

ELECTRODIALYTIC REMEDIATION OF CCA-TREATED WOOD IN LARGER SCALE

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Abstract

A pilot plant for electrodynamic remediation of CCA-treated wood in larger scale has been designed and tested at DTU. Several process parameters were investigated, and it was found that the use of collecting units and soaking of the wood prior to the electrodynamic process had a positive influence on the remediation process. There is a tendency towards easier remediation of wood chips < 2cm, than larger wood size fractions. The influence of the electrode distance could not be fully investigated due to the experimental setup but it is expected that the use of collecting units will keep any influence to a minimum. The best remediation efficiency was obtained in an experiment with an electrode distance of 60 cm, and 100 kg wood chips. In this experiment 87% Cu, 81% Cr and >95% As was removed. Only one other experiments was analysed for As and here 95% was removed. The electrode distance was 1.5 m and the results indicate that As may be the easiest removable of the Cu, Cr and As investigated here. This is very encouraging since As is the CCA components of most environmental concern.

Keywords

CCA-treated waste wood, electrodynamic remediation, oxalic acid, phosphoric acid, pilot plant

Introduction

The service life of wood treated with CCA (Chromated Copper Arsenate) may be 30 years or even more due to the strong fixation of CCA in the wood. The strong fixation also means that when the wood is removed from service, a large proportion of the copper (Cu), chromium (Cr) and arsenic (As) is still present and will enter the waste stream unless actions are taken to prevent this. The amount of treated wood being removed from service is expected to increase dramatically over the next few decades, making an environmentally safe handling of the wood desirable.

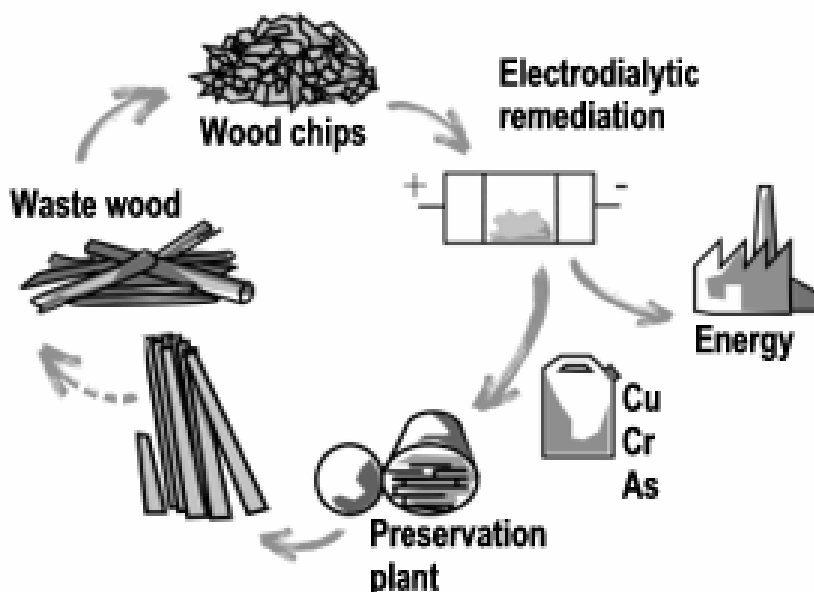


Figure 1 Proposed life cycle for CCA treated wood

In figure 1 a proposed life cycle for CCA-treated wood is presented. The CCA treated waste wood is chipped and the Cu, Cr and As are removed using electrodiolytic remediation. Afterwards the wood may be used as bio fuel since it no longer contains CCA, thereby utilising the energy resource of the wood. The removed Cu, Cr and As may be used for the production of new CCA. Since the use of CCA is being restricted in most of the world, the metals may be used in other parts of the industry instead or stabilized for safe disposal.

