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Influence of wood species, treatment method and biocides concentration on leaching of copper–ethanolamine preservatives

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Abstract

Cu–ethanolamine-based preservatives are currently the most important alternatives for classical chromated-copper formulation. However, emissions of Cu from wood impregnated with copper–ethanolamine-based preservatives are still higher compared to emissions from wood preserved with copper–chromium based preservatives. In order to elucidate leaching of copper from specimens treated (brushed, soaked or vacuum-impregnated) with different copper–ethanolamine containing biocides of two different concentrations the following research on specimens made of Norway spruce (*Picea abies*), Scotch pine (*Pinus sylvestris*) and Beech (*Fagus sylvatica*) were performed. The results showed that leaching is significantly affected by the wood species used. The lowest leaching rates were determined in specimens made of spruce, while the highest ones were determined in beech wood. Concentration of active ingredient influences the Cu fixation as well. Unfortunately, ethanolamine at higher concentration causes depolymerisation of lignin macromolecules, which results in increased copper leaching.

Keywords: Copper; Ethanolamine; AAC; Leaching; Fixation; Wood species; Retention; Impregnation

1. Introduction

Copper effectiveness against wood decay fungi makes it an important constituent of several classical, novel and proposed wood preservatives. Among them, copper–amine-based preservatives are currently the most attractive ones, due to foreseen limitations of arsenic and/or chromium in CCA and/or CCB. Ethanolamine is reported as the most suitable amine source in several researches, and it is used for several emerging preservative systems including alkaline copper quat (ACQ), copper dimethyl-dithio-carbanate (CDDC), Cu–HDO and copper azole (CA) [1,2].

The fixation of copper–amine system is still not completely examined yet. It is clear that the role of amine ligand is particularly important, as amine can affect stability, polarity and solubility of the copper–amine complex. Cupric ions are prone to form complexes with ethanolamine through amino and hydroxyl groups in aqueous solution due to formation of a five-member ring complex. These processes are significantly affected by pH of the medium. If the copper–amine complexes are bound in wood by physical interaction, they will be leached out of wood easily by water. To be well fixed in wood cells, the copper–amine complexes have to interact with wood through chemical reactions [3]. Carboxylic and phenolic hydroxyl groups in wood are the most important active sites for interactions with copper [4,5].

The most important weaknesses of copper–amine preservatives is still quite high leaching compared to classical copper–chromium preservatives. Emissions of copper from wood impregnated with copper–amine preservatives can be reduced with proper copper–amine molar ratio and addition of different hydrophobic agents. Octanoic acid is one of the chemicals that significantly decrease copper leaching from wood. This carboxylic acid has multiplicative effect, besides hydrophobic; there are new less water soluble complexes formed between copper–amine and octanoic acid in the preserved wood which decreases leaching as well [3,6]. Additionally, octanoic acid has

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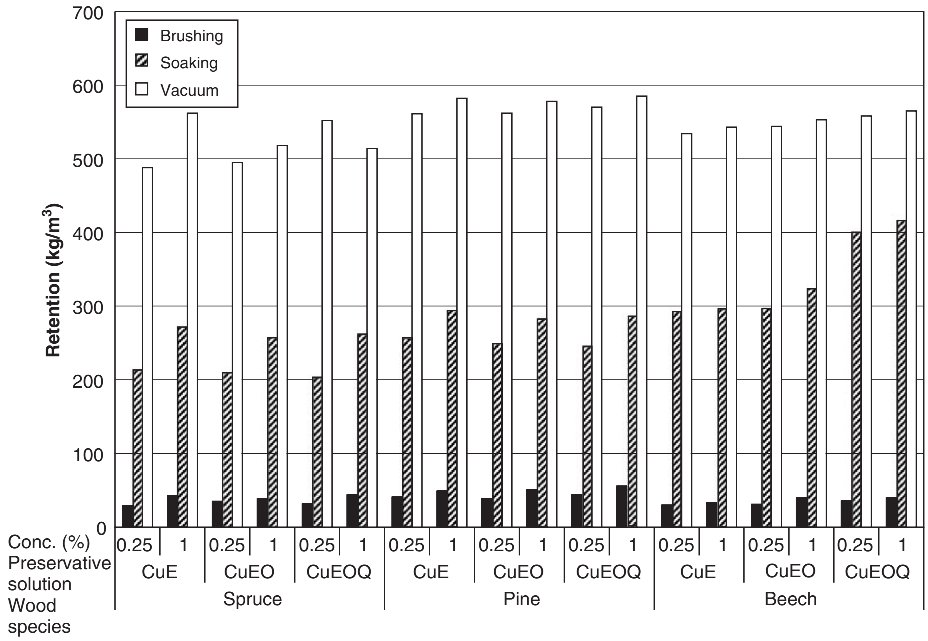

