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Electrodialytic Removal of Heavy Metals from Different Solid Waste Products

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ABSTRACT

A variety of heavy metal polluted waste products must be handled today. Electrochemical methods have been developed for remediation of polluted soil. One of the methods is the electrodialytic remediation method that is based on electromigration of heavy metal ions and ionic species within the soil matrix, and a separation of the soil and the process solutions, where the heavy metals are concentrated, with ion exchange membranes. For remediation of some soils, such as calcareous soils, it is necessary to add an enhancement solution. It was shown in a laboratory experiment that ammonium citrate could be used when removing Cu and Cr from a soil with 25% carbonates. The final concentrations of

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the elements were below the target values after the remediation. A question of whether the electrodialytic remediation method can be used for other waste products arose. Preliminary experiments showed that the method could be used for removal of different heavy metals from impregnated wood waste, fly ash from straw combustion, and fly ash from municipal solid waste incineration. The best result was obtained with the wood waste where more than 80% of each of the polluting elements Cu, Cr and As was removed in a 7-day experiment in which oxalic acid was used as enhancement solution. From the straw ash, 66% of the Cd was removed, but 64% of the fly ash dry mass dissolved during the treatment. In this actual experiment, no enhancement solution was used but that will be necessary to avoid dissolution of the ash to such a high extent. For the fly ash from waste incineration, ammonium citrate was tested as enhancement solution and in 14 days 62% Cd, 53% Cu, 6% Pb, and 31% Zn were removed. The preliminary results were thus promising for developing the electrodialytic method to other products than soil, although more research is needed especially in finding the best enhancement solutions for each product.

Key Words: Heavy metals; Solid waste; Electrodialysis; Electrokinetic remediation; Enhancement solution.

1. INTRODUCTION

The process of electrodialysis in which ion exchange membranes are used has been known since 1948. At this time, the interesting aspects were desalination of potable water and brackish water to drinking water and concentration of seawater for salt production.[1] Later electrodialysis has been used for other separation processes (e.g., in the food industry or in wastewater treatment).

Different electrochemical methods to decontaminate heavy metal polluted soils using a DC electric current as a cleaning agent have been under development since the late 1980s, and some of the methods have been implemented, whereas others are in the state of field implementation. These methods are based on the transport processes electromigration and/or electroosmosis.

One of the electrochemical soil remediation methods is the electrodialytic soil remediation, which combines the process of electrodialysis with soil remediation. The method differs from the other electrochemical soil remediation methods by the use of ion exchange membranes. The soil is placed in the desalination compartment instead of the normal electrolyte solution to be desalted in conventional electrodialysis. One advantage in the use of ion exchange membranes is that the products from the electrode processes will not enter the soil, which means that the conditions in the soil compartment are easier to control. The decisive factor for the electrochemical soil remediation processes is the ability to desorb the heavy metals from the soil to ionic form in the soil solution during the process. When the heavy metals are present as ions, they are transported out of the polluted soil by electromigration. This fact may lead to a question of whether the electrochemical remediation methods can be used for removal of heavy metals from other solid waste products if it is possible to transform the heavy metals to ionic form in these wastes too. This article reports experimental results from electrodialytic treatment of soil as well as impregnated wood waste, fly ash from straw combustion, and municipal solid waste incineration (MSWI) fly ash.

2. ELECTRODIALYTIC REMEDIATION

Electrodialytic remediation of solid waste products started to develop in 1992[2] and was patented in 1995 (PCT/DK95/00209). The method was first developed for remediation of heavy metal polluted soil. Because soil characteristics are varying from site to site and because the heavy metals act differently in the soil, it is beneficial to characterize the polluted soil carefully before starting the remediation.[3] Dependent on this characterization, a proper enhancement solution is chosen to aid desorption of the heavy metals, if necessary, and a combination of membranes is chosen. The basic cell is shown in Fig. 1.

To choose the best combination of membranes *in the anode end* it is important to know if the soil contains a considerable amount of anions that preferably should not participate in the anode processes. If so, membrane A must be a cation exchange membrane (CAT) to prevent these ions to enter the surface of the anode. Examples of unwanted anions could be Cl^- which would lead to production of toxic chlorine gas and F^- which would lead to the formation of HF, an acid that can destroy the anode material. If no enhancement solution is needed, membrane B is an anion exchange membrane (AN). If enhancement solution is needed, membrane B is chemically neutral fabric/filter paper (FP) to supply the waste with the enhancement solution by electroosmosis during the remediation process. When the present anions do not have influence on the anode process, then membrane A can be either a CAT, an AN, or there may be only one compartment in the anode end depending on

