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1 Utilisation of electrodiallytically treated sewage sludge ash in mortar

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6

7 **ABSTRACT**

8 Phosphorous is a scarce resource and there is a need to develop methods for recovery of this
9 irreplaceable nutrient from secondary resources, e.g. from sewage sludge ash (SSA). Today SSA is
10 most often disposed of and the resource is lost. In the present study, about 90 % phosphorous was
11 recovered from SSA by electrodialytic separation in a bench scale set-up, and the particulate residue
12 after the extraction (SSA-ED) was evaluated for use as cement replacement in mortar. The SSA-ED
13 and untreated SSA were grinded for 0sec, 30 sec and 10 min in order to obtain fractions with
14 different degrees of fineness. Each fraction was tested as cement replacement with 20% substitution
15 in mortar. The technical and aesthetical properties of mortars containing the two SSAs were
16 compared to the properties of ordinary mortar. The SSA-ED was acidic; however, this did not
17 significantly influence the mortar properties on short term investigated here. For example, the
18 compressive strength of the mortar with SSA-ED only decreased by 8% compared to ordinary
19 mortar. The workability of mortars with SSA or SSA-ED was reduced compared to the reference.
20 The colour of mortar with SSA-ED was warm reddish, and more intense than the colour of the
21 mortar with SSA. The intense colour was due to the increased concentration of hematite during ED.

22 This study showed potential for separating SSA to two resources by combining electrodialytic
23 extraction of phosphorous and subsequent utilization of the residual mineral ash in mortar.

24 **Keywords:** SSA, electrokinetic remediation, phosphorous, heavy metal, fineness

25 **Graphical abstract**

27 **INTRODUCTION**

28 Sewage sludge ash (SSA) is the residue from thermal treatment of sewage sludge, most frequently
29 incineration, at wastewater treatment plants. Phosphorous in SSA is generally not plant available,
30 and thus the SSA has no fertilizer value and thus the common practice is landfilling of the SSA. The
31 natural deposits of phosphorous are rapidly depleting with the current consumption rate, and in such
32 a speed that phosphorous already today is regarded as a scarce element. This is alarming as
33 phosphorous is an irreplaceable element for all living organisms. Drivers to find appropriate
34 applications for SSA instead of landfilling was initially to solve a waste problem due to increasing
35 quantities of SSA [1-3] rather than the phosphorous reuse. Extensive research was carried out for
36 the purpose of investigating possibilities to use SSA in production of construction materials in
37 general and in cement based materials specifically [4-6]. Over the last decade, research on SSA
38 utilisation has developed alongside the developments of waste management policy. The overall aim
39 of the waste hierarchy in the European directive on waste [7] is to encourage EU member states to
40 “reintroduce as much material as possible into production processes” [8]. By the introduction of the

41 waste hierarchy, the conception of waste has also changed from the perception of waste as a
42 problem to regarding waste as a resource [8]. This change is also reflected in studies on SSA
43 utilisation, in which SSA is referred to as “secondary material” [6] and “useful material” [4]. When
44 considering SSA as a resource, the main resource of interest in SSA is the relatively high content of
45 phosphorous, which generally is 5 – 10 wt% [5].

46 In the Resource Strategy by the Danish Government in 2013, the target is to reuse 80 % of
47 phosphorous from sewage sludge (including SSA) by 2018. To reach this goal, efficient methods to
48 recover the phosphorous from SSA are required and different methods are currently under
49 development. The methods are grouped in two: thermochemical treatment or wet chemical
50 extraction [4]. A drawback for the latter group is that in acid extraction, which is the method that
51 achieves the highest percentage of phosphorus separation, the heavy metals are also extracted [9,
52 10], which hampers the use of the recovered phosphorous in fertilizer production. To obtain a clean
53 phosphorous product, different processes for separation of phosphorous and heavy metals have been
54 suggested, such as pH adjustment [11, 12], sulphide precipitation [11], cation exchange [9, 11] and
55 electrodialytic separation [13, 14]. The first three separation methods require a two-step treatment:
56 first extraction then separation. In electrodialytic separation, the phosphorous extraction and heavy
57 metal separation occur simultaneously.

58 Electrodialytic separation first developed for soil remediation, and was recently further developed
59 for extraction of phosphorous from SSA with simultaneous heavy metal separation. Fig. 1 shows
60 the patented two-compartment electrodialytic cell [15].

61 The anode is placed directly in a suspension of SSA and water. The cathode is placed in a separate
62 compartment and a cation exchange membrane separates the two compartments. When a DC
63 current is applied, the pH of the suspension decreases as protons are generated at the anode from

64 electrolysis. Once pH reaches below 2, P and a part of the heavy metals are extracted. The heavy
65 metal cations electromigrate to the catholyte passing the cation exchange membrane and thus the
66 heavy metals are separated from the suspension, where phosphorus remains. Studies by Ebbers et
67 al. [16] and Ottosen et al. [13] have shown that it is possible to recover more than 90% P with this
68 experimental set-up in laboratory scale (25-50 g SSA treated) and that the extracted phosphorous is
69 pure from heavy metals and can be processed further to fertilizer [13].

