



Thermal behavior and reaction to fire of European beech (*Fagus sylvatica*) treated with various salts and mineralization formulations

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1. Introduction

Wood is used as a construction material since ancient times. However, its attribute as a flammable material capable of catching fire is one of the greatest concerns for its usage in various applications in construction. Building elements made of wood such as constructive elements, facades, ceilings, walls or floorings made of wood can increase the fire load of a building and contribute to spreading of a flame. According to the European standard EN 13501-1, materials are classified in various classes in respect to their reaction to fire. According to the requirements which are demanded in the EN 13501-1, the majority of solid wood and wood products is classified in class D [1]. One way to reduce these drawbacks and improve wood's burning class is to use fire retardants. An assumed goal for a successful fire retardant for wood is to achieve the burning class B, which is frequently required for higher, larger or public buildings in many national building codes [2]. There is a wide variety of different fire retardants for wood. They can be categorized according to their mode of action, their chemical composition, or their application method [3–6]. A lot of fire retardants contain halogen, phosphorus or heavy metal and thus, are under discussion of being ecological concern or under suspicion for being harmful to humans and animals [3,7–10]. There is a demand for the substitution of those chemicals by non-hazardous substances. Different alternative approaches were investigated during the last years for wood and wooden products like: silica-based formulations such as water glass and alkoxysilane treatments, various inorganic/mineral fillers or nanocomposites [11–16]. Another promising approach is the mineralization of solid wood by means of a wood modification with slightly water-soluble minerals. Natural mineralization or fossilization, such as phosphatization, carbonization or silification describes the long process of substituting the wood structural compound with minerals [17]. Artificial mineralization by means of wood modification, on the other hand, describes the process of depositing minerals in the cell lumens and cell walls. Various authors describe artificial mineralization processes to

incorporate calcium carbonate (CaCO_3) in wood which leads to improved fire retardancy [18–21]. Guo et al. [22] demonstrated a successful treatment of wood with the phosphorous based mineral struvite to improve fire retardancy. Franke and Volkmer [23,24] treated oak and beech with an in-situ precipitation of the mineral calcium oxalate in a two-step impregnation process. It was shown that the mineralization treatment led to an improved fire retardancy. Calcium oxalate is the salt of the organic acid oxalic acid. It occurs according to its hydrate form as the mineral whewellite or weddellite. It is known to be formed by plants such as rhubarb against herbivores or in humans as kidney stones. Calcium oxalate is slightly water soluble (0.7 mg/l) and therefore might be suitable as a highly fixed fire retardant for solid wood.

The focus of the study is to investigate the thermal behavior and the reaction to fire of calcium oxalate treated beech (*Fagus sylvatica*). Since in-situ precipitation of calcium oxalate is carried out in a 2-step process, two formulations are applied to precipitate calcium oxalate in the wood. Both formulations consist of two water soluble salts. Potassium oxalate is used as a precursor in both formulations. As a second salt calcium chloride, respectively calcium acetate is used as precursor. Special emphasizes of the investigations is set on the impact of the precursor alone, the byproducts produced in the reaction, as well as pure and fixed calcium oxalate achieved after carrying out a leaching protocol on the performance against fire. Furthermore, the impact of the retention on the reaction to fire was investigated.

2. Experimental

European beech (*Fagus sylvatica*) was selected for all treatments. The beech specimens which were intended Scanning Electron Microscopy coupled with an Energy Dispersive X-ray Analysis (SEM-EDX) and for the thermogravimetric analysis (TGA) were cut into pieces with dimensions of 20 mm × 20 mm × 35 mm (radial × tangential × longitudinal), while specimens intended for mass loss calorimeter (MLC) measurements were cut into the dimensions of 18 mm × 100 mm × 100

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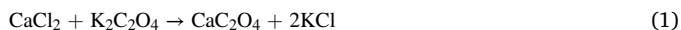
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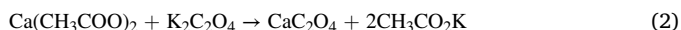
mm (radial × tangential × longitudinal).

Three water soluble salts namely calcium chloride (CaCl₂), potassium oxalate (K₂C₂O₄) and calcium acetate (Ca(CH₃COO)₂) were used as treatment agents. These salts were selected according to Eq. (1) and Eq. (2) to obtain an *in-situ* precipitation of calcium oxalate (CaC₂O₄) and the corresponding reaction by-product (potassium chloride KCl; respectively potassium acetate CH₃CO₂K):

Formulation 1:



Formulation 2:



Each salt was diluted in deionized water in two different concentrations. An overview of the treatments and concentrations, as well as the corresponding abbreviations for the various treatments used in the following text, are given in Table 1. Specimens were impregnated with the aqueous salt solutions in a pilot-scale autoclave with following parameters: First, a vacuum of 100 mbar was applied for 30 min. Secondly, the specimens were impregnated with 8 bar of pressure for 6 h. This process is in line with typical impregnation settings that are also used in industrial processes for wood impregnation. The time of 6 h was selected because of preliminary study that show that 6 h are sufficient to achieve a good penetration into the wood of the impregnation agents. Specimens which were impregnated two times were dried under room climate conditions to appr. 20 % moisture content (MC) between the first and the second impregnation step. Due to the high hygroscopic properties of CaCl₂, some CaCl₂ treatments (CC_{high}, as well as CC/PO_{high} and CC/PO_{low}), which undergo two impregnation steps, were dried in a vacuum kiln at 40 °C and 100 mbar to achieve sufficient low moisture content.

Specimens with pure CaC₂O₄ (CO) were obtained by treating beech twice, applying the same parameters and precursors as for the combination PO/CC_{high} (Table 1). The specimens were treated twice to increase the WPG and made it comparable to treatments that did not undergo a leaching process. Subsequently, water-soluble unreacted salts and water-soluble by-products were removed by applying two consecutive leaching cycles. Leaching cycles were carried out by submerging specimens in deionized water and expose them to a vacuum of 200 mbar

Table 1

Overview over the various treatments, the applied measurements, the mixing ratios of the used salts, as well as the abbreviations for each particular treatment.

Chemical 1	Chemical 2	Mixing ratio Chemical 1: H ₂ O	Mixing ratio Chemical 2: H ₂ O	Tests	Abbreviation
Calcium chloride	–	420 : 1000	–	MLC, TGA	CC _{low}
Calcium chloride	Calcium chloride	420 : 1000	420 : 1000	MLC	CC _{high}
Potassium oxalate	–	360 : 1000	–	MLC, TGA	PO _{low}
Potassium oxalate	Potassium oxalate	360 : 1000	360 : 1000	MLC	PO _{high}
Calcium acetate	–	309:1000	–	MLC, TGA	CA _{high}
Calcium acetate	Calcium acetate	309 : 1000	309 : 1000	MLC	CA _{high}
Potassium oxalate	Calcium chloride	180:1000	210 : 1000	MLC	PO/CC _{low}
Potassium oxalate	Calcium chloride	360 : 1000	420 : 1000	MLC, TGA	PO/CC _{high}
Potassium oxalate	Calcium acetate	180:1000	155 : 1000	MLC	PO/CA _{low}
Potassium oxalate	Calcium acetate	360 : 1000	309 : 1000	MLC, TGA	PO/CA _{high}
Potassium oxalate	Calcium chloride	360 : 1000	420 : 1000	MLC, TGA	CO

for 1 h. Afterwards, specimens were kept in the water for 7 days. The water was changed one time each day. Finally, the specimens were dried under room conditions and the whole leaching protocol was repeated.

