



# Electrodialytic removal of heavy metals from different fly ashes Influence of heavy metal speciation in the ashes

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## Abstract

Electrodialytic remediation, an electrochemically assisted extraction method, has recently been suggested as a potential method for removal of heavy metals from fly ashes. In this work, electrodi-alytic remediation of three different fly ashes, i.e. two municipal solid waste incinerator (MSWI) fly ashes and one wood combustion fly ash was studied in lab scale, and the results were discussed in relation to the expected heavy metal speciation in the ashes. The pH-dependent desorption charac-teristics for Cr differed between the two MSWI ashes but were similar for Cd, Pb, Zn and Cu. Thus, it was expected that the speciation of Cd, Pb, Zn and Cu was similar in the two ashes. However, in succeeding electrodi-alytic remediation experiments significant differences in removal efficiencies were observed, especially for Pb and Zn. In analogous electrodi-alytic remediation experiments, 8% Pb and 73% Zn was removed from one of the MSWI ashes, but only 2.5% Pb and 24% Zn from the other. These differences are probably due to variations in pH and heavy metal speciation between the different ashes. Cd, the sole heavy metal of environmental concern in the wood ash, was found more tightly bonded in this ash than in the two MSWI ashes. Approximately 70% Cd was removed from both types of ashes during 3 weeks of electrodi-alytic remediation, although the total concentration was a factor of 10 lower in the wood ash. It was suggested that complex Cd-silicates are likely phases in the wood ash whereas more soluble, condensed phases are dominating in the MSWI ashes.

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## 1. Introduction

Fly ashes from municipal solid waste incineration (MSWI) contain high concentrations of several heavy metals, and due to the potential leaching of these heavy metals and other toxic components, the MSWI fly ashes are regulated as hazardous waste in Denmark and many other countries. According to the Danish environmental legislation, MSWI fly ash is defined as a hazardous waste which requires stabilisation before permanent land filling. Until suitable stabilisation methods have been developed, the fly ash must be deposited only temporarily, or exported for handling in other countries. The definition hazardous waste is linked to the leaching properties of heavy metals and other toxic component in the waste, and therefore, and given the fact that MSWI fly ash at present not is approved for reuse, no limit values have been defined for the concentration of heavy metals in the stabilized ashes. Instead, the long-term stability of the ashes should be proven through leaching tests, etc.

At present no stabilisation methods have been finally accepted by the Danish environmental authorities. Therefore, to minimise pollution of the environment and meet the legislative demands for stabilisation, new treatment methods for detoxification of MSWI fly ash and/or for the recovery of metals should be considered.

Biomass, as for instance wood, straw and energy crops, is a renewable, CO<sub>2</sub> neutral energy source. The combustion residues from the process of biomass combustion contain important plant nutrients such as K, P and Mg. Therefore, the ashes are considered recycled to agricultural fields and forest soils as fertilisers. However, the reuse of bio-ashes as fertilizers is limited due to high concentrations of the toxic heavy metal Cd, especially in the fly ash fractions. In Denmark, the limit value for Cd in wood ash for recycling is 15 mg/kg DM [1]. Cd bio-accumulates and dietary intake is the dominant pathway for human exposure to Cd [2].

Electrodialytic remediation, an electrochemically assisted extraction method originally developed for remediation of heavy metal polluted soil [3], has recently been suggested as a potential method for removal of toxic heavy metals from fly ashes from both municipal solid waste incineration [4,5] and biomass combustion [6]. In this present study, electrodialytic removal of heavy metals from two MSWI fly ashes and one wood combustion fly ash is compared and discussed in relation to the expected heavy metal speciation.

## 2. Speciation of heavy metals in the different fly ashes

The speciation of heavy metals in fly ashes and other combustion residues is highly influenced by the metal's behaviour and fate during the combustion process. More volatile metals, as for instance Cd, may vaporise during combustion and subsequent condense out on the surface of fly ash particles when the flue gas cools down downstream of the boiler. Thereby, the fly ash becomes enriched in volatile elements whereas the bottom ash is depleted in these elements. Non-volatile elements, on the other hand, are highly retained in the bottom ashes. Cd, Pb and Zn have all been found to be enriched in the fly ash fractions due to initial volatilisation whereas Cu and Cr to a great extent are retained in the bottom ashes [7].

