-7 days of EDS of SSA-A and between 7-10 days of SSA-
239 B (figures 3 and 4). The P extraction corresponds to the time where pH reaches below 2 (table 1), which
240 again corresponds to the finding for SSA-A, reported in (Ottosen et al. 2013) for chemical extraction in
241 HNO₃ where 50-60% P was extracted at pH 2 and 85-100% P at pH of about 1 from this ash. Results
242 with two-compartment EDS was reported in (Ebbbers et al 2015a) with SSA from the same plant as SSA-
243 A of the present investigation but with lower L:S (10 vs. 14) and the same current. The lower L:S
244 prolonged the extraction time slightly as the buffering capacity of the suspension increases with ash
245 amount. In (Ebbbers et al 2015a) about 80% P was extracted during 7 days.

246 For both SSAs prolonging EDS after the time where full P extraction was obtained meant a loss of P into
247 the cathode compartment (figures 3(d) and 4(d)). After 14 days of EDS the lost P was approximately
248 18% for both ashes. When terminating the experiments at the point where maximum P extraction is
249 obtained the loss of P into the cathode compartment is about 10% from both ashes and this loss seem
250 hard to hinder. As the two compartments are separated by a CEM, which hinder transport of anions, the
251 P transported into the catholyte may have been transported as neutrally charged complexes by diffusion
252 due to the concentration difference in the two compartments or by electromigration as cationic species
253 may be formed e.g. from the reactions: $\text{Al}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{AlH}_2\text{PO}_4^{2+}$ or $\text{Al}^{3+} + \text{H}_2\text{PO}_4^{2-} \rightarrow \text{AlH}_2\text{PO}_4^+$
254 (Nordstrom & May, 1989). During the two experiments with duration of 14 days A7 and B4, 45% and
255 32% Al was transported into the cathode compartment, respectively, and it is possible that some of the
256 Al had formed positively charged complexes with P.

257 Incineration of sewage sludge is used worldwide, but an emerging technology is low-temperature
258 gasification, which allows energy production from biomass resources like sewage sludge with high
259 contents of low melting point ash compounds, which can cause boiler operational problems in the more
260 traditional incineration (Skoglund et al. 2013). Viader et al. (2015) tested two compartment EDS (at L:S
261 10 and an applied current of 50 mA) from ash from gasification of two different municipal sewage
262 sludges from a plant where P was captured 50% biologically and 50% chemically (with Fe and Al
263 chlorides) and a plant where P was mainly removed biologically with a minor amount of Fe salts (this
264 latter was co-gasified with wheat straw pellets). During 7 days 26% and 90% P was recovered by EDS,
265 respectively. The low P-extraction from the first ash was suggested being due to low-soluble Fe-
266 phosphates formed during the gasification. This hypothesis is supported by the good EDS result from the
267 other ash, with only a minor content of Fe. Even though the SSA from the present investigation originates
268 from sludge where Fe-salts were used for P precipitation, the EDS extraction of P is not hampered by

269 this, probably because iron oxides are formed during incineration rather than iron phosphates, so the
270 choice of thermal process influences P extractability from the ash. The possible EDS for extraction of P
271 and separation of heavy metals from SSA was shown being dependent on the precipitation chemicals
272 used at the WWWT in (Ottosen et al 2014), so this is the case for both gasification and incineration ashes.
273

274 **3.4 Heavy metal removal**

275 As well as P, the heavy metals were mobilized faster from SSA-A than SSA-B (figures 3 and 4). The
276 mobilization of Cu and Zn was faster than Pb from both ashes, i.e. Zn and Cu were mobilized at a higher
277 pH. The nature and proportion of minerals controlling the mobilization behavior of the different heavy
278 metals from sewage sludge ash have not yet been studied in-depth. The mineralogy in SSA represents an
279 assemblage of crystalline and amorphous phases and it is a very complex system. However, the finding
280 that Pb is mobilized to a lesser extent than Cu and Zn is in accordance to findings from chemical
281 extraction in acid for SSAs (Ottosen et al. 2013), three compartment EDS (Ottosen et al 2014, Guedes et
282 al. 2014), two-compartment EDS (Ebberts et al 2015a) and it is also a general finding using three-
283 compartment EDS for treatment of different ash types e.g. municipal solid waste incinerator fly ash
284 (Pedersen et al 2003) and wood ash (Ottosen et al 2007).