After the treatment, all specimens were dried at 103 °C until constant weight and the Weight Percentage Gain was calculated according to Eq. (3).

$$\text{WPG} = \frac{m_1 - m_0}{m_0} \times 100; \% \quad (3)$$

Where WPG is the weight percentage gain (in %), m₁ is the absolute dry weight after treatment (in g) and m₀ is the absolute dry weight before the treatment (in g).

In a final step leftovers of salts and minerals that are precipitated on the specimen's surface were removed carefully with a steel brush.

Prior to testing, all specimens were stored in a climate chamber at 20 °C and 65 % relative humidity until weight constancy and the MC was calculated according to Eq. 4

$$\text{MC} = \frac{m_1 - m_{\text{salts}} - m_0}{m_0} \times 100; \% \quad (4)$$

Where MC is the moisture content at 20 °C and 65 % relative humidity (in %), m₁ is the weight after treatment at 20 °C and 65 % relative humidity (in g), m_{salts} is the weight of the impregnated salts (in g) and m₀ is the absolute dry weight before the treatment (in g).

Distribution and determination of the physico-chemical characteristic of the salts are performed with SEM-EDX. The SEM-EDX measurement was performed with a SEM Hitachi TM3030 SEM instrument coupled with a Bruker Quantax 70 EDX system EDX support. One specimen for each treatment was taken for measurements directly after the treatment, as well as after carrying out the leaching protocol. The transversal section of the specimens was smoothed with a microtome blade. Subsequently, the specimens were sputtered with a gold-palladium layer with a sputter coater.

The thermal behavior of the treated specimens was characterized by Thermogravimetric Analysis (TGA) using a TG 50 (Mettler Toledo). Prior to testing, specimens were milled carefully to a fine powder. A sample weight of 10–15 mg was used, and the measurements were carried out under nitrogen gas with a purge rate of 40 ml/min⁻¹ and a heating rate of 10 °C/min⁻¹, ranging from 30 °C to 800 °C. Each specimen was tested three times to ensure reproducibility. Derivative Thermogravimetry (DTG) was obtained by calculating the first derivative. In TGA/DTG investigations only one concentration of the salts solutions was applied (Table 1). In addition to the treated wood samples, the pure salts as obtained from the vendor, as well as after a precipitation treatment were tested within the same settings. Pure CaC₂O₄ was obtained by mixing water-diluted K₂C₂O₄ and CaCl₂ and subsequently filtering the solution with cellulose filter paper.

The evaluation of the reaction to fire was carried out with a Mass Loss Calorimeter (MLC) (FireTestingTechnology, West Sussex, UK) with an extra Thermopile and chimney for heat release assessment. The HRR were calibrated using a series of defined flow steps of methane gas. The tests were performed according to a modified ISO 5660-1. The MLC method deviates mainly from the ISO 5660-1 standard by using thermocouples for heat release rate instead of oxygen depletion as done in the cone calorimeter. The MLC method does not analyze dripping or smoke. The treated as well as the untreated specimens were stored in a climate chamber at 20 °C and 65 % relative humidity prior to testing. The samples were then covered with aluminum foil from 5 sides, leaving one face open. A heat flux of 50 kW/m² was used, and each test was carried out for 1800 s after the specimen ignited. The time to ignition (TTI), the total heat release (THR), and the maximum heat release rate (pHRR) were recorded for five specimens for each treatment, as well as for the untreated control.

3. Results & discussion

3.1. Weight percentage gain and moisture content

The WPG and the MC of the specimens at 20 °C and 65 % relative humidity are presented in Table 2. The impregnation with single salts leads to different WPGs in respect to the various salts and salt solution concentrations. Single salt treatment with the PO_{low} and PO_{high} displays higher WPGs compared to treatments with CC_{low} and CC_{high}, as well as CA_{high}/CA_{low}. An increase with the second impregnation step was achieved for PO_{high} and CA_{high}. In contrast, a second impregnation with CaCl₂ did not lead to a pronounced increase of the WPG of CC_{high}. It is probable that due to the strong hygroscopic character of CaCl₂, salts were leached out during storage and drying of the specimens and thus, no clear differences between one and two-step impregnation were detected.

The impregnation with the second salt (CaCl₂; respectively Ca(CH₃COO)₂) led to an increased WPG of all 2-step mineralized specimens. This speaks for a sufficient uptake of the second salt to achieve reaction of the precursors in CaC₂O₄ mineralized beech. However, the WPGs achieved for the formulations PO/CC_{low} (30.0 %) and PO/CC_{high} (43.5 %) are higher compared to PO/CA_{low} (21.9 %) and PO/CA_{high} (39.4 %). Before leaching, a WPG of 54.5 % was achieved by a double impregnation of the formulation PO/CC_{high}. Subsequent leaching led to a final WPG of CO treated beech of 29 %. These values are probably obtained due to a high amount of reacted and fixed CaC₂O₄. Comparable results after carrying out a leaching protocol were achieved for a comparable treatment by Franke and Volkmer [23].

It is well known that treatments of wood with salts cause increased moisture adsorption [25–29]. For the treatment with the single salts K₂C₂O₄ and Ca(CH₃COO)₂ only small or negligible increase of the MC at both WPGs were observed. In contrast, the treatment with CaCl₂ lead to a MC around 50 % which is beyond the fibre saturation point of wood, which is around 30 % MC for most of European wood species [30]. After the 2-step mineralization, an increased MC for all treatments were observed. Treatment PO/CC_{high} and PO/CC_{low} have lower MC compared to the treatments CC_{high} and CC_{low} where only CaCl₂ is impregnated. This indicates a reaction to CaC₂O₄ and the corresponding by-product (KCl). Furthermore, PO/CC_{low} with lower WPG showed a higher MC

Table 2

WPG and MC of the treated beech wood and the untreated control specimens prior to the MLC test. Standard deviation in parentheses.