70 A question now arises, whether the remaining mineral residue is an additional resource. A possible
71 application for the SSA-ED could be as cement replacement in concrete. The CO₂ emission from
72 cement production is responsible for about 5% of the anthropogenic emission. Cement is the
73 essential “glue” in concrete, and one way to lower the general CO₂ emission related to concrete is to
74 use materials with pozzolanic activity or filler effect as partly cement replacement. Research
75 combining extraction of phosphorous and using the treated SSA as cement replacement is scarce.
76 Donatello et al. [9] studied the use of sulfuric acid to recover phosphorous from SSA and use the
77 acid washed SSA in mortar. They found that the sulphate from the acid influenced the properties of
78 the mortars negatively compared to the untreated SSA. SSA-ED will not contain similar high
79 sulphate content. The aim of the present work is to investigate the potential for combining
80 electrodialytic extraction of phosphorous from SSA and the use SSA-ED as cement replacement in
81 mortar.

82 **MATERIALS AND METHODS**

83 SSA from Avedøre, BIOFOS was used in the experiments, a wastewater treatment plant operating
84 in the Copenhagen area, Denmark. The SSA was from mono-incineration of sewage sludge and it
85 was sampled in May 2014. Iron salts were used at the wastewater treatment facility to precipitate P
86 and the sewage sludge was incinerated in a fluidized bed combustor at about 850°C.

87 **Analytic procedures in ash characterization**

88 Characterization was made with dried ash and cement. Concentrations of Cu, Pb, Zn and Cd were
89 measured with ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) after pre-
90 treatment in accordance to DS259: 1.0 g ash and 20.0 ml (1:1) HNO₃ was heated at 200 kPa
91 (120°C) for 30 minutes and filtered through a 0.45 µm filter prior to the analysis. Leaching
92 experiments for Cu, Pb, Zn and Cu were made according to DS/EN 12457-3 part 1 at L/S 2, mixing
93 40 g material and 80 ml distilled water for 24 hours. Ash pH and conductivity were measured by
94 suspending 10.0 g ash in 25 ml distilled water. After 1 hour agitation pH and conductivity were
95 measured directly in the suspension with Radiometer electrodes. Water content was measured as
96 weight loss after 24 hours at 105°C (calculated as weight loss over the weight of the wet sample).
97 Loss on ignition (LoI) was found after 30 minutes at 550°C and additionally after 30 minutes at
98 950°C. Five replicates of each of these analyses were made. Solubility in water was evaluated by
99 suspending 50.0 g ash in 500 ml distilled water and agitated for 1 min, after settling the water was
100 decanted and another 500 ml distilled water added. This was repeated until the ash was washed
101 three times. Finally, the suspension was filtered and the ash dried and weighed. Major oxide
102 composition was estimated from semi-quantitative analysis by X-ray fluorescence (XRF) on
103 powder samples by an external laboratory. The particle size distribution was measured by laser
104 diffractometry. Ash mineralogy was studied by X-ray powder diffraction (XRD), for identification
105 of major crystalline phases. The instrument was a PANalytical X'Pert Pro operating at 45 mA and
106 40 kV applying Cu K α radiation with a 2 Θ X'Celerator detector. The samples were scanned in the
107 range of 4-100 2 Θ within 2.5 hours. The diffractograms were interpreted by using the ICDD PDF-4
108 database for minerals and the main peaks were identified.

109 **Electrodialytic bench-scale experiment**

Fig. 2 shows the ED bench-scale set up. It was built in a plastic container (60x40x32 cm). Two anodes were placed directly in the suspension. The cathodes were placed in cathode units, which were boxes with circulating catholyte. One side of the box (facing into the container) was a cation exchange membrane (27 x 37 cm²) from Ionics. Both cathodes and anodes were platinum coated titanium meshes (4 x 20 cm²).

The catholytes (25 l each) were prepared by mixing 21.5 g of NaNO₃ with 50 ml of 1:1 HNO₃ into 25 l of distilled water. Each of the two cathode units had a separate catholyte circulation system.

The SSA suspension prepared for the experiment had a liquid to solid (L:S) ratio of 10.3. First, 28 l distilled water was added to the anolyte compartment. Thereafter 3 kg of SSA was mixed into 3 l of distilled water in a separate tank and added gradually to the anolyte to make the full suspension.

The SSA was kept suspended to avoid sedimentation in the container by three overhead stirrers (vos 14 /VWR).

A power supply (Blanko- Model Q J-3003C III) maintained a constant current. Each pair of electrodes shared the same power supply, however, independently connected to separate outlets.

