



# Electroremediation of straw and co-combustion ash under acidic conditions

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## ABSTRACT

Biomass, such as wood and straw, is currently used in EU as a renewable energy source for energy production and this application is expected to rise in coming years. Combined heat and power installations produce fly ash, which is considered hazardous waste. The fly ash management issue should be addressed before biomass combustion is considered a truly sustainable technology. The electro-dialytic process is a remediation technique able to assist the management of fly ash. For this work, straw and co-combustion of wood ash are briefly characterized and their electro-dialytic treatment is carried out under acidic conditions.

Straw ashes presented high removal rates for Ca, Cu, Cr and particularly for Cd, which has been reduced to a level below the established by Danish regulations. Acidification also induced a high dissolution and a lower pH of the ash. Fly ash from co-combustion of wood presents similarities with wood ash alone. However, further characterization should be carried out before any comparison regarding applicable legislation. Under acidic conditions, the electro-dialytic treatment was not effective for the co-combustion wood ash. The heavy metals appeared in the least soluble fraction of this ash and lowering the pH of such an alkaline material does not mean sustainability and may hinder its reuse.

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## 1. Introduction

Biomass, such as wood, straw and energy crops, is an important renewable and CO<sub>2</sub> neutral energy source in Europe. Biomass resources are closely linked to EU energy policy, where decreases in CO<sub>2</sub> emission are considered necessary and the use of renewable sources for the production of energy plays an important role. The White Paper on Renewable Energy sets the EU quantitative targets for renewable energy until 2010 in 12% of the total energy production. In 2005, according to the European Commission dossier on biomass [1], 4% of the energy outcome in EU was from wood (3%) and straw (1%) combustion. There is an overall pressure on renewable energy sources, where combustion of biomass represents an important resource for the combined heat and power (CHP) production. CHP installations are high technology plants where incineration of biomass and fossil may be combined or combusted alone. As incinerators, the remaining fractions of the process possess an intrinsic hazardousness, especially fly ash. According to the guidelines from the Danish Environmental Protection Agency [2], bottom ashes from straw and wood combustion will in most cases meet the demands for category H3 and T3, respectively. This

enables direct use of bottom ash from biomass combustion on agricultural fields [3]. Nevertheless, the fly ashes from biomass combustion usually present Cd concentrations that may exceed the top category, H1 and T1, which implicates ash deposition in landfill [4]. Therefore, limitations of deposition of fly ash have been established in 5 mg Cd kg<sup>-1</sup> for straw ash and 15 mg Cd kg<sup>-1</sup> for wood ash, both in the disposal of 500 kg of ash as fertilizer in the soil with the restriction of 5 years interval [2,4,5]. Besides their eventual hazardousness, these fly ashes have a fertilizing value relying on its K, Mg and P content [4,6], where removal of heavy metals could enable the (re)application of Danish regulations.

Since bio ashes do not present the toxicity level of other fly ashes (e.g. resulting from municipal solid waste incineration) [7], reutilization could be a sustainable management option for these residues after the removal of heavy metals. The electro-dialytic process (EDR) is a remediation technique first described for heavy metal contaminated soil [8]. The method combines an electric DC field as cleaning agent with the use of ion-exchange membranes, allowing the regulation of ion fluxes in a cell arrangement first developed at the Technical University of Denmark. Details can be found elsewhere, e.g. [9,10]. The EDR has been successfully applied for the removal of Cd in straw ash [5,6] and Pedersen [4] and Pedersen et al. [11] studied its application to wood ash.

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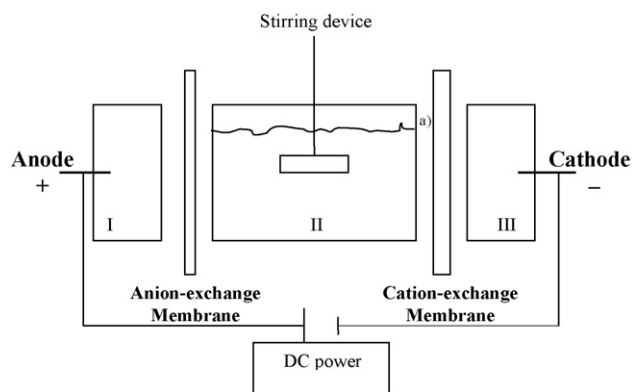
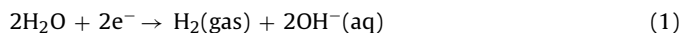


Fig. 1. Setup design for the studied electrochemical experiments. I: anode compartment; II: central compartment; III: cathode compartment; and (a) volume level in the electrochemical cell with the ash suspension (adapted from Pedersen [4]).