285

286 At day 10 the pH in both ash suspensions reached approximately 1 (table 2). At this point the mobilized
287 percentages were:

288 SSA-A: 88% Cu, 42% Pb and 80% Zn

289 SSA-B: 41% Cu, 39% Pb and 29% Zn

290 After this point pH stabilized in both experimental series and the mobilization of the heavy metals
291 stopped.

292

293 Jensen et al. (2006) reported remediation results for Pb from soil fines in a three-compartment
294 electro-dialytic cell. The distribution of Pb in the cell over time was reported in a similar way as figures
295 3 and 4 in the present work. The work by Jensen et al. (2006) clearly illustrated how the removal of Pb
296 underwent four phases:

- 297 (1) a “lag-phase”, where removal was substantially absent
- 298 (2) a high removal rate involving dissolution of Pb into the soil solution
- 299 (3) low removal rate, where the already dissolved Pb was removed from solution
- 300 (4) no further Pb-removal was obtained as the treatment proceeded.

301 The same four phases can be used to describe the removal of the heavy metals from the SSAs in the
302 present investigation. The “lag-phase” (1) is the phase until the buffering capacity of the ash is exceeded
303 and the suspension reaches an acidification level, where the heavy metal is released (2). The duration of
304 this phase was dependent on both the buffering capacity of the SSA and the actual heavy metal. The
305 treatment should be finished by the end of phase (3) or at latest at the beginning of phase (4) because
306 further treatment does not lead to any improvements but only increased energy consumption. In the actual
307 experiments this point is related to the stabilized pH at about 1, after which the major current carrier will
308 be H⁺ ions. Similar phases are thus found during electro-dialytic treatment of soil fines and sewage sludge
309 ash. The focus in this investigation is recovery of P and simultaneous removal of heavy metals and it is
310 important to finish the treatment to hinder significant loss of P into the catolyte.

311 The four phases are easiest distinguished for Cu and Zn in SSA-B (figure 4). Phase (1) is approximately
312 5 days; Phase (2) between 5 and 7 days; Phase (3) is between 7 and 10 days, though not seen as a
313 decreased removal rate compared to the previous phase, but only from the stop in heavy metal removal

314 of the already mobilized part, Phase (4) is after 10 days, where the distribution of Cu and Zn does not
315 change over time. The phases have different durations for Cu and Zn in SSA-A (figure 3). Phase (1) was
316 less than 3 days the change from phase (2) to (3) is around 5 days, as hereafter the concentration in the
317 solution of the suspension decreases. This means that the removal rate in the applied electric field is
318 faster than the rate with which heavy metal release from the ash occur. Phase (4) starts at about day 10.
319 In relation to Pb both were within phase (3), even with the longest durations. The optimal duration at the
320 conditions of the present investigation is about 7 days for Ash-A and 10 days for Ash-B. Distinguishing
321 the separation process into these phases can be useful when optimizing EDS as the experimental
322 conditions can be optimized for each phase.

323

324 **3.5 The treated ash**

325 The concentrations of Cu, Pb and Zn in the ash decreased over time in Ash A while they increased in ash
326 B during EDS (table 2). This distinct difference shows that whereas the heavy metals are found in
327 relatively high concentrations in the soluble ash particles of Ash A (under conditions of EDS) they are
328 found in the least soluble particles in Ash B. This underlines the different characteristics of the two SSAs
329 even though they are both from mono-incineration of sewage sludge in fluidized bed at 850°C. The final
330 concentrations of Cu and Zn were 3-4 times higher in Ash B after 14 days of EDS even though the initial
331 concentration was lower. This might influence the possible uses of the ashes in construction materials,
332 where high heavy metal concentrations can hamper the use.

333

334 **3.6 Purity of the filtrate with P**

335 The salt produced from evaporation of the water from the filtrate in experiment A6 (where the extraction
336 of P and separation of heavy metals had reached slightly into phase 4, i.e. the heavy metal cations are

337 transported into the catholyte) is evaluated in relation to the heavy metal concentrations by comparison to
338 the limiting values for use of waste on agricultural land in Denmark (Miljøstyrelsen 2010). There are two
339 sets of concentrations; the first is on a dry matter basis and the second are P related concentrations. The
340 latter is only given for Pb and Cd of the four heavy metals of the investigation. The limiting values are
341 shown in table 3. Soil contamination with Cd from phosphate fertilizer is a major issue. The Cd content
342 in the salt was 0.9 mg Cd/kg, which is higher than the Danish limiting value of 0.8 mg Cd/kg (table 3).
343 The Cd contamination level in common P fertilizers ranges from trace to 300 mg/kg of dry product
344 (Gupta et al 2014), and thus the Cd concentration in the salt is in the lower end of fertilizers. The P related
345 concentration in the salt was 3.7 mg Cd/kg P which was less than the limiting value. An average Cd
346 content in European fertilizers is 138 mg/kg P (Davister 1996) and the salt contains significantly less.
347 The total concentrations of Cu, Pb and Zn in the salt were all below the limiting values. In addition, the
348 P related limiting value for Pb was by far met in the salt.

