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## **AN EVALUATION OF THE INFLUENCE OF HEAT TREATMENT ON THE PRESERVATIVE RETENTION IN ASH WOOD (*FRAXINUS EXCELSIOR* L.)**

*As high temperature followed by preservation may cause many different, sometimes contrary changes in wood properties, the aim of this paper was to determine the retention and possible distribution of copper containing preservative in ash wood with an X-ray spectrometer. Two solutions corresponding to the final retention 2 and 4 kg/m<sup>3</sup> were applied as preservative for model laboratory scale low-pressure preservation of ash wood. Before preservation was made, samples were heat treated for 2 or 6 hours at 180°C, apart from the control samples. The mapping option of the X-ray spectrometer was applied and the surface on the half-cut cross-section was analysed. Copper was acknowledged as the retention indicator. On the basis of the results obtained, it can be assumed that the heat treatment improves the treatability of samples with the parameters used. Longer treatment durations increase the uptake of the preparation solutions.*

**Keywords:** ash wood, heat treatment, preservation, preservative retention, XRF, Cu

### **Introduction**

The heat treatment of wood increases its dimensional stability and biological durability, without the necessity of application of additional chemicals [Yildiz et al. 2006]. It is also applied to raise aesthetical properties of the material. However, some of the mechanical properties deteriorate for example tensile strength, modulus of rupture and modulus of elasticity all decrease [Boonstra et al. 1998]. It was indicated that the physical parameters of modified wood decrease more rapidly when the conditions of modification are more severe, e.g. when the air environment instead of anaerobic conditions are applied or a closed system without atmosphere exchange [Stamm 1956]. In practice, wood is most often treated in the temperature range of 160°C to 220°C (manufacturers and

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R&D institutions like VTT Technical Research Centre of Finland or different literature sources e.g. Wang et al. [2013] or Percin et al. [2015]) during a specified time. Detailed parameters of the process are dependent mainly on the final application of the modified material, the level of its conversion and size of the particular elements. Thermal modification may be performed in different non-oxidative environments (superheated steam, nitrogen, oil, combustion gases), employed to avoid material degradation.

Manufacturers, experienced with different applications of their products (oak, ash, beech and pine are the tree species most often heat treated in Poland) in outdoor conditions (garden furniture, terraces, facades) and as indoor floor materials and furniture concluded that these woods should be additionally preserved against insects and fungi, especially species where durability is still insufficient despite the heat treatment. The process of preservation after heat treatment will give different effects, because heat treatment results in changes of the hygroscopic properties of wood. It reduces equilibrium moisture content (EMC) as well as tangential and radial swelling. Permeability of heat-treated wood is significantly lower in comparison to untreated one [Finish Thermowood Association 2003]. The plasticisation of lignin leading to a reorganization of the lignocellulosic polymeric components of wood seems to be the most probable explanation of the wettability change. High temperatures, generally used for wood heat treatment, are not necessary to modify its hydrophilic properties, which can be modified at lower temperatures [Hakkou et al. 2005].

The process of wood preservation has been widely examined for decades [MacLean 1952] and this topic is still inexhaustible [Mohareb et al. 2010; Helsen et al. 2007]. The heat treatment of wood was the issue studied by Chaouch et al. [2010], Gunduz et al. [2010] and Hill [2006]. However, the influence of both modification techniques (applied simultaneously) on wood properties has not often been examined. The preservation of heat-treated wood may be problematic because treatment causes the increase of hydrophobic properties (mainly a decrease of EMC of about 50%) and a following difficulty of wood penetration with water based preparations [Yildiz and Gümüşkaya 2007] as it consists in diffusion rather than capillary effects. Bastani et al. [2015] denoted that heat treatment had no effect on apparent sessile drop contact angles in Scots pine and beech suggesting difficulties with impregnation. According to Kwon and Ayırlmis [2016] the thickness swelling and water absorption of the specimens significantly decrease with increasing treatment temperature, in particular at 190°C. There were some attempts to preserve heat-treated wood with classic oils for surface saturation realized by the submersion in chosen preservatives or pressure preservation with the application of autoclaves. Kartal et al. [2008] assumed that the addition of preservative (containing boron) before the heat treatment at high temperatures would protect the examined wood of Japanese cedar (*Cryptomeria japonica*) against the loss of strength. But the results were not unequivocal, they were highly dependent on the treatment

temperature. Strength changes are caused by the decomposition of wood components – depolymerisation of carbohydrates with the acetic acid molecule splitting off from acetyl branches and hemicelluloses content decrease, which increases the Klason lignin content. Tomak et al. [2011a and 2011b] studied the influence of heat treatment in oil of beech and pine wood with the addition of boron based preservative. The coefficient of the preservative absorption in heat-treated wood was 20% higher than in unmodified wood. However, results obtained by Ahmed et al. [2013] indicates that thermally modified samples had lower treatability than control samples. More structural changes after thermal modification, especially in birch, significantly reduced the preservative uptake and distribution.