This work aims to study the EDR process applied to fly ash from combustion of straw and co-combustion of wood with no assisting agent and in an acidic environment.

Among the electrochemical reactions taking place in the EDR system (Fig. 1), the reduction and oxidation of water on the inert electrodes are important ones [12]. The half reaction at the cathode is



and the anode half-reaction is

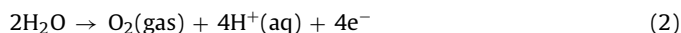


Fig. 1 presents the schematic setup of the EDR cell used in laboratory. The anion-exchange membrane (Fig. 1) is not a perfect rectifier and the  $\text{H}^+$  ions are expected to pass from the anode into the central compartment of the cell [13,14]. Since the cation-exchange membrane is permeable to cations,  $\text{H}^+$  ions are free to also pass between the central compartment and cathode. Catholyte alkalization is controlled through its acidification usually by the addition of nitric acid [9,15,16]. Acidification, or a low pH during EDR, enhances the removal of heavy metals and has been well documented in, e.g. [9,14,15].

However, it may also induce the solubilization of species, such as alkali earth metals and calcium salts, which in the case of ash promotes its dissolution together with a lower pH of the ash.

Moreover, parameters such as the addition of a stirring device to the stationary cell or the combination of an assisting agent to the polluted media [3,4,17,18] may enhance the mobility of the heavy metals species inside the EDR cell.

## 2. Materials and methods

### 2.1. Ashes

The two fly ashes, ST and CW (described below), were collected at the electrostatic precipitators, in CHP plant Avedøre unit 2, Copenhagen, Denmark. This is a cogeneration plant flaming natural gas, fuel oil, straw or co-combusting wood pellets with assisting fuels, being the world largest straw fired boiler. Each fuel is combusted separately and the parameters optimized per fuel in order to obtain a maximum efficiency. Although no quantifications of annual fly ash production were found in CHP Avedøre unit 2 documentation [19]; estimation is possible based on Strehler [20].

- ST ash: corresponds to the fly ash generated during the combustion of straw and straw pellets. Straw is a by-product resulting

from the growing of crops and they are dependent on the type of Danish agriculture. No pre-selection of straw by type before combustion is referred in [19]. The CHP boiler has a capacity of 150,000 ton/year [19], being the annual production of straw ash estimated on approximately 6450 ton/year (calculated from the 4.3% ash content of straw [20]).

- CW ash: is the abbreviation of the fly ash resulting from the co-combustion of wood pellets/fuel oil/natural gas, in the proportion of 11/1.5/4, respectively. Wood pellets are prepared from wastes of parquet floors and table tops, where no pre-selection of wood type is proceeded prior to combustion [19]. Once the total consumption of wood in Avedøre unit 2 is of 280,000 ton/year [19], the resulting CW ash is grossly estimated on approximately 1120 ton/year (calculated from the ash content of wood of 0.4% referred in [20]).

### 2.2. Analytical methods

For the determination of the water content, fly ashes were dried for 24 h in a heating closet at 105 °C. Ash dissolution was quantified by suspending fly ash in distilled water, in a L/S ratio of 4, for 24 h. The suspension was then filtered through 0.45 μm, dried at 105 °C for 24 h and weighted. The difference between initial and final dry weight corresponds to the soluble fraction.

pH was measured in the suspension of 2.5 g of dried fly ash in 12.5 ml distilled water, for 1 h, using a combined Radiometer pH electrode. After the fly ashes digestion in a pressurized assisted microwave (10 ml concentrated  $\text{HNO}_3$  + 0.25 g of dry ash). Ca, Cr, Cu and Cd were determined by atomic absorption spectrophotometry in flame (FAAS) or graphite furnace, depending on the limiting concentrations of the sample. The chloride content was measured in distilled water extractions of 24 h (in a L/S of 2.5) by Dionex ionchromatograf, DX120. For every procedure, a series of three replicates was carried out.

X-ray diffraction (XRD) analysis were performed by a Philips PW 1050/25 (vertical Goniometre) with automatic divergence slit, 0.2° receiving slit and 1.0° scatter slit at a spectrum of  $2\theta$  from 5° to 65°.

### 2.3. Electrochemical experiments

For the remediation of fly ashes, an electrochemical cell was used (Fig. 1). The electrochemical cell was made from Plexiglas with a central compartment of 10 cm long and an internal diameter of 8 cm. Through a hole placed in the middle of this compartment (Fig. 1), a stirrer was placed to stir the ash slurry. The stirrer was a flexible plastic flab, with about 5 cm and 6 mm width, fastened to an insulated wire and was powered by a "Heto" motor with a rotation velocity of 1300 rpm.

