UNIVERSITÀ DEGLI STUDI FIRENZE

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“Nanotechnologies for the restoration of alum-treated archaeological wood”

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Introduction

Wood is a complex material, made mainly of cellulose, which has been widely used for the realisation of different objects and artworks.

Several mechanisms, such as acid hydrolysis and oxidation, might promote the degradation of this material, inducing the depolymerisation of the cellulose chains and the loss of mechanical strength. The degradation pathways of this material are still under study, as well as the short/long term effects of the conservation treatments that have been proposed so far. Particularly complex is the treatment of waterlogged wood: in fact, as the excess of water is released, the object shrinks and decreases in size. Different conservation approaches have been proposed and applied with the aim of preserve the wood surface and maintain unvaried the dimensions of the objects during the drying of the wood. From the mid-19th century to the 1960s in Scandinavia, heated alum solutions, $KAl(SO4)_2 \cdot 12H_2O$, were the most commonly used treatment for waterlogged wood. The rational behind this was to replace the water in the wet degraded wood with alum, lending structural support and enabling it to dry without collapse. However, the treatment with alum has several side effects: it does not fully and uniformly penetrate the wood, which is still prone to collapse. Moreover, the objects treated with this method show low pH values due to the development of highly acid regions.

The Oseberg ship (Viking Ship Museum, Norway)

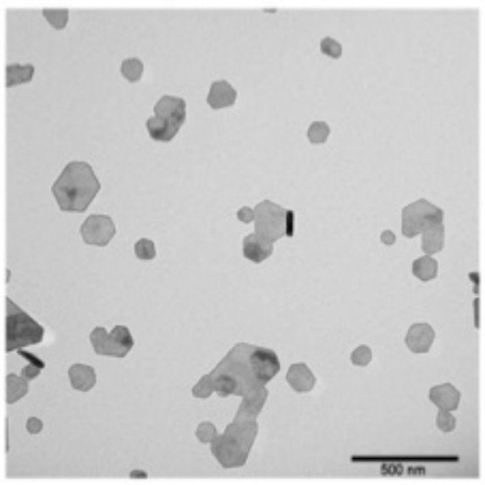
Aims

The aim of this research was to design a conservation protocol for archaeological waterlogged woods that have been treated with alum, such as the wooden objects of the “Viking Ship Museum” in Oslo. The artefacts of this collection show low pH values due to the treatment with alum. Thus, the first conservation approach tested was the use of calcium hydroxide nanoparticles dispersed in low chain alcohols as deacidifying agents.

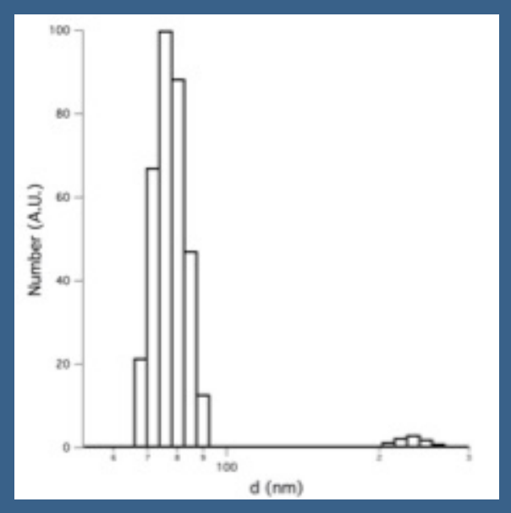
Materials and methods

Archaeological wood samples (both softwood and hardwood samples) dated to 975-1150 AD have been used. The samples were found in 2005 in a site called Presterød (Tønsberg in Norway) and treated in 2013 with a “boiled” alum solution for 24h and air dried.

Calcium hydroxide nanoparticles were synthesized in an autoclave system working at high temperature and pressure.



TEM image shows that particles are hexagonal platelets with a high degree of ordering and thickness of about 20-30 nm



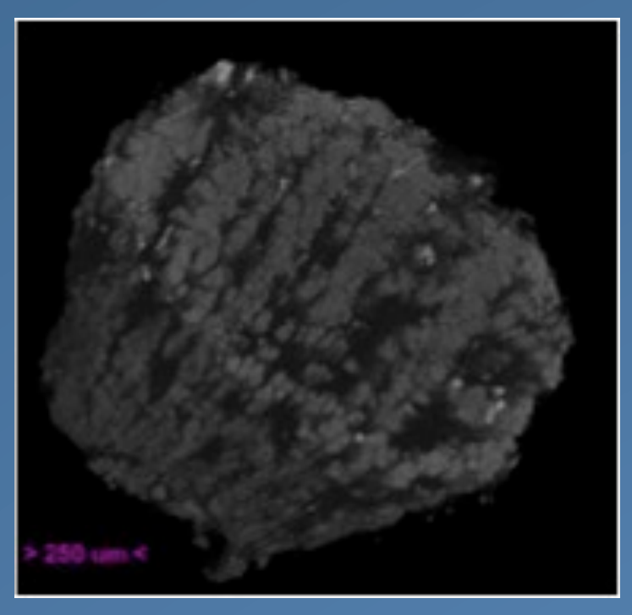
Size distribution of $Ca(OH)_2$ nanoparticles dispersed in ethanol obtained by DLS

