

Electrodialytic removal of Cd from biomass combustion fly ash suspensions

Kirkelund, Gunvor Marie; Ottosen, Lisbeth M.; Damø, Anne Juul

Published in:
Journal of Hazardous Materials

Link to article, DOI:
[10.1016/j.jhazmat.2013.02.004](https://doi.org/10.1016/j.jhazmat.2013.02.004)

Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Kirkelund, G. M., Ottosen, L. M., & Damøe, A. J. (2013). Electrodialytic removal of Cd from biomass combustion fly ash suspensions. *Journal of Hazardous Materials*, 250-251, 212-219. DOI: 10.1016/j.jhazmat.2013.02.004

DTU Library

Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Electrodialytic removal of Cd from biomass combustion fly ash suspensions

Gunvor M. Kirkelund^{a,*}, Anne J. Damoe^b, Lisbeth M. Ottosen^a

^a Department of Civil Engineering, Technical University of Denmark, Denmark

^b Department of Chemical and Biochemical Engineering, Technical University of Denmark, Denmark

HIGHLIGHTS

- ▶ Electrodialytic remediation could be used to remove Cd from biomass fly ash suspensions.
- ▶ Cd limiting concentrations in the fly ash were met for reuse as fertilizer.
- ▶ pH below 2 in the fly ash suspension was determining the effectiveness for Cd removal.

ARTICLE INFO

Article history:

Received 14 December 2012

Received in revised form 28 January 2013

Accepted 4 February 2013

Available online xxx

Keywords:

Biomass combustion

Fly ash

Cd

Electrokinetic remediation

Reuse

ABSTRACT

Due to relatively high concentrations of Cd, biomass combustion fly ashes often fail to meet Danish legislative requirements for recycling as fertilizer. In this study, the potential of using electrodialytic remediation for removal of Cd from four different biomass combustion fly ashes was investigated with the aim of enabling reuse of the ashes. The ashes originated from combustion of straw (two ashes), wood chips, and co-firing of wood pellets and fuel oil, respectively. A series of laboratory scale electrodialytic remediation experiments were conducted with each ash. The initial Cd concentration in the ashes varied between 8.8 mg Cd/kg (co-firing ash) and 64 mg Cd/kg (pre-washed straw ash), and pH varied from 3.7 (co-firing ash) to 13.3 (wood ash). In spite of such large variations between the ashes, the electrodialytic method showed to be sufficiently robust to treat the ashes so the final Cd concentration was below 2.0 mg Cd/kg DM in at least one experiment done with each ash. This was obtained within 2 weeks of remediation and at liquid to solid (L/S) ratios of L/S 16 for the pre-washed straw ash and L/S 8 for the straw, co-firing and wood ash.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Straw and wood chips are gaining increased importance as alternative to fossil fuels in power production as biomass is renewable and CO₂ neutral. The Danish power producers incinerate 1.0 Mtonnes straw, 0.2 Mtonnes wood chips and 0.2 Mtonnes straw/wood annually after 2005 [1]. The only bi-products produced from biomass combustion are, besides flue gas condensate, ash residues rich in plant nutrients such as K, P and Mg, which ideally should be recycled as soil fertilisers and/or liming agents. However, elevated concentrations of Cd in bio ash possess potential environmental risk and restrictions in reuse as fertilizer exists [2–4]. In Denmark recycling of bio ashes is regulated on the basis of the content of Cd [5].

Cd and Cd compounds are highly volatile during combustion of biomass and are released from the fuel bed as gaseous compounds

[6,7]. When the flue gas temperature decreases downstream of the boiler, the volatilised compounds may condense on residual fly ash particles or aerosols, which are subsequently trapped in the dust removal filters. Hence, an enrichment of Cd in the fly ashes compared to the bottom ashes during combustion of biomass has been reported [4,8]. The ash fractions that most often fail to meet the Danish regulatory demands are the fly ashes, whereas the bottom ashes often meet even the most restrictive limits [9].

It has been estimated that the yearly production of bio ashes from Danish CHP (combined heat and power) plants and district heating plants was about 28,000 tonnes straw ash and 3000–4000 tonnes wood ash in 2000 [9]. These amounts are expected to double towards year 2012. Two thirds of the produced straw ash is currently recycled to the agricultural fields and the rest is landfilled, whereas practically all wood ash is landfilled [9]. Although it may be possible and beneficial to recycle a larger fraction of these ashes in the future, it is expected that around 2700 tonnes straw ash and an unknown fraction of the wood ashes will still have to be landfilled or remediated each year due to a too high Cd concentration [9]. It is problematic and expensive to deposit the fly ash fractions because the ashes are unstable and Cd is easily leached in contact with water.

* Corresponding author at: Department of Civil Engineering, Technical University of Denmark, Kemitorvet, Building 204, DK-2800 Lyngby, Denmark.
Tel.: +45 45 25 17 30; fax: +45 45 88 59 35.

E-mail address: gunki@byg.dtu.dk (G.M. Kirkelund).

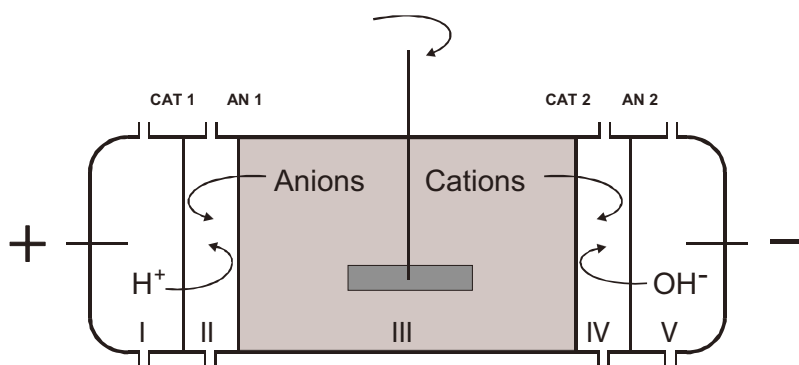


Fig. 1. Electro-dialytic remediation in principle. CAT=cation exchange membrane. AN=anion exchange membrane. The polluted medium is placed in compartment III. Electrolytes are circulated in all electrolyte compartments (compartments I, II, IV and V). CAT 1 and AN 2 are optional.

