Short Note

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Treatment of European beech with a new wood fire retardant agent based on *in situ* deposition of calcium oxalate

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Abstract: European beech (*Fagus sylvatica* L.) was impregnated in a two-step process with aqueous solutions of potassium oxalate and calcium chloride successively. These compounds are intended to react *in situ* to the water-insoluble salt calcium oxalate and the reaction by-product potassium chloride. In order to assess the treatability, the solid uptake after the first impregnation and after the treatment was examined. The fixation of the precipitated salts was measured in leaching tests according to the European standard EN 84. The reaction to fire of mineralized beech was tested following the standard ISO 11925-2. A weight percentage gain of appr. 35% indicates a sucessful treatment of the beech with the mineralization agents. The weight percentage gain after leaching indicates a sufficient fixation of calcium oxalate in the wood. Furthermore, results from flammability tests indicate improved fire resistance due to the mineralization.

Keywords: mineralization, reaction to fire, wood modification

Introduction

Mineralization of wood is a natural process which occurs during fossilization of wood. It is a long-term process and involves the accumulation of non-organic materials, such as silicon, calcium carbonate or phosphor in the wood, resulting in the preservation of the wood (Buurman 1972). According to Fengel (1991), the process of natural mineralization can be subdivided into coalification and silicification. Coalification describes the transformation of the cell wall substances into highly condensed compounds, whereas silicification characterizes the substitution of the cell wall substances by various minerals. There are existing approaches to achieve artificial mineralized wood material by means of substitution of the wood compounds. For example, Fritz-Popovski et al. (2013) successfully replicated the cellulose structure with a silicone by means of substituting these compounds in wood.

However, artificial mineralization of wood denotes in the field of wood modification a filling of the voids in the wood structure by means of impregnation of liquid solutions. Until today, various approaches have been developed to achieve artificial mineralized wood to overcome various drawbacks of wood, such as insufficient natural durability or poor dimensional stability. Artificial mineralization based on silicon was widely investigated and a comprehensive amount of formulations in combination with wood was investigated as summarized by Mai and Militz (2004a,b). One obtained feature, which was observed for almost every silicon-based treatment, was improved fire retardancy.

Another approach of artificial mineralization of wood is the *in situ* precipitation of water-insoluble salts inside the wood to obtain a material with improved properties, e.g. improved fire retardancy. Merk (2016) precipitated calcium carbonate in European beech and Scots pine and obtained modified wood with improved fire retardancy. Likewise, investigations by Khelfa et al. (2013) evidenced improved fire retardancy of birch treated with $MgCl_2$ and $NiCl_2$.

In this study, calcium oxalate [$Ca(COO)_2$] was intended to precipitate *in situ* of European beech (*Fagus sylvatica* L.). $Ca(COO)_2$ is hardly water soluble and thus promises a proper fixation inside the wood by means of resistance against leaching effects that are caused by

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water. Therefore, two water-soluble salts, namely calcium chloride ($CaCl_2$) and potassium oxalate [$K_2(COO)_2$], were impregnated in the wood in a two-step impregnation process successively. This results in the precipitation of $Ca(COO)_2$ and the corresponding by-product potassium chloride (KCl).

$Ca(COO)_2$ is found in nature, e.g. as kidney stones or in various plants such as rhubarb (*Rheum rhabarbarum* L.) as protection against herbivores. Furthermore, $Ca(COO)_2$ is known to be a by-product of the wood degradation process caused by copper-tolerant wood-destroying fungi (Stephan et al. 1996).

This study aimed to investigate the treatability of beech wood with ionic salt solutions and a resulting precipitation of $Ca(COO)_2$. Furthermore, the effect of this treatment regarding wood with retarded reaction to fire properties was investigated.

