

# The use of an electric field for the removal of alum from treated wooden objects

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## **Abstract**

In this paper the removal of sulfate and aluminum ions from waterlogged alum treated wood with the use of an applied electric field is in focus. Removal of alum is seen as the first step towards re-conservation of the wood with e.g. PEG. Alum treated wood samples from the Hjortspring finds (app. 350 BC) was used in this investigation and a total of six experiments are presented here. An electric DC field was applied across the wood for 4-20 days. A constant current of 1-5 mA was applied and the corresponding voltage drop initially low, often below 10 V. At the end of the experiments sulfate has moved as expected towards the positively charged electrode (anode) and after 20 days only 10% of the sulfate was left in the wood. The majority of the sulfate was removed with the use of the electric field. It was shown that it is possible to apply the electric field and remove sulfate in both experiments with and without presoaking. Aluminum tended to be removed more slowly and even after 20 days only minor amounts of aluminum was removed from the wood, The power consumption was low, only 1.6 Wh after 20 days. An increase in pH near the anode was found in some of the experiments. The reason is not obvious and further experiments are needed to evaluate the reason for this. Total removal of alum was not obtained in the experiments reported here, but the high conductivity and the transport of the measured ions due to the electric field indicates that an applied electric field as a method for removal of alum and other unwanted ions from treated objects should be further investigated. Research is ongoing and distribution of potassium after treatment will be measured in the near future.

## 1. INTRODUCTION

Alum is not used for conservation of waterlogged wood today, but it was widely used in Denmark, Norway and Sweden up until 1960. This means that many important finds have been treated with alum, including the Hjortspring find, an Iron Age find from Denmark and the Norwegian Oseberg find, considered the most richly ornamented Viking Age find in the world.

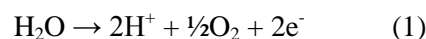
In alum treated wood, the ingress of alum into the wood was limited to the outermost mm, and the inner part of the object has thus been left unimpregnated. The shape of the object may thus be preserved, but the untreated wood in the center has often shrunk during drying, causing internal cracking. Even after drying, the crack formation is ongoing and this may be attributed to mechanical tension and ongoing decay of the wood. The alum treatment made the wood heavy and brittle, but the strength of the wood was not improved. Alum treated wood is also subject to structural pulverization which may eventually cause the total destruction of the artifact. The disadvantages of the alum treatment method have resulted in different attempts at re-conservation. At the Danish National Museum this is presently done by extraction of alum in water at room and elevated (80°C) temperature, followed by re-conservation with PEG. The water is changed multiple times during the extraction until the removal of alum has ended (monitored by conductivity measurements).

A Nordic collaboration involving the Technical University of Denmark, the National Museum of Denmark, the University of Oslo, and the Swedish National Heritage Board are currently trying to work across borders in an attempt to solve the problems of the alum-treated wood.

One attempt is to investigate the possibilities of removing alum from the wood by electromigration. In this method an electric DC field is applied across the wood sample and the alum ions ( $K^+$ ,  $Al^+$  and  $SO_4^{2-}$ ) are transported by the electric field out of the wooden object.

At the Technical University of Denmark the use of an electric DC field to transport ions in porous materials has been a research area for the last 15 years. Initially the method was developed for removal of heavy metals from polluted soils, but it has also been used for e.g. removal of copper, chromium and arsenic from impregnated waste wood [1] and in-situ impregnation of wood with copper or boron [2]

When an electric field is applied across a moist porous material, the electric current is carried by ions in the water matrix of the material. This is known as electromigration. The ions will move according to their charge, positively charged ions (cations) will move towards the negatively charged electrode (cathode) and negatively charged ions (anions) will move towards the positively charged electrode (anode). In the electrodes current is carried by electrons and at the electrodes the current change from being carried by ions to being carried by electrons and vice versa. At the anode oxidation takes place and at the cathode reduction processes occurs. The transported ions takes part in the electrode processes and with inert electrodes, oxidation and reduction of water also takes place. At the anode acid is produced:



and at the cathode base is produced:



The electrode processes (1) and (2) will result in pH changes near the electrodes and the produced ions will also move in the electric field, so an acidic front will emerge from the anode and an alkaline front from the cathode unless actions are taken to prevent this. In the experiments reported here the electrodes are placed in a clay poultice designed at DTU [3] that are used to neutralize the acid at the anode and to some extent it is also capable of hindering the alkaline front from emerging. In addition to pH control, the poultice also serves as a reservoir for the removed alum ions and ensures an optimal contact between the electrodes and the wood without damaging the wood.

