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Effect of oxalic, acetic acid, and ammonia on leaching of Cr and Cu from preserved wood

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Abstract Wood treated with CCB (chromated copper borate) has an expected service life of 20–50 years, depending on conditions of service and method of treatment. After this period, treated wood is discarded as special waste. Due to toxic elements (Cu, Cr, and B) in such treated wood, burning and landfill disposal are not considered as environmentally sound solutions. Chemical extraction seems more promising. The principle of the method is to convert fixed biocides in wood into soluble form and leach them out of the wood. In order to elucidate this process, copper(II) sulfate, potassium dichromate, and CCB-treated samples were leached using five different agents, namely, water, an aqueous solution of oxalic or acetic acid, and an aqueous solution of oxalic or acetic acid with ammonia. Afterwards, the amounts of leached copper and chromium were determined. In a parallel experiment, electron paramagnetic resonance measurements of wet- and dry-leached and unleached samples were performed in order to determine the paramagnetic complexes that were formed. The highest chromium leaching was achieved with the aqueous solution of oxalic acid, as chromium was converted into water-soluble chromium oxalate. While the mixture of oxalic acid and ammonia resulted in the highest copper leaching, EPR observation revealed that in this case water-soluble complexes of copper, oxalic acid, and ammonia were formed. We found out that oxalates formation is not the only mechanism responsible for copper or chromium leaching. High acidity may play an important role too.

Introduction

Chromated copper arsenate (CCA) and chromated copper borate (CCB) have been the most important commercial wood preservatives for more than

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50 years. Furthermore, during the past 20 years, the usage of copper/chromium-based preservatives has grown dramatically (Huang and Cooper 2000). Approximately 21 million m^3 of CCA-treated lumber were produced annually in the United States in 1996 and production is still increasing (Cole and Clausen 1996). In Germany they used to treat 1.5–2.0 million m^3 of wood annually with more than 1000 t of chromium and 600 t of copper (Stephan et al. 1996a).

CCA- or CCB-treated wood has an expected service life of 20–50 years, depending on conditions of service and method of treatment. After this period, treated wood is discarded as waste. The disposal of CCA- or CCB-treated waste wood will cause a major environmental problem when removed from service, because of the toxic metals concentrated in such wood. Cooper (1993) estimated that the volumes of CCA-treated wood removed from service in the United States will rise from one million m^3 in 1990 to 16 million m^3 in 2020. Currently, some options for dealing with waste CCA- or CCB-treated wood include: reuse, recycling, incineration, use as fuel, and landfill disposal (Kartal and Clausen 2001). The disposal of preservative-treated wood into landfills is considered to be the least preferred method, as the portion of preservative biocides in treated wood is only small compared to the total volume. Furthermore, the capacities of special dumps are limited and public approval for new facilities is extremely low (Stephan and Peek 1992). Recent recycling research has provided several methods for environmentally more acceptable solutions; namely, biological methods using either copper-tolerant fungal strains (Stephan et al. 1996a) or bacteria (Clausen and Smith 1998) and chemical extraction methods (Stephan et al. 1996b). The principle of both methods is to covert insoluble heavy metals in waste wood into soluble form through acidification with organic acids. Converted heavy metals are then leached from the wood. Thus, both the remediated wood fibre and the metals could be reclaimed. Acidification can be caused either by chemical treatment or by exposure to fungi. The most frequently used acids in this process are oxalic and acetic acid (Clausen and Smith 1998). Oxalic acid is a small organic acid with two low pK values (pK$_1$=1.27; pK$_2$=4.26) (Skoog et al. 1992). The mentioned acid is often produced in great quantities by brown rot fungi (Green et al. 1991; Humar et al. 2002a) and is associated with brown rot colonization of wood (Jellison et al. 1997).

Oxalic acid reacts with insoluble chromium in wood to form a soluble form of chromium oxalate; thus, chromium can be leached out of wood. On the other hand, an insoluble complex of oxalic acid and copper is formed; consequently, copper oxalate remains in the wood even after extensive leaching (Stephan and Peek 1992; Humar et al. 2002a). In order to leach copper oxalate, ammonia could be added into the leaching solution. If this is done, copper becomes soluble and can be leached out of wood.