Materials and methods

European beech (*Fagus sylvatica)* was selected for the study. Precipitation of $Ca(COO)_2$ and the reaction by-product KCl was initiated according to Eq. 1. The reactants potassium oxalate monohydrate [$K_2(COO)_2$] (99% purity) and calcium chloride hexahydrate ($CaCl_2$) (98% purity) were obtained from Sigma Aldrich® (St. Louis, MO, USA).

$$K_2(COO)_2 + CaCl_2 \rightarrow Ca(COO)_2 + 2KCl \quad (1)$$

The impregnation solutions were prepared by diluting the corresponding salt in deionized water in the ratio given in Table 1. The ratio was selected in accordance to stoichiometric calculations to ensure a theoretically maximum conversion of the reactants inside the wood.

The aqueous ionic salt solutions were impregnated in a two-step impregnation process in a pilot-scale autoclave. The impregnation of each step consists of a vacuum-pressure cycle. Thereby, a vacuum of −95 mbar was applied for 20–30 min, following a pressure of 500 mbar for 1 h. After the first step, the $K_2(COO)_2$ impregnated specimens were dried at room conditions to approx. 20% moisture content prior to the impregnation of $CaCl_2$.

The solid uptake after the first impregnation step as well as the weight percent gain (WPG) after the second impregnation step were determined based on the absolute dry weight according to Eq. 2 on 24 specimens with the dimensions of 35×35×200 mm³. The absolute dry weight before and after the mineralization treatment was determined in a kiln dried at 103 °C until a constant weight was reached.

$$\text{Solid uptake / WPG} = \frac{w_1 - w_0}{w_0}; \% \quad (2)$$

where solid uptake is the theoretical uptake of the precipitated reactants after the first impregnation step and WPG is the theoretical uptake of the assumed reaction products $Ca(COO)_2$ and KCl, respectively. Furthermore, w_1 is the absolute dry weight after each impregnation step in grams, and w_0 is the absolute dry weight before impregnation in grams.

A leaching test following the specifications noted in the European standard EN 84 was performed to estimate the fixation of $Ca(COO)_2$ and the by-product KCl in the wood. Thereby, the specimens were submerged in deionized water and exposed to a vacuum of 40 mbar for 20 min. Subsequently, the specimens were kept in the water for 14 days. During the leaching process, the water was changed periodically for a total of 10 times.

Reaction to fire tests were carried out according to the standard ISO 11925–2 with six mineralized beech specimens as well as six untreated beech specimens with the dimensions of 250×90×20 mm³. A flame was set with a metallic cylinder equipped with a cone-like point with an angle of 45°. The reaction to fire test involves several stages. First, the flame is positioned approx. 1.5 mm below the edge of the sample. The length of the flame was 20 mm and the flux of the air was 0.6–0.8 $m^3 s^{-1}$. Afterward, the specimens were exposed to the fire for 105 s. Subsequently, the time the wood stays burning after the flame is retired was recorded and the extent of the flame trace was measured after the test. Thereby, the length and width of the flame trace was measured and presented as the sum of both.

Results and discussion

The solid uptake after the first impregnation step as well as the WPG after the second step and after leaching are presented in Figure 1.

After impregnation of the first reactant [$K_2(COO)_2$], the European beech displayed a solid content uptake of 22.7%. Subsequently, after the second impregnation step ($CaCl_2$), the beech specimens had a WPG of 35.1%. The WPG after the second step indicates that the impregnation of $CaCl_2$ is not sufficient to achieve a full conversion to $Ca(COO)_2$ and KCl. However, it is conceivable that some amount of $K_2(COO)_2$ is leached out during the second impregnation step of $CaCl_2$ and thus, lead to a lower WPG as expected. In order to determine the successful mineralization process, leaching tests according to the EN 84 can serve as a first indicator for the treatment. The educts are water soluble [$CaCl_2 = 811\ g \cdot l^{-1}$ at 20°C and $K_2(COO)_2 = 360\ g \cdot l^{-1}$ at 20°C], as well as the

Table 1: Mixing ratio of the reactant:H_2O (w:w) and ratio of the reaction educts, as well as the reaction products.

