Utilisation of electrodialytically treated sewage sludge ash in mortar

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ABSTRACT

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

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

INTRODUCTION

Sewage sludge ash (SSA) is the residue from incineration of sewage sludge at wastewater treatment plants. Phosphorous in SSA is generally not plant available, and thus the SSA has no fertilizer value and thus the common practice is landfilling of the SSA. The natural deposits of phosphorous are rapidly depleting with the current consumption rate, and in such a speed that phosphorous already today is regarded as a scarce element. This is alarming as phosphorous is an irreplaceable element for all living organisms. Drivers to find appropriate applications for SSA instead of landfilling was initially to solve a waste problem due to increasing quantities of SSA [1-3] rather than the phosphorous reuse. Extensive research was carried out for the purpose of investigating possibilities to use SSA in production of construction materials in general and in cement based materials specifically [4-6]. Over the last decade, research on SSA utilisation has developed alongside the developments of waste management policy. The overall aim of the waste hierarchy in the European directive on waste [7] is to encourage EU member states to "reintroduce as much material as possible into production processes” [8]. By the introduction of the waste hierarchy, the conception of waste has also changed from the perception of waste as a problem to regarding waste as a resource [8]. This change is also reflected in studies on SSA utilisation, in which SSA is referred to as “secondary material” [6] and “useful material” [4]. When considering SSA as a resource, the main resource of interest in SSA is the relatively high content of phosphorous, which generally is 5 – 10 wt% [5].

In the Resource Strategy by the Danish Government in 2013, the target is to reuse 80 % of all phosphorous by 2018, including phosphorous from SSA. To reach this goal, efficient methods to recover the phosphorous from SSA are required and different methods are currently under development. The methods are grouped in two: thermochemical treatment or wet chemical extraction [4]. A drawback for the latter method is that in acid extraction the heavy metals are extracted together with the phosphorous [9, 10], which hampers the use of the recovered phosphorous in fertilizer production. To obtain a clean phosphorous product, different processes for separation of phosphorous and heavy metals have been suggested, such as pH adjustment [11, 12], sulphide precipitation [11], cation exchange [9, 11] and electrodialytic separation [13, 14]. The first three separation methods require a two-step treatment: first extraction then separation. In electrodialytic separation, the phosphorous extraction and heavy metal separation occur simultaneously.

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

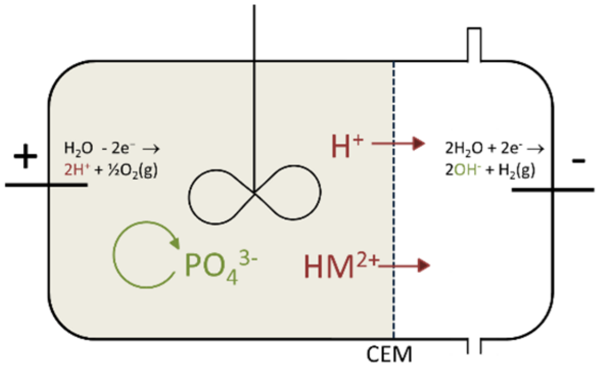

Fig. 1 The two compartment electrodialytic set-up for treating a material suspension. CEM-cation exchange membrane

The anode is placed directly in a suspension of SSA and water. The cathode is placed in a separate compartment and a cation exchange membrane separates the two compartments. When a DC current is applied, the pH of the suspension decreases as protons are generated at the anode from electrolysis. Once pH reaches below 2, P and a part of the heavy metals are extracted. The heavy metal cations electromigrate to the catholyte passing the cation exchange membrane and thus the heavy metals are separated from the suspension, where phosphorus remains. Studies by Ebbers et al. [16] and Ottosen et al. [13] have shown that it is possible to recover more than 90% P with this experimental set-up in laboratory scale (25-50 g SSA treated) and that the extracted phosphorous is pure from heavy metals and can be processed further to fertilizer [13].

A question now arises, whether the remaining mineral residue is an additional resource. A possible application for the SSA-ED could be as cement replacement in concrete. The CO_2 emission from cement production is responsible for about 5% of the anthropogenic emission. Cement is the essential "glue" in concrete, and one way to lower the general CO_2 emission related to concrete is to use materials with pozzolanic activity or filler effect as partly cement replacement. Research combining extraction of phosphorous and using the treated SSA as cement replacement is scarce. Donatello et al. [4] studied the use of sulfuric acid to recover phosphorous from SSA and use the acid washed SSA in mortar. They found that the sulphate from the acid influenced the properties of the mortars negatively compared to the untreated SSA. SSA-ED will not contain similar high sulphate content. The aim of the present work is to investigate the potential for combining electrodialytic extraction of phosphorous from SSA and the use SSA-ED as cement replacement in mortar.

