

INFLUENCE OF ETHANOLAMINE ON LIGNIN DEPOLYMERIZATION AND COPPER LEACHING FROM IMPREGNATED WOOD

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ABSTRACT

Copper-ethanolamine based wood preservatives are replacing several classical copper-chromium based solutions, due to foreseen ban of chromium. Fixation of copper-ethanolamine based wood preservatives is not as good as fixation of copper-chromium ones. The main object of this manuscript was to prove, that ethanolamine primarily enables copper fixation, but later this chemical is the prime reason for insufficient fixation of copper-ethanolamine formulations. Presumably, since ethanolamine causes depolymerization of lignin and hemicelluloses, what consequences in increased leaching. In order to prove that presumption, Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*) wood specimens were impregnated with three different aqueous solutions consisting of copper-ethanolamine and additives/co-biocides of three different concentrations. After four weeks of fixation, those specimens were leached for seven days. Mass change after leaching was measured gravimetrically. Modulus of elasticity (MoE) was determined using non-destructive technique. In parallel, copper, nitrogen and carbon contents were analysed in leachates and carbon and nitrogen content were measured in leached and un-leached wood blocks as well. The results showed that presence of ethanolamine in preservative solutions results in MoE change. In leachates significantly increased carbon as well as copper contents was determined. Carbon contents in leachates from impregnated wood were significantly higher than in the leachates from control specimens. There was good correlation between organic carbon in leachates and copper leaching. The main source of organic carbon was wood components. Therefore, we believe, that our hypothesis of ethanolamine induced lignin depolymerization is confirmed.

KEY WORDS: Norway spruce, beech wood preservation, ethanolamine, depolymerization, performance, leaching

INTRODUCTION

Due to increased environmental awareness and foreseen ban of chromium based preservatives in EU (BPP 98/8/EC 1998) and voluntarily removal of copper-chromium-arsenic based preservatives from residential application in US and Canada (Townsend and Solo-Gabriele 2006), copper-ethanolamine wood preservatives are becoming the most important formulations for preservation of wood in ground contact (use class IV). Copper-ethanolamine complexes mainly react with lignin and there are two types of reaction mechanisms proposed. In a ligand exchange reaction mechanism, copper-ethanolamine complexes exchange ligands with wood and release one or two amine molecules (Thomason and Pasek 1997). In the second possible reaction mechanism, non-charged species of copper-ethanolamine complexes are transformed into charged species during process of impregnation. Functional groups (carboxyl and phenolic groups) can react with the charged species to form a stable wood-copper-ethanolamine complex (Zhang and Kamdem 2000). Unfortunately addition of ethanolamine can not ensure so good copper fixation as chromium compounds (Temiz et al. 2006). We presume that one of the reasons for insufficient fixation of copper-ethanolamine preservatives originates in the fact, that ethanolamine causes lignin depolymerization, resulting in leachable complexes of copper-ethanolamine-lignin monomers. Due to this lignin degradability, ethanolamine can be used even for pulping (Claus et al. 2004). However, lignin degradation in the presence of ethanolamine is not completely clarified. The most important reaction of lignin depolymerization is the cleavage of β -aryl ethers adjacent to carbonyl functions (Wallis 1976). Another lignin degradation mechanism was reported by Petrič and co-workers (Petrič et al. 2004) They stated that there are free radicals formed during interaction of wood with ethanolamine, which causes degradation and discoloration, very similar to UV degradation.

Our previous reports indicates, that high temperature fixation of copper-ethanolamine treated wood results in increased copper leaching, presumably because of the fact that temperature accelerated lignin depolymerization (Humar and Žlindra, in press). However, in the past researches we only suspect that ethanolamine induced depolymerization is the key factor for increased copper leaching. The main object of this manuscript was to prove this presumption. Elucidation of this phenomenon is of significant importance, in order to develop more effective and environmentally friendly copper-ethanolamine based wood preservatives.

