Evaluation of assisting agents for electrodialytic removal of Cd, Pb, Zn, Cu and Cr from MSWI fly ash

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Abstract

Different assisting agents (0.25 M ammonium citrate/1.25% NH_3, 0.25 M Na-citrate, 2.5% NH_3, DI water) have been used for aiding the removal of heavy metals during electrodialytic treatment of municipal solid waste incineration (MSWI) fly ash. In this study, the effectiveness of the different agents was evaluated. The heavy metal speciation in solution was discussed and simulated at the different conditions using the geochemical equilibrium model Visual MINTEQ. The heavy metals examined were Cd, Pb, Zn, Cu and Cr.

The 2.5% NH_3 solution was the best assisting agent for removal of Cd, probably due to formation of stable tetraammine complexes; whereas the best Pb removal was obtained with 0.25 M Na-citrate (Pb forms very stable chelates with citrate). The best compromise for removal of all five metals was obtained with the 0.25 M ammonium citrate/1.25% NH_3 solution.
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1. Introduction

Fly ashes from, e.g. wood combustion and municipal solid waste incineration (MSWI) are usually very alkaline in nature, having a pH ranging between 10 and 12, sometimes even higher [1–3]. The high pH is caused by a high content of metal oxides and hydroxides, predominantly of Ca (CaO, Ca(OH)$_2$). At these high pH values, most heavy metals in the fly ashes are considered immobile. However, due to a very high initial content of several heavy metals in MSWI fly ashes, there is a high potential risk of harmful environmental
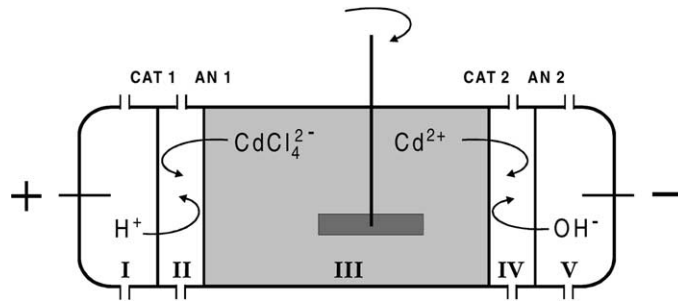
Fig. 1. The principle of electridialytic remediation of fly ash.

impact when these ashes are deposed of. In many countries, fly ashes and other residues from MSW incineration are considered hazardous waste which needs special handling.

Leaching properties, speciation and enhanced extractability of heavy metals in MSWI fly ashes have been studied intensively in several studies, often for the purpose of finding possible methods for the stabilization and/or reuse of ashes and metals [1,4–8].

Previously, electrodialytic remediation has been introduced as a possible new extraction method [9]. In electrodialytic remediation, which was originally developed for remediation of heavy metal polluted soil [10], the fly ash is suspended in an aqueous phase and placed between two electrodes. A sketch of the electrodialytic remediation cell is shown in Fig. 1.

When a low voltage dc current is applied, the ions in the ash slurry (in compartment III) begin to migrate in the electric field either toward the positive electrode (anode) or toward the negative electrode (cathode), depending on their speciation. As a result, the ions are transported out of the ash slurry and into the electrolyte solutions in compartment II or IV, from where they can be separated by conventional methods (e.g. electroplating, ion exchange, or precipitation). Ion exchange membranes are used to separate the ash slurry from the electrolytes, thereby preventing ions from the electrolytes from (re-)entering the ash slurry. During the remediation, the ash slurry is stirred continuously, and the electrolyte solutions in compartments I, II, IV and V are circulated to ensure good electrical contact between electrodes and the electrolyte solutions and remove produced gasses.

It has been shown that the electrodialytic remediation method enhances the extractability of heavy metals in MSWI fly ashes compared to more traditional extraction methods [9]. When combining the electrodialytic treatment with the addition of an appropriate assisting agent to the ash slurry before and during remediation, it is possible to improve the desorption of one or more heavy metals specifically, thereby improving the extraction efficiency considerably for targeting metals compared to basis experiments using only water or acid as assisting agents.

When choosing an assisting agent, the following factors should be considered: (1) which metal(s) to extract; (2) which chemicals may suite the metal(s) of concern (acids, bases, others); (3) the nature of the fly ash (pH, chemical composition, etc.). Many heavy metals are soluble at low pH, and therefore, acids may be useful assisting agents in some cases. Some metals, e.g. Pb and other amphoteric metals, are soluble at very high pH values as well as at low pH values, and in these cases, it may be appropriate to use bases

for extraction. However, complexing or chelating agents may be the best choice in many cases. The formation of stable complexes/chelates may bring heavy metals in solution at pH values where they are otherwise insoluble (neutral to high pH), and it may be possible to find selective complexing/chelating agents, favouring the metal(s) of concern.