MATERIALS AND METHODS

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

Analytic procedures in ach characterization

Characterization was made with dried ash and cement. Concentrations of Cu, Pb, Zn and Cd were measured with ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) after pre-treatment in accordance to DS259: 1.0 g ash and 20.0 ml (1:1) HNO_3 was heated at 200 kPa (120°C) for 30 minutes and filtered through a 0.45 μm filter prior to the analysis. Ash pH and conductivity were measured by suspending 10.0 g ash in 25 ml distilled water. After 1 hour agitation pH and conductivity were measured directly in the suspension with Radiometer electrodes. Water content was measured as weight loss after 24 hours at 105ºC (calculated as weight loss over the weight of the wet sample). Loss on ignition (LoI) was found after 30 minutes at 550ºC. Five replicates of each of these analyses were made. Solubility in water was evaluated by suspending 50.0 g ash in 500 ml distilled water and agitated for 1 min, after settling the water was decanted and another 500 ml distilled water added. This was repeated until the ash was washed three times. Finally, the suspension was filtered and the ash dried and weighed. Major oxide composition was estimated from semi-quantitative analysis by X-ray fluorescence (XRF) on powder samples by an external laboratory. The particle size distribution was measured by laser diffractometry. Ash mineralogy was studied by X-ray powder diffraction (XRD), for identification of major crystalline phases. The instrument was a PANalytical X'Pert Pro operating at 45 mA and 40 kV applying Cu Kα radiation with a 2Θ X'Celerator detector. The samples were scanned in the range of 4-100 2 Θ within 2.5 hours. The diffractograms were interpreted by using the ICDD PDF-4 database for minerals and the main peaks were identified.

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 cm^2) from Ionics. Both cathodes and anodes were platinum coated titanium meshes (4 x 20 cm^2).

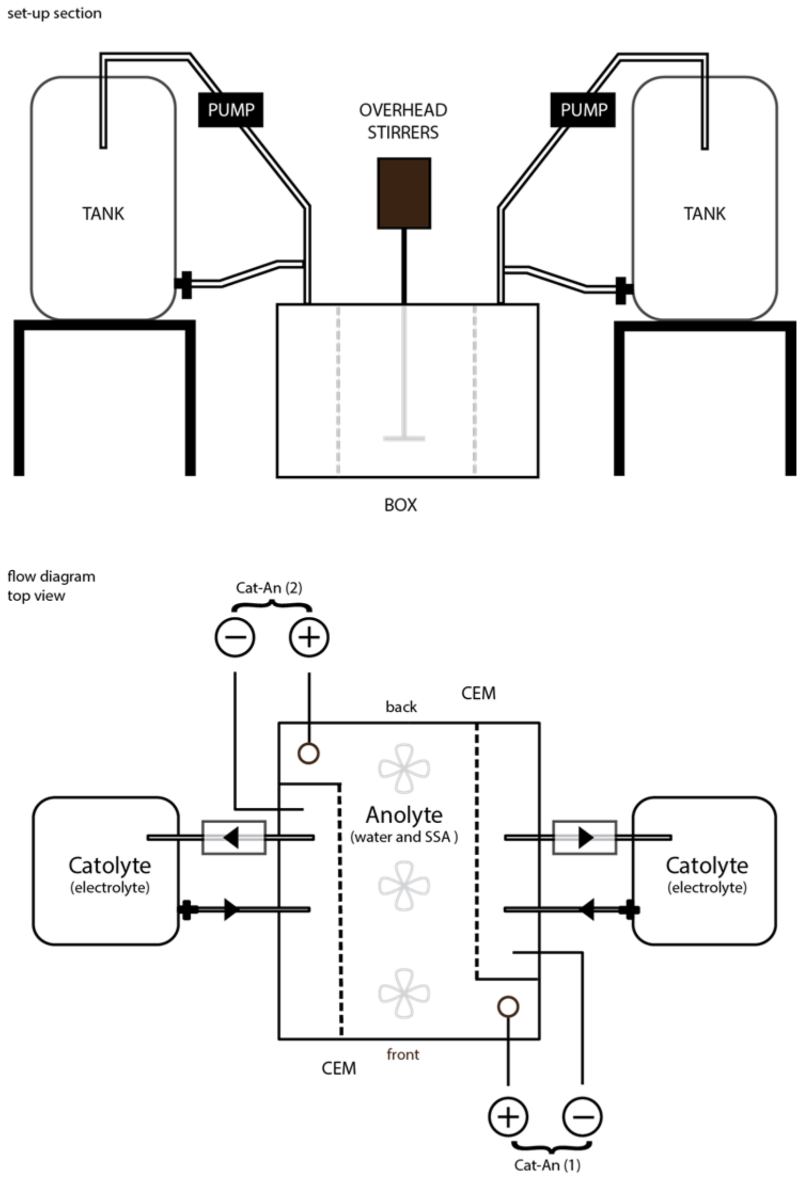

Fig. 2 The bench scale electrodialytic experimental setup, CEM-cation exchange membrane

The catholytes (25 l each) were prepared by mixing 21.5 g of $NaNO_3$ with 50 ml of 1:1 HNO_3 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 HNO_3 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 electrodialytic experiment. LoI, water content, water solubility, concentrations of Cd, Cu, Pb and Zn (ICP-OES) and P (XRF) and mineralogy (XRD) were measured in the ED treated and dried ash.

