Wood Treated with Nano Metal Fluorides – Relations between Composition, Size, and Durability

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von

M.Sc. Shirin Mustaquim Usmani

Präsidentin der Humboldt-Universität zu Berlin
Prof. Dr.-Ing. Dr. Sabine Kunst

Dekan der Mathematisch-Naturwissenschaftlichen Fakultät
Prof. Dr. Elmar Kulke

Gutachter/innen:

1. Prof. Dr. Erhard Kemnitz
2. Dr. Ina Stephan
3. PD Dr. Rüdiger Plarre

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....Die Fragen selbst liebzuhaben....

....Vielleicht lebst du dann allmählich

eines fernen Tages in die Antwort hinein

-Rainer Maria Rilke-

Abstract

In this study, nanoscopic particles of magnesium fluoride (MgF_2) and calcium fluoride (CaF_2) also known as nano metal fluorides (NMFs), were evaluated for their potential to improve wood durability. Even though these fluorides are sparingly soluble, their synthesis in the form of nano-sized particles turns them into promising candidates for wood preservation. Their distinct property of low-water solubility is proposed to maintain long-lasting protection of treated wood by reducing the leaching of fluoride.

Analytical methods were used to characterize the synthesized NMFs and their distribution in treated wood specimens. Transmission electron microscopy images showed that these fluoride particles are smaller than 10 nm. In nano metal fluoride (NMF) treated specimens, aggregates of these particles are uniformly distributed in the wood matrix as confirmed with scanning electron microscopy images and their corresponding energy-dispersive X-ray spectroscopy maps. The fluoride aggregates form a protective layer around the tracheid walls and block the bordered pits, thus reducing the possible flow path for water absorption into wood. This is reflected in the reduced swelling and increased hydrophobicity of wood treated with NMFs.

The biocidal efficacy of NMFs was tested against brown-rot fungi (*Coniophora puteana* and *Rhodonia placenta*), white-rot fungus (*Trametes versicolor*), and termites (*Coptotermes formosanus*). The fungal and termite tests were performed in accordance with the EN 113 (1996) and EN 117 (2012) standards, respectively. Prior to fungal tests, the NMF treated wood specimens were leached according to the EN 84 (1997) standard. Compared to untreated specimens, the NMF treated wood specimens have a higher resistance to decay caused by brown-rot fungi, white-rot fungus, and termites. Although all NMF treatments in wood reduce the mass loss caused by fungal decay, only the combined treatment of MgF_2 and CaF_2 has efficacy against both brown-rot fungi and white-rot fungus. Similarly, wood treated with the combined NMF formulation is the least susceptible to attack by *C. formosanus*. It is proposed that combining MgF_2 and CaF_2 changes their overall solubility to promote the release of fluoride ions at the optimal concentration needed for biocidal efficacy against fungi and termites.

In this thesis, it was proven that even after leaching, sufficient fluoride was present to protect NMF treated wood from fungal decay. This shows that NMFs are robust enough for above ground contact outdoor applications of wood, where permanent wetness cannot be avoided according to Use Class 3.2, as per the EN 335 (2013) standard. Also, they pose a low risk to human health and the environment because they are sparingly soluble. Since NMFs significantly reduce the decay of wood, the CO_2 fixed in it will be retained for longer than in unpreserved wood. Overall, the novel results of this study show the potential of NMFs to increase the service life of building materials made from non-durable wood.

Keywords: Nano metal fluorides, solubility, wood protection, fungi, termites

Kursfassung

In dieser Arbeit werden die nanoskaligen Partikel von Magnesiumfluorid (MgF_2) und Calciumfluorid (CaF_2), die als Nano-Metallfluoride (NMFs) bekannt sind, auf ihr Potenzial zur Verbesserung der Beständigkeit von Holz-basierten Materialien untersucht. Obwohl diese NMFs nur schwer löslich sind, werden sie durch ihre Synthese in Form von Nanopartikeln zu vielversprechenden Kandidaten für den Holzschutz. Ihre besondere Eigenschaft der geringen Wasserlöslichkeit ist Grundlage dafür, einen langanhaltenden Schutz des behandelten Holzes aufrechtzuerhalten, indem die Auslaugung von Fluorid reduziert wird.

Die Partikelgröße der synthetisierten NMFs und ihre Verteilung in behandelten Holzproben wurde charakterisiert. Transmissionselektronenmikroskopische Aufnahmen zeigen, dass die Fluoridpartikel kleiner als 10 nm sind. Rasterelektronenemikroskopaufnahmen und der zugehörigen energiedispersiven Röntgenspektroskopie zeigen, dass Aggregate dieser Partikel eine homogene verteilung in der untersuchten Holzmatrix von behandelten Proben. Die Fluoridaggregate bilden eine Schutzschicht um die Zellwände und blockieren deren Hoftüpfel, dadurch ist der mögliche Fließweg für die Wasseraufnahme ins Holz eingeschränkt. Dies zeigt sich in einem verminderten Quellen und erhöhter Hydrophobie des mit Nano-Metallfluorid (NMF)-behandelten Holzproben.

Die biozide Wirkung der NMFs wurde entsprechend der Normen EN 113 und EN 117 gegen Braunfäulepilzen (*Coniophora puteana* und *Rhodonia placenta*), am Weißfäulepilz (*Trametes versicolor*) und den Termiten (*Coptotermes formosanus*) geprüft. Vor den Pilztests wurden die mit dem NMF behandelten Holzproben nach EN 84 ausgelaugt. Im Vergleich zu unbehandelten Proben weist das mit Fluorid behandelte Holz eine höhere Beständigkeit gegen Fäulnis durch Braunfäulepilz und Weißfäulepilz, sowie gegen Termitenfraß auf. Obwohl alle NMF-Behandlungen den durch Fäulnis verursachten Masseverlust des Holzes reduzieren, zeigt nur eine kombinierte Behandlung mit MgF_2 and CaF_2 eine höhere Wirksamkeit sowohl gegen Weißfäulepilz als auch Braunfäulepilz. Außerdem wird Holz, das mit der NMF Kombination behandelt wurde, am wenigsten von *C. formosanus* angegriffen. Offenbar verändert sich die Gesamtlöslichkeit in der Kombination von MgF_2 und CaF_2 so, dass Fluorid in einer für eine biozide Wirkung gegenüber Pilzkulturen und Termiten erforderlichen optimalen Konzentration freigesetzt wird.

Die Ergebnisse dieser Arbeit zeigen, dass auch nach einer Auswaschung ausreichend Fluorid im Holz verbleibt, um es vor Zersetzung zu schützen. Dies bedeutet, dass NMFs robust genug sind für Anwendungen im Freien mit Bodenkontakt der Nutzungsklasse 3.2 nach EN 335. Darüber hinaus stellen sie aufgrund ihrer sehr schlechten Wasserlöslichkeit ein geringeres Risiko für die menschliche Gesundheit und Umwelt dar. Da NMFs die Zersetzung von Holz deutlich unterdrücken, bleibt das darin gebundene CO_2 länger fixiert als in unbehandeltem Holz. Die neuartigen Ergebnisse dieser Arbeit zeigen das Potenzial von NMFs, die Lebensdauer von Baumaterialien aus nicht haltbarem Holz zu erhöhen.

Stichwörter: Nano-Metallfluoride, Löslichkeit, Holzschutz, Pilze, Termiten

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List of abbreviations

ASE	Anti-swelling efficiency
DIN	Deutsches Institut für Normung
EG	Ethylene glycol
EMC	Equilibrium moisture content
EN ***, ENV ***	European standard, followed by number
ET	Ethanol
Lac	Lactic acid
NMF	Nano metal fluoride
NMFs	Nano metal fluorides
WPG	Weight percent gain

Chemicals

Ag	Silver
aq	Aqueous
B_2O_3	Boric oxide
C	Carbon
Ca	Calcium
CaF_2	Calcium fluoride
CC	Chromated copper
Ce	Cerium
CeO_2	Cerium oxide
CFK	Chromium fluoride copper
Copper HDO	Bis-(N-cyclohexyldiazeniumdioxy)-copper
Cu	Copper
CuO	Cupric oxide
DOT	Disodium octaborate tetrahydrate
F	Fluoride
H	Hydrogen
He	Helium
HF	Hydrogen fluoride
M^+	Metal cation
M(OR)	Metal alkoxide
Mg	Magnesium
MgF_2	Magnesium fluoride
M-OH	Metal hydroxide
n	Metal valence
NaF	Sodium fluoride
Ne	Neon

OH	Hydroxide
SiO_2	Silicon dioxide/Silica
TiO_2	Titanium dioxide
Zn	Zinc
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide
ZrO2	Zirconium dioxide

Techniques

BSE	Back-scattered electron
CA	Contact angle
CP	Cross polarization
DLS	Dynamic light scattering
EDX	Energy dispersive X-ray spectroscopy
HAADF	High-angle annular dark field
STEM	Scanning transmission electron microscopy
HR	High resolution
MAS	Magic angle spinning
NMR	Nuclear magnetic resonance
TEM	Transmission electron microscopy
X-ray micro-CT	X-ray micro-computed tomography
XRD	X-ray diffraction

Symbols

GJ	One billion joules
cm	Centimeters
δ	Chemical shift (ppm)
ºC	Degrees centigrade
eV	Electron volt
€	Euros
ν	Frequency
g	Grams
hPa	Hectopascal
Hz	Hertz
h	Hours
KHz	Kilohertz
kPa	kilopascal
kV	Kilovolt
L	Liter

MHz	Megahertz
mW	Megawatt
µl	Microliter
µm	Micrometer
µs	Microseconds
mg	Milligram
ml	Milliliter
mm	Millimetre
mV	Millivolt
M	Molar (mol/L)
nm	Nanometer
ppm	Parts per million
Pa	Pascal
RH	Relative humidity
θ	Scattering angle
s	Seconds
PDF	Powder diffraction file
λ	Wavelength

1. Introduction

In this introductory chapter, the importance of wood preservation in construction is outlined along with the aims and objectives of the current study. This is followed with an overview of the composition and the structure of wood, the organisms, and the insects that can decay and damage it. Lastly, common active ingredients used in wood preservatives are mentioned along with improvements in their formulations as nanoparticles.

1.1 Importance of wood preservation in construction

Wood is a renewable raw material harvested from forests to produce timber for the building sector. As a construction material, timber has broad appeal due to its wide-ranging attributes from its low-cost to its low-energy consumption. The cost of constructing a roof made with timber is significantly lower than steel.[1] Embodied energy is the amount of non-renewable energy consumed in the construction of a building, which includes the acquisition of raw materials, their processing, and transportation. Timber requires less energy for transportation and construction because of its lower weight.[2] Consequently, timber has lower embodied energy than concrete or steel, which makes it a preferred material for construction.[3] A wooden house has an embodied energy of 232 billion Joules (GJ), much lower than a house made of concrete (396 GJ) or of steel (553 GJ).[4] In addition to having a higher embodied energy than timber, the production of steel requires the mining of raw materials such as iron ore, which damages the landscape for many years.[2] Similarly, the production of concrete requires the extraction of sand from river beds and sea floors, creating an imbalance in the local aquatic ecosystem.[2] In contrast, terrestrial damage is minimized with a harvested forest that can be regenerated to produce more trees.[5] Therefore, wood is an economical and sustainable alternative to high-cost and energy-intensive construction materials.

In the context of climate change mitigation, timber has the lowest carbon footprint compared to cement and steel.[2] A wood-framed building has lower net CO_2 emissions compared to a concrete-framed building.[6] Unlike cement and steel, wood as a construction material can function as a carbon sink.[2] Specifically for the European Union, increasing the use of engineered wood products was estimated to store 46 million tons $CO_{2\text{-eqv}}$ per year by 2030.[7] Globally, replacing cement and steel with timber in new building projects for urban dwellers is estimated to store up to 20 gigatons of carbon.[2] Overall, climate mitigation strategies should include the promotion of durable wood products, as they play an important function in carbon storage over their long service life.

To maintain their long service life, wood products need to be protected from damage caused by organisms, insects, weathering, and fire. Warm temperatures and high humidity are optimal conditions for the growth of organisms and insects on wood products. Invasive insects such as the Formosan subterranean termite, *Coptotermes formosanus* cause extensive economic damage to wooden structures in tropical regions.[8] Future models predict that climate change will cause the Formosan species to move towards temperate climates that will make timber houses in these regions vulnerable to termite damage as well.[9] In temperate zones, coniferous trees are the primary source of timber, commonly damaged by fungi. Moisture accumulation in timber houses is prone to attack from fungi belonging to the Basidiomycota phylum. In Europe, *Coniophora puteana* and *Serpula lacrymans* are the commonly observed fungi in damaged timber buildings.[10] Chemical treatment and restoration of a house decayed by wood rot is estimated to cost around 10,000 €.[11] An increase in temperature and humidity due to global warming will also create more favorable conditions for fungal colonization and termite infestation of timber houses with the consequent economic losses.[12]

The damage to wooden structures can be prevented by protecting them from decay. One method of protection is impregnation with wood preservatives. Treating wood products with preservatives has played a significant role in reducing their decay. Since 1909, the use of preservatives in timber has saved over 4000 million trees from being felled in the United States.[5] Another advantage is that naturally non-durable species can be treated with preservatives and used to manufacture wood products where previously only durable species were applicable.[5] Thus, wood preservation is an important method to extend the service life of a renewable construction material and consequently for the conservation of forests.

A wood preservative needs to meet the criteria listed below for commercial use.[13,14]

1) Biocidal activity: Wood preservative needs to be biocidal to wood-destroying organisms such as fungi and insects such as termites.
2) Permanence: Besides toxicity, the wood preservative needs to be stable within the wooden material and should have a low leaching tendency. For example, borates are biocidal, albeit highly water soluble. Therefore, fixatives are needed to inhibit their leaching from wood.

3) Treatability: A preservative needs to be evenly distributed in the wood matrix. Various methods can be applied to improve their treatability, such as pressure treatment to force the preservative into wood.
4) Non-corrosive and non-harmful to wood: The preservative should not cause corrosion to metal fastenings. Also, the impregnation of wood with the preservative should not reduce its mechanical strength and increase its inflammability.
5) Safety: An ideal preservative will be safe for handling during timber treatment and for the consumer of the end product.
6) Cost: The preservative should be cost-effective and readily available in sufficient quantity for application.
7) Environmental impact: The active ingredient in the preservative should not be hazardous to aquatic and mammalian life or other non-target organisms.

1.2 Aims of the study

In the history of wood protection, the biocidal efficacy of fluoride compounds is well documented.[15] Current fluoride compounds used in wood preservatives cannot be applied alone because they are highly water soluble. Thus, they are combined with a fixative such as chromium to minimize their leaching from wood.[15] However, the use of chromium is restricted in several European countries because of its detrimental impact on the environment.[16] Consequently, there has been a steady decline in the use of fluoride for wood preservation. Therefore, there is a need for finding an alternative method to overcome their solubility limitation such that fluoride compounds can be used without the need for additional fixatives. One such alternative would be to use sparingly soluble fluoride compounds such as magnesium fluoride (MgF_2) and calcium fluoride (CaF_2). The challenge is how to impregnate low-water soluble compounds into wood. This is where the size of these compounds can be the key to solving this challenge.

Formulations of active ingredients as nano-sized particles are widely available as commercial wood preservatives.[16] For instance,h micronized copper particles are supposed to be homogeneously distributed in wood and available for protection from fungi.[17] Besides copper, nano formulations of boron, another commonly used active ingredient in wood protection has also been tested for biological resistance.[18,19] Yet, current review of literature on nano-based wood treatments does not report on formulations of any fluoride compounds that have been evaluated as preservatives.[20,21]

The following dissertation addresses this gap by evaluating nanoscopic form of metal fluoride particles known as “nano metal fluorides” to protect wood from fungi and termites. In this study, nano-sized particles of magnesium fluoride (MgF_2) and calcium fluoride (CaF_2) are referred to as nano metal fluorides (NMFs). There are three attributes of NMFs that could make wood more durable. First, compared to current fluorides used as wood preservatives, MgF_2 and CaF_2 are sparingly soluble in water due to which their susceptibility to leaching will be lower, and therefore they will remain in a sufficient concentration in wood to prevent decay. Also, due to their low-water solubility, they pose less risk to vertebrates. Second, these metal fluorides impregnated in the form of nano-sized particles can penetrate deeper into the wood matrix and minimize the likelihood of fungal colonization. Third, once impregnated into wood, these sparingly soluble fluorides do not liberate hydrogen fluoride (HF), which was observed in fluoride treated wood in the past.[12]

These low-water soluble fluorides can remain as a “reservoir” inside treated wood from which “free” fluoride ions will be released in small doses when the moisture content in wood reaches a level to promote their solubility. For instance, the high humidity in the surrounding environment that increases the moisture content of wood will also trigger the release of “free” fluoride ions from their low-water soluble form deposited in the matrix. The high humidity is also an important physiological requirement for fungal colonization of wood. Thus, the release of “free” fluoride ions coincides with the initiation of fungal attack of wood, which is an ideal scenario for its protection. Thereby, the moisture content of wood plays the role of the sensor, which “signals” the NMFs to release the fluoride ions that can counteract the attack from fungi and termites. The hypothesis is that the nanoscopic size of metal fluorides will enable their impregnation and even distribution inside wood, and their low-water solubility will create a reservoir from which release of “free” fluoride ions is regulated to protect the end product during its storage and subsequent service life. Thus, the low-water solubility, the nano-size of these metal fluorides, and their reduced toxicity to vertebrates are the properties that make them promising candidates for research as wood preservatives.

The aim of this thesis is to determine the durability of wood treated with nano metal fluoride (NMF). The following objectives are set.

1. Characterization of NMFs and their distribution inside wood after treatment.
2. Material properties of wood treated with NMFs.
3. Biocidal efficacy of NMF treated wood against fungi and termites.
4. Possible protection mechanism of NMF treated wood.

1.3 Wood: composition and structure

Wood is an economically important raw material. In the European Union, Germany had the highest production value (greater than 47 billion €) from wood-working industries in 2017.[22] Wood is a material of choice for construction because of its desirable properties such as high strength to weight ratio, functionality, good thermal insulation, and aesthetics.[23] These properties of wood are due to its unique composition as a biopolymer consisting of cellulose, hemicelluloses, lignin, and a minor number of extractives. Cellulose provides tensile strength, while hemicelluloses and lignin support the cellulose framework to give wood its elasticity.[5] A brief description of these constituents of wood are provided below.

1.3.1 Cellulose, hemicellulose, and lignin

Cellulose is the most abundant organic polymer on Earth and constitutes the largest proportion of wood.[24] The building block of cellulose is cellobiose, which is a polysaccharide consisting of glucose units linked together by β-glucosidic bonds (Fig.1.1). The intramolecular linkages between OH-groups of the glucose units give stiffness to the cellulose chain. The degree of polymerization (DP) in a cellulose molecule was calculated to be in the range of 9000 to 15,000.[24] Wood-derived cellulose has at least 65% crystalline regions.[24]

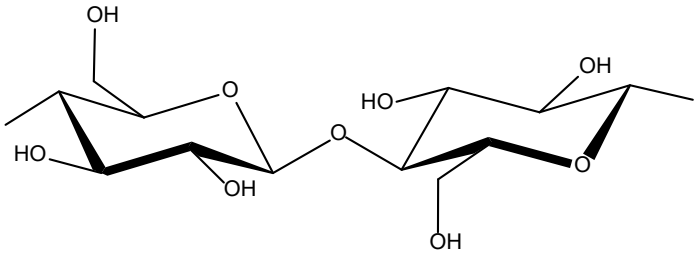
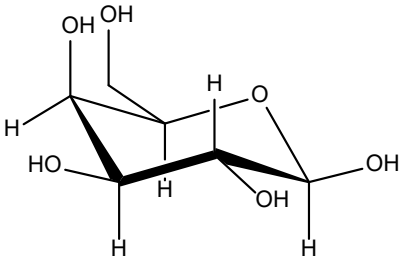
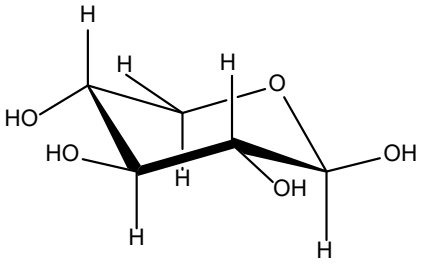


Fig.1.1 Chemical structure of cellobiose.

Similar to cellulose, hemicelluloses are also formed of polysaccharide polymers. They differ from cellulose as they have a lower DP (500 - 3000) and are composed of more than one kind of sugar.[25] Some sugars found in hemicellulose are D-galactopyranose and D-xylopyranose (Fig.1.2).[24] Hemicelluloses are connected to cellulose and provide structural support to the tree.



D-galactopyranose



D-xylopyranose

Fig.1.2 Sugar monomer components of wood hemicellulose.

