

Consumption of O₂, evolution of CO₂ and reduction of Cr(VI) during fixation of chromium based wood preservatives in wood

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Abstract Norway spruce dust was impregnated with aqueous solutions of chromated copper wood preservatives. Immediately after treatment, observation of CO₂ evolution and O₂ consumption were performed. Significant quantities of CO₂ were released during reaction of chromium (K₂Cr₂O₇) containing solutions with wood or brown rotted wood. Nevertheless, during reaction of cellulose with these preservatives we did not observe evolution of CO₂. The presence of copper did not influence on concentration of CO₂. Opposite to CO₂ evolution, treatment of wood and brown rotted wood resulted in O₂ consumption. The oxygen concentration decrease in the measuring chamber was approximately 5 times greater than increase of concentration of carbon dioxide. Electron paramagnetic resonance (EPR) observations of chromium fixation showed that chromium is reduced from Cr(VI) to Cr(III) with Cr(V) as an intermediate on wood, brown rotted wood and cellulose. However, the reduction on wood and brown rotted wood was faster than the reduction on cellulose, as determined from changes of Cr signals in EPR spectra. So, evolution of CO₂ and consumption of O₂ as well as EPR signals of Cr species thus indicate that brown rotted wood, consisting of lignin and hemicelluloses in contact with Cr(VI) reacts more intensively than cellulose, and possibly, oxidation mechanisms of lignin and cellulose with Cr(VI) are different.

Introduction

Knowledge of the fundamental interactions of copper and chromated copper (CC) based preservatives with wood is important in understanding how these materials protect wood from decay, and as a basis for the design of future generations of wood preservatives. A number of research groups have studied the chemical interactions between CC preservatives and wood. The key features are known but due to their complexity, the mechanisms involved are still not fully elucidated and further research is needed to gain a better understanding

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of the processes involved (Richardson 1993; Pohleven et al. 1994; Hughes 1999).

Evolution of CO₂ during fixation of chromium-based preservatives in wood is well known (Williams and Feist 1984; Ruddick et al. 1993; Porandowski et al. 1998; Jorge et al. 1999). Despite of great commercial importance of chromium based preservatives, complete mechanism of decarboxilation is still not understood. Porandowski et al. (1998) proposed that decarboxilation occurred during reaction of chromium with hydroxyl groups on lignin, cellulose or hemicellulose. Similarly, Hon and Chang (1985) suggested that large amounts of Cr(VI) are reduced to Cr(III) with all three substrates. Pizzi (1990a, 1990b) proposed an incomplete reduction of Cr(VI). Cr reacts with the lignin component of wood to form stable complexes, but further portions of Cr appear to be weakly bound, or just precipitated, on wood carbohydrates, possibly cellulose. It is known, that during fixation more than one Cr(V) species are present (Yamamoto and Ruddick 1992). Cr(V) in wood is quite long-lived and can still be detected two years after impregnation (Petrič et al., unpublished). This is a rather surprising result, taking into account the known instability of Cr(V) species in the presence of oxidants and reductants (Farrel and Lay 1992).

The role of Cr(V) in the fixation process of chromated copper based preservatives is still not well explained. It was the aim of our work to throw light on occurrence of Cr(V) and more generally reduction of Cr(VI) to Cr(III) during fixation of CC preservatives in wood, by the method of electron paramagnetic resonance (EPR), and to see whether there is a relationship between evolution of CO₂ and consumption of O₂ from wood and reduction of Cr(VI) in wood.

Materials and methods

Measurements of CO₂ and O₂ concentrations

Norway spruce (*Picea abies* Karst) sapwood was ground into sawdust (Mesh 40). Afterwards, 20 g of air-dry sawdust were put into the measuring chamber (V ≈ 400 ml) (Fig. 1) and treated with 40 ml of a preservative solution. The following preparations were used for impregnation:

- aqueous solution of copper(II) sulfate (CuSO₄ × 5H₂O) (c_{Cu} = 0.75%) and potassium dichromate (K₂Cr₂O₇) (c_{Cr} = 1.25%) (CC)
- or aqueous solution of copper(II) sulfate (Cu) (c_{Cu} = 0.75%)
- or aqueous solution of potassium dichromate (Cr) (c_{Cr} = 1.25%)
- or distilled water.