From characterisation studies of MSWI fly ashes it has previously been found that oxide and chloride phases of Pb and Zn are enriched at/near the surface of the fly ash particles. Pb sulphates, elemental Pb and Zn, and Zn bromides and silicates have also been detected [8]. Analyses of the fly ash bulk mineralogy have revealed existence of Pb silicates and Zn sulphates [8]. Due to the relatively low concentrations of Cd in most fly ashes, Cd compounds have only been identified in a few studies. However, according to Evans and Williams [9] Cd arsenates and sulphates have been found in MSWI fly ashes, and Dahl [10] has reported the existence of complex Cd compounds, probably silicates or sulphates, in biomass combustion fly ashes. Thermodynamic modelling has suggested  $\text{CdCl}_2$  and  $\text{CdO}$  as probable condensed phases in both MSWI fly ashes and biomass combustion fly ashes [7,10].

### 3. Experimental

#### 3.1. Analytical methods

The following analytical methods were used in this work: total metal concentrations in the ash samples were found using atomic absorption spectroscopy in flame (FAAS) after microwave assisted pressurised digestion in concentrated  $\text{HNO}_3$  at a liquid-to-solid (L/S) ratio of 20 (method modified from Danish Standard DS 259). pH in the ashes was measured with a pH-electrode in 1 M KCl at a liquid-to-solid ratio of 5. Water content was found as loss of weight after drying at  $105^\circ\text{C}$  and content of organic matter ( $C_{\text{comb.}}$ ) was found as loss on ignition ( $550^\circ\text{C}$ ).

#### 3.2. The experimental ashes

Two MSWI fly ashes and one wood chips combustion fly ash were used for this study. MSWI fly ash 1 (GR) was obtained from a small incineration plant on Nuuk landfill, Greenland, and MSWI fly ash 2 (VF) was obtained from the mass-burn facility “Vestforbrænding”, Denmark. At the points of sampling (the electrostatic precipitators), the gas streams had not been exposed to flue gas cleaning additives (e.g. lime). The wood combustion ash (FA) was obtained from the cyclone on Ebeltoft district heating plant, a grate-fired wood chips combustion plant in Denmark. Some characteristics of the experimental fly ashes are given in Table 1. As seen from Table 1 the natural pH of all three fly ashes is very alkaline (between 10.8 and 13.3). The high concentrations of Ca, which are originated only from Ca presence in the fuel (no lime addition), contribute to the very high pH of the ashes (in the form of  $\text{CaO}$ ) [11]. The GR ash has a quite high content of organic matter, indicating that the combustion has been incomplete. The concentration of heavy metals is very high in the two MSWI fly ashes. Whereas the concentrations of Cd, Zn and Cu are comparable in the two MSWI ashes, quite large variations are seen for Pb and Cr. These variations are most likely due to varying concentrations of the metals in the waste fuel, although other factors, such as the amount of Cl in the fuel, may have influenced too. It has previously been shown that even small portions of Cl in the waste may decrease the volatilisation temperature of especially Pb with several hundred degrees, leading to significant Pb volatilisation during

Table 1  
Some characteristics of the experimental fly ashes

Parameter	MSWI 1 (GR)	MSWI 2 (VF)	WOOD (FA)
Water content (%)	2.2	0.7	0.9
Loss on ignition (%)	11.4	1.3	1.0
pH	10.8	12.2	13.30
Ca (mg/kg DM)	85500	140000	237000
Cd (mg/kg DM)	280	240	28
Pb (mg/kg DM)	4000	8050	110
Zn (mg/kg DM)	22650	17150	n.m.
Cu (mg/kg DM)	1370	1570	n.m.
Cr (mg/kg DM)	3000	280	n.m.

n.m.: not measured.

incineration and subsequent enrichment in the fly ash fractions [7]. Thus, large variations in Pb vaporisation and distribution between bottom ashes and fly ashes have been reported in different studies [7]. Important sources of Pb in municipal solid waste are batteries, plastics and pigments [12]. Significant variations in Zn vaporisation have been reported too [7]. Sources of Zn in the waste are various, e.g. scrap metal, organometallics, printing ink, papers and plastics [12]. The volatility of Cd, Cu and Cr is less influenced by variations in fuel composition or combustion conditions. Cd, which is a highly volatile metal, is generally almost completely vaporised at normal incineration temperatures and consequently highly enriched in the fly ashes. Cu and Cr are both quite non-volatile and to a great extent retained in the bottom ash [7,12].

### 3.3. Batch leaching experiments

Batch leaching experiments were performed on the three experimental fly ashes to compare the leaching characteristics of the heavy metals. Different concentrations of HNO<sub>3</sub> were used to find the pH-dependent heavy metal desorption. The possibilities of extracting the heavy metals at neutral and alkaline conditions instead of at low pH were examined too, using 0.5 M ammonium citrate, adjusted to different pH values with 25% NH<sub>3</sub>, as a desorption agent. All batch leaching experiments were performed by mixing 1.0 g of dry, homogenised ash with 25 ml of the extraction agent in a 50 ml plastic bottle and extract for 3 days with constant shaking. After that, pH was measured in the liquid phase, the sample was filtrated and the filtrate analysed for selected metals on FAAS.