In order to elucidate the role of acids in these processes, copper, chromium, and CCB-impregnated samples were leached with different leaching solutions containing oxalic or acetic acid and ammonia. After leaching, electron paramagnetic resonance (EPR) measurements of treated samples were performed. EPR is a very useful method, which allows the observation of species with unpaired electrons like Cu(II), Cr(III), and Cr(V). This method was successfully applied in the field of wood preservation (Pohleven et al. 1994; Hughes et al. 1992; Zhang and Kamdem 2000; Ruddick et al. 2001). However, to the best of our knowledge, there are not any data in the literature on the use of EPR for the investigation of changes of wood and copper-based preservatives in impregnated wood after oxalic or acetic acid extraction.

Material and methods

Sample preparations

Norway spruce sapwood (*Picea abies* Karst) samples of dimensions $1.5 \times 2.5 \times 5$ cm^3 (longitudinal direction) were vacuum impregnated with a 5% CCB solution (34% $CuSO_4 \times 5H_2O$; 37.3% $K_2Cr_2O_7$; 28.7% H_3BO_3) according to the EN 113 procedure (ECS 1989). Some samples were impregnated with copper or chromium solutions only. The concentration of copper or chromium in these solutions was comparable to the concentrations of Cr or Cu in the original CCB solution. The treatment of specimens resulted in a solution uptake of about 360 kg/m^3. Later, the samples were conditioned for four weeks, the first two weeks in closed chambers, the third week in half-closed ones, and the fourth week in open ones. The conditioned samples were then oven dried (75°C) for 5 days in order to ensure the complete reduction of chromium. After that they were weighted and conditioned at 20°C and 65% RH.

Leaching procedure

A laboratory study was conducted to examine and compare the effect of distilled water, distilled water containing 2% oxalic acid or acetic acid, and distilled water containing 2% oxalic acid and 2% ammonia or acetic acid and ammonia on copper and chromium leaching, as seen from Table 1. Leaching of Cu and Cr was determined according to the modified European standard EN 1250 (ECS 1994). Three conditioned samples per treatment were put on shaker and positioned with a ballasting device. After that, 250 g of leaching solution was added. The leaching solution was replaced after 24-h periods for a total of 4 days. Afterwards, atomic absorption analyses (AAS) of water were preformed in order to determine the percentages of leached copper and chromium. The experiment was preformed in three parallel leaching procedures for each treatment. The leached samples were analysed too. Half of the samples were oven dried (323 K) and the other half remained wet. Afterwards EPR measurements of both wet and dry samples were performed.

EPR measurements

EPR experiments were performed at room temperature on a Bruker ESP-300 X-band spectrometer (microwave frequency 9.62 GHz, microwave power 20 mW, modulation frequency 100 kHz, modulation amplitude 0.1 mT). We cut off four matchstick-like samples ($40 \times 1 \times 1$ mm^3) of each wood specimen and inserted them one by one into a resonator. Thus, EPR measurements of each observation were replicated twelve times per treatment. EPR measurements were taken of the oven-dried specimens as well as on the wet ones. Additionally, EPR spectra of the leached water were recorded. The components of the EPR parameters (tensor g and hyperfine splitting tensor A) were determined directly from the spectra, where possible.

Results and discussion

Copper(II)-sulfate-treated specimens

From the samples treated with copper(II) sulfate, only 32% of the copper leached out of wood (Table 1). The reason for such low copper leaching originates from the fact that the leaching regime in our experiment was not the most severe, as we wanted some metals to remain in the samples in order to perform EPR analysis.