The duration of the experiment was 24 days and a constant current of 0.4 A was applied to each electrode pair for the first two days and 1.0 A for the remaining 22 days. The pH of the catholytes was adjusted with 1:1 HNO₃ after 2, 4, 11 and 15 days, when the pH of the catholyte was above 2.

The pH and electrical conductivity (EC) were measured regularly in the SSA suspension at two places (named back and front, see Fig. 2). Samples of the SSA suspension were collected regularly, filtered, and the target elements were measured in the filtrate by ICP-OES.

After the ED experiment, the SSA suspension was filtered, dried at 50°C until the liquid had evaporated, crushed lightly by hand in a mortar, and finally stored in sealed plastic bags. Target elements, pH and conductivity were measured in the filtrate, SSA and catholyte at the end of the

133 electro dialytic experiment. LoI, water content, water solubility, total and leaching concentrations of
134 Cd, Cu, Pb and Zn (ICP-OES) and P (XRF) and mineralogy (XRD) were measured in the ED
135 treated and dried ash.

136 **Mortar preparation and testing**

137 Before the SSA and SSA-ED (here referred to as test materials) were used in mortar, they were
138 grinded for 0 sec, 30 sec and 10 min using a vibratory cup mill (FRITSCH - pulverisette 9). The
139 grain size of the SSA and grinded samples are shown in Table 1. The grinded test materials were
140 used for the production of test binders that consisted of 80 % of cement and 20 % either SSA or
141 SSA-ED. In total mortar 8 mixes were produced (Table 2) The basic recipe, which was used for the
142 mortar production, was 75 % sand, 25 % binder and a water/binder ratio of 0.5. The sand was a
143 coarse grained sea-sand (0 – 4 mm) and the cement used was CEM II/A-LL 52.5R. This particular
144 type of cement has a reduced CO₂ footprint compared with ordinary portland cement as up to 20 %
145 of the cement clinker is replaced by limestone filler.

146 The mortar was prepared in a Hobart mixer with the capacity of 5 liters. Binder (either cement or
147 cement and SSA) was placed in the bowl, and the water was added. The mixer was switched on for
148 30 sec at low speed. The sand was added during the next 30 sec, and then the mixer was switched to
149 high speed and the mixing continued for another 30 sec. The mixer was stopped and the paste
150 adhering to the inside of the bowl was within the next 30 sec removed by a scraper. After 60 sec of
151 rest, the stirring process proceeded and the paste was stirred at high speed for another 60 sec.

152 The compaction procedure was executed by a vibrating table at a frequency of 53 Hz. The mortar
153 was placed in the mould within the first 30 sec and the mortar was vibrated for another 90 sec. The
154 mortar samples were sealed in plastic for 24 hours, demolded and cured in water vertically placed in
155 a sealed plastic box. The two series were cured in separate boxes because the leaching of the

156 mortars in the two series was expected to be different. $M\text{-SSA}_{0\text{sec}-10\text{ min}}$ were cured for 28 days and
157 $M\text{-SSAED}_{0\text{sec}-10\text{ min}}$ for 40 days. The extended curing time applied for $M\text{-SSAED}_{0\text{sec}-10\text{ min}}$ may have
158 influenced the compressive strength result. But because the strength increase levels out after 28
159 days, the two series, $M\text{-SSA}_{0\text{sec}-10\text{ min}}$ and $M\text{-SSAED}_{0\text{sec}-10\text{ min}}$, are roughly compared though taking
160 the difference in the curing time applied into account.

161 Three prismatic specimens (160mm x 40mm x 40mm) were cast in each mould. After curing they
162 were cut into 6 equal test samples (80mm x 40mm x 40mm). For the determination of the
163 compressive strength a Toni 3000 compression machine was used. The pH was measured and
164 mineralogy investigated on crushed samples for the three different mortars.

165 The flow value expresses the workability of mortar with untreated and grinded SSA. Preparation of
166 mortars followed DS/EN 191-3+A3 (DS 2009) and the tested mortars are those listed in Table 2.
167 The flow value was determined according to DS/EN 1015-3 (DS 1999). A truncated conical mould
168 (50 mm high, internal diameter 100 mm at the bottom and 70 mm at the top) was uniformly filled
169 with mortar. The mould was removed, and the mortar exposed to jolting by slowly raising the
170 mould 2 cm vertically and dropping it, 15 times at a rate of one pr. second at a flow table. The mean
171 diameter (d_{mean}) from two measurements of the subsequent mortar diameter in two directions at
172 right angles was found. The procedure was repeated twice for each mixture.