Additionally, the same experiment was repeated with brown rotted wood (BRW) as a model for lignin, with Na-cellulose as a model for cellulose, and L+ glucose. BRW was obtained from untreated wood exposed to brown rotting fungi (*Coniophora puteana* ZIM L009 and *Gloeophyllum trabeum* ZIM L017 (Raspor et al. 1995)) for 4 month.

Immediately after impregnation with preservative solutions, measurements were performed. Concentrations of CO₂ and O₂ in the system were measured every 10 s for at least 7 hours. All measurements were preformed in three parallels, not showing any significant differences between them. An infra red gas analyzer (0–3000 ppm; ±5 ppm) was used for carbon dioxide detection and galvanic sensor for O₂ measurements (0–25%; ±0.01%).

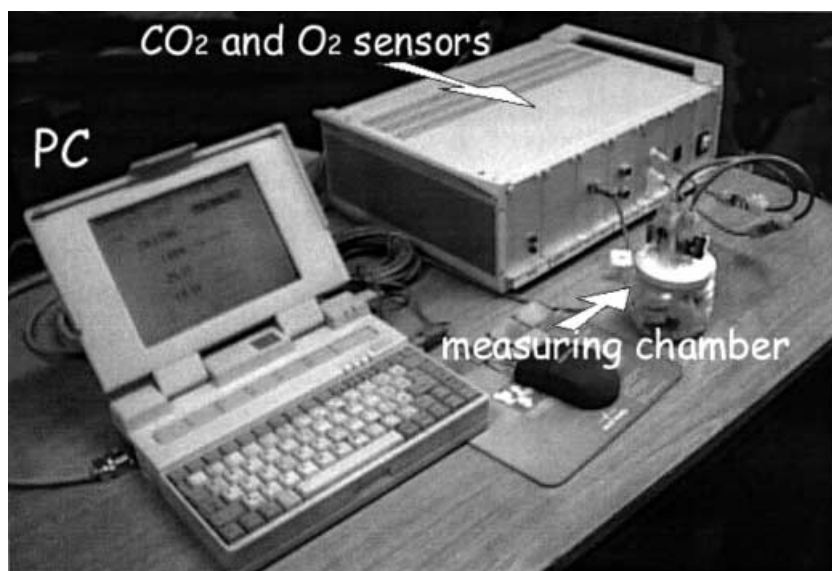
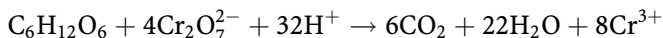


Fig. 1. The system for measuring evolution of CO₂ and consumption of O₂

EPR measurement

For Electron Paramagnetic Resonance (EPR) measurements, very fine wood sawdust (Mesh 130), brown rotted wood (as a model for lignin) or Na-cellulose were prepared. Approximately 0.1 g of dust was treated with 0.2 ml of aqueous solution of potassium dichromate ($c_{Cr} = 1.25\%$) and put into a capillary tube. Afterwards, EPR measurements started. The first measurement was performed after 5 minutes and the last one after 2 weeks of drying at 75°C. Measurements were performed at 75°C using 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). For comparison, some samples were measured also at room temperature. Additionally, we made same experiments with L+ glucose and a K₂Cr₂O₇ solution, as it is reported that in this case Cr(III) and CO₂ are formed, (Davidson 1941; Hughes 1999):



Results and discussion

Measurements of CO₂ and O₂ concentrations

As expected, fixation of chromium based wood preservatives resulted in evolution of CO₂. From wood treated with the aqueous solution of potassium dichromate, large amount of carbon dioxide was released. CO₂ concentration increased from initially 300 ppm to a maximum of 3500 ppm after 7 hours of reaction (Table 1).

Furthermore, we observed very intense evolution of CO₂ from BRW, impregnated with chromium containing solutions (Table 1). In some cases, concentration of carbon dioxide increased after 7 hours of reaction, from initially 500 ppm to 3300 ppm respectively (Fig. 2). Thus, the whole wood reacts with chromium at

Table 1. Changes in CO₂ concentration after 7 hours of reaction of wood or its components with aqueous solutions of chromium and/or copper based preservatives

Treatment	Substrate Wood Change in CO ₂	Lignin concentration [ppm]	Cellulose	/
CC	+1600 ± 200	+2300 ± 230	0	+400 ± 150
Cr	+1500 ± 150	+2500 ± 250	0	+500 ± 200
Cu	0	0	0	+350 ± 200
Water	0	0	0	-150 ± 50
No treatment	0	0	0	0

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a rate not very different from that of BRW. In experiments with spruce Na-cellulose we did not observe any evolution of CO₂ as a result of reaction of cellulose with chromium and/or copper containing wood preservatives (Table 1). Based on these results, we presume that cellulose is not involved in decarboxilation. Therefore, we believe that lignin functional groups have the main role in evolution of CO₂ during reduction of chromium in wood, as suggested also by Jorge et al. (1999). On the other hand, Cr³⁺ interactions with cellulose are mainly based on Van der Waals forces (Pizzi 1990a).