Mortar preparation and testing

Before the SSA and SSA-ED (here refered to as test materials) were used in mortar, they were grinded for 0 sec, 30 sec and 10 min using a vibratory cup mill (FRITSCH - pulverisette 9). The grain size of the SSA and grinded samples are shown in Table 1. The grinded test materials were used for the production of test binders that consisted of 80 % of Cement and 20 % either SSA or SSA-ED. In total mortar 8 mixes were produced (Table 2) The basic recipe, which was used for the mortar production, was 75 % sand, 25 % binder and a water/binder ratio of 0.5. The sand was a coarse grained sea-sand (0 – 4 mm) and the cement used was CEM II/A-LL 52.5R. This particular type of cement has a reduced CO_2 footprint compared with ordinary portland cement as up to 20 % of the cement clinker is replaced by limestone filler.

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 interval	Cement	Sand	Water
M -Ref$_f$	÷	÷	450 g	1350 g	225 g
M-(…*)$_{0\text{ sec}}$	90 g	0 sec	360 g	1350 g	225 g
M-(…*)$_{30\text{ sec}}$	90 g	30 sec	360 g	1350 g	225 g
M-(…*)$_{10\text{ min}}$	90 g	10 min	360 g	1350 g	225 g

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

The compaction procedure was executed by a vibrating table at a frequency of 53 Hz. The mortar was placed in the mould within the first 30 sec and the mortar was vibrated for another 90 sec. The mortar samples were sealed in plastic for 24 hours, demolded and cured in water vertically placed in a sealed plastic box. The two series were cured in separate boxes because the leaching of the mortars in the two series was expected to be different. M-SSA$_{0\text{sec -10 min}}$ were cured for 28 days and M-SSAED$_{0\text{sec -10 min}}$ for 40 days. The extended curing time applied for M-SSAED$_{0\text{sec -10 min}}$ may have influenced the compressive strength result. But because the strength increase levels out after 28 days, the two series, M-SSA$_{0\text{sec -10 min}}$ and M-SSAED$_{0\text{sec -10 min}}$, are roughly compared though taking the difference in the curing time applied into account.

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

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

For evaluation of the colour differences another type of samples were casted in moulds made from film faced ply wood as desribed in detail in [17]. 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 3). 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 SSA during ED; Pb from 170 to 420 mg/kg and Zn from 2100 to 2600 mg/kg. While the decreased concentrations of Cd and Cu show that they were extracted to a higher extent than the overall ash dissolution, the increased concentrations of Pb and Zn showed that they were extracted to a lesser extent. Taking the SSA dissolution into account, the Pb content was higher in SSA-ED than in the original SSA, which reflect an inhomogeneity in Pb concentration and that the initial sample did not represent the SSA treated by EDR. For Zn, about 38% was removed. The heavy metal mobilization was significantly less than in the lab experiments with SSA from the same plant [13], where 85% Cu, 40% Pb and 77% Zn were mobilized.

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 %				
$P_2O_5^*$	0.2 (0.1*)	20.6 (9*)	2.3 (1*)	-
Al_2O_3	4.9	8.3	6.6	SiO_2+ Al_2O_3+ Fe_2O_3 >70 %
SiO_2	20.1	18.6	39.4	
Fe_2O_3	5.4	15.7	27.3	
SO_3	4.7	19.2	0.3	< 3.0 %
Na_2O	0.7	1.2	0.8	Alkalies < 5 %
K_2O	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 %

The ED recovery process

As a constant current was applied to the electrodes during the ED experiment, the voltage varied as a result of varying resistivity. The voltage generally decreased between both sets of electrodes, 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 very same range in the two electrode sets. The pH decreased due to the electrolysis at the anodes, and the conductivity of the SSA suspension did subsequently increase. Conductivity and pH in the suspension during the experiment are shown in Fig. 3, and the measurements in the two sampling points (back and front) are varying only very little at every time of analysis.

The experiment can be separated into four zones based on pH: (I) pH decreases from 7 to 3 during over the first approximately 69 hours, (II) pH stabilizes between 2 and 3 until 356 hours, (III) pH decreases gradually to 1 until about 475 hours (approximation as data points were not analysed here), and (IV) pH stabilizes at 1 for the remaining hours of the experiment. The oxidation rate of H_2O at the anode was constant (after 2 days) due to the constant current applied, and thus the rate of H^+ produced was constant. The pH in the suspension is buffered by the SSA in Zone II, and this corresponds to the finding in (Kappel et al. 2017, submitted), where a titration curve showed an ash buffering capacity around pH 2-3. In zone III, this buffering capacity was overcome, at pH decreases. In zone IV it is expected that the current is nearly exclusively carried by H^+ ions, which at this point are present to a very high extent in the suspension. The conductivity of the suspension is almost linearly increasing over the duration of the experiment irrespectively of pH, showing the release of ions from the SSA during the buffering period in zone II.

