

INFLUENCE OF THE COPPER-ETHANOLAMINE SOLUTIONS pH VALUE ON COPPER FIXATION IN WOOD

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ABSTRACT

Fixation of copper-ethanolamine based wood preservatives is significantly affected by composition, concentration and pH value of preservative solution. Influence of solution pH on copper leaching from Norway spruce wood, treated with different copper-ethanolamine based aqueous solutions with different pH values is described. Copper fixation was determined according to the modified ENV 1250 procedure. Results showed that copper leaching was affected by the pH values of preservative solutions. In general, better copper fixation was determined at specimens treated with copper-ethanolamine solutions of lower pH values. This relationship was more evident at spruce wood treated with preservatives of higher concentration than at the lower. Furthermore, influence of pH was more evident at pure copper-ethanolamine preservatives, than at solutions that besides copper and ethanolamine contain boron, quaternary ammonium compounds and/or octanoic acid.

KEY WORDS: leaching, wood preservation, pH value, Norway spruce, impregnation, biocides, amines

INTRODUCTION

Copper-ethanolamine based wood preservatives will be predominant formulation for protection of wood in soil contact in the following years, due to established limitations on copper-chromium based wood preservatives. However, fixation of the copper-ethanolamine based preservatives is still not comparable to the copper-chromium ones. Emissions of the biocides from copper-amine treated wood can be reduced with proper copper-amine molar ratio and addition of different hydrophobic additives. Octanoic acid is one of the chemicals that significantly decrease copper leaching from impregnated wood (Petrič et al. 1998). This carboxylic acid has heterogeneous effect: beside hydrophobic, there are new less water soluble complexes formed between copper-amine and octanoic acid in the preserved wood what improves copper fixation. Additionally, octanoic acid has

fungicidal effect itself, what results in improved resistance of impregnated wood against copper tolerant fungi and insects (Breeuwer et al. 1997).

Although copper-amine preservatives are utilized for approximately two decades, complete mechanisms of fixation are not elucidated yet. The loss of amines due to volatilization of amines and the precipitation of insoluble copper salts was for many years thought to be the principal fixation mechanism, similar as at copper-ammoniacal preservatives (Dahlgren and Hartford 1972, Pohleven et al. 1994). Even as this may be an important fixation mechanism for copper-ammoniacal based preservatives, it cannot be the mechanism for copper-amine complexes as the amines have higher boiling points. Wood is a weakly acid substrate, in which functional groups, such as carboxyl groups and phenolic groups served as active sites for interactions with copper. Two types of reaction mechanisms for copper-ethanolamine fixation are 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 another possible reaction mechanism, noncharged 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). Copper fixation to wood was found to depend largely upon the solution concentration and pH. Higher pH values of the treating solutions resulted in more stable copper-amine complexes, which will not promote a good interaction between wood and copper-ethanolamine complexes (Zhang and Kamdem 2000). Therefore, it would be of significant commercial interest, to improve copper fixation in copper-ethanolamine wood preservatives through adjusting of the pH. Influence of pH at various copper-ethanolamine based wood preservatives on copper fixation is the topic of this paper.

MATERIAL AND METHODS

For this experiment three types of copper (II) sulphate and 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 (Humar et al. 2005). 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 one was the most complex. It consisted of copper (II) sulphate, ethanolamine, octanoic acid and alkyl diethyl benzyl ammonium chloride (CuEOQ). Concentration of the alkyl diethyl benzyl ammonium chloride equals to copper one. For impregnation aqueous solutions of two different copper concentrations were used, 0.5 and 0.1 %, respectively. The pH values of some preservative solutions were adjusted using H_2SO_4 or NaOH. When changing pH values, special attention were given to prevent formation of precipitates. In total 30 different preservatives were prepared. List of solutions used and final pH values can be resolved from Tab. 1.

For impregnation specimens made of Norway spruce (*Picea abies*) of $1.5 \times 2.5 \times 5.0$ cm were prepared. Orientation and quality of the wood meet requirements of the standard ENV 1250 (1994) and EN 113 (1989). Spruce blocks were vacuum impregnated according to the EN 113 procedure (1989). The treatment of the wood specimens resulted in a solution uptake of about 400 kg/m^3 .