Splinters cut from the alum-treated samples were immersed for 12 hours in the $Ca(OH)_2$ nanoparticles dispersion in ethanol (c=5g/L) and then left to dry in the air at 25 °C and 50% RH for 28 days.

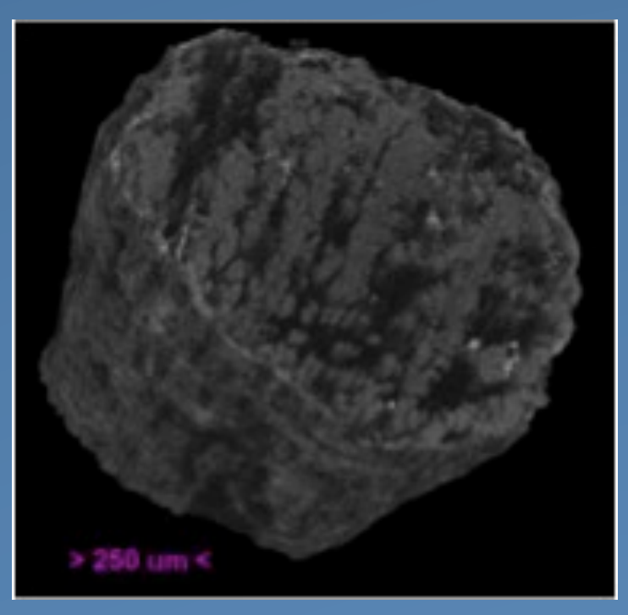
Samples were analysed, before and after the deacidification treatment, with Micro Tomography Micro-CT SkyScan 1172, Differential Thermogravimetry (SDT-Q600 Thermo Gravimetric Analyser), operating between 25°C and 1150°C at a heating rate of 10°C/min under nitrogen flow (100 mL/min) and with FTIR Bio-Rad FTS 40A. pH values were measured using a pH paper indicator by depositing a droplet of distilled water over the wood surface.

Results

pH measurements and Micro-CT images. The deacidification treatment raised the pH of the Norwegian samples from a starting value of 2.5 up to 5.



AaHW 0001, micro-CT 3D image about internal structure (before of deacidification treatment)



AaHW 0001, micro-CT 3D image about internal structure (after deacidification treatment)

Thermal Analysis

Thermograms of wooden samples in general show pyrolysis peaks of cellulose, hemicellulose and lignin. For the samples treated with alum, the peaks of cellulose and hemicellulose disappear and thermograms are characterised only by the pyrolysis peak of lignin (Tp) and of the products of alum combustion.
Main thermal reactions of alum:

1. Between 50 and 350 °C: endothermic: dehydration in several steps

$KAl(SO_4)_2 \cdot 12H_2O \rightarrow KAl(SO_4)_2 + 12H_2O$

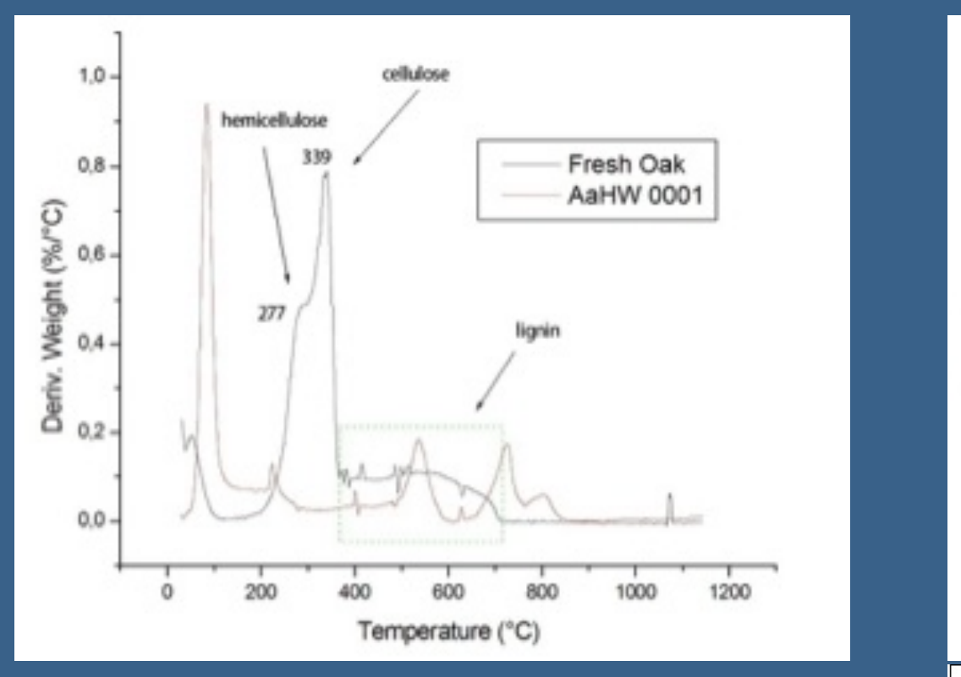
2. Solid phase decomposition

$KAl(SO_4)_2 \rightarrow K_2SO_4 + Al_2(SO_4)_3$

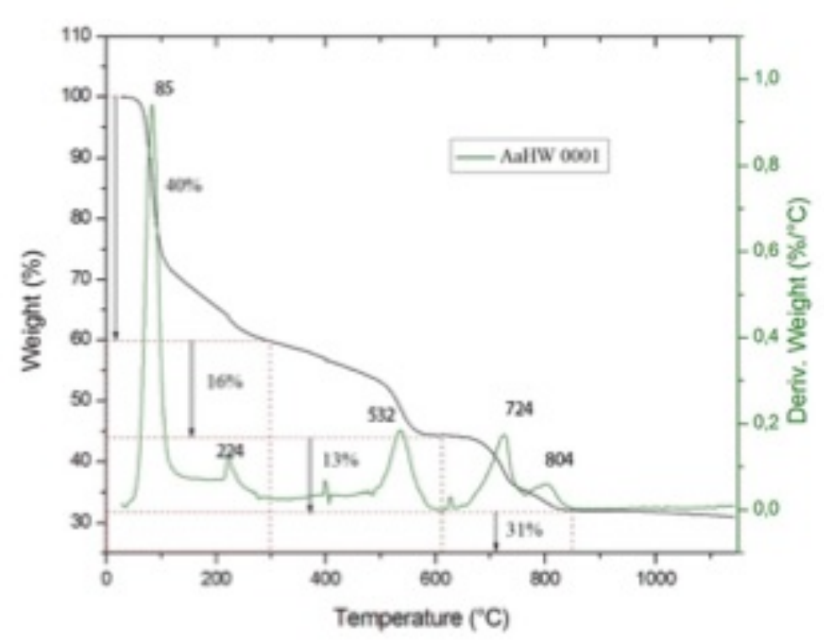
3. Between 750 and 950 °C decomposition of $Al_2(SO_4)_3$

$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$

4. At about 1100 °C: endothermic: decomposition of K_2SO_4

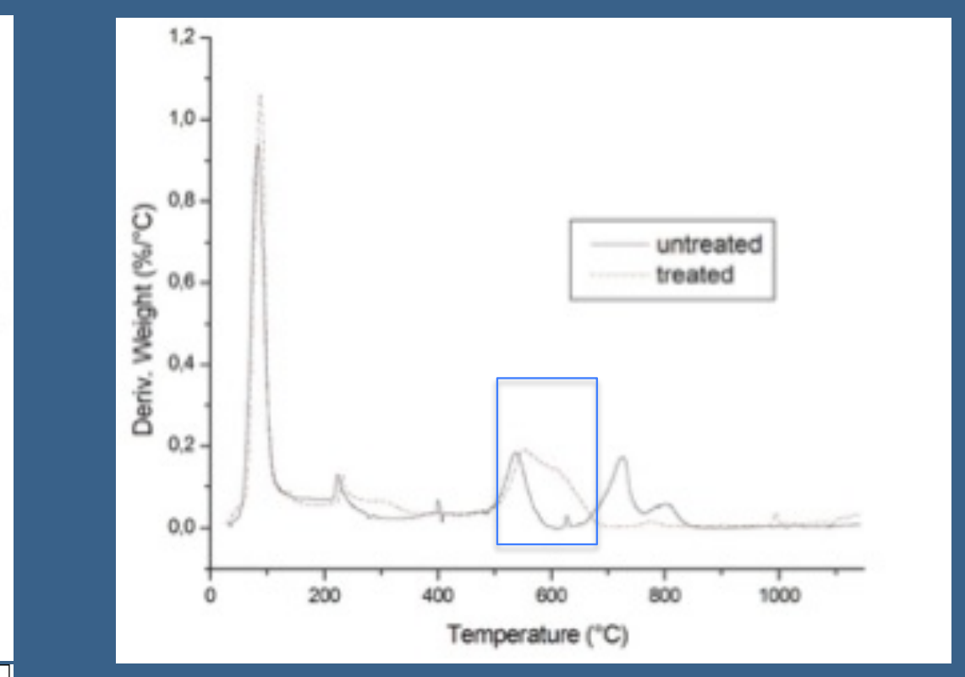


Comparison between DTG curves of fresh oak and alum-treated sample



	Water content	Lignin content	SO_3 moles of $Al_2(SO_4)_3$	Al_2O_3
AaHW 0001	40%	16%	13%	31%