Electrodiolytic remediation is a method developed and patented at the Technical University of Denmark (DTU). Initially the method was developed for removing heavy metals from polluted soil. The method uses a direct electric current as a cleaning agent and combines it with the use of ion exchange membranes to separate the electrolytes from the soil. Good results have been obtained, and subsequently the method has been tested on a wider range of materials including fly ash, sludge, harbour sediments and impregnated waste wood.

In laboratory scale experiments CCA-treated waste wood has been remediated both as sawdust and wood chips with encouraging results. In sawdust app. 95% Cu, 90% Cr and more than 96% As has been removed [1] and in remediation of wood chips, removal results of more than 90% Cu and app. 85% of both Cr and As has been obtained [2].

Based on the good results obtained in the laboratory, the upscaling of the electrodiolytic remediation has now been started. In the experiments presented here, between 94 kg and 469 kg wood chips was used in each experiment, compared to the 50-70 grams used for experiments in laboratory scale.

Electrodiolytic remediation (EDR)

EDR uses a direct electric current as a cleaning agent and combines it with the use of ion exchange membranes to separate the electrolytes from the wood.

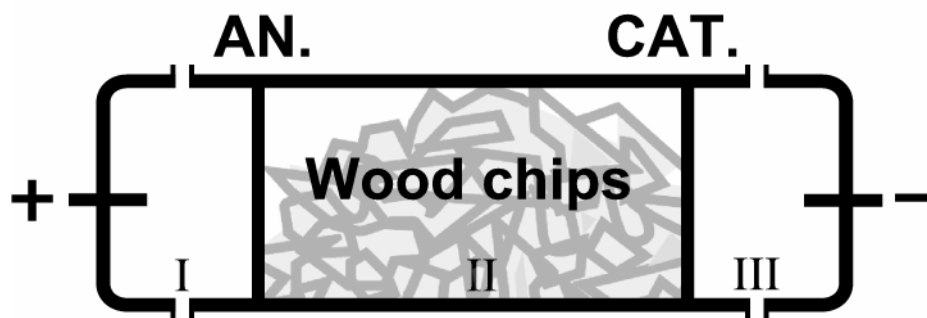


Figure 2 Schematic presentation of an electrodiolytic cell. Compartment I and III is the anode and cathode compartment respectively, the wood chips are placed in compartment II.
AN: Anion exchange membrane, CAT: Cation exchange membrane

The laboratory cell consists of three compartments: an anode compartment (I), a cathode compartment (III) and a middle compartment (II) containing the wood chips (figure 2). The catholyte is separated from the middle compartment by a cation exchange membrane, a membrane that only allows positive ions – cations - to pass. The anolyte is separated from the middle compartment by an anion exchange membrane, a membrane that only allows negative ions – anions- to pass. When an electric potential is applied to the electrodes, the current in the cell will be carried by ions in the solutions. Accordingly Cationic species will migrate towards the cathode and anionic species will migrate towards the anode. With ion exchange membranes placed as described above, no current carrying ions can pass from the electrode compartments into the middle compartment, while ions can be transported from the middle compartment into the electrode compartments. In this system the current is thus prevented from carrying highly mobile ions from one electrode compartment through the middle compartment into the other electrode compartment. Furthermore competition between such highly mobile ions from the electrode compartments and the ions in the middle compartment is avoided. The electro-dialytic remediation method is described in further details in [3] & [4]

Experimental

Wood

The wood used in the experiments was supplied by RGS90, the largest recycling company in Denmark. From a large pile of demolition wood waste app. 10 m³ of impregnated wood was collected. By visual inspection it can be very difficult to see if old (weathered) wood is impregnated or not, therefore Chromazurol S, a colour reagent turning blue in contact with Cu was used to identify the impregnated wood. After sorting, the wood was chipped and divided into three size fractions (< 2cm, 2-4 cm and > 4cm) by sieving. In table 1 the mean concentration of Cu, Cr and As in the wood is given.

Table 1 Mean Concentration \pm 95% CL of Cu, Cr and As in Waste Wood

	ppm (mg/ kg wood)
[Cu]	1279 \pm 66
[Cr]	1334 \pm 91
[As]	837 \pm 114

Mean values are based on 179 samples for Cu and Cr and 95 samples for As.

