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The Influence of Sample Origin on the Leachability of Wood Preservatives

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Several studies have been conducted on impregnability of the raw material and large variations have been found. The leaching of wood preservatives into nature is a problem, especially agents that consist copper. Leachability of i. e. copper has been studied by several authors. This study tries to set the variation of leachability of Wolmanit CX-8 and Tanalith in system, evaluating the origin of a tree and the origin of a sample.

Samples of Scots pine sapwood (*Pinus Sylvestris*) (20×20×50 mm) were treated with the wood protection agents Wolmanit CX-8 and Tanalith. The variation in leachability within trees, between trees and between different stands of Scots pine (in Norway and Denmark) was studied. The samples were climatized, impregnated with preservatives and leached according to standard EN84.

The study indicates differences between the products. Stand location and samples position in a tree play a role in preservative leaching from wood, favouring southern located trees to be more prone to loosing preservative. Also the lowest part of the tree does not fixate preservatives as well as the upper parts.

Keywords: copper-containing wood preservatives, EN84, leaching, RoF, Scots pine.

1. INTRODUCTION

Wood is a natural and traditional building and construction material with good native properties. It is relatively light and strong. Its appearance and properties differ a lot between species and even between trees, so there is a wide variety in material to choose from for all kind of uses. Wood products are used indoors as well as residential and other outdoor constructions. The weak point in wood usage is that the material is susceptible to degradation by many different organisms: termites, fungi, so the good native qualities are challenged daily. To overcome shortcomings, wood is treated with different preservatives. Another choice would be plastic lumber, a competitor for solid lumber which is believed to be dimensionally more stable, does not photodegrade and does not have such high maintenance requirements. But to be sure about the certainty of this statement further research is required [1].

Wood preservatives nowadays face many requirements, a protection agent has to make wood resistant to fungi, termites and weather degradation. Plus they have to be in accordance with environmental norms. The consumer is also becoming more eco-aware and – conscious, therefore industry must adapt to more nature friendly standards.

There are still some questions arising concerning elements currently used in wood preservation, e. g. copper. Copper is an essential micronutrient for most living cells. Though, in larger doses, it acts as an algaecide, bactericide, fungicide and moldicide [2] and when leaches out from wood it can become a hazard to the nature, especially to the aquatic life-forms [3].

Copper-based wood preservatives have been widely used for a long time, but have gone under some restrictions because of environmental concerns. Chromated copper arsenate CCA, for instance, has been banned in most countries. Replacing CCA are chromium- and arsenic- free wood preservatives, containing copper, and organic co-biocide such as triazoles or Cu-HDO as well as amines as complexing agents for the copper. Fixation process for these preservatives is different than for CCA. Copper fixates in the wood by reaction of the amine complexing agent with the wood material at the same time forming insoluble copper compounds, pH-difference between the solution and the wood is the main key in this process [4].

The aim of this study is to see if the raw material influences fixation and leachability of wood preservatives. The research was designed to discover the variation in leachability within and between trees. The preservatives used in this study are used all over the world. Similar studies using the same raw material have been made on treatability by Larnøy et al.(2008), Lande et al. (2009) and Zimmer (2009), who found correlations between latitude, sample height, radial position, annual ring width, tree height, method of drying and treatability. The highest significance on treatability was proven to be from the impregnation liquid [5 – 7].

2. EXPERIMENTAL DETAILS

2.1. Materials

For these tests, trees from three Scots pine (*Pinus sylvestris*) stands, two in Norway and one in Denmark, were sampled. All stems were divided into 5 sections of 60 cm at 0, 25, 50, 75 and 100 % distance from ground after removing the top end of the trunk. Within these sections a centre block with width of 75 mm with north-south orientation was cut out and parted in two. The block was parted exactly through the pith. Wood samples from sapwood with dimensions of (20 × 20 × 50) mm³ were cut out in as many layers as the radial size allowed. In sum, 956 samples were used for the tests. The samples were conditioned at 65 % relative humidity and 20 °C until

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equilibrium moisture content was reached. Cross sections were sealed with a two component sealer "Pyrotect-2K-Aussen-Schutzlack 1720-7100-302" (Dreisol Coatings GmbH) to ensure that no liquid could pass the longitudinal pathways.