## 2. EXPERIMENTAL CONDITIONS

The wood used for these experiments are alum treated samples from the Hjortspring find. The experimental setup is shown in figure 1. The wood is placed between two mesh electrodes, which are placed in a clay poultice. The anode (to the right) is an inert titanium electrode and the cathode (left electrode) is steel. A DC power supply (HP3612A) is used and a constant current is applied to the electrodes.

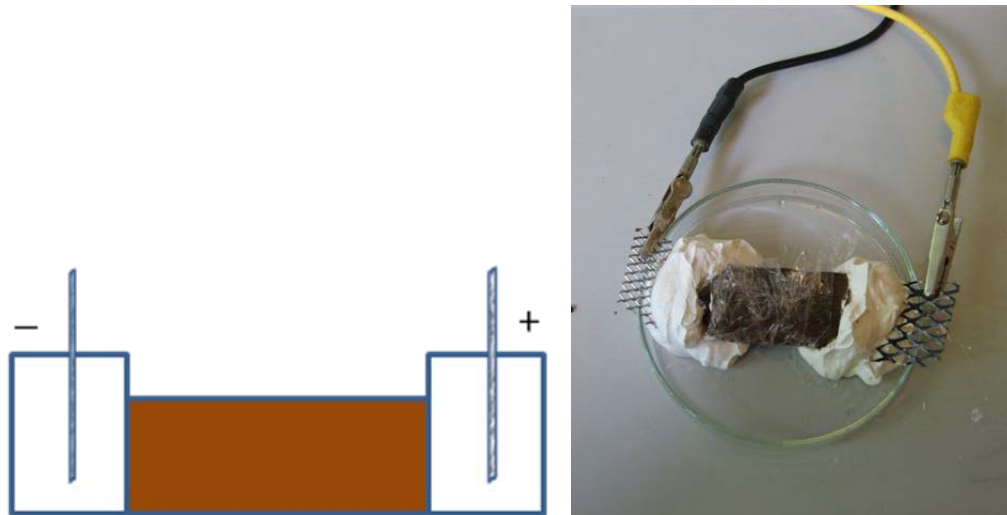


Figure 1: experimental setup. The wood sample is placed between two electrodes placed in poultice. Right picture: experimental setup of experiment A1.

The wood sample is orientated with the length of the sample between the electrodes.

In some of the experiments the wood was presoaked in water before the electrokinetic treatment.

During the experiment current and voltage drop is monitored and in some cases the current is adjusted to optimize the electro migration. The clay poultice is changed during the experiments to evaluate the transport rate of aluminum and sulfate during the experiments and also the change of poultice is used as a solution if the voltage drop (and thereby resistance) increases drastically. The experimental conditions are summarized in table 1. A1 was the longest running experiment (20 days) and A2 was a reference experiment to A1 with no current applied. In A3 the current was increased to initially 5 mA and later 3 mA. Experiment A4 was placed in a desiccator, above water (RH close to 100%) to avoid the wrapping of the sample in plastic. In A5 we used same setup as in A4, but without soaking the sample in water first. In A6 the sample was placed outside the desiccator and only slightly covered with a piece of plastic to protect the setup from spills etc. from the work in the laboratory. Sample A1-A4 was soaked prior to the experiment, sample A5 and A6 was not.