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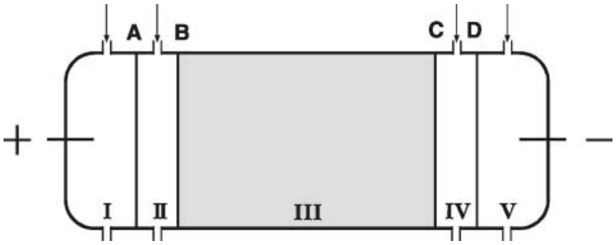

Figure 1. Basic laboratory cell for choice of membrane combination. The membranes A, B, C, and D can be either a cation exchange membrane, an anion exchange membrane, or a chemically inert fabric dependent on the actual medium to be remediated.

the enhancement solution. If, e.g., the enhancement solution must be kept alkaline, membrane A is an AN; if the enhancement solution can be decomposed by anodic oxidation, the A membrane is a CAT.

In the cathode end of the cell, the choice of membrane combination depends on other factors. If the soil contains metals that are readily electrodeposited, it may be necessary to choose membrane D to be an AN to protect the cathode from these elements. The volume of the cathode can increase considerably by electrodeposition, and this can cause problems in full-scale remediation. If membrane D is chosen to be an AN, membrane C should be a CAT in the cases in which an acidic environment in the polluted matrix is beneficial to the remediation action to avoid OH^- from the electrode process. In some cases, it is sufficient with only one compartment in the cathode end, too, and then the membrane is most often a CAT, or in some cases FP.

During recent years electrodialytic remediation of other porous waste products than soil has started to develop. Some of these products are impregnated wood waste and different types of fly ash.

3. SOLID WASTE PRODUCTS CONTAINING HEAVY METALS

The electrodialytic process was tested for removal of heavy metals from four different solid waste products: polluted soil, impregnated wood waste, fly ash from straw combustion, and fly ash from municipal solid waste incineration (MSWI fly ash) (Table 1). A short introduction to the problems with these waste products and the bonding of heavy metals in each product is given in the following.

Table 1. Concentration of pollutants in the different waste products.

Soil	Wood waste	Straw ash	Waste incineration ash
Cu 3300 mg/kg	Cu 430 mg/kg	Cd 11.2 mg/kg	Cd 240 mg/kg
Cr 1060 mg/kg	Cr 840 mg/kg		Pb 8050 mg/kg
	As 589 mg/kg		Zn 17,150 mg/kg
			Cu 1570 mg/kg

3.1 Polluted Soil

Soils have been polluted with heavy metals from different industrial sources as, e.g., wood preservation plants, tanneries, and wire production. The pollution may pose a risk to surface water and groundwater quality; furthermore, plant uptake is the first step of accumulation of the toxic metals in the food chain. In the soil, the heavy metals are retended by different mechanisms dependent on the soil characteristics and the actual heavy metal. The main retention mechanisms for heavy metals in soils are cation exchange, specific adsorption with surface ligands to form mainly covalent bonds with the lattice ions, organic complexation, and precipitation.[4]

3.2 Impregnated Wood Waste

Wood has been impregnated by metal salts for about 150 years and since the 1960s CCA (Cu, Cr, and As) has been the most widespread combination for the preservation process. The CCA is a very efficient preservative due to a good fixation of the metals in the wood, but on the other hand, the metals are still in the wood when it is removed from service. This makes impregnated wood waste a problematic type of waste to handle, and the amount of wood waste can be expected to increase in the years to come. The way the wood waste must be handled varies from country to country. Incineration, often in combination with an extended flue gas cleaning to avoid As emission, is a widespread method to decrease the waste volume, but it results in a chemically unstable ash product that is highly toxic due to the high content of Cu, Cr, and As. In Denmark, it is not allowed to incinerate the wood that is preserved with metal salts. This wood must be separated from other waste products and stored in special landfills until treatment technologies, which ensure reuse of the metals and use of the energy resource of the wood, are developed.[5]

The complex fixation mechanisms of CCA are still not well understood. However, the most dominant reaction during the fixation is the reduction of Cr(IV) in the treating solution to Cr(III) through oxidation of wood components. Cu also reacts directly with wood, by ion exchange. A series of condensation reactions occur during the fixation involving two or even all three elements.[6]

3.3 Fly Ashes

Biofuels (e.g., straw) are becoming increasingly important worldwide as a present and future alternative to fossil fuels. After combustion, the remaining ashes contain several minerals that are essential to agricultural soils, and it would be beneficial to return the ashes to the soil. One problem is thought that the concentration of Cd in the straw ash often is quite high and furthermore a high percentage of this Cd is highly mobile.[7] In the straw ash, much of the Cd is present as soluble $CdCl_2$.[7]