In the case of the highly alkaline fly ashes, which usually have very high acid neutralization capacities too, it seems unreasonable to use acids as assisting agents. Huge amounts of acid will be necessary to lower the pH sufficiently, and besides, considerable amounts of harmless compounds will dissolve. The smaller the amount of harmless ions in solution, the better removal efficiency can be obtained in EDR. Therefore, choosing suitable complexing/chelating agents or alternatively bases as assisting agents seems most rational.

2. Chelating agents in combination with electrodialytic remediation

Most of the metals in the periodic system are able to form complexes or chelates. The higher valence of the metal ion, the more stable are the complexes and chelates formed. In particular, the transition metals may form a large variety of complexes and chelates. The stability of complexes of some common divalent metal ions is predicted to follow the following order [11]:

$$Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg \tag{1}$$
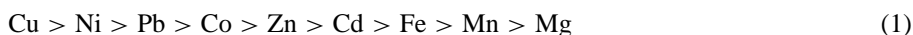
This order is independent of the nature of the ligands involved. The stability of metal complexes and chelates may nevertheless be greatly dependent on the nature of other positive ions in the solution [11].

Citrate, which is a naturally occurring chelating agent, forms stable chelates with several heavy metals and has previously been used for extraction of heavy metals from polluted soils [12,13]. On the basis of promising batch extraction experiments conducted in an earlier study [14], citrate was selected as an assisting agent for the electrodialytic removal of Cd, Pb, Zn Cu and Cr from MSWI fly ash in this study. The citrate was used either in combination with NH_3 as ammonium citrate (Experiment 4) or in combination with NaOH as Na-citrate (Experiment 3). The other assisting agents used in this study was NH_3 (Experiment 1) and DI water (Experiment 2). NH_3 can form stable tetraammine complexes with Cu, Zn and Cd at high pH [15].

If the chelation between citrate and heavy metals in electrodialytic remediation experiments on fly ash is assumed to follow the order of stability expressed in Eq. (1), citrate chelates of Cu and Pb will be more stable than those of Zn and Cd. Chelates of trivalent metal ions (e.g. Cr(III), Fe(III)) will be even more stable.

An expected citrate chelate to be formed with the divalent metal ions (Me^{2+}) is the monovalent, negatively charged $[MeCit]^{1-}$, according to the following equilibrium equation:

$$Me^{2+} + Cit^{3-} \Leftrightarrow [MeCit]^{1-} \tag{2}$$

According to Martell [11], who discussed chemistry of metal chelate compounds, such large monovalent chelate ions may have very small ionic mobility compared to the smaller, divalent metal ions. Martell [11] referred results where electrodialysis was used as a method to indicate chelation in certain cases where the chelate has a negative charge. Electrolytic

migration towards the anode is then an indication of a negative ion. The method turned out to have some serious limitations. An attempt to demonstrate the existence of calcium citrate chelates in blood serum by electrodialysis failed, except when a large and unnatural amount of citrate was added to the serum. However, it was not possible to conclude that the chelate was absent either [11]. It was suggested that the lack of positive results in that study was a consequence of a very small ionic mobility of the large monovalent chelate ion compared to that of the smaller, divalent calcium ion. Also, the trivalent citrate ion would carry most of the negative charge [11]. The equilibrium equation of the dissociation of the 1:1 chelate is

$$Ca^{2+} + Cit^{3-} \Leftrightarrow [CaCit]^{1-} \tag{3}$$

It was suggested that even as little as 10–20% dissociation of the chelate would be sufficient to prevent migration of $[CaCit]^{1-}$ to the anode [11]. Furthermore, the more rapid migration of the citrate ion would tend to cause further dissociation of the chelate during the electrodialysis [11].

Green et al. [16] studied the feasibility of using electrodialysis to extract divalent metal ions from citrate salt solutions and found that, at pH 6, the rates of transfer of anionic citrate complexes through the anion exchange membrane were extremely low (current efficiency < 0.05% for Cu and Ni). They suggested that species such as $[NiCit]^-$ and $[Cu_2H_{-2}Cit_2]^{4-}$ are too bulky to transfer through the anion exchange membrane. At a pH of 1, on the other hand, it was possible to remove Cu and Ni (as Cu^{2+} and Ni^{2+}) with a current efficiency of around 25% through the cation exchange membrane, though co-transport of Na^+ occurred at comparable rates. When using H_3Cit rather than Na_3Cit as the citrate source, current efficiencies around 50% were obtained. Therefore, they concluded that electrodialytic separation of metals from citrate solutions should include acidification of the solution to a pH of 1–2, which facilitates the removal of metals in their uncomplexed form.

