

**TESTING CONTENT OF COPPER IN SCOTS PINE WOOD
(*PINUS SYLVESTRIS* L.) AFTER PRESERVATIVE TREATMENT**

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ABSTRACT

Testing content of copper in pinewood (*Pinus sylvestris* L.) after preservative treatment. An attempt was made to vacuum pressure treatment of pinewood (*Pinus sylvestris* L.) in laboratory conditions. Wolmanit® CX-10 was chosen as a wood preservative. Copper is the active component in this preservative. The analysis of copper content inside wood samples was made after treatment. Measurements were made on XRF spectrometer with an option of point, linear and mapping analysis. The results show that copper compounds absorption grade inside wood depends in a high degree on the preservative concentration.

KEY WORDS: preservative treatment, copper, XRF spectrometer

INTRODUCTION

Nowadays the copper compounds are not applied as wood preservatives independently, but they are a part of preservatives compositions. It is because of their low toxicity in relation to warm-blooded organisms and relatively low price (Krajewski 2001). Complex organocopper compounds are one of the most important preservatives containing copper. These compounds can be divided into following groups:

1. Agents containing Cu-HDO (bis-(N-cyclohexyldiazoniumdioxy)-copper). They are classified as hardly leaching. Their fungicidal value is lower than $1 \text{ kg}\cdot\text{m}^{-3}$, oral toxicity for rats comes to about $860 \text{ mg}\cdot\text{kg}^{-1}$. That is why these agents were acknowledged as environment-friendly. Wolmanit® CX-10 is the well-known trade product belonging to this group of preservatives. It is sold as a navy-blue water-soluble concentrate. Cu-HDO, inorganic copper and boron compounds are the active ingredients. Wolmanit® CX-10 is assigned to protect wood against domestic fungus and insects; it is use in the hazard class from 1 to 4. This preparation is assigned for pressure-vacuous method (Dr. Wolman GmbH 2004). Wolmanit® CX-10 is produced by German firm "Dr Wolman", which

belongs to the BASF group. “Dr Wolman” was the leading manufacturer of preservatives called “Wolman salts”, which were consisted of chromium compounds. The requirements for biocides, which were more and more rigorous, made the producer substitute chromium with active ingredients which are more environment-friendly (which can be copper). Wolmanit® CX-10 is certified by, among others, National Institute of Hygiene (No. B-1679/94), Building Research Institute (No. 546/94), Wood Technology Institute (no. 1/ITD/94).

2. Alkaline copper quaternary ammonium compounds (ACQ) – they consist of water-soluble cationic surfactants – quaternary ammonium compounds (QAC), which consolidate in wood on the ion exchange basis. These compounds are strongly poisonous for fungus and microorganisms. Ammonia copper compounds are the second component, which make the ACQ preservatives also insecticidal (Krajewski, Witomski 2005).
3. Complex compounds of triazole polymers and copper (polymerized copper complexes – PCC). These compounds consist of triazole polymers and copper salts, e.g. copper acetate. Complex compounds are modified using aliphatic amines to gain chemical structures of higher stability and make the penetration into wood deeper (Krajewski et. al. 1997). Krajewski (1999) states that there is the synergy of compounds from ACQ and PCC groups. This is the phenomenon of constant character. It can be used to decrease the content of active compounds in preservative, what means production cost decrease and the reduction of environment pollution.

Agents containing Cu-HDO, specifically Wolmanit® CX-10 is the object of interest in this paper.

Quality of the wood treatment depends on the proper penetration of the preservative into wood structure. The aim of this paper is to examine the possibility of the treating quality monitoring using modern X-ray spectrometer. It is going to be realised basing especially on the “mapping” and “line scan” options of the spectrometer, which can present the copper concentration gradient on the wood sample surface.

The “line scan” option of XRF spectrometer was used with success by Vives et al. (2005). In this paper authors were examined the gradient of some metals content in treated wood samples (CCA preservative). Siegele et al. (2008) applied the mapping option of X-ray spectrometry (particle induced x-ray emission – PIXE) to localise trace metals in the structure of metal accumulating plants. It arises from this papers that methods based on X-ray spectrometry could be applied to examine the degree of absorption of metals from the preservative solution penetrating wood samples.