Different methods for reducing the content of Cd in bio ashes have been suggested, including ash washing [9], thermal treatment [10], optimisation of the combustion process itself [2], and, as in this present work, electrochemical extraction [3,11–13].

1.1. Electro-dialytic remediation

Electro-dialytic remediation is a separation technique based on the principle that ions in solution will electromigrate in an electric field. The method was first developed for removal of heavy metals from soils [14]. The principle is illustrated in Fig. 1.

Originally, the soil was placed in the demineralization compartment (compartment III in Fig. 1) as stationary and water saturated [14]. Later it was shown that for treatment of fine-grained materials as fly ashes and harbour sediment it is beneficial to treat a stirred suspension instead [3,15]. In the case of e.g. straw fly ash, a high percentage of the ash consists of easily soluble particles, as alkali-chlorides, and thus the mass and volume decreases during the treatment [11], which is an operational problem in the stationary cell. The removed heavy metals can be recovered from the electrolytes by conventional methods, e.g. chemical precipitation or electro-deposition.

To mobilise the heavy metals, acidification is necessary and in electro-dialytic remediation this happens due to water splitting at the anion exchange membrane [16–18]. Water splitting occurs at the anion exchange membrane when the limiting current of the membrane is exceeded. The optimum current for the electro-dialytic remediation is when the limiting current for the anion exchange membrane is exceeded, whereas not for the cation exchange membrane. In the stirred electro-dialytic set-up, it has been shown that current densities above 0.8 mA/cm^2 can result in the unwanted water splitting at the cation exchange membrane for soil suspensions [19]. The same study showed significant influence of the L/S ratio on the optimal current density and this is higher at low L/S ratios of the suspension.

In this study, electro-dialytic remediation was applied to four different types of biomass combustion fly ashes. The objectives were to investigate how pH is developing in the ash suspension during remediation and how pH affects the Cd removal. Further, the final Cd concentrations will be compared to Danish limit concentration for reuse of biomass ash as fertilizer.

2. Materials and methods

2.1. The experimental ashes

Four different ashes were included in the study and all originated from biomass fired power plants in Denmark:

- *Straw*: straw fly ash obtained from the straw boiler at the multi-fuelled CHP plant Avedøre Unit 2, Copenhagen.
- *Co-firing*: fly ash from co-firing of fuel oil and wood obtained from the multi-fuel boiler at Avedøre Unit 2, Copenhagen. The multi-fuel boiler is capable of burning combinations of wood, fuel oil and natural gas.
- *Wood*: wood fly ash from grate-firing of wood chips at Køge power plant, Køge.
- *Pre-washed straw*: grain size fractionated straw fly ash from the straw boiler at the multi-fuelled CHP plant Avedøre Unit 2, suspended in water for removal of easily soluble salts and cadmium. The pre-washed straw ash was a by-product (sludge phase) obtained from a demonstration project investigating heavy metal removal from ashes by a combination of washing, pH-adjustment and grain size fractionation (PSO FU project 2201).

The pre-washed straw ash was obtained as a suspension; all the other ashes were obtained naturally dry, from the electrostatic precipitators.

2.2. Analytical procedures

Metal and element concentrations (Pb, Zn, Cu, Ni, Fe, K, Na, Mn, Ca) were measured in aqueous phase by atomic absorption spectroscopy (AAS) in flame (GBC-923) and Cd by graphite furnace (Perkin Elmer 5000 HGA) after a modified digestion of DS 259 [20]. During microwave digestion 0.1–0.3 g dry ash and 10 ml concentrated HNO_3 for 30 min at 135 Psi. Metal and element analyses of the ashes were made in at least three replicates. Concentrations are given per dry weight of ash.

Chloride content in the ashes was measured by potentiometric titration with AgNO_3 on the eluent after extraction with distilled water (L/S=5, 48 h). pH was measured in aqueous phase with a “Radiometer” digital pH-meter after 1 h contact between ash and 1 M KCl (L/S=5). Water content was found as loss of weight after drying to constant weight at 105°C and loss on ignition was measured at 550°C . All chemicals used were of analytical grade.

Cadmium desorption as a function of pH was found through a series of batch extraction experiments with different concentrations of nitric acid (HNO_3), where 1.0 g of dry ash was mixed with 25 ml HNO_3 (concentrations between 0.0 and 1.0 M) in 50 ml plastic bottles and extracted for 3 days with constant agitation. Afterwards, pH was measured in the aqueous phase, the sample was vacuum filtered ($45 \mu\text{m}$) and the filtrate was preserved with HNO_3 before analysed for Cd using AAS. K, Ca, Fe and Mn were also measured on AAS for the straw and co-firing ashes.

Table 1
Experimental conditions for the different electro-dialytic remediation experiments.

Experiment	Ash type	Ash amount (g DM)	Cell type
S1	Straw	50	5 compartments
S2	Straw	75	5 compartments
S3	Straw	100	5 compartments
CF1	Co-firing	50	5 compartments
CF2	Co-firing	100	5 compartments
W1	Wood	50	5 compartments
W2	Wood	75	5 compartments
W3	Wood	100	5 compartments
PW1	Pre-washed straw	~50	3 compartments
PW2	Pre-washed straw	~27	3 compartments
PW3	Pre-washed straw	~25	3 compartments