At the end of the experiments the wood piece was divided into four slices and dried at 40°C for 48 hours before the analysis. The slices are numbered 1-4 with slice 1 being closest to the anode and slice 4 closest to the cathode. Concentration of aluminum and sulfate was measured in the wood, clay poultice and the soaking solution. Aluminum was measured with ICP after pressurized digestion of 0.25 g wood in 10 ml concentrated nitric acid. Sulfate was measured with ion chromatography after extraction of the wood sample in distilled water for 1 hour with a wood: water ratio of 1:8 w/w. The extractions was also used for measuring pH of the samples.

Table 1. Experimental conditions

Experiment	Dimensions <sup>1</sup> (l,w)/mm	soaking	Current /mA	Duration/days	Set up	Poultice change
A1	50,35	45 min.	1	20	Wrapped in plastic	Day 1, 8,15
A2	46,35	1.5 hour	0	20	Wrapped in plastic	None
A3	53,23	3 hour	3-5	4	Wrapped in plastic	Day 1
A4	32,32	1,5 hour	2	9	In desiccator, above water	Day 7
A5	37,28	None	1-2	7	In desiccator, above water	Day 5
A6	42,24	None	2	9	On table	Day 2,5

<sup>1</sup>length and width of the sample. The height was between 10 and 18 mm.

### 3. RESULTS AND DISCUSSION

In table 2 the distribution of sulfate and aluminum after the experiments are shown with the charge and energy consumption of the experiments. The charge consumption is an expression of how much charge was moved in the experiment and the energy consumption is an expression of how difficult is was to move the charge. In two experiments with the same charge consumption, higher energy consumption is a sign of higher resistance in the system. The lowest energy consumption was seen in A1 and this was also the experiment with the highest charge transfer.

Due to difficulties with the analytical equipment all measurements of sulfate and aluminum was done at the same time; after the end of experiment A6. This made it impossible to design a setup for one experiments based on the removal rate of sulfate and aluminum in the previous experiments. The results imply that it would have been possible to obtain higher removal rates of at least sulfate if the duration of the experiments had been prolonged. This is taken into consideration in the ongoing research.

Table 2: Results from experiment A1-A6

	Charge transfer (C)	Energy consumption (Wh)	Distribution of SO <sub>4</sub> at the end of the experiments (mg/% of total)				Distribution of Al at the end of the experiments (mg/% of total)			
			Soaking	Anode clay	Cathode clay	Wood	Soaking	Anode clay	Cathode clay	Wood
<b>A1</b>	1686	1.6	<b>187</b> (26%)	<b>400</b> (56%)	<b>57</b> (8%)	<b>72</b> (10%)	<b>16</b> (23%)	0	<b>0.5</b> (1%)	<b>52</b> (76%)
<b>A2</b>	-	-	<b>260</b> (26%)	<b>66</b> (7%)	0	<b>681</b> (68%)	<b>28</b> (19%)	0	0	<b>120</b> (81)
<b>A3</b>	533	7.4	<b>232</b> (24%)	<b>93</b> (10%)	<b>9</b> (1%)	<b>640</b> (66%)	<b>21</b> (13%)	0	0	<b>139</b> (87%)
<b>A4</b>	1509	8.4	<b>121</b> (14%)	<b>102</b> (11%)	<b>9</b> (1%)	<b>660</b> (74%)	<b>12</b> (9%)	0	<b>1</b> (1%)	<b>123</b> (91%)
<b>A5</b>	1091	11.7	0	<b>84</b> (12%)	<b>1</b> (0%)	<b>590</b> (87%)	0	0	0	<b>136</b> (100%)
<b>A6</b>	1453	13.5	0	<b>180</b> (10%)	<b>31</b> (2%)	<b>1562</b> (88%)	0	0	<b>1.5</b> (0%)	<b>320</b> (100%)

