LEACHING OF COMMONLY USED IMPREGNATION AGENTS AFFECTED BY WOOD PROPERTIES

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ABSTRACT

The objective of the study was to assess the influence of wood properties on copper leaching from wood treated with preservatives.
Scots pine (*Pinus sylvestris* L.) trees were harvested from two different stands in Norway and one in Denmark. Sapwood was cut to samples (20 x 20 x 50mm) in as many layers as the radial size allowed. Within this material, it is possible to trace the individual sample to its original position in the stem. Approximately half of the samples were treated with Wolmanit CX-8 and half with Tanalith. All samples were conditioned, impregnated with preservatives and leached according to EN84. Copper and boron content in water samples was determined by an ICP (Inductively Coupled Plasma) technique. The variation in leachability within trees, between trees and between different stands was studied.
Statistical analyses showed that trees from the south are more prone to leaching and that samples from the lowest part of the tree fixate less preservative than those from the upper parts. In addition, drying method of the sample had an influence and differences were also noted between products used in the study.

Key words: Copper-based wood preservatives, EN84, leaching.

INTRODUCTION

Wood is a renewable resource with many positive qualities but the wood industry faces challenges due to the changing environmental policies about the use of wood preservatives. Preservatives containing arsenic and chromium have been banned from the market. There have been studies indicating that copper in other systems is not so strongly bound (Habicht et al. 2003, Temiz et al. 2006) and the preservatives used in this study are common copper-based impregnation solutions.
Copper is naturally occurring element, mostly present in surface waters and is an essential micronutrient for plants and animals at low concentrations (Kapustka et al. 2004). At elevated concentrations, it may become toxic to aquatic life forms. Toxicity concentrations are species and water body dependent (Aquatic life ambient… 2007).
The objective was to assess the dependence of leachability on different wood properties of Scots pine. Previous studies have been made on permeability of wood that used the same raw material (Larnøy et al. 2008, Lande et al. 2010, Zimmer et al. 2009). It was

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found that treatability was affected by latitude, the origin of the sample with respect to vertical and horizontal stem position, tree height and method of drying.

MATERIAL AND METHODS

Wood samples

Three Scots pine stands were chosen for this study, two from Norway and one from Denmark. Nine trees were harvested from each site, 27 trees in total. After removing the top of the tree, the stem was divided into 5 sections of 60 cm. Sections were taken from 0, 25, 50, 75 and 100% of remained tree height. From each of the section a block of 75 cm width with north-south orientation was sawn. Blocks were split exactly through the pith. The two halves of each block were either “air dried” or “kiln dried”. Drying method for the north and south pole was randomly selected.

Only sapwood was chosen for this study, heartwood was removed. Samples with dimensions of approximately 20 x 20 x 50 mm were cut out in as many layers as the radial size allowed. In total, 931 samples were tested.

After cutting, samples were conditioned at 65% RH and 20°C until equilibrium moisture content was reached. To prevent the liquid flow in the longitudinal direction, cross sections of the samples were sealed with a two component sealer (Pyrotect-2K-Aussen-Schutzlack 1720-7100-302, Dreisol coatings GmbH, Germany).

This set of samples was impregnated with Wolmanit CX-8 and Tanalith, which are two widely used wood protection solutions.

478 samples were treated with Wolmanit CX-8, which is a chromium free, copper- and boron-based wood preservative consisting of 2.8% Bis-(N-cyclohexyldiazeniumdioxy)-copper (Cu- HDO), 13.04% Copper hydroxide carbonate and 4% boric acid.

459 samples were impregnated with Tanalith, which 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.

Impregnation

Impregnation was performed at 6 bar for 10 min. Wood samples were weighed immediately after impregnation to calculate respective uptake values.

Leaching

Test samples were conditioned in the same way as it had been done before impregnation (65% RH and 20°C till equilibrium moisture content).