Leaching was performed according to the modified ENV 1250 (1994) procedure. In order to speed up experiment, following two modifications were done: instead of five three specimens were positioned in the same vessels and water mixing was achieved with shaking on shaking device instead of magnetic stirrer. Nine specimens per solution/concentration/treatment were put in

three vessels (three specimens per vessel) to have three parallel leaching procedures. Afterwards, specimens in the vessel were positioned with a ballasting device. 300 g of distilled water were added and the vessel with its content was shaking with the frequency of 60 min⁻¹. Water was replaced daily for seven times in ten subsequent days. Leachates from the same vessel were collected and mixed together. Afterwards, atomic absorption spectroscopy (Varian SpectrAA Duo FS240) analysis of the leachate was performed. Percentages of leached copper were calculated from the amount of retained copper determined gravimetrically and amount of copper in collected leachates.

Tab. 1: Influence of pH value of copper-ethanolamine based preservative solutions on leaching of copper ethanolamine based preservatives from Norway spruce wood. Standard deviations are given in the parenthesis.

Preservative solution	Copper concentration in preservative solution (%)	pH adjustment	pH value	Percentages of Cu leached (%)
CuE	0.1	increased	11.3	3.5 (0.3)
		medium increased	10.7	2.7 (0.4)
		unchanged	9.8	3.6 (0.1)
		medium lowered	9.3	3.6 (0.3)
		lowered	8.7	3.9 (0.2)
	0.5	increased	11.9	8.0 (0,6)
		medium increased	10.8	7.2 (0,5)
		unchanged	9.9	7.3 (0,1)
		medium lowered	9.3	7.1 (0,2)
		lowered	8.6	6.5 (0,4)
CuEO	0.1	increased	11.5	5.0 (0,2)
		medium increased	10.8	6.3 (0,6)
		unchanged	9.9	4.0 (0,2)
		medium lowered	8.6	3.7 (0,3)
		lowered	9.2	5.0 (0,3)
	0.5	increased	12.0	7.9 (0,5)
		medium increased	11.0	9.4 (0,3)
		unchanged	10.0	7.0 (0,7)
		medium lowered	9.3	5.9 (0,2)
		lowered	8.6	4.5 (0,1)
CuEOQ	0.1	increased	11.2	5.9 (0,2)
		medium increased	10.4	6.9 (0,1)
		unchanged	9.4	4.0 (0,1)
		medium lowered	8.9	4.4 (0,3)
		lowered	8.5	5.7 (0,2)
	0.5	increased	11.5	9.3 (0,4)
		medium increased	10.5	20.3 (0,9)
		unchanged	9.4	10.0 (0,0)
		medium lowered	8.8	7.9 (0,1)
		lowered	8.2	16.0 (0,8)

RESULTS AND DISCUSSION

From results presented in Tab. 1 and Fig. 1, it can be seen, that composition and concentration of the preservative solution influence copper fixation. Relationship between those parameters and copper fixation is well elucidated in the literature already (e.g. Humar et al. 2007). In general, our results showed that, the preservative solutions of lower concentration perform better than ones of higher concentration. From specimens treated with aqueous solution of low concentration in average 4,5% of copper was leached, while almost two times higher copper leaching rates were determined at spruce wood treated with preservatives of higher concentration (8,9%). There are two potential reasons for this occurrence. Firstly, the number functional groups that can form stable complexes (hemicelluloses an lignin carbonyl and hydroxyl groups) is limited, thus when wood is treated with solutions of higher concentrations, there are higher percentages of copper/ethanolamine complexes that remained deposited in wood cell lumina which are more prone to leach from wood. On the other hand, when specimens are treated with the solution of the lowest concentration, the pH of the preservative solution is usually lower, what reflects in better fixation as well (Zhang and Kamdem 2000).

However, addition of octanoic acid to preservative solutions of higher concentration improves copper fixation, but it did not have an effect on the fixation at wood specimens treated with copper ethanolamine preservative 0 the low concentration. Octanoic acid improves fixation, due to its hydrophobic effect. Unfortunately addition of other cobiocides (boron and quaternary ammonium compound) increases copper leaching (Tab. 1). We were not able to identify reasons for that occurrence, but comparison of pH values and leaching data shows, that we can not explain this phenomenon with pH related mechanisms. It was accepted, that aqueous solutions with lower pH values, exhibited better performance, but there was no such trend determined.