Table 1. Percentages of leached Cu and Cr from the preserved wood using different leaching agents: distilled water (H_2O), distilled water containing 2% oxalic acid (Ox), distilled water containing 2% oxalic acid and 2% ammonia (OxN), 2% acetic acid (Ac), and 2% acetic acid and 2% ammonia (AcN). Standard deviations are presented in brackets

Preservative	Leaching agent	Cu leached [%]	Cr leached [%]
CCB	H_2O	1 (0.1)	0 (0.1)
	Ox	13 (2.3)	53 (0.3)
	OxN	48 (2.4)	27 (1.4)
	Ac	40 (2.2)	21 (1.2)
	AcN	24 (2.1)	8 (0.6)
$CuSO_4 \times 5H_2O$	H_2O	32 (0.7)	–
	Ox	12 (1.1)	–
	OxN	63 (3.2)	–
	Ac	37 (0.3)	–
	AcN	34 (0.2)	–
$K_2Cr_2O_7$	H_2O	–	1 (0.1)
	Ox	–	54 (1.5)
	OxN	–	23 (0.1)
	Ac	–	7 (0.7)
	AcN	–	4 (0.1)

The leaching procedure lasted 4 days, and consisted of four cycles only. Furthermore, the amount of leaching water was relatively low compared to the amount prescribed in the EN 1250 procedure. Leaching of copper, carried out according to the standard procedure (ECS 1994), resulted in a significantly higher copper loss of 49.5% (Humar et al. 2001a). In cases when leaching was performed according to an even more severe leaching procedure EN 84 (ECS 1992), even higher amounts of leached copper were reported (66.1%) (Hughes 1999). EPR spectra and parameters of the leached copper-treated samples did not significantly differ from the spectra of unleached ones (control). In both cases the EPR parameter $g_\perp$ was 2.077 (Fig. 1). The same values are reported in the literature (Pohleven et al. 1994; Hughes et al. 1992; Humar et al. 2001b). As no changes were observed in the spectral parameters, we presume that the remaining copper is of a similar form as the copper in the specimens before leaching. On the other hand, the leaching of copper-sulfate-treated specimens caused a decrease in the intensity of the Cu(II) EPR signal due to copper removal.

The leaching of the copper-sulfate-treated samples with the aqueous solution of acetic acid (Ac) resulted in a 15% higher copper loss than leaching with water only (Table 1). One of the possible explanations for this occurrence may be acidity, as it could release absorbed copper (Clausen and Smith 1998). The copper that remained in the wood had different EPR parameters than the copper of unleached samples. The shift of the $g_\perp$ value from 2.077 for the control samples to 2.073 for the samples leached with acetic acid was noted. The possible reason for this shift is the reaction between the copper in wood and acetic acid. During this reaction copper acetate could be formed. Addition of ammonia to the solution of acetic acid (AcN) did not increase the leaching of copper; rather, it even decreased it to the same amount as observed for leaching with water only (AcN in Table 1). On the other hand, an even higher shift of the EPR value $g_\perp$ was observed, from an initial 2.077 to 2.066 in the samples leached with a mixture of acetic acid and ammonia. The EPR parameters of the remaining copper in acetic acid/ammonia leached wood ($g_\perp$=2.066, g_{II}=2.227, and A_{II}=17.3 mT) indicate that the sur-

AcN

Ac

OxN

Ox

Free radical

Cu(II)

H₂O

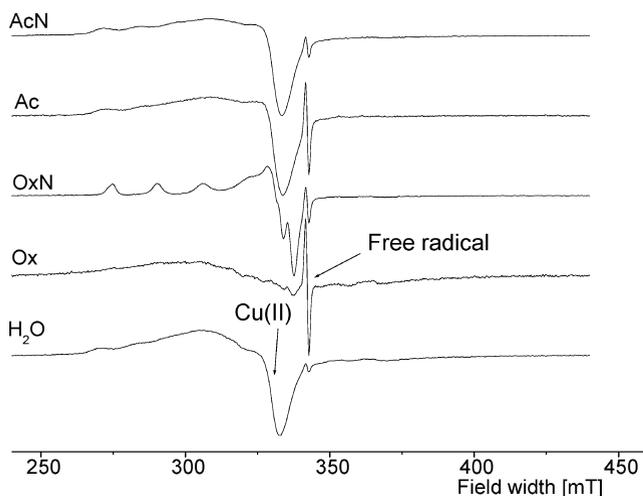250   300   350   400   450

Field width [mT]

