

The Presence of Sulfuric Acid in Alum-conserved Wood – Origin and Consequences

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Abstract

Art objects and archaeological finds have undergone restoration and conservation treatments in the past ca two hundred years. One does not need to be a prophet to forecast that historical conservation and restoration treatments and their consequences will be an issue that conservators and conservation scientists will meet with increasing frequency. Among wooden objects, conservation using alum salts has played and still plays an outstanding role: it was widely used in Scandinavia, but also worldwide. Today many objects are damaged or threatened by the consequences of this treatment. The objects are brittle and have a tendency to disintegrate. It is assumed that the presence of sulfuric acid plays a central role in the still active deterioration process.

The alum-conservation method

An understanding of the observed deterioration of the alum-treated finds from Oseberg is the subject of investigations presented in this paper. These finds represent the world's richest collection of wooden objects from the Viking Age. The objects, found in a grave mound on the 'Oseberg farm' near Tønsberg, Norway, were part of a burial ritual in 834 AD for two women of high standing. In 1904, the objects were recovered in a highly fragmented and waterlogged state. Many of the wooden artifacts were conserved using the alum-conservation method and they are now threatened by a slow, active deterioration caused by the method originally used to preserve them.

The treatment used for the Oseberg find is described in excavation publications as well as in archival material. The artefacts were treated as follows:

The fragments were immersed in large tanks of concentrated alum solution, heated to ca 90° C. The solution penetrated the wood, the alum salts recrystallized and supported the structure, allowing the artefacts to be dried with minimal dimensional change. Maintaining the fragment's dimensions allowed the pieces to be fitted together. The fragments were then impregnated with linseed oil and reconstructed using metal screws, pins, fills and modern wood. The reconstructed object was finally lacquered. Objects treated in this way include the three sleds, and wagon now displayed at the Viking Ship Museum in Oslo, in addition to hundreds of smaller finds.

The role of sulfuric acid

Recent collections surveys indicate the wood is highly acidic (pH 1) and mechanically weak, due to the formation of new cracks and extension of existing cracks formed during drying. It is thought that the low pH value of alum-treated wood is the main cause of active deterioration of the remaining wood polymers.

Experiments reproducing the Oseberg treatment were applied to freshly excavated archaeological poplar, fresh poplar, cellulose paper and lignin. FTIR analysis demonstrated that the alum treatment affects all samples at both RT and 90°C, with more degradation at 90°C. Aluminum ions, released from the alum salt upon dissolution, react with water to form various soluble and insoluble aluminum hydroxide species. This reaction is enhanced at higher temperatures, which explains the higher acidity obtained in alum solutions after heating (pH 0-2,5) than unheated solutions (pH 3,5-4). Precipitates formed in alum solutions heated to 90°C were identified by XRD to be aluminum hydroxide-salts, demonstrating the potential for mixtures of salts to also have been precipitated inside the Oseberg wood. Decomposition of alum in solution was compared with its decomposition/dehydration in solid form when heated.

The present contribution discusses the immediate effects of high acidity on newly alum-treated archaeological wood analyzed by FTIR, and compares it with Oseberg wood treated with alum 100 years ago. It also suggests a possible mechanism of acid formation. This knowledge will aid in designing preservation and re-treatment strategies.

1. INTRODUCTION

The preservation of archaeological wood has been and still is a challenge to conservation specialists due to its altered chemical structure and the heterogeneous nature of deterioration. One of the earliest methods to conserve this material was developed by C.B. Herbst in the 1850's and applied to the highly degraded waterlogged wooden finds from Viemose, Denmark [1]. Hot solutions of alum salts were used to impregnate the degraded wood such that it could maintain its dimensions upon drying. As it was one of the few methods available for treating waterlogged degraded wood [2], the alum conservation method gained recognition in museums worldwide. It was in use until the late 1950's when it was replaced by polyethylene glycols as an improved alternative.

During the 100-year use of the alum method, several variations of the method were applied to waterlogged wood. Varying concentrations of the alum salt, the temperatures used and the addition of compounds, such as glycerol are documented in older journals [1] [3].