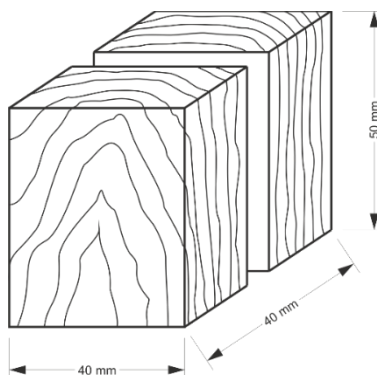
According to Jin and Archer [1991] copper ions react with functional groups such as carboxyl, carbonyl and phenolic hydroxyl and become immobile in the wood. Heat treatment might influence the amount of copper ions leached from treated wood because of various chemical changes in the wood.

Systematic investigation of the influence of heat treatment on the retention and distribution of the preservative is still to be done. As high temperature, and different types of preservatives may cause many different, sometimes contrary changes in wood properties (dependent also on wood species), the first aim of this paper was to determine the influence of heat treatment of two different durations on the retention of preservative containing copper in the ash wood structure. The second purpose was to show the possible distribution of preparation in the structure of ash wood samples with the application of the mapping option of an X-ray fluorescence spectrometer, which cannot be found in current literature.

## Materials and methods

The wood samples used for analysis were obtained from ash (*Fraxinus excelsior* L.) wood, the part of the heartwood without colouring. Its chemical composition was as follows: 81.8% of holocellulose (with the application of sodium chlorite) including 47.3% of cellulose (determined with Kürschner-Hoffer method) and 34.5% of hemicelluloses [Gawron 2012]. Samples with dimensions of 40 mm × 40 mm × 50 mm (parallel to the grain), as shown in figure 1, were divided into 3 groups of 4. Group 1 was treated as control one (samples 1-4). Group 2 was heat treated in the air at a temperature of 180±5°C for up to 2 hours (samples 5-8). Group 3 was heat treated in the same conditions with the duration increased to 6 hours (samples 9-12). The process of the thermal modification was performed in a laboratory oven with thermo-circulation. It consisted of: (stage 1) initial wood drying at 100 ±1°C for a duration of 12 hours; (stage 2) achieving a temperature of 130°C with a 15°C/h gradient and initial warming of the material for 1 hour; (stage 3) achieving the treatment temperature of 180°C with a 10°C/h gradient; (stage 4) final warming

at 180°C within 2 or 6 hours; (stage 5) cooling of the material until the ambient temperature is reached with a 10°C/h gradient. All stages of the experiment were performed in the air atmosphere.



**Fig. 1. Samples dimensions and grain orientation**

Samples from each group were then preserved with a watersoluble preparation, pH –  $9.6 \pm 0.5$ , containing the following active substances: 5% of boric acid, 16.3% of copper (II) hydroxycarbonate and 3.5% of Cu-HDO. Two samples from each group were treated with the solution corresponding to a final content of 2 kg of the preparation in 1 m<sup>3</sup> of wood (sample numbers 1, 2, 5, 6, 9, 10) and 4 kg/m<sup>3</sup> (sample numbers 3, 4, 7, 8, 11, 12). A model process of pressure preservation was used, applied earlier in previous paper [Gołofit et al. 2012].

All of the samples were placed in beakers with solutions. The beakers were placed in a Shell Lab vacuum dryer and pressure was reduced to 10 kPa. After 20 minutes, the pressure was raised to atmospheric pressure level and samples were left in the solution for a further 20 minutes.

The final contents of 2 and 4 kg/m<sup>3</sup> were achieved using the following procedure: samples with the earlier specified dimensions were subjected to a model pressure preservation process with distilled water. After determining the amount of water which penetrated the samples (weighting), the final concentration of the preparation was calculated: 5 g/1000 g of water for the final content of 2 kg/m<sup>3</sup> of wood and 10 g/1000 g of water for the final content of 4 kg/m<sup>3</sup>.

Preserved samples were then half-cut parallel to the grain. The obtained surfaces were analysed by the mapping method available in XRF Spectro Midex M spectrometer. The mapping was performed with a resolution of  $23 \times 18$  and each measuring point (screen 2 mm  $\times$  2 mm) was exposed for 30 seconds.

In order to compare preservative retention, copper on the analysed surfaces was examined. The results of the described measurements were so-called impulse counts of copper. For each surface, the average copper impulse counts were calculated. Additionally, values for both halves of each sample were

averaged. The comparison of the calculated values allowed the influence of heat treatment on the preservative retention to be determined.