Pilot plant



Figure 3 The pilot plant in use. Wood chips in yellow plastic nets are placed between collecting units, where the Cu, Cr and As from the wood is collected. The end units contains the electrodes, and are named electrode units.

A pilot plant has been designed for the remediation of up to 2 m³ treated wood waste. Figure 3 shows the pilot plant in use. It consists of a box that is app. 3 meter long, 1 meter wide and 1 meter high. Inside the box, there are ribs for every 35 cm and at these ribs it is possible to place a collecting unit or an electrode unit. When the full capacity of the plant is in use, the electrode units are placed in each end of the box, thereby giving a distance between the electrodes of 3 meters. The electrode units may also be placed at the ribs, thereby allowing the distance between the electrodes to vary from 30 cm to 3 meters. The pilot plant is in principle only an upscale of the laboratory set up, but some adjustments have been made in the up scaling. Due to the larger size, the distance between the electrode compartments (where the ions are collected in laboratory scale experiments) may become a limiting factor on the remediation time or efficiency. To compensate for this, collecting units are introduced. Collecting units are placed between the electrode units and have a cations exchange membrane on one side and an anion exchange membrane on the other side. The membranes make it possible to trap the ions inside the units. By introducing the collecting units, the distance the ions have to travel before being captured can be reduced to 30 cm. The amount of wood to be treated may vary between app. 300 l and 2 m³.

A total of seven pilot plant remediation experiments are presented here, and in table 2 the experimental conditions for the experiments are outlined

Table 2 Experimental Conditions.

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp.6	Exp. 7
Electrode distance (cm)	60	60	60	60	90	150	270
Wood (kg)	94	106	97	99	178	248	469
Duration (days)	11	11	21	15	15	21	21
Wood fractions	M	M	M	M	F/M/L	M	F
Collecting units	1	0	1	1	2	4	8
Current (A)	1.4-2	2	2-5	0.2-3	2-3	2-3	1-1.5
Voltage (V)	24-25	14-18	30-58	14-60	23-29	40-63	23-39
Additive	Water	Water	Water	5% oxalic acid	Water	Water	Water
Soaking solution /duration (hours)	5% oxalic acid/48	5% oxalic acid/48	0,5 M H ₃ PO ₄ /18 5% oxalic acid/24	-	0,5 M H ₃ PO ₄ /18 5% oxalic acid/24	0,5 M H ₃ PO ₄ /18 5% oxalic acid/24	0,5 M H ₃ PO ₄ /24 5% oxalic acid/24

In Exp. 4 oxalic acid was used as electrolyte solutions. In all other experiments 0.01 M NaNO₃ was used. Wood fractions: Fine (F) <2 cm, Medium (M) 2-4 cm, Large (L) >4 cm.

In all the experiments the current strength was kept as high as possible. In exp. 1 and 2 the max current strength possible was 2 A. For exp. 3-7 the power supply was replaced and the max. current strength was 5 A. In all experiments the current strength was initially kept constant, but due to increasing resistance the current strength had to be reduced during the experiments. In all experiments but exp. 4, the wood was soaked before remediation. After soaking the wood was placed in the pilot plant and covered with tap water and the current was applied. In the electrode units and collecting units 0.01 M NaNO₃ was circulated. During the remediation, the pH was kept below pH 2 in the units to prevent precipitation. After remediation the distribution of Cu and Cr was measured in all seven experiments. The content of Cu and Cr was measured in the soaking solutions, the units, in the middle compartments and in the wood. Wood samples were analysed using microwave assisted acid digestion and the concentration of Cu and Cr was measured on AAS. The distribution of As was only measured in exp. 3 and exp. 6 due to the fact that the analysis had to be made outside the department and at high costs.

Results

The influence of different parameters on the remediation result has been investigated. The interpretation are here based on only seven experiments in total, ad no two experiments are alike. It is therefore emphasised that it is to be regarded as tendencies rather than definite conclusions on the matter of remediation in larger scale.