### 3.4. Electrodialytic remediation experiments

The laboratory cells used for electrodialytic remediation experiments in this study were made of Plexiglas cylinders, designed and developed at the Technical University of Denmark. A typical laboratory cell consists of three compartments, as sketched in Fig. 1. The fly ash is suspended in an aqueous phase (water or a desorption agent) and placed in compartment II. The electrodes, which are made of inert material (platinized titanium) are placed in compartments I and III, respectively. In each of compartments I and III, electrolyte solutions

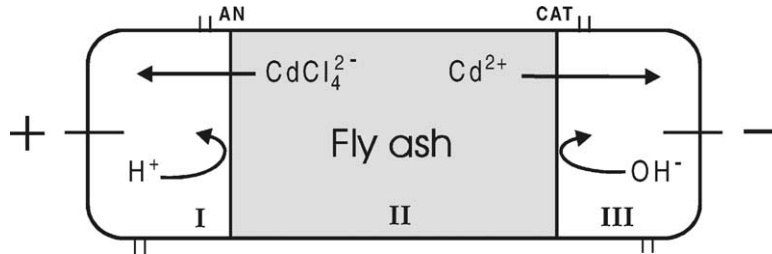


Fig. 1. The principle of electro-dialytic remediation. AN, anion exchange membrane; CAT, cation exchange membrane.

are circulated in separate systems. When an electric dc current is applied to the system, the ions in the ash suspension and electrolytes will begin to migrate in the electric field, either toward the anode or towards the cathode, as current carriers. The three cell compartments are separated by ion exchange membranes, placed in the electro-dialytic way, thereby allowing ions in the ash suspension to be transported through the membrane and into the electrolyte solutions in compartments I or III but preventing transport of ions (with opposite charge) in the opposite direction. In this way, no current is wasted in transporting ions from one electrolyte compartment, through the ash suspension and into the opposite electrolyte compartment. As a result of the remediation process, the heavy metals and other ions removed from the ash suspension will be concentrated in compartments I or III, from where they can be precipitated or separated with conventional methods. Thereby, no new waste products should be generated.

The laboratory cell can be modified in different ways to improve the remediation process. Extra liquid compartments are sometimes inserted between the electrodes and the ash suspension; in one or both sides of the cell. The extra compartments can either serve to prevent the ions removed from the ash suspension from reaching the electrodes by inserting extra ion exchange membranes in front of the electrodes, or to facilitate increased transport of water or desorption agents into the ash suspension by inserting passive membranes adjacent to the ash suspension. Another modification of the cell is to introduce continuous stirring of the ash suspension during remediation. This modification makes it easier to maintain homogeneous conditions (as for instance a constant pH value, which is sometimes a key parameter for the remediation process), inside the ash suspension. A disadvantage of using continuous stirring is that it requires a higher L/S ratio in the ash suspension.

#### 3.4.1. Experiments 1 and 2: comparison between MSWI fly ashes

The electro-dialytic remediation experiments 1 and 2 were carried out on the two MSWI fly ashes. Compared to the cell shown in Fig. 1, the following modifications were made: an extra compartment with a passive membrane (filter paper) adjacent to the ash was inserted in the cathode side, thereby allowing a desorption agent (ammonium citrate) to enter the ash from the cathode side. In the anode side, a concentration compartment was applied by inserting a cation exchange membrane in front of the electrode. A sketch of the cell is shown in Fig. 2. A mixture of 0.5 M ammonium citrate and 2.5%  $\text{NH}_3$  was added to the ash as a

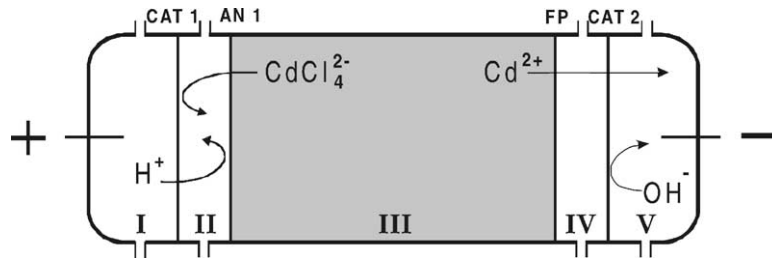


Fig. 2. The electroalytic remediation principle used in experiments 1 and 2. CAT, cation exchange membrane; AN, anion exchange membrane; FP, filter paper.

desorption agent to a water content of approximately 50%, before the ash was placed in the cell. The two remediation experiments were run for 10 weeks each with a constant current of 40 mA applied. The removal of Cd, Pb, Zn, Cu and Cr was compared.