Treatment of wood only with the aqueous solution of copper(II) sulfate, without chromium, did not cause release of CO₂. As expected, the presence of copper(II) sulfate in chromium based preservatives, also did not result in additional release of CO₂. Thus, we proved the statement of Porandowski et al. (1998), that copper(II) sulfate does not influence on evolution of CO₂ during fixation. As at wood, treatment of BRW or cellulose with copper(II) sulfate also did not cause release of CO₂.

It has to be mentioned that L+ glucose is sometimes regarded as a simple model for cellulose or even wood (Michell 1993; Wright and Banks 1989). However, our decarboxilation results with L+ glucose were completely different for cellulose. While from treated glucose, significant amounts of CO₂ were released, no evolution of CO₂ was observed during the reaction with cellulose. This is one more confirmation, that L+ glucose cannot be used as a model for cellulose.

During the reactions, we were also measuring concentrations of oxygen. Prominent changes in O₂ concentrations during reaction of chromium(VI) and copper(II) containing preservatives with wood or its components were observed (Fig. 2). In the available literature there are no reports on observation of O₂ consumption during fixation of chromium containing wood preservatives in wood. We observed a decrease of oxygen concentration in the system only in the cases where decarboxilation occurred (Table 2). For example, at wood, treated with aqueous solution of K₂Cr₂O₇, approximately 1500 ppm of CO₂ was released and more than 8000 ppm of O₂ was consumed. The oxygen concentration decrease was approximately 5 times greater than the increase of carbon dioxide. The same changes happened also at BRW impregnated with chromium based aqueous solution, but not with impregnated cellulose. As can be seen from similar shapes of both CO₂ and O₂ concentration curves (Fig. 2), CO₂ evolution and O₂ consumption occur simultaneously; thus, we presume that decarboxilation and consumption of oxygen are connected. Porandowski et al. (1998) and Ostermeyer and coworkers (1989) proposed some mechanisms of fixation reactions of chromium with wood components and in both proposed reaction mechanisms, consumption of O₂ was suggested. However, in our measurements we directly