MATERIAL AND METHODS

Sample preparation and leachates analysis

Samples ($0.5 \times 1.0 \times 20.0$ cm³) were made of Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*) wood. Orientation and quality of the wood meet requirements of the standard EN 113 (1996). For impregnation of the samples three different ethanolamine based aqueous solutions were used as resolved from Tab. 1. Control samples were impregnated with water only. First set of solutions consists of ethanolamine (EA), second one of copper(II) sulphate and ethanolamine (CuE), while the third one consists of copper(II) sulphate, ethanolamine, octanoic acid, sodium borate and alkyl diethyl benzyl ammonium chloride (CuEOQ). For impregnation, initial aqueous solutions were dissolved to have three different concentrations as seen from Tab. 1. Wood blocks were vacuum treated according to the EN 113 procedure (1996). The samples were then conditioned for four weeks: the first two weeks in closed chambers, the third week in half closed chambers, and the fourth week in open ones. Following conditioning, half of the samples were leached according to the modified EN 84 procedure for seven days (1994) Specimens were

soaked in the same water during leaching. Afterwards, leached and non-leached samples were oven dried (103 °C), and their initial masses were determined. Copper, carbon and nitrogen contents were determined in all collected leachates. Copper concentrations were determined with FLAAS (Varian SpectraAA Duo FS240). Experiment was performed in seven replicates. Total and organic carbon contents were determined with TOC analyzer Shimadzu TOC-5000A according to ISO 8245. Total nitrogen contents were determined with UV-Vis spectrometer Varian Cary 50 after the oxidative digestion with peroxodisulfate in autoclave (ISO 11905-1).

Tab. 1: Chemical composition of preservative solutions used

Preservative solution	Concentration of preservative solution	C _{Cu} (%)	C _{EA} (%)	C _{OA} (%)	C _{quat} (%)	C _B (%)
EA	Low (L)	0	0.577	0	0	0
	Medium (M)	0	2.885	0	0	0
	High (H)	0	5.770	0	0	0
CuE	Low (L)	0.1	0.577	0	0	0
	Medium (M)	0.5	2.885	0	0	0
	High (H)	1.0	5.770	0	0	0
CuEOQ	Low (L)	0.1	0.577	0.081	0.1	0.048
	Medium (M)	0.5	2.885	0.405	0.5	0.238
	High (H)	1.0	5.770	0.810	1.0	0.476
Water	/	0	0	0	0	0

EA – ethanolamine, OA – octanoic acid, quat – quaternary ammonium compound,

Evaluation of modulus of elasticity

Modulus of elasticity (MoE) was determined before impregnation, after conditioning of impregnated specimens and after leaching. Specimens were oven dried prior MoE measurements. Because of difficulties encountered in measuring the axial vibrations, flexural vibration modes were used to characterize elastic parameters. Considering the hypothesis of the homogeneity of geometrical and mechanical properties along the sample, basic dynamics theorems can be applied to obtain the motion equation of lateral vibrations. Analysis was performed on specimen with clamped-free end conditions. During the test the lateral displacements of vibrating sample in damped vibration with known vibration mode was measured. As, an inductive proximity sensor was used, a small piece of metal foil of neglected mass was glued on the surface of each sample. The damped frequency was obtained by FFT analysis of the exponentially decayed displacement signals detected in time domain. For determination of Young modulus of samples we used the frequency equation deduced from Bernoulli model, which was assumed as acceptable because of the relatively high length-to-depth sample ratio, (E - Young modulus (N/m^2), ν - natural frequency (s^{-1}), $C = 3.51563$ – constant derived from Bernoulli equation, ρ – density ($kg\ m^{-3}$), l – free sample length (m), h – sample height (m)). Measurements were performed on seven replicates.

Chemical analysis (CNS) of wood

Prior nitrogen and carbon analysis, wood blocks, that was used for MoE measurements, were milled into particles (MESH 80) and homogenized. Approximately, 0.2 g of an oven dry sample was combusted in the oxygen atmosphere at 1350°C in LECO 2000-CNS analyzer to determine carbon and nitrogen content.

RESULTS AND DISCUSSION

The complete volume of the specimens was impregnated with preservative solutions, since they were made of sapwood, they have rather high surface volume ratio and efficient procedure was used for treatment. Norway spruce specimens in average retain 430 kg/m³ and beech wood ones retain 510 kg/m³ of preservative solutions. There were no statistically significant difference observed between different preservative solutions and concentrations.