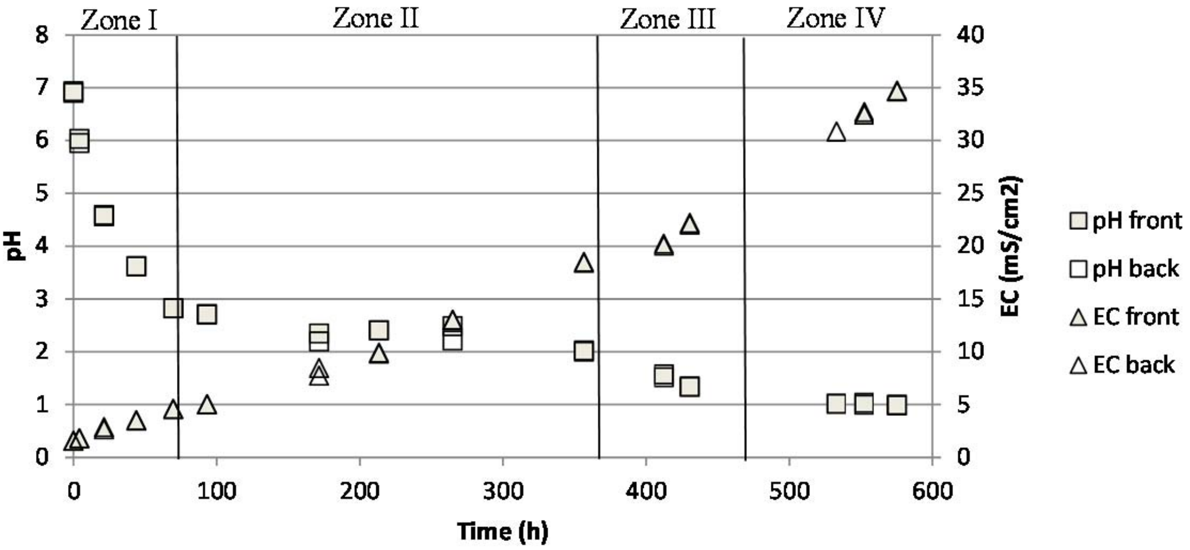

Fig. 3 pH and conductivity on the SSA suspension during the ED experiment

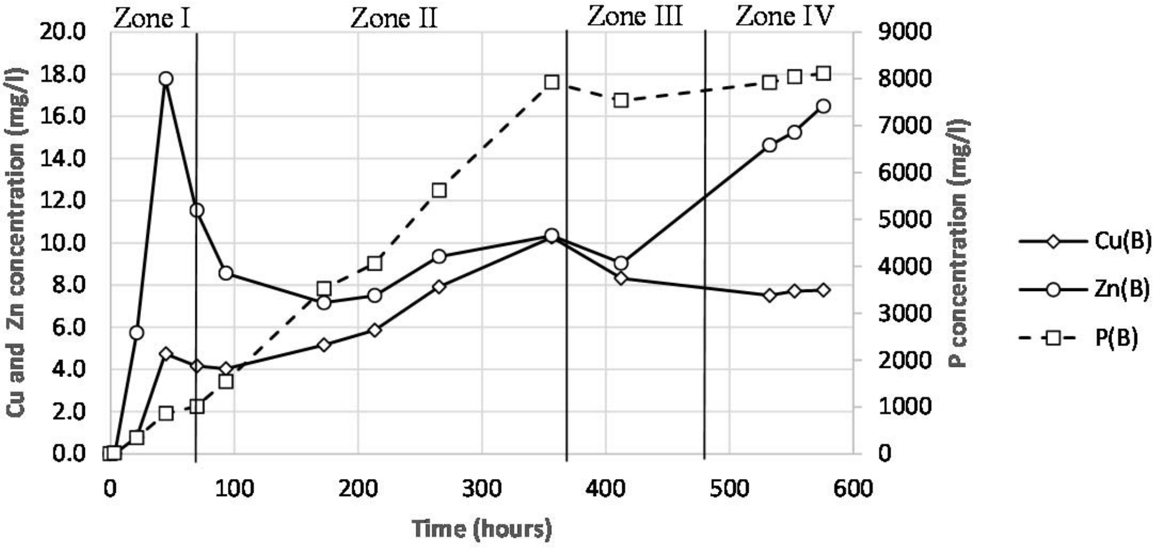

Fig. 4 Concentration of Cu, Zn and P during ED in the liquid of the SSA suspension. The horizontal lines corresponds to the zones in acidification (Fig. 3)

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

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

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

Characteristics of raw and treated ash

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

The heavy metal content and leaching for the cement and SSAs are seen in Table 4 and the concentrations are compared to limit values for reuse of non-hazardous materials for geotechnical purposes [18], as there are no limits for reuse in construction materials. The leaching concentrations of Cu, Pb and Zn in the SSA-ED exceeded these limits, mostly because the SSA after electrodialytic treatment is acidic. Incorporation of ED treated MSWI fly ashes with high leaching concentrations in mortars have shown comparable leaching levels to a reference mortar for Cd, Cu, Pb and Zn, probably because the metals were incorporated in the alkaline mortar matrix [19]. However, the leaching of the SSA-ED containing mortars should be studied to ensure that there is no unacceptable environmental impact of this use.