In the past decade, surveys carried out by several museums have shown that alum-treated wood is unstable [4] [5] [6]. A major preservation challenge is that it is wood that has been treated by what is today an obsolete method; we simply do not know enough about it. Conservation records before 1960, if they exist at all, contain sparse information about the alum treatment. And because it is no longer in use, practical knowledge about applying this method (and the pitfalls it entails) has been lost. Though obsolete, newer generations of preservation specialists are faced with securing the thousands of objects treated with alum.

An understanding of the observed deterioration of the alum-treated finds from Oseberg is the subject of investigations presented in this paper. These finds represent the world's richest collection of wooden objects from the Viking Age. The objects, found in a grave mound on the 'Oseberg farm' near Tønsberg, Norway, were part of a burial ritual in 834 AD for two women of high standing. In 1904, the objects were recovered in a highly fragmented and waterlogged state.

The treatment used for the Oseberg find is described by Brøgger and Rosenqvist [3] [7] as well as in archival material [8]. The most deteriorated wood (e.g. birch/alder and maple) – which included several hundred objects and fragments, of which a significant number bear spectacular surface carvings – was treated as follows:

The fragments were immersed in large tanks of concentrated alum solution, heated to ca 90°C. The solution penetrated the wood, the alum salts recrystallized and supported the structure, allowing the artifacts to be dried with minimal dimensional change. Maintaining the fragment's dimensions allowed the pieces to be fitted together. The fragments were then impregnated with linseed oil and reconstructed using metal screws, pins, fills and modern wood. The reconstructed object was finally lacquered.

Recent collections surveys indicate the wood is highly acidic (pH 1) and mechanically weak, due to the formation of new cracks and extension of existing cracks formed during drying [4] [9]. FTIR spectra of Oseberg's alum-treated wood show by the broadening of the bands between 1800 – 1610 cm⁻¹, that the lignin is heavily degraded (oxidized), and it is generally much more deteriorated at all bands when compared to freshly excavated archaeological wood. Although the wood is mechanically weakened, it is likely the effects of the long term exposure to high acidity that have caused the material to become weaker over the 100 years since its conservation. We believe the low pH values are causing a slow, active deterioration within the wooden fabric¹. Low pH values are reported for most of the alum-treated objects in Denmark and Sweden [5] [6]. The source of acidity, however, has not been previously studied.

¹ It should be emphasized that a relatively large proportion of the alum treated wood from the Oseberg find was fortunately surface-treated with linseed oil. In contrast to the powdery, disintegrating mass of 'wood' beneath it, this coating (which has penetrated at the most ca 5 mm across the grain) has ensured the survival of the finely carved surfaces, due to its consolidating effect. Whether this coating proves to be a potential barrier to neutralizing and strengthening agents remains to be tested, but so far its preserving effect is unquestionable.

1.1 Aim of this study

Our starting point has been to understand the origin of the low pH measured in the wood. By answering this, we can evaluate whether the remaining alum salts represent a future threat to the objects or whether they are stable. In other words: must the alum be removed in order to stabilize the wood? This is an important question, because of the great risk involved in removing the alum salts from the most highly reconstructed objects, such as the sleds, wagon, and many others. By minimizing handling of these fragile finds, we also minimize risk of irreparable damage.

Experiments carried out:

1. Reproduction of the alum-treatment method used to conserve the Oseberg finds, based on general contemporary descriptions by Brøgger [3], without the addition of linseed oil or lacquer. Variation of the temperatures and concentrations of alum salts relative to the published method were also investigated.
2. The effect of pH on samples at different temperatures using sulfuric acid solutions was also studied. The pH range used for the sulfuric acid approximately mimics the pH ranges recently measured on the alum-treated wood.
3. Wood that was newly treated with alum in these experiments was compared with alum-treated Oseberg woods.
4. Effect of heating alum salts, in the solid state and in solution was studied.

2. MATERIALS AND METHODS

2.1 Sample description

The samples used in this study included fresh poplar (from a reference set), archaeological poplar cut into 1 cm thick sections from a 20 cm long fragment, (Viking Age, excavated in 2005 and stored at 4°C in water), chromatography paper (representing cellulose, Schleicher & Schuell, cat.no. 3001614) and extracted softwood lignin (Sigma Aldrich, cat.no. 471003). Archaeological wood samples were identified by light microscopy.