Solutions of Wolmanit CX-8 and Tanalith were used for impregnation procedure. 487 samples were treated with Wolmanit CX-8 and other 469 with Tanalith. Wolmanit CX-8 is a liquid copper- and boron-based wood preservative consisting of 2.8 % bis-(n-cyclohexyldi-azeniumdioxy)-copper (Cu-HDO), 13.04 % copper hydroxide carbonate and 4 % boric acid. Tanalith is a water-borne wood preservative based on copper and co-biocides consisting of 22.5 % copper carbonate, <45 % 2-aminoethanolcarbonate, 0.49 % tebuconazole, 4.9 % boric acid and <5 % di-2-ethylhexylphthalate.

2.2. Impregnation

The same impregnation schedule was used for all specimens. Samples were not tended to be penetrated fully to observe how the differences in permeability are correlated with the leachout of the preservative, hence the solutions were impregnated into wood by using pressure of 6 bar for 10 min. Wood samples were then removed from the treatment solution, wiped lightly and weighed immediately after impregnation to calculate respective uptake values.

2.3. Determination of treatability

Level of treatment is often determined by retention of preservatives or liquid uptake per volume of wood. These variables are too closely related to permeability and wood density. The lower the density the higher the void volume and therefore the permeability is better as well. Hence liquid will fill voids faster.

Larnøy et al. and Lande et al. introduced the concept of the ratio of filling (RoF) [5]. The RoF was employed to obtain a value of treatability independent of wood density. Treatability is now determined by the liquid ratio of filling of the void volume. The void volume of the respective sample is calculated following Eq. (1) and Eq. (2) expresses the ratio of filling (RoF). The RoF is influenced only by permeability and impregnation conditions. Since the impregnation conditions are kept the same throughout the tests, permeability will be the only factor affecting penetration velocity. As long as impregnation conditions avoid a full treatment of the samples, the RoF will be a justified method to measure treatability. High permeability will lead to fast liquid flow and result in a high RoF.

$$V_{void} = V_{12\%} - V_{cellwall} - V_{water} + V_{swell} \; ; \quad (1)$$

$$RoF = V_{uptake} / V_{void} \times 100 \quad [\%] \; ; \quad (2)$$

where V_{void} is the void volume in wood, $V_{12\,\%}$ is the volume of the sample at 12 % MC, $V_{cellwall}$ is the volume of the cell wall material, V_{water} is the volume of water at 12 % MC, V_{swell} is the potential increase in volume due to swelling and V_{uptake} is the volume of the treating liquid.

To calculate the void volume, moisture content (MC) was adopted with 12 %, when the specific gravity of the wooden substance was assigned with 1.5 and the water bound in the cell walls was set with a gravity of 1.1 [8]. The cumulative volume due to swelling from 12 % MC to fibre saturation is expressed in V_{swell}, which is necessary to take into account as long as impregnation fluid is based on water and responsible for a swelling of the material. The impregnation liquid in Equation 2 was set at a specific gravity of 1.05 [5].

2.4 Leaching procedure

After impregnation the samples were conditioned again at 65 % relative humidity and 20 °C until equilibrium moisture content was reached.

Treated samples were leached according to standard EN84. [9] Test vessels with the samples covered with sufficient amount of deionized water were placed in the impregnation vessel, where vacuum of 0.04 Bar was established. It was held for 20 min. After vacuum the samples were maintained in the water for 2 h, before the water was changed. The specimens were covered with deionized water again and remained for 14 days in the water. 5 ml of the leaching water was collected and combined from each of the vessel for chemical analyses. Water changes took place ten times (including the change after impregnation in 2 h). Copper and boron content of water in which the test specimens had been immersed was determined by ICP (Inductively Coupled Plasma) technique. For neutralizing the water sample for ICP hydrochloric acid (HCl) was added to the sample.

To discover the sources of variance, analyses of leachouts with tree location, sample`s position (vertical and horizontal) and sample`s exposition (northern or southern side of the tree) were performed.

Statistical analyses were executed with JMP 8.0 by SAS Institute Inc.

3. RESULTS

To determine the treatability, ratio of filling (RoF) was calculated. The distribution range for both solutions is basically the same, between 10 % – 45 % of the wood sample is filled with liquid (Figs. 1, 2).