Table 4: Heavy metal content in the experimental materials

Heavy metals (mg/kg)	Cement	SSA	SSA-ED	Category 3 [18]
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 (µg/l)				
Cd	<20	<20	35	40
Cu	<20	<20	4,730	2,000
Pb	<20	<20	92	70
Zn	<20	<20	48,500	1,500

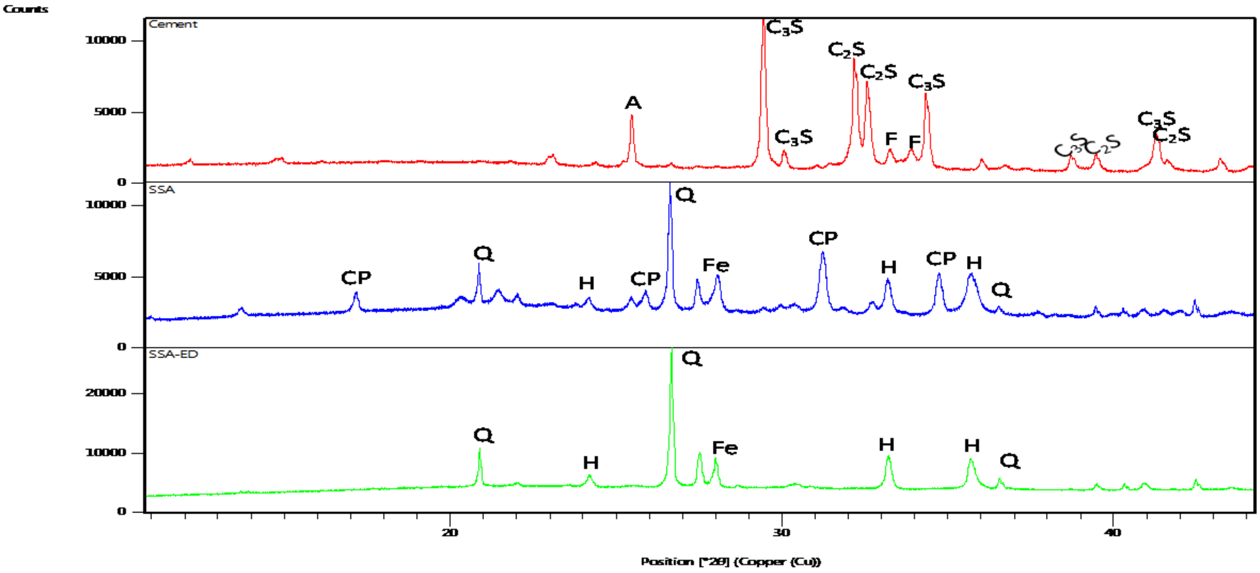

Fig. 5 XRD diffractograms for cement and SSA samples A- anhydrite, Q – quartz, H- hematite, CP-calcium phosphate, Fe – feldspar, C_3S – alite, C_2S – belite, F - ferrite

There were no similarities in the mineralogy between cement and the SSA samples, as seen in Fig. 5. The cement consisted, as expected, of the main cement minerals C_3S (alite), C_2S (belite) and C_4AF (ferrite). Celite (C_3A) was not detected in the diffractogram, which could be due to peak overlap, having the main peak at 33.15 (°2Θ) and ferrite with major peaks at 33.53 (°2Θ) and 33.92 (°2Θ). Rietveld analysis on Portland cement has previously shown 6.5 % C_3A compared to 63.6 %

C_3S, 8.9 % C_2S and 14.2 % C_4AF [20]. Anhydrite ($CaSO_4$) was also found in the present cement. The main difference between the raw and ED treated SSA, was the removal of calcium phosphate in the ED treated ash, which could be expected due to the overall P removal (Table 3). Otherwise SSA and SSA-ED were mineralogically consisting mainly of Q (quartz), Fe (feldspar) and H (hematite).

Mortar properties

The XRD diffractograms for the three different mortars (M-ref, M-SSA and M-SSA-ED the two latter with non-grinded SSA) are seen in Fig. 6. The main mineralogical phases in the mortars were similar regardless of the substitution of cement with SSA. Quartz (SiO_2), the plagioclase feldspars albite ($NaAlSi_3O_8$) and K-spar ($KAlSi_3O_8$), calcite ($CaCO_3$) and the hydration product portlandite ($Ca(OH)_2$) were the main identified minerals. The diffractograms did not show any of the minerals found in the SSAs (Fig. 5). This is likely due to the dominating minerals from the sand, the cement hydration and the dilution effect since SSA only replaced 20 % of the cement. Quartz and feldspars are the most common minerals in sand from Danish sand pits [21] and this is coherent with finding these as the main minerals in the mortars. The pH for all the mortars was 12.3, which shows that the acidic electrodialytic treated SSA did not significantly affect the pH of the mortar on a short term basis.