Unlike cellulose and hemicelluloses, lignin is composed of heterogeneous, alkyl-aromatic polymers.[26] They form a complex arrangement of phenolic units around the main building blocks; guaiacyl, syringyl, and *p*-hydroxyphenyl.[24] Lignin binds with hemicelluloses but not with cellulose. In addition to providing strength and rigidity to the tree, lignin acts as a shield to protect the main structural components of cellulose and hemicelluloses.[27] However, lignin can be degraded by ultraviolet rays, which results in discoloration of wood. [28]

The main components in wood are arranged in an interconnected network (Fig.1.3). In the wood cell, the cellulose polymers are arranged into fine threads (microfibrils) through van der Waals forces and intermolecular hydrogen bonds. The hemicelluloses attach to the microfibril surface and enable the microfibrils to slip past each other.[29] These microfibrils are held together by intermolecular hydrogen bonds to form large threads (macrofibrils).[25] The lignin molecules interpenetrate the fibrils to strengthen the cell walls.[27]

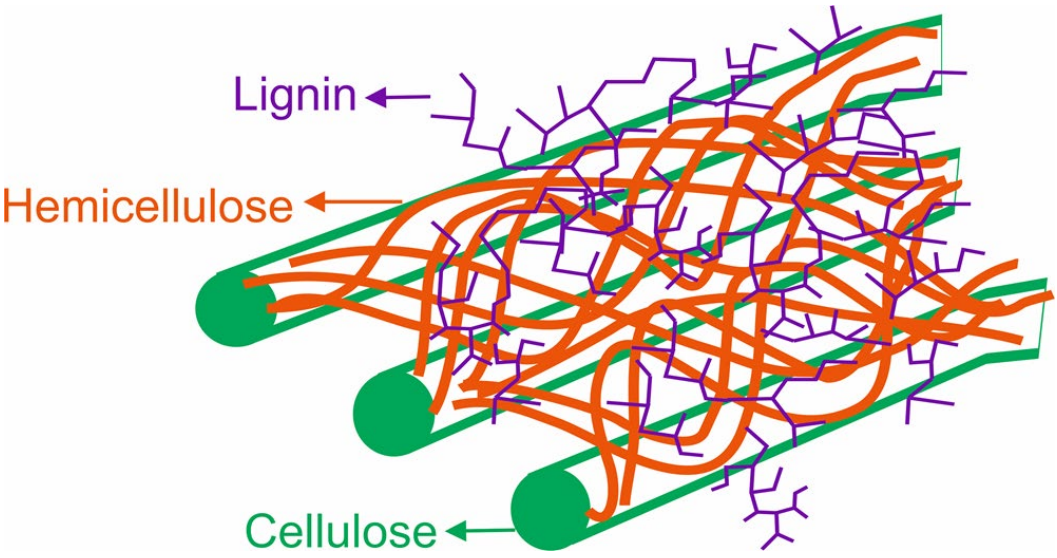


Fig.1.3 Schematic representation of the interaction of wood polymers in the secondary cell wall. Image created by S.M. Usmani.

A wood cell is made up of a primary wall, a thick secondary wall that is subdivided into three layers (S1, S2, and S3), and the lumen (Fig.1.4). The middle lamella is composed of a lignin-pectin complex and glues the cells together.[29] The wood cell progression begins in the primary cell wall formed of loosely packed microfibrils.[30] The S1 and S3 layers are relatively thinner compared to the S2 layer. The transition of a cell from earlywood to latewood is determined by the S2 layer, which consists of closely packed microfibrils oriented 10-20° relative to the fiber axis.[31] An increase in the microfibril angle is related to the reduction in mechanical strength of wood which can be an indicator of wood decay.[32]

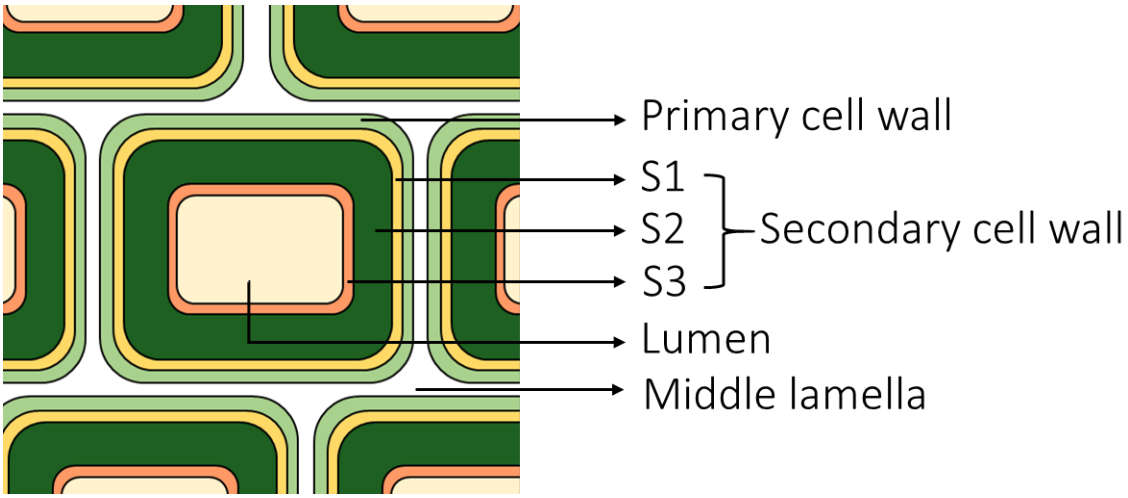


Fig.1.4 Schematic representation of wood cell wall components. Image created by S. M. Usmani.

1.3.2 Heartwood and sapwood

In wood, cells are arranged such that the older region is in the center, known as heartwood. In a cross-cut section of a tree trunk shown in Fig.1.5, the inner, darker region of heartwood is surrounded by the lighter sapwood area that performs the function of conduction and storage (Fig.1.5). The sapwood is formed of living cells which are converted into heartwood as they die.[29] Most extractives such as resins and pine pitch are found in the heartwood.[24] Depending on the wood species, the percentage of extractives varies and can play a role in color, smell, and natural durability of wood.[24] For instance, the intense color of mahogany is due to the type and quantity of extractives in its heartwood, while water resistance in teak heartwood is due to deposits of waxes and oils.[33] Even though extractives are formed in the sapwood as byproducts of cellular metabolism, no species of wood

contains durable sapwood.[31,33] Preservative treatment can impart durability to sapwood, making it a useful product for building long-lasting wooden structures.

Fig.1.5 Cross-cut section through a tree outlining the heartwood and sapwood regions. Image taken by S. M. Usmani.

1.3.3 Wood species

Some species widely used in testing of wood preservatives are Scots pine (*Pinus sylvestris*), which is an evergreen species (softwood) and beech (*Fagus sylvatica*), a deciduous species (hardwood). A brief description of the two types follows.

Evergreens are found in the temperate regions where distinct seasonal changes result in the formation of annual (growth) rings. In evergreens, two cell systems are interconnected.[31] The longitudinal cells run from root to crown, providing support and conduction to the tree. These are known as tracheids. There are two types of tracheids that cater to seasonal change as shown in Fig.1.6. During the beginning of the season, conduction is the primary function of the tracheids. Therefore, cell diameters are large and walls are thin in earlywood tracheids.[30] As the season progresses, support takes precedence over conduction, causing the cells to become narrow and thick-walled, now known as latewood tracheids.[30] They also contain bordered pits that allow liquid to flow between neighboring cells, as shown in Fig.1.6. The other cell system is aligned radially from bark to pith. In this system, conduction takes place through ray tracheids. Nutrition is stored in brick-shaped parenchyma cells which are similar to ray tracheids, that also contain pits to transport liquid between neighboring cells.[30]

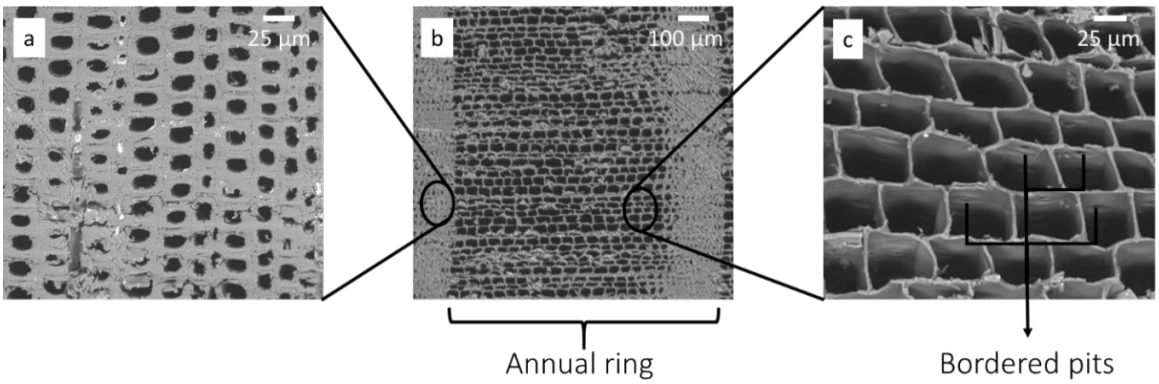


Fig.1.6 Cross-cut section of Scots pine in back-scattered electron image showing tracheids (a) latewood tracheids (b) annual ring (c) earlywood tracheids with bordered pits. Image created by S. M. Usmani.

In addition to the tracheids and parenchyma cells, there are resin canals found in the longitudinal and radial directions. Resin is secreted into these canals by specialized parenchyma cells known as epithelial cells.[5] Resin acts as a natural barrier against wood-degrading organisms. To replicate the natural resistance of wood, extractive formulations such as tannins continue to be evaluated for use as preservatives, but their efficacy remains low compared to current commercial preservatives used in wood products.[34]

Unlike evergreens, fibres are the principal cells in deciduous species that provide mechanical strength.[31] Fibres are similar to tracheids, but shorter.[5] Conduction in deciduous trees takes place in long pipe like cells known as vessels. They come in varying sizes depending on species and may contain a single large opening or several smaller ones.[5] Longitudinal parenchyma cells contain storage tissues. Similar to resin canals in evergreens, some deciduous species have gum canals.

The cellular arrangement of the wood species determines its permeability. Scots pine sapwood has a lower permeability than beech.[35] This is because fluid transport in evergreen trees is regulated by bordered pits that are not found in deciduous trees. Tension stress such as drying can result in aspiration of the bordered pits which can block liquid flow.[30] Therefore, drying of wood before preservative treatment can lead to aspiration of bordered pits in earlywood tracheids of Scots pine sapwood. Consequently, less than the expected amount of preservative enters the matrix reducing the protection of treated wood from decay. Thus, the permeability of wood is an important characteristic that can determine the future durability of a treated wood product.

1.4 Wood-degrading fungi and termites

Fungal decay is generally classified into three ecological types depending on structural damage to wood; white-rot, brown-rot, and soft-rot. Both white-rot and brown-rot fungi can break-down cellulose, but only the former can degrade lignin. Soft-rot can degrade cellulose, hemicellulose, and lignin to a small extent. A brief description of their decay mechanism follows.

1.4.1 White-rot fungi

White-rot fungi have a complex enzyme set-up that enables them to degrade cellulose along with lignin. The cellulase enzyme complex is made up of three main groups; endo-1,4-ß-glucanases, two types of exo-1,4-ß-glucanases, and glucohydrolases.[36] Cellulose and hemicellulose are broken down by cellulases. Lignin is degraded by oxidative enzymes such as peroxidases and laccases, and the resultant heterogeneous aromatics are metabolized by the fungi.[35] Instead of sequential degradation of lignin, cellulose, and hemicellulose, some white-rot fungi can decay both carbohydrates and lignin at the same time, this is known as simultaneous white-rot.[37] Simultaneous white-rot is observed in *Trametes versicolor*, a white-rot fungi.[37] After a white-rot attack, wood is reduced to a fibrous mass and has a bleached appearance (Fig.1.7).[38] These fungi predominantly attack hardwoods, and as such are not commonly observed in timber buildings in the northern hemisphere, which are mostly made using conifers.[37]

Fig.1.7 Beech wood decayed by *T. versicolor*. Image taken by S. M. Usmani.

1.4.2 Brown-rot fungi

Some common brown-rot fungi are *Coniophora puteana, Gloeophyllum trabeum*, and *Rhodonia placenta*.[39] They preferentially attack softwoods and are commonly observed in wooden structures built with conifers in temperate regions. Brown-rot fungi degrade

mostly carbohydrates and cause limited damage to lignin. They induce the production of hydroxyl radicals to depolymerize lignin and expose cellulose for degradation.[26] During wood decay, brown-rot fungi form oxalic acid to lower the pH of their microenvironment and initiate non-enzymatic and enzymatic breakdown of cellulose.[39] A non-enzymatic oxidative mechanism using iron-dependent Fenton chemistry is used by brown-rot fungi to depolymerize carbohydrates.[26,40] Brown-rot remove hemicellulose sugars such as xylose and mannose before cellulose sugars. Strength loss due to brown-rot attack is associated with the hydrolysis of hemicellulose. The rapid depolymerization of cellulose causes wood to shrink, as shown in Fig.1.8.[38] Although both wooden specimens presented in Fig.1.8 have shrunk, their appearance is remarkably different, with *C. puteana* leaving dark stains and *R. placenta* causing deep cracks.

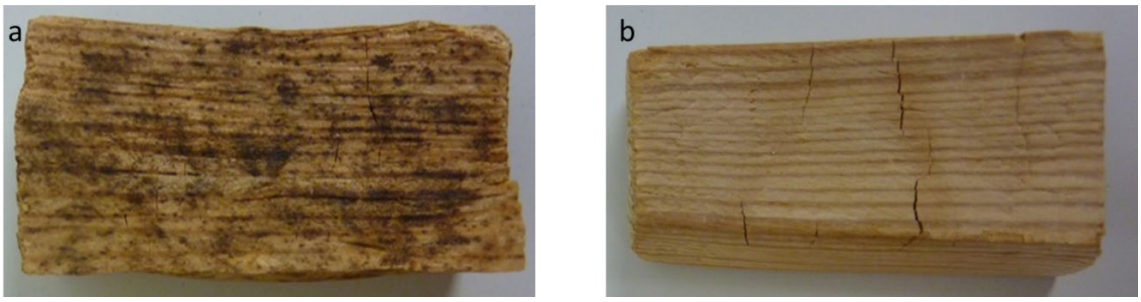


Fig.1.8 Wood specimens damaged by (a) *C. puteana* and (b) *R. placenta*. Image taken by S. M. Usmani.

1.4.3 Soft-rot fungi

Soft-rot decay is caused by ascomycetes and deuteromycetes.[40] It is similar to white-rot in that all cell wall constituents may be degraded, but they degrade relatively less lignin.[40] This might be because many ascomycetes have a complete cellulase system like white-rot fungi. Additionally, soft-rot decay is characterized by longitudinal cavities in wood, as this allows them to attack less lignified portions of the cell wall. However, soft-rot differ from white-rot and brown-rot as besides wood they can decay plant debris as well. Also, they can attack water saturated wood such as submerged wooden poles, which cannot be attacked by white-rot and brown-rot fungi.[37] Soft-rot fungi may cause stain, discoloration, and appearance of cracks in wood.[5,37]

1.4.4 Termites

Termites are known as Isoptera, which refers to the two pairs of straight wings that are characteristic of reproductive adults.[41] Traditional ecological classification of termites is based on how they digest lignocellulose. Higher termites (Termitidae) have only intestinal bacteria. Lower termites called as "subterranean" have both symbiotic protozoa and bacteria to digest cellulose.[41] They live in colonies comprising of large number of termites. The soldiers in the colony are distinguished with their dark brown head and protruded mandibles, while workers have a white head and body (Fig.1.9). Subterranean termites such as *Coptotermes* and *Reticulitermes* can cause damage to goods and services. The genus *Reticulitermes* is found mostly in Europe and the *Coptotermes* species is found in tropical and sub-tropical regions.[42,43] Among the genus *Coptotermes*, the species *Coptotermes formosanus* is native to China and the most economically important invasive insect.[44] Globally, the estimated cost of damages to goods and services due to attack by *C. formosanus* was reported to be greater than 30.2 billion US $ per year.[44] The United States of America alone spends over 1 billion US $ yearly on termite control and repair to damaged wooden structures and homes.[45] Thus, preservatives that can inhibit termite attack are crucial for extending the service life of wooden structures and prevent economic losses to the built environment.

Fig.1.9 *C. formosanus,* worker (left) and soldier (right). Image taken by S. M. Usmani.

Although subterranean termites produce cellulases to metabolize lignocellulose, the resultant amount is insufficient to meet their nutritional needs. Therefore, termites have evolved a symbiotic relationship with diverse micro-organisms found in the hindgut of worker termites such as protist, *Pseudotrichonympha grassii,* as shown in Fig.1.10.[46] These micro-organisms facilitate in the digestion of lignocellulose. Initially, the amorphous region of the cellulose is partially degraded by the endoglucanase produced in termites, after which the product travels to the hindgut, where the gut protists depolymerize the crystalline region of cellulose.[47] The end product of lignocellulose degradation is mainly acetate, which is utilized by the termites as a carbon and energy source.[47] An understanding of how the protists population react to active ingredients in wood preservatives can be used to increase their biocidal efficacy against termites.

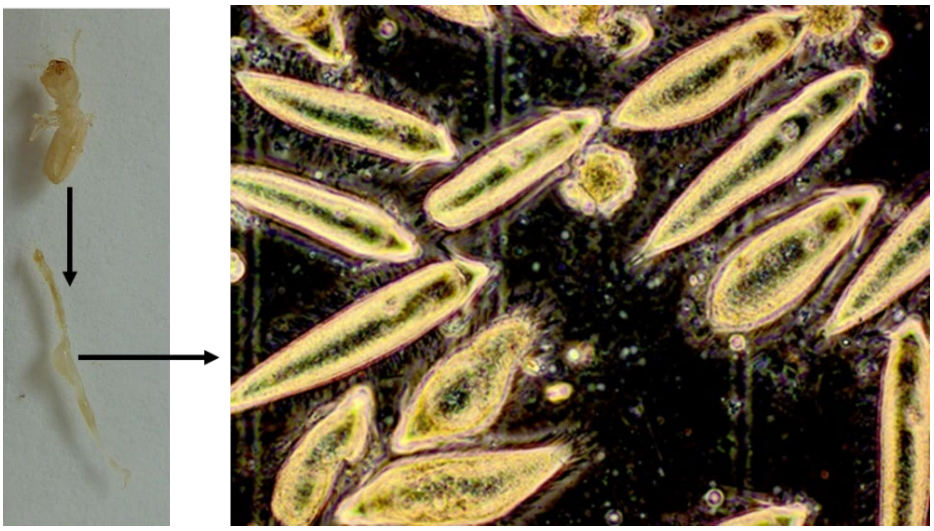


Fig.1.10 *C. formosanus* worker with removed gut and the corresponding gut protists, *P grassii*. Image taken by S. M. Usmani.

1.5 Wood preservation

In the wood-working industry, preservatives provide economic and environmental benefits by extending the service life of the wood product. In the European Union itself, approximately 18 million cubic meters of timber were pressure treated with wood preservatives.[48] In Germany, the durability of wood and wood-based products is categorized based on their potential service conditions into “Use Classes” (EN 335: 2013) as shown in Table 1.1.[49]

Table 1.1 Summary of Use Classes applicable for chemically treated wood [49]

Use Class		Service condition
1		Indoor use with ≤ 70% air humidity which requires preservatives for prevention of insects.
2		Indoor use with air humidity > 70% and outdoor use (without weathering) that requires preservatives for prevention of insects and fungi.
3	3.1	Weatherproof wood products that are placed outdoors (above ground with limited water contact) need preservatives to prevent decay caused by fungi and insects.
	3.2	Weatherproof wood products that are placed indoors (wet rooms) and outdoors (above ground with prolonged water contact) need preservatives to prevent decay caused by fungi and insects.
4		Wood which is in permanent contact with ground or fresh water that needs the same preservatives as in Use Class 3.
5		Wood used in the marine environment that need preservatives to protect from marine organisms.

In general, wood preservatives can be classified based on their solubility as oil-borne or water-borne.[50] The earliest known preservative is oil-borne creosote, which continues to be used in some countries to protect railway sleepers. At present, most oil-borne wood preservatives such as pentachlorophenol are restricted because of their detrimental impact on the environment.[51] Simple salts such as zinc chloride ($ZnCl_2$) and sodium fluoride (NaF) were some of the earliest water-based preservatives.[50] The use of these salts declined as they were found to leach out from wood when exposed to water. Consequently, they were substituted with wood preservatives containing active ingredients such as copper and boron.

1.5.1 Copper and boron

Copper is a widely used active ingredient for wood preservation. Since the early 1950s, copper was combined with chromic acid and arsenic pentoxide for wood fixation. In the 1990s, when arsenic and hexavalent chromium came to be classified as human carcinogens, their use became restricted to industrial applications.[52] Consequently, several alternatives were developed to replace chromium and arsenic in preservative

formulations.[51] Some well-known replacements are alkaline copper quaternary ammonium salts, copper HDO [bis-(N-cyclohexyldiazeniumdioxy)-copper], and copper azoles. Combination of copper with quaternary ammonium compounds has proven efficacy against insects and copper tolerant fungi.[50] It was observed that ammonia plays a role in expanding the cell walls to improve the distribution of copper into wood.[50] Copper is also combined with azoles, which are used in agricultural applications. Although triazoles have low mammalian toxicity, their production costs are high.[50] Some triazoles used in combination with copper are propiconazole and tebuconazole.

Copper is closely followed by boron, another well-known active ingredient used in wood preservatives. In addition to their high biocidal activity, boron compounds have low mammalian toxicity. Also, brown-rot fungi have not developed resistance to boron as they have to copper.[53] These properties of boron have resulted in its increased use in wood products.[50] Disodium octaborate tetrahydrate (DOT) is a well-known boron compound used in wood preservation.[53] Other borate formulations common in wood treatment are sodium tetraborate, borax, and boric acid. As borates are non-flammable, the treated wood product is flame retardant as well. Despite their advantages, borate compounds are limited by their high leachability. Therefore, their use is restricted to above ground contact applications where they are not directly exposed to weathering conditions such as rain. To overcome the leaching susceptibility of boron in ground contact applications, it is used in combination with other biocides. For instance, borate when combined with copper and chromium for outdoor ground contact applications is effective against soft-rot.[53] Copper is also combined with boric acid in an amine-based formulation known as copper HDO.[50] However, unlike copper, boron loses its efficacy on fixation.[53] Research efforts are ongoing to develop formulations that will result in partial mobility of boron inside wood after fixation, which is necessary for its biocidal action.