Fig. 1. EPR spectra of dry copper-sulfate-treated Norway spruce wood samples after leaching with: distilled water (H₂O), distilled water containing 2% oxalic acid (Ox), distilled water containing 2% oxalic acid and 2% ammonia (OxN), 2% acetic acid (Ac), and 2% acetic acid and 2% ammonia (AcN)

roundings around the copper ion have changed compared to the copper in the samples leached with water ($g_\perp$=2.077, g_{II}=2.366, and A_{II}=12.5 mT). EPR parameters of Cu(II) with high A_{II} and low g_{II} values are typical for a copper atom complexed with nitrogen atoms (Pohleven et al. 1994; Hughes et al. 1992; Zhang and Kamdem 2000). Thus, we presume that at least one part of the copper in wood reacted with ammonia and formed complexes of copper and ammonia. As the EPR signal of this compound overlaps the EPR signal of copper sulfate in wood, we could not precisely determine the exact type of this copper complex.

Leaching of the samples with the aqueous solution of oxalic acid resulted in the lowest copper losses. No more than 12% of copper was leached from the samples (Ox in Table 1). This result was expected, as it is well known that copper reacts with oxalic acid and, consequently, insoluble copper oxalate is precipitated in the wood (White et al. 1997; Humar et al. 2002a). This fact was further supported by EPR spectroscopy, as the EPR spectrum of the copper-sulfate-treated sample after leaching with oxalic acid had the same line shapes as reported in the literature for copper oxalate (Srivastava et al. 1980), with the measured g_0 value of 2.175 and a linewidth of about 43 mT (Fig. 1). Furthermore, from this spectra it can be seen that all the copper that remained in the samples was in the form of copper oxalate. In contrast to the samples leached with oxalic acid solution, the highest copper loss (63%) was found for the samples leached with a leaching agent containing oxalic acid and ammonia (OxN in Table 1). We believe that copper oxalate and ammonia react and a new, soluble complex of copper, oxalic acid, and ammonia is formed. This correlates well with the literature data (Stephan et al. 1996a; Humar et al. 2002a) and was further supported by EPR spectroscopy. EPR spectra and parameters ($g_\perp$=2.067, g_{II}=2.286, and A_{II}=15.7 mT) of copper-sulfate-treated wood after leaching with oxalic acid and ammonia are typical for copper(II) surrounded by nitrogen atoms (Hughes et al. 1992; Pohleven et al. 1994; Zhang and Kamdem 2000). This is even more evident from the EPR spectra of the wet wood samples treated with copper sulfate after

leaching with ammonia and oxalic acid. Instead of an anisotropic spectrum, we can see a typical isotropic Cu(II) EPR signal ($g_0=2.151$, $a_0=6.1$ mT) (Fig. 4), with the same parameters as the EPR signal of an aqueous solution of copper(II) sulfate, oxalic acid, and ammonia. Furthermore, the mentioned isotropic spectrum of Cu(II) in wood differs from the isotropic spectrum of the aqueous solution of copper(II) sulfate/ammonia without oxalic acid ($g_0=2.124$, $a_0=7.3$ mT). This shows that the copper in wood after leaching with the solution of oxalic acid and ammonia (OxN) was dissolved and could easily diffuse from the wood; this resulted in intense copper leaching. On the other hand, the anisotropic copper(II) EPR signals observed in wet samples leached with a solution of acetic acid (Ac) and acetic acid with ammonia (AcN) indicate that copper was at least slightly adsorbed in wood (Fig. 4). The shape of these spectra is typical for copper not surrounded by nitrogen (Pohleven et al. 1994). Thus, we believe, that the dissolved part of the copper did not react with the ammonia.

Potassium-dichromate-treated samples

EPR spectra of potassium-dichromate-treated wood provided us less information than the EPR spectra of copper-treated wood. The chromium in the formulation is present as a diamagnetic Cr(VI). During the fixation process, Cr(VI) is reduced to paramagnetic Cr(III) via Cr(V) as an intermediate. Cr(III) has three unpaired electrons and gives a broad peak. On the other hand, Cr(V) has only one unpaired electron, thus giving sharp peaks in comparison to Cr(III) (Hughes et al. 1992; Humar et al. 2002b). EPR signals of chromium(III) and chromium(V) are well resolved as seen in Fig. 2.