349

350 The concentrations of macro elements (P, Ca, Al and Fe) in the salt are shown in table 3. A SEM-EDX
351 investigation of dry salt verified that the macro elements in the salt were only those given in the table 3.
352 As aimed for, the salt had a very high content of P (24% per weight) and calculated to P_2O_5 this
353 corresponds to 56% per weight, which is higher than the economic grade of phosphate rock ranging from
354 25% to 37% (Gupta et al 2014). In case evaporation is chosen as method for further processing the filtrate
355 towards use in fertilizer, it is of importance that the water soluble fraction of P in the salt was very high
356 (92%), which is very positive. Fe and Al phosphates are poorly soluble, and these could constitute a part
357 of the salt, but as 66% Fe and 60% Al were in a water soluble form, less than half of these elements can
358 be present as poorly soluble phosphates. In addition, the concentrations of Fe and Al were very low
359 compared to that of P. On a molar basis there were 9% Al and 0.5% Fe in relation to P, so the maximum

360 loss of water soluble phosphorous compounds due to precipitation of Al and Fe phosphates would be
361 less than 10%. The molar ratio between Ca and P in the salt was 0.17, but as both elements have high
362 water solubility poorly soluble calcium phosphates are not formed. Calcium dihydrogen phosphate is
363 soluble in weak acid and is the suggested form. The major part of the salt crystals is considered to be
364 phosphoric acid crystals, which are colorless and hygroscopic crystals, exactly as experienced for the
365 crystals formed in this project. The salt had good quality for use in fertilizer production i.e. high water
366 solubility of P and a low concentration of heavy metals, however, full evaporation at 50°C is time and
367 energy consuming so chemical precipitation could be a better solution. Important is though the low
368 content of impurities in the filtrate, which allows for further processing towards fertilizer production.

369

370 **4. CONCLUSION**

371 SSA was used as secondary resource for P recovery in the present investigations. SSAs from two different
372 municipal wastewater treatment plants were included. The SSAs contained slightly less P than phosphate
373 rock used in commercial fertilizer production and more heavy metals. Simultaneous recovery of
374 phosphorous and separation of heavy metals from SSA was obtained in a two-compartment
375 electro-dialytic cell. The SSA was initially suspended in distilled water at the anode compartment and
376 during application of an electric DC field, pH decreased in the suspension due to electrolysis at the anode.
377 The acidification caused mobilization of P and heavy metals. In the applied electric field the heavy metals
378 were transported over the cation exchange membrane into the catholyte. Higher extractions of P were
379 obtained by EDS from both SSAs compared to chemical extraction at the same pH. A longer duration of
380 the EDS process to reach high P extraction was needed for one of the ashes, 10 days vs. 7 days, (as it had
381 higher buffer capacity). Recovery of 80-90% P was obtained (defined as the fraction in the solution of

382 the anode compartment) with less than 20% of the original heavy metals for both ashes. A P-salt was
383 produced from the filtrate and the salt had a low content of impurities, which allows for further processing
384 towards fertilizer production.

385

386 **5. ACKNOWLEDGEMENTS**

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391 **6. REFERENCES**

392

393 Aydin, I.; Aydin, F.; Saydut, A.; Bakirdere, E.G.; Hamamci, C. Hazardous metal geochemistry of
394 sedimentary phosphate rock used for fertilizer (Mazıdag, SE Anatolia, Turkey). *Microchemical Journal*,
395 **2009** *91*, 63–69

396 Cyr, M.; Coutand, M.; Clastres, P. Technological and environmental behaviour of sewage sludge ash
397 (SSA) in cement-based materials. *Cement Concrete Res*, **2007**, *37*, 1278-1289

398 Davister, A. Studies and Research on Processes for the elimination of cadmium from phosphoric acid.
399 *OECD Proceedings - Fertilizers as a Source of Cadmium. IOMC*. 1996 Paris. p. 21-30.