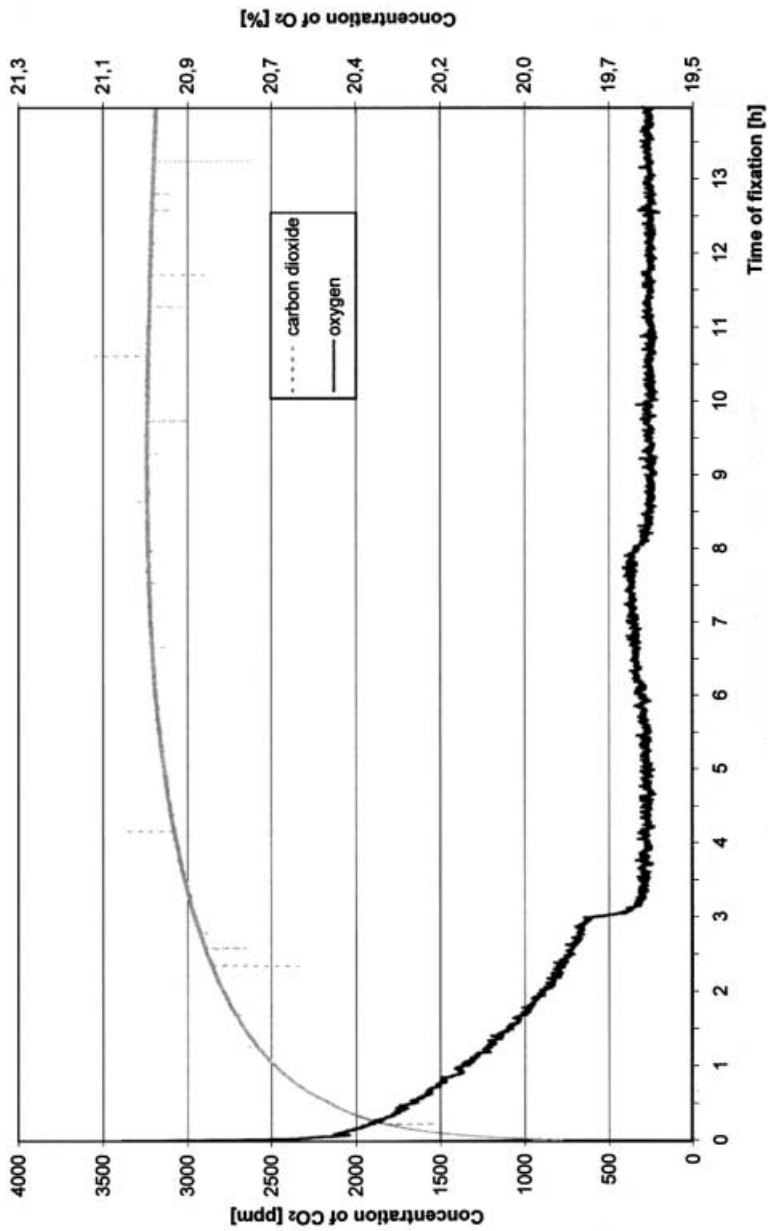


Fig. 2. Changes in concentration of CO₂ and O₂ during reaction of brown rotted wood (lignin) with chromium containing aqueous solution (K₂Cr₂O₇)

Table 2. Changes in O₂ concentration after 7 hours of reaction of wood or its components with aqueous solutions of chromium and/or copper based preservative

Treatment	Substrate Wood Change in O ₂	Lignin concentration [%]	Cellulose	Control
CC	-0.8 ± 0.1	-1.2 ± 0.1	0	0
Cr	0.6 ± 0.1	-1.0 ± 0.1	0	0
Cu	0	0	0	0
Water	0	0	0	0
No treatment	0	0	0	0

showed that O₂ is consumed during decarboxilation of wood, as a result of treatment of wood with chromium based preservatives.

During our experiments, we also observed a slight increase of CO₂ concentrations when chromium and/or copper containing solutions were put into the measuring system (Table 1). The reason for this increase may possibly be slight air pressure changes in the measuring chamber during measurements.

EPR measurements

As usual for wood based systems, EPR spectra of BRW and wood contained the signals of free radicals and manganese. Free radical signals ($g_0 = 2.003$) were observed in the EPR spectra of untreated wood samples, as well as on the spectra of chromium treated ones. Intensity of this signal did not vary between parallel measurements. g value of 2.003 lies well within the range, specific for heteroatomic organic radicals, containing oxygen. Such radicals may originate from photo-degradation of wood or its components. (Dobbs 1974; Harańczyk 1999)

Immediately after impregnation of wood or its components (lignin or cellulose), manganese(II) signal appeared ($g_0 = 2.009$ $a_0 = 9.6$ mT) (Figs. 4 and 5). But two hours after treatment, Mn signal completely disappeared.

However, by our investigations we would like to find correlation between reactions of Cr and decarboxilation. In interpretation of EPR spectra of impregnated wood or BRW or cellulose, we focused on Cr spectra. Very shortly after treatment of wood or wood component models, narrow Cr(V) signal appeared ($g_0 = 1.978$). This is not a surprising result, since it has been shown that Cr(VI) is reduced to Cr(III) with Cr(V) as an intermediate (Yamamoto and Ruddick 1992; Ruddick et al. 1994). This is also well correlated with the fact that the reduction of Cr(VI) to Cr(V) is faster than the reduction of Cr(V) to Cr(III) (Mahapatro et al. 1980). In our spectra, Cr(V) signals were present in treated wood, as well as in treated BRW and cellulose. These observations are in contradiction with the results described in the previous chapter (3.1). During the reaction of cellulose with chromium based preservatives, reduction of chromium occurred in spite of fact that decarboxilation was not observed in this case. Thus, the described chromium reduction and decarboxilation process cannot be directly associated. It has to be mentioned, that Cr(V) signals in BRW are much more intense than in treated cellulose (Figs. 4 and 5). Oxidation in cellulose with Cr(VI) is more difficult than oxidation in BRW. It does not end with decarboxilation, while oxidation in BRW (as model for lignin) finishes with the evolution of CO₂. The intensities of Cr(V) signal were decreasing with time after treatment, as a consequence of further reduction of Cr(V) to Cr(III). At wood and particularly BRW, the main decrease occurred during first 15