2.3. Apparatus

The electro-dialytic remediation cell used in the present remediation experiments was made of cylindrical Plexiglas® compartments. It consisted of either three (I, III, V) or five (I–VI) compartments (see Fig. 1). If the cell consisted of three compartments the removed salts and heavy metals will be concentrated in compartment I and V. The demineralization compartment was 10 cm long and with an internal diameter of 8 cm. Ash suspensions with varying amounts of ash and a total volume of app. 400 ml were placed in the demineralization compartment. An electrolyte solution (500 ml of 0.01 M NaNO₃, pH < 2 adjusted with HNO₃) was circulated in each of the electrolyte compartments using Pan World magnetic pumps with a flow rate of 2.6 l/min. An IKA RW11 Basis Lab Egg motor was used to stir the ash suspension during remediation (app. 1500 rpm). The stirrer, which was especially designed for the cell, was made of a flexible plastic flap fastened to a glass rod. The total length of the flap was 5.5 cm and the width was 6 mm. The electrodes were made of platinum coated titanium wire (diameter 3 mm) obtained from Permascand. A Hewlett Packard E3612A power supply was used to maintain a constant electric dc current. The ion exchange membranes were obtained from Ionics, anion exchange membrane 20 SZRA B02249C and cation exchange membrane CR67 HUY N12116B, which have transport numbers 0.95 and 0.97 respectively [21]. The ion exchange membranes can be reused after an experiment, as Hansen et al. [22] found that the membranes kept their transport numbers and permselectivity after 3 months use in electro-dialytic soil remediation experiments, where pH ranged from 1.5 to 11.

2.4. Electro-dialytic remediation experiments

Two or three electro-dialytic remediation experiments were made with each ash type and eleven experiments were made in total. In the experiments with the straw ash, the wood ash and the co-firing ash, the amount of ash in the cell varied between 50 and 100 g (dry) ash to 400 ml distilled water, whereas other remediation parameters were kept constant. Experimental conditions are seen in Table 1.

In the experiments with the pre-washed straw ash, 400 ml ash suspension (dry matter content approximately 12.5%) was used in each experiment. The aqueous phase was either the original suspension water (experiment PW1), or it had been washed once (experiment PW2) or twice (experiment PW3). The residual dry matter content decreased due to the washing process, as more salts were dissolved when adding fresh water to the suspension (solubility controlled dissolution). On the other hand, the residual Cd concentration in the ash increased as Cd was more resistant to dissolution. The suspension water was first separated from the ash particles by centrifugation, then the supernatant was removed

by decantation, and the removed volume was replaced by 300 ml distilled water. The washing supernatants were measured for Cd.

All experiments were run for 2 weeks at a constant current of 40 mA, corresponding to a current density of approximately 0.8 mA/cm². The current was chosen based on previous studies [19] as the optimal current to prevent water splitting at the cation exchange membrane during the experiments. This resulted in varying voltage drop, which was monitored daily. pH was measured in the electrolytes and adjusted with 5 M HNO₃ if pH > 2. This was especially done in compartment VI (Fig. 1) of the electro-dialytic cell, to avoid precipitations in the electrolyte due to the production of OH⁻ by the electrode reaction at the inert electrode. Furthermore, 10 ml aqueous samples were taken from the electrolytes to follow the development in Cd concentration over time. In experiment PW1, Fe, K and Mn were also measured in the electrolytes. pH was measured in the ash suspension daily, except in experiment S1 and CF1.

After the experiments the membranes and electrodes were soaked in 1 M and 5 M HNO₃, respectively, to release precipitated metals. The ash suspension was filtered through a 45 µm filter and digestions made on the filtered ash sample. The digestions and filtered liquid were measured for Cd on AAS. pH was measured on dry ash. The aqueous phase, the electrolytes, the membranes and the electrodes were all analysed for Cd.

3. Results and discussion

3.1. Ash characterisation

The results from the initial characterisation of the four ashes are given in Table 2, where the limit values for reuse for heavy metals also are seen. pH dependent desorption of Cd in HNO₃ is illustrated in Fig. 2A and pH dependent desorption of Fe, K, Mg and Ca in the straw and co-firing ash in Fig. 2B and C.

The Cd concentration in the straw and pre-washed straw ashes was above the limit value. No limit exists for the co-firing ash, as it cannot be reused as fertilizer according to the current legislation [5]. Still, the Cd concentration in the co-firing ash was below the limit for the wood ash. It is still interesting to investigate these two ashes, as there also exists a maximum total load of Cd that is allowed to be added to the agricultural land [5]. When comparing the concentrations of other metals, the concentration of Ni was almost 200 times the limit value that for the co-firing ash. The high content of Ni, which probably originates from the fuel oil, may cause environmental concern in relation to potential reuse of the ash. Although recycling of ashes from co-firing of biomass and fossil fuels is currently not allowed, alternative reuse options for the remediated ash could be considered, e.g. reuse in construction materials or as a filler material. The Pb concentration was above the limit value only for the pre-washed straw ash. In the following, only Cd will be studied as it is considered the most problematic.

Whereas pH was slightly acidic in the straw ash, the pre-washed straw ash and in the co-firing ash (pH 5.5, 5.7 and 3.7, respectively), pH was alkaline in the wood ash (13.3). The high pH in the wood ash was probably due to a high content of alkaline oxides, especially CaO [23,24], which also corresponds to a much higher Ca content in this ash.

The loss on ignition was relatively low in the wood ash and higher in the straw, the co-firing and pre-washed straw ash. A low loss on ignition is an indication of good burn-out of the fuel.

When comparing the pre-washed straw ash with the raw straw ash, significant differences in element concentrations appeared, although the two ashes were originally produced in the same straw-fired boiler. The differences indicate changes in the ash composition due to the pre-washing treatment. In the raw straw ash the

Table 2
Characterisation results (mean values \pm standard deviation) for the four ashes.