400 Donatello, S.; Cheeseman, C.R. Recycling and recovery routes for incinerated sewage sludge ash
401 (ISSA): A review. *Waste Management* **2013**, *33(11)*, 2328-2340

402 Donatello, S.; Freeman-Pask, A.; Tyrer, M.; Cheeseman, C.R. Effect of milling and acid washing on the
403 pozzolanic activity of incinerator sewage sludge ash. *Cement Concrete Comp*, **2010a**, *32*, 54-61

404 Donatello, S.; Tong, D.; Cheeseman, C.R. Production of technical grade phosphoric acid from incinerator
405 sewage sludge ash (ISSA). *Waste Management*, **2010b**, *30*, 1634–1642

406 Ebbbers, B.; Ottosen, L.M.; Jensen, P.E. Comparison of two different Electrodialytic Cells for Separation
407 of Phosphorus and Heavy Metals from Sewage Sludge Ash, *Chemosphere*, **2015a**, *125*, 122-129

408 Ebbbers, B., Ottosen, L.M., Jensen, P.E. Electrodialytic treatment of municipal wastewater and sludge for
409 the removal of heavy metals and recovery of phosphorus, *Electrochimica Acta*, **2015b**. In Press.

410 Franz, M. Phosphate fertilizer from sewage sludge ash (SSA). *Waste Management*, **2008**, *28*, 1809-1818

411 Guedes, P.; Couto, N.; Ottosen, L.M.; Ribeiro, A.B. Phosphorus recovery from sewage sludge ash
412 through an electrodialytic process. *Waste Management*, **2014**, *34*, 886–892

413 Gupta, D.K.; Chatterjee, S.; Datta, S.; Veer, V.; Walther, C. Review. Role of phosphate fertilizers in
414 heavy metal uptake and detoxification of toxic metals. *Chemosphere*, **2014**, *108*, 134–144

415 Jensen, P.E.; Ottosen, L.M.; Ferreira, C. Kinetics of Electrodialytic Extraction of Pb and Soil Cations
416 from Contaminated Soil Fines in Suspension, *Journal of Hazardous Materials*, **2006**, *138*(3), 493-499

417 Miljøministeriet, Miljøstyrelsen (Danish EPA) Anvendelse af affald til jordbrugsformål (In Danish).
418 Vejledning No. 1, 2010

419 Nordstrom, D.K.; May, H.M. Aqueous equilibrium data for mononuclear aluminum species. In
420 *Environmental Chemistry of Aluminium*. G. Sposito. CRC Press, Boca Raton, FL 1989, pp 29-53

421 Ottosen, L.M.; Jensen, P.E. Kirkelund, G.M. Electrodialytic separation of phosphorous and heavy metals
422 from two types of sewage sludge ash. *Separation Science and Technology*, **2014**, *49*, 1910–1920

423 Ottosen, L.M.; Kirkelund, G.M.; Jensen, P.E. Extracting phosphorous from incinerated sewage sludge
424 ash rich in iron or aluminum. *Chemosphere* **2013**, *91*(7), 963-969

425 Ottosen, L.M.; Pedersen, A.J.; Hansen, H.K.; Ribeiro, A.B. Screening the possibility for removing
426 Cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method

427 *Electrochimica Acta* **2007**, 52(10), 3420-3426

428 Pedersen A.J.; Ottosen, L.M.; Villumsen, A. Electrodialytic removal of heavy metals from different fly
429 ashes. Influence of heavy metal speciation in the ashes. *Journal of Hazardous Materials* **2003**, B100, 65-
430 78, 2003

431 Skoglund, N.; Grimm, A.; Ohman, M.; Bostrom, D. Effects on Ash Chemistry when Co-firing
432 Municipal Sewage Sludge and Wheat Straw in a Fluidized Bed: Influence on the Ash Chemistry by
433 Fuel Mixing, *Energy & Fuels*, 2013, 27, 5725-5732

434 Takahashi, M.; Kato, S.; Shima, H.; Sarai, E.; Ichioka, T.; Hatyakawa, S.; Miyajri, H. Technology for
435 recovering phosphorous from incinerated wastewater treatment sludge. *Chemosphere*, **2001**, 44, 23-39

436 Tirado, R., Allsop, M. Phosphorus in agriculture: problems and solutions. Greenpeace Research
437 Laboratories Technical Report (Review) 02-2012 (greenpeace.org).

438 Touaibia, D.; Kerdjoudj, H.; Cherif, A.T. Concentration and purification of wet industrial phosphoric
439 acid by electro-electrodialysis (Technical note). *Journal of Applied Electrochemistry*, **1996**, 26, 1071-
440 1073

441 Viader, R.P., Jensen, P.E., Ottosen, L.M., Ahrenfeldt, J., Hauggaard-Nielsen, H. Electrodialytic
442 extraction of phosphorus from ash of low-temperature gasification of sewage sludge
443 2015, *Electrochimica Acta*, In Press.