Four electrochemical experiments were carried out: Experiments 1 and 2 using the ST ash, for 10 and 14 days, respectively, and Experiments 3 and 4 were carried out on CW ash for 10 and 14 days, respectively. Before the EDR period started, a washing of the ash was carried out. The procedure was similar to ash dissolution, but instead of filtering the suspension, a decantation was used to grossly separate the solid from the liquid. The remaining suspension was filled up to L/S of 4 using distilled water.

Anion-exchange membrane 204 SZRA B02249C and cation-exchange membrane CR67HUYN12116B from Ionics were used to separate the central compartment from the anode and cathode compartment, respectively. Platinum coated electrodes from Permascand were used as working electrodes and a power supply (Hewlett Packard E3612A) maintained a constant current of 40 mA. This corresponds to a current density higher than the empirically calculated  $0.8 \text{ mA cm}^{-2}$ , since the central compartment is not totally filled with the ash suspension (Fig. 1). As anolyte and

**Table 1**  
General characteristics of the straw ash (ST) and the co-combustion ash (CW)

Parameter	ST	CW	Straw ashes	Wood ashes
pH	5.9 ± 0.04	12.0 ± 0.2	5.9 <sup>a</sup> /5.5 <sup>b</sup>	13.9 <sup>a</sup> /13.3 <sup>b</sup> /13.3 <sup>c</sup>
Water content (%)	1.2	0.4	–	–
Ash dissolution (%) <sup>d</sup>	61	13	–	–
Mineral species	Fe <sub>2</sub> O <sub>3</sub> , KCl, K <sub>2</sub> SO <sub>4</sub> , MgCO <sub>3</sub>	CaSO <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub> , MgCO <sub>3</sub> , Mg <sub>2</sub> SiO <sub>4</sub> , SiO <sub>2</sub>	–	–
Cl content (%) <sup>e</sup>	21	0.3	30–31 <sup>a</sup>	0.44–0.46 <sup>a</sup>
K (%)	–	–	26–29 <sup>a</sup>	5.6–5.9 <sup>a,c</sup>
Ca (mg kg <sup>-1</sup> )	3700 ± 1.4	87 280 ± 4.8	7600–8600 <sup>a</sup> /4200 <sup>f</sup>	250 000–290 000 <sup>a</sup>
Cd (mg kg <sup>-1</sup> )	11.3 ± 0.01	22.4 ± 0.6	10 <sup>b</sup> /18 <sup>b</sup>	29 <sup>a</sup> /12 <sup>b</sup> /28 <sup>c</sup>
Cr (mg kg <sup>-1</sup> )	13.5 ± 0.43	185.0 ± 1.3	2 <sup>a</sup>	170 <sup>a</sup> /330 <sup>a</sup>
Cu (mg kg <sup>-1</sup> )	81 ± 11	232 ± 3.4	37 <sup>a</sup>	225 <sup>a</sup>

Heavy metal concentrations measured in other Danish straw ashes and in wood ashes is also shown.

<sup>a</sup> Ref. [21].

<sup>b</sup> Ref. [16].

<sup>c</sup> Ref. [11].

<sup>d</sup> Of total weight.

<sup>e</sup> Water soluble fraction (L/S ratio = 2.5).

<sup>f</sup> Ref. [23].

catholyte, 500 ml of 0.01 M NaNO<sub>3</sub> was used. The pH value of the catholyte solution was daily adjusted to about 2 by addition of concentrated HNO<sub>3</sub> solution.

At the end of the experiments the suspension in the central compartment was filtered at normal pressure. Ash digestion with acid was preceded, according to the methods described in Section 2.2. The electrodes and membranes were rinsed in 5 M HNO<sub>3</sub> and 1 M HNO<sub>3</sub>, respectively, and the concentration of Ca, Cd, Cr and Cu measured. Volume and concentration of Ca, Cd, Cr and Cu in the solution of the three compartments were also determined by FAAS.

### 3. Results and discussion

#### 3.1. Ash characterization

Table 1 systematizes the ST and CW ash characteristics, as well as fly ash from wood and straw characterization obtained on previous studies [7,16,21–23]. The main purpose is to establish a parallelism between wood ash and CW ash, where ash is the result from wood, fuel oil and gas co-combustion. In terms of legislation, Denmark only allows the application of bio ashes (from straw or wood) in agricultural fields [2]. This short description serves to verify the adequacy of legislation application to CW ash. Comparing heavy metal concentrations, CW and wood ash are very similar [7,11,21]. Furthermore, CW ash has a Cd concentration slightly higher than the requested in Danish regulations (22 mg Cd kg<sup>-1</sup> in CW vs. 15 mg Cd kg<sup>-1</sup> in [2]). However, an analysis only based on Cd concentrations is not sufficient. Some mineral composition is not equivalent and Cr and Ca concentration were higher in the wood ash alone [7]. Steenari et al. [22] have documented the presence of CaCO<sub>3</sub> in wood ash samples but Lima et al. [7] refuted this mineral existence in CW ash.

