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INFLUENCE OF WATER PROPERTIES ON LEACHING OF COPPER-BASED PRESERVATIVES FROM TREATED WOOD

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ABSTRACT

Copper amine based preservatives will be one of the most important wood preservatives in the coming decades and will likely replace copper-chromium containing ones. However, the leaching of copper from copper-ethanolamine treated wood is still higher in comparison to copper-chromium treated wood. In order to improve copper fixation octanoic acid is introduced to the preservative formulation. This acid performs well when leaching experiments were performed with distilled water. In this research we were interested in how a kind of water (see water, tap water, distilled water, water from river and artificial humic acid solution) influences copper leaching. Experiments were carried out according to modified EN 1250 procedure. The highest copper leaching was determined at artificial humic acid solution. We believe that affinity of humic acid to metal ions is the prime reason for increased copper leaching. On the other hand, the lowest leaching rates were determined at specimens leached with water from river or distilled water. Formulation of preservative solution influences leaching as well. The lowest leaching was generally determined at specimens treated with aqueous solution of copper, ethanolamine and octanoic acid.

KEY WORDS: wood preservatives, copper, ethanolamine, CCB, emissions, leaching, water properties

INTRODUCTION

Wooden products used outdoor are exposed to abiotic and biotic factors that can results in severe deterioration and in the last stage even in complete failure of construction. However, when wood is used for construction purposes, decay processes needs to be slowed down or even stopped. In order to prolong useful life of wood, it is impregnated with different biocides.

Copper-based fungicides are successfully applied long time ago. They were combined with chromium to enable fixation and arsenic to improve performance against copper tolerant fungi and insects (Richardson 1997). Due to arsenic toxicity, its use in the field of wood protection is not desired in the major part of European countries (Humar et al. in press). However, the situation is currently changing even more with the introduction of the Biocidal Products Directive (Anon. 1998). This directive will likely ban the use of chromium in wood preservatives, thus new solutions to enable copper fixation needs to be introduced. Similar trends are foreseen in North America as well (Temiz et al. in press). Amines seem the most appropriate replacement for chromium. Particularly ethanolamine is reported as the most promising copper fixative in numerous 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) (Cao and Kamdem 2004; Humar et al. 2003).

The fixation of copper-ethanolamine preservatives in wood is still not as effective as at copper-chromium based ones. In order to improve fixation of those solutions, hydrophobic agents can be introduced to this system. Octanoic acid seems particularly suitable, as it has as hydrophobic as well as limited fungicidal effect (Schmidt 1984). However, octanoic acid performed well when leaching tests were performed with distilled water, but there are only a few data available on emissions of copper from wood impregnated with copper-ethanol-octanoic acid formulation performed with water from natural environment.

In our study, treated specimens were leached with different waters types in order to simulate different possible end uses of impregnated wood; wood in contact with fresh water, see water and particularly to elucidate leaching of the biocides from impregnated wood in contact with moorland, rich of organic acids, particularly humic acid. Installing utility poles or treated structures in contact with these wet, organic sites may alert their protection efficiency and environmental impact (Lebow 1996).

This research will enable decisions where copper-ethanolamine treated wood could be used. As copper-ethanolamine wood preservative will likely compete with classical copper-chromium ones, specimens impregnated with commercial formulation of copper, chromium and boron (CCB) were included into this research as well.

MATERIAL AND METHODS

Wood specimens

Specimens were made of Norway spruce (*Picea abies*) sapwood. For leaching wood blocks of 1.5 × 2.5 × 5.0 cm were prepared. Orientation and quality of the wood meets requirements of the standard ENV 1250 (1994) and EN 113 (1989).

Treatment solutions

For impregnation of the specimens, four different copper based wood preservative solutions were used. The main emphasis was given to copper ethanolamine based ones. They consisted of copper(II) sulphate and ethanolamine where copper ethanolamine molar ratio was set constant (1:6). The first solution contains copper and ethanolamine only (CuE), while the second one contains octanoic acid as well (CuEO). The molar ratio between copper 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). Concentration of the alkyl diethyl benzyl ammonium chloride equals copper one (1%). For comparison, classical copper chromium and boron based solution (CCB) of 5% (34% $CuSO_4 \times 5H_2O$; 37.3% $K_2Cr_2O_7$; 28.7% H_3BO_3) was chosen.

Impregnation

Spruce blocks were vacuum impregnated according to the EN 113 procedure (1989). The treatment of the wood specimens resulted in sufficient uptakes, and the whole specimens volumes were impregnated with respective preservative formulation. The specimens were afterwards conditioned for four weeks, the first two weeks in closed chambers, the third week in half closed and the fourth week in open ones. Prior to leaching specimens were stored at 25 °C, 65% RH.