Treatment		WPG %	MC at 20 °C/65 rh %	
Control		*	9.8	
Single salt	CC _{low}	29.2 (0.6)	47.0 (2.7)	
	CC _{high}	32.4 (2.6)	52.8 (5.6)	
	PO _{low}	25.4 (0.8)	10.6 (0.3)	
	PO _{high}	42.5 (0.8)	12.1 (0.8)	
	CA _{low}	18.4 (1.6)	9.1 (0.5)	
	CA _{high}	28.0 (4.3)	9.3 (1.6)	
2-step mineralization	PO/ CC _{low}	30.0 (2.8)	20.0 (4.8)	
	PO/ CC _{high}	43.5 (4.7)	13.2 (2.2)	
	PO/ CA _{low}	21.9 (2.1)	11.3 (0.6)	
	PO/ CA _{high}	39.4 (5.3)	15.6 (1.8)	
	2-step mineralization and subsequent leaching	CO	29.2 (0.1)	9.0 (0.8)

compared to PO/CC_{high}. This might be explained by insufficient reaction and leftovers of CaCl₂ in the wood. Treatments containing Ca(CH₃COO)₂ lead to higher MC than the single salt impregnations with K₂C₂O₄, respectively Ca(CH₃COO). Thereby, higher WPGs lead to higher MC. This phenomenon might be attributed mainly to the reaction by-product CH₃CO₂K. This becomes more probable when looking at the CO specimens which undergo a leaching protocol. Here, the MC was at a similar level to untreated beech wood. The MC also indicates that the highly hygroscopic precursors and by-products, namely CaCl₂ and KCl, were leached out and mainly CaC₂O₄ was left. To support this assumption SEM-EDX measurements were carried out before and after mineralized specimens underwent the leaching protocol. The results are displayed in Fig. 1. Before leaching, the elements Ca, Cl and K were detected. This indicates the presence of the precursors calcium chloride and potassium oxalate, simultaneously. Moist of the precipitated crystals were found in the cell lumen of the vessels. However, indications for the presences of the precursors simultaneously was also found in the lumen of the fibres and also some indication was found for a penetration into the cell wall (Fig. 1 left; spot 4). The distribution was not to found homogeneous over the specimens but frequently. After leaching the EDX signals that are attributed to the precursors calcium chloride (Cl) and potassium oxalate (K) disappeared. The presence of calcium indicates a precipitation of the slightly water-soluble mineral calcium oxalate. In comparison to the state of the mineralized wood before leaching, less cell lumina seemed to be filled with crystals. The crystals were found also in the lumen of the vessels, as well as in the lumen of the fibers. However, no traces of the minerals were found in the cell lumen (Fig. 1 right, spot 5). This indicates insufficient crystallization in the cell lumen. Additionally, Franke et al. [31] demonstrated a comparable behavior of mineralized beech.

3.2. Thermogravimetric analysis

The thermal behavior of the pure salts, as well as of the treated and untreated beech was determined by means of TGA and DTG. The thermal properties for the single salts, after mixing them according to Formulation 1 and Formulation 2 and after removing the reaction by-products (KCl, respectively CH₃CO₂K) to obtain pure CaC₂O₄, is presented in Fig. 2. The TGA of CC displayed a pronounced weight loss in an early stage (below 200 °C) with a DTG peak at 156 °C. This is attributed to the release of water. Subsequently, CC do not show further degradation which is indicated by no mass loss up to 800 °C. This demonstrates the strong thermal stability of the inorganic salt CaCl₂. TGA of PO also showed mass loss in the early stage until appr. 150 °C with a DTG peak at 117 °C. This first stage is attributed to the release of water and water of crystallization due to the increasing of the temperature [32]. A further stage of mass loss between 570 °C and 640 °C with a DTG peak at 615 °C indicates degradation of K₂C₂O₄ to K₂CO₃ + CO [32]. In the same way as for CC and PO, the first stage of mass loss of CA is attributed to the evaporation of water and water of crystallization [33]. The next stage from appr. 430 °C until 510 °C is attributed to the degradation of Ca(CH₃COO)₂ to CaCO₃ and CO₂ and finally, between appr 650 °C and 800 °C the CaCO₃ degrades under release of CO₂ to the thermal stable CaO [33]. The mass loss of CA is of appr. 70 % during the test period, much higher than for CC (19 %) and PO (25 %).

PO/CC consists of precipitated Ca₂C₂O₄ and KCl, and PO/CA of precipitated Ca₂C₂O₄ and CH₃CO₂K. Both formulations showed an initial mass loss below 100 °C which can be attributed to the release of adsorbed water. In contrast, the first stage of mass loss for CO, which only consists of Ca₂C₂O₄ starts at above 100 °C with a DTG peak at 195 °C and is attributed to the release of water of crystallization [34]. PO/CC also displayed a mass loss in this temperature range with a peak at 180 °C. PO/CA did not show a relevant mass loss in this region. The next stage of mass loss is above 400 °C and was detected for PO/CC, PO/CA as well as for CO. Most probably, this is attributed to the degradation processes of Ca₂C₂O₄ and CH₃CO₂K (for PO/CA) [33,34]. Additionally, DTG of PO/CA showed two peaks in the temperature range

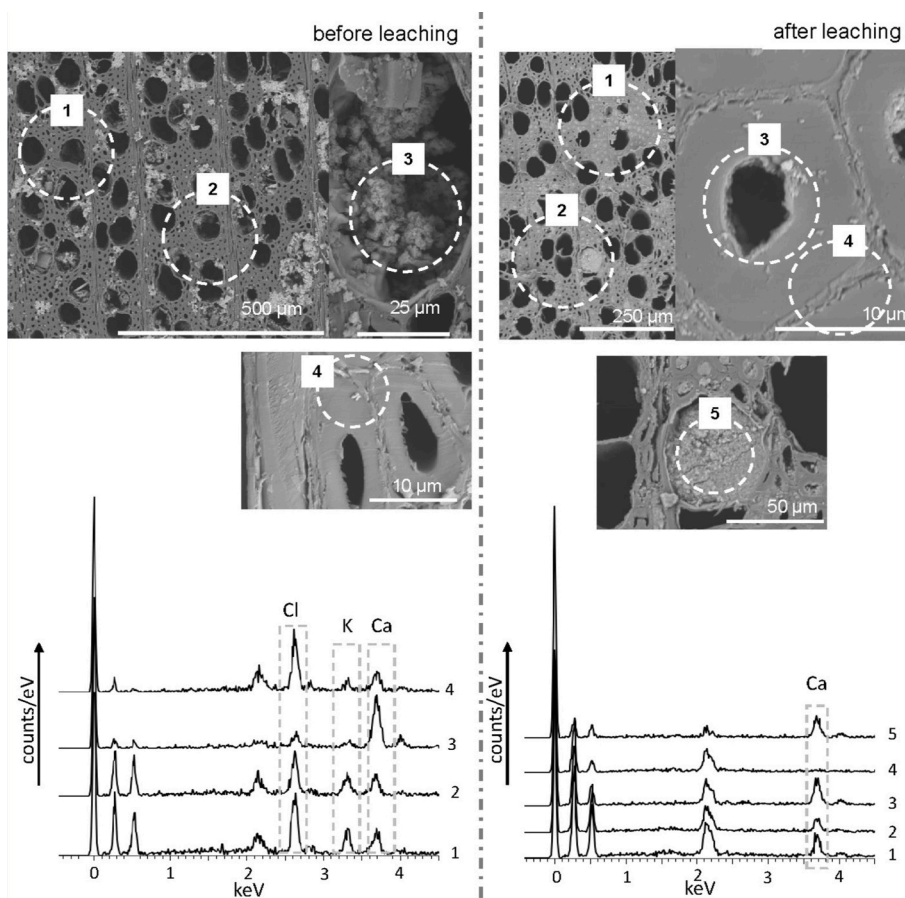


Fig. 1. SEM-EDX measurements of PO/CC treated beech before leaching and after leaching to remove water-soluble by-product and unreacted precursors to obtain a material that only contains calcium oxalate.