As shown in table 2, the removal of sulfate is dominantly towards the anode. This is expected since sulfate ions are negatively charged. For no obvious reasons sulfate is only measured in the anode clay and not also in the cathode clay in experiment A2. This was not expected, since no current was applied in this experiment, and the transport here from the wood into the clays is due to passive diffusion alone. It is however seen that the removal is six times higher in A1 where current was applied. The highest removal of sulfate was obtained in experiment A1, where only 72 mg (10%) was left in the wood after the experiment. It is highly likely that even higher removal could be obtained if the duration of the experiment was prolonged. In figure 2 the voltage drop of the experiments are seen and for experiment A1 the voltage drop did not exceed 4 V at any time during the experiment. This implies very low resistance in the system and a longer duration would be possible. In experiment A3 a current of 3 mA was applied initially, and since the voltage drop was low, the current was increased to 5 mA the next day. This however was too high and the voltage drop increased considerably during the next three days. A reduction of the current to 3 mA decreased the voltage drop, but only for a few hours and the experiment was therefore ended. The removal of sulfate to the anode was lower than in A1 even when it is taken into consideration that the charge transfer was lower in A3. This is often seen in electrokinetic experiments of this type, where the stressed situation caused by too high resistance, may not be fully reversible. In A4 the lower current and the change of setup to the desiccator resulted in a lower resistance of the system. The resistance increased significantly after nine days (see figure 2) and the experiment was ended. The low removal rate of sulfate (11%) is discouraging since the charge consumption is in the same range as A1, but it is likely that a higher removal of sulfate could be obtained if the clay poultice was replaced with new instead of ending the experiment.

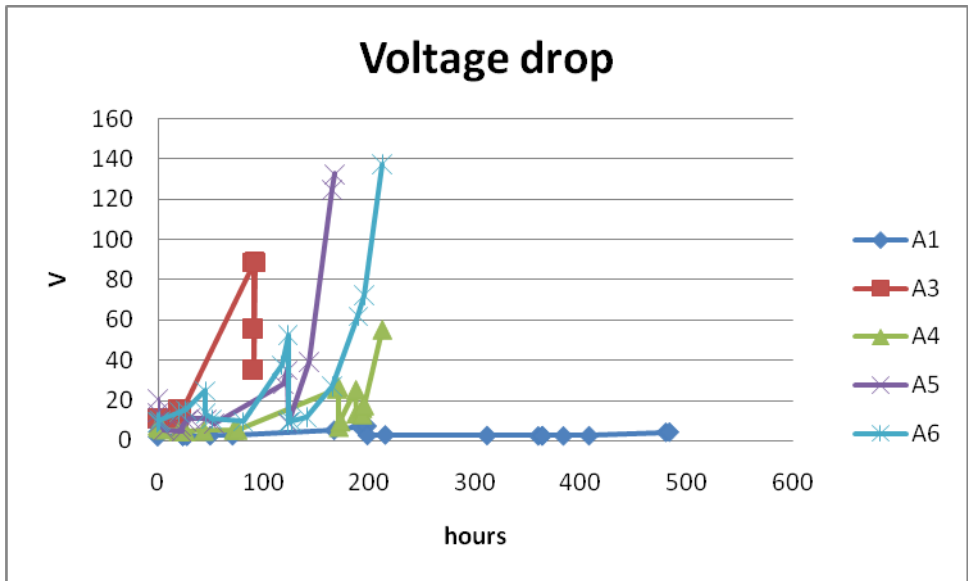


Figure 2: voltage drop in experiment A1 and A3-A6.

In A5 and A6 the objective was to investigate the possibilities of removing alum from wood without presoaking. A5 was the first step, where the wood sample was placed in high RH (in a desiccator above water). The results showed that it was possible to apply the field without presoaking and 84 mg (12%) of the sulfate was found in the anode poultice at the end of the experiment. As in experiment 4 a higher removal seems likely if the poultice clay was replaced instead of ending the experiment after seven days. Since the electric field was easily applied to the dry sample in the desiccator, A6 was made with the intention to investigate if a high humidity was necessary for the success of the experiment. In A6, the setup was placed at a table in the laboratory and the results were very promising. It was possible to remove 180 mg (10%) of the sulfate in this experiment and with poultice replacement additional removal of sulfate is foreseen.

The removal of aluminum was not successful. The best result was obtained in experiment A6, where 1.5 mg aluminum was removed. The removal seems to be towards the cathode, indicating aluminum being present as cations, however higher removal to either side is preferred before the speciation may be identified.