Mass of the oven dry specimens increased after impregnation. The lowest dry retention was observed at ethanolamine treated specimens and the highest one at specimens treated with the most complex solution CuEOQ. Retention, expressed weight percent gain, was higher at spruce wood specimens than at beech ones. For example, treatment of the Norway spruce with ethanolamine aqueous solution of the highest concentration, resulted in mass gain of 7.8% while treatment of the parallel specimens made of beech, resulted in weight gain of 4.1%. At beech specimens, more wood substrate retains less preservative solutions than spruce wood specimens. Relationship between solution uptake and density of spruce specimens was 1.13, and 0.75 at beech ones (Tab. 2). However, it should not be overlooked that mass gain showed that, even after drying of the ethanolamine treated specimens at 103°C, ethanolamine did not completely evaporate from wood (Tab. 2). In spruce wood specimens impregnated with the ethanolamine solution of the medium concentration in average 87.5% and in beech wood 69.5% of ethanolamine remained in wood.

After leaching, weight of impregnated specimens was determined again. Ethanolamine treated and leached spruce specimens have almost the same mass than observed before impregnation. Additionally, weight of the leached ethanolamine impregnated beech wood was even lower than before impregnation (Tab. 2). On the first look this indicates, that most of the ethanolamine were released from wood during leaching as its fixation is not sufficient. While, CNS results showed, that considerable amounts of ethanolamine remained in wood even after leaching (Tab. 2). Thus some other components besides ethanolamine must leach from wood. Analysis of the leachates revealed increased nitrogen as well as carbon concentrations. Concentration of organic carbon in leachates from beech wood impregnated with ethanolamine solution of the highest concentration was almost ten times higher than at leachates from untreated specimens (Tab. 3). We presume that increased carbon levels did not come from ethanolamine only, but from depolymerised wood components as well. Average carbon-nitrogen ratio in leachates from impregnated wood was 3.27 at spruce and 4.12 beech ones, what is considerably higher than at ethanolamine itself (1.71). This is clear evidence, that there are some other organic-compounds besides ethanolamine leached from wood. In order to determine wood components in leachates, they were oven dried, and an FTIR spectrum of the dry residue was determined, revealing that there are peaks assigned to aromatic rings as well as to carbohydrates identified. According to the literature data (Claus et al. 2004, Petrič et al. 2004), we consider depolymerization of lignin, and leaching of the depolymerised lignin fragments, as one of the possible mechanism, that could explain higher carbon contents in collected leachates. This presumption is further supported by comparison of beech and spruce masses after leaching. Ethanolamine treated beech specimens losses more weight after leaching in comparison to spruce one (Tab. 2), presumably due to the higher lignin content. Lignin depolymerization is oxidative process, as there are significant amounts of oxygen consumed during fixation of copper-ethanolamine wood preservatives (Humar et al. 2003). Additional proves for lignin depolymerization is vanilla like smell during oven drying and colour changes of ethanolamine treated wood. Ethanolamine treated specimens became more brownish, because of the quinone formation (Petrič et al. 2004). Furthermore, microscopy analysis of differentially coloured slices revealed, that there was significantly less lignin determined in earlywood, while

anatomy structure of latewood remained almost the same (Humar et al. 2007). However, besides lignin there is possibility that there are some other components, particularly extractives leached from wood. Ethanolamine can form water soluble soaps with fatty acids extractives, for example.

Tab. 2: Properties of Norway spruce and beech wood impregnated with different ethanolamine containing aqueous solutions before and after leaching