#### 3.4.2. Experiments 3 and 4: comparison between MSWI fly ash and wood fly ash—removal of Cd

Remediation experiments 3 and 4 were carried out on MSWI fly ash 2 (VF) and the wood combustion fly ash, respectively. The electroalytic remediation principle in these two experiments was also modified in comparison to the cell in Fig. 1. Concentration compartments were inserted in both sides, and continuous stirring of the ash suspension was introduced, using a flexible plastic stirrer driven by a “Heto” motor with a rotating velocity of 1300 rpm. The stirrer as well as the ash slurry was introduced into the ash compartment through holes in the top of the cell. Extra liquid could be added through these holes as well if necessary. A sketch of the stirred cell is shown in Fig. 3. Experiments 3 and 4 were both run for 3 weeks with a constant electric current of 40 mA applied. A 0.25 M ammonium citrate/1.25 M  $\text{NH}_3$  mixture was added to the ashes as desorption agent at a L/S ratio of approximately 6.7, corresponding to a water content of 87%. The removal of Cd was compared.

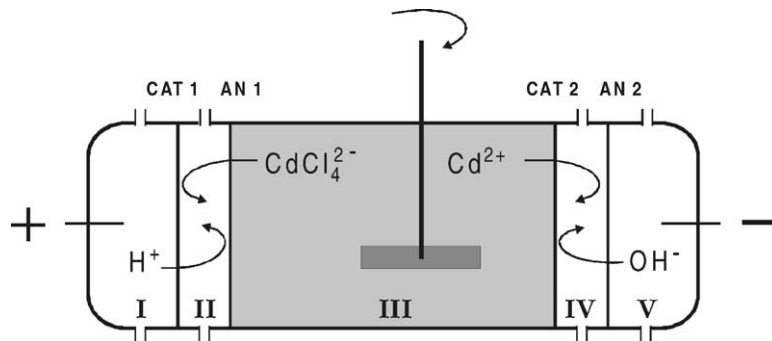


Fig. 3. The electroalytic remediation principle used in experiments 3 and 4. CAT, cation exchange membrane; AN, anion exchange membrane.

Table 2  
Experimental parameters for the remediation experiments carried out

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Fly ash	GR	VF	VF	FA
Duration (weeks)	10	10	3	3
Current (mA)	40	40	40	40
Total charge passed (mol)	2.6	2.4	0.75	0.75
Initial ash weight (g)	355*	415*	75	75
Desorption agent	0.5 M ammonium citrate/2.5% NH <sub>3</sub>	0.5 M ammonium citrate/2.5% NH <sub>3</sub>	0.25 M ammonium citrate/1.25% NH <sub>3</sub>	0.25 M ammonium citrate/1.25% NH <sub>3</sub>
Water content (%)	49% water	47% water	87% water	87% water
Electrolyte I	2.5% NH <sub>3</sub>	2.5% NH <sub>3</sub>	2.5% NH <sub>3</sub>	2.5% NH <sub>3</sub>
Electrolyte II	0.25 M ammonium citrate/1.25% NH <sub>3</sub>	0.25 M ammonium citrate/1.25% NH <sub>3</sub>	0.25 M ammonium citrate/1.25% NH <sub>3</sub>	0.25 M ammonium citrate/1.25% NH <sub>3</sub>
Electrolyte IV	0.25 M ammonium citrate/1.25% NH <sub>3</sub>	0.25 M ammonium citrate/1.25% NH <sub>3</sub>	0.01 M NaNO <sub>3</sub> , pH < 2	0.01 M NaNO <sub>3</sub> , pH < 2
Electrolyte V	0.01 M NaNO <sub>3</sub> , pH < 2	0.01 M NaNO <sub>3</sub> , pH < 2	0.01 M NaNO <sub>3</sub> , pH < 2	0.01 M NaNO <sub>3</sub> , pH < 2

\* Dry weight includes the dry weight of the ammonium citrate used as desorption agent (~19% (w/w) in experiment 1, ~17.5% (w/w) in experiment 2.

In all four experiments carried out, the inner diameter of the ash compartment (compartment III) was 8 cm and the length was 10 cm. The ion exchange membranes used were obtained from “Ionics” and the electrodes were platinum coated titanium wire ( $\varnothing = 3$  mm) from “Permascand”. 250 ml of electrolytes were circulated in each of compartments II and IV, and 500 ml of electrolytes were circulated in each of compartments I and V, using “Pan World” magnetic pumps with a flow rate of 2.6 l/min. A “Hewlett-Packard E3612A” power supply was used to maintain a constant electric current. Voltage drop and electric current was noted every day during the remediation period and pH was measured in the electrolytes. pH in the electrolyte compartments was adjusted with 1:1 HNO<sub>3</sub> or NaOH if necessary to maintain the present values.