The solvent in wood preservative formulation can improve the distribution of preservative in the wood matrix. A study done by Amofa reported on the role of ethylene glycol (EG) in wood treatment.[54] The study reported that the formulation of boron using EG as a solvent facilitated its diffusion in wood by causing it to swell, that in turn opened the cell wall matrix.[54] The swelling is due to the strong affinity between EG and the hydroxyl groups in the wood matrix. Additionally, the relatively low vapor pressure of ethylene glycol reduced its evaporation and prolonged the cellular movement of boron inside wood.[54] In addition to facilitating diffusion, ethylene glycol reduced the potential

water absorption capacity of wood. The decrease in the available water sorption sites is a consequence of physio-chemical interaction between EG and wood. Therefore, moisture content measured in EG treated wood was significantly lower than water treated wood.[54] Another advantage reported by Amofa was that pine wood treated with boric acid in EG solution was found to leach less boron.[54] Concerning human health and environmental safety, EG biodegrades rapidly in soil and surface water (within 28 days), it is non-carcinogenic, and poses no risk to human health.[55,56] Hence, EG is an ideal solvent for wood preservative formulations that is safe for handling and improving the distribution of preservative inside wood.

1.5.2 Chemical wood modification

Chemical modification is another method to protect wood. In chemical modification, the hydrophilic hydroxyl groups of the cell wall polymers are converted into hydrophobic groups to significantly reduce the moisture content of wood. The advantage of chemical modification is that the treatment is non-biocidal. Therefore, the environmental and health risks of chemically modified wood are negligible. Chemical modification methods such as acetylation and furfurlyation are already commercialized for wood protection.[57] In furfurylation, wood is polymerized with furfuryl alcohol (produced in agricultural wastes) using catalysts and heat.[20] A furfurylated wood product is resistant to marine borers.[20] In acetylation, acetic anhydride reacts with the wood hydroxyl groups that results in the formation of wood acetate and acetic acid.[20] However, the acetylation process has been applied to only two types of wood; radiata pine and alder.[57] More research is ongoing to apply chemical modification in other wood species as well.

For instance, lactic acid, a non-toxic chemical has been studied to chemically modify beech wood. Lactic acid-based treatments on beech improved its dimensional stability and biological resistance to *C. puteana* and *T. versicolor*. The treatment involves a curing step at 160°C for 48 h for *in-situ* polymerization of lactic acid oligomers inside wood.[58] A simpler strategy could be to use lactic acid itself as a solvent for suspension of an inorganic active ingredient such as boron or fluoride. Thereby, a synergistic effect on biocidal efficacy can be investigated similar to that reported for ethylene glycol and boron and discussed in the previous section (1.5.1).[54]

1.5.3 Fluoride preservatives

Fluoride used to be an important active ingredient in wood preservative formulations before the prevalence of copper and boron. Fluoride formulations became prevalent during the World War I when the German State Railway had to find a replacement for creosote, which was used to protect railway sleepers but was in scarce supply.[59] In 1887, the first patent for impregnation of wood with fluoride compounds was made by Thompson, followed by several patents from Malenkovic and Wolman.[31,60] In these earlier treatments, a mixed solution of sodium fluoride and zinc chloride followed with heating led to a precipitate of zinc fluoride in the wood matrix.[31] In 1907, Wolman patented an improved treatment using potassium fluoride for protection of mine timbers.[31] This treatment was subsequently replaced with sodium fluorosilicate, a cheaper and widely available compound.[31] In 1909, Malenkovic developed an improved formulation known as "Basilit", a mixture of 88% NaF and 12% dinitrophenolanilin, which was later modified to dinitrophenol by Wolman.[31] However, dinitrophenol was found to be corrosive and was eventually replaced with dichromates. In addition to reducing corrosion, dichromates were found to improve the fixation of fluorides in wood. The resultant fluoride and dichromate formulation was known as "Wolmanit U" or "Basilit U", where U stands for unleachable.[15]

In 1909, Netzsch did a comprehensive study on the biocidal efficacy of fluorides for wood preservation. He found that the toxicity of fluoride to fungi was proportional to the amount of fluorine in the compound.[61] In addition, HF itself was more toxic than simple metallic salts because of the activity of the free hydrogen.[61] Moisture content of wood plays an important role in the diffusion of fluoride ions in the wood. Becker confirmed that the fluorides diffuse with moisture to the decayed area within wood.[15] Diffusion of fluoride was initiated when the wood moisture level reached 17% to 19% and increased linearly with the rising water content.[15] He also reported that fluoride in the wood matrix continuously establishes new equilibria based on the fluctuations in the moisture content.[62] Therefore, the biocidal action of fluoride is regulated by the moisture content of wood.

During wood treatment, fluoride penetrates mostly in the axial direction, followed with the radial, and the least in the tangential direction in the ratio of 6:4:3.[15] Bifluorides were found to penetrate deeper than silicofluorides.[15] Becker reported that 1 kg/m^3 of fluoride in wood could be sufficient to protect against fungal degradation.[15] For eradication of wood-destroying beetle larvae, surface treatment with 100 g bifluorides salt per m^2 was required.[15] With NaF, the fluoride content of 0.45 kg/m^3 was needed for biocidal efficacy.[15]

In another study, NaF at even lower retention of 0.33 kg/m^3 had efficacy against wood-degrading fungi, albeit without leaching.[63]

A composition of chromium, fluoride, and copper (CFK) was developed by Desowag-Bayer, which has efficacy against soft-rot fungi.[15] Besides this formulation, a mixture of copper naphthenate and NaF was reported to have efficacy against brown-rot (*R. placenta*) and white-rot (*T. versicolor*) fungi.[64] In this treatment, the dissociated fluoride from NaF aided in the diffusion of copper for better protection of wood.[64] Even stand-alone treatment of particleboard with NaF at low retention is resistant to decay caused by fungi and termite (*C. formosanus*).[65] NaF is also toxic to mold fungi (*Aspergillus niger*), House Longhorn beetle (*Hylotrupes bajulus*), and termites (*Reticulitermes flaviceps*).[31,66,67] Besides this, fluorides are also used in remedial treatment of wood.[63] Overall, fluorides at low concentrations have demonstrated efficacy against a wide-range of wood-degrading fungi and insects.

Moreover, treatment with fluoride does not alter the physical properties of wood. Fluoride salts are acidic or neutral, and therefore they do not reduce the mechanical strength of wood as observed with the use of alkaline liquids.[15] X-ray emission of timber showed that fluoride salt prevented the shrinkage of wood by blocking the cell wall cavities.[15] In contrast to copper, fluorides do not stain wood or have an odor, unlike creosote. Regarding anti-corrosion, partial hydrolysis of silicofluorides results in HF formation, which is corrosive to iron screws used for fastening in wooden structures.[15] However, NaF has no effect on any type of metal fastening.[15] Also, a study showed that the optimized combustion of fluoride treated wood did not result in a higher concentration of stacked pollutants compared to those released from the combustion of untreated wood.[68] Another study found that fluoride concentration in treated wood ash was not significantly higher than pure wood ash.[69] These studies show that fluoride treated wood poses a low risk to the environment at the end of its service life.

Despite their multiple advantages as highlighted above, the main limitation of fluoride compounds remains their high susceptibility to leaching. Becker (1973) reported that a short rainfall can remove more than 50% injected fluoride salts if used without fixatives.[15] Studies on NaF treated wood specimens found that fluoride was lost during leaching, which resulted in their high mass losses due to fungal and termite attack.[65–67,70] Their high susceptibility to leaching has contributed to the decline of fluoride compounds in wood preservative formulations. Table 1.2 summarizes the number of fluoride-based

wood preservatives used in Germany from the list published by *Deutsches Institut für Bautechnik* (DIBt).[71–73] The empty column in Table 1.2 is because the German Building Institute did not include any fluoride compounds (water-based) in the DIBt list of wood preservatives for 2016.[73]

Table 1.2 Summary of approved fluoride-based wood preservatives in Germany

Mixtures	Listed products		
	1981[71]	1997[72]	2016[73]
Chromium/fluorine	9	-	-
Fluorosilicates	12	2	-
Bifluorides	11	1	-
Chromium/fluorine/boron	6	9	-
Chromium/fluorosilicates/zinc/copper	-	2	-
Total	38	14	0

From Table 1.2, it is seen that in 1981 there were 38 fluoride mixtures available in the market, which declined to 14 in 1997, and zero were listed in 2016 because no applicant (company) applied for commercial approval of fluoride-based wood preservatives. This is because boron has gradually replaced fluorine in many wood preservative formulations.[53] Even though boron compounds are highly water soluble, they are preferred due to their low mammalian toxicity. To bring back fluorides into production as commercial wood preservatives, the problem of their high susceptibility to leaching must be solved. One method to overcome the leaching limitation would be to evaluate sparingly soluble fluorides synthesized as nanoparticles for protection of wood from fungi and termites.

1.5.4 Nanoparticles as wood preservatives

Nanoparticles with their distinct physical properties of small size and increase in specific surface area have opened an exciting technological route to improve the distribution of active ingredients into wood. The distribution of nanoparticles in the wood structure is dependent on their diameter and the type of wood species used in the treatment. As discussed in the earlier section (1.3.3), beech wood is relatively more permeable than Scots pine. Differences in permeability can determine if nanoparticles of a specific diameter can be introduced in a particular wood species. For instance, beech wood could be treated with

silica (SiO_2) particles which were 350 nm in size, whereas in treatment of Scots pine wood, their particle size was limited to 70 nm.[74] Therefore, the particle size and type of wood species are important variables to consider during treatment of wood.

Micronized copper (Cu) preservatives with particle sizes ranging from 1 nm to 250 µm are now estimated to comprise 50% of the commercial Cu containing wood preservative market in North America.[75] Besides Cu, studies have evaluated efficacy of other nano formulations for wood protection. Unleached wood treated with nano zinc borate is resistant against brown-rot fungi; *C. puteana* and *R. placenta*.[18,19] Similar resistance to brown-rot fungi was reported for unleached wood specimens treated with titanium dioxide (TiO_2) that was prepared using sol-gel synthesis.[76] Another study reported that unleached wood treated with nano zinc borate has efficacy against white-rot fungus, *T. versicolor*. However, the same treatment in wood resulted in high mass loss caused by brown-rot fungus, *Tyromyces palustris*.[77] With respect to leaching, it is reported that nano formulations of Cu and zinc (Zn) are more leach resistant compared to their soluble metal oxide counterparts.[78] Mantanis et al. (2014) found that coating with acrylic emulsion also reduces the leaching of nano zinc borate from wood.[77]

Leach and biological resistance of several nanoparticles namely zinc oxide (ZnO), boric acid (B_2O_3), cupric oxide (CuO), TiO_2, cerium oxide (CeO_2), and tin oxide (SnO_2) were evaluated against fungal decay by Terzi et al. (2016).[79] They found that only wood specimens treated with nanoparticles of ZnO are resistant to leaching and against brown-rot fungus, *Gloeophyllum trabeum*.[79] Still, the same nano-based treatments in wood are not resistant to decay caused by *T. versicolor*.[79] Subsequent work by Bak, et al. (2018) found that increasing the concentration of nano ZnO formulation to 5% for wood treatment made even the leached specimens resistant to *T. versicolor*.[80] Yet, this higher concentration of ZnO nanoparticles in wood after leaching was not sufficient to protect from *C. puteana*, a widely observed fungi in decayed wooden houses in Europe.[80] One nano-based treatment that is reported to have efficacy against *C. puteana* after leaching was TiO_2/Cerium (Ce) in Spruce wood.[81] However, the efficacy of TiO_2/Ce treatment in wood specimens has not been evaluated for either white-rot fungi or termites.

Several research studies have assessed wood treated with nano formulations for protection from termites. In a termite test with *C. formosanus*, the specimens treated with nano-B_2O_3 and then leached caused 100% termite mortality, although the lowest mass loss (4.2%) was observed for specimens treated with nano-CuO.[79] In another test, nano ZnO

treated wood specimens that were leached led to mass losses below 2% caused by *Reticulitermes grassei*.[82] Wood treated with nano ZnO was also found to protect from termites, *R. flavipes*.[83] Among all the nano-based treatments that have been evaluated so far, nanoparticles of ZnO and TiO_2 in various formulations have shown the most promising results. The former protected wood from white-rot fungus and termites, while the latter from brown-rot fungus. However, there is no one nano-based treatment that is reported to protect wood against both types of fungi and termites. Therefore, further improvements are needed such that one nano-based treatment of wood provides broad protection from different types of decay instead of developing tailor-based preservative formulations.

1.6 Nano metal fluorides

Sol-gel synthesis is a widely used, low-cost, and easy to scale-up method for synthesis of oxidic nanoparticles. It also offers more control over synthesis parameters to modify the shape, size, and structure of the nanoparticles.[84] These characteristics have led sol-gel synthesis to become an established process in various industrial applications such as thin-films and catalysts.[84] Some metal oxide nanoparticles synthesized and tested using this procedure for wood protection are SiO_2 and TiO_2, which were described in the previous section (1.5.4).[85]

Sol-gel synthesis involves hydrolysis of a metal alkoxide precursor followed with a condensation reaction between terminal hydroxyl groups.[86] In the solution state known as "sol", the metal oxide particles are in a colloidal suspension which has a lower viscosity than the final network structure called "gel". The sol-formation can be controlled by various factors such as pH, temperature, and reactant concentration. These parameters can influence the sol state or the gel state of the resultant metal oxide.

The flexibility of sol-gel synthesis allows the use of different metal alkoxide precursors which undergo acid-catalyzed hydrolysis through nucleophilic substitution. In sol-gel synthesis, M-OH is formed via the co-ordination of a metal cation, M^{n+} with a water molecule. Following hydrolysis, the hydroxyl groups can undergo condensation with –OR groups to form -M-O-M- cross-linked gel network accompanied with the release of water or alcohol. The formation of a highly viscous gel poses a challenge for wood treatment. To overcome this limitation, wood is either dip-coated with the precursor solution or it is immersed in the precursor solution for *in-situ* polymerization of the resultant metal oxide.[85]

An immersion treatment does not result in uniform distribution of nanoparticles over a greater area in the wood matrix.[81] A treatment where the wood is directly treated with the sol would be a more effective strategy in pushing the nanoparticles deeper into wood. To implement such a strategy, the sol-gel synthesis procedure would need to be optimized such that wood can be treated with the sol and delay or minimize the formation of the gel. In this way, a colloidal suspension of nanoparticles with small diameters can be impregnated in the wood matrix. Once inside, the eventual aggregation of nanoparticles will function to block the micro/nano-pores in wood cells and minimize the entry of fungal hyphae. The formation of a stable sol requires control over the sol-gel process, which can be achieved via the fluorolytic sol-gel route used to synthesize nano metal fluorides (NMFs).

In 2003, the typical hydrolysis reaction of sol-gel was modified to fluorolysis for the synthesis of novel nanoscopic metal fluoride particles by Kemnitz, et al.[87] In fluorolytic sol-gel synthesis route, hydrogen fluoride is used to fluorinate the metal alkoxide precursor. It is a well-known method for synthesis of sparingly soluble fluorides such as magnesium fluoride (MgF_2) and calcium fluoride (CaF_2). MgF_2 is found as a rare mineral known as "Sellaite" and CaF_2 is a naturally occurring mineral (also called "Fluorspar").[88] MgF_2 is used in the production of aluminium and CaF_2 is used in the production of HF, an important chemical needed for synthesis of various fluoride materials.[89] MgF_2 has a rutile structure and CaF_2 has a cubic structure.[90,91] Both are sparingly soluble, with CaF_2 (16 mg/L) having a lower solubility than MgF_2 (130 mg/L).[92]

In fluorolytic sol-gel synthesis, the reaction is between M^{n+} cation from the metal alkoxide and stoichiometric amounts of HF resulting in the formation of M-F bonds (Fig.1.11). It involves the direct attack of fluoride at the uncoordinated M center that results in the formation of M-F-M bridges instead of the M-O-M network seen during hydrolysis.[93] The donating solvent molecules stabilize the highly distorted metal fluoride particles in the sol state while preventing the formation of regular MF_6-octahedra.[94] The colloidal properties of the system (sol and gel formation) are controlled by optimizing the reaction conditions such as the type of solvent and precursor. Specifically, for wood treatment, the synthesis conditions are optimized to form a clear sol as shown in Fig.1.11. A stable sol-state with low viscosity will improve the distribution of metal fluoride nanoparticles into the matrix for better protection of wood from decay.

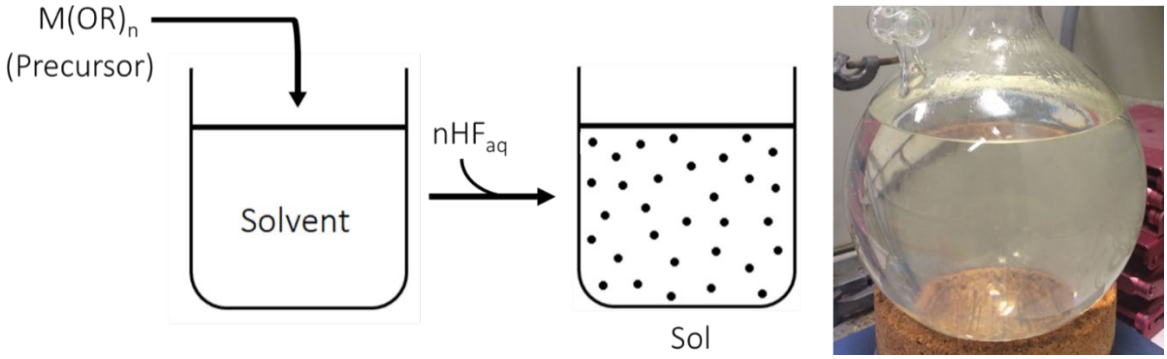


Fig.1.11 Schematic of fluorolytic sol-gel synthesis and an example of a clear CaF_2 sol (right), where M(OR) = metal alkoxide and n = metal valence. Image created by S. M Usmani.

NMFs have been evaluated for a broad range of applications such as catalysis,[90,95] optical thin films,[96] antireflective coatings,[97,98] biodegradable plastics,[99] and dental.[100] The more electronegative fluoride results in a stronger Lewis acidic character of metal fluorides, which is not observed in metal oxides.[88] MgF_2 nanoparticles prepared with fluorolytic sol-gel synthesis have a large surface area of 300 m^2/g for Lewis acid sites that can be optimized to produce catalysts tailored according to specific reactions.[90] Silicon plates spin-coated with MgF_2 sol result in a transparent layer with thickness as low as 19 nm that can be used in optical coatings.[96] Glass substrates coated with MgF_2 nanoparticles show high mechanical stability and antireflective properties with a minimum reflectance of 0.2% at 600 nm.[97] Furthermore, it was reported that the addition of CaF_2 to MgF_2 coating improved its mechanical stability such that it is even scratch resistant to coarse steel wool.[98] Mechanical properties of low molecular polylactic acid used to make biodegradable plastics are improved with the synthesis of CaF_2 nanoparticles in lactic acid.[99] Thus, properties of several materials are improved with the inclusion of NMFs.

Also, metal fluorides in the form of nanoparticles have been studied for various biological applications. Low concentrations of CaF_2 nanoparticles were reported to be antibacterial and non-toxic to mammalian cells.[101] Notably, the nano-size and the less ordered lattice structure of CaF_2 nanoparticles make them more soluble than the macro-sized CaF_2.[100] The higher solubility means that an oral rinse containing nano-sized CaF_2 will result in a larger fluoride deposition to provide better protection from dental caries than macro-sized CaF_2.[100] This result was in agreement with another study, that reported nanocomposites containing CaF_2 had high fluoride release which were also mechanically durable.[102] Nanoparticles of CaF_2 and MgF_2 also showed higher remineralization of early

dental caries lesions than NaF.[103] In one study, the combination of ZnO and MgF_2 nanoparticles reduced the growth of gram-positive bacteria which are responsible for respiratory tract infections.[104] They also found that the combination of both nanoparticles resulted in lower leaching compared to their respective individual coating on Cochlear implant, which is used as a hearing aid.[104] More importantly, the combination of ZnO and MgF_2 at a low concentration (0.08 wt%) did not have an adverse effect on human dermal fibroblast cells that were isolated from the auditory canal.[104] Also, catheters coated with MgF_2 nanoparticles were shown to be antibacterial and had no adverse effect on human cell lines.[105] The toxicity of fluoride compounds in vertebrates is dependent on their solubility. Studies done on rats found that CaF_2 and MgF_2 posed a lower risk to renal and hepatic organs compared to NaF that has a higher solubility (40 g/L).[106] Overall, NMFs have demonstrated their antibacterial activity and biocompatibility for use in medical applications.

Yet, no studies have reported on the biological resistance of wood treated with nanoparticles of either CaF_2 or MgF_2. As far back in 1926, the use of sparingly soluble fluorides such as CaF_2 and MgF_2 was proposed as an alternative to highly soluble fluorides as they would be more environmentally safe.[107] So far, extensive literature search did not turn up results that tested the viability of these sparingly soluble fluorides to protect wood from decay. One of the reasons results from these tests have not been reported is because wood treatment with sparingly soluble compounds can be challenging. To overcome this limitation, metal fluorides can be synthesized as nanoparticles to improve their treatment and subsequent distribution into the wood matrix. The following study presents the first results on the durability of wood treated with sparingly soluble metal fluorides.

2. Characterization

This chapter presents results from the characterization of nano metal fluorides (NMFs) and the resultant treated wood.

2.1 Composition and particle sizes of nano metal fluorides

Fluorolytic sol-gel synthesis is a well-established method and past studies have already characterized MgF_2 and CaF_2 nanoparticles.[88,108] Specifically for the current study, a novel equimolar combination of MgF_2 and CaF_2 was synthesized in a single sol using fluorolytic sol-gel synthesis. The following is the characterization of the NMF combination sol and its comparison with stand-alone NMF sols.

2.1.1 X-ray diffraction (XRD)

The Fig.2.1 shows the XRD patterns of xerogels from NMF sols. The xerogels of MgF_2 and CaF_2 matched the respective reference patterns of MgF_2 and CaF_2.