444 Werther J., Ogada, T. Sewage sludge combustion. *Prog Energ Combust Sci* **1999**, 25, 55–116
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	Duration (days)	Dissolved ash (%)	Final pH in suspension	Final concentrations in ash Cu/Pb/Zn (mg/kg)
A1	3	27.2	2.1	540/180/1160
A2	5	44.5	1.7	390/220/1050
A3	7	50.8	1.6	250/170/1030
A4	10	54.3	1.1	210/160/840
A5	10	53.7	1.1	260/150/950
A6	10	53.9	1.1	260/140/1010
A7	14	53.9	1.0	210/120/930
B1	5	26.2	4.3	600/120/2900
B2	7	42.8	2.1	510/140/2700
B3	10	64.7	1.2	690/140/4200
B4	14	65.5	1.0	700/140/4100
B5	16	63.7	1.1	690/130/4100

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448 *Table 1: The duration and SSA varied between the experiments. Shown are also for the SSA the final pH, dissolution during*
449 *the experiment and concentrations of Cu, Pb and Zn.*

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	Ash A	Ash B
pH (H ₂ O)	9.6 ± 0.1	12.4 ± 0.1
Conductivity (mS/cm)	2.8 ± 0.2	10.3 ± 0.1
Loss on ignition (550°C) (%)	0.5 ± 0.05	3.0 ± 0.12
Solubility in water (g/kg)	15	66
Water soluble Cl (mg/kg)	25 ± 1	860 ± 8
P (g/kg)	110 ± 1.1	72.3 ± 2.1
Al (g/kg)	21.6 ± 0.3	14.1 ± 4.4
Zn (mg/kg)	2030 ± 14	2180 ± 65
Cu (mg/kg)	700 ± 3.6	480 ± 12
Pb (mg/kg)	115 ± 2.3	81 ± 2.5
Cd (mg/kg)	3.2 ± 0.1	2.2 ± 0.2

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Table 2: Characteristics of the two investigated SSAs.

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	P	Al	Ca	Fe	Cu	Pb	Zn	Cd
Total concentration (mg/kg)	244,000	18,700	55,400	2,200	248	91	460	0.9
P related concentration (mg/kg P)					1,020	370	1,900	3.7
Soluble in water (mg/kg)	224,000	11,300	53,500	1,460	240	22	430	0.5
Water solubility (%)	92	60	97	66	97	24	94	56
Limiting value (mg/kg)					1,000	120	4,000	0.8
Limiting value (mg/kg P)					-	10,000	-	100

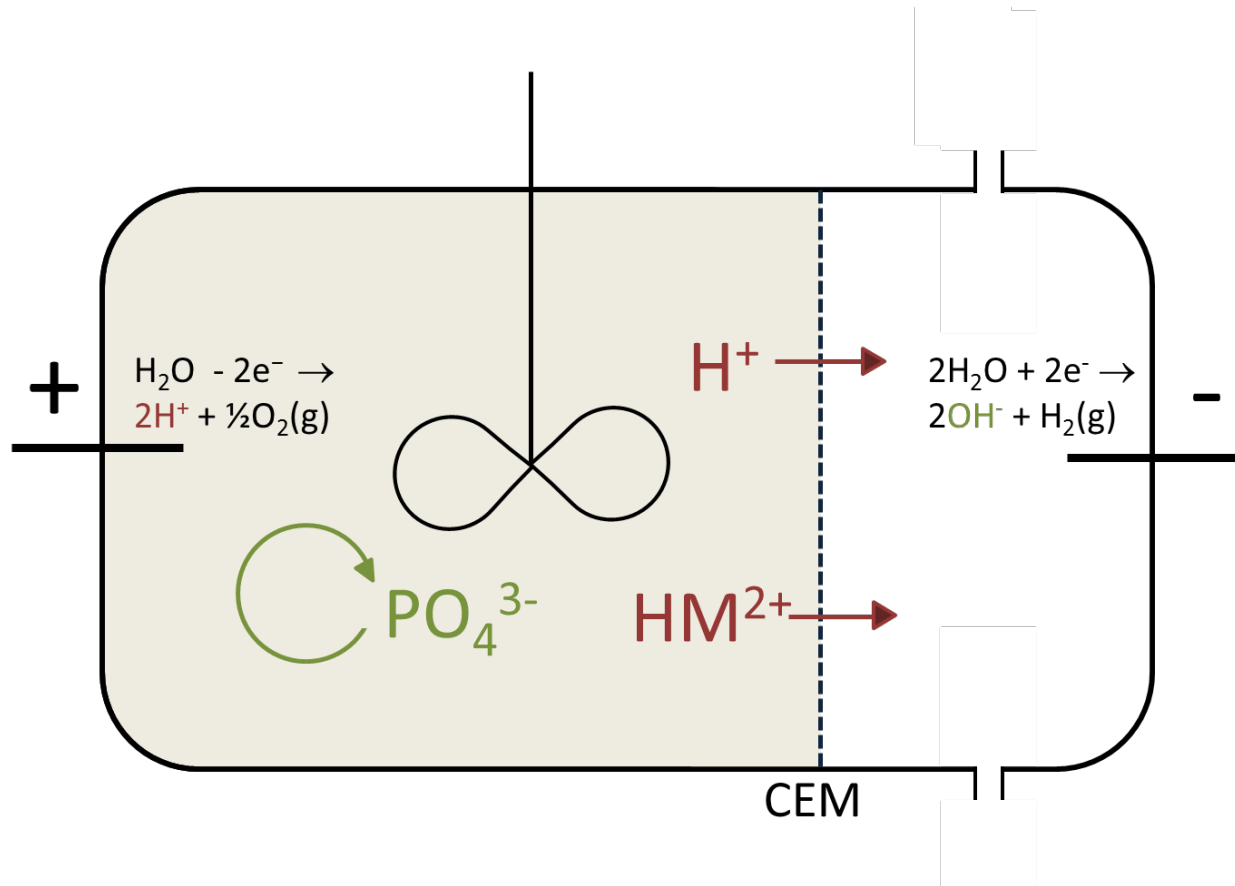
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459 *Table 3: Total concentrations, phosphorous related concentrations, water soluble concentrations and water solubility of*
460 *different chemical elements in the salt produced from experiment A6. The limiting values are from (Miljøstyrelsen 2010).*