Leaching of chromium-treated samples with water resulted in insignificant chromium leaching. Only 1% of the chromium was leached out of wood (Table 1). EPR spectra and parameters of the leached chromium-treated samples did not significantly differ from the spectra of the unleached control ones. In both cases similar EPR parameters, $g=1.982$ and a linewidth of $\Delta H=48$ mT, were observed (Fig. 2). However, we observed one significant change. The intensity of the Cr(V) EPR signal significantly decreased by 93% (Table 2). A similar observation is reported by Hughes et al. (1992). As we did not determine Cr(V) EPR signal in leachates, we presume that the water somehow affected the chromium reduction.

However, the addition of acetic acid to water increased chromium leaching. A chromium loss of 7% was determined (Table 1). The EPR signal of Cr(III) remained almost the same; thus, we suspect that the acetic acid did not effect the chromium coordination environment. The possible reason for increased leaching is the acid environment itself, as a significant correlation between the pH value of the leaching agent and chromium loss is known (Stephan and Peek 1992). Acid may have reversed the chromium fixation process. Thus, high acidity may be the key to "unfix" heavy metals in wood (Clausen and Smith 1998; Shiau et al. 2000). The addition of ammonia into an aqueous solution of acetic acid decreased the chromium leaching (AcN in Table 1), and no changes in the Cr(III) EPR signal were observed either. Similar to water leaching, the signal of Cr(V) in the EPR spectra of both acetic acid (Ac) and acetic acid/ammonia (AcN) leached samples almost completely disappeared. A decrease of 99.3% of the intensity of this signal was observed, which was even more prominent than in samples leached with water only (Fig. 2, Table 2). The reason for this decrease seems similar as that described for samples leached only with water.

The highest chromium leaching was observed in the presence of oxalic acid. Leaching of chromium-treated samples with oxalic acid resulted in a 54% chro-
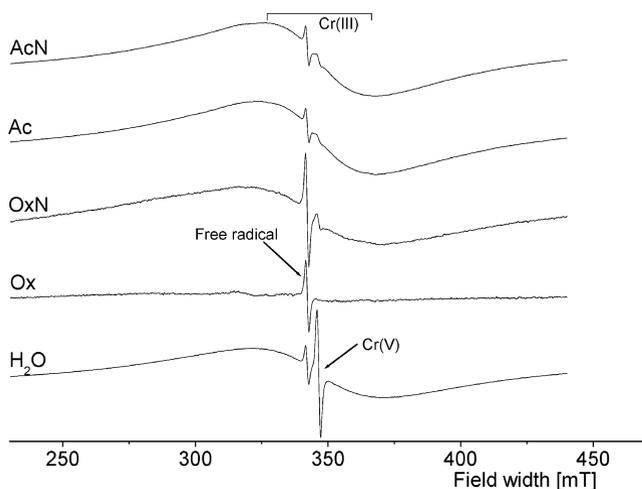
Fig. 2. EPR spectra of dry potassium-dichromate-treated Norway spruce wood samples after leaching with: distilled water (H_2O), distilled water containing 2% oxalic acid (Ox), distilled water containing 2% oxalic acid and 2% ammonia (OxN), 2% acetic acid (Ac), and 2% acetic acid and 2% ammonia (AcN)

Table 2. Intensity of Cr(V) EPR signal on EPR spectra of treated Norway spruce samples after leaching with different leaching agents: distilled water (H_2O), distilled water containing 2% oxalic acid (Ox), distilled water containing 2% oxalic acid and 2% ammonia (OxN), 2% acetic acid (Ac), and 2% acetic acid and 2% ammonia (AcN). Standard deviations are presented in brackets