173 Metal leaching from mortars were made similarly as for the test materials according to DS/EN
174 12457-3 part 1 and the mortars were hand crushed prior to the mixing with distilled water. The
175 buffering capacity of the mortars was determined according to Reddy et al. [17] by firstly preparing
176 a suspension of the test material mixed in water (6.7 % w/v) secondly stirring the suspension for 30
177 min before pH was measured. Successive 1 ml of concentrated HCl were added every 30 min and
178 pH was measured thereafter. This was repeated every 30 min until pH was below 2.

For evaluation of the colour differences another type of samples were casted in moulds made from film faced ply wood as described in detail in [18]. The dimensions of these moulds were 100x100x30mm. Paper cuttings were used to make both rough and smooth surfaces of the hardened mortar, and a circular shape was cut out of the lining paper using a circle cutter. The paper was moistened under running water for a few seconds. Before the frame was mounted, the wet paper cutting was placed at the base of the mould and evened out with the means of a wall paper brush.

RESULTS AND DISCUSSION

Phosphorous and heavy metals in the SSA before and after ED

The investigated SSA contained 20.6 wt% P_2O_5 (found from the XRF analysis), which corresponds to 9.0 wt% P (Table 3). The P concentration in the investigated ash is slightly lower than in the previously investigated SSA batches from the same facility, 10wt% [10], 12wt% [16] and 11wt% [13], however, the concentration is within the general range (5 – 10 wt% P) reported by Cyr et al. [5].

The initial SSA amount in the experiment was 3 kg, and with a P concentration of 9 wt% the total mass of P was 270 g. During ED, P was extracted from the SSA, and the concentration was decreased to about 1.0 wt% P (2.3 % P_2O_5) in SSA-ED. In ED lab scale experiments from [13] where successful P extraction was obtained from SSA from the same incineration plant, about 50% SSA dissolved, and the same range of dissolution is expected in the present bench-scale experiment. Thus approximately 15 g P was still bound in the SSA after ED, corresponding to 6% of the total.

The concentration of Cd and Cu decreased in the SSA during ED (Table 4). The Cd concentration decreased from 2.8 mg/kg to 0.5 mg/kg (corresponding to 91% removal taking the 50% dissolution of SSA into account) and the Cu concentration decreased from 590 mg/kg to 460 mg/kg (61% removal). This is on the contrary to the concentrations of Pb and Zn, which both increased in the

202 SSA during ED; Pb from 170 to 420 mg/kg and Zn from 2100 to 2600 mg/kg. The reason for the
203 increased Zn concentration was that 38 % Zn was removed, while the dissolution of SSA was 50 %.
204 The Pb removal was very limited. The increased Pb concentration in the SSA-ED cannot be
205 explained by dissolution alone. The Pb concentration of the initial SSA can vary greatly, which was
206 seen in another study on the similar SSA, where fifteen replicates of the untreated ash were
207 analyzed and a high variability of Pb was observed (208 ± 100 mg/kg) [19]. Therefore, the Pb
208 removal cannot be sufficiently quantified. The Cu, Pb and Zn mobilization in the present study was
209 significantly less than in the lab experiments with SSA from the same plant [13], where 85% Cu,
210 40% Pb and 77% Zn were mobilized.

211

212

213

214 **The ED recovery process**

215 As a constant current was applied to the electrodes during the ED experiment, the voltage varied as
216 a result of varying resistivity. The voltage generally decreased between both sets of electrodes,
217 from 30.8 V to about 10 V for Cat-An1 and 30.2 V to 10.8 for Cat-An 2, i.e. the voltage was in the
218 very same range in the two electrode sets. The pH decreased due to the electrolysis at the anodes,
219 and the conductivity of the SSA suspension did subsequently increase. Conductivity and pH in the
220 suspension during the experiment are shown in Fig. 3, and the measurements in the two sampling
221 points (back and front) are varying only very little at every time of analysis.

222 The experiment can be separated into four zones based on pH: (I) pH decreases from 7 to 3 during
223 over the first approximately 69 hours, (II) pH stabilizes between 2 and 3 until 356 hours, (III) pH
224 decreases gradually to 1 until about 475 hours (approximation as data points were not analysed
225 here), and (IV) pH stabilizes at 1 for the remaining hours of the experiment. The oxidation rate of
226 H₂O at the anode was constant (after 2 days) due to the constant current applied, and thus the rate of
227 H⁺ produced was constant. The pH in the suspension is buffered by the SSA in Zone II, and this
228 corresponds to the finding in [20], where a titration curve showed an ash buffering capacity around
229 pH 2-3. In zone III, this buffering capacity was overcome, as pH decreases. In zone IV it is
230 expected that the current is nearly exclusively carried by H⁺ ions, which at this point are present to a
231 very high extent in the suspension, and have a higher mobility than the other ions of the solution.
232 The conductivity of the suspension is almost linearly increasing over the duration of the experiment
233 irrespectively of pH, showing the release of ions from the SSA during the buffering period in zone
234 II.