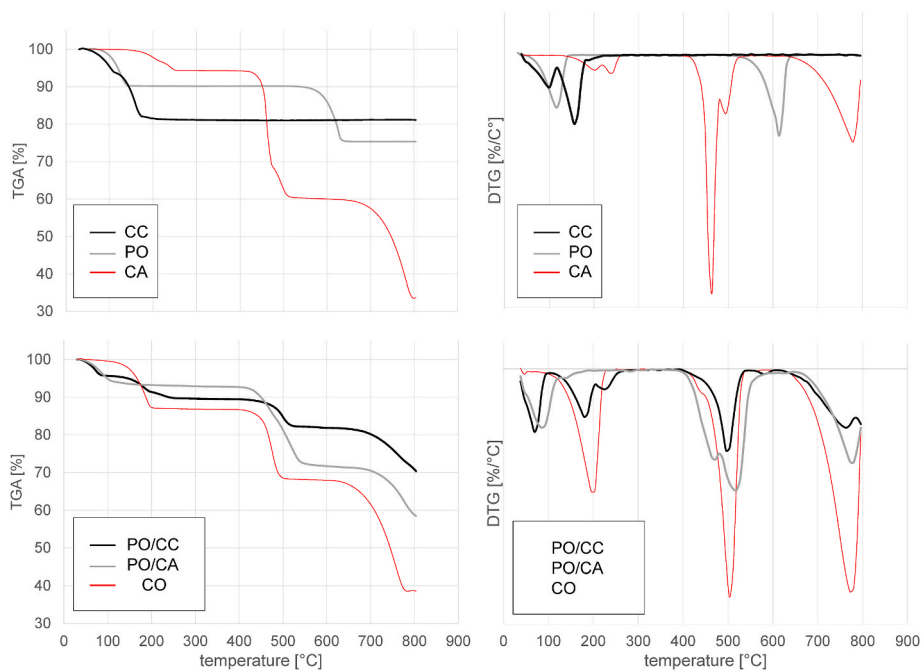


Fig. 2. TGA and DTG plots of the pure single salts (above) and after precipitation reaction of both applied formulations, as well as after filtering the by-products (below).

of 470 °C and 520 °C. The last stage of decomposition is found up from 650 °C. Thereby, PO/CC and PO/CA indicated a retarded on-set and DTG peaks at higher temperatures compared to CO. Thus, an impact of the reaction by products on the decomposition is assumed.

TGA and DTG plots of the treated beech, as well as untreated beech are displayed in Fig. 3. The mass loss of untreated wood in the first stage (below 100 °C) is characterized by the evaporation of water [35]. The second stage begins at appr. 300 °C and is attributed to thermal decomposition of hemicelluloses, celluloses, and lignin. The DTG plots show 2 prominent peaks at appr. 340 °C and at 400 °C in this range. The first peak (here appearing as a shoulder) is mainly attributed to the release of volatile gases from hemicelluloses, where the second peak is mainly attributed to the decomposition of celluloses [35–38]. Lignin degrades over a wider temperature range and is therefore overlapped by degradation peaks from cellulose and hemicellulose [39].

In the temperature range below 200 °C, all the treated beech specimens showed a mass loss which can be attributed to the release of water, respectively water of crystallization. A pronounced peak in DTG curves which can be attributed to the release of water of crystallization was detected for the 2-step mineralization treatments, namely PO/CC at 140 °C, for PO/CA at 170 °C and for CO at 165 °C. Compared to the pure salts, and in combination with wood, this peak seems to appear at lower temperatures. Furthermore, for PO/CC this peak is at significant lower temperatures compared to PO/CA and CO. Maybe, the presence of wood as well as the presence of chlorine, might affect the binding of water of crystallization during the in-situ crystallization. Since water cools down and withdraws energy from the flame, the presence of water of crystallization might contribute to an improved flame retardancy and might have a positive influence on fire protective properties.

In the second stage, all treatments: single salt impregnation, 2-step mineralization treatment, and 2-step mineralization with subsequent leaching, caused shifts on the on-set of the decomposition temperature to lower temperatures compared to the untreated beech. Thereby, the chlorine containing treatments CC and PO/CC display the most pronounced shifts. A comparable behavior of the chlorine-free treatments was demonstrated. Additionally, peaks of the DTG curves indicate the altered thermal behavior of beech caused by the treatments. Two peaks

were determined for chlorine containing treatments CC (230 °C and 280 °C) and PO/CC (275 °C and 350 °C), where the chlorine-free treatments display one peak in this temperature ranges (PO at 314 °C, CA at 369 °C, PO/CA at 330 °C and CO at 345 °C). It is assumed that halogens containing salts may catalyze the dehydration of holocellulose and thus, lead to decomposition at lower temperatures [40,41]. At the same time, it is known, that also the ions of alkali metals potassium and calcium have catalytic effects [42,43]. Liu et al. [44] demonstrated the impact of various potassium-based salts such as KCl and K_2CO_3 as catalyst on the dehydration and char forming of cellulose. Other inorganic salts and minerals show a comparable behavior in combination with wood [20,45–47]. Furthermore, the temperature where the peak appeared might also be affected by the WPG. Bakirtzis et al. [48] demonstrate that a higher amount of the inorganic salt sodium bicarbonate leads to lower peak temperatures in DTG curves of treated celluloses.

The weight loss and DTG peaks occurring at temperatures above 450 °C are mainly attributed to degradation processes of the impregnated salts and appear in accordance to the measurements carried out with the pure salts. Additionally, DTG Peaks at 500 °C for treatments PO/CC, PO/CA as well as CO indicated a reaction to $Ca_2C_2O_4$.

3.3. Reaction to fire determined in the mass loss calorimeter

The reaction to fire of the treated beech was determined with a MLC. It should be noted that the Cone Calorimeter method is normally applied in order to determine the PHHR and THR of a material. The Cone Calorimeter is a bench-scale test which measures the oxygen consumption of a burning material at a defined energy. According to Babrauskas [49] the PHHR and the THR of a material are directly related to oxygen consumption [50]. In contrast most of the Cone Calorimeter measurement methods, measures the mass loss of a sample under defined energy input. Likewise with the oxygen consumption measured in cone calorimeter, the pPHR and THR of a material can be indirectly measured by the mass loss of a material or with a thermopile in MLC measurements. It is reported that the accuracy of a MLC is poorer compared to a Cone Calorimeter [51,52]. It is also reported that high