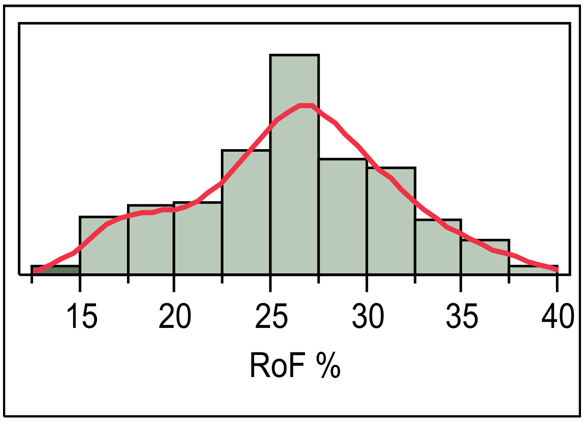

Fig. 1. Distribution of the ratio of filling (%) for samples treated with Wolmanit CX-8

Correlating Wolmanit CX-8 and Tanalith leachouts with the RoF, a trend could be observed: the higher the RoF the higher the leachout, for both copper and boron in both preservatives (Figs. 3, 4). Correlation was stronger for B leaching where the R^2 converged in a maximum of 0.66

(Fig. 5). For Cu leaching only a slight trend occured ($R^2 > 0.1$) (Figs. 3, 4). *P* values were <0.001 for all the Figures.

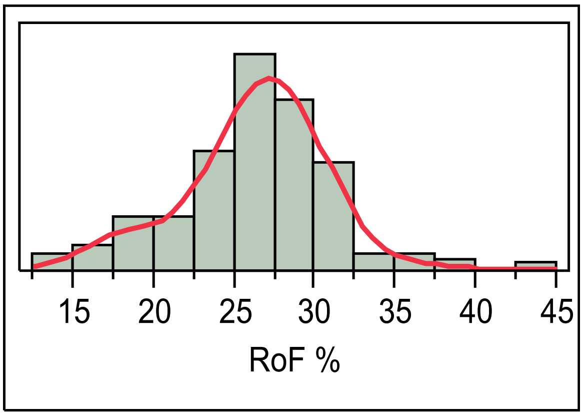

Fig. 2. Distribution of the ratio of filling (%) for samples treated with Tanalith

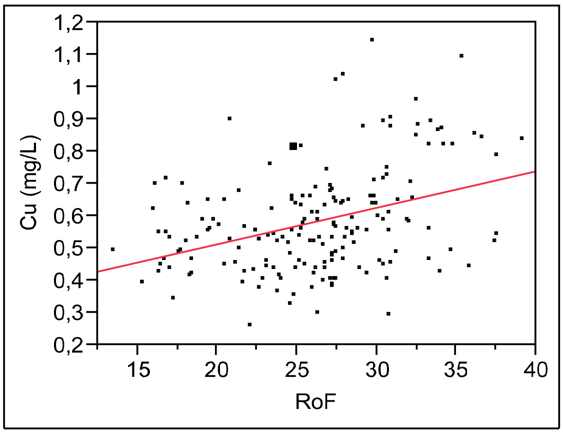

Fig. 3. Fit line between RoF and Cu leachout from Wolmanit CX-8 treated samples ($R^2 = 0.138$)

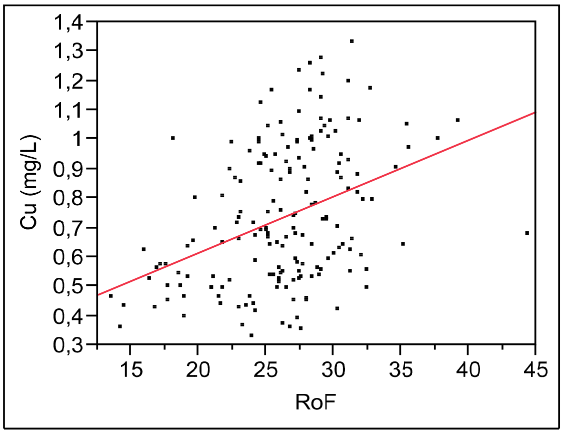

Fig. 4. Fit line between RoF and Cu leachout from Tanalith treated samples ($R^2 = 0.145$)

Screening on possible variables to discover what influences preservatives leaching out did not give any moderate correlations ($R^2 > 0.01$) or significant differences (95 % confidence level) for exposition or for the horizontal position of the sample, but the correlation was found for harvesting latitude and for the vertical position of the sample.