A serious drawback for incineration of municipal solid waste is the production of chemically unstable flue gas purification products that are rich in heavy metals. At present, these products are most often disposed at special landfills. The MSWI fly ash is one of the flue gas purification products that is very rich in heavy metals. The composition of the MSWI fly ash is highly complex. The MSWI fly ash contains two general particle morphologies: (1) an extremely fine grained, polycrystalline, aggregated platelet material containing many volatile elements such as Cl, K, Na, S, and Pb and (2) spherical aluminosilicates particles.[8] Eighmy et al.[8] performed a comprehensive study to characterize speciation behavior of major and minor trace elements in electrostatic precipitator ash from a Canadian MSW incineration plant. The Zn species identified were K_2ZnCl_4, $ZnBr_2$, $ZnCl_2$, ZnO, $Zn_4Si_2O_7(OH)_2 \cdot 2H_2O$, and metallic Zn; the Pb species were $Pb_3O_2SO_4$, $Pb_3Sb_2O_7$, $PbSO_4$, $PbCl_2$, PbO, $Pb_5(PO_4)_3Cl$, and metallic Pb; the Cu species identified was $BaCuO_2$ and the Cd species was $Cd_5(AsO_4)_3Cl$.

4. ENHANCEMENT SOLUTIONS TO ELECTRODIALYTIC TREATMENT OF THE DIFFERENT WASTE TYPES

To be mobile in the electric field, the heavy metals must be present in ionic form or as charged species. Thus, it is necessary to desorb the heavy metals during the process, and for this purpose it may be beneficial to add an enhancement solution to the waste matrix.

4.1 Soil

Remediation experiments have been performed with various soil types polluted by different heavy metals. It has been concluded that the soil type and the combination of heavy metals are determining whether an enhancement solution must be added to the soil to desorb the heavy metal. Non-calcareous soils that are polluted by heavy metals such as Cu, Zn, and Cd, which will desorb from the soil in an acidic environment, can be remediated by the electrodialytic process without any use of enhancement solution. During the remediation process, the soil becomes acidified from the anode end toward the cathode end due to water splitting at the anion exchange membrane, and when the acidic front reaches all through the soil volume, the remediation action is ended.[9,10]

In other soil systems, use of an enhancement solution is beneficial or even necessary. It has been shown that ammonia can be used as a proper enhancement solution in different cases. For remediation of a soil polluted by As and Cu, ammonia can be used as enhancement solution. As is mobile in the high pH region that is caused by the ammonia, and charged copper tetra amine complexes are formed which mobilize Cu as well.[11] Ammonia has also been shown to be a good enhancement solution in the case of a calcareous soil polluted by Cu[12] because the copper tetraamine complexes formed are mobile in the high pH region. Here the calcareous parts in the soil will not dissolve as it would be in the case where the acidic front is developed.

In this article, an experiment with a calcareous soil (25% carbonates) that is polluted by Cu and Cr from wood preservation is reported. It was previously shown[13] that ammonia cannot be used as enhancement solution for Cr removal. The experiment described here investigates the usefulness of ammonia citrate at $\mathrm{pH} = 8$ as enhancement solution. The citric part is expected to form mobile complexes with both Cu and Cr. If the concentration of citrate is not added in excess compared with all the elements it forms complexes with, ammine complexes with Cu can be expected to form too. At $\mathrm{pH} = 8$, the calcareous parts in the soil are not expected to dissolve.

4.2 Wood Waste

For electrodialytic treatment of impregnated wood waste, in the form of sawdust, it has been shown that oxalic acid is a good enhancement solution.[14] Oxalic acid and copper form(s) anionic complexes, most likely $\mathrm{Cu(Ox)_2}^{2-}$. Oxalic acid also forms anionic species with chromium, e.g., $\mathrm{Cr(Ox)_3}^{3-}$. Arsenic is expected to be mobile in the acidic environment.[14]

4.3 Fly Ash

In straw ash, approximately 50% of the Cd is soluble in water and the pH of this fly ash is about 5.9,[7] and it may be possible to remove the Cd without use of enhancement solution.

Enhancement solution is necessary in the case of the MSWI fly ash. The pH in these ashes is much higher (about 12), and the buffering capacity of the fly ash is so high that the process of acidification would be extremely slow. Thus, an enhancement solution is necessary to use the electrodialytic method to remove the heavy metals. Ammonium citrate at pH of about 9 has been suggested as enhancement solution for this fly ash. Complexes can be expected to form between either the ammonia or the citrate part of this enhancement solution and the heavy metals.

5. EXPERIMENTAL SECTION

5.1 Analytical Section

To find heavy metal concentrations in the soil, the soil was treated as prescribed in Danish Standard DS 259 Determination of metals in water, sludge, and sediments—General guidelines for determination by atomic absorption spectrophotometry: 1.0 g dry soil and 20.0 mL (1:1) HNO_3 were heated at 200 kPa (120°C) for 30 min. The liquid was separated from the solid particles by vacuum through a nuclepore filter and diluted to 100 mL. Danish standard 259 was used for the straw ash, too.