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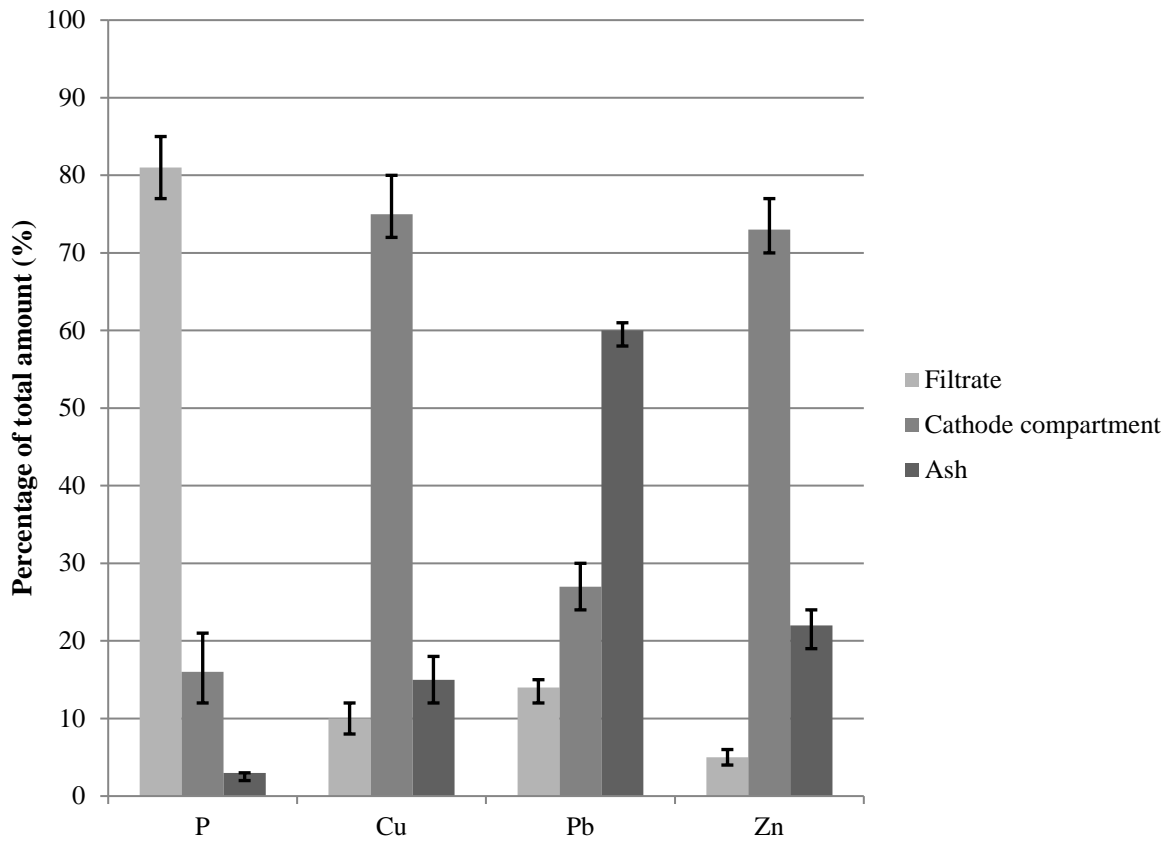
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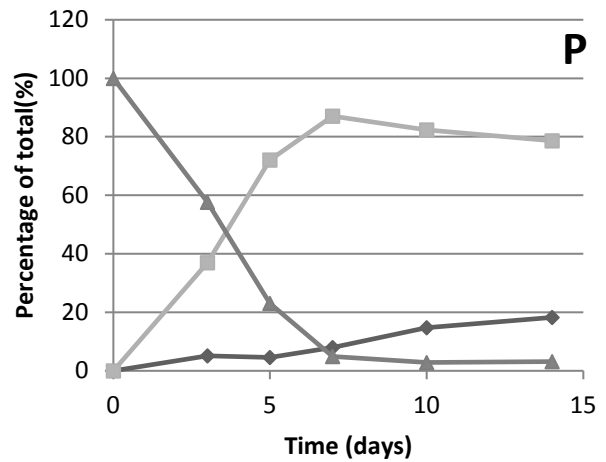
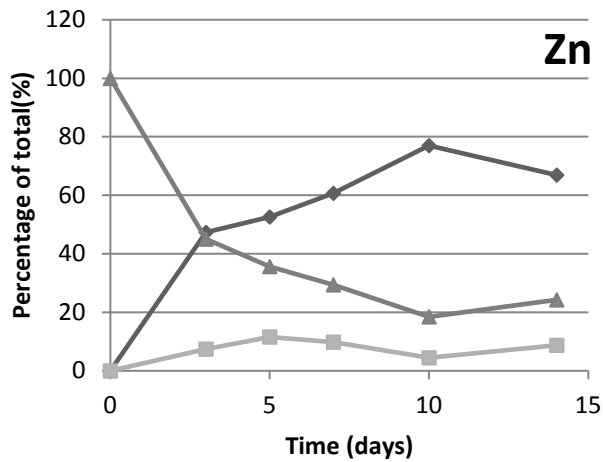
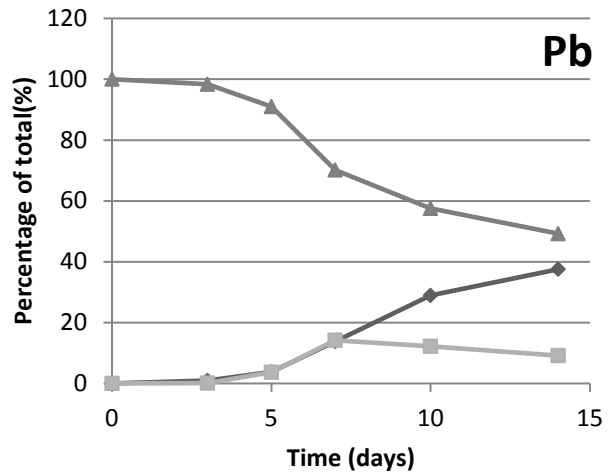
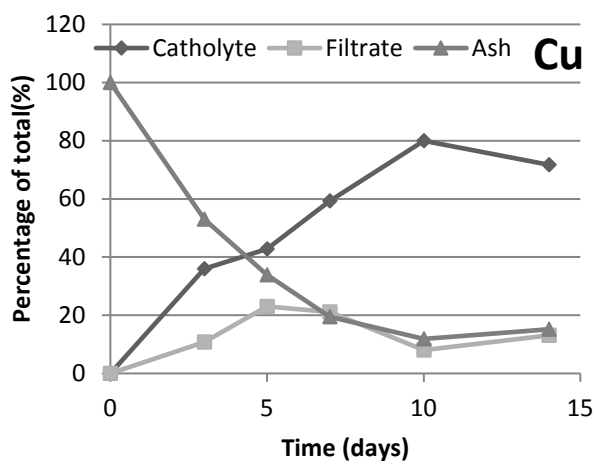
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466 *Figure 1: Two-compartment electrochemical cell for simultaneous P recovery and heavy metal separation from*
 467 *sewage sludge ash. The compartments are separated by a cation exchange membrane (CEM). The ash is*
 468 *suspended in water in the anode compartment. During the application of current, the suspension is acidified*
 469 *from electrolysis at the anode (reaction shown in the figure). In the acidic environment the P and heavy metals*
 470 *are brought into solution and the heavy metal cations (HM^{2+}) are transported into the catholyte by*
 471 *electromigration.*