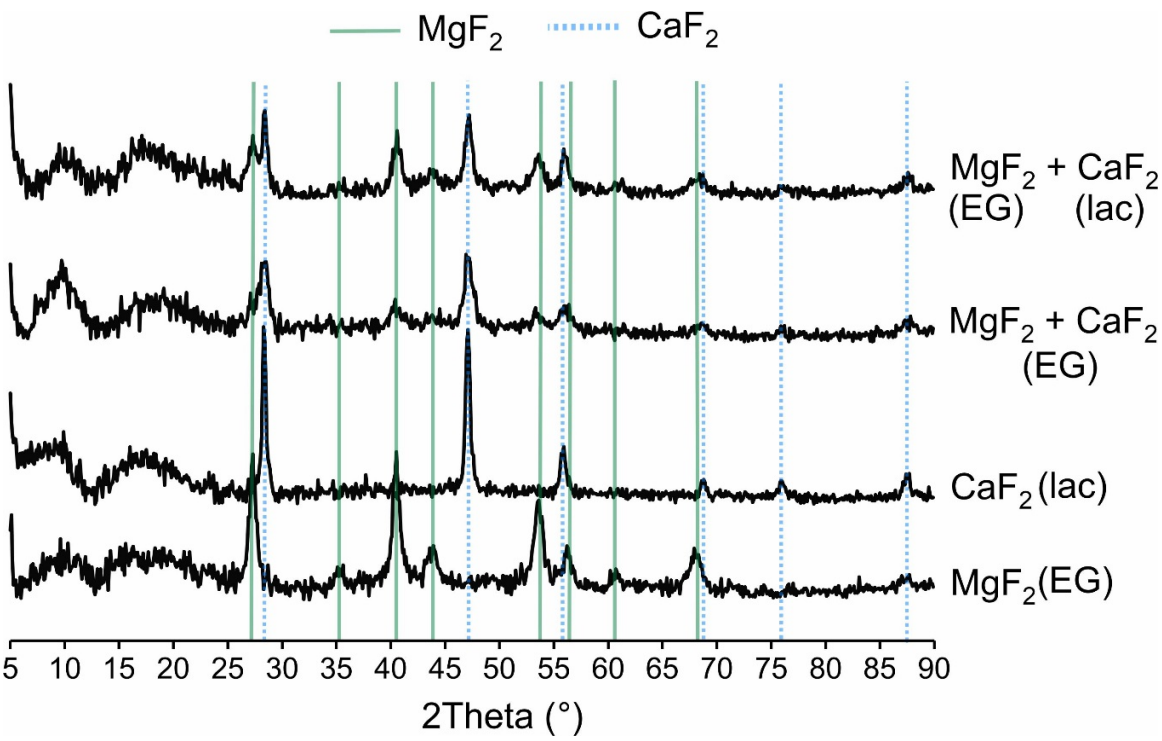


Fig.2.1 XRD patterns of xerogels in different solvent formulations, ethylene glycol (EG) and lactic acid (lac). The vertical lines are the reference peaks from MgF_2 (PDF 41-1443) and CaF_2 (PDF 35-0816).[109]

In Fig.2.1, the reflection peaks in the xerogel of the combination of MgF_2 and CaF_2 in a single sol in ethylene glycol (EG) matched with the respective reference patterns of MgF_2 and CaF_2. Similarly, the reflection peaks from the xerogel of the combination of MgF_2 sol in ethylene glycol (EG) and CaF_2 sol in lactic acid (lac) could be attributed to reference reflections of MgF_2 and CaF_2. Thus, the XRD diffraction patterns confirmed that the NMF combination formulations were composed of MgF_2 and CaF_2.

2.1.2 Dynamic light scattering (DLS)

After confirmation of composition, the hydrodynamic diameter of the nanoparticles was determined with DLS. The hydrodynamic diameter of a nanoparticle includes not only the particles but everything bound to the particle surface. The distribution of the hydrodynamic diameter of the nanoparticles in the NMF sols is presented in Fig.2.2.

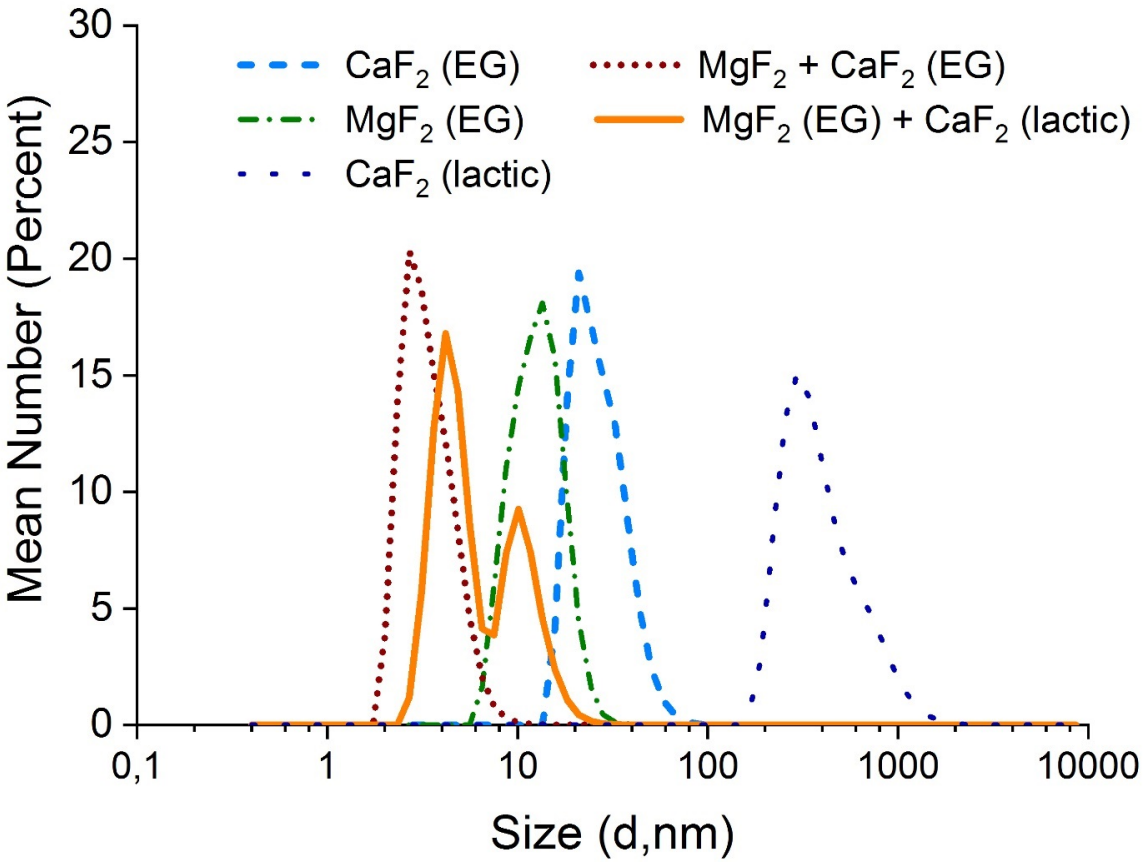


Fig.2.2 Hydrodynamic diameter of nanoparticles in NMF sols in different solvent formulations, ethylene glycol (EG) and lactic acid.

The nanoparticles in a single sol of MgF_2 (EG) sol have a hydrodynamic diameter of 14 nm (Fig.2.2). The CaF_2 nanoparticles synthesized in EG have a hydrodynamic diameter of 21 nm, whereas CaF_2 nanoparticles synthesized in lactic acid had a larger hydrodynamic diameter. Strong binding of several layers of lactic acid (linked by hydrogen bonding) could have led to a hydrodynamic diameter much larger than the diameter of the "pure" CaF_2 particle.

For the single sol combination of MgF_2 and CaF_2 in EG there is only one peak at 4 nm. However, for the combination of MgF_2 (EG) and CaF_2 (lac) there are two peaks, at 5 nm and 10 nm. The two peaks were caused by two types of particles with different sizes. This is the expected behavior when mixing two separately synthesized sols. However, in the one-step sol synthesis, the two particles influence or direct each other leading to a more uniform particle size. To get a clearer picture of the mean particle size distribution of "pure" nanoparticles of metal fluorides in different formulations without the influence of solvent, they were characterized by TEM.

2.1.3 Transmission electron microscopy (TEM)

High resolution-transmission electron microscopy (HR-TEM) images in Fig.2.3 reveal that the mean particle size distribution of NMFs is smaller than 10 nm. The sizes of the MgF_2 and CaF_2 nanoparticles in the one-step sol are similar to separately synthesized sols.

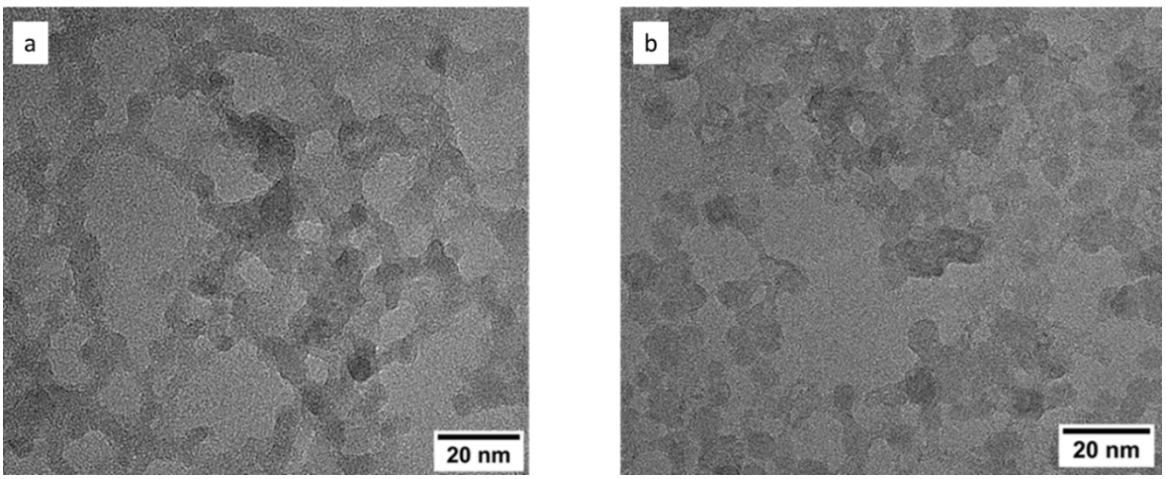


Fig.2.3 HR-TEM image of MgF_2 and CaF_2 nanoparticles (a) synthesized together in one sol with ethylene glycol as solvent (b) combined from two sols, one in ethylene glycol and the other in lactic acid.

In contrast to HR-TEM images, the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images show that a larger proportion of particles with sizes smaller than 5 nm are present in the one-step sol (Fig.2.4a) than the combination of two separate sols (Fig.2.4b). Thus, combining sols causes more nanoparticles to aggregate resulting in their larger size. It is also observed that there is a large difference in size of the nanoparticles from the one-step synthesis (Fig.2.4a) than the separately synthesized sols (Fig.2.4b). This variation in particle size could influence their eventual distribution, with the smaller particles able to penetrate rapidly and deeper into wood during treatment.

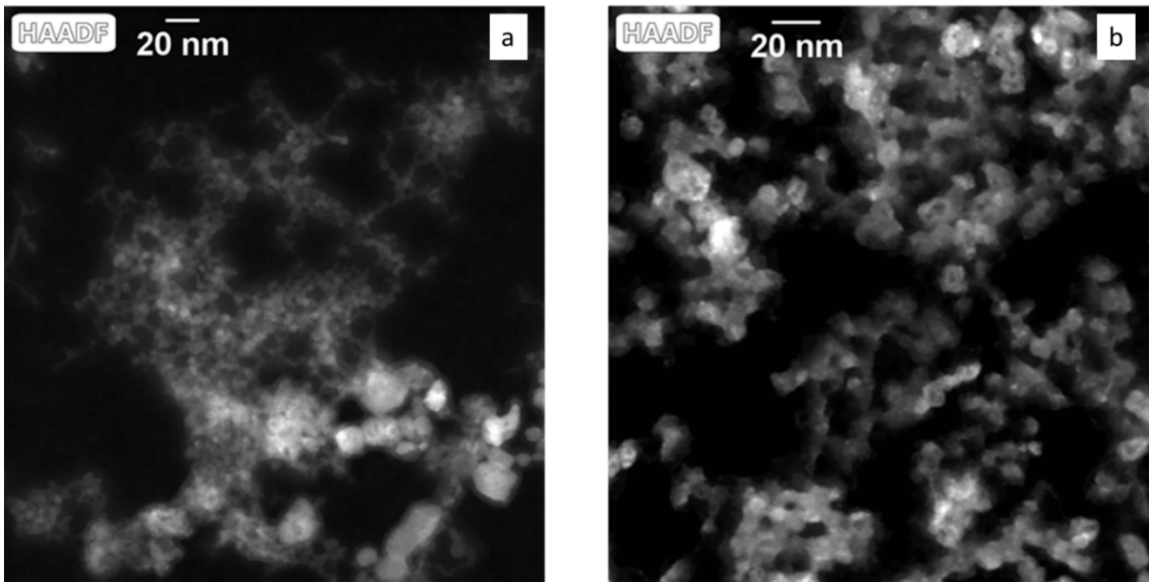


Fig.2.4 High-angle annular dark field-STEM image of MgF_2 and CaF_2 nanoparticles from (a) one-step sol in ethylene glycol as solvent (b) combined from two sols, one in ethylene glycol and the other in lactic acid.

Elemental mapping was done on the associated HAADF-STEM images in Fig.2.4, to determine the composition of MgF_2 and CaF_2 nanoparticles in the combined formulations. From Fig.2.5, it is confirmed that nanoparticles in the single sol are composed of fluorine (F), calcium (Ca), and magnesium (Mg). It is also observed that there are larger aggregates of CaF_2 (Fig.2.5a,b) than MgF_2 (Fig.2.5a,c).

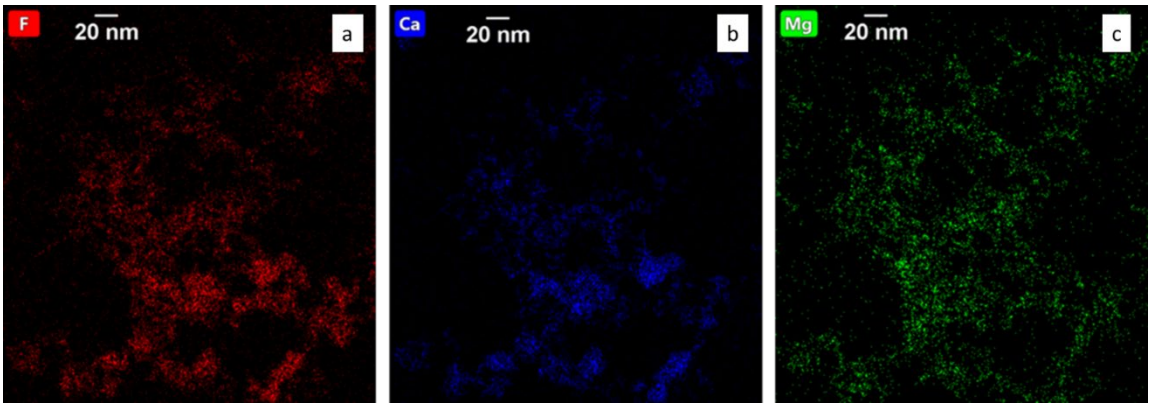


Fig.2.5 Elemental map of (a) Fluorine (b) Calcium (c) Magnesium in MgF_2 and CaF_2 nanoparticles synthesized together in one sol with ethylene glycol as solvent.

Similarly, elemental maps in Fig.2.6 show that the nanoparticles are composed of F, Ca, and Mg in the combination formulation from separately synthesized sols. Here, the difference between the size of the MgF_2 and CaF_2 nanoparticles (Fig.2.6) is smaller than those observed in the previous elemental maps (Fig.2.5). The chemical composition information from EDX is complementary to the results from the XRD diffraction patterns in Fig.2.1. The results from this section demonstrate that particles of metal fluorides are small enough to distribute over a greater area inside the wood matrix during treatment.

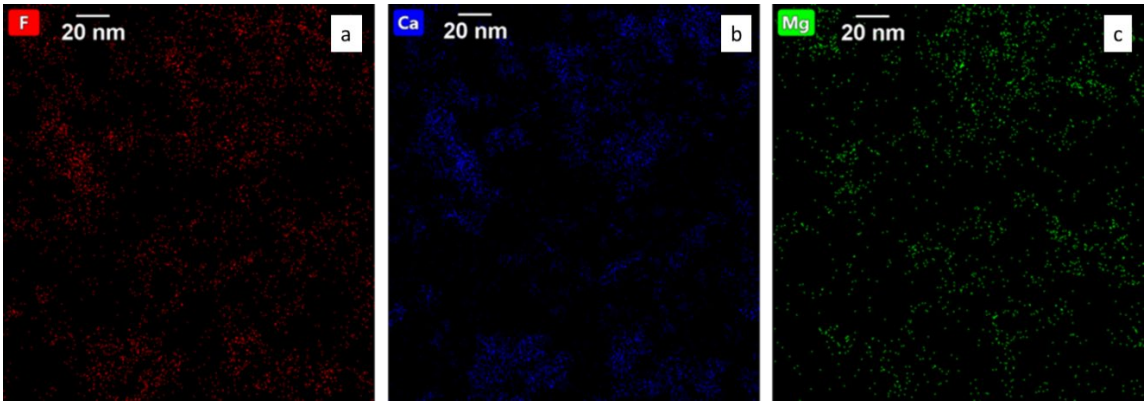


Fig.2.6 Elemental map of (a) Fluorine (b) Calcium (c) Magnesium in MgF_2 and CaF_2 nanoparticles combined from separately synthesized sols of MgF_2 in ethylene glycol and CaF_2 in lactic acid.

2.2 Wood treated with nano metal fluorides

In this section, wood treated with NMFs is characterized by various analytical techniques to determine their inclusion and distribution inside wood.

2.2.1 Powder XRD

The Fig. 2.7 compares the powder XRD diffraction patterns of Scots pine specimens; untreated and treated with the combination of MgF_2 and CaF_2 (unleached and leached).

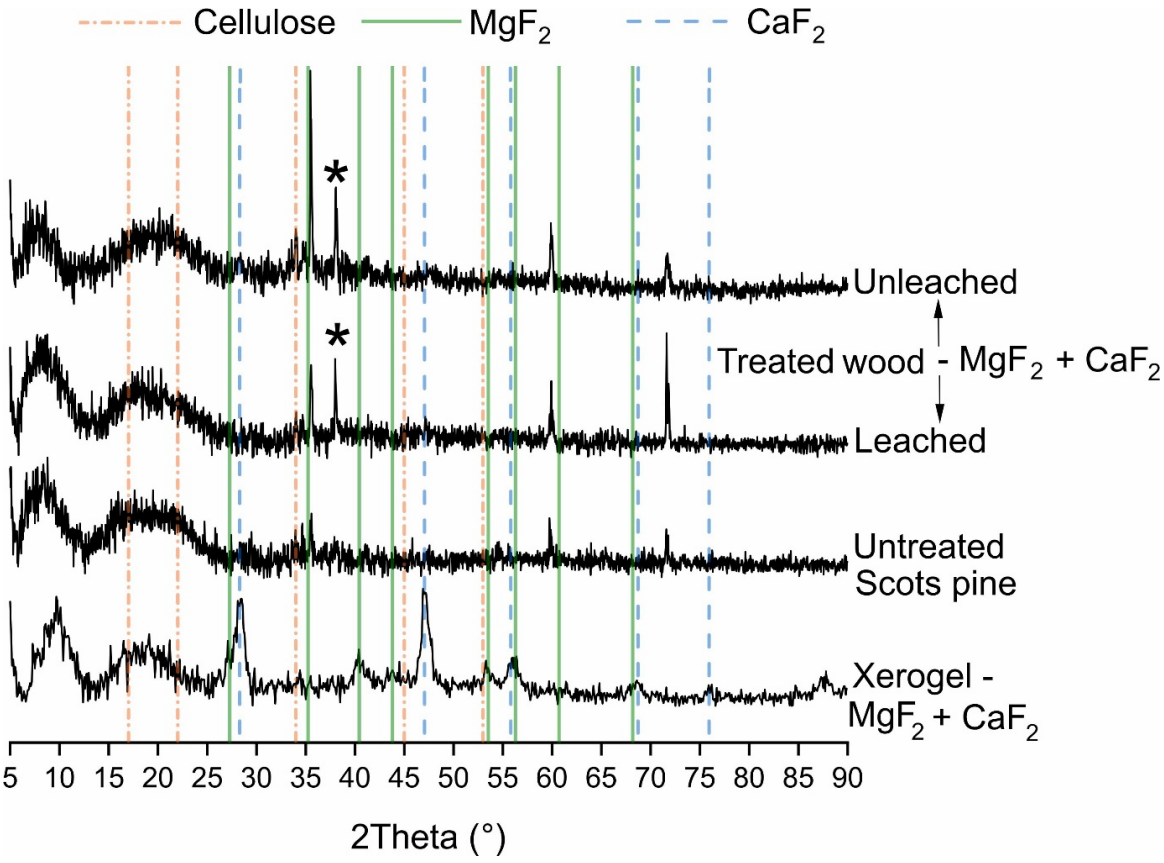


Fig.2.7 Comparison of powder XRD patterns of untreated Scots pine, NMF treated wood, and NMF xerogel. The orange vertical (dash-dot) lines are reference reflections from untreated Scots pine.[110] The green vertical (solid) lines are the reference peaks from MgF_2 (PDF 41-1443) and the blue vertical (dash) lines are the reference peaks from CaF_2 (PDF 35-816).[109] The asterisk highlights the reflection seen only in NMF treated wood (unleached and leached).