235 The concentrations of Cu, Zn and P in the filtrate of the SSA suspension during the ED experiments
236 are shown in Fig. 4. Cu represents the heavy metals of which the concentration decreased in the
237 SSA during the treatment and Zn the heavy metals for which the concentration increased.

238 An almost linear release of P over time is seen during the first two zones, where after the P
239 concentration in the filtrate remains almost constant. Thus the P extraction was finished with Zone
240 II, and the experiment could have been stopped here after about 360 hours. The P was thus
241 extracted during the period, where the SSA had a buffering capacity around 2-3. It is commonly
242 reported, that SSA contains whitlockite, e.g. [9]. Whitlockite is a group of structurally complex Ca-
243 metal-phosphates, and as whitlockites are acid soluble, these minerals are dissolved during the ED
244 treatment, and may contribute to the buffering capacity in Zone II; however, the large amorphous
245 phase in SSA makes the pattern difficult to distinguish. The ED experiment could have been
246 stopped at the end of zone II, as no more P was recovered after this period. The concentration of P
247 was at this point about 8 g/l in the filtrate and with approximately 31 l filtrate this gives about 250 g
248 P totally in the filtrate, which is by far the major part of the P initially in the ash (270 g).

249 The continuation of the experiment after the maximum extraction of P (zone II) with zone III and
250 IV was not only an excessive use of energy, but it also decreased the quality of the filtrate as the Zn
251 concentration increased (mainly in zone IV). The separation of heavy metals in this zone is not
252 efficient as the pH is so low, that hydrogen ions will be by far the main charge carrier. Thus it is
253 highly important to stop the ED process at the right time. At the end of zone II, the concentrations
254 of both Cu and Zn were about 10 mg/l, which corresponds to 310 mg. Initially the 3 kg of ash
255 contained 1.8 g Cu and 6.3 g Zn. Thus 18% Cu and 5% Zn was found in the filtrate.

256 **Characteristics of raw and treated ash**

257 Table 3 shows characteristics for the cement, SSA and SSA-ED. The requirements for use of coal
258 fly ash (DS/EN 450-1:2007) in concrete are shown in the table for comparison, to evaluate the
259 general quality of the SSAs. The pH of the SSA decreased from 9.3 to 3.5 during ED. The water
260 solubility was low for both SSAs and should thus not lead to any volume changes when used in
261 mortar. The LoI increase for the cement from 550°C to 950°C is due to the limestone filler in this
262 type of cement and all LoIs met the requirements. The XRF analysis shown as oxide weight
263 percentages in the materials (Table 3) showed that while the weight percentage of Fe_2O_3 increases
264 the weight percentage of Al_2O_3 decreases during ED. The weight percentage of SiO_2 increases,
265 showing that Si was mainly present in the part of the SSA, which was not dissolved during ED. In
266 SSA-ED the weight percentages of Al_2O_3 , Fe_2O_3 and SiO_2 summed up to 73 % of the mass, whereas
267 in the SSA the sum of these major oxides was 43 %. Comparing these weight percentages to the
268 requirements for coal fly ash used in concrete it was seen that the ED treatment made the SSA more
269 eligible for use in concrete. Also the reduction in SO_3 due to the ED treatment is favourable for the
270 SSA as material. The content of CaO was also greatly reduced in the SSA-ED, which can be linked
271 to the lower pH and that Ca-containing minerals and phases will dissolve at acidic pH. This will
272 also mean that the buffer capacity of the SSA-ED has been reduced and this together with the acidic
273 pH could negatively influence the properties of the mortar when used as substitution for cement.

274 The heavy metal content and leaching for the cement and SSAs are seen in Table 4 and the
275 concentrations are compared to limit values for reuse of non-hazardous materials for geotechnical
276 purposes [21], as there are no limits for reuse in construction materials. Both the leaching results in
277 this study and the limit values [21] are based on the DS/EN 12457-3 part 1 leaching test. The
278 leaching concentrations of Cu, Pb and Zn in the SSA-ED exceeded these limits, mostly because the
279 SSA after electrodialytic treatment is acidic. The leaching from SSA-ED was 14% Cd, 4% Cu and
280 Zn and 0.04 % Pb compared to the total concentrations in this ash.

281

282 There were no similarities in the mineralogy between cement and the SSA samples, as seen in Fig.
283 5. The cement consisted, as expected, of the main cement minerals C_3S (alite), C_2S (belite) and
284 C_4AF (ferrite). Celite (C_3A) was not detected in the diffractogram, which could be due to peak
285 overlap, having the main peak at 33.15 ($^{\circ}2\theta$) and ferrite with major peaks at 33.53 ($^{\circ}2\theta$) and 33.92
286 ($^{\circ}2\theta$). Rietveld analysis on Portland cement has previously shown 6.5% C_3A compared to 63.6%
287 C_3S , 8.9% C_2S and 14.2% C_4AF [22]. Anhydrite ($CaSO_4$) was also found in the present cement.
288 The main difference between the raw and ED treated SSA, was the removal of calcium phosphate in
289 the ED treated ash, which could be expected due to the overall P removal (Table 3). Otherwise SSA
290 and SSA-ED were mineralogically consisting mainly of Q (quartz), Fe (feldspar) and H (hematite).