In figure 4 the concentration of Cu, Cr and As in the wood after remediation is shown.

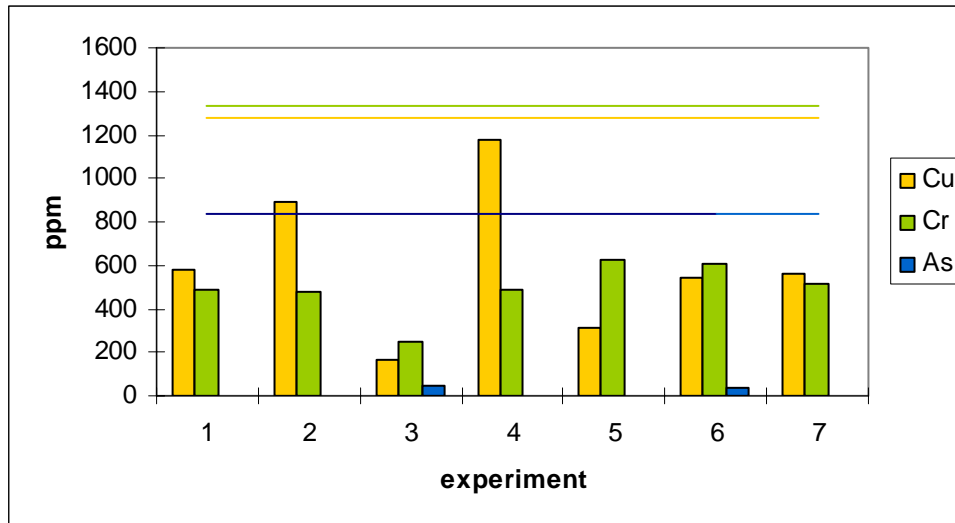


Figure 4 The concentration of Cu, Cr and As in the wood after remediation. Concentration of As is only measured in exp. 3 and exp. 6. Horizontal lines indicate initial concentration.

As seen in figure 4 the content of all three metals have been reduced in the wood in all seven experiments. In the following sections the results are discussed in relation to different process parameters.

Collecting Units

In experiment 1 and 2 the setup is similar except for the use of a collecting unit in exp.1. The purpose was to illustrate the influence of the collecting unit on the remediation by comparing the two experiments.

In figure 4 the concentration of Cu and Cr in the wood after remediation is illustrated by comparing exp. 1 and 2. It seems that the remediation of Cu is improved by the use of a collecting unit to shorten the way the ions have to travel before being collected. On the other hand, no effect is seen for Cr. To further investigate the differences in Cu remediation, the distribution of removed Cu after remediation in the two experiments is compared in figure 5.

As can be seen in figure 5, a larger amount of Cu was removed in the experiment where a collecting unit was placed (exp. 1). The amount of Cu found in the units after remediation is more than three times larger in experiment 1 and the amount of Cu present in the middle compartments is higher in exp. 2, where the ions have to travel a greater distance before being captured in a unit. The reason for the large difference in Cu removal is not connected with the use of a collecting unit alone. In stead it may be connected with the fact that the soaking liquids from exp. 1 were reused in exp. 2. The Cu removed during soaking is more than four times larger in exp. 1. The possibility of reusing soaking solutions have been tested in laboratory scale and the results (not shown) indicated that it may be used up to 4 times without any influence on the remediation efficiency. Thereby no influence by the reuse of the soaking solution was anticipated. However, the apparent reduced removal of Cu during soaking, when the soaking solution has been used before seems to point in the other direction. Further investigation is needed to verify if the reuse of soaking solutions have an influence on the remediation efficiency in larger scale. For the present series the soaking solutions has been used and reused three times in total in all experiments except exp. 1 and 3.