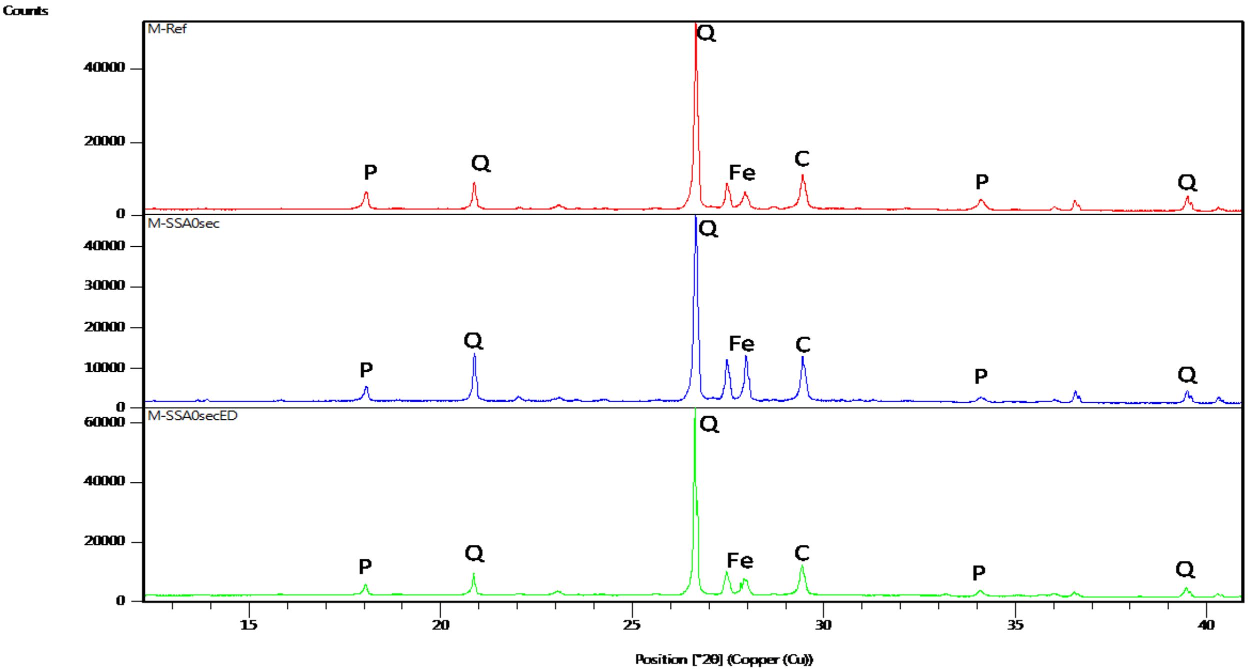

Fig. 6 XRD diffractograms for mortar samples. P- portlandite, Q-quartz, C, calcite, Fe – feldspar

The compressive strength was slightly lower when the mortars contained SSA as well as SSA-ED compared to the reference mortar (Fig. 7a), but the SSA-ED still gave compressive strengths above 50 MPa for all tested mortars, which is sufficient for most uses of concrete. For the mortar with SSA, the compressive strength increased in accordance to an increase in the fineness of the SSA particles (Fig. 7b). This finding corresponds to results reported in the studies of Pan et al., and Donatello et al. [9, 22]. In these two studies, it was found that the specific surface area did not increase significantly even though the fineness of the particles did due to the grinding. Therefore, it was suggested that the SSA particles had a porous structure with many open pores, adding to the overall specific surface area. As consequence of the high open porosity, the available water in the system was reduced, which could have inhibited the hydration process of the clinker minerals [9] as well as the workability of the mortars [22]. The improved compressive strength (Fig. 7) and workability (Fig. 8) found for M- $SSA_{30\ sec}$ and M-SSA_{10min} supports this assumption. Furthermore, the fineness of a pozzolanic material is important for the hydration process, because fine particles provide extra nucleation sites due to large surface areas and at the same time extra space in the system for hydration products to form and develop at the early stage [23]. In case the fine particles are without pozzolanic activity, they may improve the strength from a filler effect.

Even though the d50 were quite similar for SSA and SSA-ED (Table 1) the graduation differs. The d10 was 14 µm for SSA and 3 µm for SSA-ED, and thus SSA-ED had the largest fraction of the finest particles. At the same time, SSA-ED also had the largest fraction of the coarsest particles, as d90 was 817 µm compared to 356 µm for the SSA. Thus, the grain sizes differed more in SSA-ED than in SSA. After grinding SSA-ED for 30 sec the d90 is still coarser than in the SSA. The increased concentration of Si (Table 3) in SSA-ED, of which a large fraction is present in quarts (Fig. 5) may be related to this. The quarts may originate from the sand in the fluidized bed, i.e. relatively coarse particles, and quarts is not easily grinded to finer particle sizes. Still after 10 min grinding, the SSA-ED has larger d90 than SSA. The increase in compressive strength with increasing fineness found for M-$SSA_{0sec\text{-}10min}$ was not as apparent for M-SSA-$ED_{0sec\text{-}10min}$ due to the larger particle sizes (Fig. 7b). The compressive strength increased from 51 MPa to 55 MPa when grinding the SSA-ED for 30 sec, but the longer grinding (finer particles) did not give further strength increase. This reveals that the grain size graduation obtained with the longer grinding did not improve the packing of particles.