Wood species	Preservative	Conc.	Leaching	Mass change (%)	MoE change (%)	N content (%)	C content (%)
Spruce	EA	L	No	1.2	-1.3	0.257	42.40
			Yes	0.0	1.5	0.122	43.73
		M	No	4.0	-4.8	1.075	42.25
			Yes	-0.1	0.0	0.296	44.47
			No	7.8	-13.6	1.600	41.50
			Yes	0.0	20.7	0.410	40.40
	CuE	L	No	4.1	0.4	0.210	42.52
			Yes	1.7	-2.2	0.141	42.50
		M	No	7.0	-10.2	0.835	43.37
			Yes	1.8	-3.5	0.377	41.68
			No	14.5	-9.8	2.065	42.32
			Yes	2.9	-3.7	0.566	42.98
	CuACQ	L	No	2.7	-3.2	0.368	43.32
			Yes	0.8	-3.1	0.158	41.19
		M	No	10.1	-13.8	1.128	43.22
			Yes	3.1	-2.2	0.380	41.45
			No	17.7	-24.1	1.578	43.17
			Yes	4.6	-5.5	0.553	42.92
Water	/	No	0.5	0.8	0.053	43.53	
		Yes	0.0	-0.8	0.051	43.47	
Beech	EA	L	No	0.6	-0.8	0.187	44.67
			Yes	-0.7	6.6	0.112	44.75
		M	No	2.3	-3.8	0.492	44.60
			Yes	-1.3	6.3	0.225	44.83
			No	4.1	-15.1	1.003	44.80
			Yes	-1.9	4.8	0.304	44.60
	CuE	L	No	1.1	0.8	0.172	44.75
			Yes	-0.6	4.8	0.120	44.90
		M	No	4.0	5.8	0.612	43.85
			Yes	0.4	5.8	0.247	44.28
			No	7.0	-1.2	1.005	43.77
			Yes	0.7	11.4	0.448	44.25
	CuACQ	L	No	1.5	3.3	0.182	45.03
			Yes	-0.2	9.2	0.125	44.63
		M	No	5.6	-2.8	0.617	43.87
			Yes	0.9	6.3	0.277	45.17
			No	11.1	-14.2	1.067	43.47
			Yes	2.6	2.7	0.418	44.55
Water	/	No	0.0	1.2	0.080	44.48	
		Yes	-0.8	1.3	0.065	44.53	

In most of leachates from copper ethanolamine (CuE and CuEOQ) treated wood, even higher levels of organic carbon were determined as in the ones from ethanolamine treated wood. It seems like, that copper in wood even promotes lignin depolymerization. This statement is understandable as copper is involved in several radical induced lignin degradation reactions (Petrič et al. 2004, Fackler et al. 2006). The question arises how this influence mechanical properties of impregnated wood. Non-destructive testing of MoE enables us comparison of the specimens MoE before and after treatment. However, we are aware that MoE indicates mainly changes in cellulose structure.

In order to elucidate influence of lignin depolymerization on mechanical properties and copper leaching, additional mechanical experiments, that indicate dynamic mechanical properties, should be performed. As lateral vibration is mainly in correlation with tensile strength, and lignin mainly influences on compression strength, this method is not the best one to determine these changes. Therefore, non-destructive impact test would be more suitable to determine lignin changes.

Tab. 3: Basic characteristics of leachates after seven days of leaching of Norway spruce or beech wood specimens impregnated with ethanolamine containing preservative solutions. TC – total carbon, IC – inorganic carbon, OC – organic carbon, N – nitrogen, Cu – copper

Wood species	Preservative	Conc.	TC (mg/l)	IC (mg/l)	OC (mg/l)	c _N (ppm)	c _{Cu} (ppm)
Norway spruce	EA	L	321.3	34.9	286.4	79.7	0.6
		M	1180	78.0	1102.0	327.8	1.3
		H	3007.2	281.8	2725.4	644.9	1.4
	CuE	L	269.6	20.1	249.4	80.3	6.0
		M	1016.7	32.2	984.5	380.2	86.7
		H	2089.2	92.3	1996.9	811.3	360.3
	CuACQ	L	400.4	17.8	382.6	105.8	8.7
		M	1464.3	62.2	1402.1	410.4	87.1
		H	2290.5	95.2	2195.3	725.9	308.0
	Water	/	66.1	9.2	56.9	13.7	0.1
Beech	EA	L	488.3	59.9	428.4	89.5	1.7
		M	1507.3	112.0	1395.2	380.5	0.6
		H	2451	197.8	2253.2	700.6	0.7
	CuE	L	477.4	39.2	438.2	85.3	21.2
		M	1950.9	38.0	1912.9	439.6	88.2
		H	2410.5	52.4	2358.1	783.7	142.1
	CuACQ	L	637.7	40.5	597.2	128.2	30.6
		M	1646.6	29.7	1616.9	365.4	62.0
		H	3050.4	57.7	2992.6	780.7	187.6
	Water	/	287.8	38.2	249.5	28.2	0.9