Leaching was done according to EN84. Samples were covered with deionized water in an amount of approximately five times the volume of the sample and placed in the impregnation vessel. Samples were held in 0.04 bar of vacuum for 20 min. After vacuum, the samples stayed in the water for 2 h before the water was changed for the first time. Specimens were submersed in deionized water for 14 days. From every sample` s vessel, 5 ml of leaching water was collected, combined and submitted for chemical analyses. Water changes and collecting of water samples were done ten times (including the water change after impregnation in 2 h).

Table 1: Schedule for taking leaching samples.

Day	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Amount (ml)	5 5	5	-	-	5	5	5	5	5	5	-	-	-	5	50

Chemical and data analysis

Elements of interest in the leaching water were copper and boron. For tracing the amount of leachates from the samples, the leaching water was analyzed via ICP (Inductively Coupled Plasma) technique. For ICP the water samples were neutralized with hydrochloric acid (HCl).
To discover the sources of variance, results of leach-outs were correlated with different physical and anatomical wood properties. To determine the treatability of the wood samples and to find relations to leaching, ratio of filling (RoF) was calculated (Eq.1, 2), which relates the filled volume to the void volume that can be filled. It shows how much of the possible void volume is actually filled with liquid (Larnøy et al. 2008).

$$V_{void} = V_{12\%} - V_{cellwall} - V_{water} + V_{swell} \qquad (1)$$
$$RoF = V_{uptake} / V_{void} \times 100 \quad [\%] \qquad (2)$$

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
V_{uptake} is the volume of the treating liquid

Variables used are summarised in Table 2.

Table 2. Overview of variables used in the study.

Variables	Abbr.	Type	Comment
Location	Loc	nom	- Denmark - Norway, S-E - Norway, mid-E
Latitude	Lat	cont	56°- 61° North
Tree ID	T	nom	27 trees
Tree height	TH	cont	12-27 m
Tree age	TA	cont	18-300 years
Exposure side	ES	nom	North or South side of log
Diameter at breast height	DBH	cont	15-46 cm
Sample Height	SH	cont	0.3-20 m, 1-5 layers from the stem
Radial position	RP	cont	Registered as year after heartwood
Density	D	cont	393 -696 kg m^{-3}
Annual ring width	AR	cont	0.4-3.1 mm
Method of drying	MDr	nom	- Kiln dried at 60 °C (a) - Air dried at 20 °C (n)
Sample layer	SL	nom	1-4 layers of sapwood
Impregnation liquid	IL	nom	- Wolmanit CX-8 (W) - Tanalith (T)
Cu leachout	CuL	cont	Response variable

Statistical analyses were executed with JMP Pro 9 by SAS Institute Inc.

When promising variables were discovered, a linear mix model was generated. Linear mix model subsumes different variables simultaneously. The parameter estimates show how much the variable contributes to the response and the test statistics expresses if the effect is significant.

For the present model (Table 4), variables that showed correlations or significant difference when describing leaching were used as fixed effects. Individual tree was taken as a random effect meaning that the effect is selected by chance from a larger sample pool.

The mixed model can be written

$$Y = \mu + T_i + l_D + f_1 + a_a + b_T + g(RoF) + e_{iD1aT}$$

RESULTS AND DISCUSSION

Variations influenced by raw material in sapwood penetration have been found in former studies (Larnøy et al. 2008, Lande et al. 2010, Zimmer et al. 2009), which could mean that leaching of preservatives is also affected by wood properties.

Some samples (both Wolmanit CX-8 and Tanalith treated pieces) were regarded as outliers according to Mahalanobis and Jackknife Distances and, therefore, excluded from the analysis.