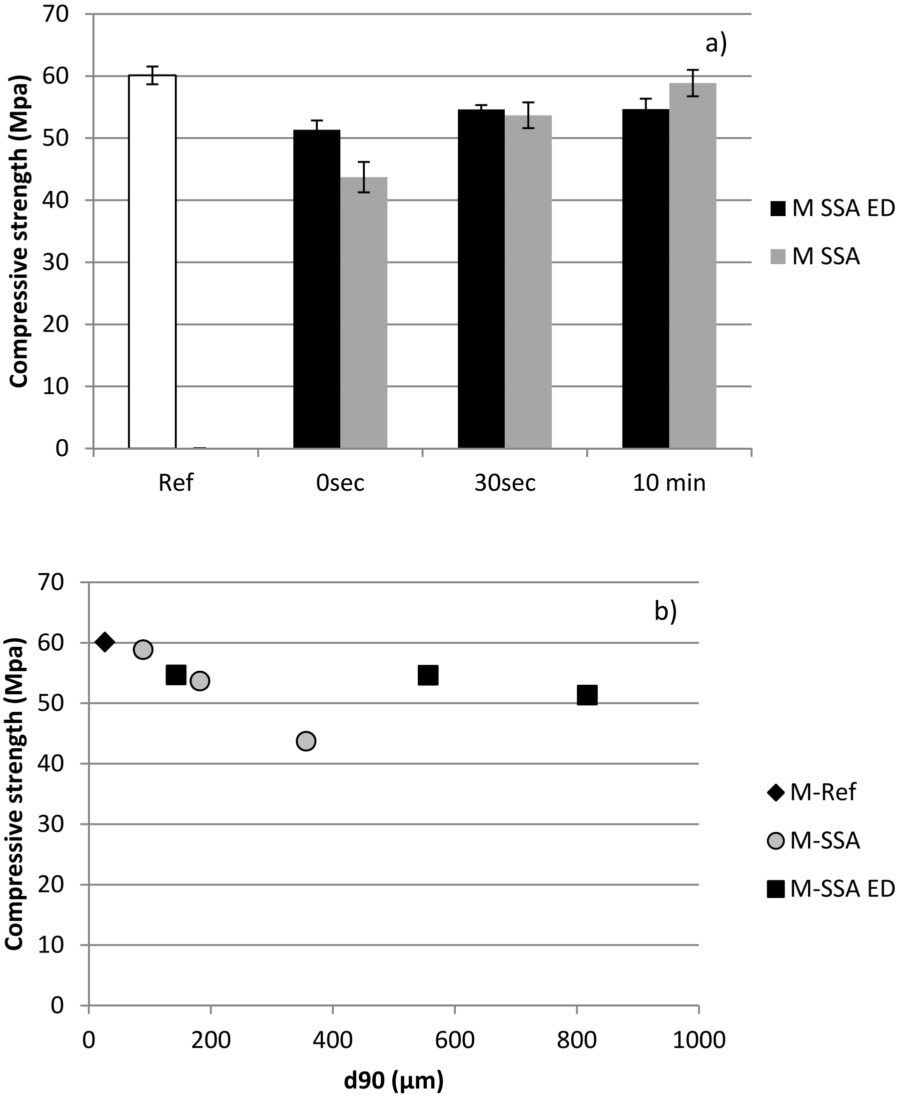

Fig. 7 Compressive strength of the mortars by a) grinding time and b) d90 in the SSA

The workability expressed by flow value spread (Fig. 8) was lower for all mortars with SSA and SSA-ED than for the flow value of the reference mortar. The lower workability was also experienced during the mortar mixing where the SSA mortars were dryer. Increased fineness is generally expected to improve the workability, which was also seen here, especially for the SSA with the grinding time of 10 minutes. The flow value for mortar with grinded SSA increased as expected but smaller particle sizes of SSA-ED$_{30sec\ -10min}$ had no influence on the flow value and did not improve the workability of M-SSAED$_{30sec-10min}$. An irregular morphology of SSA particles is likely adding to a lower workability [24] as well as the porous structure of SSA particles must be expected to influence the workability negatively, in that the pores absorbs water from the mixture [9, 22].

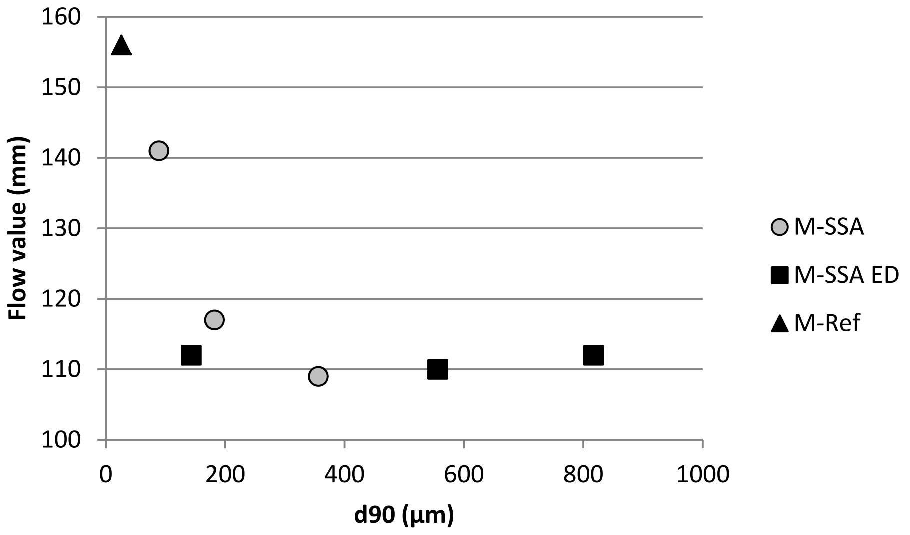

Fig. 8 Workability of the mortars expressed by the flow value spread. The d90 value is for the SSA part of the SSA mortars and for the cement in the reference mortar

Fig. 9 shows the colours of the mortar samples M-SSA$_{\text{0sec-10min}}$ and M-SSAED$_{\text{0sec-10min}}$.