When conducting electrodialytic remediation experiments on fly ash with citrate or other chelate forming agents added, these effects may be expected to influence the electrodialytic removal of heavy metals too.

3. Materials and methods

The experimental fly ash was an electrostatic precipitator ash obtained from "Vestforbrænding", a mass-burn MSWI facility in Copenhagen, Denmark. At the point of sampling (the electrostatic precipitator), the flue gas stream had not been exposed to any air pollution control additives. The plant is equipped with wet scrubbers for flue gas cleaning.

Prior to the electrodialytic remediation experiments, the ash was characterised with respect to pH, water content, loss on ignition and content of target heavy metals and major elements (Ca, K, Cl); the pH-dependent heavy metal desorption in different chemicals (potential complexing/chelating agents (ammonium citrate, Na-citrate and NH_3) and acid and alkaline extractions (HNO_3 and NaOH)) were found using 3-day batch extraction experiments at a liquid-to-solid (L/S) ratio of 25.

The following electrodialytic remediation experiments were carried out: (1) an experiment with 2.5% NH_3 added to the ash as assisting agent; (2) a basis experiment with DI

Table 1
Experimental conditions for the four electrodialytic remediation experiments

Parameter	Experiment 1 (NH$_3$)	Experiment 2 (water)	Experiment 3 (Na-citrate)	Experiment 4 (ammonium citrate)
Assisting agent	2.5% NH$_3$	DI water	0.25 M citric acid adjusted to pH 10 with NaoH	0.25 M ammonium citrate in 1.25% NH$_3$
Voltage drop	3.3–9.5	3.6–5.9	2.7–9.0	3.1–7.3
Electrolyte +1 (compartment I)	2.5% NH$_3$, pH adjusted to >9	0.01 M NaNO$_3$, pH adjusted to <2	2.5% NH$_3$, pH adjusted to >9	2.5% NH$_3$, pH adjusted to >9
Electrolyte +2 (compartment II)	2.5% NH$_3$, pH adjusted to >9	0.01 M NaNO$_3$, pH adjusted to <2	0.25 M Na-citrate, pH adjusted to >9	0.25 M ammonium citrate in 1.25% NH$_3$
Electrolyte −2 (compartment IV)	0.01 M NaNO$_3$, pH adjusted to <2	0.01 M NaNO$_3$, pH adjusted to <2	0.01 M NaNO$_3$, pH adjusted to <2	0.01 M NaNO$_3$, pH adjusted to <2
Electrolyte −1 (compartment V)	0.01 M NaNO$_3$, pH adjusted to <2	0.01 M NaNO$_3$, pH adjusted to <2	0.01 M NaNO$_3$, pH adjusted to <2	0.01 M NaNO$_3$, pH adjusted to <2

water added to the ash as assisting agent; (3) an experiment with 0.25 Na-citrate (made of citric acid and NaOH, pH approximately 10) added to the ash as assisting agent; (4) an optimized experiment with a mixture of 0.25 M ammonium citrate and 1.25% NH_3 added to the ash as assisting agent.

In all electrodialytic remediation experiments, initially 75 g of fly ash was placed in the cell (compartment III; $\varnothing = 8$ cm, $L = 10$ cm), and the compartment was filled up with approximately 500 ml of the assisting agent (corresponding to a L/S ratio of approximately 6.5). Extra assisting agent (or water) was added to the ash during the remediation period if necessary (if the ash dried out due to de-watering/evaporation). "Pan World" magnetic pumps with a flow rate of 2.6 l/min were used to circulate the electrolyte solutions in compartment I (500 ml), II (250 ml), IV (250 ml) and V (500 ml). A "Heto" motor with a rotation velocity of 1300 rpm was used to rotate the stirrer, which was made of flexible plastic. The electrodes were made of platinised titanium wire ($\varnothing = 3$ mm) obtained from "Permascand". The ion exchange membranes were obtained from "Ionics". All remediation experiments were run for 2 weeks with a constant electric dc current of 40 mA applied (0.8 mA/cm^2). The experimental conditions for the four experiments are summarized in Table 1.

After remediation, the ashes were de-watered on filter paper if a separate aqueous phase was abundant, and the (de-watered) ashes were dried at 105 °C over-night and homogenized. Water content in the ashes was found as loss of weight (%) after drying, and pH in the dry ashes was measured (in doublets) with a "Radiometer" combined pH electrode in 1 M KCl and $L/S = 5$ after 1 h of contact. Ashes, electrolytes, electrodes, membranes and aqueous phases (when abundant) were analyzed for the five metals on a "Perkin-Elmer 5000" FAAS (flame atomic absorption spectrophotometer).