The heavy metal content in the impregnated wood waste as well as in the two fly ashes was measured after pretreatment using microwave assisted pressurized digestion in concentrated HNO_3. Concentrations of Cu, Zn, Cr, and Cd were determined by using AAS in flame. Arsenic was determined by using ICP-MS.

The pH was measured in 1 M KCl at a liquid-to-solid ration (L/S) of 2.5 for soil and straw ash and (L/S) of 5 for the MSWI ash. After 1 hr of contact time, pH were measured by a Radiometer pH electrode.

5.2 Characteristic of the Experimental Waste Products

The *soil* was polluted with Cu and Cr from wood preservation. The soil was calcareous with a carbonate content of 24% (measured by a volumetric calcimeter method). The pH of the soil was 7.4, and the organic content expressed in loss on ignition was 3.4%. The fine fraction of the soil ($<63\ \mu m$) was 23.4%.

Woodchips from the outermost 3 cm of an out-of-service electricity pole was used. The length of the wood chips was from 1 to 5 cm, and the diameter was maximum 1 cm. The pole was a *Picea abies L*, treated with 12 kg "K33" (CCA-B) per m^3 sapwood in 1962 by Collstrop A/S. The pole was removed from service in 1999.

The *straw ash* was a filter fly ash taken from electrostatic precipitation of flue gas from a Danish straw fired power plant at Masnedø. The straw ash consisted of 30–31% chlorine and 26–29% potassium; pH was 5.9. More information about this ash is found in Ref.[7]

The *MSWI fly ash* was sampled from the electrostatic precipitator of the Danish MSWI plant "Vestforbrænding." At the point of sampling, the gas stream had not been exposed to any flue gas cleaning additives (e.g., lime). The ash was alkaline with a pH of 12.2.

5.3 Description of Remediation Experiments

The laboratory cells used were made of Plexiglas or glass. The ion exchange membranes were obtained from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum-coated titanium electrodes from Permascand were used as working electrodes, and a power supply (Hewlett Packard E3612A) was used to maintain a constant current. The composition of the cells for the remediation experiments varied depending on the waste products; see Table 2. The choice of enhancement solution and solutions in the outer compartments is given in Table 3.

Air-dried soil was mixed with the ammonium citrate to a water content of 14.1% before the soil was carefully filled into the central compartment by hand. Altogether, there were 883 g dry matter of soil in the cell. The wood chips (32.2 g dry matter) were placed in the central compartment and added oxalic acid. Two experiments were performed with the straw ash and the only parameter that differed between these experiments was the duration: 7 days and 24 days. The straw ash was mixed with distilled water to a water content of 39% initially and the dry weight of the ash for the experiments was approximately 136 g. The MSWI fly ash was remediated as stirred slurry with an L/S of 6.7. The initial amount of ash was 75 g dry matter.

The electrical parameters for the experiments, are given in Table 4.

At the end of the experiments, the membranes were treated with 1 M HNO_3 to extract the heavy metals that were adsorbed within the membrane

Table 2. The composition of the cells for the experiments with the different waste matrices.

	Number of compartments	Membrane A	Membrane B	Membrane C	Membrane D	Length central compartment (cm)	Diameter of cell (cm)
Soil	5	AN	FP	FP	CAT	10	8
Wood	3	—	AN	CAT	—	5	8
Straw ash	5	CAT	AN	CAT	AN	13	4
MSWI fly ash	5	CAT	AN	CAT	AN	10 (stirred)	8

The table corresponds to Fig. 1.

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Table 3. Experimental parameters for the electrodialytic remediation experiments.

	Enhancement solution	Cathode side of cell	Anode side of cell
Soil	1 M amm. citrate pH = 8	I: 0.01 M HNO_3 + 0.01 M $NaNO_3$	V: 0.01 M HNO_3 + 0.01 M $NaNO_3$
		II: 0.5 M amm. citrate, pH = 8	IV: 0.5 M amm. citrate, pH = 8
Wood	2.5% oxalic acid[a]	Saturated oxalic acid[b]	2.5% oxalic acid
Straw ash	Only addition of water	I and II: 0.01 M HNO_3 + 0.01 M $NaNO_3$	IV and V: 0.01 M HNO_3 + 0.01 M $NaNO_3$
MSWI fly ash	0.25 M amm. citrate in 1.25% NH_3[c]	I: 2.5% NH_3	V: 0.01 M HNO_3 + 0.01 M $NaNO_3$
		II: 0.25 M amm. citrate in 1.25% NH_3	IV: 0.25 M amm. citrate in 1.25% NH_3

[a] The wood chips were water saturated and volumes in the central compartment between the wood was filled with 2.5% oxalic acid.