MATERIAL AND METHODS

Samples of Scots pine (*Pinus sylvestris* L.) (one board isolated from sapwood without defects) were examined. 15 samples with size 5 × 2.5 × 1.5 cm were made.

Vacuum pressure treating were carried out using Wolmanit® CX-10 in laboratory conditions in the Shell Lab vacuuous dryer connected to Büchii vacuuous pump. Penetration of pure water into wood sample was examined at first. It was necessary to calculate the preservatives concentration which corresponds to desirable retention of active substance into wood sample. Samples were divided into five groups of three. Each group was treated in the other way before analysis.

First group (samples 1, 2, 3) – treated with pure water (control samples).

Second group (samples 4, 5, 6) – treated with Wolmanit® CX-10 solution, concentration corresponding to 1 kg.m⁻³ retention.

Third group (samples 7, 8, 9) – treated with Wolmanit® CX-10 solution, concentration corresponding to 2 kg.m⁻³ retention (I hazard class).

Fourth group (samples 10, 11, 12) – treated with Wolmanit® CX-10 solution, concentration corresponding to 3 kg.m⁻³ retention (II and III hazard class).

Fifth group (samples 13, 14, 15) – treated with Wolmanit® CX-10 solution, concentration corresponding to 4 kg.m⁻³ retention (IV hazard class).

Following parameters were used in applied wood samples treating system: Vacuum pressure in the treating chamber was 0.1 MPa, vacuum time – 20 minutes. After vacuum process system was vented and preservative could penetrate wood samples, which lasted consecutive 5 minutes. In the next step treated wood samples were dried in room temperature during four days.

Copper content was analysed after treating using Midex M Spectro XRF spectrometer. Three measurement methods were applied (Krutul et. al. 2008):

Point scan – examines elements content in the indicated sample point. This method was applied to all samples.

Line scan – examines elements content gradient on the specified line (in this case consisted of fifty measuring points). Samples were cut in the centre along fibres (similar method of sample preparation was applied by Block et al. 2007); measuring line was led in the centre of uncovered surface. One sample from each group was analysed with this method.

Mapping – examines elements content gradient on the specified sample surface. The sample with the highest copper content (sample No. 15) was analysed with this method.

RESULTS AND DISCUSSION

Treated samples point scans

Samples No. 1, 2 and 3, which were not treated, contain only trace amount of copper. It proves that copper detected in treated samples 4-15 (much higher amount) originates from copper compounds contained in preservative. Higher assumed preservative retention corresponds to higher copper content in analysed material (Fig. 1). The mean copper content in samples with assumed retention of 2 kg.m⁻³ is above twice higher than in samples with assumed retention of 1 kg.m⁻³. Retention of 3 kg.m⁻³ causes the copper content rise in relation to results for 2 kg.m⁻³ retention. The copper content in samples with retention of 4 kg.m⁻³ is much higher than for 3 kg.m⁻³ retention. The differences in increments can be caused by wood anisotropy and invisible differences in wood composition.

Tab. 1 shows the results of particular point scans made on samples from the fifth group (preservative retention – 4 kg.m⁻³). Copper content near sample fronts is about twice higher than in the sample centre.

The copper content in treated wood changes depending on preservative concentration (corresponding to assumed retention – Fig. 1) and the distance of examined point from the sample front (Tab. 1).

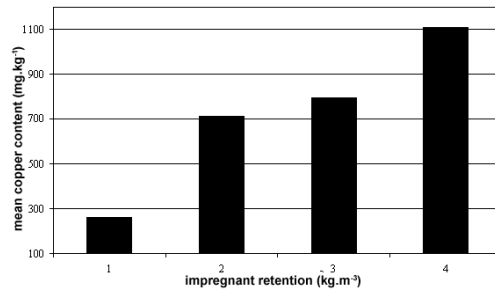


Fig. 1: The mean copper content in scots pine wood (*Pinus sylvestris* L.) in relation to particular impregnant retentions

Tab. 1. Copper content in front parts and centre of scots pine samples (*Pinus sylvestris* L.) from the fifth group

Sample No.	Scan position	Copper content (mg.kg ⁻¹)	Absolute error (mg.kg ⁻¹)	Copper content mean value (mg.kg ⁻¹)
13	front	1087	1	1107
	centre	722	1	
	front	1222	1	
14	front	1316	1	
	centre	707	1	
	front	1429	2	
15	front	1160	1	
	centre	721	1	
	front	1598	2	

Treated samples line scans

The changes of copper content in treated Scots pinewood samples (*Pinus sylvestris* L.) are showed in the Fig. 2. Results for samples from each group are presented.