At the end of the experiments, the ashes were dried (105 °C, 24 h), and the ashes as well as the electrolytes, membranes and electrodes were analysed with respect to heavy metal content on FAAS. pH and water content in the ashes was also measured. Due to the high L/S ratio, the ashes from the stirred experiments (experiments 3 and 4) were de-watered on filter paper prior to drying to separate the solids from the liquid phase, and the liquid phase was analysed for heavy metals too. The ashes from experiments 1 and 2 were segmented into five slices of 2 cm each from anode to cathode prior to drying. The experimental parameters for the different remediation experiments are shown in [Table 2](#).

## 4. Results and discussion

### 4.1. Batch leaching experiments

The desorption characteristics for Cd, Pb, Zn Cu and Cr in the two MSWI fly ashes, as found by batch leaching experiments, are illustrated in [Fig. 4](#). In [Fig. 5](#), the desorption characteristics for Cd in the wood fly ash, is plotted.

[Fig. 4](#) reveals similar desorption characteristics (in HNO<sub>3</sub>) for Cd, Pb, Zn and Cu in the two MSWI fly ashes in spite of different initial concentrations of especially Pb. Chromium, on the other hand, is relatively more mobile in the VF ash than in the GR ash, probably due to a much lower total concentration (assuming that the desorption of Cr is solubility controlled). It is also seen from [Fig. 4](#) that citrate has a positive effect on the extraction of all five examined heavy metals in the two MSWI fly ashes, especially at alkaline conditions. 95–100% Cd, 69–80% Zn, 32–60% Pb, 67–75% Cu and 6–17% Cr are extracted from the two MSWI fly ashes at a pH around 9 using ammonium citrate (and NH<sub>3</sub>) as extraction agent. Only very small amounts of the metals are extracted at similar pH values when using HNO<sub>3</sub> as the extraction agent (0–3%). Due to the very high alkalinity of the ashes, it demands huge amounts of acid and dissolution of many (harmless) Ca compounds to lower the pH in the ashes only moderately, therefore, extraction of heavy metals at neutral or alkaline conditions is preferable during electro-dialytic remediation.

From [Fig. 5](#), it is seen that ammonium citrate has a positive effect on the desorption of Cd from the wood ash too. The effectiveness of ammonium citrate is though quite pH-dependent. The maximum desorption (approximately 70%) is achieved in the pH range between 7 and 9. The relative amount (%) Cd extracted from the wood ash is lower than the relative amount extracted from the MSWI fly ashes, in spite that the total concentration