According to Table 1, the studied ST ash may be regarded as representative of a typical Danish straw ash in what concerns Cd, Cu and Cr, since their concentrations are in the range of previously studied. Dissimilarities were observed between ST and CW ash (Table 2). CW ash is an alkaline material, with low dissolution and poor chloride content, while ST ash has a lower pH, close to neutral, high ash dissolution and high chloride content.

Cd and Cr are the most toxic heavy metals here under review. Cd is present in phosphate fertilizer and sludge [24] and once spread in agricultural fields can be adsorbed by biosphere. This explains, to certain degree, the presence of Cd in straw and wood. Since Cr(III) is present in straw and wood as a minor constituent [21,25], oxidation of Cr is possible and hence Cr(VI) should be studied due to its hazardousness.

#### 3.2. Electrodialytic experiments

ST and CW ash characteristics after EDR are presented in Table 2. The acidic conditions during EDR are mainly due to the acidification of the anolyte and its maintenance at low pH during EDR. H<sup>+</sup> is the main free ion in the electrolyte solution, and this makes it as the most abundant and prone ion to exchange across anion-exchange membrane as a co-ion (phenomenon explained in detail by Hansen [26] and Ribeiro [14]). Once H<sup>+</sup> enters central compartment, and the buffering capacity is surpassed, fly ashes are thus acidified, and the longer the contact with acidic conditions, the more acidic the fly ash will get. ST ash has a natural neutral pH and a lower buffering capacity when compared to highly alkaline CW ash. Remediation time does not show its effect on the ST ash, in terms of pH, being only necessary 10 days to lower the ash pH to 2. However, CW ash presented a pH of 10 and 7 at the end of Experiments 3 and 4, respectively.

**Table 2**  
Fly ashes heavy metal content after electrodialytic experiments, together with final pH and percentage of ash amount recovered after experimental time

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Ash	ST	ST	CW	CW
Ash recovery (%) <sup>a</sup>	6.5 ± 2	4.9 ± 2	79.4 ± 2	70.1 ± 2
Ash pH	2.0	2.1	10.0	7.1
Ca (mg kg <sup>-1</sup> )	3900 ± 0.75	3520 ± 0.57	94100 ± 18.6	86550 ± 2.1
Cd (mg kg <sup>-1</sup> )	13.1 ± 0.8	4.2 ± 0.6	20.2 ± 0.01	19.9 ± 0.01
Cr (mg kg <sup>-1</sup> )	40.2 ± 3.1	11.7 ± 0.2	236 ± 0.9	234 ± 1.2
Cu (mg kg <sup>-1</sup> )	139 ± 0.1	57.7 ± 0.1	292 ± 0.14	282 ± 0.11

<sup>a</sup> Of total initial weight.

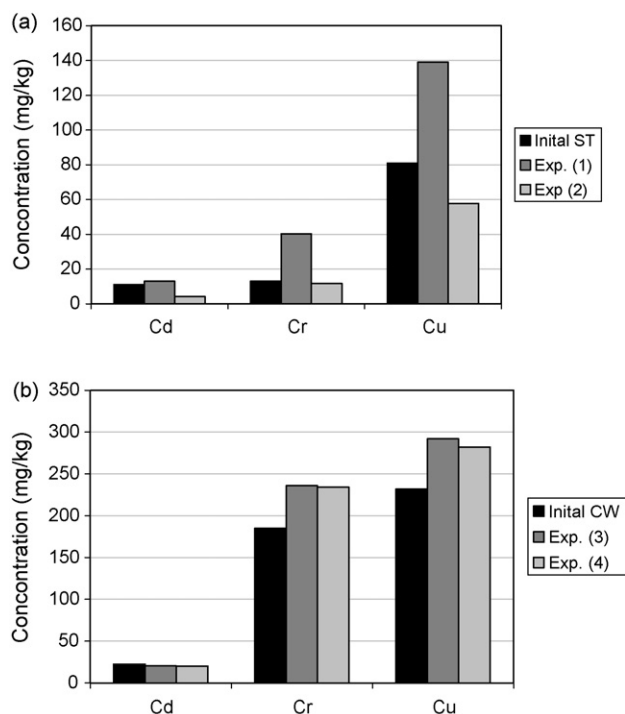


Fig. 2. Initial ash concentrations of Cd, Cr and Cu and the corresponding concentrations in the treated ashes (a) ST ash and (b) CW ash.