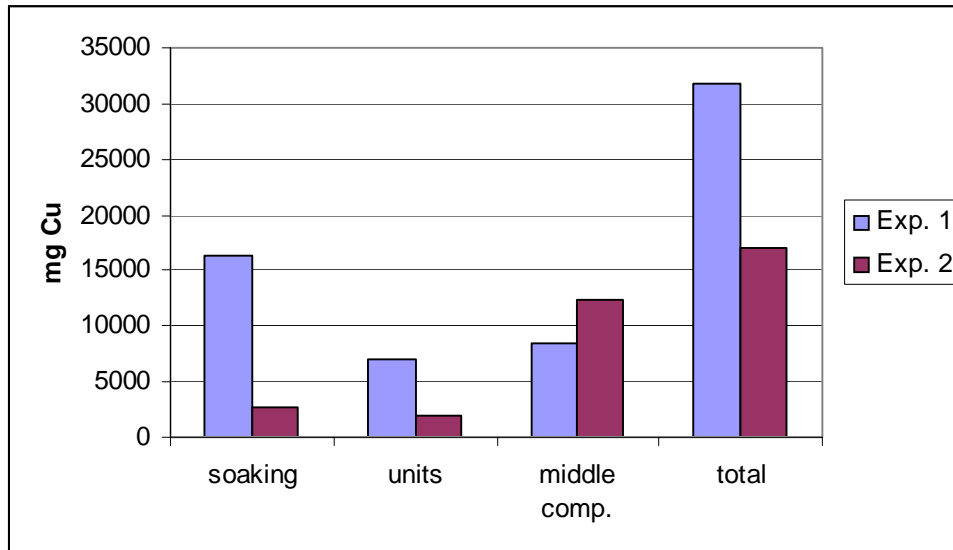


Figure 5 Distribution of removed Cu in experiment 1 (with collecting unit) and experiments 2 (without collecting unit). The term “units” in the figure covers both collecting unit and electrode units.

Soaking

In exp. 4 the wood was not soaked before remediation, but placed directly in the pilot plant. Oxalic acid was used as an additive in the middle compartments and in the units. The experiment had to be stopped after 15 days because of technical problems. The resistance increased dramatically, forcing the current strength to a value below 0.2 A. It was later discovered that the anode was broken. During the experiment the current strength had to be decreased due to extreme gas evolution in the cathode compartment that resulted in malfunction of the circulating pump. As seen in figure 4 the remediation of Cu was greatly reduced in this experiment (exp. 4) compared to exp. 1 where the oxalic acid was used in the soaking procedure, and not during the electrodynamic remediation process. In the remaining experiments, soaking was used.

Two different soaking solutions were tried in this series. In the first two experiments oxalic acid was used, and in the subsequent experiments dual soaking in phosphoric acid and oxalic acid was used. The change in soaking solution was based on a series of laboratory experiments with different acids and combinations of acids, and the use of phosphoric acid, followed by oxalic acids gave the best results in laboratory scale. By comparing exp. 1 and 3 it seems that the change in soaking solution had a profound impact on the remediation (see figure 4). In figure 6 the distribution of Cu and Cr after remediation are shown for exp. 1 and exp. 3. The remediation is increased for both metals by the dual soaking and larger proportions have been removed during soaking in exp. 3 compared to exp. 1