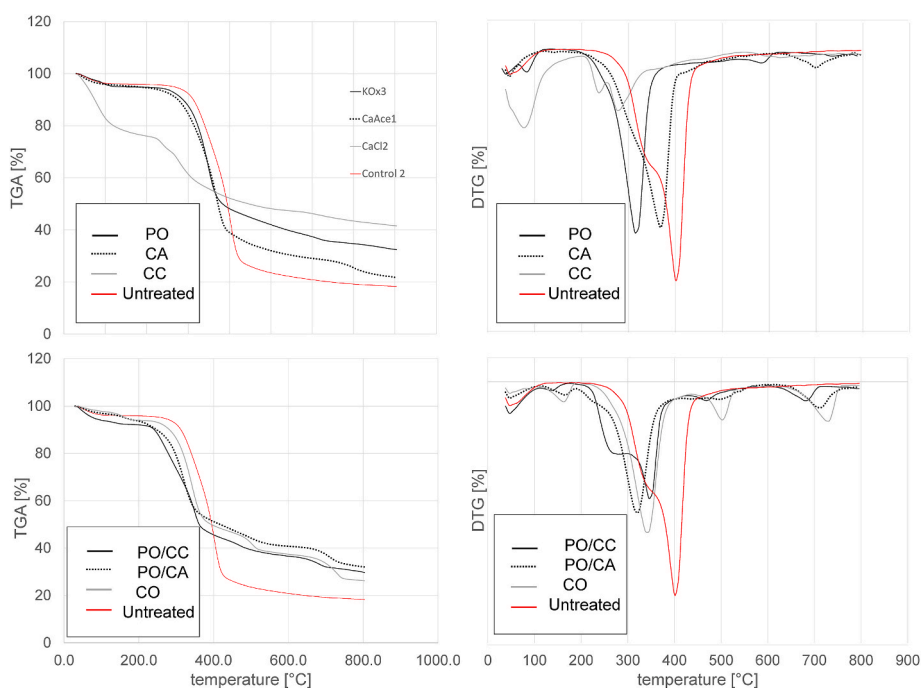


Fig. 3. TGA and DTG plots of beech treated with the single salts (above) and after 2-step mineralization process (below), as well as after leaching to obtain pure CaC_2O_4 and an untreated beech.

moisture in a material has an impact on the pHRR, as well as the THR obtained from MLC measurements. Moisture can be interpreted as heat release, misleadingly. This might lead to inaccuracies of the obtained results and might become an issue for specimens with high moisture. However, as explained in the Material and Method section, the authors used thermopiles that were installed in the chimney to overcome this problem, as it was also demonstrated by Diitenberger et al. (2013) [52].

The most relevant measures to evaluate the performance of the treated beech are listed in Table 3. The Time to Ignition (TTI) is a strong indicator for evaluating the fire-retardant properties of a material during a bench scale test like MLC testing. The TTI is used as a parameter in some models to predict the outcome for large scale tests such as the single burning item test [53,54], although, the TTI is known to have a high variation [55]. High variation in TTI was observed for all tested treatments, as well as for the untreated control. A pronounced impact of a single salt treatment on the TTI was nevertheless determined for CC_{low} and CC_{high}. Partially, some of the specimens treated with CC_{low} or CC_{high} did not ignite during the 1800 s test period. The impact of the other single salt treatments on the TTI showed only a slight improvement compared to untreated beech. Specimens which underwent the 2-step mineralization process show a comparable behavior to the single salt treatments. A clear difference between PO/CA_{high} and PO/CA_{low} was measured, where no difference between PO/CC_{high} and PO/CC_{low} was detected. Thus, the role of the WPG from this test might play only a minor role on the TTI. Other wood related factors such as thermal conductivity or heat capacity, which are related to the wood density, might be more decisive factors for ignition of the specimens [56,57]. Furthermore, the initial moisture content might affect the TTI more than the treatment itself. Long and Chew [58] demonstrated an increase of the TTI from absolute dry beech (TTI = 23 s) to beech with 11 % MC (TTI = 45 s). However, Simms and Law [59] demonstrated that even small variations in moisture have an impact on the ignition of wood. Thus, the milieu of condition before testing of 20 °C and 65 % RH for the described experiments might have an impact on the TTI compared to specimens, that are stored in 23 °C and 50 % RH as demanded in the standard. Simkovic et al. [60] measured a TTI of 31 s for beech conditioned at 23 °C and 55 % RH in a cone calorimeter with the same parameters used in the given experiment with the MLC. This underlines, that the deviation from the milieu demanded in the standard might be small. At the same time, it demonstrated that results for TTI obtained from the MLC equipped with thermopiles are comparable to those obtained in a Cone Calorimeter. After leaching, CO treated specimens have a clearly shorter TTI and simultaneously a lower MC compared to the other 2-step mineralization treatments. The role of the reaction by-products (KCl, respectively CH₃CO₂K) on the TTI still remained unclear.

Table 3

Results from MLC testing of beech wood treated with the single salts and after 2-step mineralization process, as well as after leaching to obtain pure CaC₂O₄.

treatment		TTI [s]	THR [MJ/m ²]	pHRR [kW/m ²]	Time to pHRR [s]	Mass loss [%]	
Control	Specimens ignited/specimens tested	35 (14)	173.9 (9.0)	328.9 (28.6)	626 (44)	93.5 (1.2)	
Single salt	CC _{low}	4/5	1537 ^a (330)	55.3 (19.1)	82.7 (23.5)	1740 (231)	61.6 (8.6)
	CC _{high}	2/5	1740 ^a (230)	40.6 (8.9)	54.6 (23.4)	1537 (331)	23.8 (19.4)
	PO _{low}	5/5	46 (3)	123.1 (6.9)	239.5 (27.0)	765 (25)	68.9 (1.2)
	PO _{high}	5/5	65 (11)	116.6 (10.9)	197.7 (24.9)	903 (17)	60.6 (0.7)
	CA _{low}	5/5	59 (9)	174.1 (17.3)	318.0 (9.1)	785 (29)	80.4 (0.8)
2-step mineralization	CA _{high}	5/5	50 (2)	165.3 (17.3)	271.9 (28.9)	826 (25)	76.4 (1.7)
	PO/CC _{low}	5/5	68 (18)	105.0 (9.7)	109.2 (11.37)	1122 (139)	64.2 (0.8)
	PO/	5/5	72 (7)	117.8 (10.4)	126.4 (22.5)	1083 (106)	60.2 (2.1)
	CC _{high}						
	PO/CA _{low}	5/5	37 (9)	122.0 (19.9)	244.9 (36.7)	789 (57)	74.3 (1.6)
2-step mineralization and leaching	PO/	5/5	79 (23)	121.1 (11.0)	181.6 (36.7)	1075 (102)	64.8 (3.3)
	CA _{high}						
	CO	5/5	44 (4)	118.2 (6.5)	141.0 (19.8)	912 (36)	71.2 (1.5)

^a Not all specimens ignited, TTI is based solely on the specimens which ignited.

The Total Heat Release (THR) can serve as an indicator for the fire load of a material [57]. The THR during the test period (1800s) of untreated beech was 173.9 MJ/m². It was shown that the THR was strongly reduced by the single-salt treatments CC_{high} (40.6 MJ/m²) and CC_{low} (55.3 MJ/m²), as well as clearly reduced for PO_{high} (116.6 MJ/m²) and PO_{low} (123.1 MJ/m²). In contrast, CA_{high} (165.3 MJ/m²) and CA_{low} (174.1 MJ/m²) treatments did not lead to a notable reduction of the THR compared to untreated beech. All specimens which underwent the 2-step mineralization process had their THR reduced in comparison to the untreated beech specimens. Moreover, the THR of all treatments, even after leaching, are in a comparable range. PO/CC_{high} (117.8 MJ/m²) and PO/CC_{low} (105.0 MJ/m²) treatments did not affect the THR in a greater range than PO/CA_{high} (121.1 MJ/m²) PO/CA_{low} (122.0 MJ/m²), or CO (118.2 MJ/m²). Differences between the treatments are within the variability of the measurement. Furthermore, no differences on the THR between high and low WPGs within one treatment were detected.