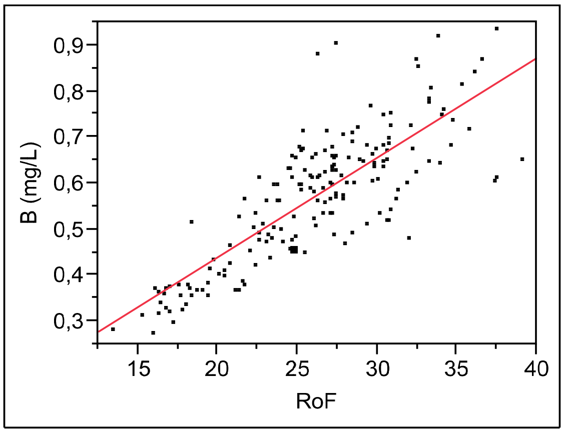

Fig. 5. Correlation between RoF and B leachout from Wolmanit CX-8 treated samples ($R^2 = 0.662$)

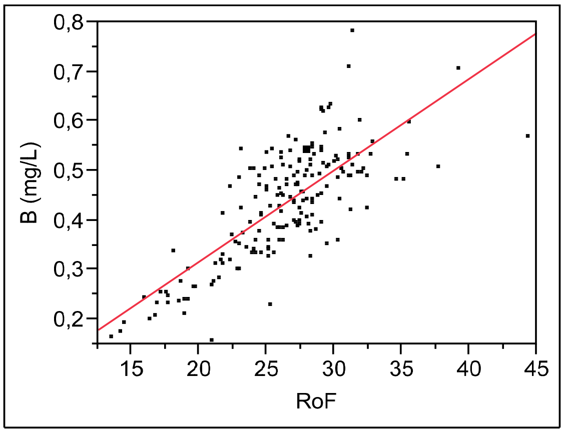

Fig. 6. Correlation between RoF and B leachout from Tanalith treated samples ($R^2 = 0.587$)

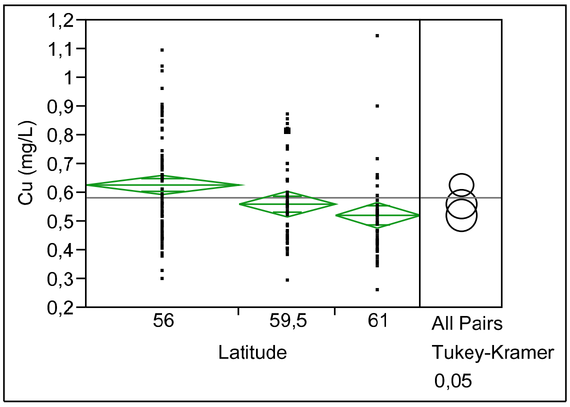

Fig. 7. Cu leachout correlation with latitude for Wolmanit CX-8 treated samples

According to Larnøy, treatability varies greatly between latitudes, favouring southern stands to be more permeable [5]. While correlating latitude with the leachout of the elements Cu and B a trend could be observed. Northern stands tend to leach out less preservative. This factor implies that the more permeable the wood is, the higher the leaching rate. This tendency was noted for both Wolmanit CX-8 and Tanalith treated samples and for both elements analyzed – Cu and B. However for Tanalith the trend was stronger. Tukey-Kramer test indicates that all stands significantly differ from each other as the circles are not overlapping (95 % confidence level) (Figs. 7, 8).

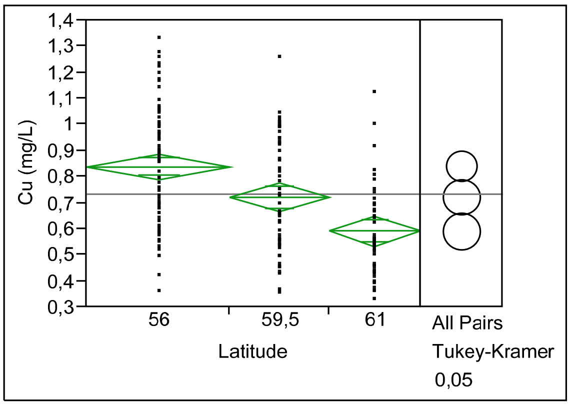

Fig. 8. Cu leachout correlation with latitude for Tanalith treated samples

Correlating sample`s vertical position in a tree with Cu and B leachouts, gives a trend of lower part of the trunk leaching out more than the upper part. Tukey Kramer shows significant difference between lowest and highest part of the tree, especially in Wolmanit CX-8. In this preservative the lowest part significantly differs from the other groups. Other groups were found to be alike and are demonstrated in concurrent circles (Figs. 9, 10).