[b] 100 g/L.

[c] L/S = 6.7 mL/g). Amm. Citrate = ammonium citrate.

Table 4. Electrical parameters for the remediation experiments.

	Current density (mA/cm^2)	Voltage range (V)	Duration (days)
Soil	1.0	4.0–9.3	78
Wood	0.8	2.8–3.2	7
Straw ash	5.6	5.5–28.0	7 and 24
MSWI fly ash	0.8	2.8–8.2	14

during the process. The cathode was rinsed in 5 M HNO_3, too. The volume of the solution in the outer compartments was measured and so was the concentration of heavy metals. In the experiment with soil and straw ash, the matrix in the central compartment was sliced into five slices, and the heavy metal concentration was measured twice in each slice. In the experiment with the wood chips, the concentration was measured in six different pieces of wood chips and in the solution in the central compartment. In the MSWI fly ash experiment in which the ash was a stirred suspension, the concentrations of the heavy metals was measured in both fly ash and solution.

6. RESULTS

6.1 Soil

The experiment lasted for 78 days and during this period the solutions in the four compartments were replaced with new solutions three times. The amount of Cu and Cr removed over time is shown as a function of time in Fig. 2. At the cathode, 4.6 mg Cu was precipitated during the experiment, which corresponds to 0.2% of the total Cu amount.

The normalized concentration profiles in the soil are shown in Fig. 3. The carbonate content in the soil varied between 21.3% and 23.7% after the experiment.

6.2 Impregnated Wood Waste

At the end of the experiment, the Cu concentration in the wood chips varied between 0 and 44 mg/kg, and the Cr concentration varied between 35 and 177 mg/kg. The samples from the microwave digestion were mixed before analyzing As; thus, only the average concentration of 150 mg/kg is known.

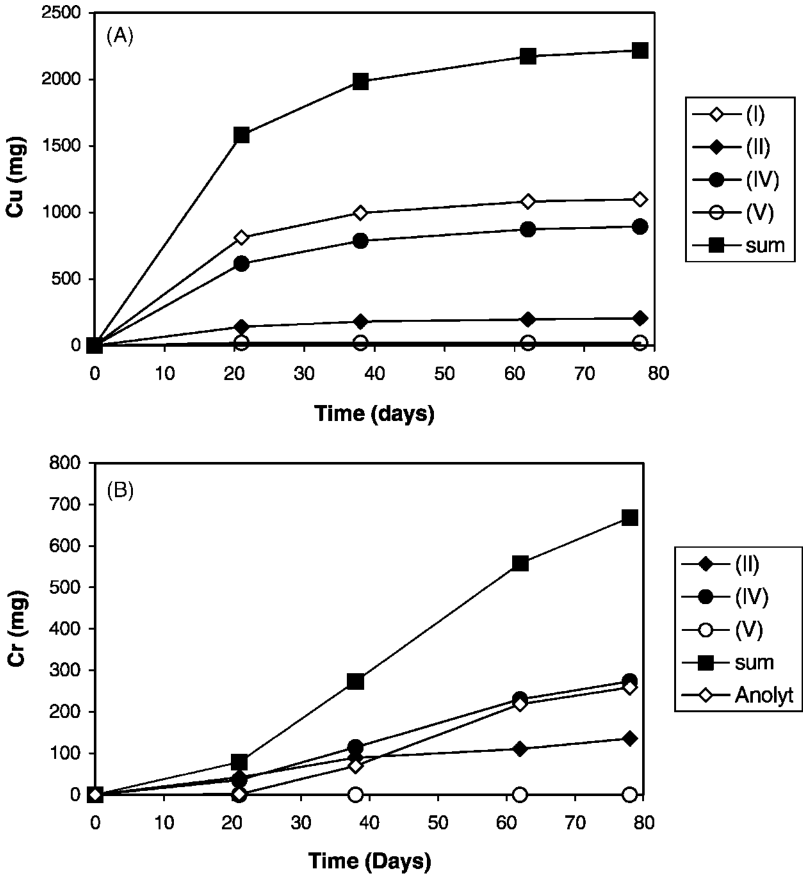

Figure 2. The amount of (A) Cu and (B) Cr found in the different electrolyte solutions in the cell as a function of time. The sum of curve is shown, too.

The distribution on percent of the heavy metals in the experimental cell at the end of the experiment is shown in Fig. 4.