Fig. 1. Retention of preservative solution after brushing, soaking or vacuum impregnation of the specimens made of three different wood species, with different copper–ethanolamine aqueous solutions.

fungicidal effect itself, which results in improved quality of impregnated wood [3] (Fig. 1).

However, in most of the previous reports on copper leaching or fixation [3,4], experiments were performed on specimens made of single wood species, impregnated according to standard vacuum procedures only. From the application point of view it would be of great interest to compare copper leaching in specimens made of different wood species and preserved with different techniques with preservatives of different concentrations. In order to elucidate those issues, the following research was performed.

2. Material and methods

2.1. Specimens

Specimens were made of the three most important European non-durable woods: Norway spruce (*Picea abies*), Scotch pine (*Pinus sylvestris*) and Beech (*Fagus sylvatica*). For specimens, only sapwood part was chosen. The dimensions ($1.5 \times 2.5 \times 5.0$ cm) and orientation of the samples meet requirements of the standard EN 1250 [7]. In total 486 specimens were prepared. For each combination of treatment, preservative and concentration, nine specimens were prepared, which were leached in three individual vessels.

2.2. Treatment solutions

For impregnation of the specimens three different copper(II) sulphate, ethanolamine aqueous solutions were used. Copper ethanolamine molar ratio was constant (1:6) in all of the preservative formulations. This molar ratio is rather high in order to achieve dissolution of all wood preservative ingredients. The detailed properties of preservative solutions are explained in the article of Humar and coworkers [8]. The first solution contains copper and ethanolamine only (CuE), while the second one contains octanoic acid as well (CuEO). The molar ratio of Cu and octanoic acid was 1:1. The third solution was the most complex. It consisted of copper(II) sulphate, ethanolamine, octanoic acid and alkyl diethyl benzyl ammonium chloride (CuEOQ). The Concentration of CuEOQ equals to the copper one. For impregnation, aqueous solutions of two different copper concentrations were used. At the highest one, Cu concentration was 1.0%, while at the other one, a four times lower Cu concentration of 0.25% was chosen.

2.3. Impregnation

Specimens were treated with preservative solutions using three different procedures. Specimens (162 in all) were brushed two times with the selected aqueous solution. Another 162 specimens were soaked into the respective preservative solution for 24 h, while the last third of the specimens were vacuum-impregnated according to the EN 113 procedure [9]. Various treatments of the wood specimens resulted in different solution uptakes that can be seen form Table 1. Later, the specimens were conditioned for 4 weeks, the first 2 weeks in closed chambers, the third week in half-closed and the fourth week in open ones, and afterwards stored at 25 °C, 65% RH.

Table 1
Results of the ANOVA test (0.95)

Wood species	Preservative solution	Cu conc. (%)	Treatment		
			Brushing	Soaking	Vacuum
Spruce	CuE	0.25	B	A	A
		1	B	D	B
	CuEO	0.25	A	B	A
		1	A	C	B
	CuEOQ	0.25	A	C	AB
		1	B	EF	B
Pine	CuE	0.25	B	E	B
		1	B	E	C
	CuEO	0.25	B	E	AB
		1	C	D	C
	CuEOQ	0.25	C	F	BC
		1	C	F	B
Beech	CuE	0.25	C	DE	AB
		1	C	FG	D
	CuEO	0.25	B	DEF	B
		1	C	F	D
	CuEOQ	0.25	C	F	C
		1	C	FG	D

Influence of wood species, preservative solution and concentration on copper leaching was analysed.Differences between treatments are not seen from this table.Each column represents its own group.