Water used

For leaching five different water types were utilized, tap water, distilled water, water from Ljubljanica river, see water (Adriatic see) and artificial humic acid (Sigma) solution (AHS) as model for water from moorland like described by Cooper et al. (2000). The concentration of humic acid in artificial humic acid solution (AHS) was 0.3%.

Leaching procedure

Leaching was performed according to the modified ENV 1250 (1994) procedure. In order to speed up the 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 a shaking device instead of magnetic stirrer.

Nine specimens per solution/water type were put in three vessels (three specimens per vessel) to have three parallel leaching procedures. In total 60 vessels were prepared. Than the specimens in the vessel were positioned with a ballasting device. 300 g of water were added and the vessel with its content was shaken with the frequency of 60 min^{-1}. Water was replaced daily for seven subsequent days. Leachate from the same vessel was 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 amount of copper in collected leachate.

RESULTS AND DISCUSSION

For this research, specimens made of Norway spruce wood were used, as this material is very frequently used for outdoor construction applications in middle Europe. The retention of preservatives in these specimens is very high (Tab. 1). On average, specimens retained 26.09 kg/m^3 of CCB. The highest retention of 66.09 kg/m^3 was determined at specimens impregnated with solution CuEOQ. Although it has to be considered, that there are significant amounts of ethanolamine and octanoic acid present included in this preservative and those compounds do not have pure fungicidal effect but they were introduced into the preservative solution in order to improve copper fixation. Recommended retention levels for wood used in use class 4 (ground contact or fresh water contact) are usually significantly lower. Willeitner (2001) reported that a retention of maximum 14 kg/m^3 of CCB or 5 kg/m^3 of copper-ethanolamine based Wolmanit CX-8 are sufficient to protect nondurable wood in ground contact. In contrary, the Nordic Wood Preservation Council recommends notably higher retention levels. For example, retention of 36 kg/m^3 of copper-amine.

quat are recommended for wood to be used in ground contact. These approved retentions based on a minimum 5 years field testing in accordance with relevant standards in two sites being (Hughes 2004). Retention levels are recommended for wood products of larger dimensions, where outer part of wood retained more preservatives than inner ones. We assume that the retention of the outer parts are treated according to the requirements of the Nordic Wood Preservation Council, corresponds to the retention of active ingredients at our specimens.

Tab. 1: Retention of wood preservatives. Standard deviations are given in parenthesis

Wood preservative	**Retention [kg/m^3]**	**Retention of non-volatile components [kg/m^3]**
CCB	26.09 (4.7)	26.09 (4.7)
CuE	54.41 (9.7)	22.04 (3.9)
CuEO	56.64 (8.3)	21.18 (3.1)
CuEOQ	66.09 (9.9)	29.74 (4.4)

As expected, the best fixation was determined at specimens impregnated with copper-chromium based preservative CCB. From CCB impregnated specimens leached with distilled water, on average 0.1% of retained copper released (Tab. 2). Similar results were determined when water from river was utilized instead. Immersion of the specimens to water from sea or river resulted in slightly higher emission rates of 0.2 %. On the other hand, the highest leaching rates from CCB impregnated specimens were measured after leaching with artificial humic acid solution (AHS). From these specimens on average 1.2% of Cu was released, what is more than ten times higher emission as from the specimens leached with distilled water (Tab. 2). There are several reasons for the observed occurrence. First, AHS is acidic (Tab. 3) what may have reversed the chromium fixation process. Some researchers reported already that high acidity may be the key to "unfix" copper in wood (Stephan and Peek 1992). If chromium is reduced from Cr(III) to Cr(VI) form, copper is dissolved. Furthermore, humic acids contain many organic functional groups such as carboxylic, phenolic, hydroxyl, amine, and quinone groups, which provide a number of different potential binding sites for metal ions (Chen and Wu 2004). Therefore, new soluble complexes between copper and humic acid are formed, what results in increased leaching as well.

Leaching of copper from spruce wood specimens impregnated with copper-ethanolamine based aqueous solution was significantly higher in comparison to CCB treated specimens. At wood impregnated with copper-ethanolamine aqueous solution (CuE) 7.1% of Cu was determined in distilled water after seven days of leaching. This value is almost 100 times higher than determined at CCB treated specimens. Similar, copper leaching rates were determined when distilled or see water were utilized instead, indicating that, copper fixation in the presence of ethanolamine is still not as good as in the presence of chromium as fixative, and it is not influenced by water properties. Therefore, it has to be considered what is environmentally more acceptable; low emissions of chromium and copper from CCB impregnated wood or significantly higher emissions of copper and no chromium from Cu-ethanolamine treated wood. On the other hand, retentions of copper-amine preservatives were considerably higher than the recommended ones. Therefore, there might not be enough functional groups in wood to ensure efficient fixation of copper-ethanolamine complexes.