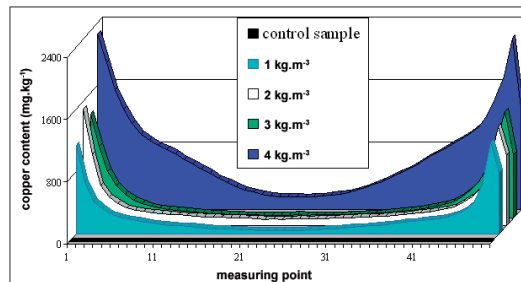


Fig.2: The copper content in wood samples for different impregnants retentions and control sample (line scans)

All of the data courses (excluding control sample) are of the same character. Copper content values decrease in the direction of the diagram centre. The comparison of treated samples with control sample proves that whole volume of treated samples was penetrated with the preservative.

Analysis of first five measuring points (Fig. 3.) shows that preservative retention of 4 kg.m^{-3} causes the highest copper content. Higher preservative retention causes consolidation of higher copper amount. Similar amount of copper consolidates in samples with retention 2 and 3 kg.m^{-3} . Copper content is higher in the sample with 2 kg.m^{-3} retention than in the sample with 3 kg.m^{-3} retention in the first measuring point. It can be caused by wood defect that is present in this place. Copper content in the sample with retention 1 kg.m^{-3} is insignificantly lower than in samples with retention 2 kg.m^{-3} and 3 kg.m^{-3} , especially in the 3rd, 4th and 5th measuring point.

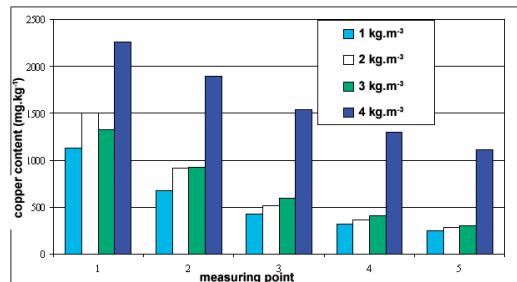


Fig. 3: Copper content in treated scots pine (*Pinus sylvestris* L.) wood samples analysed by the line scan method (five initial measuring points)

Uhl et al. (2001) measured the wood preserver distribution (Cu-HDO) to the depth of 0.45 mm and their analysis didn't show much variations. It seems that copper concentration decreases in the depth more than 1 mm, as it is shown in the Fig. 2 and 3.

Treated sample mapping

Sample No. 15 was analysed. The copper content gradient on this sample surface is showed in the Fig. 4.

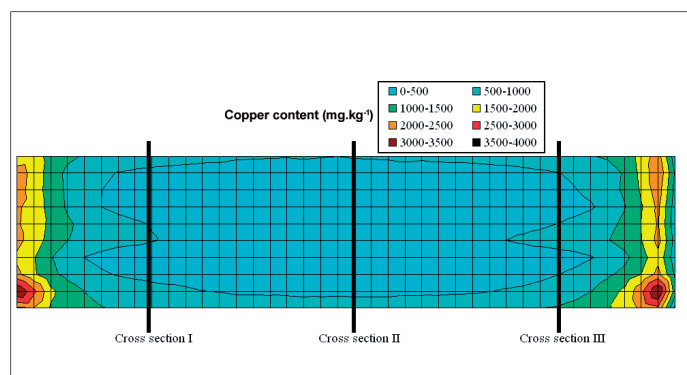


Fig. 4: Mapping of the copper content in the sample No. 15

Zones with the highest copper content values (above 2500 mg.kg^{-1}) are situated in the lower part next to the sample fronts. Zones with values above 1500 mg.kg^{-1} are situated up to two points from sample fronts. Copper content values in the range of $500 - 1000 \text{ mg.kg}^{-1}$ were observed along sample longer sides. Values in this range were also observed in the half of the sample height in form of “wedges” situated from 6th to 10th measuring point from sample fronts. Remaining, central sample zone contains less than 500 mg.kg^{-1} of copper.