Parameter	Ash			
	Straw	Co-firing	Wood	Pre-washed straw
pH	5.5 \pm 0.0	3.7 \pm 0.0	13.3 \pm 0.0	5.7 \pm 0.0
Water (%)	0.4 \pm 0.2	0.2 \pm 0.1	0.4 \pm 0.1	87.5
Loss on ignition (%)	8.0 \pm 0.2	12.4 \pm 1.1	2.2 \pm 0.1	9.0 \pm 0.3
Cl ⁻ (%)	20	0.7	3.2	2.8
Cd (mg/kg)	18.0 \pm 0.6	8.8 \pm 0.4	12.1 \pm 0.6	64 \pm 1.6
Cd limit (mg/kg) [5]	5		20	5
Cu (mg/kg)	79.0 \pm 79.0	137 \pm 5.0	303 \pm 3.0	370 \pm 105
Zn (mg/kg)	572 \pm 11	1331 \pm 29	800 \pm 6.0	1271 \pm 206
Pb (mg/kg)	92.7 \pm 3.9	74.0 \pm 4.0	102 \pm 2.0	194 \pm 23
Pb limit (mg/kg) [5]	120	120	120	120
Ni (mg/kg)	15.0 \pm 1.4	10,900 \pm 180	77.0 \pm 1.8	35.3 \pm 7.6
Ni limit (mg/kg) [5]	60	60	60	60
K (g/kg)	485 \pm 12	49.1 \pm 3.0	323 \pm 0.0	291 \pm 18.6
Ca (g/kg)	2.7 \pm 0.1	9.5 \pm 1.4	113 \pm 3.6	12.1 \pm 1.0
Fe (g/kg)	2.0 \pm 0.1	15.9 \pm 0.5	3.8 \pm 0.5	2.6 \pm 1.3
Mn (g/kg)	0.075 \pm 0.003	4.8 \pm 0.1	10.2 \pm 0.4	0.90 \pm 0.1

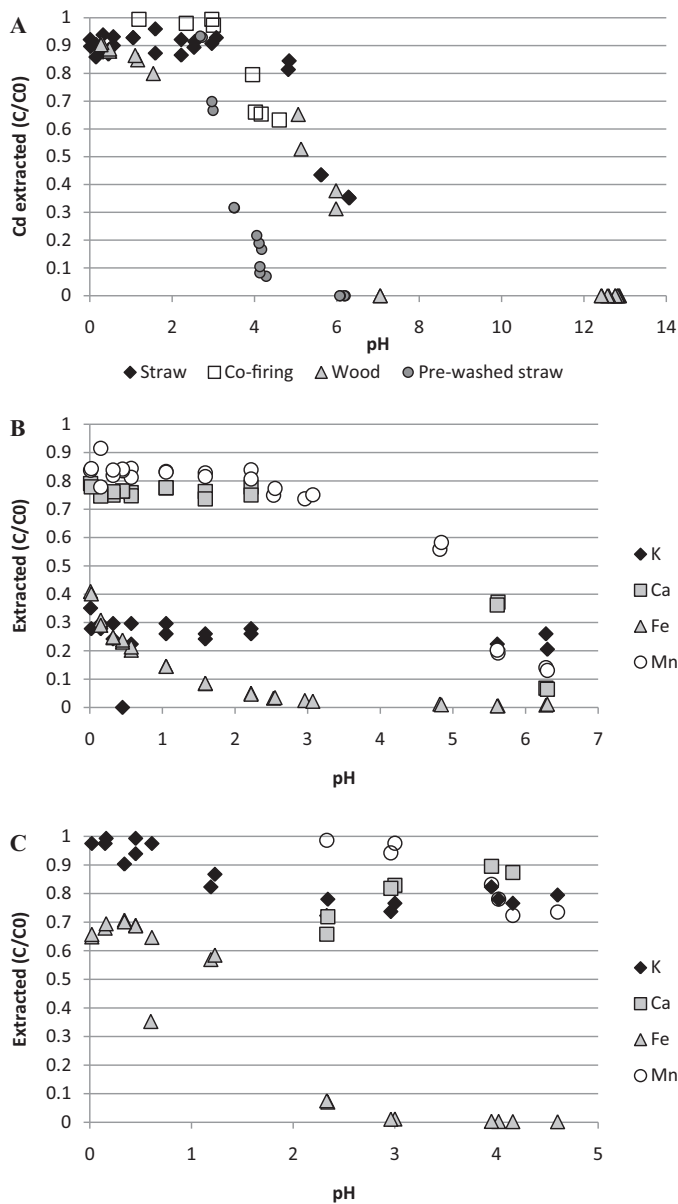


Fig. 2. pH dependent desorption. (A) Cd in the four ashes. (B) K, Ca, Fe and Mn in the straw ash. (C) K, Ca, Fe and Mn in co-firing ash.

chloride content was as high as 20%, whereas it was only 3% in the pre-washed straw ash, and the K content was reduced from almost 500 g/kg DM to less than 120 g/kg DM. This indicates washout of KCl and other easily soluble chlorides. On the other hand, Cd, Cu, Zn, Pb, Ca, Fe and Mn increased in concentration in the pre-washed straw ash compared to the raw straw ash. This enrichment can be explained by a mass loss of the ashes when easily soluble salts are washed out, leading to a concentration of the remaining elements in the ash residue [25].

It is seen from Fig. 2A that for all four ashes, desorption of Cd was highly pH dependent. The pH at which Cd started to desorb from the ash was lower in the pre-washed straw ash (around 4) compared to the other ashes (around 6). This was probably because the more soluble part of the Cd had already been washed out and the remaining Cd in the pre-washed straw ash is not soluble at the natural pH (5.7) of this ash. In the wood ash Cd was immobile at pH values above 7, meaning that no Cd was released at the natural pH of this ash (13.3). For the straw ash around 40% Cd was water soluble at the natural pH (5.5) and for the co-firing ash the water soluble fraction of Cd was as high as 80% (natural pH 3.7). On the basis of these observations, it is expected that the straw ash and the co-firing ash will be easier to remediate compared to the wood ash and the pre-washed straw ash.

It is seen from Fig. 2B that the desorption of Ca, Mn and Fe in the straw ash was pH dependent, whereas K desorption seemed solubility controlled. In the co-firing ash (Fig. 2C), higher amounts of K, Ca, Fe and Mn were extracted than from the straw ash. Only Fe showed pH dependent behaviour in the investigated pH range in the co-firing ash.