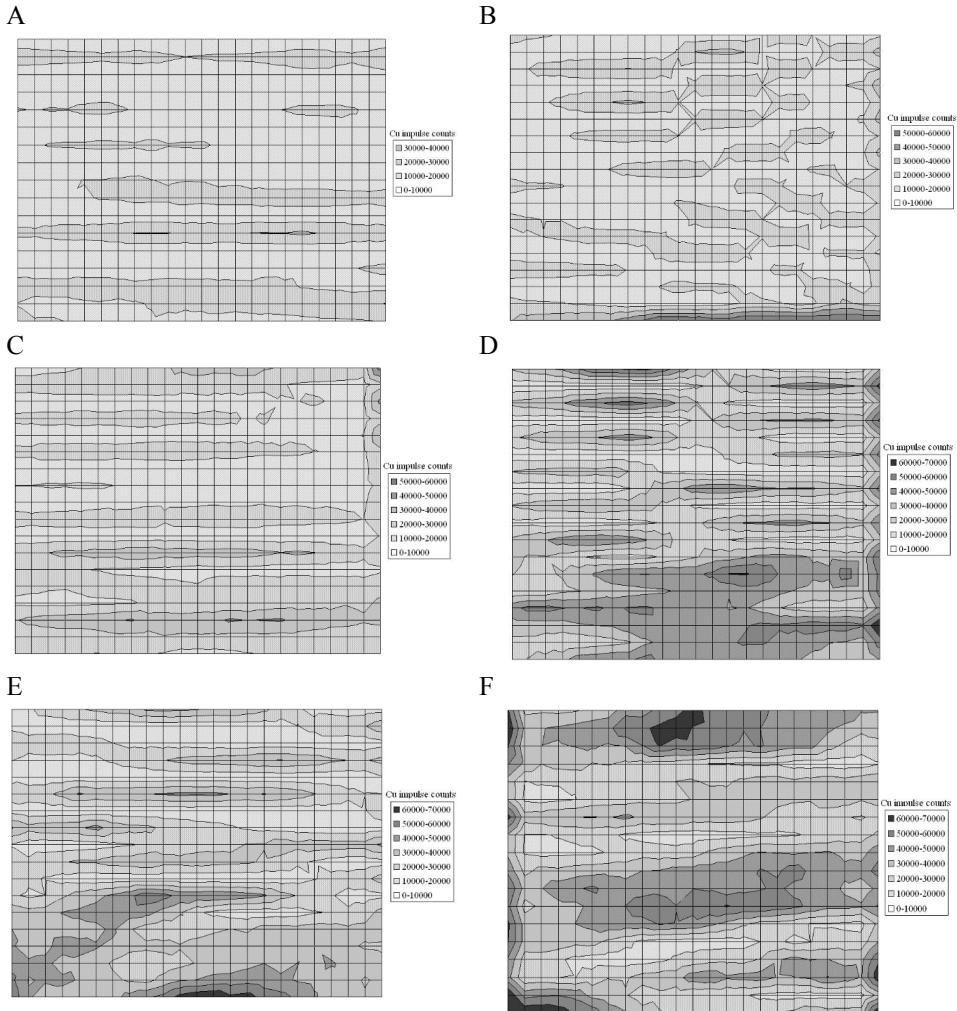
## Results and discussion

Figures 2A and 2B present the gradient of copper impulse counts on the cross-section of samples no 1 and 3 correspondingly from group 1 (control samples preserved without heat treatment). On both graphs, impulse counts values in the range of 10000-20000 and 20000-30000 are dominant. This second range is much more visible for in sample no 3. This is caused by a higher concentration of the preservative. Longitudinal areas of higher impulse counts (reaching deep inside the sample structure) are observable on both figures. This is probably enhanced by the fact that ash is the studied species. The phenomenon of deep longitudinal penetration of ash wood was observed by Zielenkiewicz et al. [2013].

Figure 2C shows the copper concentration map (isocurves) on the cross-section of sample no 5 which was heat treated for 2 hours at a temperature of 180°C before preservation. The longitudinal areas of raised copper content are visible as in previous figures. However, there are much more of them in relation to the control samples, additionally an area with the range of impulse counts of 30000-40000 appears. It means that heat treatment caused the extension of free spaces availability or an increase in the volume of these spaces, because of the destruction of the tracheid walls, ray tissues and pit deaspiration [Awoyemi and Jones 2011]. It is also suggested that thermal degradation of the hemicelluloses makes the entire polymer complex more permeable for liquids [Terziev and Daniel 2002], because of the significant pectins degradation. This effect is more easily visible in figure 2D, where the results obtained for sample 7 are presented (preserved in a solution with a higher concentration).