Composition	Reactant 1 $K_2(COO)_2$ ($C_2O_4K_2$:H_2O)	Reactant 2 $CaCl_2$($CaCl_2$:H_2O)	Educts $K_2(COO)_2$:$CaCl_2$	Product $Ca(COO)_2$:KCl
Mixing ratio (w:w)	1:2.8	1:2.1	1:1.3	1:1.2

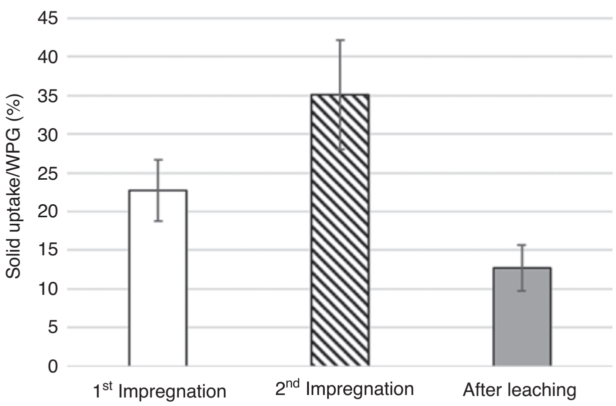

Figure 1: Solid uptake after the first impregnation step, the WPG after the second step, as well as the WPG after leaching of $Ca(COO)_2$ mineralized beech.

reaction by-product KCl (347 $g \cdot l^{-1}$ at 20°C) and thus, they are assumed to be easily washed out, whereas $Ca(COO)_2$ is poorly water soluble (0.07 $g \cdot l^{-1}$) and is expected to be fixed inside the wood. After leaching, a WPG of 12% is left over in the wood. Presuming a theoretical conversion rate of 100%, the WPG after leaching is in good agreement with the calculated conversion ratios between $K_2(COO)_2$ and KCl. This supports the hypothesis that during the second impregnation step, some amounts of $K_2(COO)_2$ are leached out. In the case of insufficient conversion, the amount of leached out chemicals would be higher. However, the precise rate remains unclear and more work has to be carried out to strengthen this assumption.

The effect of the mineralization with $CaCl_2$ and $K_2(COO)_2$ to obtain $Ca(COO)_2$ in beech regarding the reaction to fire is presented in Figure 2. The burning trace of the untreated beech samples is clearly bigger than the trace of the mineralized beech samples (Figure 2a). Furthermore, the time the wood stays burning after the flame is retired is almost eliminated for the mineralized beech (Figure 2b).

The results from the flammability test indicate that the treatment can improve the inflammability of beech wood. For the mineralized beech, the flame path was reduced to 6.1 mm compared to the untreated beech (10.3 mm). Additionally, the time the wood stayed burning after flame retirement was almost eliminated for the mineralized wood, whereas the untreated wood stayed burning on average for 34 s. Browne (1958) categorized various possible mechanisms of the action of a fire retardant. The most likely theory matching with the treatment is that the salts insulate the wood and exchange of heat as well as pyrolyzing gases are limited. Additionally, the precipitated salts, and in particular chlorides, have a high hydrophilic effect resulting in a higher equilibrium moisture content compared to the untreated wood (Furuno et al. 1992). This could also contribute to the reaction of the mineralized wood against fire. Interior applications with special