3.2. Electrodialytic remediation experiments

The voltage drops over the cells in the experiments were lower than 9V in all the experiments. The final Cd concentration in the ash (mg Cd/kg DM) and the final pH value in the ash suspension is seen in Table 3. There was not sufficient amount of ash to measure pH in the ash after experiment S1 and CF1. The Cd recovery was calculated as recovered amount of Cd in percentage of the initial amount and was 85–120% for the different experiments. As much as 90% of the straw ash was dissolved in the experiments, for wood ash up to 70% and 50% for the co-firing ash, due to wash out of salts and other easily dissolvable compounds.

It is seen from Table 3 that for the straw ash, the co-firing ash and the pre-washed straw ash the Cd concentration was reduced significantly in all electro-dialytic remediation experiments. For straw ash, the concentration was reduced to below the limit value for Cd.

Table 3
Cd concentration and pH in the ash after electrodiolytic remediation. n.m. – not measured.

Experiment name	Initial Cd conc. (mg/kg DM)	Final Cd conc. in ash (mg/kg DM)	Final pH in ash suspension
S1	18	1.9	n.m.
S2	18	3.4	0.7
S3	18	2.9	0.8
CF1	8.8	0.6	n.m.
CF2	8.8	0.7	1.2
W1	12.1	1.9	1.0
W2	12.1	8.7	5.6
W3	12.1	19.4	6.5
PW1	64	3.5	1.3
PW2	86.7	2.0	1.1
PW3	112	1.8	1.7

Despite a significantly higher initial Cd concentration (64 mg/kg) in the pre-washed straw ash, the final concentration was as low as 1.8 and 2.0 mg Cd/kg in the experiments with initial water change, and 3.5 mg Cd/kg in experiment PW1. The tendency of increased remediation efficiency in the experiments with change of the water phase is probably due to a smaller amount of non-target ions in solution. When fewer ions are present in the solution, less current is wasted on transporting these ions at the expense of the heavy metal ions. In experiment W3 with wood ash, the Cd concentration

increased compared to the initial concentration and the highest final pH was also observed in this experiment.

When comparing the remediation results in Table 3 with the Cd desorption curve in Fig. 2A, there seems to be a close correlation between the obtained remediation efficiency and the final pH value in the suspension. In all experiments with the straw ash, the co-firing ash and the pre-washed straw ash the pH in the ashes was lowered to between 0.7 and 1.7 after remediation. According to Fig. 2A, Cd is highly mobile in the ashes at such low pH values. For the wood ash, the remediation efficiency decreased with increasing initial amount of ash in the cell. In the experiments on the wood ash, the final pH lay between 1.0 and 6.5, and the Cd concentration increased with increasing pH. Whereas the Cd concentration was reduced significantly in the experiment with the low final pH (1.0), it was only reduced slightly, or even increased, in the other two experiments, in which the final pH was 5.6 and 6.5, respectively. According to Fig. 2A Cd is insoluble in the wood ash at pH values around 6.5, and at pH 5.5 less than 50% is mobile. The immobility of Cd at the present pH, combined with a significant mass loss in the ash due to dissolution of salts, may explain the increased Cd concentration in the wood ash compared to the initial concentration in experiment W3.

The observed decrease in ash pH during electrodiolytic remediation is a consequence of the previously described acidification process due to water splitting and/or acid leakage from the anolyte and catholyte. This acidification process can be further illustrated

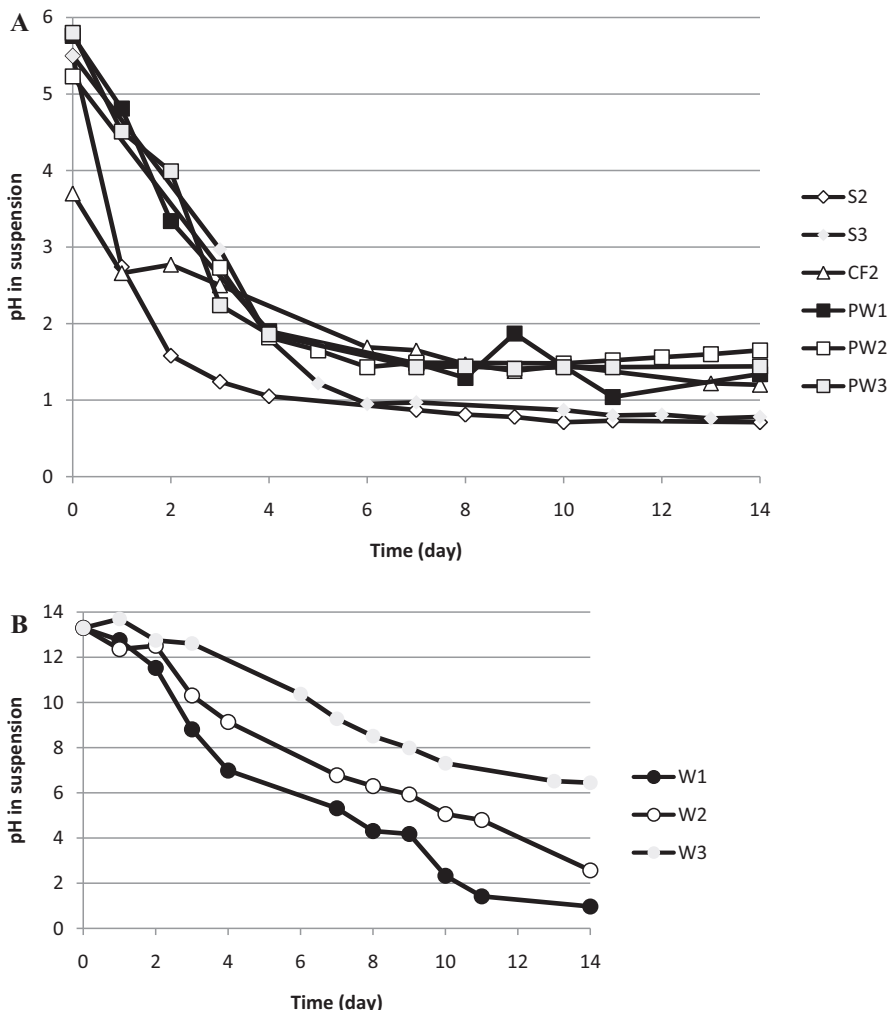


Fig. 3. pH in the ash suspension during electrodiolytic experiments. (A) Experiments with straw, co-firing ash and pre-washed straw ash. (B) Wood ash experiments.