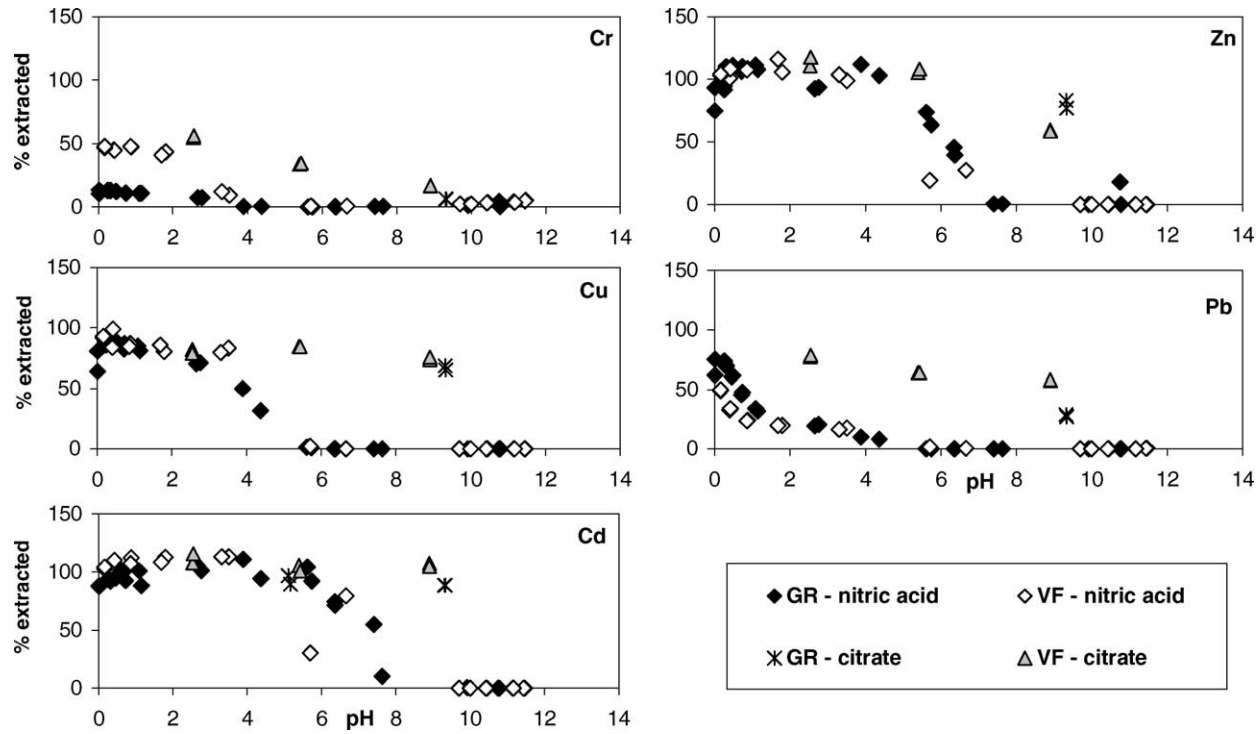


Fig. 4. Metal extraction as a function of pH in batch extraction experiments on the two MSWI fly ashes using citric acid/ammonium citrate or HNO<sub>3</sub>.

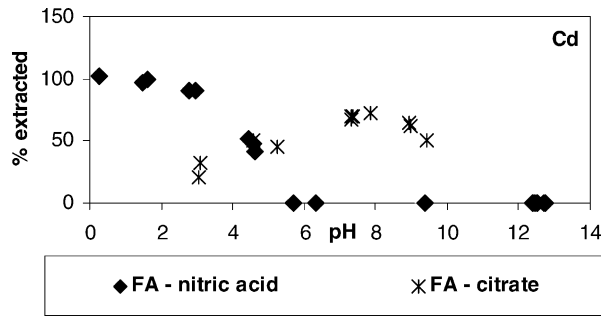


Fig. 5. Cd extraction as a function of pH in batch leaching experiments on the wood fly ash (FA) using citric acid/ammonium citrate or  $\text{HNO}_3$ .

of Cd in the wood ash is only about 10% of that in the MSWI ashes. The pH at which Cd starts to desorb using  $\text{HNO}_3$  as leaching agent is lower in the wood ash too, approximately 5, against 6–7 in the MSWI ashes. These leaching characteristics indicate that the Cd compounds present in the wood ash are generally less soluble than those in the MSWI ashes.

According to Evans and Williams [9] who studied heavy metal adsorption onto fly ash in waste incineration flue gases, the capture of Cd onto fly ash particles is mainly a physical adsorption at relative low temperatures, but at higher temperatures, chemical reactions (chemisorption) between Cd and aluminosilicate may take place too, forming a complex Cd–aluminosilicate. The chemisorption of Cd is a surface phenomenon and once all the potential sites are occupied and the surface layer is saturated, further condensation will be by physical adsorption [9]. This chemisorption mechanism may explain the apparently different speciation of Cd in the wood ash compared to the MSWI fly ashes. Due to the much lower concentration of Cd in the wood ash, it is likely that the majority of the Cd in this ash is bonded as aluminosilicates as a result of chemisorption whereas in the MSWI fly ashes the major part of Cd is probably present as condensed phases.

#### 4.2. Electrodialytic remediation experiments

Mass balances for each metal in the four electrodialytic remediation experiments are shown in Table 3. Removed metals (mg) represent the metals found in the electrolytes, membranes and on the electrodes at the end of the experiments. The mg in solution represents the metals found in the aqueous phase in the stirred experiments (experiments 3 and 4). In Table 4, pH, water content and dry weight of the ashes after remediation are listed. The current efficiencies, defined as the percentage of the total charge passed the cell carried by the different (removed) heavy metals in the four experiments, are listed in Table 5. It is assumed that all metals carry a charge of 2 ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{CrO}_4^{2-}$ ). The percentage removed metals and the fraction found at the anode side in experiments 1 and 2 are illustrated in Figs. 6 and 7.