Fig. 2a shows ST ash initial and final Cd, Cr and Cu concentrations. It is seen at the end of Experiment 1, with 10 experimental days, these metals were more concentrated in the ash compared to initial conditions, indicating that they were present in the least soluble fraction of the ash. However, at the end of Experiment 2, i.e. extra 4 days of experimental time and acidic conditions, Cd was reduced to 63%, Cr 13% and Cu 29%. Emphasizing Cd content, Experiment 2 had 4.2 mg Cd/kg, below the 5 mg Cd kg<sup>-1</sup> defined by Danish regulations. Cd is expected to be as soluble CdCl<sub>2</sub> [6,7], explaining the high mobility of the metal. Table 2 shows that ST ash presented a weight loss of 93–95% after EDR, showing that ST ash is a highly soluble material with a high content of soluble salts, such as alkali and chloride [7,21]. The massive weight loss also represents a drawback in the valorization of electrodiolytic treated ST ash.

Fig. 2b also shows initial and final Cd, Cr and Cu concentrations for CW ash. Cr and Cu increased their concentrations after EDR treatment. Cd is an exception, presents the same concentration before and after EDR. In CW ash case, increasing remediation time did not improve removal efficiencies. Like in ST ash, the increase on metal concentrations after EDR suggests that metals are present in the least soluble fraction of the ash, strongly bond to the matrix. The acidification induced dissolution as well, but in a more modest percentage in CW ash 20–30% (Table 2). The matrix acidification did not release the metals to large extent, meaning that they were not easy to ionize. Cd may be trapped or bound to oxides (CdO) or silicates (CdSiO<sub>4</sub>) in CW ash while Cr was trapped or bind to oxides (Mg<sub>2</sub>SiO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) or hydroxides [7]. The remediation efficiencies for Cu and Cr are considered null, where Experiments 3 and 4 presented a removal of 1% of Cd.

### 3.2.1. Heavy metal migration

The evolution of pH along experimental time on compartment II, where the ash material was placed, is shown together with Cd, Cr and Cu concentrations on the electrolytes, compartments I and III (Figs. 3 and 4). The pH of compartments I and III was maintained

at 2. Ca was removed from the figures due to its high concentration in comparison to the other studied metals. The high Ca migration and high concentration in the electrode compartments shows that Ca is removed prior to the other metals, although it has an inferior ionic mobility or diffusion coefficient [17,27]. Current is then wasted transporting Ca instead of the target heavy metals.

Fig. 3 presents Experiments 1 and 2 metals variations. Only 5 experimental days were sufficient to lower ST ash suspension pH to 2 (Fig. 3). Together with a decrease of pH in the central compartment, the metals started to increase in the electrolytes, i.e. the low pH mobilized the metal species in the ash suspension enabling their passage through the ion-exchange membranes and into the respective electrolyte. During Experiment 1, Cu appeared as the most mobile, crossing both anion and cation-exchange membranes. However, Cu presented a descending trend in the last days during Experiment 1 and a more oscillatory pattern during Experiment 2. This is mainly due to electrode deposition [3,17]. Metal ions undergo electrodeposition according to thermodynamic principle, and depending on the metal present in the fly ash, electrode deposition may occur [28]. Therefore, when metal ions deposit at the electrode, a subsequent drop in their concentration will occur in the electrolyte (Fig. 3). Furthermore, during Experiment 2, Cr shows some migration activity to the anode and Cd to the cathode. Cd is found to be as soluble CdCl<sub>2</sub> or bound to aluminosilicates in ST ash [7,21], which allows a promptly solubilization in neutral or acidic conditions. This may explain the high migration of Cd as a cation in Experiments 1 and 2, probably in the form of Cd<sup>2+</sup> [6].

Fig. 4 shows CW ash experiments (3 and 4). It is seen that 10 days of EDR time were necessary to lower the pH into 2. Although the ash suspension was acidified, the final fly ash still had a pH of 10 and 7, in Experiments 3 and 4, respectively. Fig. 4 also shows Cr increasing on the anolyte or compartment I, and Cu on the catholyte or compartment III. An oscillatory behavior was also observed for Cu, the same as in ST ash, but with higher variability (Fig. 4). Electrodeposition of this metal at the cathode is also expected and probably the metal species in CW ash is the same as in ST ash, probably Cu<sup>2+</sup> [3,17,28]. The displacement of Cr to the anode unveils an anionic Cr fraction, most likely CrO<sub>4</sub><sup>2-</sup> or Cr(VI). The identification of Cr(VI) through an ion-exchange method has been tried by Johnson [29] and may be explored in an electrodiolytic system. According to Pohland-Schwandt [25], Cr(VI) solubility rises from pH 5 until pH 12. Anionic Cr concentration increased in compartment I, as well as the ash suspension in the central compartment decreased its pH to 2. Comparing ash suspension pH (2) with pH of the ash at the end of experiments (7 and 10; Table 2), there is a significant discrepancy. This pH gap could make Cr(VI) to be released from the matrix and into the anode compartment. Cr was found to be trapped or bound to oxides (Mg<sub>2</sub>SiO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) or hydroxides in CW ash [7]. However, the migration of Cr towards the cathode during Experiments 3 and 4 was not significant. The most likely Cr form present in CW ash is an anionic Cr, but no decisive conclusions are possible before further developments.