Change of pH of preservatives of the lowest concentration consisting of copper and ethanolamine (CuE), did not have significant effect on performance of copper. From specimens treated with the solution CuE of the lowest pH of 8.7 in average 3.9% of copper was leached, while from the parallel specimens treated with the most alkaline CuE formulation with pH of 11.3, even lower copper losses were measured (3.5%). However, difference between those two values is statistically insignificant. Stability of the copper-ethanolamine complexes did not play an important role as we believe that there were enough easily accessible reactive function sites available in wood. Secondly, buffering capacity of this solution was relatively low in comparison to more concentrated solutions tested and therefore pH values of preservative solutions decreases in contact with acidic wood with high buffering capacity, what diminished influence of the initial pH values. However, at spruce blocks treated with CuE formulation of the lowest concentration the best copper fixation in this experiment was determined (Tab. 1).

On the other hand, pH affect copper fixation at specimens impregnated with solution CuE of the highest concentration, more notably. There was very tight correlation ($r^2 = 0.863$) determined between, pH value of the preservative solution CuE ($c_{Cu} = 0.5\%$), and copper leaching from impregnated Norway spruce (Fig. 1). From the specimens treated with solution CuE of the lowest pH (8.6) in average 6.5% of copper was determined in leachate, while almost 25% higher copper losses were measured at wood specimens treated with similar solution of the most alkaline pH of 11.9 (Tab. 1). This data indicates that pH has effect on fixation of copper-ethanolamine system if concentration of preservative solutions is high enough.

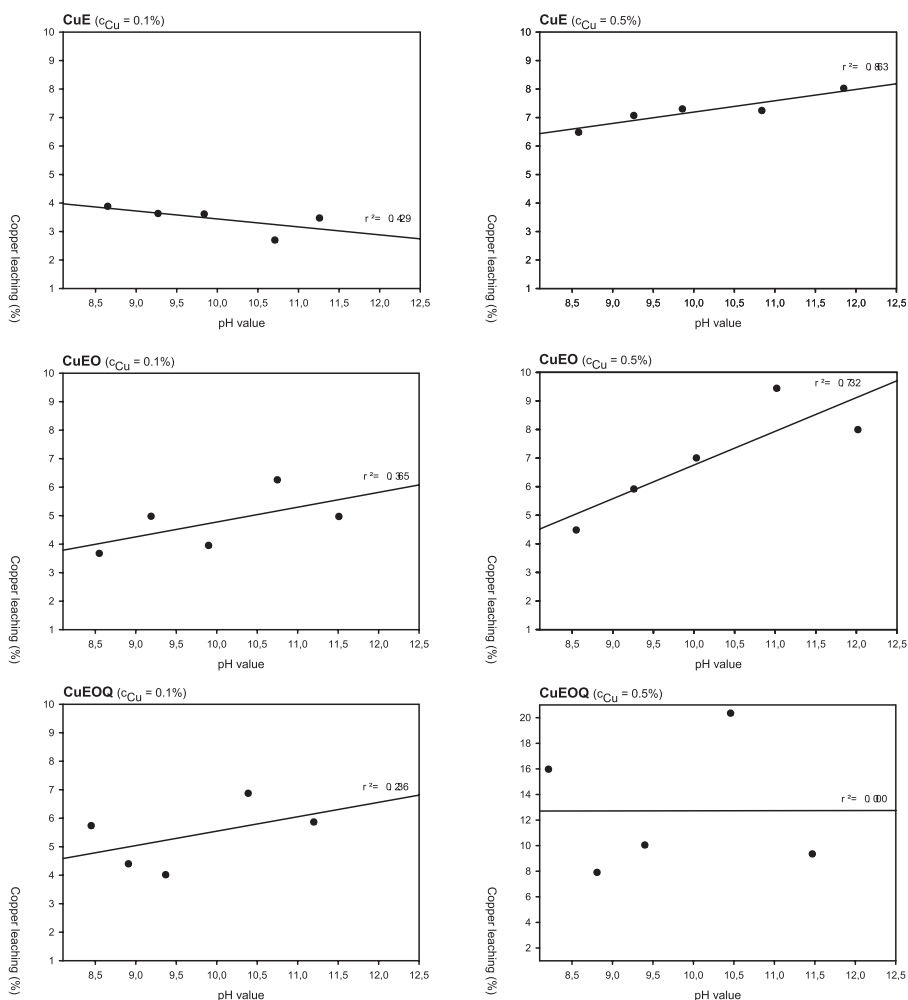


Fig. 1: Correlation between pH values and copper leaching from Norway spruce wood treated with different copper-ethanolamine based wood preservatives.