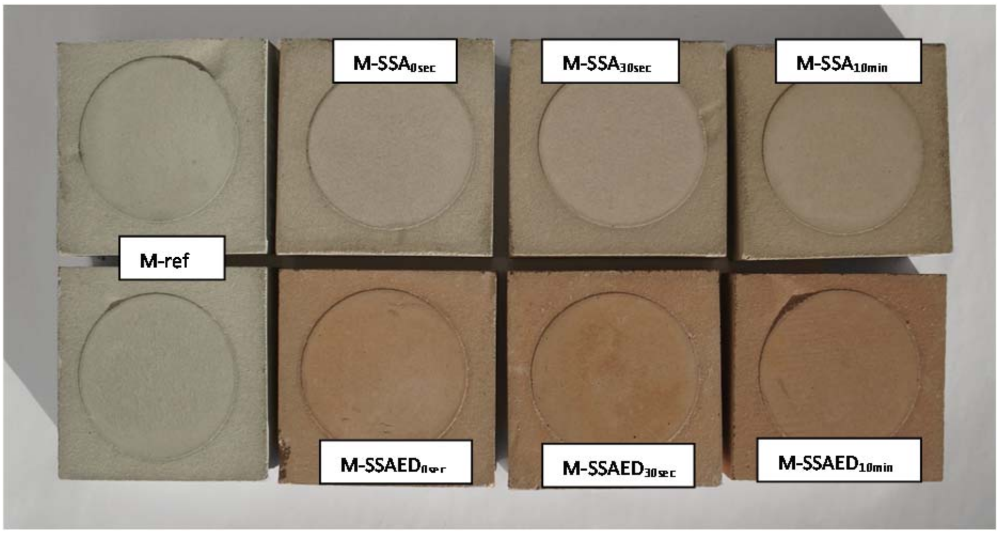

Fig. 9 Colours of the experimental mortars

The three mortars with SSA-ED$_{\text{0sec-10min}}$ all had a more intense red colour than the mortars with SSA$_{\text{0sec-10min}}$. The colour originates from the hematite (Fe_2O_3, see Fig. 5), and the concentration of Fe was higher in SSA-ED than SSA (Table 3). The saturated red colour was similar for all three samples with SSA-ED$_{\text{0sec-10min}}$ whereas the colours of M-SSA$_{\text{0sec-10min}}$ evolved slightly in the intensity as the particle size of the SSA decreased. Grinding the ash means larger surface area, which results in the slightly stronger colour of the grinded mortars with SSA. Thus, the colours of M-SSA$_{\text{0sec-10min}}$ were induced by the physical changes of the SSA whereas the colours of M-SSAED$_{\text{0sec-10min}}$ most likely were due to the chemical changes of SSA-ED. It is possible that a very low content of CaO together with a higher content of Fe for SSA-ED (Table 3) may have caused the significant colour change of M-SSAED$_{0sec\text{-}10min}$ compared to faint colours of M-SSA$_{0sec\text{-}10min}$. It is known from the composition of minerals in clay that a high content of Fe together with a low content of CaO generates the red colour known in bricks [25]. The rough and smooth surfaces made by the paper cuttings were made to unfold the aesthetical qualities of the mortar. The rough and smooth surfaces are basic elements of architecture and therefore important for architects and to experience architecture awareness of these elements are necessary [26]. The difference between the smooth parts which are the spherical part of the samples in Fig. 9 and the rough part, accentuate the colours of the mortars. From Fig. 9 it can be seen that the visual difference in the colour tones between rough and smooth parts are clearer for the samples with SSA than for samples with SSAED. The colours of M-SSAED$_{0sec\text{-}10min}$ may be conceived as an intrinsic property of the material which aesthetically can be used in the build environment for exposed concrete structures.

CONCLUSION

- Electrodialytic separation extracted 90 % of phosphorous from the SSA. The electrodialytic treatment reduced the pH of the SSA from 9.3 to 3.5, however, no immediate influence of the acidic pH of the ash were seen from the results of the mortar testing. The acidic pH though increased the heavy metal leaching of the electrodialytically treated SSA and the leaching properties should be studied further for the mortars containing the SSA.
- Compressive strengths over 55 MPa were achieved for mortars with SSA, although the compressive strength decreased when replacing cement with SSA compared to the reference (60 MPa).
- The fineness and mineralogy of the SSA changed due to the electrodialytic treatment, probably influenced by the dissolution of the ash constituents at the acidic pH.
- The red color intensified in the mortar with SSA-ED compared to the SSA, into a color 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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