The peak heat release rate (pHRR) serves as a simplified indicator for the efficiency of a fire retardant [57,61]. In addition to the pHRR, the propagation of the HRR during the test period of one characteristic plot for each treatment and the untreated control are displayed in Figs. 4 and 5. Typically, wood provides two peaks during a test in the MLC. The first peak appears shortly after ignition and the second peak is indicative for the time that the rear face reaches a temperature of appr. 300 °C [56, 57]. The pHRR for almost all treatments and the untreated control is

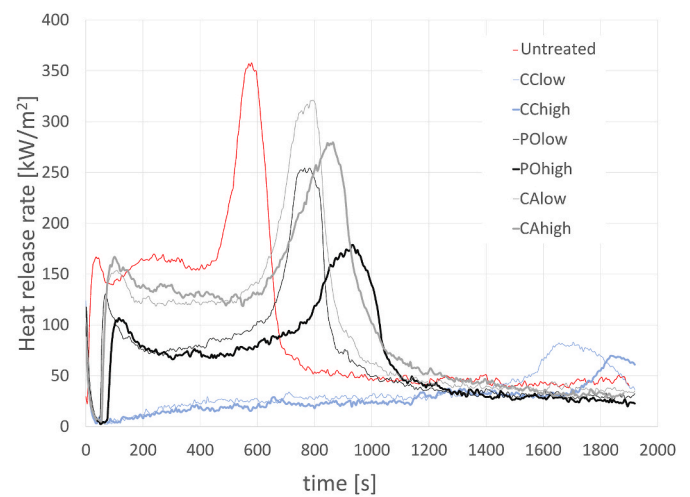


Fig. 4. Plot of the release rate (HRR) of single salt treated beech at two different WPGs and of an untreated control.

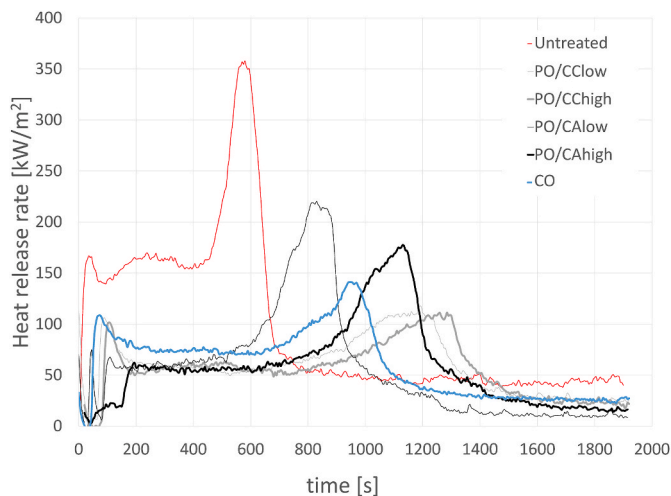


Fig. 5. Plot of the heat release rate (HRR) of the two-step mineralized treated beech at two different WPGs after leaching to obtain CaO_2C_4 mineralized beech, as well as of an untreated control.

attributed to the second peak. The pHRR for untreated beech was measured with an average of 328.9 kW/m^2 and appears after 626 s of testing. This is in line with findings from various Cone Calorimeter tests of untreated beech. Grexa et al. (1997) [62] measured a pHRR of untreated beech at 50 kW/m^2 after appr. 630s with a peak maximum of appr 360 kW/m^2 [62]. Merk et al. (2016) obtained a pHRR in a cone calorimeter of $402 (61 \pm) \text{ kW/m}^2$ for untreated beech [19], but their specimens were only 10 mm thick. This indicates that the results obtained from the MLC equipped with thermocouples are in a comparable range to those achieved from Cone Calorimeter.

The chlorine containing treatments have the strongest impact on reducing the pHRR. With pHRRs of 54.6 kW/m^2 (CC_{high}) and 82.7 kW/m^2 (CC_{low}), single salt treatment with CaCl_2 lead to the highest reduction. Additionally, the pHRR of CC_{high} and CC_{low} is attributed to the first peak and appeared after 1740 s and 1537 s, respectively. 2-step mineralization formulations $\text{PO/CC}_{\text{high}}$ (126.4 kW/m^2) and $\text{PO/CC}_{\text{low}}$ (109 kW/m^2) which also contain chlorine strongly reduced the pHRR of the wood. Together with the chlorine-free single salt treatments, the 2step mineralization treatments also caused a pronounced reduction of pHRR and delayed the achievement of the pHRR. Higher WPGs indicate a reduction of the pHRR and delayed the time until the pHRR is reached to a greater extent than the low WPGs within the same treatment. The single salt treatments CA_{high} (271.9 kW/m^2) and CA_{low} (318.0 kW/m^2) provide the poorest reduction of pHRR of all treatments. Leaching of the by-product to obtain pure CaC_2O_4 caused a lower pHRR in the CO treatment (141.9 kW/m^2) compared to the 2-step mineralization treatments $\text{PO/CA}_{\text{high}}$ (181.6 kW/m^2) and $\text{PO/CA}_{\text{low}}$ (244.9 kW/m^2). It must be noted that the CO treatment had lower WPG (29.2 %) compared to the CA_{high} , but reduced pHRR to a greater extend. The single salt treatment PO_{low} , on the other hand, with a WPG of 25.4 %, comparable to the WPG at CO, presented a less pronounced reduction in the pHRR than CO. PO_{high} , with a WPG of 42.5 %, also showed poorer reduction in pHRR compared to CO. It is discussable if CO might have contained residuals of chlorine which were not leached out to cause these remarkably good results. However, according to the measured MC, it is evident that only small traces of chlorine might have remained in the wood. In this case, the impact of these residuals on the pHRR might be neglectable.

The mass loss at the end of the testing period was reduced by the various treatments. Hautamäki et al. (2020) [63] suggest a correction of the mass loss by subtracting the impregnation agent from the dry wood mass. As demonstrated in TGA measurements, most of the applied salts are not thermal stable at temperatures below $800 \text{ }^\circ\text{C}$. CA displayed more

pronounced mass loss compared to PO or CC in TGA experiments. Subtracting the wood dry mass from the residual non degraded salts and minerals might be challenging. Additionally, the increased MC compared to the untreated beech must be considered in interpretation of the mass loss at the end of the test period. However, visual assessment of the specimens after the treatments showed the effectiveness of all applied salts. Some examples are displayed in Fig. 6. The treated specimens indicated greater amounts of leftovers compare to the untreated beech. Differences between the various mineral and salt treatments or between the various WPG within one treatment cannot be assessed by visual evaluation. However, by take a look into the mass loss rate of the various treatments a trend is observable (Figs. 7 and 8). Besides CC_{high} and CC_{low} all treatments had the same characteristic curve compared to the untreated control, but slowed down the mass loss. As for the other measured characteristic values, treatments containing chlorine displayed the greatest impact on the mass loss rate. Nevertheless, after leaching out the chlorine, CO treated wood still displayed a significant slower mass loss compared to untreated wood. This might be indicative for a reduced flamesread due to the treatments. The treatments with the higher WPGs also indicate to slow down the mass loss to a greater extend.