Both in the wood and in the poultice, pH was measured after extraction in distilled water. The results are presented in figure 3.

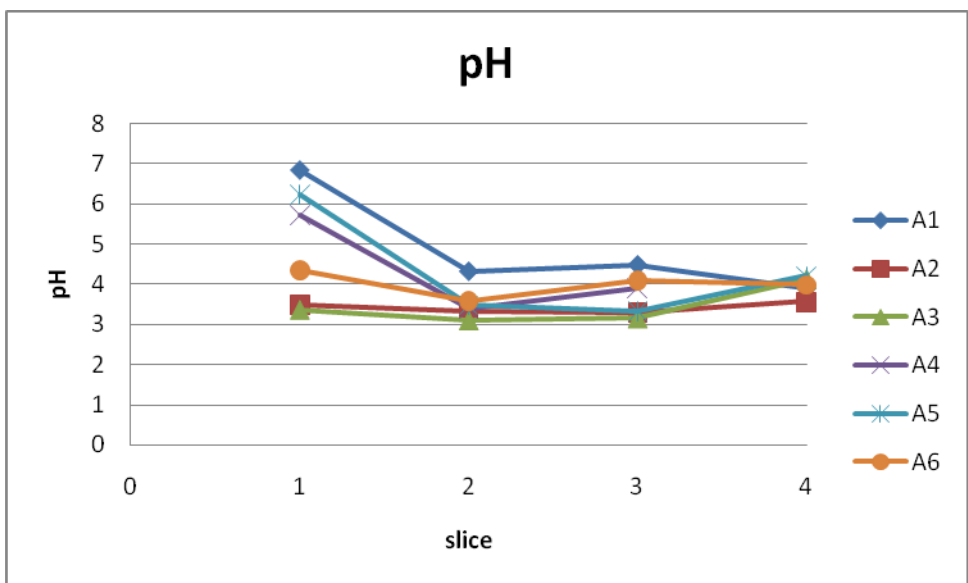


Figure 3: pH in wood at the end of the experiments. Slice 1 closest to the anode, slice 4 closest to the cathode.

In experiment A2 no current was applied and this may be used as a reference for A1, since the samples for A1 and A2 were cut from the same piece of wood. In A2 pH is between 3 and 4 all through the wood. In the rest of the experiments the initial pH is unknown, however a series of pH measurements were made on different pieces of alum treated wood and using the same method for pH measurements, pH values between 2 and 4 was measured. In experiment A1, A4 and A5 a significant increase of pH is seen in the wood near the anode. The reason for this is not clear, however it seems evident that the clay poultice is capable of neutralizing any acid being produced at the anode. It is most likely caused by redistribution of ions in the wood. Further investigations are needed to evaluate why the increase in pH is seen in these experiments and not the others.

#### **4. CONCLUSIONS**

The objective was to investigate the possibility of using an applied electric field to remove alum (aluminum, potassium and sulfate) from treated wood. Due to analytical reasons, the distribution of potassium has not yet been measured, but the results will hopefully be available in the near future.

A series of six experiments are reported here and in all the experiments where current was applied, sulfate was removed to some degree. The removal was towards the anode, in agreement with sulfate ions being negatively charged. The removal of aluminum was very low and insignificant. It should however be taken into consideration that removal rates of potassium were not measured. It is highly likely that potassium was also moved towards the cathode by the applied electric field and possibly more easily than aluminum. This may be part of the reason for the lack of aluminum removal. Also aluminum may be present as an oxide, either charged or uncharged or precipitated. More information of the aluminum speciation is needed to establish this.

In experiments where presoaking was used, a significant amount of sulfate and aluminum was removed in the soaking step. This may be the preferred method, since the current then targets the more unavailable ions in the wood. However there may be situations where soaking of the wood is unwanted and the results from experiments A5 and A6 shows that this is also possible with the electrokinetic method. Research is ongoing and experiments with longer duration and more frequently poultice clay replacements are planned.

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