Prior to FAAS analysis, 0.4 g sub-samples of the remediated ashes were pre-digested in 10 ml concentrated HNO_3 using microwave assisted pressurized digestion (135 psi, 30 min), vacuum filtered, and diluted to 50 ml with DI water. (The digestion method was modified from the Danish Standard "DS259" for determination of metals in soil and sediments). Membranes and electrodes were soaked in HNO_3 (1 and 5 M, respectively) to release the metals prior to analysis. All metal analyses on the remediated ashes were made in duplicates or triplicates, the initial metal analyses (Ca, K and heavy metals) of the raw fly ash were made in five replicates. Initial Cl content in the ash was measured in aqueous solution with a Cl-selective electrode, and loss on ignition was found as loss of weight after heating to 550 °C. All chemicals used were of analytical grade.

4. Results and discussion

4.1. Ash characterisation and pH dependent heavy metal desorption

Initial metal concentrations and other characteristics of the experimental fly ash are given in Table 2. The pH dependent heavy metal desorption (% metal desorbed as a function of final pH in solution) for potential complexing/chelating agents (ammonium citrate, Na-citrate and NH_3) and acid and alkaline extractions (HNO_3 and NaOH) are shown in Fig. 2. The concentration of ammonium citrate and Na-citrate was 0.5 M with respect to citrate (pH

Table 2
Characteristics of the experimental fly ash

Parameter	Mean
Water content (%)	0.7
Loss on ignition (%)	1.3
pH (L/S = 5)	12.2
Cl (%)	21.5
Ca (mg/kg DM)	140100
K (mg/kg)	37200
Cd (mg/kg DM)	241
Pb (mg/kg DM)	8070
Zn (mg/kg DM)	17140
Cu (mg/kg DM)	1570
Cr (mg/kg DM)	285

adjusted with NH_3 or NaOH, respectively). An amount 2.5 and 5% NH_3 solutions were used for the NH_3 extraction. The concentrations of HNO_3 and NaOH (acid and alkaline extractions) were varied to obtain a wide range of pH values. The L/S ratio was 25 in all extractions.
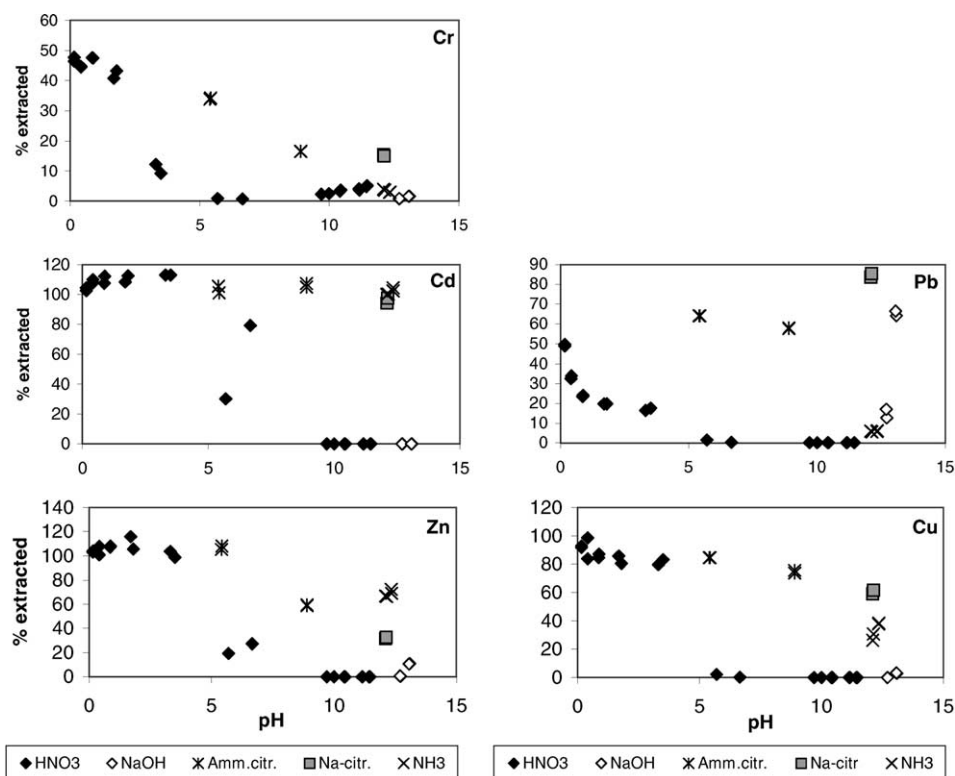

Fig. 2. The pH dependent heavy metal desorption with different assisting agents.