6.3 Straw Ash

The cadmium content in the different slices of ash at the end of the two experiments is given in Fig. 5 as final Cd mass divided with initial Cd mass. The values in Fig. 5 are given in this way due to a loss in dry matter of the ash

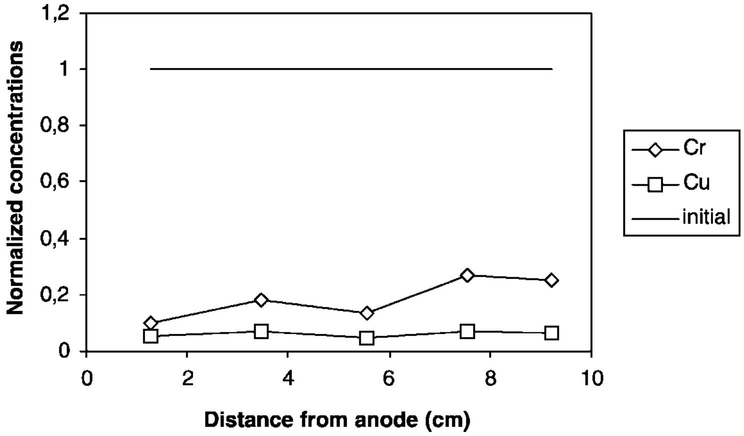

Figure 3. Normalized concentration profiles in the soil at the end of the remediation.

during the experiments. The loss of dry matter was 25% in the experiment of 7 days and 64% in the experiment of 24 days. In the longest experiment, about two-thirds of the cadmium was removed from the ash about 80% of the removed cadmium was removed to the anolyte, and about 20% was found in the catholyte and the cation exchange membrane. During the experiments, the pH of the fly ash was lowered from 5.2 to less than 2.

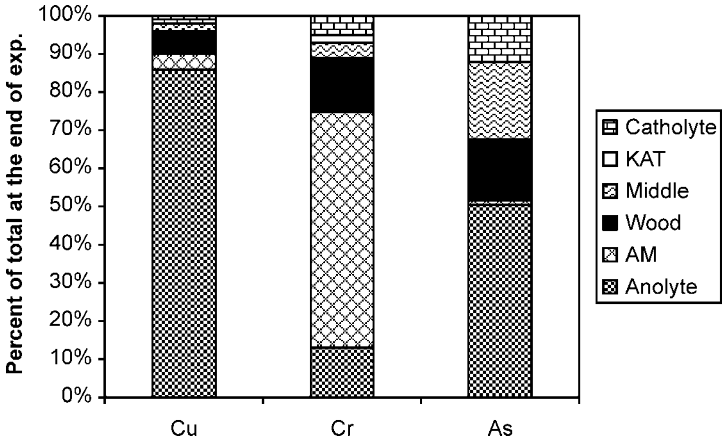

Figure 4. Distribution of Cu, Cr, and As in the electrodialytic cell at the end of the experiment performed with wood chips. (Modified from Ref.[15]).

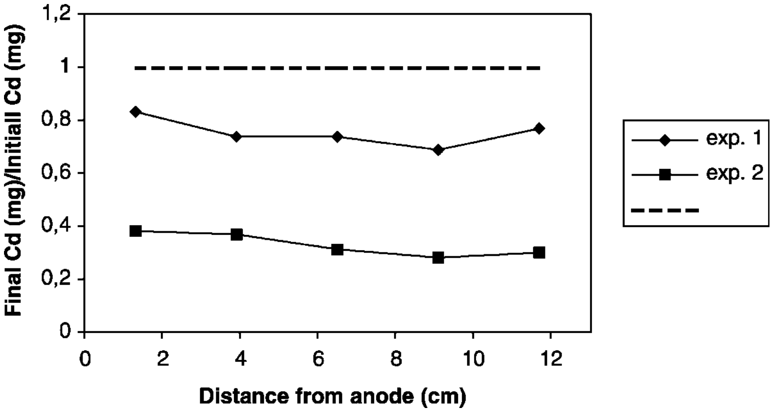

Figure 5. Final Cd (mg)/initial Cd (mg) in the straw ash at the end of experiment 1 (7 days) and experiment 2 (24 days).[16]

6.4 MSWI Fly Ash

The distribution in percent of the four heavy metals in focus is shown in Fig. 6. This figure is based on the amounts found in the different parts of the cell at the end of the experiment. The mass balances when comparing the total amounts after the experiment with the initial amount based on the initially