The increase of the heat treatment duration to 6 hours causes broadening of areas with raised copper impulse counts value. It may be observed in the figures 2E and 2F (correspondingly sample no 9 and 11). Copper impulse counts increase especially in case of sample number 11.

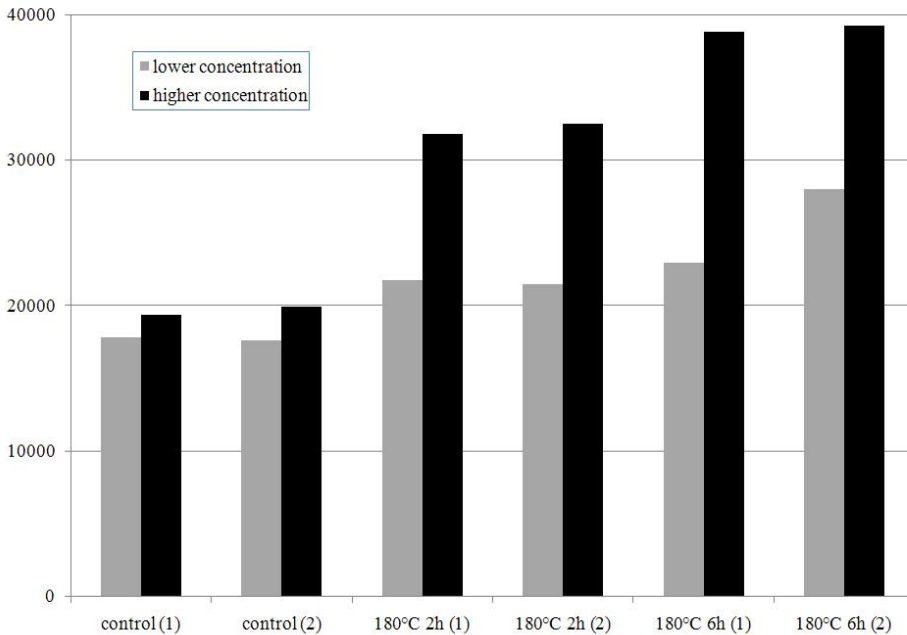
Observations made on the basis of figures 2A and 2F are similar to the comparison of the average impulse counts for all surfaces. This is shown in figure 3. A significant influence of heat treatment on the preservative retention is visible for samples preserved with a preparation with lower concentration (grey columns) as well as for ones preserved with higher concentrated preparation (black columns). Differences are more significant in the case of the preparation with a higher concentration. It is important to note the dependence of the element content in wood on its impulse counts (it is visible in fig. 3). This was stated for example in the paper by Zielenkiewicz et al. [2012]. That is why the percentage change of the impulse counts value is not equal to the percentage change of the element content.



**Fig. 2. Copper concentration gradient on the cross-section of: A – sample 1 (control, retention 2 kg/m<sup>3</sup>), B – sample 3 (control, retention 4 kg/m<sup>3</sup>), C – sample 5 (heat treatment duration 2 h, retention 2 kg/m<sup>3</sup>), D – sample 7 (heat treatment duration 2 h, retention 4 kg/m<sup>3</sup>), E – sample 9 (heat treatment duration 6 h, retention 2 kg/m<sup>3</sup>), F – sample 11 (heat treatment duration 6 h, retention 4 kg/m<sup>3</sup>)**

The presented results are not consistent with the theory of the flow of preservative migration in a preserved sample. However, they are similar to the conclusions of Tomak et al. [2011b], who stated that heat treated wood absorbs as much as 20% more preservative than untreated wood, even though the other type of preservative was applied and other species (beech and pine) were examined. Comparing this to thermally modified samples by Ahmed et al. [2013] which showed lower treatability than the control ones, authors stated that

more structural changes after heat treatment significantly reduced the uptake and changed the distribution of the preservative. Perhaps it is due to the different type of preservative and species used, but thermal wood modification caused lower copper retention (higher leakage) in research carried out by Wang et al. [2013]. It may be related to the degradation and depolymerization of the cell wall components during the treatment.



**Fig. 3. Mean copper impulse counts on analysed cross-sections of control and heat treated samples (1 and 2 mean two surfaces of the same sample obtained after half-cutting)**

## Conclusion

The presented results suggest that ash wood may be activated by the heat treatment to absorb more of the preservative. The evaporation of water during heat treatment and probably the degradation of the fibrous structure, are responsible for the increase of space volume available for preservative. Such an effect allows the application of a preservative with a lower concentration in relation to wood, which was not heat treated at all. Additional analysis must be made, however, in order to determine the percentage increase of preservative content. Moreover, the economic aspect of the eventual heat treatment process should be examined.

It is stated in literature that solvent retention may be increased after heat treatment. Our studies show that it also concerns the solutions of preservative containing copper.

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