2.2 Sample treatment solutions

A total of 16 samples of archaeological poplar were treated with test solutions at each RT and 90°C. Twelve samples each of fresh poplar, chromatography paper and lignin were treated with test solutions at each RT and 90°C. Untreated samples were used as references for treated samples.

Alum solutions

Concentrations of 2 parts alum: 1 part distilled water (4.1 M) and 4 parts alum:1 part distilled water (by weight) (8.2 M) (aluminum potassium sulfate salts (Merck, pro analysi grade), were applied to freshly excavated archaeological poplar (*populus*), fresh poplar, chromatography paper (representing cellulose) and extracted lignin for a 24-hour period. To observe the effect of temperature, all samples were treated at both room temperature and at 90°C. pH values of the alum solutions and of treated and untreated woods were taken at both RT and 90°C (after cooling), using pH strips.

Sulfuric acid solutions

Four solutions of pure sulfuric acid were also prepared using distilled water, approximately representing the range of pH (0-3) measured on the wood in previous surveys. Samples of archaeological poplar, fresh poplar, chromatography paper and lignin were mixed with each solution for 24 hours. The treated samples give an immediate indication of the aggressiveness of the acidic environment on wood polymers at both room temperature and at 90°C.

2.3 Physical properties

The basic density of wood samples was measured by comparing the oven dry weight to the waterlogged volume according to Jensen and Gregory [10]. Average density for archaeological poplar was found to be 0.125 g/ml, comparable to that previously measured for alum-treated Oseberg wood (0,1 g/ml). Fresh poplar had a density of 0,436 g/ml.

2.4 Analytical instruments

Spectroscopic measurements were carried out on a Perkins Elmer Spectrum One FTIR-ATR unit, containing a ZnSe/diamond hybrid crystal, at a resolution of 4 cm^{-1} ; 32 scans were taken from each sample. One spectrum was taken of each sample.

XRD patterns of alum salts were recorded using a Siemens D5000 powder diffractometer.

3. RESULTS AND DISCUSSION

At room temperature, alum solutions are acidic, with pH values between 3.5-4. The pH of cooled solutions which had been heated to 90°C had a broader range, from pH 0-2.5, regardless of start concentration. If we compare pH values of archaeological samples treated with alum at 90°C – the same temperature under which the Oseberg finds were treated – with that of untreated archaeological wood there is a large difference: the alum-treated poplar has a pH value of approximately 2.5, while the untreated archaeological poplar had a pH value of 5 (fresh poplar had a pH value of 4).

3.1 Alum solutions

See Table 1 for peak assignments.

Below, only preliminary results of our investigations are presented as the changes observed in the infrared spectra are not as clear as expected. Infrared spectra were normalized before interpreting changes.

For **untreated archaeological poplar**, the main constituent is lignin [11] [12] [13] [14]. There are likely cellulose remains left, but all characteristic peaks for hemicellulose (1734 cm^{-1}) and cellulose ($1371, 1158, 897\text{ cm}^{-1}$) are not visible. The lignin is generally deteriorated, which is shown by signals in the region ($1615\text{-}1750\text{ cm}^{-1}$), attributed to increased signals due to C=O groups (carboxylic acids, aldehydes and ketones) [17].

It was difficult to evaluate **alum-treated archaeological poplar** with respect to the untreated references due to their heterogeneity of condition. Samples treated at 90°C were compared with those treated at RT. All samples except one showed increased absorbance at 90°C relative to room temperature. The greatest changes in spectra are located at 1122 cm^{-1} , corresponding to combined aromatic and C-O stretches (see Fig.1). Increased absorbance at 90°C may imply increased oxidation, which would be reflected in the region between $1610\text{-}1750\text{ cm}^{-1}$, however this is not observed in our experiments.

Although the **alum-treated chromatography paper** was mechanically weaker and more brittle, infrared spectra showed only small changes after treatment.