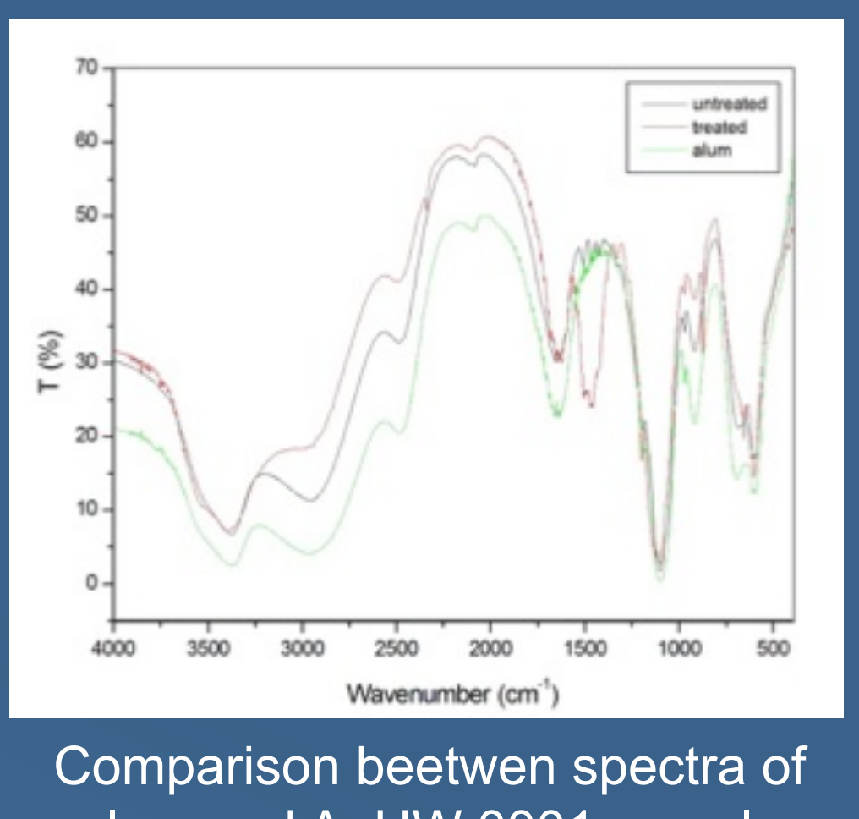
TG and DTG curves of the sample AaHW 0001 as received



Comparison between DTG curves of AaHW 0001 sample before and after deacidification treatment. After treatment Tp of lignin is increased from 532 to 548 °C

Infrared analyses of wood samples

IR spectra show that samples treated with alum solution at 90°C miss the characteristic bands of hemicellulose (1738 cm^{-1}) and cellulose (1371, 1158, 897 cm^{-1}). All spectra show a peak at 3371 cm^{-1} due to stretching of OH group, one at 1647 cm^{-1} due to the bending of hydrogen water molecules, and two other peaks at 1097 cm^{-1} and 603 cm^{-1} due to the S=O stretching and S – O stretching, respectively. There are week peaks below 600 cm^{-1} maybe due to the Al – O stretching.



Comparison beetwen spectra of alum and AaHW 0001 sample before and after treatment

The band 695 cm^{-1} can be due to the stretching vibration of $[Al(H2O)6]^{3+}$.
In the IR spectra, the absorption band with a maximum at 922 cm^{-1} is due to the pendulum vibration of water, the band at 974 cm^{-1} suggests that the vibration is due to SO_4^{2-} groups.
The spectra show weak peak of aromatic skeletal vibration of lignin at 1509 cm^{-1}.
The presence of an alkaline reservoir is suggested from peak at 1472 cm^{-1} assigned to CO_3^{2-} stretching.

Future work

- Study of the penetration of nanoparticles into the wood.
- Use of $Mg(OH)_2$ nanoparticles with a smaller size compare to $Ca(OH)_2$ nanoparticles.
- Design a new protocol base on the synthesis of hybrid nanocomposites made of TEOS and nanostructured calcium hydroxide.

References

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- Susan Braovac, Hartmut Kutzke, “*The presence of sulfuric acid in alum-conserved wood – Origin and consequences*”, Journal of Cultural Heritage 13S (2012) S203–S208.

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