From Figs. 6 and 7, it is seen that the relative Cd removal (in %) has been similar for the two MSWI fly ashes in experiments 1 and 2 (44 and 40%, respectively), although the

Table 3  
Mass balances for the four electrodialytic remediation experiments

Metal	Experiment no.	Amount (mg) start (ash)	Amount (mg) removed	Amount (mg) in solution	Amount (mg) final (ash)	Removed to anode side (mg)	Recovery (%)
Cd	1	73	32	–	34	24	92
	2	103	42	–	39	4.3	78
	3	18	13	1.9	10	1.9	138
	4	2.1	1.5	0	1.1	0.04	129
Pb	1	1085	90	–	830	81	85
	2	3075	75	–	2990	26	100
	3	605	53	50	495	45	99
Zn	1	4900	3570	–	1456	363	103
	2	7805	1885	–	4188	83	78
	3	1286	944	1.7	1244	35	170
Cu	1	375	67	–	226	13	78
	2	660	202	–	447	9.5	98
	3	118	81	1.0	36	3.5	99
Cr	1	755	17	–	687	14	93
	2	70	2.3	–	96	0.8	141
	3	21	4.6	0.3	9.9	4.3	69

Table 4  
Final ash dry weight, final pH, final water content and ash recovery (%), experiments 1–4

Experiment no.	Amount (g) DM (ash)	Final pH (range)	Water content (%) (range)	Ash recovery (%)
1	267	6.9–7.5	56–60	75
2	374	8.1–9.7	44–50	92
3	60	9.6*	71	80
4	64	9.5*	77	86

\* pH measured in aqueous phase.

Table 5  
Current efficiencies in the four electrodialytic remediation experiments

Experiment no.	Total charge passed (mole)	Current efficiency (%)				
		Cd	Pb	Zn	Cu	Cr
1	2.6	0.04	0.03	4.15	0.08	0.03
2	2.4	0.06	0.03	2.43	0.27	0.004
3	0.75	0.06	0.07	3.85	0.33	0.02
4	0.75	0.007	–	–	–	–

The current efficiency is defined as the percentage of the total charge passed the cell carried by the (removed) heavy metals. It is assumed that all metals carry a charge of 2 ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{CrO}_4^{2-}$ ).

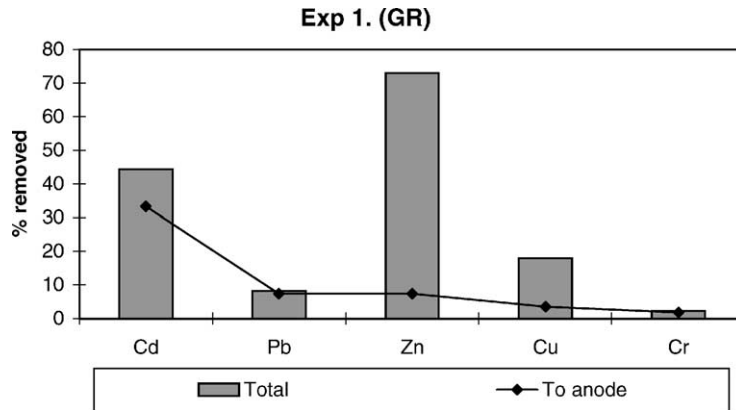


Fig. 6. Total metals removed (%) and the fraction found at the anode side, experiment 1.

migration direction differs. A larger fraction of Cd is removed to the anode side in experiment 1 compared to experiment 2, indicating a larger fraction of negatively charged Cd species (complexes). For Pb and Zn, relatively more is removed from the GR ash (experiment 1) than from the VF ash (experiment 2) (73% versus 24% for Zn, 8% versus 2.5% for Pb). The better Pb removal may be explained by a larger percentage of complexation. In experiment 1, Pb was preferentially removed to the anode side, indicating a larger fraction of negatively charged Pb species, e.g. citrate or chloride complexes, whereas in experiment 2, the majority of the removed Pb was found at the cathode side ( $\text{Pb}^{2+}$ ). For Zn, a lower final pH in ash slices in experiment 1 (see Table 4) may explain why more Zn was removed in this experiment. From the batch leaching experiments (Fig. 4) it was found that Zn begins to desorb at pH values below approximately 7.5 when acid ( $\text{HNO}_3$ ) is used as desorption agent. In experiment 1, the final pH was slightly below 7.5 in all ash slices, whereas it was higher in experiment 2 (see Table 4). The Cu removal has, on the other hand, been

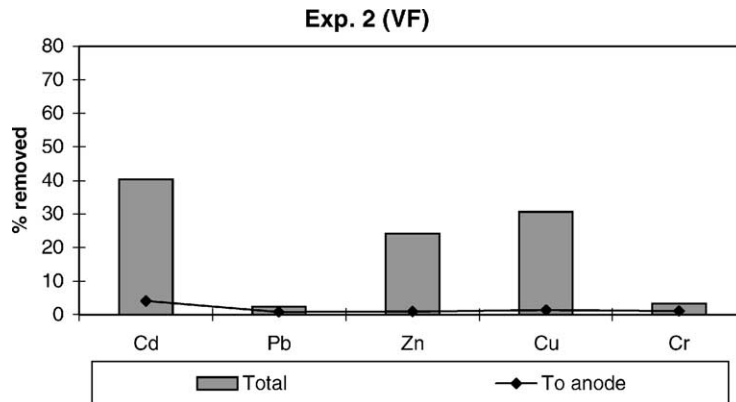


Fig. 7. Total metals removed (%) and the fraction found at the anode side, experiment 2.