Alum-treated lignin showed general greater absorbance at 90°C vs RT when comparing samples of the same concentration, except at 1131 and 1028 cm^{-1} , where RT-samples have similar or slightly higher absorbances. This is contrary to that observed for the treated archaeological poplar, and may be due to the fact that the lignin in archaeological poplar is more degraded than the treated lignin, and will therefore show different deterioration patterns. It may also be due to the fact that we are comparing a softwood purified lignin to hardwood lignin in the archaeological samples. At 1211 cm^{-1} , alum-treated samples have a distinct peak which in the controls is only a shoulder, indicating that the guaiacyl ring signal could be enhanced due to deterioration of other components [13]. The 1632 cm^{-1} peak in the control sample broadened due to increased oxidation of the lignin in the region $1620\text{-}1800\text{ cm}^{-1}$ [17]. The 1337 and 1317 cm^{-1} peaks in control disappear in the alum treated samples. These small peaks may be due to the small amounts of syringyl moieties in softwood lignin (the sample tested), which are known to be more susceptible to general decay than the guaiacyl moieties, which dominate in softwood lignins [13] [16]. Treated lignin samples showed a shift from the 1038 cm^{-1}

peak (control) to 1028 cm^{-1} for all alum solutions, possibly indicating changes due to guaiacyl lignin deterioration.

In **alum-treated fresh poplar**, the lignin and carbohydrate moieties are likely affected (as also seen in chromatography paper) but the changes are not clearly visible in the FTIR spectra, except at 1102 cm^{-1} (cellulose) and at 1734 cm^{-1} (hemicellulose), where deterioration is reflected by reduced absorbance for treated samples.

3.2 Sulfuric acid solutions

FTIR analyses showed that sulfuric acid affected all samples at both RT and 90°C . Effect of temperature and concentration of acids did not follow a clear trend. It may be related to limitations in acid production due to equilibrium effects of both aluminum and sulfuric acid [15], which is planned to be investigated more thoroughly.

3.3 Comparison of newly-treated archaeological poplar with Oseberg samples:

The alum-treated Oseberg wood analyzed originated from the same fragment (birch/alder?), which had fallen apart into 6 'slices', each slice showed a gradual increase in deterioration relative to the one before it which was *visible*. This increase in visible deterioration was also reflected in their spectra. pH values of the slices were similar (0,5-1) and did not reflect the varying visible states of deterioration.

The spectra from Oseberg wood show signals dominated by lignin (see Fig.2). As the degradation of the Oseberg wood increases, spectra where absorbance was maximized against the peak at 1118 cm^{-1} showed an increase in absorbance and in band width in all regions (lignin). All of the Oseberg woods had much broader, less-defined bands than the newly alum-treated archaeological wood. This is especially evident in the region $1590\text{-}1220\text{ cm}^{-1}$. Between $1615\text{-}1820\text{ cm}^{-1}$, absorbance also increases with increasing deterioration, showing that deteriorating lignin over time becomes increasingly oxidized to acidic groups, the most degraded sample exhibiting a clear peak at 1701 cm^{-1} . At 1029 cm^{-1} , the absorbance decreases with increasing degradation, likely of the remaining lignin (guaiacyl).

The reason for the large difference between newly treated archaeological wood and that which had been treated 100 years ago indicates an ongoing process of deterioration with time. It may be related to the general high acidity of the wood caused by the alum treatment at 90°C . Experiments with sulfuric acid solutions showed that deterioration of wood polymers at RT over only a 24 hour period can occur. Although the mechanisms involved in the breakdown of alum-treated wood cannot be elucidated through these experiments, the effects of acidic-related deterioration over time which have caused the observed stated of deterioration of the Oseberg wood are clearly reflected in infrared spectra.

3.4 The behaviour of alum salts during heating

Alum-conserved wood from Oseberg exhibits a pH of ca 1, whereas a solution of alum at room temperature has a pH of ca 3.5. The increasing acidity indicates that during treatment and/or during storage (additional) acid has been released.

Initial reconstruction experiments as used on the Oseberg finds show that temperatures of $80\text{-}100^\circ\text{C}$, lead to a decomposition of alum and the formation of sulfuric acid. Strips of cellulose paper were partly immersed in an alum solution with a concentration as used in the original treatment (2 parts alum: 1 part water), and heated to $90\text{-}95^\circ\text{C}$. The part of the paper above the solution was blackened and destroyed, indicating the action of strong acid. This observation initiated a closer consideration of the effect of heat on alum salts in solid form and in solution.