From literature, it is known that untreated Scots pine has reflections at 17°, 22°, 34°, 45°, and 53° (orange vertical dash-dot lines).[110] Although the powder XRD diffraction patterns of untreated and NMF treated wood (unleached and leached) are similar, they do

not show reflections that can be attributed to reference reflections from Scots pine. The similar XRD diffraction patterns of unleached and leached NMF treated specimen means that structurally there is no change after treatment and the subsequent leaching of wood.

The peak at 38° (asterisk in Fig.2.7) is seen only in unleached and leached NMF treated specimens. The reflection at 38° is not found in reference reflections of untreated Scots pine or MgF_2 or CaF_2. More importantly, no reflections in the diffraction patterns of NMF treated wood (unleached and leached) can be attributed to either MgF_2 or CaF_2. A reflection at 60° in NMF treated wood (unleached and leached) cannot be assigned to MgF_2 because the same reflection is also observed in the powder XRD diffraction pattern of untreated Scots pine. However, the reflection cannot be assigned to Scots pine either as it has not been reported in literature for untreated Scots pine.[110] Also, the reflection at 72° found in the diffraction patterns of both untreated and NMF treated specimens cannot be attributed to either cellulose, MgF_2, or CaF_2. As this is not the focus of the current study, research needs to be done in the future to assign the reflections at 38°, 60°, and 72° observed in NMF treated wood.

2.2.2 Nuclear magnetic resonance (NMR) spectroscopy

The ^{19}F MAS NMR spectra of Scots pine; untreated and treated with the combination of MgF_2 and CaF_2 (unleached and leached) are compared in Fig.2.8. In the ^{19}F MAS NMR spectrum of untreated Scots pine, a small signal for CaF_2 at -108 ppm was observed. The likely source of this signal is the impurities found in the rotor used in the measurement. More importantly, evidence of MgF_2 with a chemical shift of -198 ppm and CaF_2 with a chemical shift of -108 ppm were observed in the spectra of unleached and leached NMF treated wood specimens. The remaining signals in the ^{19}F MAS NMR spectra with a chemical shift of -2, -54, -162, and -206 ppm are attributed to spinning sidebands. Overall, the NMR spectra provide evidence of metal fluorides in unleached and leached treated wood.

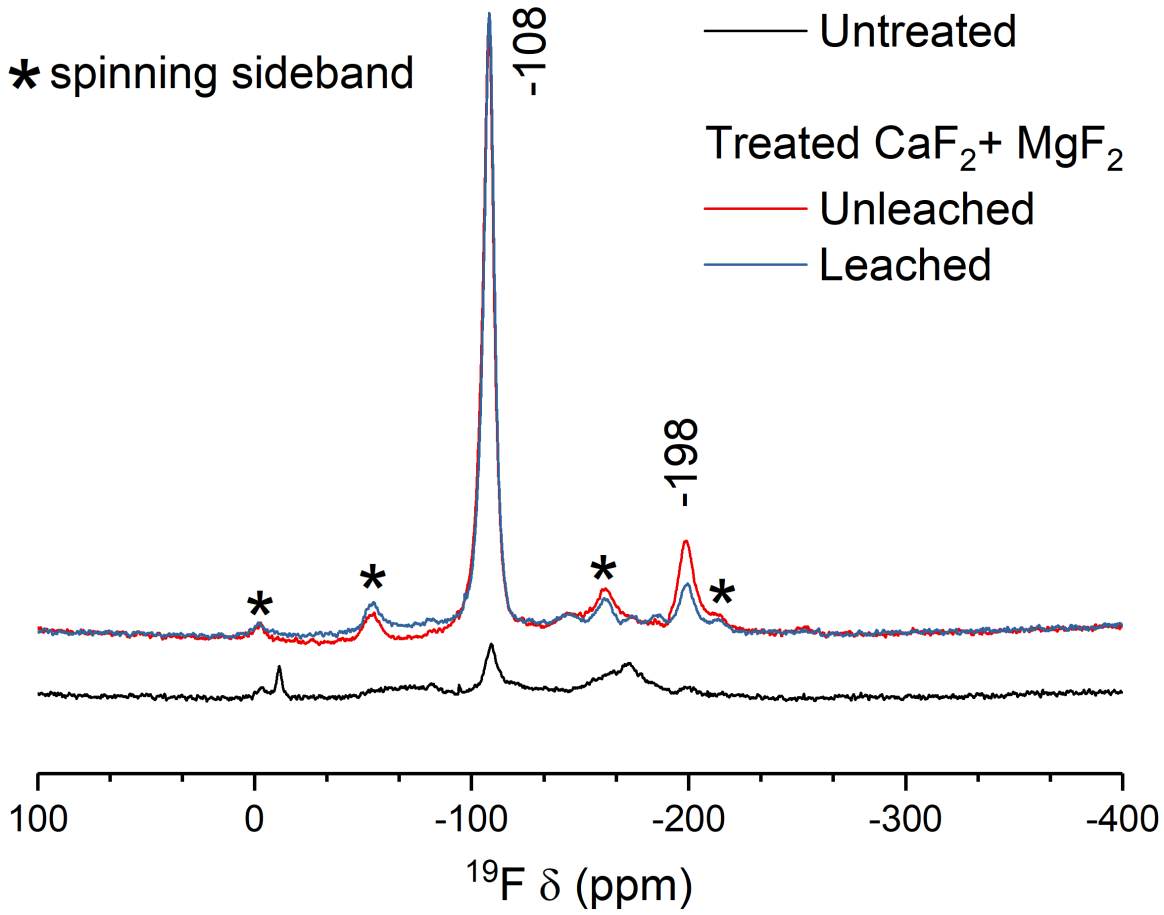


Fig.2.8 ^{19}F MAS NMR spectra (Larmor frequency - 376.4 MHz) of unleached treated wood (red), leached treated wood (blue), and untreated wood (black).

An earlier study by Krahl, et al. (2016) reported ^{19}F NMR spectra from the combination of MgF_2 and CaF_2 sols containing 15 and 30 mol% calcium, respectively.[98] In that study, the signal intensity of CaF_2 was lower than MgF_2, which was attributed to the formation of the metastable phase, $CaMgF_4$.[98] In the current study, the NMF combination formulation is different as it contains an equimolar concentration of MgF_2 and CaF_2. From Fig.2.8, it is seen that in wood treated with the NMF combination formulation, the signal of CaF_2 is much higher than MgF_2. The higher intensity of the CaF_2 signal could have an influence on the eventual biocidal efficacy of the NMF combination formulation.

It should also be emphasized that the signal intensity of the chemical shift at - 198 ppm (MgF_2) is lower in the leached treated specimen than the unleached treated specimen (Fig.2.8). This finding is consistent with the difference in solubility between MgF_2 and CaF_2. As MgF_2 has a higher water solubility than CaF_2, more amount of former leaches out of the treated specimens than the latter. Therefore, the MgF_2 signal is smaller in the leached than the unleached treated wood. Moreover, there is relatively no change in

the intensity of the CaF_2 signal between unleached and leached treated wood. Perhaps, the lower soluble CaF_2 could function as a reservoir that releases "free" fluoride ions from NMF treated wood during biocidal action against fungi and termites.

The ^{1}H-^{13}C CP MAS NMR spectra in Fig.2.9 shows the signals from the cell wall components in Scots pine; untreated and treated with the combination of MgF_2 and CaF_2 (unleached and leached). The signals detected between 62 ppm to 105 ppm correspond to polysaccharides with the signal at 56 ppm attributed to lignin methoxy groups, signals between 112 ppm to 152 ppm are from the aromatic rings, and the lone signal at 21 ppm is from the acetate groups of hemicelluloses.[111] There are no differences in the ^{1}H-^{13}C CP MAS spectra of untreated and NMF treated wood, except for the slight increase in the signal with a chemical shift of 130 ppm in the unleached NMF treated wood. The chemical shift of 130 ppm is from the aromatic groups in lignin.[111] This signal in unleached treated wood is likely from the interaction of NMFs with the aromatic groups in lignin, although it seems to be reversible. This is because in the leached NMF treated wood, the intensity of this signal was similar to untreated Scots pine.

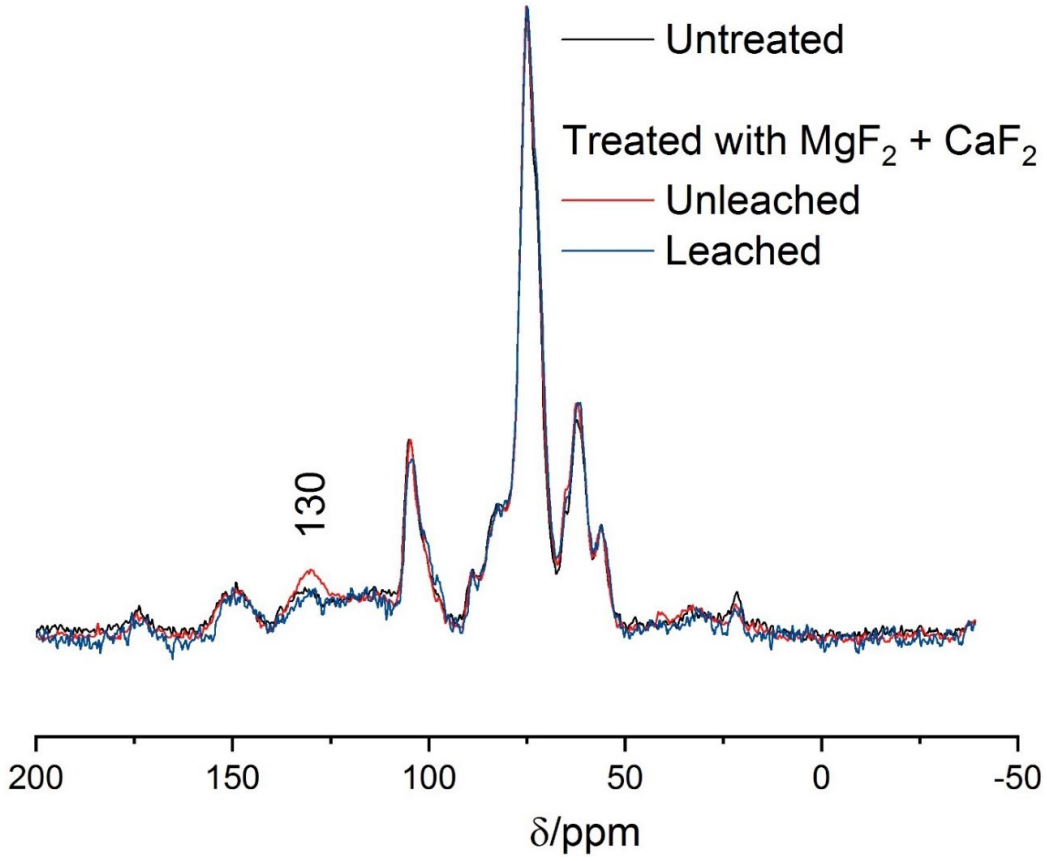


Fig.2.9 ^{1}H-^{13}C CP MAS NMR spectra (ν = 20 kHz) of unleached treated wood (red), leached treated wood (blue), and untreated wood (black).

2.3 Micro-distribution of nano metal fluorides in treated wood

The distribution of a preservative inside wood is a crucial determinant of its efficacy against wood-degrading fungi and insects. There are three cut sections in wood as shown in Fig.2.10. The following analytical techniques present information on the spatial localization of nano metal fluorides (NMFs) inside wood.

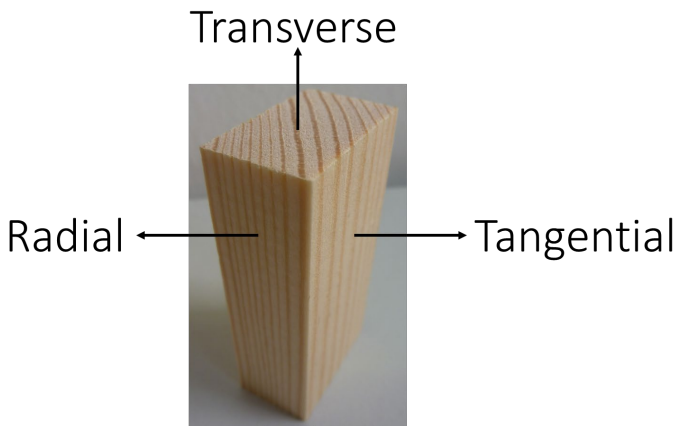


Fig.2.10 Cut sections in Scots pine wood. Image taken by S.M. Usmani.

2.3.1 Tangential section of treated wood

In Fig.2.11a, the back-scattered electron (BSE) image of the tangential longitudinal section of Scots pine wood treated with NMFs is shown. It is observed from the BSE image that the nanoparticles have aggregated over the surface of the tracheid channels. In Fig.2.11b-c, the fluoride composition of these aggregates was confirmed with EDX mapping at a higher magnification, which shows that the NMFs were present in the tracheid channels and the bordered pits. In a tree, the tracheid channels are responsible for transporting water and minerals, while bordered pits allow communication between adjacent cells in the horizontal direction.[27] In the present study, these pathways enabled the distribution of NMFs into the wood matrix. Thus, the presence of NMFs in both tracheid channels and bordered pits demonstrates that they are well distributed in the treated wood specimens.

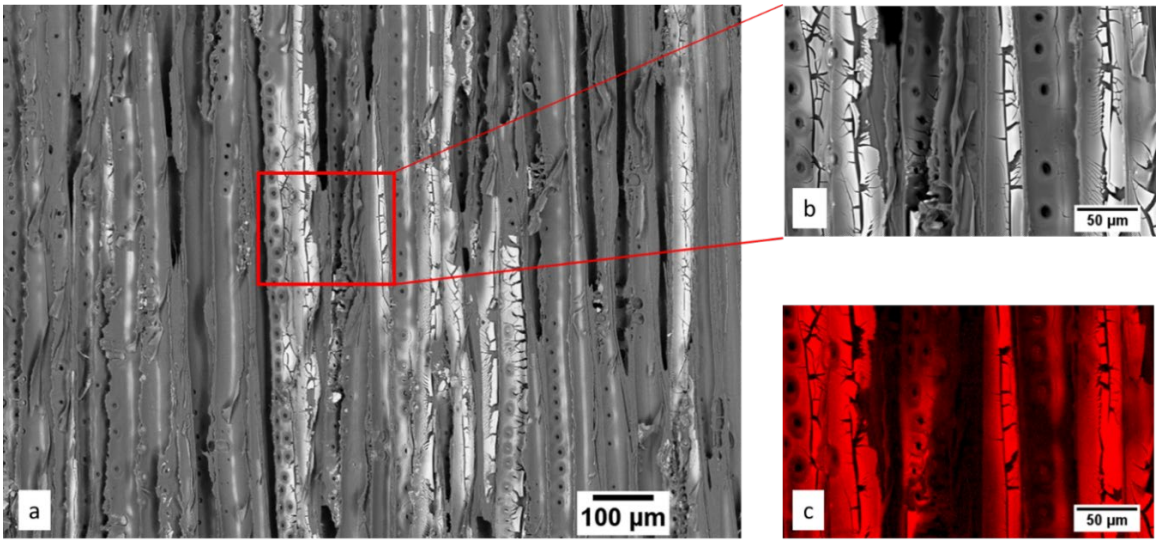


Fig.2.11 Tangential longitudinal surface of Scots pine wood treated with NMFs. BSE image showing bordered pits and longitudinal tracheids at (a) low and (b) high resolution. (c) EDX map of fluorine (red) in the longitudinal tracheids and bordered pits.

2.3.2 Radial section of treated wood

In Fig.2.12, an overview of the radial longitudinal section of treated Scots pine wood shows a high percentage of bordered pits and ray tracheids filled with aggregates. As in the tangential section from the previous section, NMF deposits were also present in the bordered pits in the radial section of treated wood. These aggregates are composed of fluoride, which was confirmed at a higher magnification with the corresponding EDX map (Fig.2.12b-c). Ray tracheids are also pathways for transporting water and minerals in wood cells, which is another route for the NMFs to penetrate and distribute within wood.

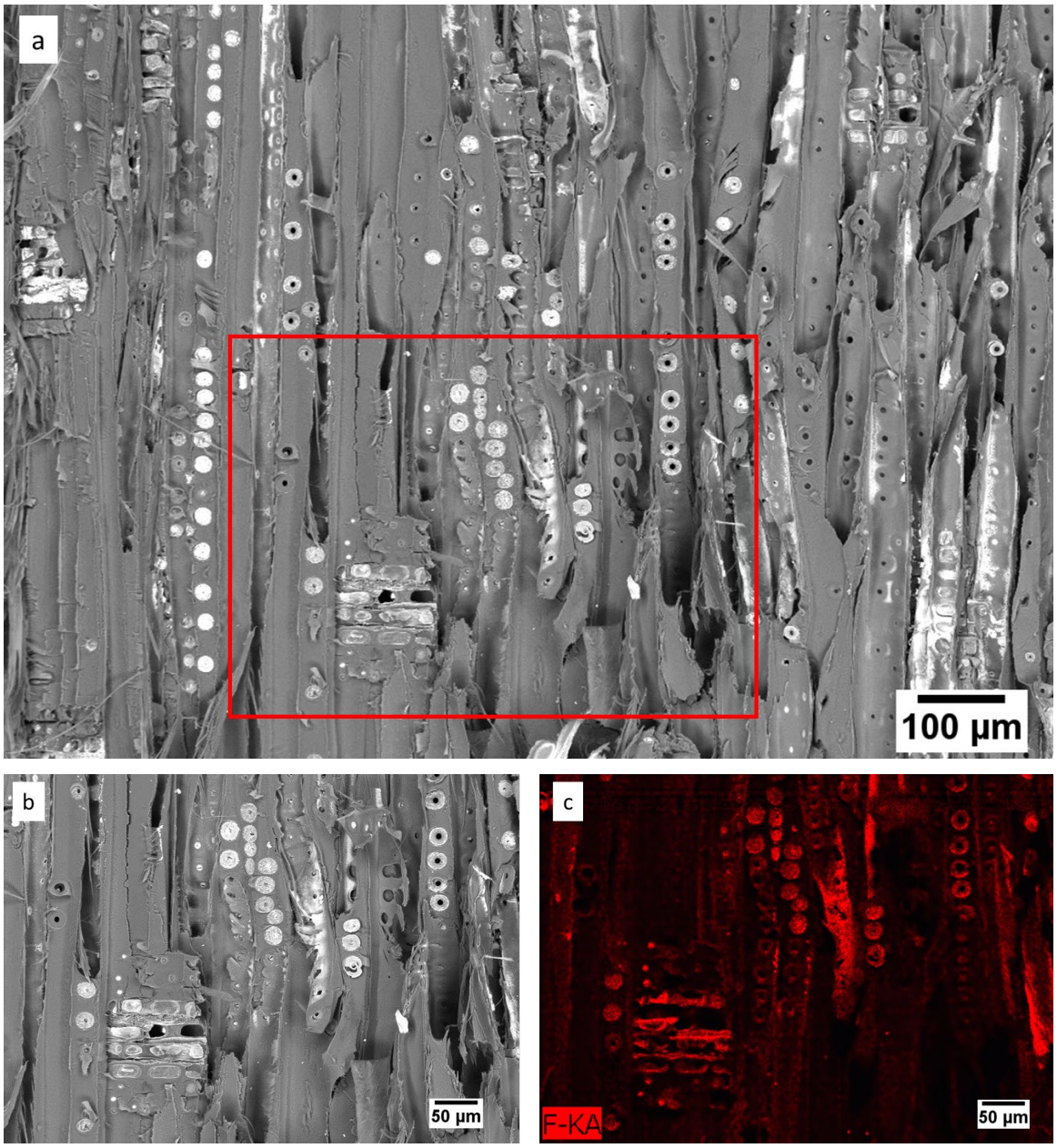


Fig.2.12 Radial longitudinal surface of Scots pine wood treated with NMF. BSE image showing bordered pits and ray tracheids (a) low and (b) high resolution. (c) EDX map of fluorine (red) in the ray tracheids and bordered pits.

In Fig.2.13, more evidence of NMFs in the ray tracheids is presented from the BSE image at an even higher magnification with its corresponding EDX map that confirms the fluoride composition of the accumulated aggregates. The NMF aggregates were mostly in the micrometer size (~10 µm).

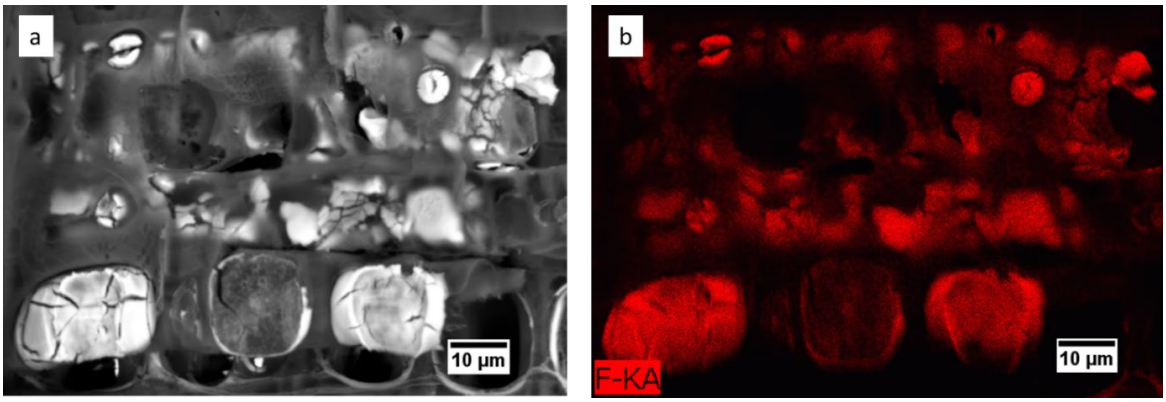


Fig.2.13 Ray tracheids of Scots pine wood treated with NMFs. (a) BSE image showing aggregates of NMF in ray tracheids (b) EDX map of fluorine (red) in the ray tracheids.