Preservative	Leaching agent	Intensity of Cr(V) EPR signal
CCB	Control (no treatment)	23.6 (0.3)
	H_2O	2.2 (0.1)
	Ox	0.0 (0.0)
	OxN	1.5 (0.1)
	Ac	0.5 (0.0)
	AcN	0.5 (0.0)
$CuSO_4 \times 5H_2O$	Control (no treatment)	–
	H_2O	–
	Ox	–
	OxN	–
	Ac	–
	AcN	–
$K_2Cr_2O_7$	Control (no treatment)	34.0 (0.4)
	H_2O	5.7 (0.3)
	Ox	0.0 (0.0)
	OxN	2.1 (0.1)
	Ac	0.5 (0.0)
	AcN	0.5 (0.0)

mium loss. Therefore, in the outer parts of the samples, neither the Cr(III) nor the Cr(V) EPR signals were detected. However, in central parts of the samples, a weak Cr(III) EPR signal was still present. We presume that, if the leaching time and periods are increased, an even higher chromium loss would be determined. The parameters of the Cr(III) EPR signal in the centre of the samples (g=2.00, line-

width=64.3 mT) differ from the parameters of the control (g=1.98, line-width=48 mT). We suspect that the reason for the described changes originates from the fact that the chromium in wood reacted with oxalic acid and this reaction resulted in the formation of a water-soluble chromium oxalate. A violet colouring of the leachate and the literature data further support our conclusion (Clausen and Smith 1998; Sharp 1975; Stephan and Peek 1992). In contrast to copper-treated wood, the addition of ammonia into an aqueous solution of oxalic acid did not increase the chromium leaching, but rather decreased it (Table 1). Furthermore, the Cr(III) EPR parameters in potassium-dichromate-treated wood after leaching with oxalic acid and ammonia did not differ from the parameters of specimens leached with oxalic acid only, which indicates that ammonia prevents the formation of chromium oxalate. The other possible explanation for this phenomenon originates from the higher pH value of the leachates (Stephan and Peek 1992).

CCB-treated samples
The leaching results of the CCB-treated samples correlate well with the results of specimens treated with either copper sulfate or potassium dichromate. The interpretation of the EPR spectra of CCB-treated samples is more difficult, because the Cu(II) and Cr(III) EPR signals are superimposed (Fig. 3). Leaching of CCB-treated samples with water resulted in insignificant copper and chromium loss (Table 1). Furthermore, the shape and parameters of the EPR spectra of the leached specimens did not differ from those in the controls, except for the dis-appearance of the Cr(V) EPR signal. This correlates well with the results of copper and chromium leaching described in the previous sections.

Leaching of CCB-treated samples with the aqueous solution of acetic acid seems more promising. A copper loss of about 40% and a chromium loss of 21% were achieved (Ac in Table 1). Thus, acetic acid releases bound copper in CCB-treated wood to the same extent as in the specimens treated with unfixed copper sulfate only. Furthermore, similar changes in the EPR spectra were observed as described for copper- or chromium-treated specimens. Therefore, we believe that during leaching with an aqueous solution of acetic acid at least a portion of the copper was released and a new complex between copper and acetic acid was formed. The addition of ammonia to the aqueous solution of acetic acid resulted in decreased copper as well as chromium leaching, compared to specimens leached with an aqueous solution of acetic acid only.