The results obtained in the MLC demonstrated the effect of various salts and mineral treatments on the reaction to fire of beech wood. In sum, all treatments lead to an improvement of the reaction to fire compared to untreated beech. In general, the differences in WPG within the same treatment reduced the pHRR and delayed the time until pHRR was reached but did not significantly affected the THR. Treatments containing the CaCl_2 showed the highest efficiency. The mode of action and the efficiency of halogens as fire retardants is known and already described [15,64–66]. A further factor that might contribute the fire-retardant properties obtained with CaCl_2 treatments is the high moisture content which occur, in particular, in the single salt chlorine containing treatments. CC_{high} and CC_{low} were related to MC above the fibre saturation point. Water in the wood matrix supports the fire retardancy and might increase the TTI [59,67,68]. However, MC above the fibre saturation point is not suitable in any commercial application since it also causes a reduction in the mechanical and physical properties of the wood [69–71] and can support fungi growth [72]. Other drawbacks of the application of CaCl_2 as a fire retardant are its corrosiveness and high leachability. The impact of chlorine on the reaction to fire is also indicated for the 2-step mineralization treatments. Thereby, the PO/CC treatments provided greater improvement of the fire-retardant properties of wood compared to the other 2-step mineralization treatments PO/CA and CO. The $\text{Ca}(\text{CH}_3\text{COO})_2$ containing treatments CA_{high} and CA_{low} , as well as 2-step mineralized $\text{PO/CA}_{\text{high}}$ and $\text{PO/CA}_{\text{low}}$, performed the weakest against fire. It is claimed by Lowden and Hull [6] that acetate serves as fire retardant by causing alteration of thermal properties However, $\text{Ca}(\text{CH}_3\text{COO})_2$ could not reduce THR, nor reduce the HRR at satisfying levels compared to the other treatments tested. Furthermore, 2-Step mineralized beech PO/CA displayed even poorer performance compared to pure $\text{Ca}_2\text{O}_2\text{H}_4$ presented by the CO treatment. This indicates that combinations between oxalate and acetate might not provide synergetic effects in the way chlorine does. In contrast, it will weaken the performance of the oxalate treatment, as indicated by the performance of CO. This becomes clear when comparing treatments with WPG in a similar range: CC_{low} , PO_{low} , CA_{high} , $\text{PO/CC}_{\text{low}}$, $\text{PO/CA}_{\text{low}}$, and CO were found to have similar WPG in a range between 25 % and 30 %. As demonstrated in SEM EDX measurements CO treatments show to have no chlorine leftovers. Thus, all the effects influencing the reaction to fire can be attributed to calcium oxalate. The fact that the minerals could not be satisfactorily fixed in the cell wall can possibly have a further influence on the reaction to fire performance. This is supported by studies from Saka et al. [73].

The order of their efficiency against fire in the MLC test can be listed as $\text{CC}_{\text{low}} > \text{PO/CC}_{\text{low}} > \text{CO} > \text{PO}_{\text{low}} > \text{PO/CA}_{\text{low}} > \text{CA}_{\text{high}}$. It is questionable why PO_{low} differs from CO so much. According to Nik-Azar

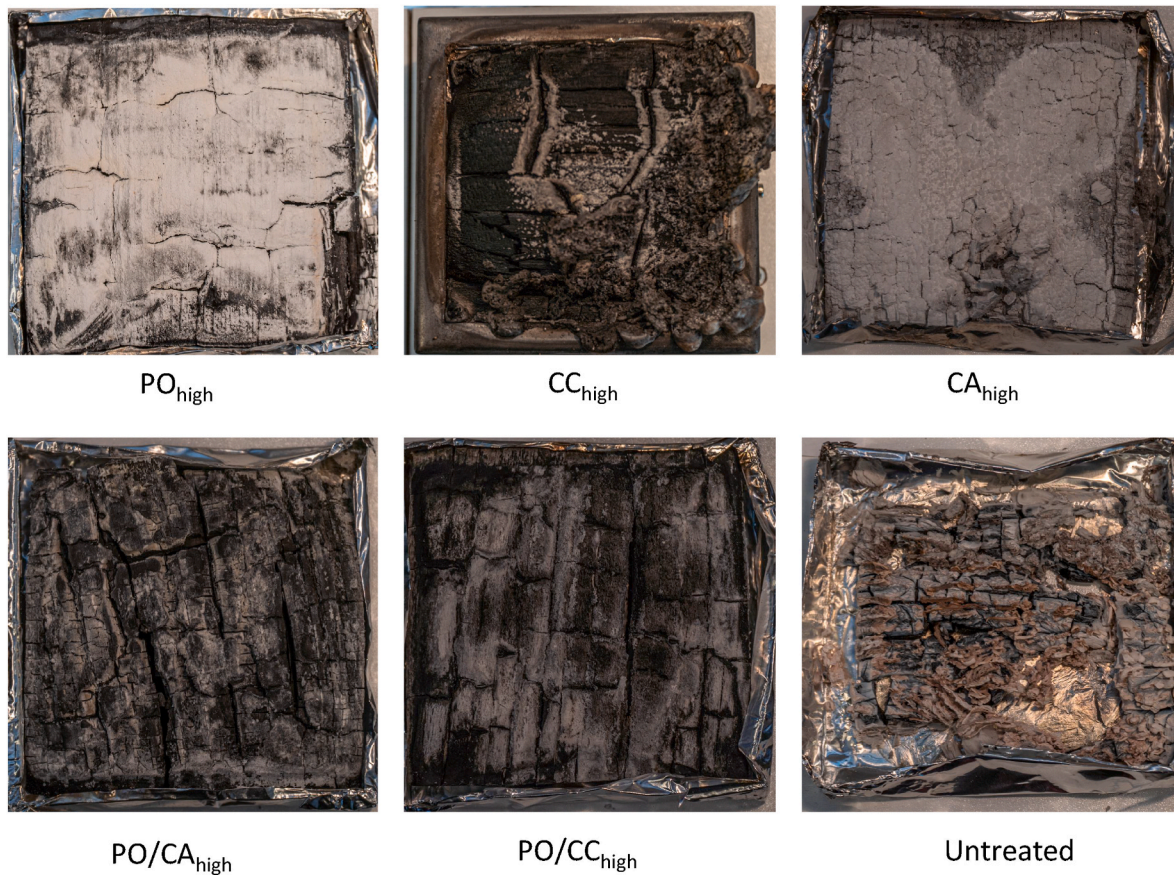


Fig. 6. Char residuals after 1800 s of MLC testing for some selected specimens.