Impregnation of the spruce as well as beech wood specimens with preservative solutions causes loss of MoE. Decrease of the MoE was the most prominent at spruce specimens impregnated with preservative solutions of the highest concentration. The highest one (-24.1%), was determined at spruce blocks impregnated with preservative CuACQ (Tab. 2). At beech wood specimens lower MoE losses were determined. We presume that there are similar reasons for difference between spruce and beech, as described for mass changes; higher retention-density ratio at spruce compared to beech. After leaching, MoE of the specimens increased again. Final MoE of the leached spruce specimens depends of concentration of preservative solutions, at specimens impregnated with more concentrated solutions higher MoE losses were determined. At leached beech specimens impregnated with copper-ethanolamine based preservatives higher MoE was determined than at unimpregnated specimens. The most prominent increase (11.4%) was determined at leached beech wood specimens impregnated with preservative CuE of the highest concentration. One of the reasons for this increase could be, that ethanolamine cause formation of free radicals in lignin (Petrič et al. 2004) after drying these free radicals enables new cross-linking of lignin fragments.

However, the most important question arises how lignin depolymerization and copper leaching are related. Leaching procedure used in this experiment was one of the most severe ones. Vacuum treatment was the first step of leaching procedure. Therefore specimens were completely soaked with water, what enable efficient diffusion of water soluble molecules from wood to leachates. This fact and high surface-volume ratio explains extensive leaching of copper active ingredients. Copper leaching from spruce wood specimens impregnated with the preservative solution CuE and CuEOQ increased with increasing concentration of preservative solutions. For instance, from spruce specimens impregnated with CuE solution of the highest concentration in average 30.3% of copper was leached while almost five times lower copper losses were determined at specimens treated with the solution CuE of the lowest concentration (6.0%). Similar ratios were observed at spruce wood treated with preservative solution CuEOQ, also. If concentration of organic carbon (OC) and copper leaching rates are compared (Fig. 1A), it can be seen that those values are tightly correlated ($r^2 = 0.93$). At specimens where higher copper leaching was determined, higher concentrations of organic carbon were determined in leachates as well. This is in line with our presumption, that copper leaching and lignin depolymerization are related. In addition, good correlation between mass change after leaching and copper losses ($r^2 = 0.96$) was determined as well (Fig. 1B). On the other hand, correlation between MoE changes and Cu leaching is less significant, but still present (Fig. 1).