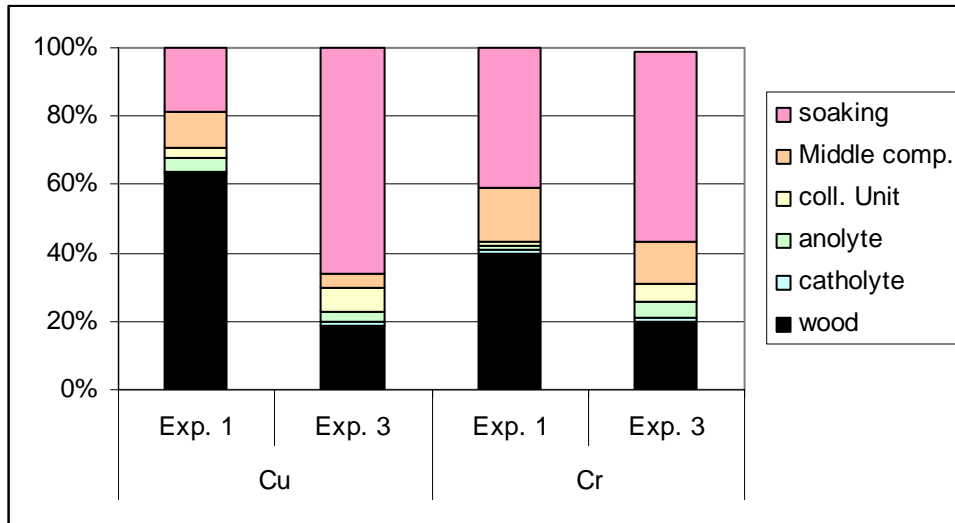


Figure 6 Distribution of Cu and Cr after remediation in exp. 1 (oxalic acid soaking) and exp. 3 (dual soaking of phosphoric and oxalic acid).

Size Fraction

In exp. 5 all three wood size fractions have been remediated at the same time. The different sizes were evenly distributed all over the pilot plant and after remediation, 24 wood samples from each of the three fractions were analysed for Cu and Cr. The concentration of both metals was significantly lower in the fine fraction than in the medium and large fraction, indicating that it may be easier to remediate wood chips with a size < 2 cm. The concentration of Cu was reduced to 127 ± 12 ppm in the fine fraction, 368 ± 67 ppm in the medium fraction and 515 ± 176 ppm in the large fraction. Overlap of the 95% CL in the medium and large fraction indicates that the difference between these two fractions is not statistically significant. However the relatively high 95% limits in the same fractions indicate a high variation. For Cr the variation is high in the large fraction where the concentration after remediation was reduced to 771 ± 294 ppm. In the medium fraction the concentration of Cr was 629 ± 95 ppm and 462 ± 35 ppm in the fine fraction. As for Cu, the concentration of Cr is significantly lower in the fine fraction, compared to the medium fraction, indicating an easier remediation of the fine fraction. The high variation in the large fraction does not make the difference between the Cr content of this fraction and each of the other two fractions statistically significant.

Electrode Distance

The electrode distance has been varied between 60 cm and 270 cm, but to evaluate the influence of electrode distance on the remediation exp. 3 and 6 are used. The two experiments are of the same duration, and the same wood size fraction and soaking solution was used in the two experiments. The electrode distance was 60 cm in exp. 3 and 150 cm in exp. 6. In figure 4 it is seen that increasing the electrode distance by factor 2.5 results in a decrease in the remediation of app. the same magnitude for both copper and chromium. The same is not true for the remediation of As. In both experiments more than 95% of the As has been removed.

The limiting factor when increasing the electrode distance may be the current strength and voltage drop. It is likely that the increase in amount of wood and electrode distance may require an increase in electric charge and voltage drop. This was not possible in these experiments due to the limitations of

the power supply and the all ready mentioned fact that the current was kept as high as possible in all experiments.

In exp. 6 only the medium fraction was used and in exp. 7 only the fine fraction was used. In figure 4 it is seen that the remediation in the two experiments seems unaffected by the fact that the electrode distance is 150 cm in one experiment and almost twice as long (270) cm in the other experiment. The reason for this may have more to do with the difference in wood fraction as discussed earlier than on the difference in electrode distance.

Discussion

A series of seven electro-dialytic remediation experiments has been presented here and different process parameters have been investigated. Due to the limited amount of experiments it is important to emphasize that the results may be viewed as trends or indications rather than absolute results.