2.4. Leaching procedure

Leaching was performed according to the modified ENV 1250 [7] procedure. In order to speed-up the experiment, the following two modifications were done: instead of five, three specimens were positioned in the same vessels and water mixing was achieved with shaking on a shaking device instead of a magnetic stirrer.

Nine specimens per solution per treatment per concentration were put in three vessels (three specimens per vessel) to have three parallel leaching procedures. In total 162 vessels were prepared. The specimens in the vessel were positioned with a ballasting device. Distilled water (300 g) was added and the vessel with its content was shaken at the frequency of 55 min^{-1}. Water was replaced daily for seven subsequent days. Leachates from the same vessel were collected and mixed together. Afterwards, atomic absorption spectroscopy (AAS) analysis of the leachate was performed. Percentages of leached copper were calculated from the amount of retained copper determined gravimetrically and the amount of copper in the collected leachates.

3. Results and discussion

3.1. Retention of preservative solutions

Different impregnation procedures resulted in various retentions. The highest solution uptakes were measured at vacuum-impregnated specimens (548 kg/m^3) and the lowest ones at the brushed ones (41 kg/m^3). The average retention of soaked specimens was in between (282 kg/m^3) (Table 1). Those uptakes are comparable with the ones reported in literature [10].

At specimens made of different wood species comparable uptakes were determined after brushing. On the other hand, the most prominent influence of wood species on retentions was noted during soaking. The highest one was determined at specimens made of beech sapwood (339 kg/m^3), followed by pine sapwood (270 kg/m^3) and spruce sapwood (232 kg/m^3) (Table 1). In vacuum-treated specimens the influence of wood species on retention was less prominent. The vacuum treatment of pine specimens resulted in the highest uptake of 573 kg/m^3, while the lowest retention of 521 kg/m^3 was measured in vacuum-treated spruce blocks (Table 1). The reasons for the observed differences can be explained by well-known anatomical features.

The composition of the preservative solution did not have a significant influence on the amount of retained biocide (Table 1). However, uptake of the preservative solution was significantly affected by concentration of the active ingredients. This difference was more evident in soaked specimens than in vacuum-treated ones. For example, in spruce specimens soaked in solution, CuE of the highest concentration, on average, retained 273 kg/m^3 of the preservative solution. But, in spruce specimens treated according to the same procedure and solution, CuE of the lowest concentration, on average 27% lower solution uptakes, were weighted (214 kg/m^3) compared to the ones treated with solution of the highest concentration. Analogous relationships were noted in specimens made of spruce or pine immersed in the preservative solution for 24 h. In wood blocks made of beech, the influence of concentration on retention was less-significant (Table 1). We believe that ethanolamine is the key substance that influences impregnability of wood. There are two important reasons that can explain the positive influence of ethanolamine. Firstly, ethanolamine decreases the surface tension of the preservative solution; therefore, it enables preservative solution to penetrate smaller voids in the wood cell walls. Secondly, some resins are soluble in ethanolamine, which results in the opening of additional paths for penetration of the preservative solution into specimens made of softwood. Solubility of resins in ethanolamine explains the increased retention at specimens impregnated with solutions of higher ethanolamine concentration at pine and spruce specimens in comparison to beech ones (Table 1).

3.2. Leaching of copper from impregnated wood

The prime interest of this research was to determine the influence of various parameters on copper leaching. The highest average leaching rates were determined in brushed specimens. This seems reasonable, as preservatives applied by this technique remained on the surface layer of the