In the previous experiments where specimens were impregnated with less preservative and thus lower retention levels were achieved, consequently lower copper losses between 1.5% and 4% were determined (Humar *et al.* 2005). However, at CuE impregnated specimens we determined the lowest emission rates when leaching with water from Ljubljanica river (4.7%). We were not able to identify reasons for this occurrence. On the other hand, similar as at CCB impregnated specimens, leaching with AHS resulted in the highest copper losses. During leaching with AHS on average 11.7% of Cu was leached (Tab. 2). Nevertheless, the differences between leaching with distilled water and AHS are not that prominent as at CCB impregnated specimens. We presume, that the acidity of the water used for leaching, does not influence copper de-fixation at CuE impregnated specimens like at CCB treated ones. It seems that affinity of humic acid to metal ions is the prime reasons for increased copper leaching from copper-ethanolamine impregnated wood.

Tab. 2: Amount of copper leached from spruce specimens impregnated with different copper based preservative solution. Standard deviations are given in the parenthesis

Wood preservative	Water type	Copper leached [%]
CCB	Tap water	0.2 [0.02]
	Distilled water	0.1 [0.00]
	River water	0.1 [0.01]
	Sea water	0.2 [0.00]
	AHS*	1.2 [0.01]
CuE	Tap water	7.2 [0.53]
	Distilled water	7.1 [1.02]
	River water	4.7 [0.03]
	Sea water	7.4 [0.05]
	AHS*	11.7 [0.94]
CuEO	Tap water	5.9 [0.41]
	Distilled water	3.8 [0.03]
	River water	4.8 [0.26]
	Sea water	5.1 [0.28]
	AHS*	7.6 [0.32]
CuEOQ	Tap water	9.7 [0.78]
	Distilled water	9.6 [0.72]
	River water	10.5 [0.33]
	Sea water	7.6 [0.41]
	AHS*	13.6 [0.17]

*AHS = artificial humic acid solution

As mentioned in introduction chapter, addition of octanoic acid to copper-ethanolamine aqueous solution notably decreases copper leaching. From specimens impregnated with CuE and leached with distilled water on average 7.1% of Cu emitted, while from parallel specimens, impregnated with copper-ethanolamine-octanoic acid solution (CuEO), copper loss of 3.8% was determined (Tab. 2). Addition of octanoic acid improved copper fixation when specimens were leached with tap water, see water and even artificial humic acid solution. We believe that octanoic acid has a multiplicative effect, beside being hydrophobic, there are new less water-soluble complexes formed between copper-amine and octanoic acid in the preserved wood what improves Cu fixation as well (Humar *et al.* 2003). However, the positive influence of octanoic acid on copper fixation was not evident when leaching was performed with water from Ljubljanica river. We were not able to identify reasons for that. We suspect that there might be some bacteria or other microorganisms present in this water that could degrade octanoic acid and disable its effect.

Tab. 3: pH values and copper content in water used for leaching

Water type	pH	c_{Cu} in water before leaching
Tap water	8.3	0.05 ppm
Distilled water	5.9	0.02 ppm
River water	8.1	0.01 ppm
Sea water	8.2	0.02 ppm
AHS*	2.5	0.11 ppm

*AHS = artificial humic acid solution

Addition of other cobiocides (quaternary ammonium compound, boron) into copper-ethanolamine-octanoic acid based aqueous solution (CuEOQ) decreases copper fixation drastically. From specimens impregnated with preservative solution CuEOQ leached with distilled water on average 9.6% of Cu was lost, what is more than 50% higher value as determined at CuE impregnated specimens (Tab. 3). Comparable leaching rates were determined at CuEOQ treated specimens leached with tap water as well. Slightly higher values were determined at specimens were water from river were utilized. However, the highest value was observed at CuEOQ treated specimens leached with AHS (13.6%). From those specimens the highest copper emissions during this testing were observed.

This opens new questions for the future work. How copper impregnated wood performs in contact with humic acid rich soil? We presume that, the durability of copper-ethanolamine treated wood is reduced, as significant amount of biocides release from wood. Additionally, pH value of wood used in contact with acidic soil decreases, what makes it more susceptible to fungal decay as well (Humar et al. 2005).

CONCLUSIONS

Emissions of copper from impregnated wood is the highest when specimens were leached with artificial humic acid solution, and the lowest when water form a river or distilled water was utilized. These data needs to be taken into consideration when using impregnated wood in contact with soil rich with rooting organic material (moor, swampland).

Leaching of copper from spruce wood impregnated with copper-ethanolamine preservatives is still significantly higher compared to copper-chromium based ones. Addition of octanoic acid decreases copper leaching irrespective of water properties used. On the other hand, addition of other co-biocides increases it.

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