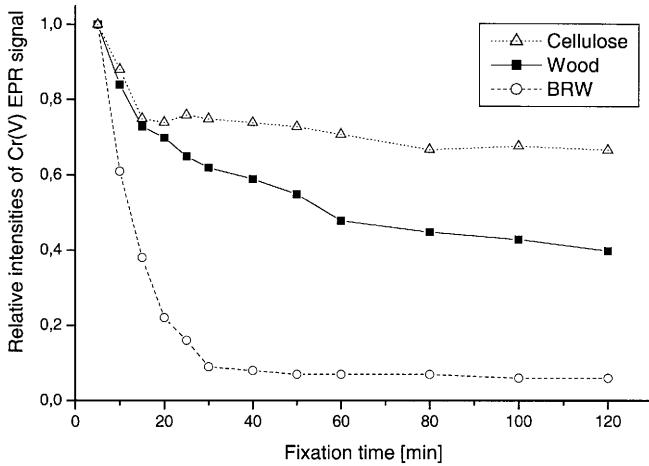


Fig. 3. Relative intensities of Cr(V) signal during fixation of chromium ($K_2Cr_2O_7$) pre-servatives with wood or its components as a function of fixation time

minutes of reaction. EPR signals of Cr(V) decreased for 62% after 15 minutes of reaction of a chromium containing aqueous solution ($K_2Cr_2O_7$) with BRW. Additional 85 minutes of this reaction resulted in almost complete 94% decrease of the Cr(V) signal. In treated wood the Cr(V) signal decreased less rapidly than in BRW, but more rapidly than in cellulose (Fig. 3). However,

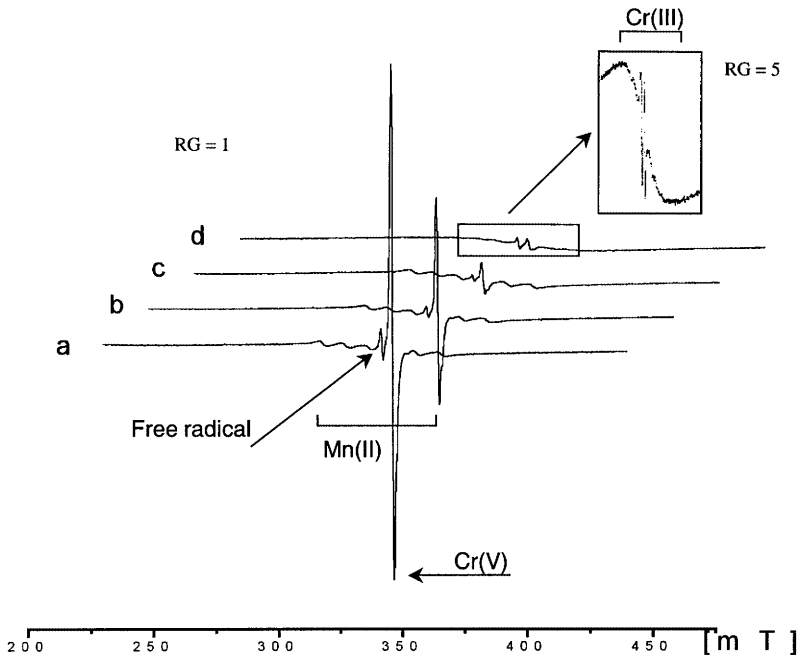


Fig. 4. EPR spectra of BRW, impregnated with aqueous solution of $K_2Cr_2O_7$ ($c_{Cr} = 1.25\%$) after 5 (a), 10(b), 30(c) and 120(d) minutes of fixation, recorded at $75^\circ C$. (RG is relative receiver gain)