3.4.1 Heating of alum solutions

A solution with a concentration of 5g/50ml was heated up to 95°C for 30 hours. A white precipitate formed, which after drying was identified by means of XRD as potassium aluminium sulfate hydroxide, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ [PDF 47-1885]. The pH value of the solution had decreased to 2.

The likely reaction is:



Precipitation of $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ is a quite slow process; nevertheless, one has to take into account that the original treatment took up to 32h, and that the same bath was used for several treatments. This leads to an enrichment of aluminum hydroxides, which results in increased acidity.

Further investigations have to be carried out to evaluate whether aluminum hydroxide compounds cause changes equilibrium over time by reacting with lignin or other wood components, which would result in an increase in acid content of the wood.

3.4.2 Heating of crystalline alum

Heating of crystalline alum leads to a loss of crystal water. However, in the literature, descriptions of the dehydration process between 20 -100°C and identification of hydrates formed in this temperature range are inconsistent and contradictory. Aside from the maximally hydrated $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ and the water-free $\text{KAl}(\text{SO}_4)_2$, the existence of different intermediate hydrates, containing 3-, 4-, 6-, 7-, 8- and 9- water molecules as defined chemical species are given in different sources.² [18] [19] [20] [21] [22]

At 92°C alum melts and the remaining crystal water evaporates. ‘Burnt Alum’ (*alumen ustum*) is formed, a porous, amorphous mass, which was used as a drug in earlier times. Further heating leads to recrystallization of water-free alum, and the formation of steklite $\text{KAl}(\text{SO}_4)_2$ [23].

Whereas the formation of ‘burnt alum’ and steklite is confirmed by our experiments, the question of the existence of different hydrates in the temperature range between 20 -100°C needs re-consideration. Initial XRD measurements indicate the presence of such compounds in alum-treated wood from Oseberg as well as from newly alum-treated wood made in reconstruction experiments. Knowledge of identity and properties of the salts existing in the Oseberg wood are important for the understanding of the behaviour of alum-conserved objects in museums at different RH levels and under fluctuating climate conditions.

4. CONCLUSION

Even if several mechanisms are likely involved in the deterioration process of the Oseberg alum-treated woods, making it difficult to elucidate completely, experiments reproducing the original alum treatment, under various conditions (temperature, concentration and pH) have led to a better understanding of the deterioration process. This knowledge will in turn be used as a foundation upon which stabilization strategies can be developed, which involve neutralization and strengthening steps.

FTIR proves that alum solutions, at both RT and 90°C, are capable of degrading cell wall material in archaeological wood and fresh wood. Extent of degradation does not always correlate with the alum concentrations used in this study (2:1 and 4:1 alum:water). Generally, the deterioration is enhanced at 90°C. Further investigations will involve the use of additional analytical techniques, such as HPLC, to identify decomposition products formed in the wood.

² In 1929, Krauss et al. stated that publications on alum salts and their hydrates are ‘*außerordentlich zahlreich [und] sich oft widersprechend*’ (very numerous and often contradictory) – this situation continues today. Powder data references exist in the ICDD data base, but they are marked as ‘questionable’.

Measured acidity of alum solutions at RT and 90°C (after cooling) are different: for RT, pH values were between 3,5-4; at 90°C measured values ranged from pH 0-2,5 regardless of start concentration. Higher temperatures increase the reaction rate of the aluminum ion with water, forming aluminum hydroxides and hydrogen ions [15].

XRD analyses of the heated alum solution identified one species of aluminium hydroxide precipitate. During treatment with alum, aluminum is likely partially precipitated onto the cell wall of the wood, and partially in the solution vessel in form of aluminum hydroxy salts with potassium and sulfate. Different forms of recrystallized salts likely exist in the wood, which have yet to be identified.

Heating of solid alum also leads to its decomposition and formation of sulfuric acid. FTIR was used to observe deterioration patterns caused by sulfuric acid solutions at pH 0, 1, 2 and 3 at RT and 90°C. Treatment of archaeological wood with sulfuric acid confirms that deterioration in wood is possible even if exposed for 24 hrs at RT. Today's highly degraded condition of the Oseberg alum-treated wood may illustrate the effect of an acidic environment over a 100-year period.