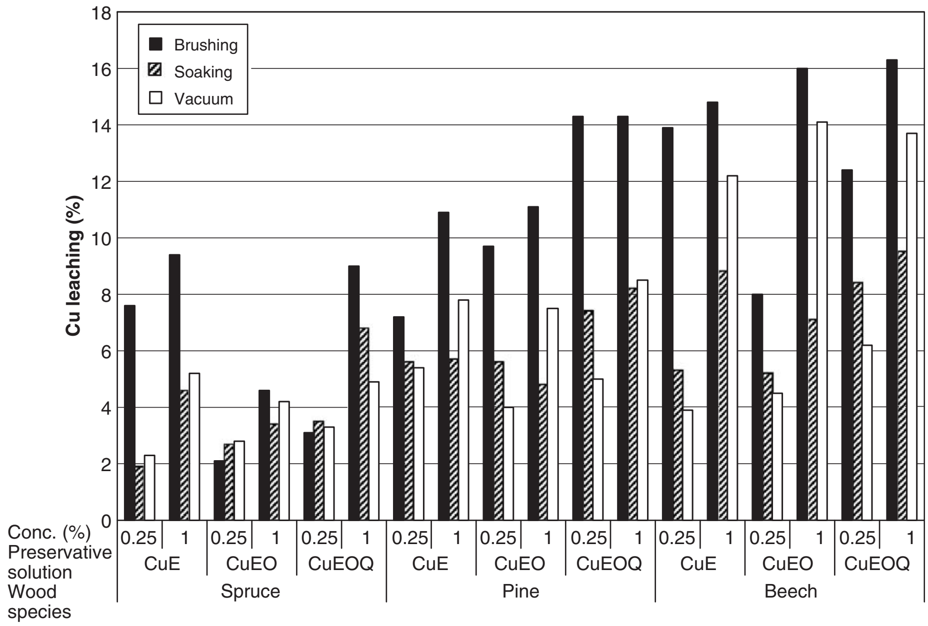

Fig. 2. Copper leaching from the specimens treated (brushed, soaked or vacuum impregnated) with different copper–ethanolamine solutions.

specimens mainly; thus, they are more susceptible to leaching (Fig. 2). We presume that soaking resulted in the best fixation rates, as the amount of preservative that enter into the specimens by vacuum treatment was too high, and there might not be enough reaction sites in wood components for fixation of copper/amine complexes.

Composition of the preservative solutions influenced leaching rates as well. In our previous researches [3,11] we reported reduced copper leaching from vacuum-impregnated Norway spruce blocks in the presence of carboxylic acids in Cu/amine preservative solution. Among different carboxylic acids, octanoic acids improved copper fixation to the highest extent. Therefore, we were interested in whether octanoic acid improves copper fixation in other wood species and in wood blocks impregnated with solutions of the lowest concentration as well. As expected, the presence of octanoic acid decrease copper leaching from specimens made of spruce wood that when brushed, soaked and vacuum-impregnated with the aqueous solution of the highest concentration. For example, from the specimens that were soaked in the formulation CuE, 4.6% of Cu was leached. If specimens were treated with a solution that besides copper and ethanolamine contains octanoic acid (CuEO), 3.4% of Cu was leached (Fig. 2). On the other hand, when spruce specimens were impregnated with preservatives of the lowest biocide concentration, octanoic acid does not influence copper leaching any more. On the contrary, there was an even slight increase of Cu leaching. From spruce blocks vacuum-impregnated with CuE, 2.3% of Cu was leached, while from the ones impregnated with CuEO 2.8% of copper was determined in the leachate. We cannot explain the reasons for the reported difference. We suspect that the concentration of octanoic acid was too low and the hydrophobic effect cannot be expressed.

Addition of other co-biocides (quaternary ammonium compound, boron) into copper–ethanolamine–octanoic acid-based preservative solution resulted in increased Cu leaching compared to both CuE and CuEO preservatives. This was evident in spruce blocks regardless of the method of treatment. Copper leaching from specimens brushed or soaked with CuEOQ was increased to 50% in comparison to blocks preserved with CuEO. However, increase of Cu leaching, due to addition of quaternary ammonium compound and boron, was least-visible in vacuum-treated spruce blocks (Fig. 2). This result seems promising as vacuum treatment is the preferred method for preservation of the most important middle-European wood species (spruce) for outdoor use.