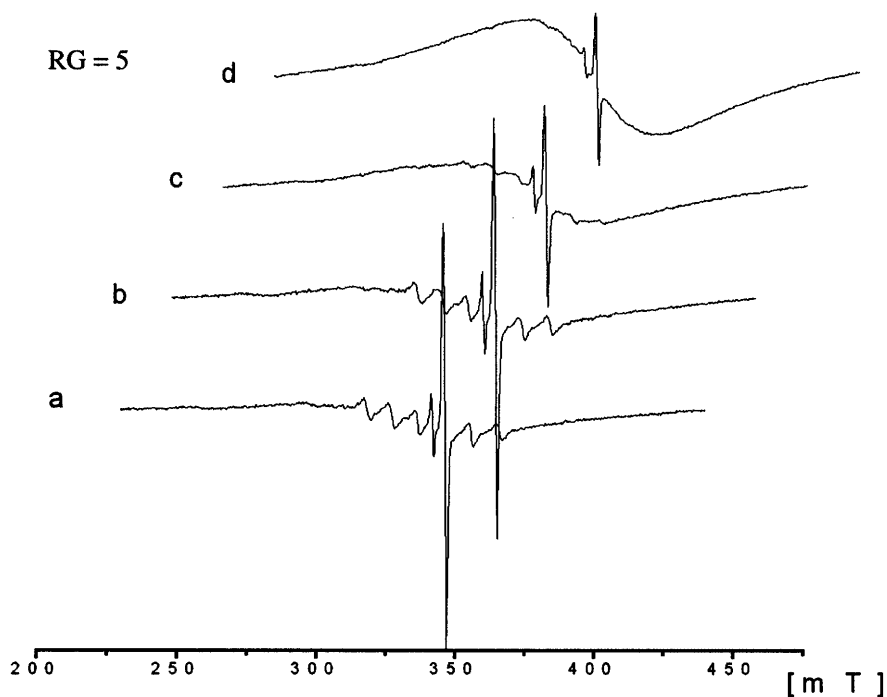


Fig. 5. EPR spectra of cellulose (recorded at 75°C) impregnated with aqueous solution of $K_2Cr_2O_7$ after 5 (a), 10 (b), 30 (c) and 120 (d) minutes of fixation

Cr(V) signal could be still detected in all substrates after 4 weeks of fixation at 75°C. The intensity of Cr(V) signal after 4 weeks, was similar to the one after 2 hours of fixation.

To conclude, during the reduction of Cr(VI) to Cr(V), we did not notice a correlation between reduction and decarboxilation. Further reduction of Cr(V) to Cr(III), takes place in all used substrates, as seen from the Fig. 3 and Figs. 4 and 5. But, decarboxilation occurs only in wood and BRW.

During our experiment with wood or its components, we noticed only one Cr(V) EPR signal, but when we used glucose instead of wood, three signals were present ($g_0 = 1.993$, $g_0 = 1.981$, $g_0 = 1.962$). Yamamoto and Ruddick (1992) reported about the same observation, for the reaction between chromium trioxide and hardwood (*Anthocephalus cadamba*).

Broad and weak chromium(III) signal appeared immediately after treatment. The intensity of this signal was increasing during the first 90 min after treatment (Fig. 4). Additional fixation did not result in significant increase of Cr(III) signal, therefore we believe that during the first 90 minutes the major reduction occurred. Intensities of chromium(III) were approximately the same so in the treated wood as well as in treated BRW and cellulose.

Conclusions

During the reaction of wood with chromium containing preservatives ($K_2Cr_2O_7$) significant amounts of carbon dioxide were released. Treatment of cellulose with aqueous solution of chromium ($K_2Cr_2O_7$) did not result in evolution of CO_2 . On the other hand, brown rotted wood as a model for lignin, reacted with chromium

with evolution of CO₂, by the same way as wood did. Therefore, we may conclude that decarboxilation occurs during reaction of chromium(VI) with lignin system and/or hemicelluloses, which are also present in brown rotted wood.

Impregnation of wood or its components with copper(II) sulfate did not cause additional release of CO₂. Therefore, the reaction of chromium and not copper, with wood or lignin is the primary reason for decarboxilation.

We also observed significant consumption of oxygen during reaction of chromium based preservatives with wood and brown rotted wood. Consumption of O₂ during oxidation of lignin with Cr(VI) was already proposed by some authors (Porandowski et al. 1998; Ostermeyer et al. 1989), but to the best of our knowledge, our measurements are the first direct evidence on the role of atmospheric oxygen in reaction of chromium based preservatives with wood.

From EPR observations we can conclude, that chromium(VI) is reduced to Cr(III) with Cr(V) as an intermediate at wood, brown rotted wood (model for lignin) and cellulose. Oxidation of wood and brown rotted wood with Cr(VI) results in their decarboxilation. But during the reaction of cellulose with chromium, decarboxilation does not take place. These results indicate that brown rotted wood, predominantly consisting of lignin and hemicelluloses in contact with Cr(VI) reacts more intensively than cellulose, and possibly, oxidation mechanisms of lignin and cellulose with Cr(VI) are different.