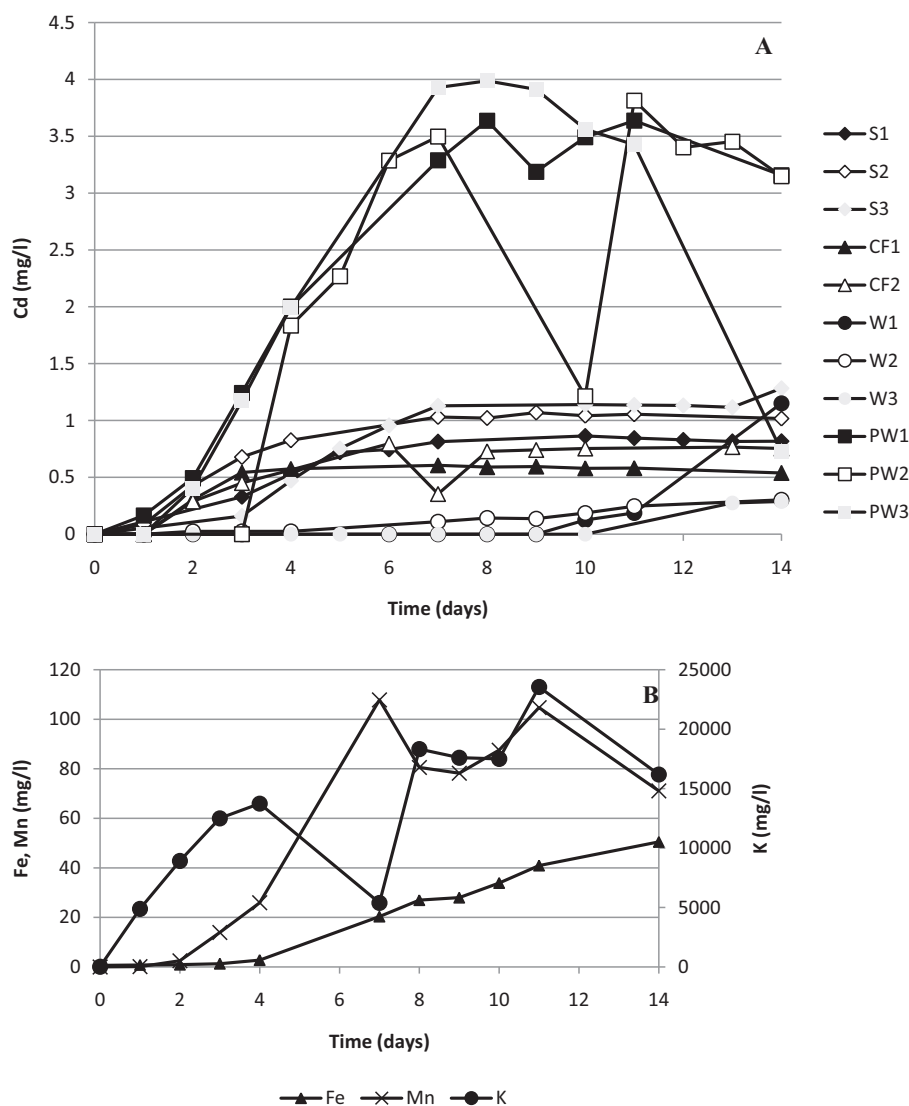


Fig. 4. (A) Cd in electrolytes and (B) Fe, Mn and K in electrolytes in experiment PW1.

by plotting the pH in the ash suspension as a function of time. For the straw and the wood ash (Fig. 3A) it was seen that the pH decrease was earlier with lower amount of ash in the suspension as there was less ash to buffer the acidification. This was not seen for the prewashed ash. The pH decrease for the co-firing ash was delayed compared the straw and pre-washed straw ash, despite lower initial pH in the ash so this ash also buffered further acidification.

Fig. 3B reveals that for the wood ash, the pH-decrease is progressing rather slowly, even for the experiment W1 with the smallest amount of ash. This ash is very alkaline and the slow pH-decrease indicates a high buffering capacity of the ash, probably caused by the high Ca concentration in the ash in the form of CaO [24].

Thus, from the above observations it seems that desorption curves combined with pH measurements of the ash during remediation may be used as a simple tool for predicting when the remediation process is finished. For Cd in the present ashes, the threshold pH seems to be around 2 for all four ashes, which was reached after 4 days (for the wood ash though only for the highest liquid to solid ratio, experiment W1). The Cd concentration in the ash is not expected to decrease significantly until pH reach below

this value, and to verify this comparison between pH of the suspension and the removed amount of Cd over time is made. Fig. 4A shows the Cd concentrations in the electrolytes during the experiments. Cd was removed to both the catholyte and anolyte during the experiments, indicating both negative and positively charged species. Comparing with Fig. 3A it is seen that the Cd removal into the electrolytes was both dependent on pH and the initial Cd concentration in the ash. However, within a series of experiments for one type of ash, the differences do not seem significant. The sudden decrease in some of the concentration profiles is most likely due to electrodeposition of Cd, especially in experiment PW1-3 where the cell only consisted of 3 compartments. The Cd removal was delayed compared to the decrease in pH, but seemed to be stabilised after 7 days of remediation. This suggests that further experiments should be made with shorter remediation times than the 14 days used in this study.