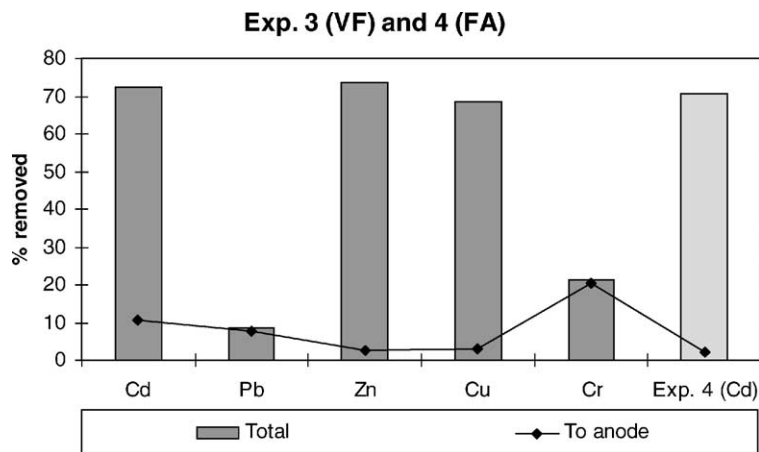


Fig. 8. Total metals removed (%) and the fraction found at the anode side, experiments 3 and 4.

slightly worse in experiment 1 compared to experiment 2 (18% versus 31%), maybe due to less complexation with  $\text{NH}_3$  as a result of the lower pH values (Cu forms very stable tetra ammine complexes with  $\text{NH}_3$ ). In both experiments, the Cr removal is very low (2–3%).

The metal removal and the fraction found at the anode side, in percentage of the initial content, in (the stirred) experiments 3 (MSWI fly ash 2) and 4 (wood fly ash) is shown in Fig. 8. From Fig. 8, it is seen that the relative fraction of Cd removed (%) is very similar in experiments 3 (MSWI fly ash 2) and 4 (wood fly ash)—approximately 70%. But as seen from Table 5, the current efficiency for Cd removal was almost a factor of 10 lower in experiment 4 compared to experiment 3, confirming the result from the batch leaching experiments (Fig. 5) which revealed that Cd was more tightly bonded in the wood ash. From Fig. 8, it is also seen that about 70% of Zn and Cu, 9% Pb and 20% Cr was removed in experiment 3. These are much better removal efficiencies than obtained on the same ash in experiment 2 (Fig. 7), indicating that the stirred cell improves the remediation process.

When comparing the current efficiencies for the different metals in experiments 2 and 3 (Table 5), it is seen that the metal removal has been significantly more effective in the stirred experiment (experiment 3) for Pb, Zn, Cu and Cr, whereas it is has been about the same for Cd. These results confirm that the use of a stirred cell improves the remediation. The highest current efficiency in experiment 3 is seen for Zn (3.85%), followed by Cu (0.33%) and Pb (0.07%). The process is still on a too early stage to make reasonable cost calculations.

## 5. Conclusion

Batch leaching experiments showed that the pH-dependent desorption characteristics of two different MSWI fly ashes were quite similar for Cd, Pb, Zn and Cu, but differed significantly for Cr. In electrodynamic remediation experiments with added ammonium citrate as desorption agent, the removal efficiencies of especially Pb and Zn varied more between

the two ashes than indicated in the batch leaching experiments. Both these metals were relatively more mobile in one of the MSWI ashes than in the other during electro-dialytic remediation, probably due to a lower final pH value in this ash and a higher degree of complexation.

A wood combustion fly ash showed other characteristics than the MSWI ashes with respect to Cd desorption. Whereas Cd was quite easily extracted from the two MSWI fly ashes Cd was more tightly bonded in the wood ash. Comparison between electro-dialytic removal of Cd from the wood ash and one of the MSWI ashes confirmed the batch leaching results: the Cd removal was much slower in the wood ash than in the MSWI ash. On the basis of literature search, it is suggested that complex Cd-silicates are likely phases in the wood ash whereas more soluble, condensed phases (CdCl<sub>2</sub>, CdO) are dominating in the MSWI ashes.

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