### 3.2.2. Mass balances

Figs. 5 and 6 present the distribution of Ca, Cd, Cr and Cu in the electrodiolytic cell at the end of the experiments. The pre-wash procedure, stated in the referred figures, aims to remove the soluble salts from the ash. Once in ionic form, these salts may waste energy, deviating current from the target of heavy metals removal. Therefore, to smooth the progress of heavy metal transport to the electrodes, a pre-wash of the material was performed [3,30].

Fig. 5 presents ST ash experiments and the partitions of each metal in the electrodiolytic cell. The pre-wash procedure seemed to be effective in the removal of soluble Cd, Cr and Cu forms from ST ash. During this procedure, 61% of the total weight is expected

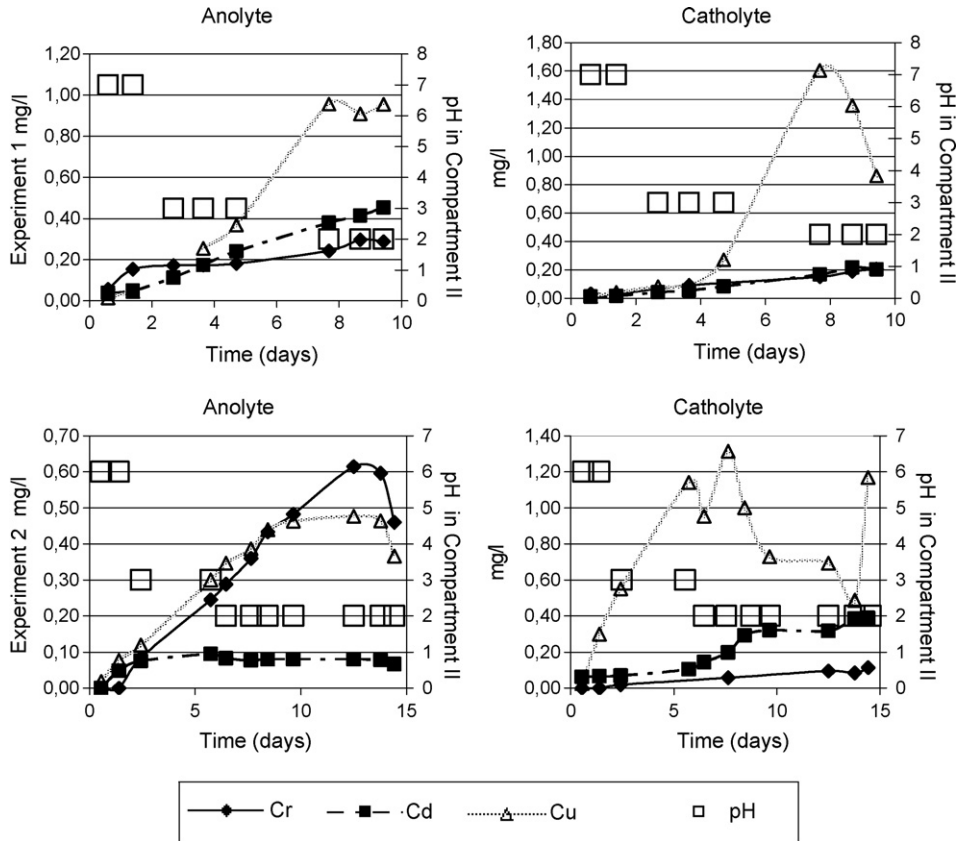


Fig. 3. Ca, Cd, Cr and Cu concentration evolution along experimental time in anolyte and catholyte in electrodialytic experiments with ST ash.