Furthermore, a significant influence of concentration of the preservative solution on leaching was observed as well. From specimens impregnated with preservative solution that contains more active substances, on average higher amounts of copper was leached, in comparison to the ones preserved with solutions of the lowest concentration. This difference was considerable as in brushed specimens as in the specimens that were soaked and vacuum-impregnated (Fig. 2). For example, in spruce blocks vacuum-treated with solution CuE of the highest concentration, 5.2% of Cu was leached, while from comparable blocks treated with aqueous solution CuE of the lowest concentration, an approximately 55% lower copper leaching rates was determined (2.3%). Similar ratios were determined in specimens made of pine too. In beech wood the influence of concentration was even more prominent. From beech specimens, either brushed, vacuum-impregnated or soaked in Cu–ethanolamine-based preservative solution of the highest concentration, most significant Cu leaching rates were determined (Fig. 2). This indicates that leaching of

Cu–ethanolamine is significantly affected by the wood species used. We believe that there must be a reason for such prominent leaching from beech specimens. The data on copper leaching seen from Fig. 2 points out that in the specimens impregnated with preservative solutions of the lowest concentration, copper is more leaching resistant than in the case when wood was treated with preservatives of the highest concentration. We believe that there are two main reasons for increased leaching in the case when specimens were preserved with solutions that contain a higher content of active ingredients. Firstly, the amount of functional groups in wood that can react with the copper/ethanolamine complex is limited, particularly the one that can form the most stable forms. Therefore, in the case of wood impregnated with an aqueous solution of copper–ethanolamine preservative of the highest concentration, there are possibly not enough functional groups to form stable complexes; thus there are higher percentages of copper/ethanolamine complexes that remain deposited in wood cell lumina which are more prone to leach from wood. Secondly, Petrič and co-workers [12] noted that during reaction of ethanolamine with wood or its components, free radicals were formed. They cause depolymerisation of lignin [13,14]. Sections of lignin that reacted with the copper/ethanolamine complex are sometimes simply cut from the lignin macromolecule and leached from wood. A radical reaction of depolymerisation is an almost newer ending process vital long after impregnation, as long as specimens are wet and ethanolamine is present. However, volatilisable ethanolamine at least partly reacts with wood. After impregnation and drying (103 °C), approximately 60% of ethanolamine that was introduced to wood during impregnation remained in wood and does not evaporate from wood even after 6 months in dry conditions [15]. Part of ethanolamine remained in wood that reacted with copper, while the other part with wood components. This ethanolamine is dissolved during leaching and causes free radical formation. Unfortunately, mechanisms of lignin degradation are not completely clarified yet. The only lignin degrading reaction due to ethanolamine specified in the literature is the cleavage of β-aryl ethers adjacent to carbonyl functions [14,16].

Ethanolamine-induced free radical depolymerisation can explain higher leaching determined at beech wood specimens compared to pine or spruce ones as well (Fig. 2). β-aryl ether bonds are more frequent in beech lignin compared to spruce lignin [17], which explains more prominent depolymerisation of beech wood caused by ethanolamine, and the consequent Cu leaching. This fact correlates to our current and earlier experiments. In our previous investigations, almost five times higher depolymerisation, expressed as increased mass losses during leaching, was observed in beech specimens compared to spruce ones [15]. We presume that there is positive correlation between Cu leaching and lignin depolymerisation. Highest depolymerisation results in more prominent leaching. Therefore, we believe that this study partially explains higher copper leaching from specimens impregnated with copper/ethanolamine solutions of higher concentration, particularly from beech wood blocks.

4. Conclusions

Leaching of copper from copper-impregnated wood is significantly affected by concentration of preservative, method of preservation and wood species. The lowest leaching rates were generally determined in Norway spruce specimens, which seems very promising, as Norway spruce is one of the most important non-durable species in Middle Europe. Furthermore, copper leaching is significantly affected by concentration of active ingredients. Lower leaching was determined in specimens treated with preservative solutions of the lowest biocides concentration. The prime reason for this presumption originates in the fact that ethanolamine in solutions of higher concentration depolymerise lignin and, afterwards, a part of copper/ethanolamine/lignin complexes can be cut from wood structure and leached from wood. Additionally, copper leaching depended on the method of treatment as well. Brushing resulted in higher leaching in comparison to vacuum impregnation or soaking procedure.

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