2.3.3 Transverse section of treated wood

BSE image of the transverse section of Scots pine wood treated with NMFs is presented in Fig.2.14.

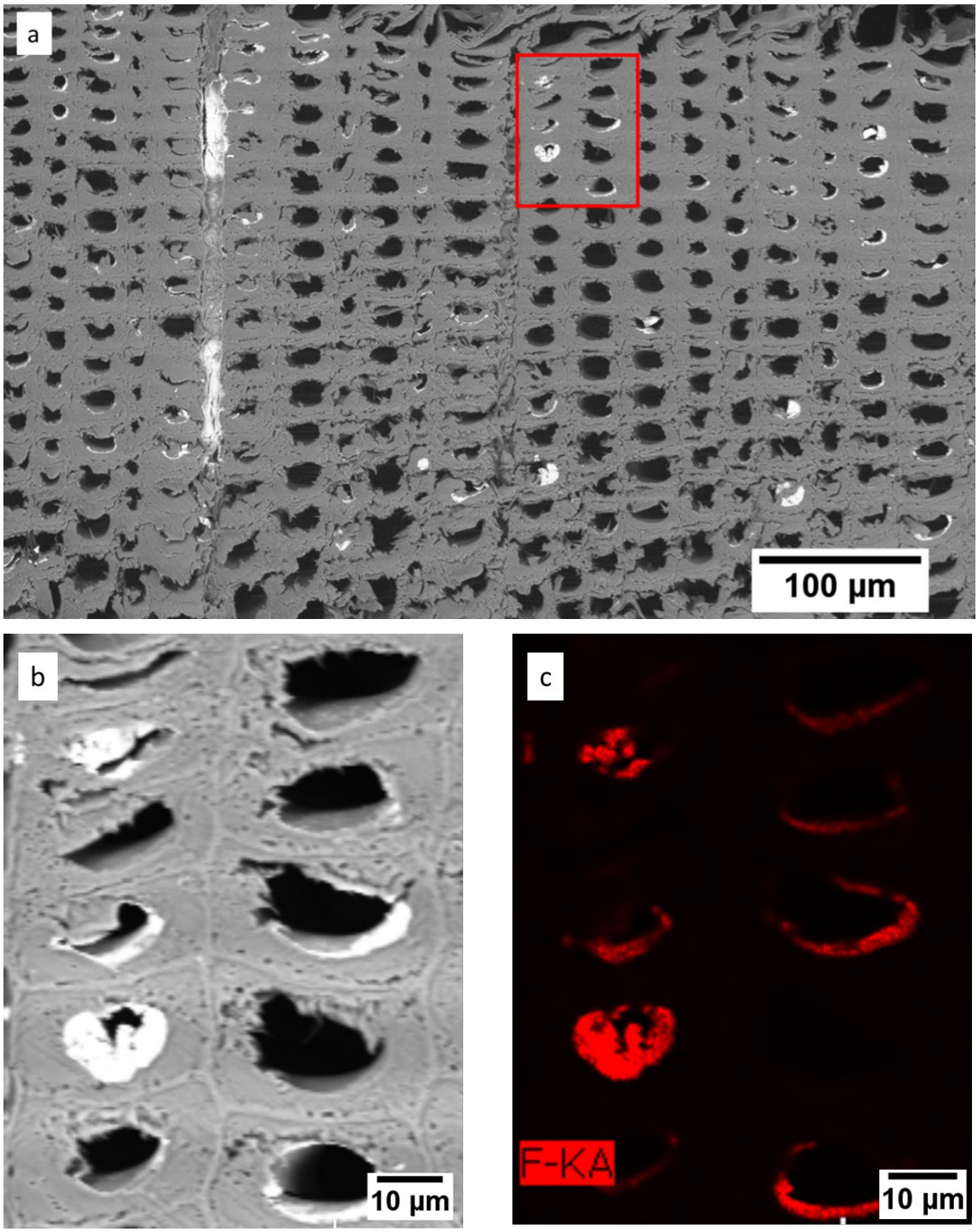


Fig.2.14 Transverse section of Scots pine wood treated with NMFs. BSE image showing aggregates of NMF in rays and latewood cell lumina (a) low and (b) high resolution. (c) EDX map of fluorine (red) in the latewood cell lumina.

In the transverse section shown in Fig.2.14b, the high-resolution BSE image of the latewood cells clearly contains deposits of NMFs in their lumina. The corresponding EDX map in Fig.2.14c confirms the fluoride composition of the deposited NMFs.

In Fig.2.15, earlywood cells are shown in the BSE image with its corresponding EDX map. In the earlywood cells, the NMFs are not present in large deposits. The larger width of earlywood cells allows greater movement of the nanoparticles which prevents the formation of larger aggregates as those observed in the latewood cells.

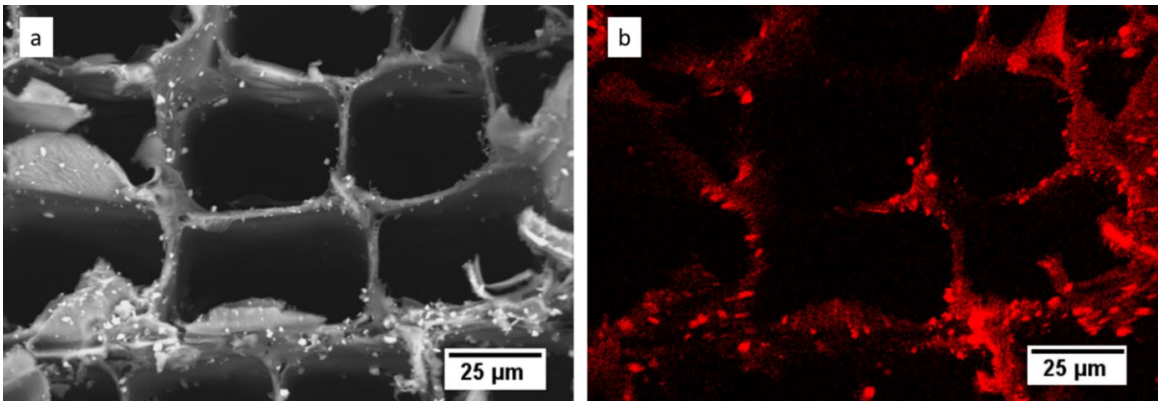


Fig.2.15 Transverse section of Scots pine wood treated with NMF. (a) BSE image showing aggregates of NMF scattered in earlywood cell lumina (b) EDX color map of fluorine (red) in earlywood cell lumina.

2.3.4 X-ray micro-computed tomography (X-ray micro-CT)

X-ray micro-CT is a non-destructive technique complementary to scanning electron microscopy and EDX. In X-ray micro-CT, series of radiographs are collected to generate a tomogram of the specimen. Thereby, it provides information on the spatial distribution of NMF in wood. Here, an X-ray micro-CT image of the transverse section from unleached NMF treated wood (Fig.2.16a) shows white spots which are evenly distributed in the lumina of the earlywood cells. These white spots are aggregates of NMFs that have deposited in the earlywood cells. However, it is difficult to confirm NMFs in the latewood cells. This is because fewer X-rays can pass through the dense latewood cells, which can also appear white as the NMF aggregates. In Fig.2.16b, it is observed that in the NMF treated wood that was leached, white deposits are present in the resin canals. This suggests that during the treatment of wood, the NMF aggregates are localized in the cell lumina. However, after

leaching they are redistributed into the resin canals, which is expected as the larger channels allow more freedom for NMFs to move within the wood matrix.

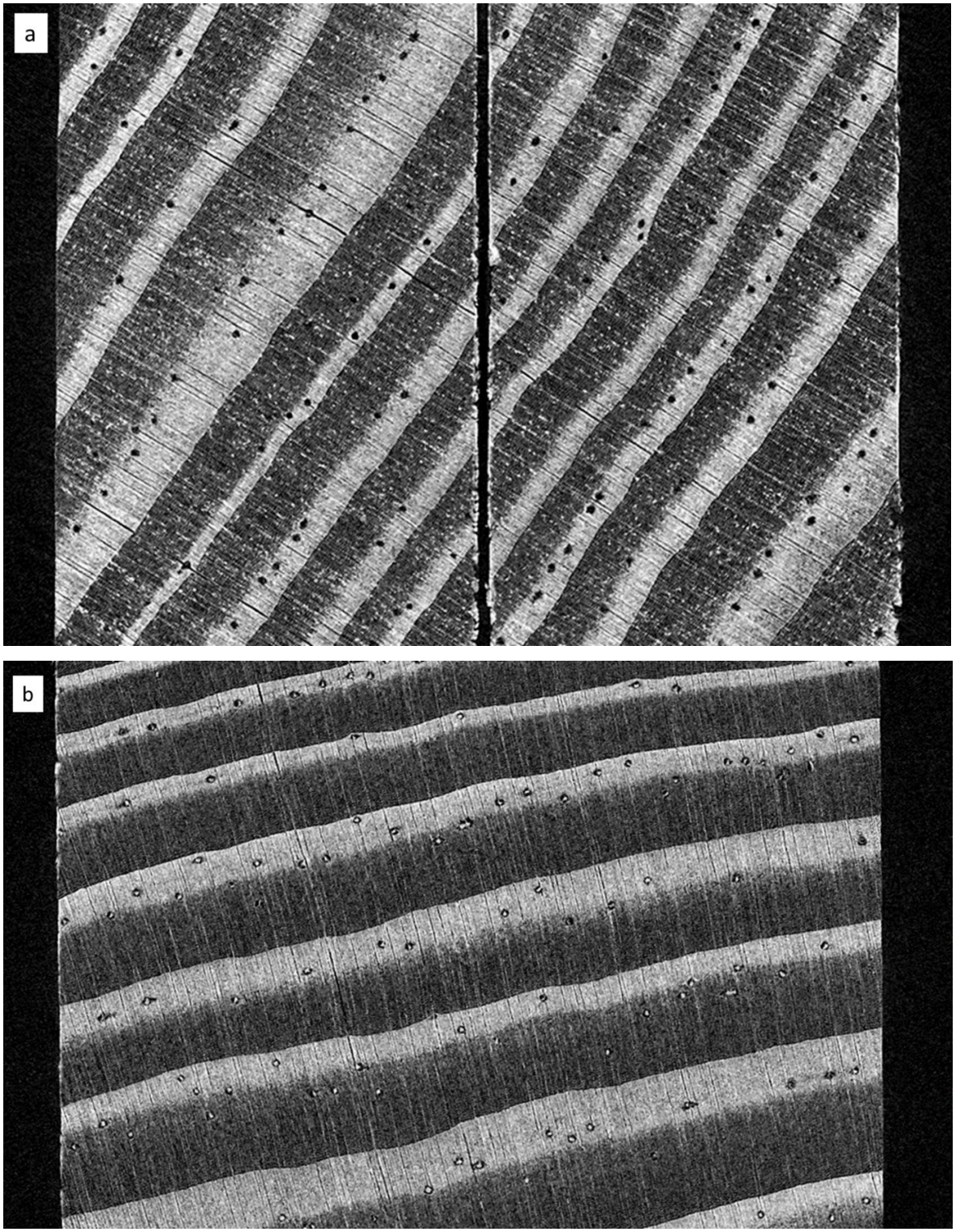


Fig.2.16 X-ray micro-CT images of the transverse section of Scots pine wood (20 mm x 15 mm) treated with NMF (a) before leaching (b) after leaching.

2.4 Summary

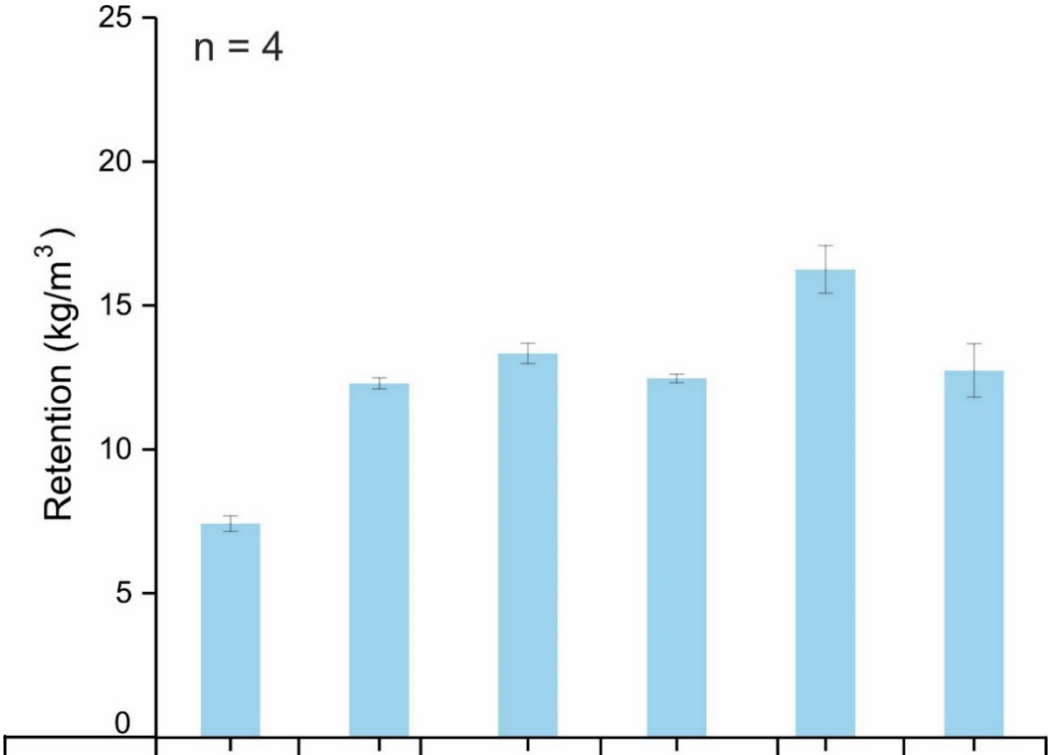
In this chapter, the composition and size of metal fluorides in the combination formulations was determined by XRD, DLS, TEM, and the corresponding elemental maps. Since the particle size of metal fluorides was smaller than 10 nm, they could distribute over a greater area inside wood during treatment. Moreover, solid-state ^{19}F MAS NMR spectrum showed that metal fluorides were present in treated wood even after it was leached. Taken together, images from electron microscopy and X-ray micro-CT provide a three-dimensional picture of the micro-distribution of NMFs in treated wood specimens. The images showed that deposits of NMFs are present in bordered pits, tracheids, latewood cells, and earlywood cells. This means that during the treatment process and later during conditioning of treated wood, agglomeration of metal fluoride particles occurred in the wood matrix. These results demonstrate that NMFs are well distributed within treated wood, a clear indicator that wood can be treated with sparingly soluble metal fluorides provided they are in nanoscopic form. This is promising for their eventual biocidal efficacy against wood-degrading fungi and insects. The next chapter presents results on the properties of NMF treated wood.

3. Properties of treated wood

To evaluate the future stability of the treated product, it is essential to consider how properties of wood change after the addition of a preservative. Ideally, the treatment of wood with a preservative should improve its dimensional stability and increase its hydrophobicity to protect it from decay. These properties of treated wood can be evaluated by measuring the equilibrium moisture content, anti-swelling efficiency, and contact angle. The following chapter presents the properties of nano metal fluoride (NMF) treated wood.

3.1 Retention

Retention is used to measure the amount of preservative remaining in wood after treatment and to estimate the weight of the treated product. From an economic perspective, preservatives that have proven biocidal efficacy with low retentions are preferred as it reduces the costs associated with treatment, processing, and shipping of a treated wood product. The Fig.3.1 shows the retention in Scots pine treated specimens.



Treatment	NaF	MgF_2	MgF_2+CaF_2	MgF_2+CaF_2	MgF_2	CaF_2
M (mol/l)	0.1	0.5	0.5	0.25 + 0.25	0.8	0.8
Solvent	H_2O	Ethylene glycol (EG)		EG lactic	EG	lactic

Fig.3.1 Retention in Scots pine treated specimens.

The NaF treated wood had the lowest retention of 7.5 kg/m^3 and MgF_2 (EG, 0.8 M) treated wood had the highest retention of 16 kg/m^3 (Fig.3.1). The rest of the treated specimens had similar retention values in the range of 12 to 13 kg/m^3.

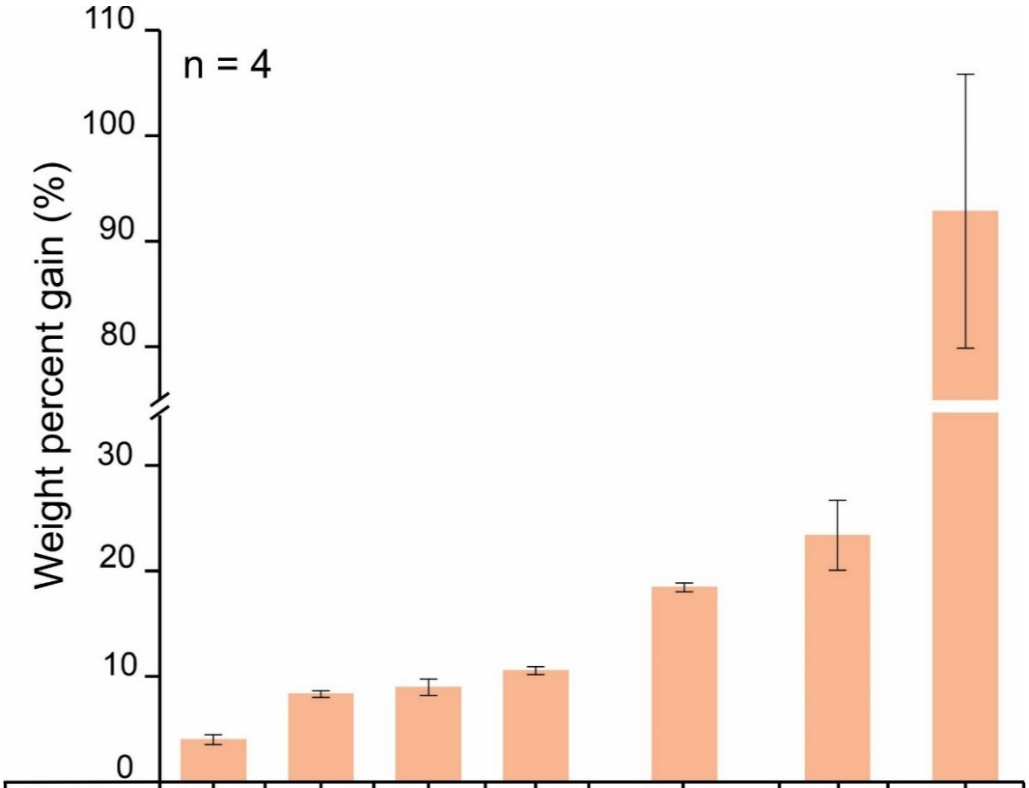
Commercial wood preservatives such as micronized copper[16] with azole co-biocides have retention in the range of 3 to 4 kg/m^3 approved for Use Class 4, much lower than the values presented in Fig.3.1. However, the retention values for NMF treated wood are comparable to retention values for wood treated with nanoparticles reported in literature.[18] Wood treated with zinc oxide nanoparticles had higher retention (45.7 kg/m^3) than those treated with nano zinc borate formulation (17.9 kg/m^3).[18] These values demonstrate the wide range of retention for nano-based treatment of wood. It is likely that the surface charge of some nanoparticles can promote their diffusion into micropores, causing a large amount to be incorporated into wood.[74] However, this needs to be confirmed for NMF treated wood in future experiments.

3.2 Weight percent gain

Weight percent gain (WPG) is the increase in the mass of wood after treatment. It is usually measured in wood that is chemically modified as an indicator of cell wall bulking. High WPG of treated wood is related to an increase in its mechanical strength.[112]

The WPG values of Scots pine treated specimens are presented in Fig.3.2. The highest WPG of over 90% was for lactic acid treated specimens, probably due to the polymerization of lactic acid monomers in wood. In comparison, the WPG of CaF_2 (lac) treated specimens was significantly lower as the aggregates of CaF_2 nanoparticles could have hindered the uptake of lactic acid molecules inside wood. From Fig.3.2, it is observed that NaF treated specimens had lower WPG as cell wall bulking was reduced with the use of water as solvent relative to lactic acid or ethylene glycol. The specimens treated with MgF_2 had significantly higher WPG than NaF treated specimens but significantly lower WPG than CaF_2 treated specimens.

Among the combination of MgF_2 and CaF_2, the single sol (EG) treated specimens had significantly lower WPG than the specimens treated in two steps with different solvents. Additionally, there was no significant difference in the WPG between MgF_2 and MgF_2+CaF_2 treated specimens as both treatments were done with only ethylene glycol as solvent. Therefore, the choice of solvent used in the NMF treatment of wood can determine its WPG and thereby its eventual mechanical strength.