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Figure 2: Repeatability of phosphorous and heavy metal distribution at the end of three similar experiments (A4-A6). Mean values are shown in solid bars and the error bars shows minimum and maximum values.



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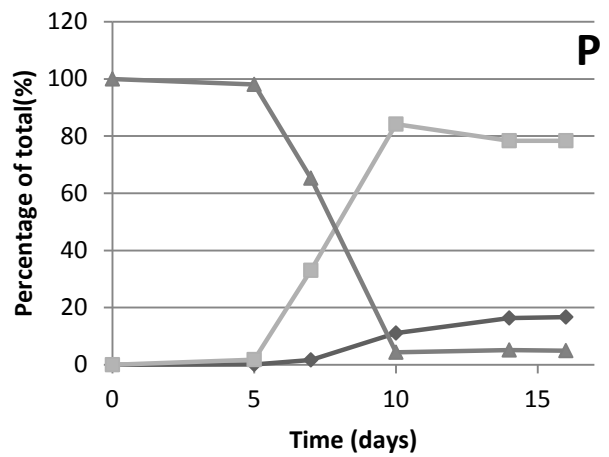
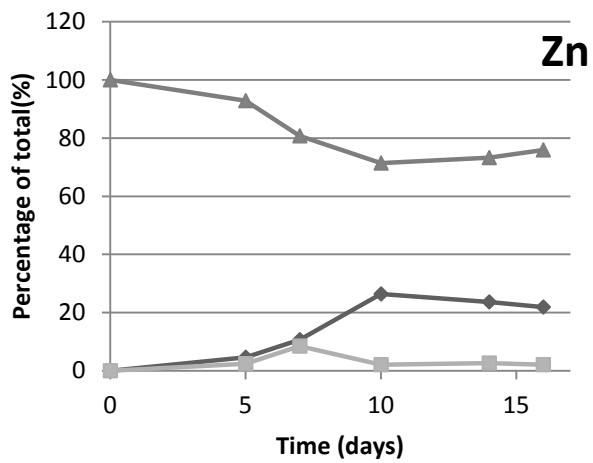
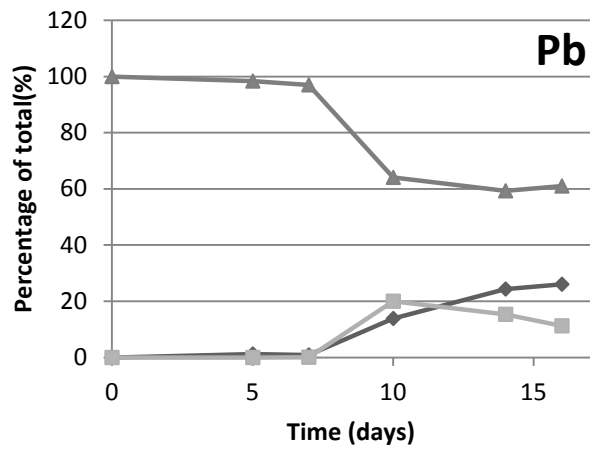
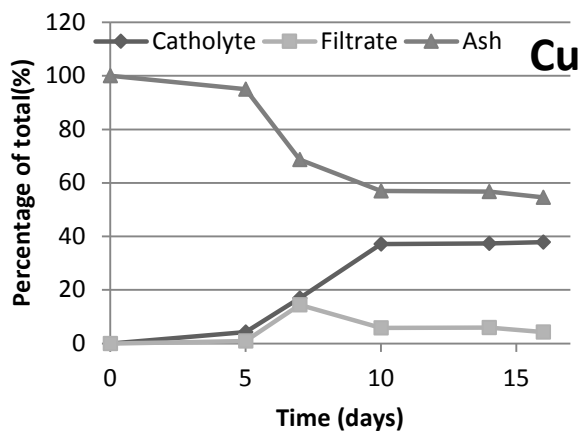
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Figure 3: Distribution of Cu, Pb, Zn and P in the two-compartment cell over time for Ash-A



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Figure 4: Distribution of Cu, Pb, Zn and P in the two-compartment cell over time for Ash-B