Further work has to be carried out to clarify whether the acid generated during treatment in alum solutions is the only source of acidity in the wood. This will involve characterization of the salts in the Oseberg wood (e.g. identity, solubility, pH sensitivities), and investigation of their behaviour. If the salts prove to be stable in relation to the future stabilization procedures applied to the wood, it is not imperative to remove them, mitigating a risky step towards the stabilization of these fragile finds.

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Table 1 gives an overview of the main bands examined in the FTIR spectra. Wavenumbers from spectra in this study are given in parentheses when they differ from references.

Wave number (cm ⁻¹)	Assignment	Reference
1734	Unconjugated C=O groups in lignin and carboxylic acid ester hemicellulose	[11]
1711 (1701)	Unconjugated C=O stretch	[12]
1665	C=O conjugated aldehyde and ketone	[17]
1650 (1632)	Adsorbed O-H; conjugated C-O cellulose	[13]
1592	Conjugated C-O; Aromatic skeletal vibration, lignin	[12]
1502 (1504)	Aromatic skeletal vibration, lignin	[12]
1462 (1458)	C-H deformation, lignin + carbohydrate	[12]
1425 (1420-1422)	C-H in-plane deformation combined with aromatic ring stretch; C-H deformation in carbohydrate + lignin;	[12]
1371	Symmetric C-H deformation carbohydrate + C-H bending carbohydrate	[11]
1330 (1337)	O-H in-plane deformation and C-H deformation, cellulose; C-O vibration syringyl lignin;	[11]
1319 (1317)	C-H vibration, cellulose; C ₁ -O in syringyl lignin;	[11]
1218 (1211)	C-O guaiacyl lignin	[12]
1158	Asymmetric C-O-C vibration carbohydrate	[13]
1122 (1119)	Aromatic skeletal and C-O stretch	[13]
1112 (1102)	Glucose ring stretch	[12]
1026 (hardwood); 1030 (softwood) (1038 shifts to 1028)	C-O primary alcohol; C-H guaiacyl lignin	[12]
898 (897)	C ₁ group frequency in cellulose + hemicellulose; C-H deformation cellulose; Glucose ring stretch, cellulose	[12]

Figure 1. Comparison of peak at 1122 cm⁻¹ for the alum treated samples of archaeological poplar. Two samples of each alum concentration (2:1 and 4:1 parts alum:water) and temperature (room temperature (RT) and 90°C).

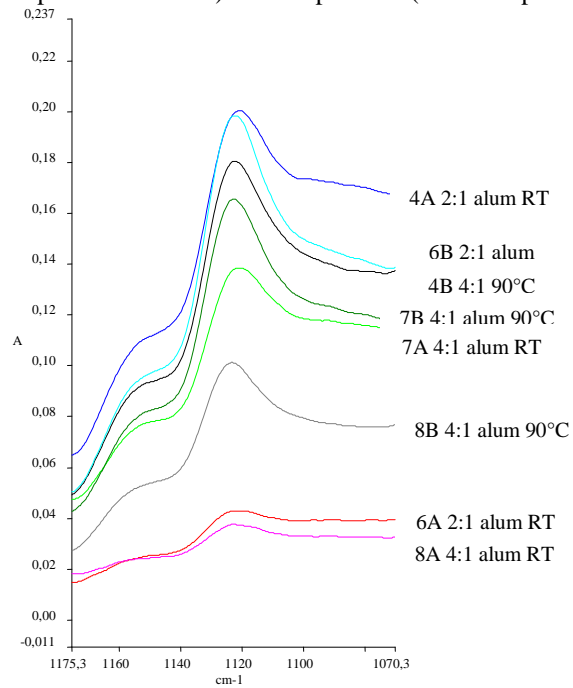


Figure 2. Comparisons of fresh poplar, untreated archaeological poplar, archaeological poplar treated with 2:1 alum:water at 90C in these studies. FTIR spectra are compared to Oseberg's alum-treated wood, conserved 100 years ago using the same method.