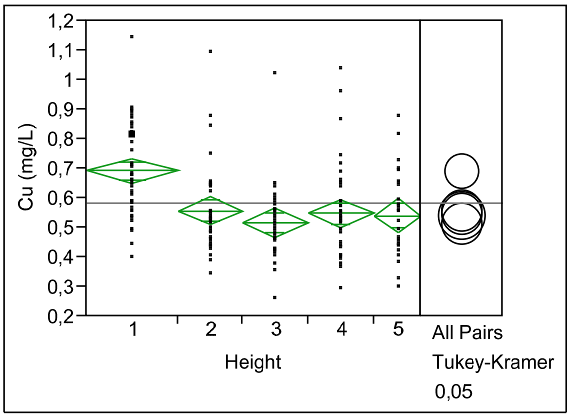

Fig. 9. Cu leachout correlation with vertical position in a tree for Wolmanit CX-8 treated samples

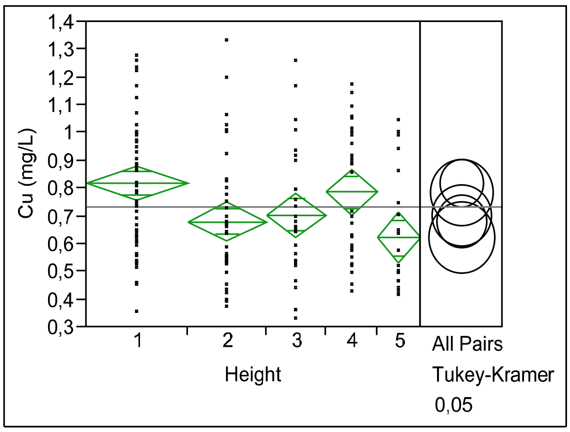

Fig. 10. Cu leachout correlation with vertical position in a tree for Tanalith treated samples

4. DISCUSSION

Depending on the study profile, leaching in literature is referred to from different aspects. Waldron et al. (2005) compiled the potential long-term leaching model by diffusion, which is based on the amount of preservative component free for emission, balanced dissociation of preservative into free water in wood and diffusion coefficients for substances percolating in different wood directions [10].

Emission of wood preservative also depends upon shape of the wood specimen. In this study the cross-sections of samples were sealed and according to Waldron this could have decreased the preservative leachout approximately five times [10].

Correlating the total amount of leachout with latitude, sample position (vertical and horizontal placement in a tree) and exposure, indicates which parameters are affecting leachability the most.

Screening showed that latitude and height in a tree have potential influence on leaching, while exposure and horizontal position of sample played minor role in copper and boron leachouts.

Figures 1 and 2 shows that ratio of filling is almost the same for Wolmanit CX-8 and Tanalith, so in this study impregnation liquid does not play a major role in influencing the RoF as described by Larnøy et al. working with Wolmanit-CX 8 and furfuryl alcohol. [5] The cause is that furfuryl alcohol and Wolmanit CX-8 differ more in molecular size than Wolmanit CX-8 and Tanalith. But as seen from Figures 3 to 6 there is a certain correlation between the amount of liquid into the wood and the amount of preservative compounds leaching out: more permeable samples emit more protection agent. The tendency applies to both Cu and B. Although, B is mentioned to be very leachable and the numbers also indicate that almost all B leached out, hence it is hard to say at first view if the raw material has a strong influence on B leaching [10, 11].

As seen from Figures 7 and 8, there is a significant difference in leaching between trees harvested from different latitudes. Latitude was found to be one of the main influences on treatability as well by Lande et al. [6] and Zimmer [7], who both used RoF to determine treatability.

It was noted that while latitude is affecting more Tanalith leachout, sample height in a tree is affecting more Wolmanit CX-8`s leaching. Figures 9 and 10 show the trend of lower part of the tree being more prone to both preservatives leaching out than the upper part. Referring to Zimmer`s work about treatability, it was found that the lowest part of the tree with the largest amount of latewood tends to be easiest to treat [7].

5. CONCLUSIONS

1. Significant correlation between ratio of filling and leaching of wood preservative (Wolmanit CX-8 and Tanalith) components was discovered.
2. Significant correlation between latitude and emission of Cu and B from preservatives was exhibited,

favouring southern stands of Scots pine emitting higher amount of preservative components.

3. The lower part of the stem shows higher leaching rate than the upper part.

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