Similar influence of pH changes as determined at CuE treated wood was observed at specimens treated with aqueous solution of copper, ethanolamine and octanoic acid (CuEO). However, at specimens impregnated with formulation CuEO of both concentrations, the highest leaching rates were not observed at the most alkaline solution, but at the ones that were impregnated with medium alkaline solutions (Tab. 1, Fig. 1). At specimens that were impregnated with the most alkaline solutions comparable leaching rates as determined at specimens impregnated with original pH values were measured. Presumably, because at CuEO solutions of higher pH values, there is more charged copper-amine complexes present in the preservative solution (Zhang and Kamdem 2000). These charged species interact with octanoic acid and form less water soluble and more leaching resistant complexes between copper, ethanolamine and octanoic acid (Humar et al. 2003).

Another reason, that could explained better fixation at the highest pH values is fact, that at higher pH values, weak acid groups in wood, are more highly dissociated, what increases their capacity to bind copper (Tascioglu et al. 2005).

Similar results as observed at CuEO treated wood were determined at specimens impregnated with the most complex wood preservative solution CuEOQ, consisting of copper, ethanolamine, octanoic acid, boron and quaternary ammonium compound. At specimens treated with CuEOQ of the low concentration ($c_{Cu} = 0.1\%$), there was almost no trend noticed between pH value and copper leaching (Fig. 1). From Norway spruce wood blocks impregnated with the formulation CuEOQ ($c_{Cu} = 0.1\%$) with the solution of the lowest pH of 8.5 almost the same copper leaching (5.7) was determined as at comparable specimens treated with the most alkaline solution CuEOQ (5.9).

At specimens treated with formulation of the high concentration ($c_{Cu} = 0.5\%$), in general the highest copper leaching rates were determined. From specimens impregnated with this solution, that has slightly alkaline pH value (10.5), in average 20.3% of copper was lost, what is the highest leaching rate determined in this experiment (Tab. 1, Fig. 1)). However, at specimens that were impregnated with solution CuEOQ of the highest pH value (11.5), copper fixation improves again. We believe that there are similar reasons for this occurrence as described for CuEO treated wood. In most cases, a pH value of CuEOQ preservatives has expectable effect on copper fixation at slightly acidified or slightly alkaline pH values, but not at extreme pH values.

However, data presented in this paper indicates, that influence of pH is quite uniform at solutions consisting of copper and ethanolamine of high concentration. But if we want to study influence of pH values on copper fixation at specimens treated with solutions that besides copper and ethanolamine contains other cobiotics, octanoic acid, boron and/or quaternary ammonium compounds, this makes situation much more complicated. There are so many factors interacting, that it is almost impossible to elucidate them all. Different active ingredients in wood preservative solution might compete for the same fixation sites in wood, and pH change might change brittle balance in freshly treated wood and makes one of the active ingredients more reactive as the other, what reflects in increased or decreased copper fixation. Nevertheless, it would be of substantial interest to elucidate not only the influence of pH values on copper fixation, but to determine its influence on fixation of other active ingredients like boron and quaternary ammonium compounds, what is significantly important from performance point of view.

CONCLUSIONS

Generally, pH values of copper-ethanolamine preservative solutions influence copper fixation in impregnated Norway spruce wood. Aqueous solutions with less alkaline pH values perform better than the ones with high pH values. However, this relationship was more obvious at more concentrated preservatives ($c_{Cu} = 0.5\%$) than at lower ones ($c_{Cu} = 0.1\%$). Influence of pH on copper fixation at spruce wood treated with preservative consisting of copper, ethanolamine and cobiotics (boron, quaternary ammonium compound, octanoic acid) was less significant, compared to specimens treated with pure copper-ethanolamine preservatives.

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