In experiment PW1, Fe, Mn and K were analysed in the electrolytes, which is shown in Fig. 4B. It was seen that the Mn removal followed, somewhat delayed, the Cd removal in experiment PW1. The Fe removal was more linear, probably present as less soluble minerals [26]. K was removed from the ash before Cd and was thus more mobile in the electric field. However, at the pH obtained in

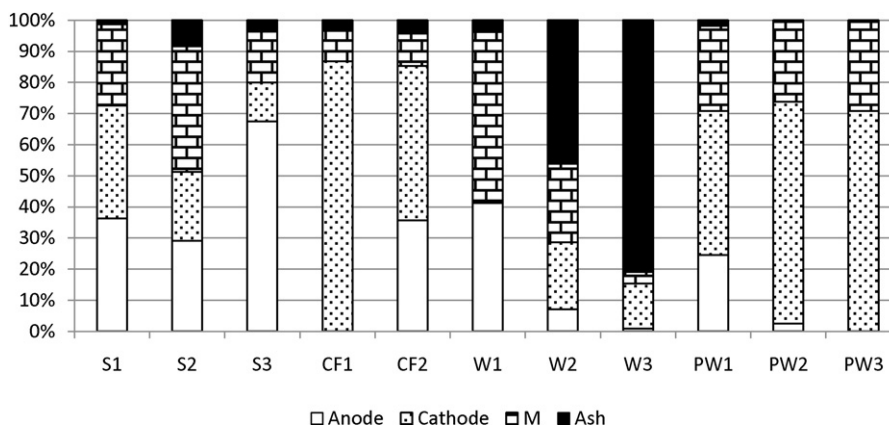


Fig. 5. Cd distribution after electrodiolytic experiments. M – middle compartment liquid.

the ash, all K was dissolved and removed by the electric current. K was removed towards the cathode in three times higher concentrations than towards the anode, indicating mainly cationic speciation. Fe and Mn were mainly removed towards the anode and cathode respectively. The large removal of K suggests that K is present in highly dissolvable phases in the straw ash also after washing and is contributing to the mass loss during electrodiolytic remediation. K was found to be present as both KCl and K_2SO_4 in straw ash [26] and further studies about the behaviour of the two minerals during electrodiolytic remediation should be made since K is important to keep in the ash for reuse purposes.

In Fig. 5, the distribution of Cd in the cell at the end of the remediation experiments is illustrated. From Fig. 5 it is seen that a significant fraction of Cd has been removed towards the anode-side of the cell in all three experiments on the straw ash. This indicates that Cd has been removed as negatively charged complexes, probably chloride complexes (e.g. $CdCl_3^-$, $CdCl_4^{2-}$) [27]. Some Cd has also been removed to the cathode side, probably as Cd^{2+} . Following the pH decrease in the fly ash suspensions and reduction of chloride content by removal by electromigration, Cd will be removed firstly towards the anode as $CdCl_4^{2-}$ and as pH decreases is removed towards the cathode as Cd^{2+} [23]. Removal of Cd towards the anode was especially seen in the experiments with straw ash and Cd has previously been found to be present in untreated ash as $CdCl_2$ [26]. A large fraction is found in solution in the middle compartment as well. This may indicate that the remediation process is still not finished, or it may be due to the presence of un-charged complexes ($CdCl_2^0$) [27], which do not electromigrate in the electric field. In the co-firing ash experiments the majority of Cd is found in the electrolytes after remediation, and only a small amount is left in the middle compartment, meaning that the separation process was successful.

For the wood ash, the remediation efficiency decreases with increasing initial amount of ash in the cell, as also seen from Table 3. After remediation a majority of the Cd is still found in the ash, or in solution in the middle compartment. Only a smaller amount is removed to the electrolytes. In the pre-washed straw ash, the distribution of Cd in the cell after remediation seems to shift towards less Cd in the anolyte and in the middle compartment when the water phase has been changed. This confirms that the easily soluble chloride, which forms negatively charged – or neutral – complexes with Cd, is removed with the water phase. Thus, significantly better separation of Cd is achieved when the soluble chlorides are removed prior to remediation.

In the literature, few experimental results on electrodiolytic removal of Cd from ashes suspended in water have been reported.

Lima et al. [13] used a similar experimental setup as in this study for straw and co-firing ashes. It was shown for the straw ash that after 10 days of remediation 70% Cd was found in the liquid in compartment III, but increasing the remediation time to 14 days, reduced this to 10%. At the same time, the Cd concentration in the straw ash was not reduced to similar low concentrations as in this study, probably due to a higher final pH in the ash. The co-firing ash had an alkaline initial pH, which resulted in less than 1% Cd removal and most Cd found in either the ash or in the liquid in compartment III. The co-firing ash in this study came from the same plant as the one used by Lima et al. [13], but the initial pH was very different. This suggests probably that ash characteristics are very dependent on the ratio of wood/fuel oil during combustion.

Ottosen et al. [12] showed Cd removals of 45 and 75% from wood ash and straw ash respectively, with similar amounts of Cd still in the liquid in the middle compartment after 14 days of remediation as seen in this study. An experiment with alkaline municipal solid waste incineration ash showed 50% Cd removal after 14 days of remediation and 40% Cd remaining in the liquid in the middle compartment [28].

The experimental results from this study and the literature show that electrodiolytically removal of Cd from fly ashes has a potential when pH in the ash solutions favours release of Cd to form charged species for electromigration.

4. Conclusion

The results from the electrodiolytic remediation experiments show a good remediation potential for all four ashes. The most important factor for a successful remediation seems to be the pH in the ash. Generally, a successful remediation seems to be achieved only when the pH decreases to below pH 2.0. This was achieved for the straw, co-firing and pre-washed straw ash within 6 days of remediation. The wood ash had a higher initial pH and a pH below 2 is only achieved when the L/S ratio in the ash suspension was high. The concentration of Cd was below the Danish regulation limits for reuse in the all electrodiolytic experiments and the ashes have thus a potential for reuse as fertilizer. However, the nutrient content should be investigated in future studies to support the findings in this study.

Acknowledgements

The authors acknowledge the financial contribution from Elkraft System and Energi E2 (PSO-F&U 3206).