Copper content gradients for three cross-sections of the sample are presented in Figs. 5, 6 and 7:

Cross-section I – 8th measuring point from the sample front.

Cross-section II – 20th measuring point from the sample front (sample centre).

Cross-section III – 8th measuring point from the second sample front.

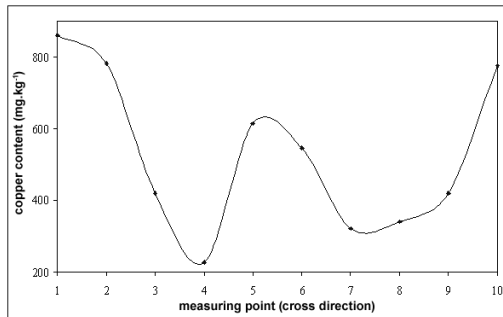


Fig. 5: Copper content in the cross-section I

Copper content in the cross-section I is about 800 mg.kg^{-1} on both sides (Fig. 5). It decreases up to the 4th measuring point level (from both sides), where its value is about $200 - 300 \text{ mg.kg}^{-1}$, and in the sample centre it rises to about 600 mg.kg^{-1} .

Copper content gradient in the cross-section II is presented in the Fig. 6. It significantly decreases from 650 mg.kg^{-1} (1st measuring point) to about 200 mg.kg^{-1} (3rd measuring point) at one side and from 500 mg.kg^{-1} (1st measuring point) to about 200 mg.kg^{-1} (2nd measuring point) at the other side. In the rest of measuring points copper content stays on the same level with insignificant rise in the sample centre.

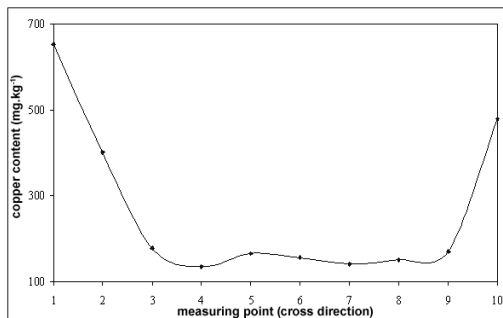


Fig. 6: Copper content in the cross-section II

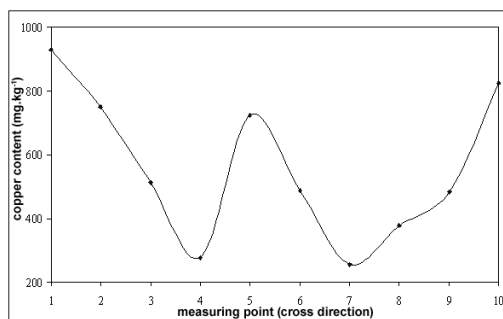


Fig. 7: Copper content in the cross-section III

Copper content gradient in the cross section III is similar to cross section I. Rise of values in the sample centre corresponds to „wedges” of higher copper content observable in the Fig. 4.

Saarela et al. (1999) were analysed the penetration of CCA preservative into wood boards. They examined copper concentration on the surface and 10 mm below. On the surface variations of Cu content are quite small, while 10 mm below the surface significant changes in content occur. It is similar to our results – first and tenth points values on all cross sections (corresponding to external surfaces) are on the same level (Figs. 5 to 7) with the exception in the tenth point on cross section II. Copper content below the surface changes significantly.

Nevertheless, according to results of Islam et al. (2009), the preservative (copper azole type B) concentration may be higher in the centre part of a sample than in the front part. It seems to be dependent on the treating process conditions or/and the type of preservative.

CONCLUSIONS

- Rise of assumed preservative retention causes higher copper amount penetration into the sample.
- Copper content in treated samples decreases in the direction of the sample centre.
- Using higher preservative concentration causes the accumulation of higher copper quantity in zones situated closer to the sample centre.
- Using of Wolmanit® CX-10 to vacuum pressure treatment enables the copper consolidation in the whole sample volume.
- The preservative penetrates samples from its fronts along fibres.
- The X-ray spectrometry seems to be a good tool to examine the treating quality.

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