291 **Mortar properties**

292 The XRD diffractograms for the three different mortars (M-ref, M-SSA and M-SSA-ED the two
293 latter with non-grinded SSA) are seen in Fig. 6. The main mineralogical phases in the mortars were
294 similar regardless of the substitution of cement with SSA. Quartz (SiO_2), the plagioclase feldspars
295 albite ($NaAlSi_3O_8$) and K-spar ($KAlSi_3O_8$), calcite ($CaCO_3$) and the hydration product portlandite
296 ($Ca(OH)_2$) were the main identified minerals. The mortar diffractograms did not show calcium
297 phosphate or hematite which was present in the SSAs (Fig. 5). This is likely due to the dominating
298 minerals from the sand, the cement hydration and the dilution effect since SSA only replaced 20%
299 of the cement. At the same time, the quartz and feldspar in the SSAs were additionally contributing
300 to the quartz and feldspars present in the mortar sand, these two minerals which are the most
301 common minerals in sand from Danish sand pits [23], thus, this is coherent with finding these as the
302 main minerals in the mortars.

303 Incorporation of ED treated MSWI fly ashes with high leaching concentrations in mortars have
304 shown comparable leaching levels to a reference mortar for Cd, Cu, Pb and Zn, probably because
305 the metals were incorporated in the alkaline mortar matrix [24]. The leaching of the SSA-ED
306 containing mortars is shown in Table 5 and gives an indication of the worst case environmental
307 impact when replacing cement with SSA compared to Danish regulation for the maximum leaching
308 concentrations for disposing inert and mineral waste [25]. The leaching of Cd and Pb from all
309 mortars was below 20 µg/l and only leaching of Cu and Zn from the mortars containing SSA could
310 be detected. For the M-SSA-ED, the leaching was reduced when the SSA was grinded, indicating a
311 better incorporation of the heavy metals in the mortar matrix. Compared to the limit values, the
312 leaching was below the values for inert and mineral waste, waste which is considered to undergo no
313 or limited chemical reactions in contact with water, respectively.

314 The pH for all the mortars was 12.3, which shows that the acidic electrodialytic treated SSA did not
315 significantly affect the pH of the mortar on a short term basis. However, as can be seen from the
316 buffering capacity of the mortars (Fig. 7), the mortar containing SSA-ED is less resistant towards
317 acidification compared to the SSA-received and the reference mortars. This could influence the long
318 term leaching from the mortars due to the weathering processes of mortar in-situ and the subsequent
319 decrease in mortar pH.

320 The compressive strength was slightly lower when the mortars contained SSA as well as SSA-ED
321 compared to the reference mortar (Fig. 8a), but the SSA-ED still gave compressive strengths above
322 50 MPa for all tested mortars, which is sufficient for most uses of concrete. For the mortar with
323 SSA, the compressive strength increased in accordance to an increase in the fineness of the SSA
324 particles (Fig. 8b). This finding corresponds to results reported in the studies of Pan et al., and
325 Donatello et al. [9, 26]. In these two studies, it was found that the specific surface area did not
326 increase significantly even though the fineness of the particles did due to the grinding. Therefore, it

327 was suggested that the SSA particles had a porous structure with many open pores, adding to the
328 overall specific surface area. As consequence of the high open porosity, the available water in the
329 system was reduced, which could have inhibited the hydration process of the clinker minerals [9] as
330 well as the workability of the mortars [26]. The improved compressive strength (Fig. 8) and
331 workability (Fig. 9) found for M- SSA_{30 sec} and M-SSA_{10min} supports this assumption. Furthermore,
332 the fineness of a pozzolanic material is important for the hydration process, because fine particles
333 provide extra nucleation sites due to large surface areas and at the same time extra space in the
334 system for hydration products to form and develop at the early stage [27]. In case the fine particles
335 are without pozzolanic activity, they may improve the strength from a filler effect.

