

"From Material to Structure" MECHANICAL BEHAVIOUR AND FAILURES OF THE TIMBER STRUCTURES

Introduction

The original roof timber of many important historical buildings in the Czech Republic is seriously corroded by ammonium phosphate and sulphate-based fire-retardant coatings. In some buildings, application of such a coating was practised repeatedly within the span of a few years, which brought about accumulation of large quantities of the salts in the timber. The effect of the corrosion is a „halcy“ wood surface. This corrosion can finally cause serious degradation of the mechanical properties of the timber. There are known cases of breakdown of some timber in USA after application of the fire-retardant and of timber roofs in the Sydney area, Australia, which were corroded by sea salt.

Currently, wood degradation by loosening of the fibrous structure is mostly regarded as an aesthetic deficiency of the historical roof timber. It is associated with a loss of information conveyed by the timber surface, such as traces of working with tools.

The problem of degraded wood structure of the roof timber is being addressed so that the degraded wood is removed mechanically to leave the “healthy” wood in place and subsequently, a neutralization solution is applied to the timber. However, this remedy was found to be efficient for a limited period of time: in a few years after application, the wood degradation process sets in again. In addition, the technology of fire-retardant coating removal is unsuitable as a method of treatment of historical heritage, and a continual thinning of the structural elements is an undesirable side effect as well.



Figure 1 – View on the Vladislav Hall building. Figure 2 – View on Prague Castle. Figure 3 – fine fibers on wood surface has appeared again after conservation treatment. Figure 4 – The most damaged timber above the Vladislav Hall. Figure 5 – Detail of the corroded wood from the figure 4. Figure 6 – Fiber sample taken by tape from the wood surface.

Current state of the attics

Attics of the Old Royal Palace (Fig. 1 and 2) were treated many times by fire-retardants based on ammonium phosphate and ammonium sulphate. As a result of the treatment, damage appeared on the wooden surface – fiberized appearance. In the period 1997-2001 the attics were investigated and treated. The pH value of the wood was measured. The values varied from 4 to 5 depends on the location. The damaged wooden surface was cleaned by brushing and then was neutralized by solutions containing CaCO₃ and boric acid. Composition of the solution was chosen depending on wood acidity. The pH values increased to 5-6 after neutralization. Then some places were treated by preservatives based on boric acid. Wood corrosion appears again after few years from the neutralization treatment as shows figure 3.

Results of roof timber examination

Wooden samples from the attics of the Old Royal Palace (fig. 5 and 6) were taken and studied by pH value measurement, by electron microscopy and by infrared spectroscopy. Measurements of climatic conditions in the attics have been carried out since May 2007.

Ammonium phosphate and sulphate-based coatings cause wood corrosion, presumably through one or more of the following processes or their combination: acid hydrolysis; decrystallization of cellulose; thermal degradation of wood. Acid hydrolysis affects mainly hemicelluloses and cellulose and brings about reduction in their molecular weight. Decrystallization of cellulose is caused by solvents and impregnations inducing wood swelling and causes reduction in the degree of cellulose crystallinity. Thermal degradation is associated with elimination of water from the hemicellulose and cellulose macromolecules, bringing about weakening of the bonds between the wood fibres. The degree of wood damage by thermal degradation depends on temperature, duration of the action and wood moisture. Higher wood moisture accelerates the thermal degradation process because hydrolysis takes place in parallel.

Various literary sources present that the corroded wood exhibits changes of moisture content and acidity. The table 1 illustrates the results of wooden samples pH values as opposed to saturated solutions pH values of ammonium phosphate and ammonium sulphate and standard wood. Determination of pH values were done in extracts prepared from the wood. The results show that pH values of corroded samples significantly differ from the standard wood. Values are approximately about 2 units lower, which indicates that acid hydrolysis could take place. Only the sample from the attic above Vladislav Hall shows high pH value 9.2. This could be caused by accumulation of high content of ammonium phosphate. In this case alkali hydrolysis could take place. Wood has lower resistance to alkali hydrolysis than acid hydrolysis. The reason is that lignin is easily hydrolysed by alkalis.

Figures 7-12 show the observation of wooden samples by electron microscopy. On the anatomical structure level, some cells of the wood exhibited breakdown of the central lamella, which is predominantly formed by lignin (Fig. 8,9,10), while other cells exhibited breakdown of the cell wall, primarily composed of cellulose (Fig. 7,9). Figures 11 and 12 image the structure of fibers which originate from the wood surface corrosion (fig. 6). Indicates that the cell walls have disintegrated into the fibrous tangle. Microscopical research says that both of the main polymers are corroded – in some cases both of them and in other cases either cellulose or lignin only. Damage of the cell walls by mechanical agent can be considered as well.

Analysis of wood samples was performed with FTIR spectrometer Bruker ISF 66v/S (Bruker, BDR) connected to a microscope Hyperion connected with Cassergrain lens for measuring transmittance spectra, detector MCT, beam splitter KBr. Measured parameters were: spectral range 4000-650 cm⁻¹, resolution 4 cm⁻¹, number of spectra accumulations 1028, apodisation Happ-Ganzel. The measured spectra were processed by a program Omnic 6.1 (Omnics Instruments Co., USA). Evaluation of changes in chemical structure was performed after bands isolation in absorption area 1200-1600 cm⁻¹ (fig. 13,14) and after relative comparison with areas of selected absorption bands of cellulose and lignin, which was calculated according to Gauss and Lorentz function. Table 2 gives information about the selected bands, which were used for the study of changes in chemical structure of wood. The relative changes in cellulose and lignin content are presented in table 3.