The positive effect of ammonium citrate and Na-citrate for desorption of all five heavy metals at neutral and alkaline conditions is seen from Fig. 2. NH_3 also enhances desorption of Cd, Zn and Cu; desorption of Cr and Pb is not influenced by NH_3.

4.2. Metal removal in electrodialytic remediation experiments

The removed fractions of Cd, Pb, Zn, Cu and Cr in the four experiments are shown in Fig. 3. It is seen from Fig. 3 that the best cumulated removal efficiency (the sum of all five metals) was obtained in the experiment with 2.5% NH_3 added. This was particularly caused by a very good Cd removal (close to 100% of the initial Cd content was removed in this experiment). The experiment added 0.25 M ammonium citrate/1.25% NH_3 as assisting agent had the second highest cumulated removal efficiency. The removal of Pb, Cu and Cr was better in this experiment compared to the NH_3 experiment whereas the Zn removal was almost equal in the two experiments.

In the 0.25 M Na-citrate/1.25% NH_3 experiment, the removal of Cd and Zn was inhibited considerably compared to the other experiments. On the other hand, the highest removal of Pb was seen in this experiment. These observations and their possible explanations are discussed further in the following section about metal speciation.

It is surprising that a large fraction of Cd was removed in the water added experiment. In fact, Cd was almost completely dissolved because a considerable amount was found in solution in the aqueous phase of the ash slurry. The explanation for the high Cd removal in this EDR experiment is probably that the pH in the ash slurry was lowered during remediation. Final pH in the ash was measured to 6.5 (1 M KCl, $L/S = 5$), which is, in fact, low enough for Cd to desorb. The pH dependent desorption experiments have shown that Cd begins to desorb when the pH in solution gets below approximately 7 (Fig. 2). In a 3-day batch extraction experiments using water as extraction agent and a L/S ratio of 25,
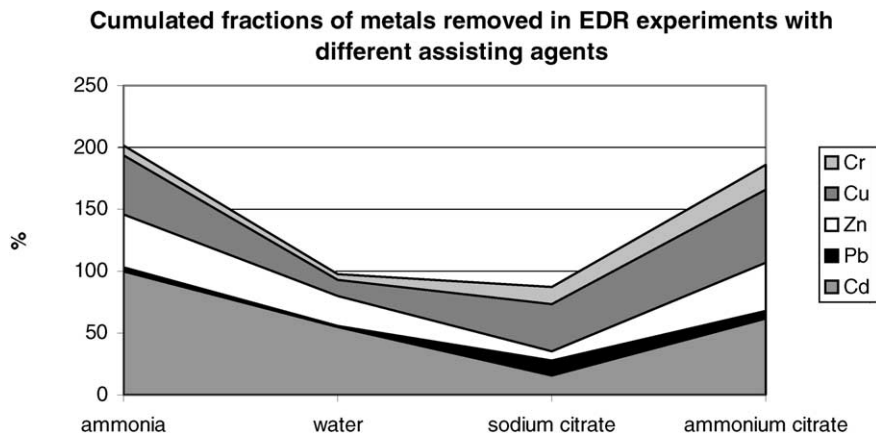

Fig. 3. Cumulated fractions of metals removed in 2-week EDR experiments with different assisting agents added. Percentage removed is defined as the amount of metals found in electrolytes, membranes and on electrodes after remediation in percentage of the initial amount.

the Cd concentration in solution was below detection limit. The final pH in solution was measured to 11.5. Another factor that may have enhanced Cd desorption in the electrodialytic remediation experiment can be alterations of chemical equilibriums in the ash slurry compared to traditional leaching/batch extraction processes. When an electric current is applied, dissolved ions are removed continuously from the ash slurry, thereby preventing solubility-controlled reactions from reaching saturation.

When comparing the batch extraction results (Fig. 2) with the electrodialytic remediation experiments (Fig. 3), it is seen that the percentage of metals extracted with citrate or NH_3 generally was higher in the batch extraction experiments. The difference was especially high for Pb extracted with Na-citrate. In the batch extraction experiment (Fig. 2), approximately 85% Pb was extracted with Na-citrate, in the electrodialytic remediation experiment it was only around 12%. There are three probable explanations for this difference: the L/S ratio; the amount of citrate available for chelation; the speciation of Pb in solution. In the batch extraction experiments, the L/S ratio was 25 whereas it was only around 6.5 in the electrodialytic remediation experiments. If the dissolution of the metals is solubility controlled, the L/S ratio will limit the amount of dissolved Pb. The amount of citrate available may be another limiting factor. The concentration of Na-citrate was higher in the batch extraction experiment (0.5 M against 0.25 M in the electrodialytic remediation experiment), and the citrate-to-Pb ratio was also higher due to the higher L/S ratio. The third possible limiting factor is the Pb speciation. If the Pb species in solution are uncharged, they will not migrate in the electric field.