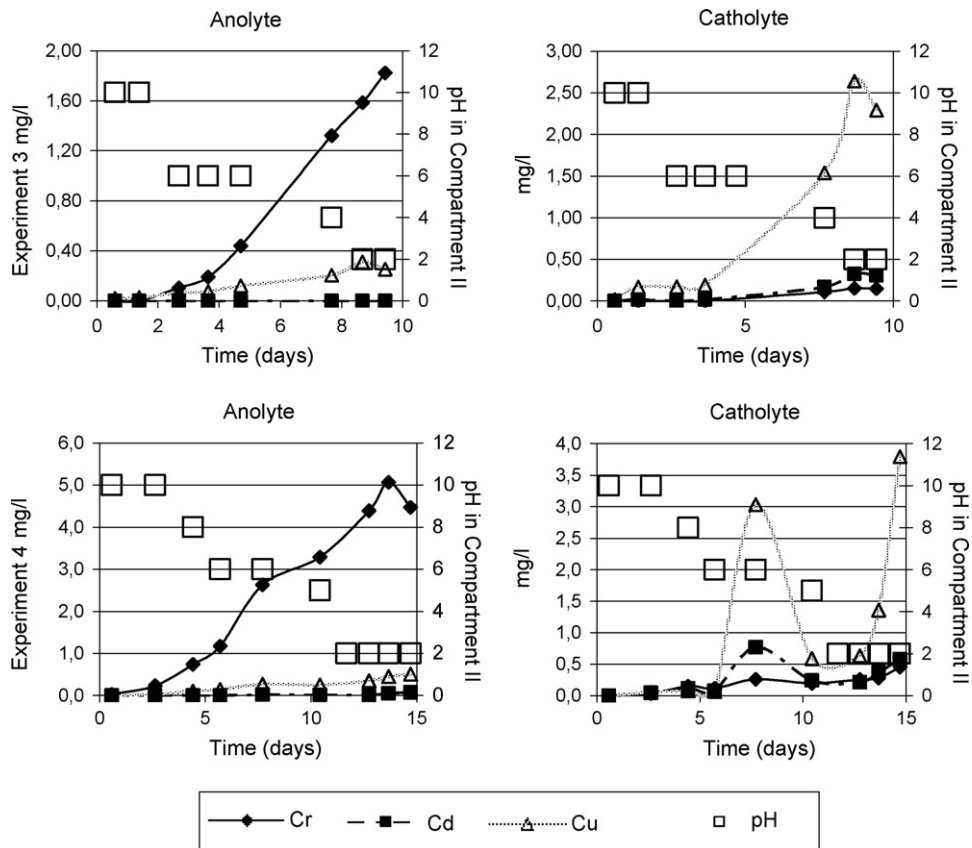
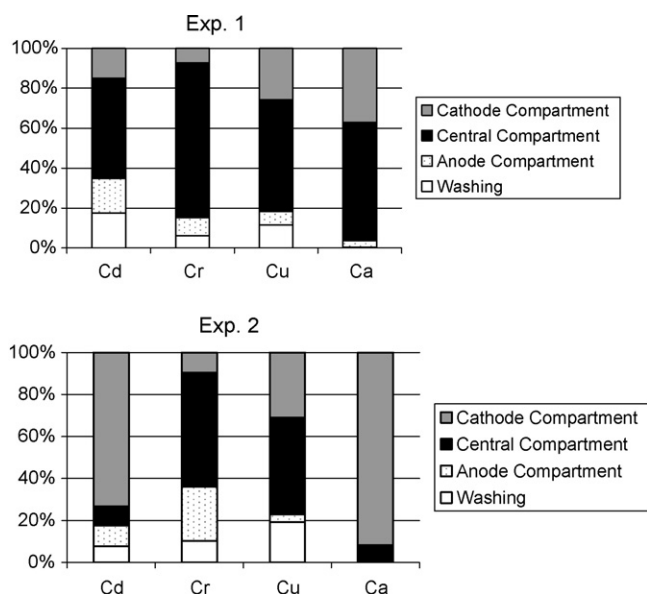


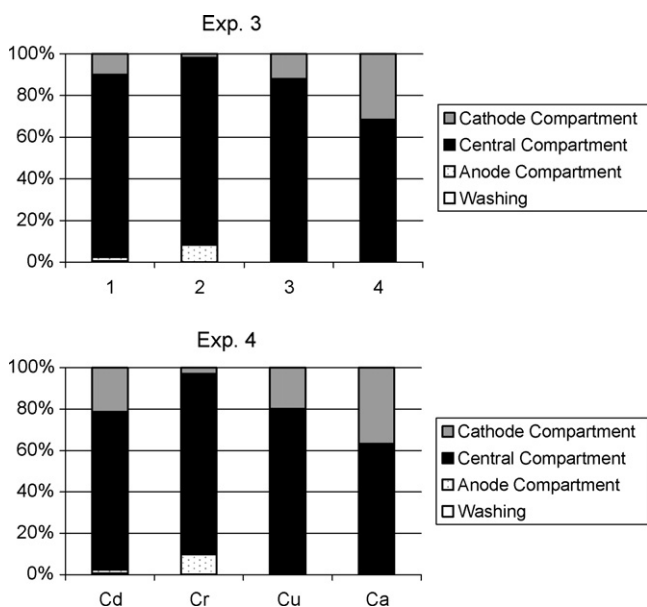
Fig. 4. Ca, Cd, Cr and Cu concentration evolution along experimental time in anolyte and catholyte in electrodialytic experiments with CW ash.