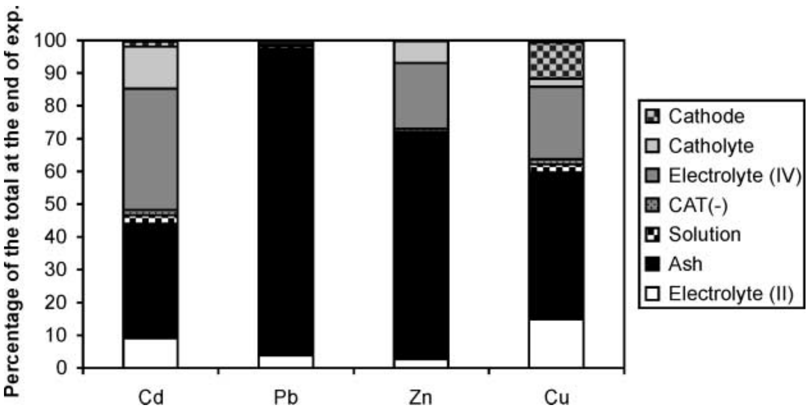

Figure 6. Distribution of Pb, Cd, Zn, and Cu in the electrodialytic cell at the end of the experiment performed with MSWI fly ash (Modified from Ref.[17]).

measured concentrations in the fly ash are 99% for Cd, 126% for Zn, 113% for Cu, and 105% for Pb.

Between 0 and 0.9% of all elements were found precipitated at the cathode, adsorbed in the anion exchange membranes, in the cation exchange membrane separating compartment (IV) and (V), and in the anolyte. These are not shown in the figure.

The mass of fly ash decreased from 75 to 71.6 g during the experiment, corresponding to a weight loss of 4.5%

7. DISCUSSION

Ammonium citrate is a very efficient enhancement solution for the actual soil. A soil pH of greater than 8 was maintained through the experiment, and the carbonate content was reduced from 24.0% to between 21.3% and 23.7%. The concentrations of Cu in the soil varied from 150 to 300 mg/kg at the end of the experiment, and the variation in Cr concentration was between 100 and 320 mg/kg. The initial concentrations of 3300 mg Cu/kg and 1060 mg Cr/kg corresponded to a soil that needs to be remediated or landfilled in Denmark. Soils with a content of less than 500 mg/kg of each of these two elements can be used for different purposes,[18] and after the remediation this goal was reached.

From Fig. 2A and B it can be seen that both Cu and Cr were removed in both directions during the remediation. No Cr and about 0.8% of the total amount of Cu were found in the catholyte and on the cathode. Both elements were concentrated in compartment IV instead of passing the cation exchange membrane into compartment V. The explanation of this is under investigation because it is an observation that is consistent with yet unpublished results with electrodialytic remediation of other wood preservation soils where ammonium citrate has been used as enhancement solution. In experiments where the cation exchange membrane is placed next to the soil instead of filter paper, no Cu was removed toward the cathode, even if the experimental setup was similar to the one of this experiment, except from the membrane next to the soil in the cathode end. In the anode end, the highest amount of both Cu and Cr was found in the anolyte as expected, but both elements were found in compartment II, too. Ammonia alone cannot be used as enhancement solution for the actual soil, because only about 2% Cr was removed in an experiment similar to the one described here, but where ammonia was used as enhancement solution.[13] In ammonia, the Cr removed was all found in the anolyte at the end of the experiment, and this may indicate that this fraction was presented as Cr(VI). In the experiment with ammonium citrate as enhancement solution, 40% of the Cr removed was found in compartment IV (i.e., removed toward the cathode). Free Cr^{3+} ions are not likely to exist at the neutral pH, and thus Cr ammine complexes can be an explanation of the cationic Cr. Ammonia cannot desorp Cr from this soil,[13] but this indicates that when the Cr is first desorbed, the ammine complexes can be formed. About 60% of the Cr was found in the electrolyte solutions in the anode end of the cell. Complexes between citrate and Cr are negatively charged, and it is expected that Cr was removed toward the anode as citrate complexes.

The remediation of Cu proceeded faster than the Cr removal. During the first 40 days of the experiment, the major part of the Cu was removed, whereas the Cr removal proceeded during the 78 days of the experiment. Only little Cr was removed during the first 20 days. It would be beneficial to increase the rate of Cr removal especially in the beginning of the experiment since the Cr removal is much slower than the Cu removal. Other concentrations and pH of ammonium citrate will be tested, as well as a longer equilibration time between addition of ammonia citrate to the soil and the start of the electrodialytic remediation.

In the wood waste experiment, it can be seen from Fig. 4 that Cu, Cr, and As were removed mainly in the direction of the anode. Arsenic was primarily moved toward the anode but was found in the liquid from the middle compartment and to some extent in the catholyte, too. At pH 2, the dominating arsenic species is H_3AsO_4, but above pH 2.2 $H_2AsO_4{}^{-}$ dominates. The fact that pH in this experiment is in the same range makes it probable that these species will be dominating in the middle compartment and in the anolyte. The fact that some arsenic is found in the catholyte indicates that also cationic species are present. According to Ref.[14] AsO^{+}, $As(OH)^{+}$, or in even more acid solutions, As^{3+} may exist and these species will move toward the cathode. Almost all the removed copper was found in the anolyte. This is in agreement with the fact that oxalic acid and copper forms anionic complexes, most likely $Cu(Ox)_2{}^{2-}$. Almost all chromium was removed toward the anode side, too, and most of the chromium was in connection with the anion exchange membrane. The anionic chromium species are probably $Cr(Ox)_3{}^{3-}$. There is also a theoretical possibility that Cr(VI) is present (as $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$ or $HCrO_4{}^{-}$), but because Cr(VI) is reduced to Cr(III) during the preservation, and given the fact that both wood and oxalic acid may react as a reducing agent, the dominating anionic chromium species is presumed to be $Cr(Ox)_3{}^{3-}$.