4.3. Speciation of metals in solution

The speciation of the metals in solution is a result of competitions between different metal complexes, metal chelates and free metal ions. The theoretical stability of citrate complexes (which have already been discussed), should preferentially lead to the following (decreasing) chelating order for the five investigated heavy metals: Cr(III)-citrate, Cu-citrate, Pb-citrate, Zn-citrate, Cd-citrate. Furthermore, Cu, Zn and Cd can form stable (positively charged) soluble tetraammine complexes with NH_3 [15] of which the $[Cu(NH_3)_4]^{2+}$ complex (tetraamminecopper) is especially stable (log $K_4 = 11.75$). Therefore, if NH_3 is present together with citrate, the ammine complexes may compete with the citrate chelates as important soluble species in the case of Cu, Zn and Cd. When looking at the preferred migration direction of the metals in the different remediation experiments (removed to anode side or cathode side, respectively), this effect seems probable. The distribution of metals in the cell after remediation (in percentage of the initial content) is shown in Fig. 4.

It is seen from Fig. 4 that almost all removed Cr has migrated to the anode. This means that Cr has been removed as negatively charged compounds, either as chromate (Cr(VI)) or Cr(III) complexes.

For Pb, the majority of the removed amount has been removed to the anode too, in the experiments added 0.25 M Na-citrate or 0.25 M ammonium citrate/1.25% NH_3. However, in the experiments added 2.5% NH_3 or water, only 22 and 42% of the Pb was removed to the anode, respectively, and only a small fraction of the Pb was removed at all. This indicates that Pb is primarily dissolved as negatively charged Pb-citrate chelates.
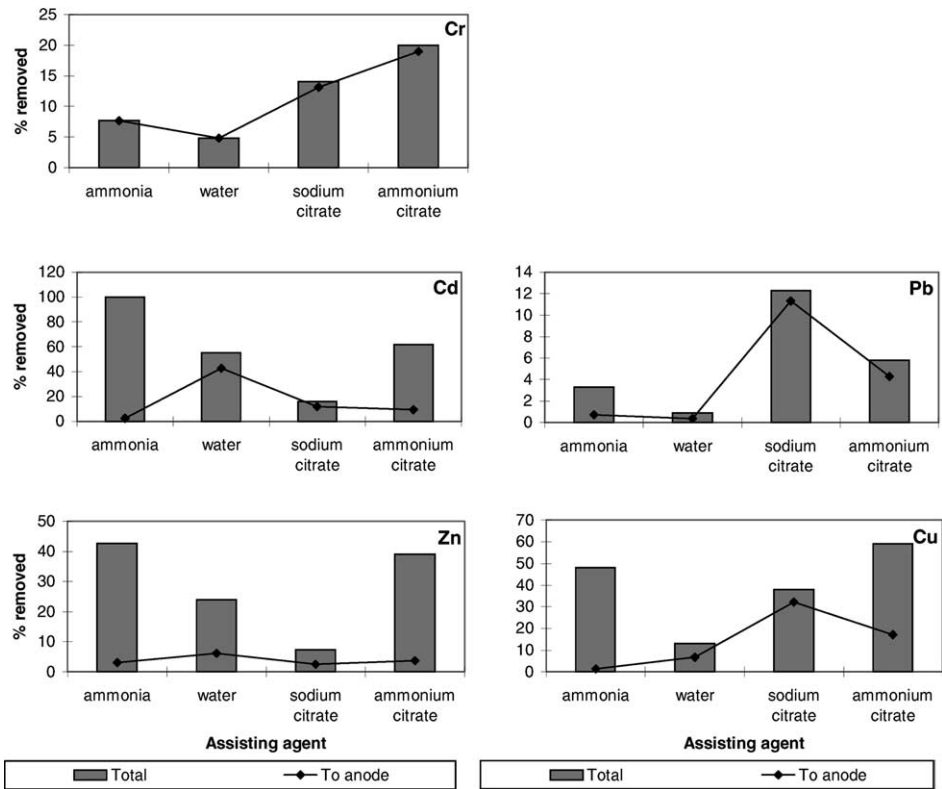
Fig. 4. Total metals removed and fraction found at the anode side (electrolytes, electrodes, membranes) of the EDR cell after remediation (%) for the four experiments (the rest of the removed metals were found at the cathode side).