References

- Davidson GF (1941) The progressive oxidation of cotton cellulose by chromic acid over a wide range of oxygen consumption. *Journal of textile institute transactions* 32:132–148
- Dobbs AJ (1974) G-factors of free radicals in fluid solution. *Electron Spin Resonance Spec. Period. Rep.* 2:281–294
- Eaton RA, Hale MDC (1993) *Wood Decay, pests and protection*. Chapman & Hall, London, Glasgow, pp 344–372
- Farrel RP, Lay PA (1992) *Comments in Inorganic chemistry*. 13:133–175
- Harańczyk H (1999) The investigation of hydration processes in horse chestnut (*Aesculus hippocastanum*, L.) and Pine (*Pinus silvestris*, L.) bark and Bast using proton magnetic relaxation. *Holzforschung* 53:299–310
- Hon DNS, Chang ST (1985) Photoprotection of wood surfaces by wood ion complexes. *Wood and Fibre Science* 17:92–100
- Hughes AS (1999) *Studies on the fixation mechanisms, distribution and biological performance of copper-based timber preservatives*. Ph. D. thesis, Imperial College of Science, Technology and Medicine, London, p 313
- Jorge FS, Santos TM, de Jesus JP, Banks WB (1999) Reactions between Cr(VI) and wood and its model compounds. Part 1: A qualitative kinetic study of the reduction of hexavalent chromium. *Wood Sci. Technol.* 33:487–499
- Mahapatro SN, Krumpolc M, Roček J (1980) Three-electron oxidations. The chromium(VI) and chromium(V) steps in the chromic acid cooxidation of 2-hydroxy-2-methylbutyric acid and 2-propanol. *J. Am. Chem. Soc.* 102:3799–3806
- Michell AJ (1993) FTIR spectroscopic studies of the reactions of wood and lignin model compounds with inorganic agents. *Wood Sci. Technol.* 27:69–80
- Ostermeyer JG, Elder TJ, Winandy JE (1989) Spectroscopic analysis of southern pine treated with chromated copper arsenate. II Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT). *Wood Chem. Technol.* 9:105–122
- Petrič M, Obadič D, Pohleven F, Schoknecht U, Šentjurc M, Electron Paramagnetic Resonance (EPR) as a method for investigations of microbiological decay process of impregnated wood. unpublished results.
- Pohleven F, Šentjurc M, Petrič M, Dagarin F (1994) Investigation of ammoniacal copper(II) octanoate in aqueous solutions and its determination in impregnated wood. *Holzforschung* 48:371–374

- Pizzi A** (1990a) Chromium interactions in CCA/CCB wood preservatives. Part I. Interactions with wood carbohydrates. *Holzforschung* 44:373–380
- Pizzi A** (1990b) Chromium interactions in CCA/CCB wood preservatives. Part II. Interactions with lignin system. *Holzforschung* 44:419–424
- Porandowski J, Cooper PA, Kaldas M, Ung YT** (1998) Evolution of CO₂ during the fixation of chromium containing wood preservatives on wood. *Wood Sci. Technol.* 32:15–24
- Raspor P, Smole-Možina S, Podjavoršek J, Pohleven F, Gogala N, Nekrep FV Rogelj I, Hacin J** (1995) ZIM: zbirka industrijskih mikroorganizmov. Katalog biokultur; Biotehniška fakulteta, Katedra za biotehnologijo, Ljubljana:98
- Richardson BA** (1993) *Wood preservation*. E & FN Spon, London, Glasgow, 226
- Ruddick JNR, Yamamoto K, Herring FG** (1994) The influence of accelerated fixation on the stability of chromium(V) in CCA treated wood. *Holzforschung* 48:1–3
- Williams RS, Feist WC** (1984) Application of ESCA to evaluate wood and cellulose surfaces modified by aqueous chromium trioxide treatment. *Colloids and Surfaces* 9:253–271
- Wright JK, Banks WB** (1989) The valence state of chromium in treated wood studied by magnetic susceptibility. *J. Wood Sci. Technol* 9:569–572
- Yamamoto K, Ruddick JNR** (1992) Studies of the mechanism of chromated-copper preservative fixation using electron spin resonance. The International Research Group on Wood Preservation, Document IRG/WP 92–3701:12