The results given there show there is a decrease of the lignin content in the samples which were taken from the wood surface (fibrous samples). Shifting of band position of CH₂ group bending vibration in cellulose to a higher wave number (from 1424 to 1430 cm⁻¹), is likely to indicate a relative increase of cellulose crystalline part as a consequence of a decrease of amount cellulose amorphous part. Creation of new bands was observed in the spectrum of sample no. 9 from the Vladislav Hall. The phenomenon may be related to oxidation of hydroxyl groups to carboxyl groups which are presented in the sample as a salt form.

The highest temperature approx. 47 °C was measured in the upper part of the attic that was close to southern tiles. In this part of the attic the temperature arose to 40 °C 9 times in summer 2007. Maximal temperature was lower in the bottom part of the attics. This indicates that the temperature is not one of the main corrosion agents (fig. 15,15).

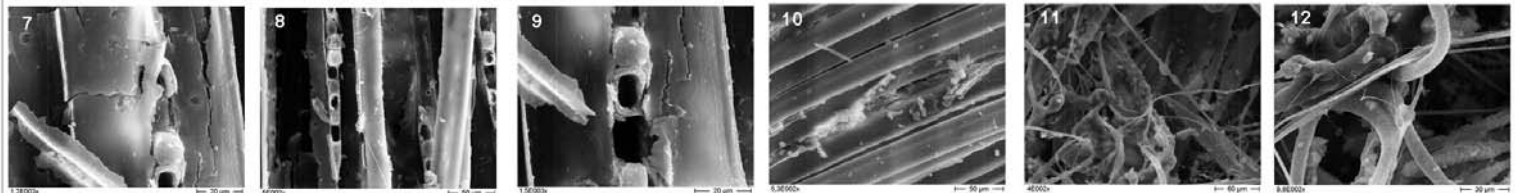


Figure 7,8,9 – A splinter from the House attic. Figure 10 – A splinter from the Vladislav Hall attic Figure 11,12 – Fibers sample from the All Saints Church attic.

Table 1. Examples of the pH values wooden sample from the Prague Castle attics

Standard wood	pH	Samples from the Prague Castle	pH
Old Pine	4.4	Attic above the House	3.2
Old Fir	5.0	Attic above the All Saints Church	4.2
Old Spruce	4.4	Attic above the Vladislav Hall	9.2
Fire Retardants			
(NH ₄) ₂ SO ₄ 18.85g/25g water			pH 5.6
(NH ₄) ₂ HPO ₄ 14.375g/25g water			pH 8.3

Table 2. Assigning vibrations to selected bands

Band intensity [cm ⁻¹]	Vibration assigning
1315	wagging vibration of CH ₂ bands in cellulose
1372	Out-of plane deformation vibration of CH bands in glucosidic ring
1428	bending vibration of CH ₂ bands in cellulose
1463	asymmetric bending vibration of CH ₂ bands in lignin
1510	C=C bonding vibration of lignin aromatic ring

Table 3. Examples of relative changes in wood composition determined by FTIR

Proportion of intensity bands areas [cm ⁻¹] / Sample	1428/1510 (Cellulose / lignin aromatic ring)	1428/1463	1372/1510 (Glucosidic ring / lignin aromatic ring)
Fr - standard	1,227	2,227	1,220
The House - no. 4	2,949	4,970	1,695
The Vladislav Hall no. 9	3,770	3,302	7,986
The Vladislav Hall no. 12	8,961	4,501	4,669

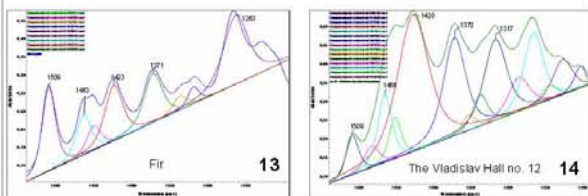
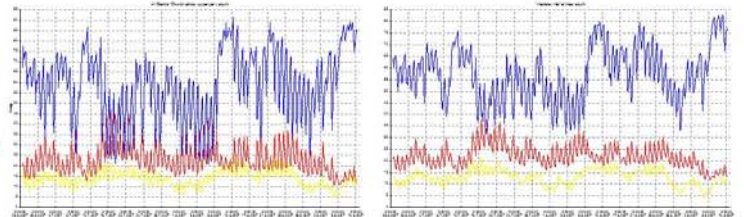


Figure 13,14 – Examples of bands isolation in absorption area 1200-1600 cm⁻¹

Relative humidity
Temperature
Dew point
Figure 15,16 – Records of climatic condition measurements



Conclusions

The results presented here show that there occurs a damage of cellulose and lignin but so far it is not possible to identify the reactions that cause their corrosion. Anyway, the initial results gained in our research will be completed in further attic examinations and measurements.

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Examination of corroded wood by ammonium phosphate and sulphate-based fire retardants – The results of the Prague Castle roof timber examination

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