For Cd, three-thirds of the removed amount was found at the anode in the experiments added water and 0.25 M Na-citrate, respectively, whereas it was only 2.4 and 15% in the 2.5% NH_3 and 0.25 M ammonium citrate/1.25% NH_3 experiments. As described earlier, Cd can form stable, positively charged tetraammine complexes with NH_3, and that is probably what has happened in the latter experiments. The preferred migration direction towards the anode in the water-added experiment indicates the existence of negatively charged Cl-complexes. As seen from Fig. 2, the lowest Cd removal was found in the 0.25 M Na-citrate experiment— even lower than in the water-added experiment. The Na-citrate must have inhibited the Cd removal, maybe due to pH changes, as a result of co-precipitation (with slightly soluble Ca-citrate) or as a result of lower ionic mobility of Cd-citrate chelates compared to Cd–Cl complexes. The latter explanation seems unlikely, however, because the amount of dissolved Cd found in the aqueous phase in the ash after remediation was considerably lower in the 0.25 M Na-citrate experiment too, compared to the water experiment.

The highest fraction of removed Cu found at the anode side was seen in the 0.25 M Na-citrate experiment (85%), indicating chelation with citrate. In the 2.5% NH_3 and 0.25 M

ammonium citrate/1.25% NH_3 experiments, Cu mainly moved towards the cathode, probably in the form of the very stable tetraamminecopper complex, which was described earlier. The lowest removal was seen in the water-added experiment. The fraction removed to the anode in this experiment probably represents Cu–Cl complexes.

For all experiments, only a minority of the removed Zn was found at the anode. This indicates that complexation with citrate and/or Cl is insignificant or that the ionic mobility of these compounds is very small. Like Cu and Cd, Zn is able to form stable, positively charged ammine complexes. As seen for Cd, the Zn removal has also been inhibited in the 0.25 M Na-citrate experiment, compared to all other experiments.

4.4. Simulated heavy metal speciation

The geochemical equilibrium model Visual MINTEQ was used to simulate the chemical speciation of heavy metals (Cd, Pb, Zn, Cu and Cr) in solution in the four different experiments.

Visual MINTEQ is capable of calculating equilibrium aqueous speciation, precipitation and dissolution of minerals, complexation, adsorption, solid phase saturation states, etc. The model uses an extensive thermodynamic database to solve the chemical equilibrium problems on the basis of parameters defined in an input file. These parameters include pH, ionic strength, initial concentration of ions, initial amounts of solids, etc. of the system to be simulated. The user has the possibility to adjust (or add new) data to the thermodynamic database (e.g. adjust stability constants), and it is possible to exclude solids from precipitation if wanted. MINTEQA2 (an earlier version of Visual MINTEQ) has previously been used to simulate leaching of MSWI fly ashes [1,5].

Due to the complexity of the fly ash system, it has not been possible to specify all potentially influencing components in this study, and, therefore, the Visual MINTEQ simulations will only be rough estimates that should be interpreted with care. Parameters for the input file were estimated on the basis of results from batch extraction experiments with the four assisting agents (water, ammonium citrate, sodium citrate and ammonia) (concentration of heavy metals in solution, pH), and from characterization of the raw fly ash (mineralogy, solubility and concentrations of major elements (Ca, K, Cl)). Varying concentrations of the assisting agents in solution were used in the simulations, since it is not actually known how large a fraction of the added assisting agent which is available for reaction with the target heavy metals (some will react with other ions, some will probably precipitate).

When comparing the Visual MINTEQ simulations with the fraction of ions collected at the anode or cathode during the EDR experiments, it has been assumed that the metal speciation does not change over time. This may actually not be quite true. The charged species in solution are removed continuously as charge-bearing ions in the electric field during remediation, leading to a depletion of ions from the ash compartment over time. This may change the chemical equilibriums. On the other hand, the ash slurry is considered ideally mixed due to the continuous stirring of compartment III, and therefore the metal speciation is regarded the same at a given time all over the electrodialysis cell.

The kinetics of complex formation and dissociation reactions are not considered to be significant owing to the long residence time in the EDR cell (the duration of the experiments

Table 3
Input parameters for the Visual MINTEQ simulations

Parameter		NH_3	Water	Na-citrate	Ammonium citrate
pH fixed at		9.5	6.5	10	9.0
Element concentrations (mg/l)					
Cd		9.8	7.7	9.3	10.5
Pb		19	1.1	278	190
Zn		460	189	227	420
Cu		20	0.1	39	47
Cr		0.4	0.1	1.7	1.9
Ca		2000	3500	1300	2000
K		1300	1300	1300	1300
Cl		50000	50000	50000	50000
Amount of finite solids (mol/l)	Lime	0.05	0.05	0.05	0.05
NH_4^+ concentration (mg/l)		1000–25000	–	–	15000
Citrate concentration (mg/l)		–	–	10000–100000	10000–100000
Na^+ concentration		–	–	15000	–

is 2 weeks). No solids were allowed to precipitate in the simulations. The input parameters used for the simulations are listed in Table 3.