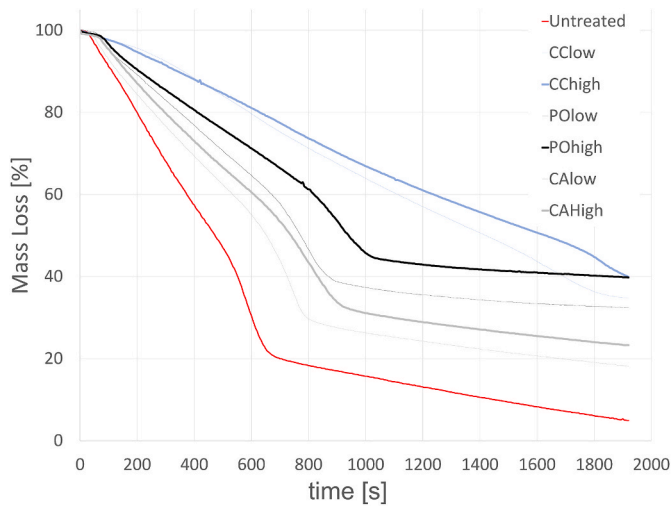


Fig. 7. Plot of the mass loss of single salt treated beech at two different WPGs and of an untreated control.

et al. (1997) potassium is a stronger cracking catalyst than calcium. On the other hand, in accordance to the TGA measurements, higher amounts of water of crystallization can also play a decisive role. Additionally, it cannot be completely excluded that residuals of chlorine remain in the specimens and thus, the performance in MLC is stronger for CO, than for PO_{low} .

No results on smoke production are currently available for the discussed treatments. However, the treatments might have the potential to reduce the smoke production. It is known from comparable treatments

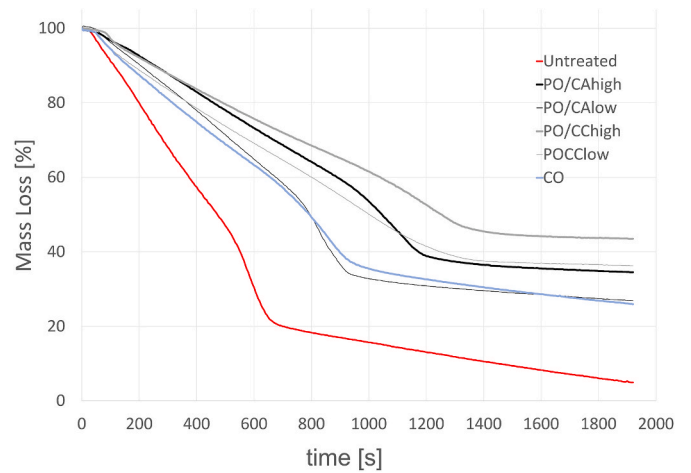


Fig. 8. Plot of the mass loss of the two-step mineralized treated beech at two different WPGs after leaching to obtain CaO_2C_4 mineralized beech, as well as of an untreated control.

such as mineralization with calcium carbonate and struvite, that these treatments reduced the smoke production of the treated wood [19,22]. Kashiwagi [74] discussed the impact of non-polymeric fillers such as calcium carbonate or silicon oxide on the smoke compression. This author [74] claimed that these inert fillers reduce the smoke generated by diluting or reducing the amount of combustible substrate and also by absorbing the heat to reduce the burning rate. It is likely that the single salts, as well as the calcium oxalate based 2-step mineralization treatments can reduce smoke production. However, this must be clarified in

further experiments.

A classification into a burning class according to EN 13501 [75] is challenging. Most woods and wood products are categorized in class D (EN 13986 [76]). The requirements for a "B" classification must be tested according to the ISO 11925-2 (single flame source test [77]) and EN 13823 (single burning item test [78]) for burning class C and higher. Investigations with the aim of predicting the burning class of wood in a bench scale test (cone calorimeter) was carried out by Kristofferson et al. [55]. The test parameters such as specimen thickness and irradiation were chosen in our study in exactly the same way as in the study by Kristofferson et al. [55]. Two main criteria for a possible B classification were defined. First a pHRR below 80 kW/m² and second, a TTI of around 200 s. However, they carried out their tests with spruce and pine. The pHRR for untreated beech is naturally twice as high than the pHRR for spruce or pine [79]. Thus, this criterion is hard to match for beech wood. However, the pHRR was clearly reduced for all treatments. In particular CO showed clearly reduced pHRR compared to untreated control. This shows the ability of a strong contribution to the fire retardant properties of beech treated with calcium oxalate. The TTI was affected clearly by the various treatments, but with the exception of CC treatments it never exceeded 200s and thus it does not match to the criteria for a B classification in a Bench scale test.

It could be demonstrated that the organic salts based on oxalate are a promising solution as fire retardant. Especially Ca₂O₂H₄ which is highly fixed in the wood, showed encouraging results in the MLC test. Compared to other likely inorganic mineralization treatments such as calcite or struvite treatments [19,20,22], the organic treatments, even with exclusion of chlorine, showed to be a promising alternative to be used as fire retardant for wood.

4. Conclusions

The objective of this study was to evaluate a 2-step mineralization process to improve the fire retardancy of beech wood. The focus was set on various formulations to precipitate calcium oxalate in wood. The single salts which are intended as precursors for the CaC₂O₄ precipitation were also investigated.

It could be demonstrated that a treatment with single salts CaCl₂, C₂O₄K and Ca(CH₃COO)₂, as well as the 2-step mineralization to obtain CaC₂O₄ in wood affects the thermal degradation of beech. All treatments shifted the pyrolysis pathway to lower temperatures compared to untreated beech. This indicates an improved fire performance by catalyzation e.g. char forming. 2-step mineralization treatments containing chlorine seem to have a greater impact on the improvement of wood thermal behavior than chlorine-free treatments. Small differences were found between single salt and 2-step mineralization treatments. An improved reaction to fire of treated beech was also confirmed in MLC test where, the impact of the reaction by-products on the response to fire was more pronounced. A strong impact was observed in all chlorine-containing treatments, in which acetate seem to have a negative impact on the reaction to fire measured by MLC but this must be seen in conjunction with the negative side effects of halogens. The retention of the salts within one treatment (single salts, as well as two-step mineralization) indicates an impact on the pHRR and on the time until the pHRR was reached. Higher retentions tend to reduce pHRR and delay the time until pHRR is reached. Over the test period, THR was not affected by different retentions within one treatment. The study showed that after leaching the water-soluble by-products and unreacted salts, the highly fixed calcium oxalate provides still improved reaction to fire compared to untreated wood. However, the performance is lower compared to specimens which contain the by-product calcium chloride.

A treatment of wood with CaC₂O₄ demonstrated that it has potential to act as a fire retardant. Products made of wood that are exposed to high humidity or weathering are feasible to be potential applications for this mineralization treatment. Maybe the biggest impact was shown of calcium oxalate on the pHRR. It is questionable if this might be enough for

obtain a material with a proper burning class for outdoor application. However, its property to reduce the pHRR and being resistant against leaching might make it to a good additive for other fire retardants for use in outdoor applications or in wet conditions.

Furthermore, tests for the performance of the formulations after exposing them to a weathering protocol must be carried out in order to evaluate a real suitability for the application as a fire retardant for outdoor applications such as facades.

CRediT authorship contribution statement

Tom Franke: Writing – original draft. **Erik Larnøy:** Investigation, Methodology, Supervision, Validation, Writing – review & editing. **Thomas Volkmer:** Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Tom Franke reports financial support was provided by Innosuisse Swiss Innovation Agency.

Data availability

Data will be made available on request.

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