References

- [1] F.J. Frandsen, Utilizing biomass and waste for power production – a decade of contributing to the understanding, interpretation and analysis of deposits and corrosion products, *Fuel* 84 (2005) 1277–1294.
- [2] M. Narodoslawsky, I. Obernberger, From waste to raw material – the route from biomass to wood ash for cadmium and other heavy metals, *J. Hazard. Mater.* 50 (1996) 157–168.
- [3] A.J. Pedersen, Characterization and electrochemical treatment of wood combustion fly ash for the removal of cadmium, *Biomass Bioenergy* 25 (2003) 447–458.
- [4] P. Vervaeke, F.M.G. Tack, F. Navez, J. Martin, M.G. Verloo, N. Lust, Fate of heavy metals during fixed bed downdraft gasification of willow wood harvested from contaminated sites, *Biomass Bioenergy* 30 (2006) 58–65.
- [5] BEK 818, Bekendtgørelse om anvendelse af bioaske til jordbrugsformål (Bioaskebekendtgørelsen), Danish Ministry of the Environment, 2008 (in Danish).
- [6] A. Ljung, A. Nordin, Theoretical feasibility for ecological biomass ash recirculation: chemical equilibrium behavior of nutrient elements and heavy metals during combustion, *Environ. Sci. Technol.* 37 (1997) 2499–2503.
- [7] L. Sørum, F.J. Frandsen, J.E. Hustad, On the fate of heavy metals in municipal solid waste combustion. Part I: devolatilisation of heavy metals on the grate, *Fuel* 82 (2003) 2273–2283.
- [8] I. Obernberger, F. Biedermann, W. Widmann, R. Riedl, Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions, *Biomass Bioenergy* 12 (1997) 211–224.
- [9] M.T. Hansen, Separation og genanvendelse af aske fra biobrændselsanlæg, dk-teknik og Miljøstyrelsen, Miljøprojekt Nr. 962, 2004 (in Danish).
- [10] J. Dahl, Chemistry and behaviour of environmentally relevant heavy metals in biomass combustion and thermal ash treatment processes, PhD dissertation, Technische Universität Graz, Graz, 2000.
- [11] H.K. Hansen, L.M. Ottosen, A. Villumsen, Electrochemical removal of cadmium from straw combustion fly ash, *J. Chem. Technol. Biotechnol.* 79 (2004) 789–794.
- [12] L.M. Ottosen, A.J. Pedersen, H.K. Hansen, A.B. Ribeiro, Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrochemical method, *Electrochim. Acta* 52 (2007) 3420–3426.
- [13] A.T. Lima, L.M. Ottosen, A.B. Ribeiro, Electroremediation of straw and co-combustion ash under acidic conditions, *J. Hazard. Mater.* 161 (2009) 1003–1009.
- [14] L.M. Ottosen, H.K. Hansen, S. Laursen, A. Villumsen, Electrochemical remediation of soil polluted with copper from wood preservation industry, *Environ. Sci. Technol.* 31 (1997) 1711–1715.
- [15] G.M. Kirkelund, L.M. Ottosen, A. Villumsen, Electrochemical remediation of harbour sediment in suspension – evaluation of effects induced by changes in stirring velocity and current density on heavy metal removal and pH, *J. Hazard. Mater.* 169 (2009) 685–690.
- [16] G.M. Nystroem, L.M. Ottosen, A. Villumsen, Acidification of harbor sediment and removal of heavy metals induced by water splitting in electrochemical remediation, *Sep. Sci. Technol.* 40 (2005) 2245–2264.
- [17] A.J. Pedersen, L.M. Ottosen, A. Villumsen, Electrochemical removal of heavy metals from municipal solid waste incineration fly ash using ammonium citrate as assisting agent, *J. Hazard. Mater. B* 122 (2005) 103–109.
- [18] L.M. Ottosen, H.K. Hansen, C.B. Hansen, Water splitting at ion-exchange membranes and potential differences in soil during electrochemical soil remediation, *J. Appl. Electrochem.* 30 (2000) 1199–1207.
- [19] P.E. Jensen, L.M. Ottosen, C. Ferreira, Electrochemical remediation of soil fines (<math><63\ \mu\text{m}</math>) in suspension – influence of current strength and L/S, *Electrochim. Acta* 52 (2007) 3412–3419.
- [20] DS 259, Determination of metals in water, sludge and sediments – general guidelines for determination by atomic absorption spectrophotometry in flame, Dansk Standardiseringsråd, 2003.
- [21] H.K. Hansen, L.M. Ottosen, S. Laursen, A. Villumsen, Electrochemical analysis of ion-exchange membranes with respect to possible use in electrochemical decontamination of soil polluted with heavy metals, *Sep. Sci. Technol.* 32 (1999) 2425–2444.
- [22] H.K. Hansen, L.M. Ottosen, A. Villumsen, Electrical resistance and transport numbers of ion-exchange membranes used in electrochemical soil remediation, *Sep. Sci. Technol.* 34 (1999) 2223–2233.
- [23] H.K. Hansen, A.J. Pedersen, L.M. Ottosen, A. Villumsen, Speciation and mobility of cadmium in straw and wood combustion fly ash, *Chemosphere* 45 (2001) 123–128.
- [24] B.M. Steenari, S. Schelander, O. Lindquist, Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB – a comparative study, *Fuel* 78 (1997) 249–258.
- [25] K.S. Wang, K.Y. Chiang, K.L. Lin, C.J. Sun, Effects of a water-extraction process on heavy metal behavior in municipal solid waste incinerator fly ash, *Hydrometallurgy* 62 (2001) 73–81.
- [26] A.T. Lima, L.M. Ottosen, A.J. Pedersen, A.B. Ribeiro, Characterization of fly ash from bio and municipal waste, *Biomass Bioenergy* 32 (2008) 277–282.
- [27] A.E. Martell, Critical Stability Constants. Inorganic Complexes, Plenum Press, New York, 1976.
- [28] A.J. Pedersen, Electrochemical removal of heavy metals from fly ashes, PhD thesis, Technical University of Denmark, Lyngby, 2002.