The simulated distribution of Cd was found quite consistent with the experimental results in the water-added experiment. The majority of the removed Cd has moved towards the anode in this experiment, indicating negatively charged Cd-species. In the Visual MINTEQ simulations of the water-added experiment, the majority of the Cd in solution was predicted to be present as either negatively charged or uncharged Cl-complexes ($[CdCl_3]^-$ and $[CdCl_2]^0$), about 40% of each. About 15% was present as the positively charged Cl-complex $[CdCl]^+$.

In the water-added experiment, the removed Cu was almost equally distributed between the anode side and cathode side, indicating both positively and negatively charged Cu species. However, in the Visual MINTEQ simulations, about 90% of the Cu in solution was predicted to be present as positively charged species (Cu^{2+}, $[CuCl]^+$ and $[CuOH]^+$) whereas the amount of negatively charged species was found insignificant. About 10% was predicted to be uncharged as $[CuCl_2]^0$.

Very little Pb was removed in the water added experiment; it may be an indication of a significant amount of uncharged Pb species in solutions. In the Visual MINTEQ simulations, Pb was predicted to be present primarily as negatively charged Cl-complexes ($[PbCl_3]^-$ and $[PbCl_4]^{2-}$ (about 50% in total), but also with a significant amount of uncharged $[PbCl_2]^0$ (35%). The remaining Pb would mainly be $[PbCl]^+$ and other positively charged species.

Zn was predicted to be distributed as about 50% negatively charged Cl-complexes ($[ZnCl_3]^-$ and $[ZnCl_4]^{2-}$), 20% uncharged Zn-chloride ($[ZnCl_2]^0$ and 30% positively charged species ($[ZnCl]^+$, Zn^{2+}) in the water-added experiment. These results were not fully consistent with the experimentally found Zn distribution. Only about one-third of the removed Zn was found at the anode side.

Cr was mobilized as negatively charged species migrating towards the anode in the water-added experiment, just as predicted using Visual MINTEQ simulations. When simulating complexation with citrate in Visual MINTEQ, the heavy metal distribution was

very dependent on the amount of citrate available (input concentrations between 10,000 and 100,000 mg/l citrate were used in the simulations). The complexation between Cd and citrate was quite weak, especially at low citrate concentrations. This may explain why Cd preferentially migrated towards the cathode (as positively charged species) in the experiment with ammonium citrate added. On the other hand, the complexation between Pb and citrate was very strong, and a considerable amount of negatively charged Pb-citrate complexes ($[PbCit]^-$) was formed. This speciation was confirmed in both the Na-citrate and the ammonium citrate added experiment. The citrate addition enhanced the Pb mobilization, and the majority of the Pb moved towards the anode. Due to the simulations, Zn and Cu should also form significant amounts of citrate complexes. However, this could not be confirmed by the experimental results in the case of Zn. Zn acted more like Cd and was found preferentially at the cathode. For Cu, the results were more consistent.

When simulating the ammonium citrate and NH_3 added experiments, Visual MINTEQ showed some limitations when calculating NH_3 complexation at high concentrations. Apparently, the very stable tetraammine complexes of Cu, Zn and Cd (e.g. $[CuNH_4]^{2+}$) are not included in the database, thereby underestimating the amount of complexation with NH_3, especially when citrate is also present. An attempt to add the stability constants to the database resulted in runtime error or program termination when all but very low NH_3 concentrations were used in the input file. Therefore, consistent results could not be achieved for NH_3 simulations.

5. Conclusion

The effectiveness of four different assisting agents (0.25 M ammonium citrate/1.25% NH_3, 0.25 M Na-citrate, 2.5% NH_3, DI water) for the removal of heavy metals (Cd, Pb, Zn, Cu and Cr) during electrodialytic treatment of MSWI fly ash has been evaluated.

It was found that for the removal of Cd, the 2.5% NH_3 solution was the best assisting agent whereas the best Pb removal was obtained with 0.25 M Na-citrate. The best compromise for removal of all five metals was obtained with the 0.25 M ammonium citrate/1.25% NH_3 solution.

When looking at the migration direction of the metals in the different experiments and comparing these results with computer simulations (Visual MINTEQ), the speciation of the heavy metals in solution could be estimated. It was suggested that Pb is primarily dissolved as negatively charged citrate chelates whereas Cu, Zn and Cd will preferentially form positively charged complexes with NH_3 when this is abundant. If water is used as assisting agent, a majority of the Cd is mobilised as negatively charged species, probably Cl-complexes. Cr is removed as negatively charged species at all examined conditions, possibly as chromate ions.

Acknowledgements

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