The use of collecting units to shorten the way the ions have to travel before being captured proved useful, especially in exp. 6 and 7 where the electrode distance was 150 cm and 270 cm respectively. In all but one experiment the wood was soaked before the electro-dialytic remediation process. When soaking was not used, the remediation efficiency decreased and in addition to that, major technical problems were encountered. The purpose of soaking is to remove the most available Cu, Cr and As first and then use the electric current to remove the less available fractions. Soaking solutions contain acid and/or complexing agents in the form of ions that will move in the electric field. If the oxalic acid or phosphoric acid was used directly in the pilot plant a large proportion of the current would be wasted on removing these ions from the middle compartment instead of Cu, Cr and As. By introducing soaking, the wood and CCA comes into contact with the acids prior to that, and the concentration of the acid (ions) in the electro-dialytic remediation is reduced. In this series the soaking in phosphoric acid followed by soaking in oxalic acid proved to be most effective.

The reuse of the soaking solutions was initially presumed to have no influence on the remediation, but when the exp. 1 and 2 was compared it seems that the removal of especially Cu during soaking was reduced. It is possible that the soaking solutions have become saturated and that some of the Cu precipitated as CuOx during the soaking in exp. 2. Thereby the amount of Cu removed during soaking in exp. 2 may be underestimated in figure 5. Even if this is the case, the measured concentration in the wood after remediation is still higher in exp. 2 than exp. 1 indication that the remediation in total was more successful in exp. 1. It may also be interpreted as an indication of precipitation of CuOx in or on the wood chips, and maybe that the precipitate dissolves to a certain extend during the remediation where the wood chips are covered with tap water.

The main conclusion based on these experiments is that the soaking is desirable for the process, but the reuse of the soaking solutions has to be investigated further.

Three different wood size fractions have been remediated and the results indicate that the remediation efficiency increases with decreasing wood size. The remediation of wood chips < 2 cm was significantly better than the remediation of the larger wood sizes. Further investigations are needed to locate the reason but lack of total soaking of the inner part of the larger fractions may be part of it. If the wood is not soaked all the way through, then it is not expected that the current will pass here, since this is believed to be the part of the chip with highest electric resistance. If the soaking solution does not reach the inner part and the current does not pass through, then the CCA will not be removed. To further investigate this possibility, laboratory experiments are planned using vacuum soaking of the wood to insure total soaking prior to the remediation.

In the upscaling process the electrode distance was one of the main factors to be evaluated. The results obtained here indicated that the remediation efficiency decreased with increasing electrode distance. The main problem in estimating the influence of the electrode distance is that the current

and voltage drop was similar in all experiments since the current was kept as high as possible in the experiments. It is believed that the voltage drop has an influence on the remediation efficiency and since the voltage drop is similar in the two extremities it may not be comparable. Instead a power supply with a higher voltage range is needed for these experiments, to ensure that the V/m may be the same in the experiments to be compared. The use of collecting units is expected to insure that the remediation time is unaffected by the electrode distance, since the distance the ions have to travel before being collected may be the same. This theory has to be verified with the above mentioned power supply.

The highest removal of both Cu, Cr and As was obtained in exp. 3, where 87% Cu, 81% Cr and more than 95% As was removed during remediation. In this experiment the electrode distance was 60 cm and just under 100 kg wood chips of medium size fraction (2-4 cm) was used. When the electrode distance was increased, the removal of Cu and Cr was decreased. In exp. 6 where the electrode distance was 150 cm and 250 kg wood was remediated, 58% Cu and 54% Cr was removed. On the other hand the remediation of As didn't decrease with increasing electrode distance. In the same experiment 96% As was removed. This is a very encouraging result since As is the CCA component of most concern and the main reason why incineration of CCA-treated wood is not allowed in Denmark. In the life cycle presented here, the wood is used as a bio fuel. In order to use CCA-treated waste wood, it is assumed that the concentration of Cu, Cr and As must be reduced to practical zero value first. Instead it is possible that remediated wood, where As has been removed and the concentration of Cu and Cr are reduced can be used in a conventional waste incineration plant. Thereby the energy resource of the wood may still be utilised.

Acknowledgements

The financial contribution of the LIFE financial instrument of the European Community are greatly appreciated.

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