The highest chromium leaching from CCB-treated specimens was found after leaching with an aqueous solution of oxalic acid. The reason for this originates from the already described chromium oxalate formation. From Fig. 3 it can be seen that the Cr(III) EPR signal completely disappeared, but the EPR signal assigned to copper oxalate remained. As copper oxalate is insoluble, it remained in the wood. The addition of ammonia to the aqueous solution of oxalic acid increased the copper leaching and decreased that for chromium, compared to the specimens treated with oxalic acid only. From the EPR spectra of the CCB-treated specimens leached with oxalic acid/ammonia the Cu(II) EPR signal of copper(II) surrounded by nitrogen is resolved (Fig. 3). The EPR spectra of the wet wood samples, treated with CCB, after leaching with oxalic acid/ammonia aqueous solution showed isotropic Cu(II) EPR signal (g_0=2.151, a_0=6.1 mT) (Fig. 4). The same spectrum was observed for the copper-sulfate-treated specimens, too. This indicates that oxalic acid and ammonia are able to unfix and dissolve copper even for CCB-treated specimens where copper is fixed.
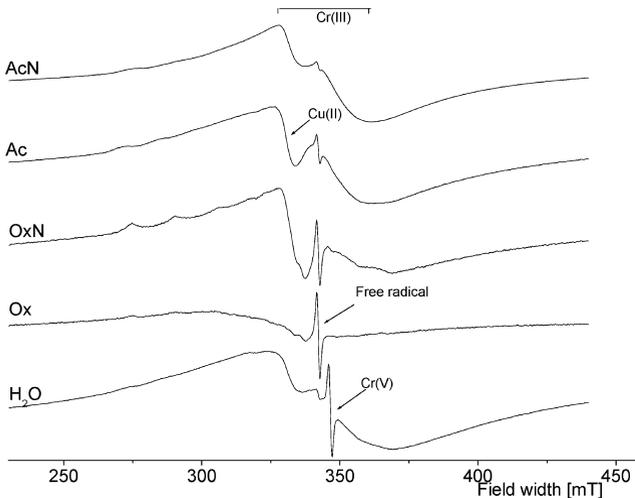
Fig. 3. EPR spectra of dry CCB-treated Norway spruce wood samples after leaching with: distilled water (H_2O), distilled water containing 2% oxalic acid (Ox), distilled water containing 2% oxalic acid and 2% ammonia (OxN), 2% acetic acid (Ac), and 2% acetic acid and 2% ammonia (AcN)
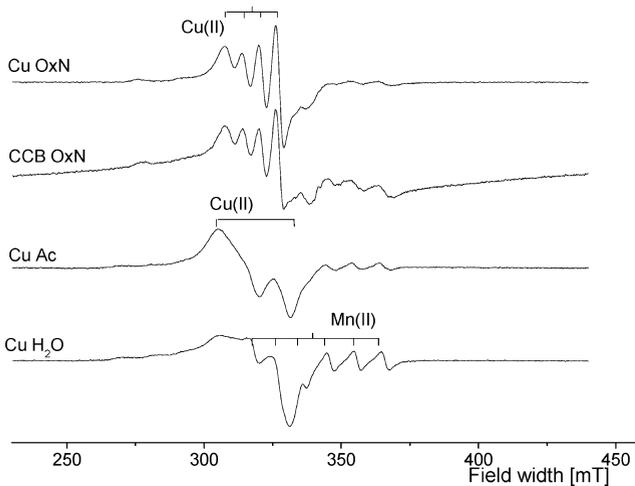

Fig. 4. EPR spectra of wet Norway spruce wood samples, previously treated with either copper sulfate or CCB, after leaching with: water (H_2O), 2% acetic acid (Ac), and distilled water containing 2% oxalic acid and 2% ammonia (OxN)

Conclusion

With this investigation, we have proven that EPR spectroscopy is a suitable method for investigating changes after the extraction of preserved wood. It provides information on chromium and copper changes in preserved wood caused by leaching, thus giving us useful information on the complexes of Cu and Cr which are formed during leaching.

From our results it can be concluded that for the best leaching of Cu or Cr out of treated wood, different procedures are needed. The highest chromium leaching

was achieved with oxalic acid extraction, while for the best copper leaching ammonia should be added into an aqueous solution of oxalic acid in order to prevent the formation of insoluble copper oxalate. Using the EPR measurements, we were able to determine the changes in copper and chromium complexes during the leaching procedure. We have proven that the leaching of CCB-treated samples with the aqueous solution of oxalic acid/ammonia caused the formation of a soluble complex made up of copper, oxalic acid, and ammonia. On the other hand, no such complex was determined when acetic acid was used instead of oxalic acid. However, we believe that the oxalate formation is not the only mechanism responsible for copper and/or chromium leaching. High acidity may reverse the chromium fixation process and thereby release heavy metals in wood. These results are very promising and have to be taken into consideration for the remediation of CCB-treated waste wood.

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