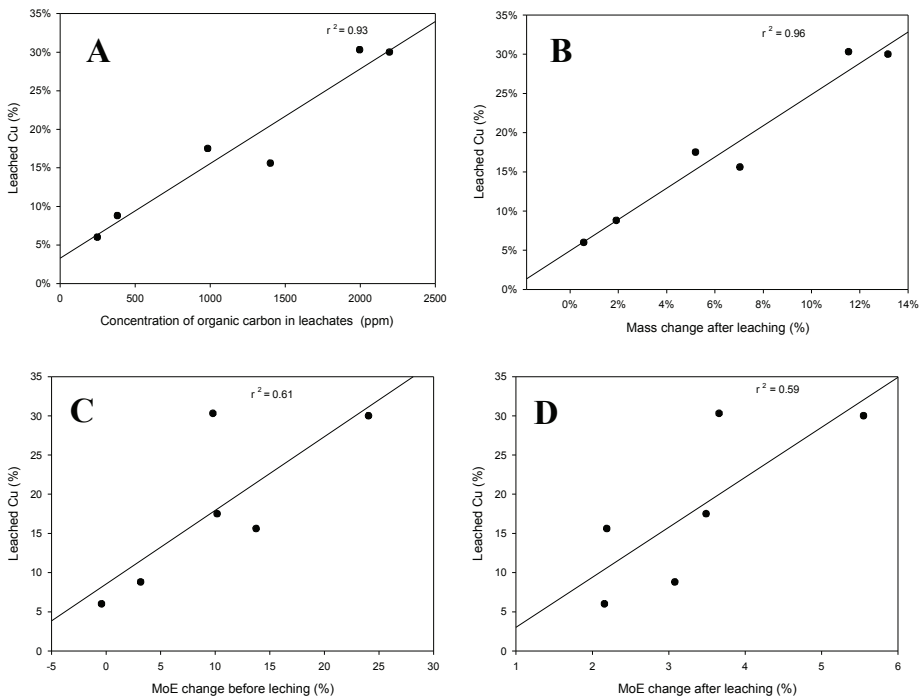


Fig. 1: Correlations between concentration of organic carbon in leachates (A), mass change after leaching (B), MoE change before (C) and after leaching (D) and copper leaching from spruce wood impregnated with different copper-ethanolamine based preservatives

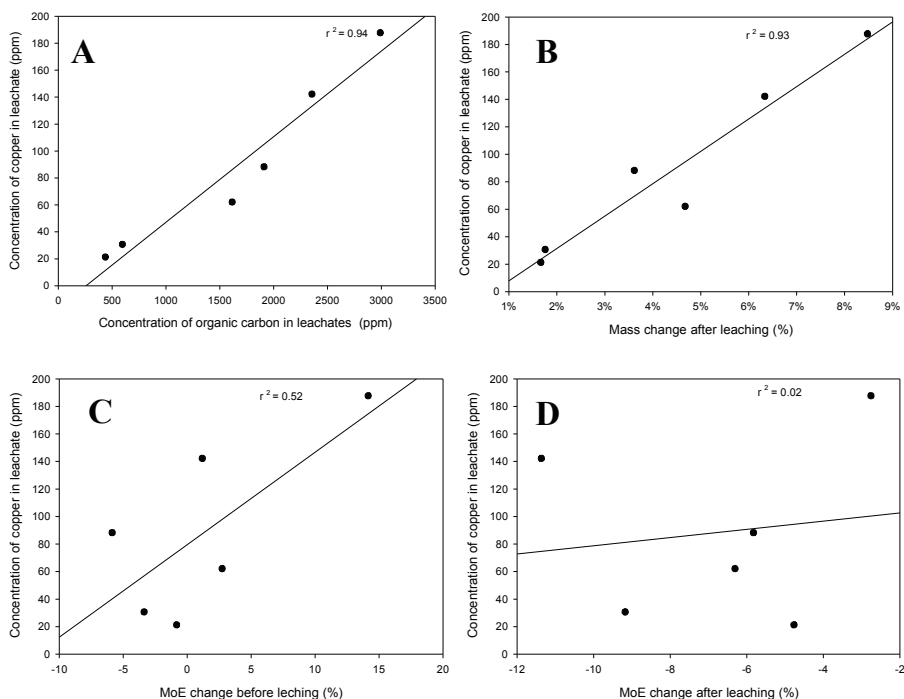


Fig. 2: Correlations between concentration of organic carbon in leachates (A), mass change after leaching (B), MoE change before (C) and after leaching (D) and copper concentration in leachates from beech wood impregnated with different copper-ethanolamine based preservatives

At beech wood, concentration of copper and organic carbon in leachates was correlated as well ($r^2 = 0.94$) (Fig. 2A). What once more indicates, that lignin depolymerization resulted in higher copper leaching. Extremely significant correlation was determined between copper concentration in leachates and mass loss after leaching ($r^2 = 0.93$) (Fig. 2B). At specimens that losses more weight during leaching, higher copper leaching rates were determined. This data indicates that copper bind to depolymerised lignin fragments, can be easily leached from the wood. Similar to spruce wood, correlation between MoE changes before leaching and copper concentration in leachates is less significant, but still present (Fig. 2C). However, there is no correlation between MoE change after leaching and copper leaching from beech wood specimens (Fig. 2D).

Conclusions

Ethanolamine in copper based wood preservatives on the first place enables copper fixation. Besides that, it causes degradation of lignin or other wood components, what results in more prominent leaching. Wood degradation reflects in higher organic carbon content in leachates, mass losses after leaching and changes in mechanical properties.

Our results indicate that copper-ethanolamine fixation could be improved. There are two most prominent options that could inhibit lignin depolymerization: addition of antioxidants and fixation in oxygen free atmosphere.

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