**Fig. 5.** Distribution of Ca, Cd, Cr and Cu in the cell at the end of the electrodialytic Experiments 1 and 2, respectively, with ST ash. Washing: concentration in the leachate resulted from ash pre-wash. Cd, Cr and Cu had an average recovery of 55%. Ca presented a recovery of 110%.

to be lost (Table 1), where many of the soluble salts are dissolved. KCl and  $K_2SO_4$  minerals are some of the minerals that attributed a fertilizing value to ST ash and are probably dissolved during pre-wash. The removal of such ion, K, decreases ST ash fertilizing value. Furthermore, pre-wash does not remove Ca, a major competitor for current carrier during EDR. Since it did not present leachability when in contact with water, Ca is considered insoluble at neutral pH. However, Ca had a high mobility during EDR, where the low pH seemed to enhance Ca mobility (Fig. 5). Together with Ca, Cd and Cu also migrated to the anode or cathode compartments out of the central compartment. Particularly during Experiment 2, the fraction of the metal passing from central to the electrode com-



**Fig. 6.** Distribution of Ca, Cd, Cr and Cu in the cell at the end of the electrodialytic Experiments 3 and 4, respectively, with CW ash. Washing: concentration in the leachate resulted from ash pre-wash. Mass balances comprised between 103% and 115%.

partments is larger than in Experiment. 1. The time factor, the only variable between the two experiments, was decisive for the high migration of the metals. Experiment 2 achievement was previously attested in Section 3.2, where a low Cd content was achieved in ST ash.

Fig. 6 presents Ca, Cd, Cr and Cu distribution in the electrodialytic cell at the end of Experiments 3 and 4. Pre-wash procedure may be neglected for the removal of Ca, Cd, Cr or Cu, confirming the low soluble salt content of CW ashes. Fig. 6 illustrates a smaller ion movement, where the larger concentration of the metals is still found on central compartment, i.e. in the ashes. Comparing Experiments 3 and 4, no significant differences are observed between metal distributions at the end of EDR. Experiment 4 showed a slightly higher mobility of Ca, Cd and Cu towards the cathode. Experiments 3 and 4 were not a success for the removal of heavy metals. Forcing the ashes to dissolve during EDR, with assistance of acidic conditions, does not seem a sustainable solution. The metals are presented in the less soluble fraction of the ash and acidifying the media in order to ionize these metals is not realistic. The matrix would continuously dissolve and metals may not be released. Furthermore, to acidify an alkaline material such as CW ash (Table 1) is not practical in a large electrodialytic scale prototype.

#### 4. Conclusion and evaluation

Similarities were found between the studied CW ash, resulting from the co-combustion of wood, fuel oil and gas, with wood ash alone. Conclusions are however frail, where further characterization should be carried out before any conclusion regarding Danish legislation on the use of CW ash in agricultural purposes.

During this study pre-wash procedure did not remove Ca from fly ashes, probably due to the ion insolubility at natural fly ash pH. Pre-wash may remove the more soluble salts from fly ash, such as soluble chlorides or nitrates, but is ineffective when it comes to removal of a major heavy metal competitor. Ca may mainly migrate due to its solubility at low pH and high concentration in the ash when compared to Cd, Cr or Cu.

The reuse of the fly ash after acidic treatment may be questioned, since the dissolution of the ash material is high, especially in ST ash, and the pH is lower than the initial. Analysing ST ash remediation, the material after EDR is an acidic material with low heavy metal content, with emphasis on the  $4.2 \text{ mg Cd kg}^{-1}$ . Based on this parameter alone, the ashes could be spread in agricultural fields according to Danish regulations. However, the low pH and the low fertilizing value, since K was mainly removed during the pre-washing, the application of such an ash into the soil would be mainly as an amendment. The electrolytes, highly concentrated with metals, could be reused in the fertilizing industry, after the lowering of Cd content. This could be possible by simply increasing the solutions pH, causing Cd to precipitate [31].

As for CW ash, acidification does not seem suitable. Forcing a highly alkaline material such as CW ash to acidify is not realistic in a large scale remediation. Furthermore, the removal of heavy metals from CW ash was null, where the acidification during the 14 days of the experiment only served to neutralize the material and to further dissolve it. Such an alkaline material could find some reuse in construction materials or as acidic soil amendment. However, the presence of Cr(VI) deserves further developments. The use of EDR in the identification of Cr(VI) could be a possibility.

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