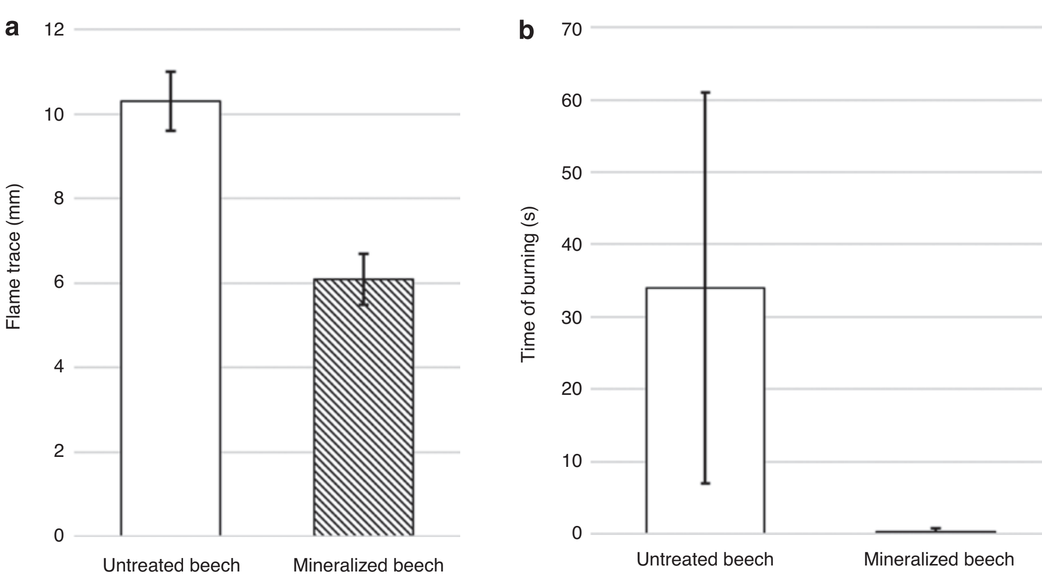

Figure 2: Reaction to fire.
Reaction to fire of the $Ca(COO)_2$ mineralized beech compared to untreated beech by means of the Flame trace (a) and by means of the time of burning after flame is retired (b).

requirements for inflammability might be a conceivable field of application for $Ca(COO)_2$ mineralized wood.

Conclusions

The feasibility of impregnation with $CaCl_2$ and $K_2(COO)_2$ to obtain $Ca(COO)_2$ in beech was demonstrated. The following conclusions can be drawn:

- A high uptake of the impregnation agents $CaCl_2$ and $K_2(COO)_2$ into European beech indicates proper treatability of this wood species to obtain $Ca(COO)_2$.
- However, a high amount of leached out chemicals was determined. It is assumed that the majority of leached out chemicals is attributed to the by-product KCl, as well as unreacted $CaCl_2$ and $K_2(COO)_2$. However, more work is needed to strengthen this assumption.
- The flammability of the mineralized beech improved compared to the untreated beech by means of the flame trace and the time of burning after the flame is retired.

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References

Browne, F.L. (1958) Theories of the combustion of wood and its control. Forest Products Laboratory Report 2136.

Buurman, P. (1972) Mineralization of fossil wood. Scr. Geol. 12:1–43.

EN 84 (1997) Wood preservatives – accelerated ageing of treated wood prior to biological testing – Leaching procedure.

Fengel, D. (1991) Aging and fossilization of wood and its components. Wood Sci. Technol. 25:153–177.

Fritz-Popovski, G., Van Opdenbosch, D., Zollfrank, C., Aichmayer, B., Paris, O. (2013) Development of the fibrillar and microfibrillar structure during biomimetic mineralization of wood. Adv. Funct. Mater. 23:1265–1272.

Furuno, T., Shimada, K., Uehara, T., Jodai, S. (1992) Combination of wood and silicate, 2: wood-mineral composites using water glass and reactants of barium chloride, boric acid, and borax, and their properties. Mokuzai Gakkaishi 38:448–457.

ISO 11925-2 (2010) Reaction to fire tests – Ignitability of products subjected to direct impingement of flame – part 2: single-flame source test. International Organization for Standardization, Switzerland.

Khelfa, A., Bensakhria, A., Weber, J.V. (2013) Investigations into the pyrolytic behaviour of birch wood and its main components: primary degradation mechanisms, additivity and metallic salt effects. J. Anal. Appl. Pyrol. 101:111–121.

Mai, C., Militz, H. (2004a) Modification of wood with silicon compounds. Inorganic silicon compounds and sol-gel systems. A review. Wood Sci. Technol. 37:339–348.

Mai, C., Militz, H. (2004b) Modification of wood with silicon compounds. Treatment systems based on organic silicon compounds – a review. Wood Sci. Technol. 37:453–461.

Merk, V. Mineralization of Wood Cell Walls for Improved Properties. Dissertation ETH Zürich, Zürich, Switzerland, 2016.

Stephan, I., Leithoff, H., Peek, R.D. (1996) Microbial conversion of wood treated with salt preservatives. Mater. Organismen 30:179–200.