In the straw ash, the Cd was found to be removed both in the direction of the anode (80%) and of the cathode (20%). In the acidic environment, Cd can be present in the ash as Cd^{2+} ions and this part will move toward the cathode. Due to the high content of Cl^{-} in the ash, $CdCl_4{}^{2-}$ complexes are likely formed, and these complexes will move toward the anode. The rate of Cd removal was almost constant in the two experiments indicating that the removal process could have proceeded further and lower concentrations could have been reached if the current was applied for a longer period. The fly ash was dissolved to a high extent during the removal process and after 24 days only 36% of the dry mass was left. Some of the ash dissolved after addition of water prior to the remediation and more of the ash particles dissolved due to the acidification of the straw ash during the process. So even though it was possible to mobilize and remove Cd from the straw ash without an enhancement solution, the next step, in the direction of developing the method for this waste product, will be to find a solution that can be added to the ash, so a minimum of the ash is dissolved and Cd at the same time is mobile. When such solution is found, the minerals in the straw ash can be used as nutrients and the Cd can be concentrated further for reuse or deposition.

During the 14-day experiment with the MSWI fly ash 62% Cd, 6% Pb, 31% Zn, and 53% Cu were removed. Pb moved toward the anode only, whereas the other three heavy metals were moved in the direction of both anode and cathode. Pb will not form positively charged amine complexes as the three other elements, but all four heavy metals investigated will form negatively charged complexes with the citrate.

The separation in the anode end was very good because the heavy metals were found in the solution in compartment (II) only, but in the cathode end the separation was poor. During the experiment, Zn, Cu, and Cd passed the anion exchange membrane into the catholyte, where both Cd and Cu deposited on the cathode.

This initial experiment with electrodialytic remediation of MSWI fly ash showed that it was possible to remove some parts of the heavy metals using ammonia citrate as enhancement solution, but still a lot of research remains before it is possible to evaluate whether the method can be used to detoxify the fly ash. Research should at first be done with other enhancement solutions to increase the mobility of especially Pb. There may be parts of the heavy metals that may be very difficult to mobilize because they are precipitated in very insoluble fly ash particles [e.g., lead hydroxypyromorphite ($Pb_5(PO_4)_3OH$)].[8] In this case it must be evaluated whether a total removal is necessary or if the method should be regarded as a stabilizing method where the mobile fraction is removed from the fly ash. The fly ash should probably still be landfilled in this case due to the remaining heavy metals, but the fly ash will not leak heavy metals and is thus not a threat to the surroundings as a leaking fly ash. The removed metals should be concentrated further for reuse, and thus a better separation than found at the cathode side in this experiment must be found.

CONCLUSIONS

The electrodialytic remediation method was first developed for removal of heavy metals from polluted soils. Most often, the heavy metals are mobilized by an acidic front that is passing the soil from the anode end toward the cathode, but in calcareous soils the buffering capacity is high and the acidic front develops too slowly for the remediation to occur within a reasonable timescale. An example of electrodialytic removal of Cu and Cr from a soil with 25% carbonates, where ammonium citrate was used as enhancement solution, showed that it was possible to remediate the soil to below the limiting values for both elements without acidifying the soil.

Preliminary experiments were made with electrodialytic remediation of other porous media polluted with heavy metals: impregnated wood waste, fly ash from straw combustion, and MSWI fly ash. For the wood waste, oxalic acid was used as enhancement solution and within 7 days 94% Cu, 86% Cr, and 84% As were removed from the wood chips. The heavy metal of concern in straw ash is Cd and in a remediation experiment of 24 days 66% of the Cd was removed without use of enhancement solution. At the same time, the fly ash dissolved due to the acidification, so only 36% of the dry mass was left and to avoid this an enhancement solution should be used. The MSWI fly ash contained high concentrations of Cd, Cu, Pb, and Zn, and by using ammonium citrate as enhancement solution in an experiment of 14 days 62% Cd, 53% Cu, 6% Pb, and 31% Zn were removed. More research must be done to optimize the remediation conditions, especially the type and concentration of enhancement solution, but the preliminary experiments showed the potential to remove heavy metals from these waste products, too.

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