Table 3: Summary of outcomes

Treatment		Dimension	N	Mean	Std dev	min	max
Wolmanit CX-8	uptake	kg m^{-3}	471	210	38	114	312
Tanalith	uptake	kg m^{-3}	448	209	32	109	290
Wolmanit CX-8	RoF	%	471	26	5	13	39
Tanalith	RoF	%	448	26	4	13	39
Wolmanit CX-8	Cu leaching	mg L^{-1}	471	0.58	0.16	0.30	1.14
Tanalith	Cu leaching	mg L^{-1}	448	0.74	0.24	0.33	1.43
Wolmanit CX-8	B leaching	mg L^{-1}	471	0.57	0.14	0.28	0.93
Tanalith	B leaching	mg L^{-1}	448	0.43	0.11	0.16	0.78

One purpose of this study was to observe how the permeability of the material is correlated with the leaching of the preservative. To get a better overview of the impregnation volume, impregnation schedule was intentionally too short for full impregnation and samples were not completely filled. Wolmanit CX-8 and Tanalith are equally distributed within the samples: both treated samples are filled approx 13-39 % (Table 3). When correlating RoF to leached out Cu amount, the results show that there are not very strong relations (R^2~0.34) which suggest that the wood properties have an influence. There is a slight trend indicating that larger amount of Cu and B leach out at higher uptakes of preservatives. This influence was more pronounced in the case of B (R^2~0.69).

The conversion from mg L^{-1} into %-s, it shows that approx 18 % of Cu leaches out from Wolmanit CX-8 samples and 23 % from Tanalith samples. Almost all of the boron leached out from the samples, independent whether they had been treated with Wolmanit CX-8 or Tanalith. It is also mentioned in the literature (Waldron et al. 2005, Ibach 1999) that boron fixates poorly in the wood and therefore it is difficult to estimate how much of the wood properties actually influence the leaching of B.

The results of the correlation between the abovementioned variables (Table 2) and the total amount of leach-out, indicates the most important parameters for leachability. Latitude, samples` vertical tree position and drying method suggest influencing leachability. Samples coming from the southern forest sites, the lowest part of the tree and that were kiln dried tended to leach out the most preservative. Lande, Larnøy and Zimmer (2008-2010) who studied treatability of Scots pine using the same stands as the present study, found that the lowest tree sectors from the southern stand is the easiest to treat.
A linear mixed model employing method of drying, impregnation liquid, latitude and tree height as fixed effects and tree as a random effect explains approximately 44% of the variation in Cu leaching.

Table 4. Model parameters to predict Cu leachout (%)

R^2			0.44	
Random effects	**Parameter**	**Var.Component**		**Pct of total**
Tree	T (i=1-10)	1.42		5.54%
Residual	e	24.25		94.46%
Fixed effects		**Estimates**	**F-ratio**	**Prob>|t|**
Method of drying	a_a	-1.74	38.15	<.0001
	a_n	1.74		
Impregnation liquid	b_W	-2.86	114.65	<.0001
	b_T	2.86		
RoF	g	-0.43	30.37	<.0001
Latitude	l_D	1.45	6.11	0.0032
	l_S	0.27		
	l_H	-1.72		
Height	f_1	3.18	11.48	<.0001
	f_2	-1.12		
	f_3	-0.85		
	f_4	0.47		
	f_5	-1.68		
Intercept	μ	30.68		<.0001

In this model, the factor “impregnation liquid” has the biggest impact on leaching. This trend was also seen for Wolmanit CX-8 and furfuryl alcohol (Larnøy et al. 2008). This might be explained by the fact that furfuryl alcohol and Wolmanit CX-8 differ more in molecular size than the solutions used here.
The drying method is also of significance. Previous studies have shown that higher drying temperature gives higher penetration values which might be due to opening of the radial and longitudinal resin canals (Booker 1990) or evaporation of volatile extractives (Lande et al. 2010). This could in turn mean that higher temperatures during kiln drying alter the chemistry of the cell wall and reduce the fixation of preservatives as compared to air dried timber.

CONCLUSIONS

The study shows the influence of the harvesting site and wood variables on the leaching behaviour of copper-based preservatives.

1. Samples taken from southern stands have higher leaching values than those from northern ones.
2. A significant correlation between vertical stem position of the samples and the emission of Cu and B from preservatives was exhibited. Preservatives leached more out from lower than from higher parts of the stem.
3. Samples that were air dried leached out less preservative than the ones that were kiln dried.

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