336 Even though the d₅₀ were quite similar for SSA and SSA-ED (Table 1) the gradation differs. The
337 d₁₀ was 14 µm for SSA and 3 µm for SSA-ED, and thus SSA-ED had the largest fraction of the
338 finest particles. At the same time, SSA-ED also had the largest fraction of the coarsest particles, as
339 d₉₀ was 817 µm compared to 356 µm for the SSA. Thus, the grain sizes differed more in SSA-ED
340 than in SSA. After grinding SSA-ED for 30 sec the d₉₀ is still coarser than in the SSA. The
341 increased concentration of Si (Table 3) in SSA-ED, of which a large fraction is present in quartz
342 (Fig. 5) may be related to this. The quartz may originate from the sand in the fluidized bed, i.e.
343 relatively coarse particles, and quartz is not easily grinded to finer particle sizes. Still after 10 min
344 grinding, the SSA-ED has larger d₉₀ than SSA. The increase in compressive strength with
345 increasing fineness found for M-SSA_{0sec-10min} was not as apparent for M-SSA-ED_{0sec-10min} due to the
346 larger particle sizes (Fig. 8b). The compressive strength increased from 51 MPa to 55 MPa when
347 grinding the SSA-ED for 30 sec, but the longer grinding (finer particles) did not give further
348 strength increase. This reveals that the grain size gradation obtained with the longer grinding did
349 not improve the packing of particles.

350 The workability expressed by flow value spread (Fig. 9) was lower for all mortars with SSA and
351 SSA-ED than for the flow value of the reference mortar. The lower workability was also
352 experienced during the mortar mixing where the test mortars were dryer. Increased fineness is
353 generally expected to improve the workability, which was also seen here for the SSA with the
354 grinding time of 10 minutes. The flow value for mortar with grinded SSA increased as expected but
355 smaller particle sizes of SSA-ED_{30sec-10min} had no influence on the flow value and did not improve
356 the workability of M-SSAED_{30sec-10min}.

357 An irregular morphology of SSA particles is likely adding to a lower workability [28] as well as the
358 porous structure of SSA particles must be expected to influence the workability negatively, in that
359 the pores absorb water from the mixture [9, 26].

360 Fig. 10 shows the colours of the mortar samples M-SSA_{0sec-10min} and M-SSAED_{0sec-10min}. The three
361 mortars with SSA-ED_{0sec-10min} all had a more intense red colour than the mortars with SSA_{0sec-10min}.
362 The colour originates from the hematite (Fe₂O₃, see Fig. 5), and the concentration of Fe was higher
363 in SSA-ED than SSA (Table 3). The saturated red colour was similar for all three samples with
364 SSA-ED_{0sec-10min} whereas the colours of M-SSA_{0sec-10min} evolved slightly in the intensity as the
365 particle size of the SSA decreased. Grinding the ash means larger surface area, which results in the
366 slightly stronger colour of the grinded mortars with SSA. Thus, the colours of M-SSA_{0sec-10min} were
367 induced by the physical changes of the SSA whereas the colours of M-SSAED_{0sec-10min} most likely
368 were due to the chemical changes of SSA-ED. It is possible that a very low content of CaO together
369 with a higher content of Fe for SSA-ED (Table 3) may have caused the significant colour change of
370 M-SSAED_{0sec-10min} compared to faint colours of M-SSA_{0sec-10min}. It is known from the composition
371 of minerals in clay that a high content of Fe together with a low content of CaO generates the red
372 colour known in bricks [29]. The rough and smooth surfaces made by the paper cuttings were made
373 to unfold the aesthetical qualities of the mortar. The rough and smooth surfaces are basic elements

374 of architecture and therefore important for architects and to experience architecture awareness of
375 these elements are necessary [30]. The difference between the smooth parts which are the spherical
376 part of the samples in Fig. 9 and the rough part, accentuate the colours of the mortars. From Fig. 9
377 it can be seen that the visual difference in the colour tones between rough and smooth parts are
378 clearer for the samples with SSA than for samples with SSAED. The colours of M-SSAED_{0sec-10min}
379 may be conceived as an intrinsic property of the material which aesthetically can be used in the
380 build environment for exposed concrete structures.

381

382 CONCLUSION

- 383 • Electrodialytic separation extracted 90 % of phosphorous from the SSA. The electrodialytic
384 treatment reduced the pH of the SSA from 9.3 to 3.5, however, no immediate influence of
385 the acidic pH of the ash were seen from the results of the mortar testing. The acidic pH
386 though increased the heavy metal leaching of the electrodialytically treated SSA and the
387 leaching properties should be studied further for the mortars containing the SSA.
- 388 • Compressive strengths over 50 MPa were achieved for mortars with grinded SSA, although
389 the compressive strength decreased when replacing cement with SSA compared to the
390 reference (60 MPa). Grinding the SSA increased the compressive strengths for both SSAs,
391 from 43 to 58 MPa for the as received SSA and from 51 to 55 MPa for the
392 electrodialytically treated SSA.
- 393 • The fineness and mineralogy of the SSA changed due to the electrodialytic treatment,
394 probably influenced by the dissolution of the ash constituents at the acidic pH.
- 395 • The red color intensified in the mortar with SSA-ED compared to the SSA, into a color
396 similar to red bricks. The red color was homogeneous in the entire mortar sample and on

both the smooth and rough surfaces. The study showed that electrodialytic treated SSA may have potentials to be utilized as resource in cement based materials especially in places where the colour aesthetically can add value to the build environment.