Treatment	NaF	MgF_2	MgF_2	MgF_2 + CaF_2	MgF_2+CaF_2	CaF_2	Lactic acid (lac)
M (mol/l)	0.5	0.5	0.8	0.5	0.25 + 0.25	0.8	
Solvent	H_2O	Ethylene glycol (EG)			EG + lac	lac	

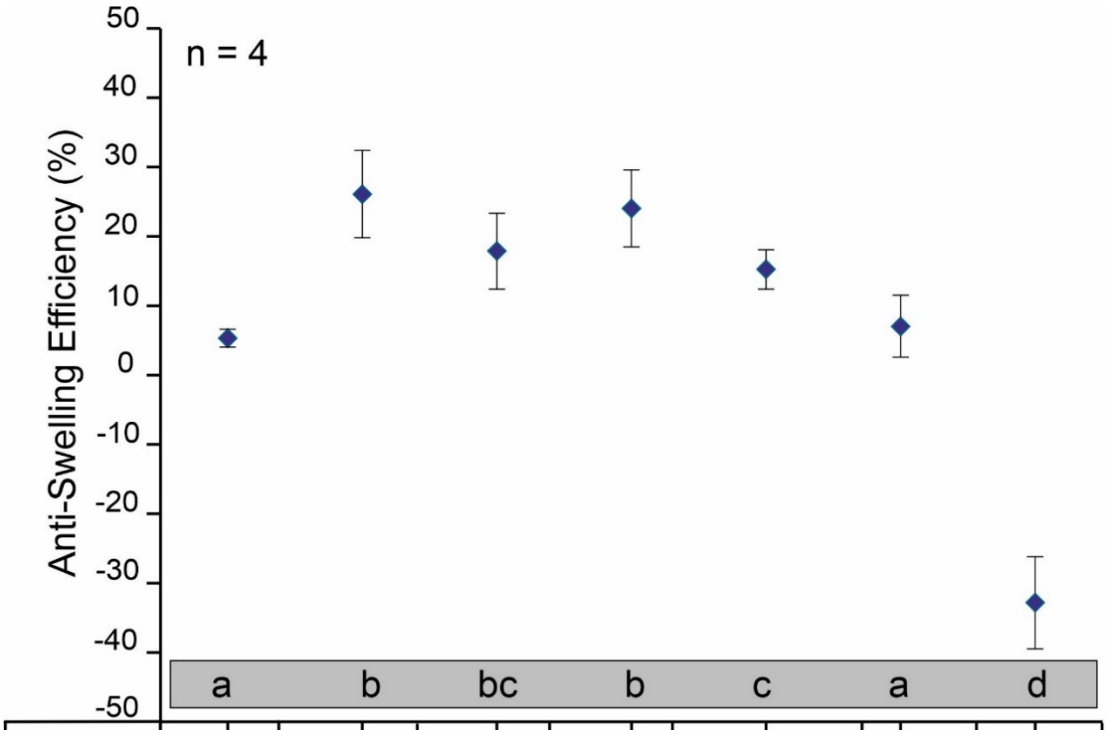
Fig.3.2 Weight percent gain in Scots pine treated wood.

These WPG values for MgF_2 treated specimens are significantly lower than that reported for acetylated pine, which has a WPG of 22.5%.[113] However, the WPG values of MgF_2 treated wood presented in this study are similar to that reported for TiO_2 sol-gel treated wood which has a WPG of 9%.[76] Thus, the WPG values reported here are similar to sol-gel treated wood and could be improved further by optimizing the solvent formulation used for NMF treatment of wood.

3.3 Anti-swelling efficiency

Anti-swelling efficiency (ASE) measures the swelling of treated wood in comparison to untreated wood. Ideally, a high ASE value of treated wood is related to an increase in its dimensional stability. In Fig.3.3, the ASE of Scots pine treated specimens are

presented. The shared letters over each treatment indicate that there is no significant difference among the treatments.



Treatment	NaF	MgF_2	MgF_2	MgF_2 + CaF_2	MgF_2+CaF_2	CaF_2	Lactic acid (lac)
M (mol/l)	0.5	0.5	0.8	0.5	0.25 +0.25	0.8	
Solvent	H_2O	Ethylene glycol (EG)			EG + lac	lac	

Fig.3.3 Anti-swelling efficiency in Scots pine treated wood. Shared letters indicate no significant difference and different letters denote a significant difference in ASE after paired t-test.

The lowest ASE (negative) was observed for lactic acid treated specimens (Fig.3.3). It could be that the addition of lactic acid led to the removal of extractives in wood leading to the rearrangement of lignin and hemicelluloses. The rearrangement caused more water molecules to penetrate the treated wood, which increased its swelling. Therefore, lactic acid increased the swelling of wood that resulted in a decrease in its dimensional stability. Ideally, an increase in WPG is related to an increase in ASE of treated wood.[112] Here, lactic acid treated wood had high WPG, followed with low ASE. This could be because the lactic acid treated specimens were not thermally cured after treatment for *in-situ* polymerization, the influence of which on dimensional stability could be assessed in future experiments.

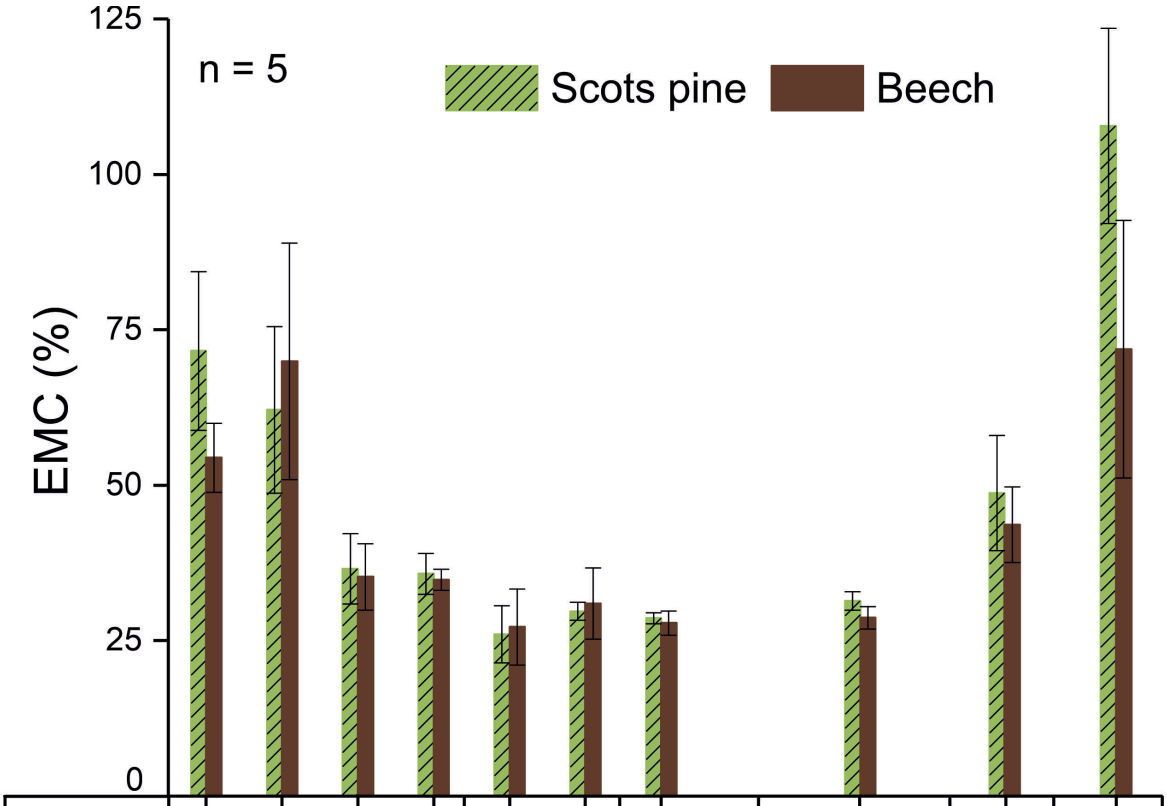
Compared to lactic acid treated specimens, the CaF_2 (lac) treated wood specimens had a significantly higher average ASE value. The CaF_2 (lac) treatment reduced the swelling of wood because the presence of CaF_2 nanoparticles inside wood could have reduced the uptake of water.

The average ASE values of CaF_2 (lac) and NaF treated specimens were similar. In contrast, MgF_2 (0.5 M and 0.8 M) treated specimens had higher and significantly different ASE values compared to CaF_2 (lac) and NaF treated specimens. Among the NMF combination formulation, specimens treated with the single sol in EG had a significantly higher ASE value than those treated with MgF_2 (EG) and CaF_2 (lac). Therefore, the dimensional stability of NMF treated wood is higher with ethylene glycol as a solvent rather than lactic acid.

The ASE values of NMF treated wood presented here are lower than those reported for TiO_2 sol-gel treated wood, which had an ASE of 34%.[76] The dimensional stability of acetylated wood is even higher with an ASE of 70%.[113] Also, a recent study found that wood treated with lactic acid oligomers and subsequently cured at 160°C had an ASE of 68%.[114] In the future, the dimensional stability of NMF treated wood could be further improved by methods such as combining it with thermal treatment.

3.4 Equilibrium moisture content

The moisture content of wood determines its susceptibility to wood decay. As described in the introduction, a high equilibrium moisture content (EMC) of wood is one of the conditions needed to initiate decay by fungi. Moisture content of 20% above wood fiber saturation (20% - 30%) is the minimum required by fungi to start colonization of wood. Thus, an ideal preservative would reduce the EMC of wood to inhibit decay. The following graph in Fig.3.4 shows the EMC in Scots pine and beech treated specimens at a temperature of 20°C and relative humidity (RH) of 65%. It is observed that treated specimens have a broad range of EMC values (Fig.3.4). Scots pine specimens treated with lactic acid had the highest EMC of over 100%. However, beech specimens treated with lactic acid had significantly lower EMC than Scots pine wood treated with lactic acid (p-value – 0.0013). This difference in the EMC of lactic acid treated specimens was due to differences in the leachability of Scots pine and beech. A higher amount of lactic acid molecules could have leached out from beech wood, which has vessels with larger diameters than from Scots pine, which has tracheids with smaller diameters.



Treatment	NaF				MgF_2		MgF_2 + CaF_2	MgF_2+CaF_2	CaF_2	lactic acid (lac)
	unleached		leached							
M (mol/l)	0.1	1	0.1	1	0.5	0.8	0.5	0.25 + 0.25	0.8	
Solvent	H_2O				Ethylene glycol (EG)			EG + lac	lac	

Fig.3.4 Equilibrium moisture content (EMC) in treated wood specimens.

In contrast to lactic acid treated specimens, the rest of the treated specimens had no significant differences between the EMC values for Scots pine and beech, as shown in Fig.3.4. The NaF (0.1 M and 1 M) treated specimens that were unleached had EMC higher than 50%. This is due to the known hygroscopic properties of NaF.[65] However, NaF treated specimens that were leached had EMC values similar to NMF treated specimens. It is evident that most NaF was lost in leaching, thus the leached NaF treated specimens were no longer hygroscopic which led to a decrease in their EMC.

The increase in the concentration of MgF_2 from 0.5 M to 0.8 M for wood treatment did not result in a proportional increase in the EMC of the specimens. Also, for the combination of MgF_2 and CaF_2 formulations, single and two-step, there was no significant difference between their EMC. Specifically, for the NMF treatment concentration of 0.8 M, the CaF_2 (lac) treated specimens had significantly higher EMC than the MgF_2 (EG) treated

specimens. Therefore, to lower the EMC of treated wood with a single NMF treatment, the use of ethylene glycol as a solvent would be preferable to lactic acid.

3.5 Contact angle

The inclusion of hydrophobic molecules in wood during its treatment can reduce its wettability. Wetting of wood is a key attribute to evaluate its adhesion, coating, waterproofing, weathering, and penetrability. The water contact angle (CA) is an essential property to determine the penetration of an adhesive in wood.[115] A surface is characterized as hydrophobic if the CA is greater than 90° and superhydrophobic when CA is greater than 150°.[116] A study reported that a larger CA of wood after its treatment resulted in a shallower penetration of the adhesive.[115] Also, as moisture is an important determining factor for decay, low wettability of wood is favorable for its preservation. Thus, wood wetting property of treated wood can be fundamental to predicting its application and the length of its service life.

Low wettability is characterized by a hydrophobic surface. Fluorine has been known to impart hydrophobicity to the wood surface. For instance, wood treated with SiO_2 nanoparticles containing fluorine had an initial CA of 168°.[117] In another study, wood coated with TiO_2 nanoparticles and capped with perfluorohexane using plasma also resulted in a CA greater than 150°.[118] In the current study, measured CA values of NMF treated wood are presented. In addition to the measurement of CA, the time taken for the water droplet to be absorbed in wood was measured. The CA of water was measured every 30 seconds until it was absorbed into the wood specimen known as complete wetting. The water droplet will take a longer time to be absorbed on a hydrophobic surface than a hydrophilic surface and is used to characterize the surface wettability of treated wood. In this section, results of unleached treated specimens are presented, followed by results of treated specimens that were leached. Lastly, the measured CA of specimens treated with the NMF combination formulations, both unleached and leached, are provided.

3.5.1 Treated wood – unleached

In the following Fig.3.5, the wettability of treated wood was compared to untreated wood by recording the change in CA over time.

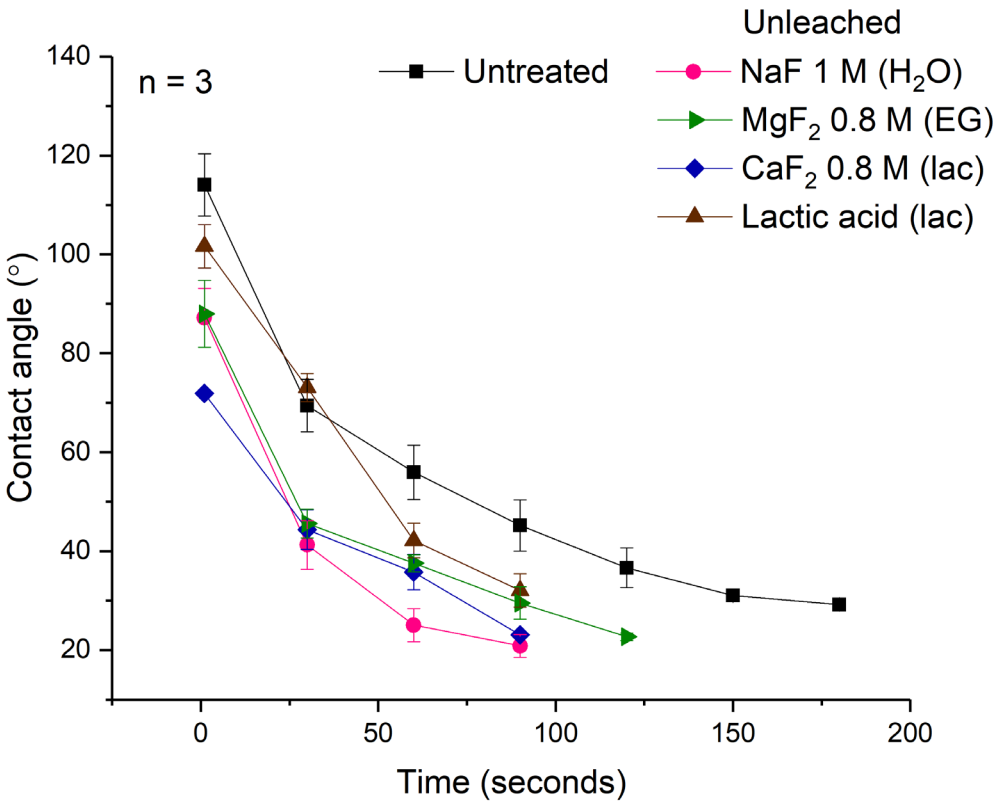


Fig.3.5 Contact angle comparison of untreated wood with unleached treated Scots pine wood. Ethylene glycol – EG, lactic acid – lac.

From Fig.3.5, it is observed that the untreated wood specimen had the highest initial CA of 114°, followed by lactic acid with a CA of 101°. The higher CA of lactic acid is due to their hydrophobic behavior, which is already known for polylactic specimens from literature.[119] The initial CA of the rest of the treated specimens was smaller than 90°, therefore their surfaces could be characterized as hydrophilic. Among these, CaF_2 (lac) treated specimens had the smallest initial CA of 72°. Thus, wood treated with CaF_2 (lac) and unleached would be more favorable to fungal colonization under humid conditions than wood treated with MgF_2 (EG) and unleached.

Of the specimens measured, the water droplet on untreated wood took the longest time for complete wetting. In comparison, complete wetting of water droplet was faster in specimens treated with NaF (1 M), lactic acid, and CaF_2 (0.8 M). Even though lactic acid treated wood had a higher initial CA than CaF_2 (lac) treated wood, the time taken for the water droplet to be absorbed was the same on both specimens. Thus, lactic acid treated wood has similar wetting behavior to CaF_2 (lac) treated wood. In summary, untreated wood has a more hydrophobic surface than unleached MgF_2, CaF_2, NaF, and lactic acid treated specimens. This could be because the solvent is still present in the unleached treated

specimens. To evaluate this assumption, CA of treated specimens that were leached were measured, and their results are presented in the next section.

3.5.2 Treated wood – leached

In Fig.3.6, the CA over time is presented for treated Scots pine specimens that were leached. For treated specimens (Fig.3.5), there was a difference in the overall wetting behavior between unleached and leached specimens. From Fig.3.6, it is observed that there was an increase in the initial CA (greater than 90°) for both MgF_2 and CaF_2 treated specimens. In contrast, the initial CA of NaF treated wood reduced from 87° in the unleached specimen to 80° in the leached specimen. Therefore, after leaching, the surface hydrophobicity decreased for NaF treated specimens but increased for NMF treated specimens.

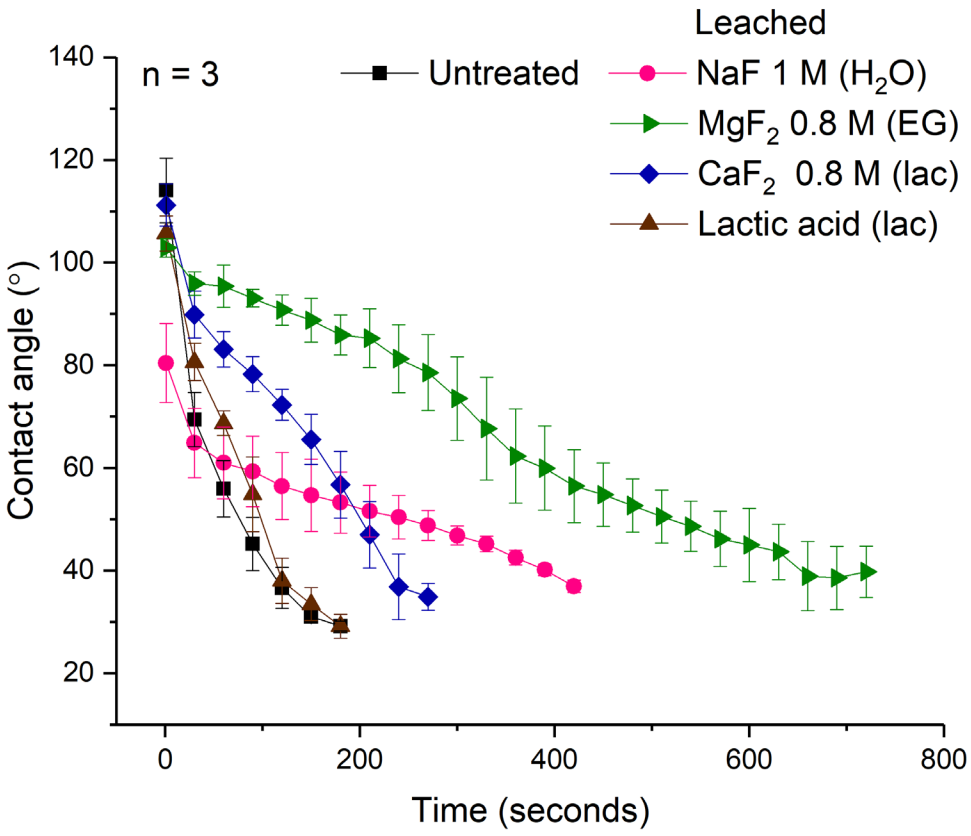


Fig.3.6 Contact angle of treated Scots pine wood specimens that were leached. Ethylene glycol – EG, lactic acid – lac.

In addition to the increase in the initial CA of the NMF treated specimens that were leached, there was also an increase in the time taken for their complete wettability. Compared to the untreated and unleached NMF treated specimens (Fig.3.5), the NMF treated specimens that were leached took a longer time for complete wettability. The longest

time was recorded for the specimen treated with MgF_2. The lactic acid treated specimen that were leached took twice as long for complete wettability compared to lactic acid treated specimen that were unleached. This could be due to the polymerization of the residual lactic acid in wood during or after leaching that eventually slowed down the absorption of the water droplet in wood. Overall, the time taken for complete wettability increased for all treated specimens that were leached. Therefore, the increase in the initial CA and the time taken for complete wettability of treated specimens that were leached relative to unleached treated specimens confirms the assumption that leaching of most of the solvent during the leaching process increases the hydrophobicity of the NMF treated wood surface.

3.5.3 Treated wood – combination of nano metal fluoride

In the following Fig.3.7, the CA over time for specimens treated with stand-alone MgF_2 (0.5 M) and the combination of MgF_2 and CaF_2 but in different formulations are presented.