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Fig. 1 The two compartment electrochemical set-up for treating a material suspension. CEM-cation exchange membrane, HM^{2+} - heavy metal cation

Fig. 2 The bench scale electro dialytic experimental setup, CEM-cation exchange membrane

Fig. 3 pH and conductivity on the SSA suspension during the ED experiment

Fig. 4 Concentration of Cu, Zn and P during ED in the liquid of the SSA suspension. The horizontal lines corresponds to the zones in acidification (Fig. 3)

Fig. 5 XRD diffractograms for cement and SSA samples A- anhydrite, Q – quartz, H- hematite, CP- calcium phosphate, Fe – feldspar, C₃S – alite, C₂S – belite, F - ferrite

Fig. 6 XRD diffractograms for mortar samples. P- portlandite, Q-quartz, C, calcite, Fe – feldspar

Fig.7 Buffering capacity to test mortars

Fig. 8 Compressive strength of the mortars by a) grinding time and b) d90 in the SSA

Fig. 9 Workability of the mortars expressed by the flow value spread. The d90 value is for the SSA part of the SSA mortars and for the cement in the reference mortar

Fig. 10 Colours of the experimental mortars

Table 1 Grain distribution of the tested materials

	d10 (μm)	d50 (μm)	d90 (μm)
Cement	1.72	8.45	26.2
SSA _{0sec}	14.1	124	356
SSA _{30 sec}	5.59	39.8	182
SSA _{10 min}	3.54	24.1	89.0
SSA-ED	2.79	101	817
SSA-ED _{30 sec}	2.22	44.1	556
SSA-ED _{10 min}	1.34	9.50	142

Table 2 Recipes of the mortars. * indicating either SSA or SSA-ED

Labelling	Ash*	Grinding	Cement	Sand	Water
		interval			
M -Ref	÷	÷	450 g	1350 g	225 g
M-(...*) _{0 sec}	90 g	0 sec	360 g	1350 g	225 g
M-(...*) _{30 sec}	90 g	30 sec	360 g	1350 g	225 g
M-(...*) _{10 min}	90 g	10 min	360 g	1350 g	225 g

Table 3 Characteristics for the experimental materials. * P content in % from the XRF analysis.

	Cement	SSA	SSA-ED	DS/EN-450-1 Requirement
Water content %	0.3	0.3	2.7	
pH	12.6	9.3	3.5	
Water solubility %	-3.6	1.5	1.3	
LOI %				
550°	0.8	0.5	4.4	Max. 9.0
950°	7.0	1.6	4.7	
Oxides %				
P ₂ O ₅ *	0.2 (0.1*)	20.6 (9*)	2.3 (1*)	-
Al ₂ O ₃	4.9	8.3	6.6	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ >70 %
SiO ₂	20.1	18.6	39.4	
Fe ₂ O ₃	5.4	15.7	27.3	
SO ₃	4.7	19.2	0.3	< 3.0 %
Na ₂ O	0.7	1.2	0.8	Alkalies < 5 %
K ₂ O	0.8	1.7	1.8	
MgO	0.5	2.3	1.0	-
MnO	0.04	0.1	0.01	-
CaO	65.8	20.9	1.0	-
TiO ₂	0.4	0.9	1.7	-
Cl	0.1	0.02	0.1	Max. 0.1 %

Table 4 Heavy metal content in the experimental materials

Heavy metals (mg/kg)	Cement	SSA	SSA-ED	Category 3 [21]
Cd	0.45	2.8	0.5	>0.5
Cu	67.5	590	460	>500
Pb	22	170	420	>40
Zn	115	2100	2600	>500
Heavy metal leaching ($\mu\text{g/l}$)				
Cd	<20	<20	35 $\pm$ 0.02	40
Cu	<20	<20	4,730 $\pm$ 170	2,000
Pb	<20	<20	92 $\pm$ 11	70
Zn	<20	<20	48,500 $\pm$ 790	1,500

Table 5 Heavy metal leaching from crushed mortar samples

	M Ref	M- SSA _{0sec}	M-SSA _{30s}	M- SSA _{10min}	M- SSAED _{0s}	M- SSAED _{30s}	M- SSAED _{10min}	Inert waste [23]	Mineral waste [23]
pH	12.5	11.6	12.5	12.4	12.6	12.6	12.6		
Cd (µg/l)	<20	<20	<20	<20	<20	<20	<20	15	300
Cu (µg/l)	<20	<20	22±6	36±8	114±11	61±24	<20	450	12,500
Pb (µg/l)	<20	<20	<20	<20	<20	<20	<20	100	2,500
Zn (µg/l)	<20	<20	34±3	39±7	128±4	38±2	29±0	1000	12,500