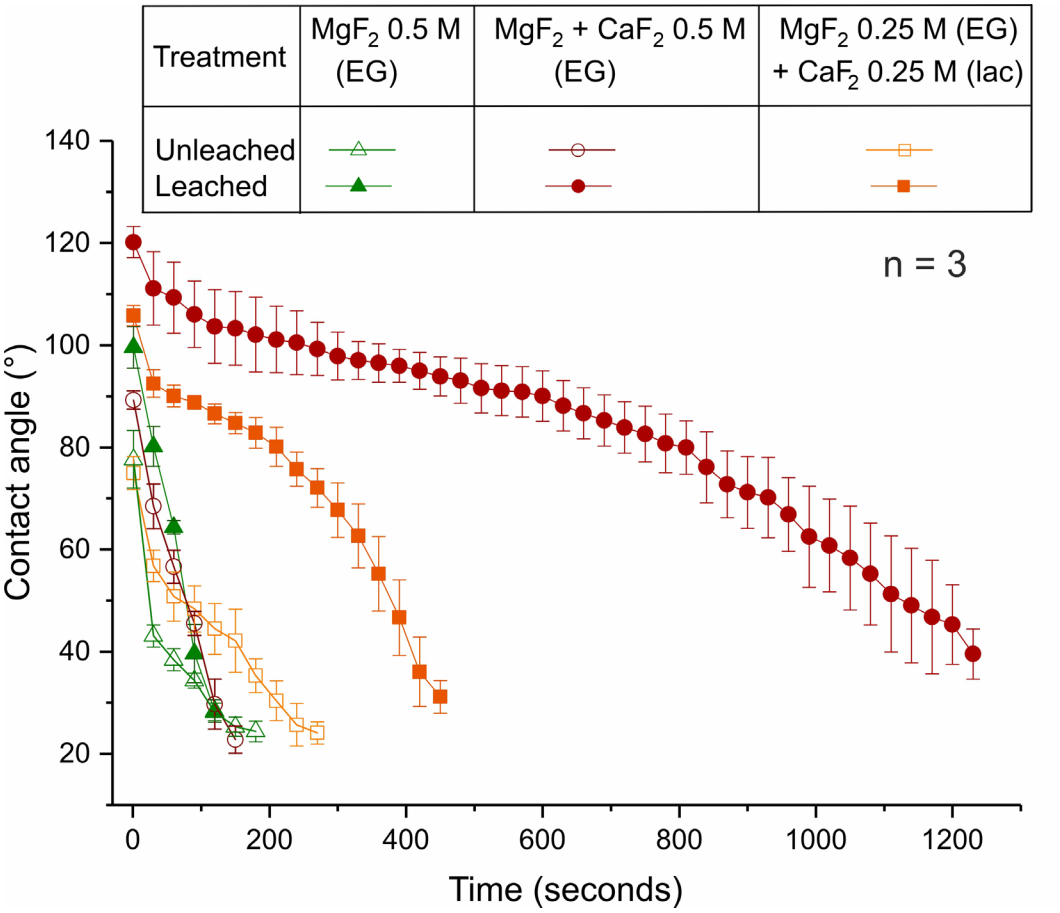


Fig.3.7 Comparison of change in contact angle for NMF treated Scots pine wood. Unleached specimens are empty symbols and leached specimens are filled symbols. Ethylene glycol – EG, lactic acid – lac.

All the treated wood compared in Fig.3.7 had the same NMF concentration of 0.5 M, but their formulations were different. The first was with only MgF_2, the second was with the combination of MgF_2 and CaF_2 in one sol in ethylene glycol (EG), and the third was with the combination of two sols; MgF_2 in ethylene glycol and CaF_2 in lactic acid.

Considering only the unleached NMF treated specimens, two observations are made from Fig.3.7. First, unleached wood treated with the single sol (MgF_2+CaF_2) in EG has a higher initial CA than unleached wood treated with the two-step combination. Second, the water droplet on the surface of unleached wood treated with the two-step combination took

longer for complete wettability than unleached wood treated with the single sol (MgF_2+CaF_2) in EG. In the unleached treated specimens, the surface of wood was more hydrophobic when it was treated with the combination of MgF_2 and CaF_2 relative to the stand-alone MgF_2.

Next, the treated specimens that were leached were evaluated to differentiate which of the two tested NMF combination formulations is better in terms of reducing the wettability of the wood surface.

Among the leached specimens, the single sol combination treatment had the larger initial CA of 120° than the two-step treatment with an initial CA of 106°. The time taken for complete wettability of wood treated with the single sol combination treatment was much longer (> 1200 seconds) than with the two-step treatment (< 500 seconds). From Fig.3.7, it is observed that on the surface of wood treated with the single sol (MgF_2+CaF_2), the water droplet had a gradual decrease in CA relative to the two-step combination treatment in which the water droplet had a steep decline in CA.

These NMF treated wood surfaces are not superhydrophobic. However, the treatment with the combination of MgF_2 and CaF_2 did improve its hydrophobicity in comparison to the untreated specimen. Overall, wood treated with the single sol of MgF_2 and CaF_2 and then leached had the most hydrophobic surface. Thus, among the NMF treated specimens it would provide the least favorable conditions for wood decay. The initial CA (120°) of the NMF treated specimen is the same as the CA reported for specimens that were thermally modified and then treated with TiO_2 nanoparticles.[120] In contrast, the CA of acetylated radiata pine is reported to be less than 80°.[121] Therefore, the hydrophobicity of NMF treated wood is better than acetylated wood and on the same level as TiO_2/thermally modified specimens. This suggests that moisture uptake in NMF treated wood would be lower and possibly slower than acetylated wood. Thus, the NMF treated specimens would reduce the likelihood of a fungal attack by reducing the moisture uptake in wood.

3.6 Accelerated ageing - leaching

An ideal preservative would have a low susceptibility to leaching such that it can extend the service life of the treated wood product. The EN 84 (1997)[122] is a leaching test modeled on creating an accelerated ageing environment for treated wood to evaluate its susceptibility to outdoor exposure conditions. Specimens treated with NMF using lactic

acid as a solvent are not reported here as the lactic acid interferes in the measurement of fluoride concentration.

3.6.1 Scots pine

The concentration of fluoride released over 15 days in leachates from Scots pine treated wood specimens in accordance with the EN 84 (1997)[122] standard is shown in Fig.3.8.

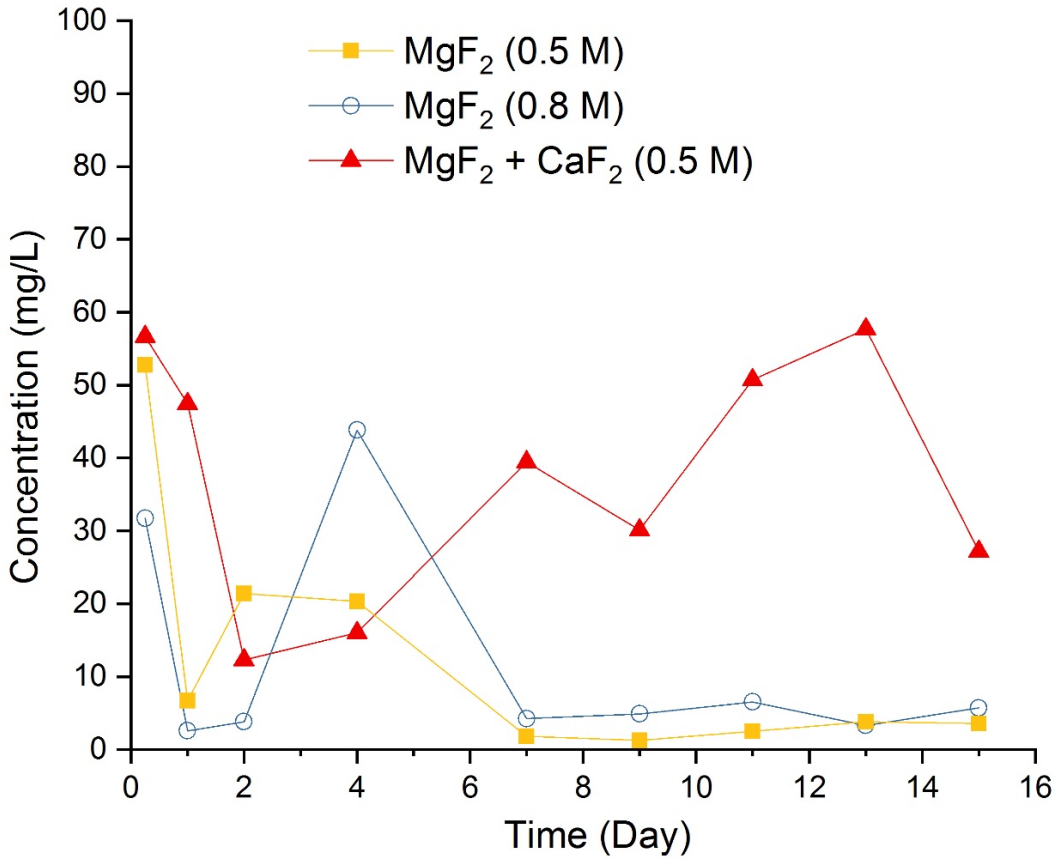


Fig.3.8 Fluoride released from NMF treated Scots pine specimens in EN 84 test. The concentration of the MgF_2 + CaF_2 system was 0.5 M.

Wood treated with MgF_2 (0.5 M) had the highest concentration of fluoride leached at the start of the experiment (Fig.3.8). In wood treated with MgF_2 (0.8 M), the highest concentration of fluoride leached was delayed until Day 4. From Day 7 onwards, the release of fluoride from specimens treated with only MgF_2 (0.5 M and 0.8 M) stabilized to very low amounts until the end of the experiment.

In contrast, specimens treated with the combination of MgF_2 and CaF_2 had two spikes in fluoride release during the duration of the experiment. The first spike was at the

beginning, followed by another spike towards the end. Unlike the stand-alone MgF_2 treatments in wood, the concentration of fluoride released from wood treated with the NMF combination formulation remained relatively higher till the end of the experiment.

Two conclusions can be made from these results. First, wood treated with the combination of MgF_2 and CaF_2 releases higher fluoride in leachates than wood treated with stand-alone MgF_2. Second, although relatively more fluoride was lost through leaching from wood treated with the combination of MgF_2 and CaF_2, the concentration did not stabilize to low levels as it did for wood treated with the stand-alone MgF_2 treatments. Thus, it is expected that the specimens treated with the NMF combination formulation and leached would have more fluoride present in them after leaching than specimens treated with only MgF_2, which could have implications for their eventual biocidal efficacy. More fluoride present after leaching would imply longer-term protection for specimens treated with the NMF combination formulation.

3.6.2 Beech

The leaching of fluoride over 15 days in leachates from NMF treated beech wood specimens following the EN 84[122] test is presented in Fig.3.9. The leaching behavior of the NMF treated beech was expected to be different from NMF treated Scots pine because of the higher permeability of the former wood species, as described in the introductory chapter (1.3.3).[35] In Fig.3.9, it is seen that the leaching trend was similar for beech wood treated with stand-alone treatment of MgF_2 (0.5 M and 0.8 M). The stand-alone MgF_2 treatments of beech wood specimens leached the highest concentration of fluoride on Day 2, after which the concentration reduced steeply over the following day. At Day 2, the concentration of fluoride leached out from specimens treated with MgF_2 (0.5 M) was lower than MgF_2 (0.8 M). Thus, more fluoride is released from wood treated with higher fluoride concentration, which is expected as more preservative is leached from wood treated with a higher concentration of preservative according to previous studies.[123] Beech wood treated with the NMF combination formulation leached a relatively higher amount of fluoride compared to beech wood treated with stand-alone MgF_2. This is similar to leaching results from Scots pine treated with the combination of MgF_2 and CaF_2 (Fig.3.8).

The combination of MgF_2 and CaF_2 treated specimens leached the highest concentration of fluoride on Day 13 of the leaching experiment. Therefore, the combination of MgF_2 and CaF_2 delayed the leaching of fluoride from beech wood. This finding is

different from what is observed in conventional wood preservatives, where most leaching occurs in the first month of the service life of wood.[123] The delay in the peak release of fluoride from NMF treated beech wood is promising as it suggests that leaching of fluoride can be slowed down. So, even in wet conditions, sufficient fluoride would be present in wood for longer-term protection from wood-degrading fungi and insects.

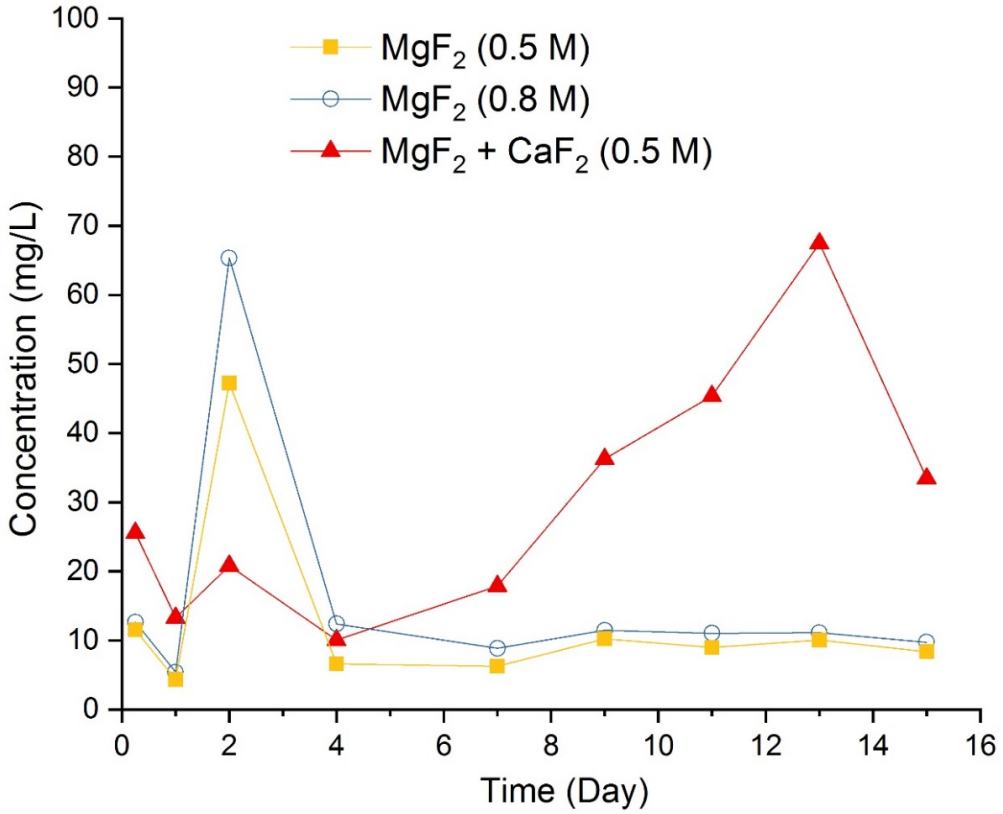


Fig.3.9 Fluoride released from NMF treated beech wood specimens in EN 84. The concentration of the MgF_2 + CaF_2 system was 0.5 M.

3.7 Summary

This chapter presented properties of NMF treated wood, which can influence its biocidal efficacy. In metal fluoride formulations, EG as a solvent is more favorable to reduce its wood moisture content and increase its dimensional stability. Moreover, treating wood with the combination of MgF_2 and CaF_2 in EG reduces the wettability of its surface. Additionally, treatment of beech wood with the NMF combination formulation delayed the leaching of fluoride. In conclusion, NMF treated wood with improved material properties can protect it from decay and damage caused by fungi and insects. The next chapter presents results on the efficacy of NMF treated wood against fungi.

4. Efficacy: Fungi

In the fungal test EN 113 (1996),[124] treated specimens are placed under severe exposure to a fungus for 16 weeks and then evaluated based on mass losses. In this test, a preservative treatment is considered to meet the biocidal efficacy requirement when the wood mass loss is equal to or less than 3% and then the resultant treated wood can be classified as durable. Unless specified otherwise, all the treated specimens were leached before the test in accordance with the EN 84 (1997) standard.[122]

This chapter begins with the results of NaF treated wood specimens against fungi. This is followed by the evaluation of solvent treated wood and then results on nano metal fluoride (NMF) treated wood. Following which, results on mass losses in wood treated with NMF in combination with copper are provided. Then results from an *in-vitro* agar test are presented. Lastly, results from the above tests were used to optimize the NMF composition and formulation for the second set of EN 113 tests.

4.1 Efficacy and limitation of NaF as a wood preservative

NaF, which has a solubility limit of 1 M, was dissolved in water for treatment with wood. The Fig.4.1 shows the mass losses in NaF treated wood caused by brown-rot fungi and white-rot fungus. Four observations can be made from the mass loss results in Fig.4.1. Firstly, wood specimens treated with NaF that were unleached had an average mass loss lower than 3% after the EN 113 test. Even specimens treated with a low concentration of 0.1 M NaF were protected against decay with no significant differences in the mass losses caused by the three fungi; *C. puteana, R. placenta,* and *T. versicolor*. Secondly, mass losses caused by fungi were similar between 0.1 M NaF and 1 M NaF unleached treated wood. Thus, a high concentration of NaF is not needed for protection from wood-degrading fungi, as even 0.1 M NaF was sufficient for biocidal efficacy against the three fungi.

The third observation from Fig.4.1 is that specimens treated with NaF, leached, and then tested were severely degraded by the three fungi. All NaF treated specimens that were leached had mass losses higher than 3%. Moreover, there was no statistical difference in the mass losses caused by the fungi to 0.1 M and 1 M NaF treated specimens that were leached. Even 1 M NaF treated and subsequently leached specimens did not provide adequate protection against any of the three fungi. Therefore, the concentration of fluoride left behind in 1 M NaF treated specimens after leaching is expectedly not enough to protect it from fungal attack.

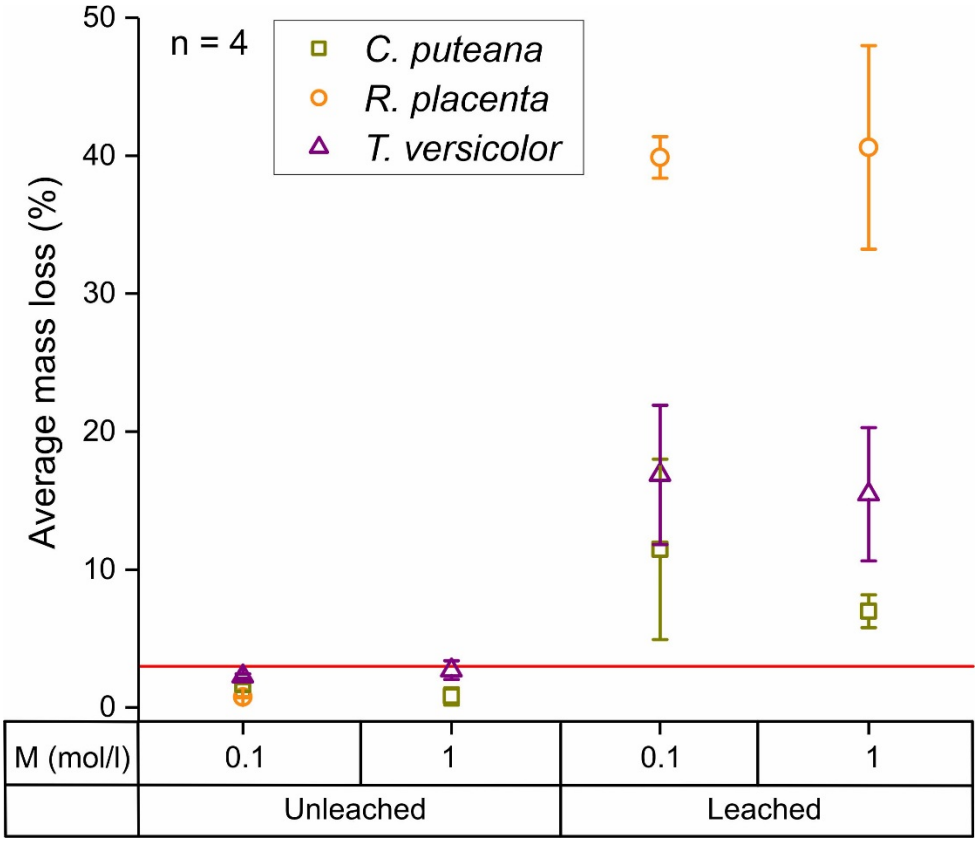


Fig.4.1 Mass loss (%) caused by fungi in unleached and leached wood treated with NaF. The red line is the mass loss cut-off at 3% for durability classification.

The fourth observation is that there were differences in the decay of NaF treated wood specimens that were leached depending on the fungi. The highest increase in mass loss after leaching was measured for NaF treated specimens against *R. placenta* and the lowest against *C. puteana*. Among the three fungi that were tested, *R. placenta* had the highest tolerance to fluoride. Therefore, a higher concentration of fluoride would be needed to protect wood from it.

The protection of NaF treated wood specimens against fungi is reduced because most of the fluoride is lost during leaching, which is expected due to its high-water solubility (40 g/L).[92] Therefore, commercial preservative formulations containing NaF also include fixatives such as chromium to prevent loss of fluoride through leaching, although its use is restricted due to environmental and health concerns. An ideal wood preservative formulation of fluoride would not need additional fixatives to minimize their leaching. This leads to the idea of using sparingly soluble fluorides such as MgF_2 and CaF_2. To impregnate these low-water soluble fluorides into wood they are synthesized as nanoparticles using

fluorolytic sol-gel synthesis. In this study, MgF_2 and CaF_2 were evaluated for their biocidal efficacy to replace traditional fluoride compounds such as NaF used in wood preservation.

4.2 First set of fungal tests

In the EN 113 test, virulence (no treatment) specimens are tested to determine that the fungal strain used for testing is performing at the optimal level. For the fungi to be considered an active strain, virulence wood specimens at the end of the EN 113 test should have a minimum mass loss of 20%.[124] The average mass loss of virulence specimens from the first set of tests are shown in Table 4.1.

Table 4.1 First set of virulence samples

Fungi	Mass loss (%)	Standard deviation
C. puteana	27.6	4.7
R. placenta	16.3	4.9
T. versicolor	21.1	2.4

The mass loss for virulence wood specimens exposed to *C. puteana* and *T. versicolor* was above 20% (Table 4.1). The mass loss for virulence specimens against *R. placenta* was 16 ± 4.9%, which suggests that the fungal strain was not active at the level required by the EN 113 standard. Although if the standard deviation value of virulence samples exposed to *R. placenta* is noted, then it could be considered as an active strain. Nonetheless, the following mass loss results for treated specimens against *R. placenta* give valuable information on the application of NMF to protect wood from fungal decay.

4.2.1 Solvent effect on wood-degrading fungi

NMFs are synthesized via sol-gel synthesis using solvents such as ethylene glycol and lactic acid. Therefore, only solvent treated wood specimens were tested to determine if they had any biocidal efficacy against fungi. The mass losses caused by the three fungi on solvent treated wood are shown in Fig.4.2. It is seen that the three solvent treatments in wood resulted in mass losses greater than 3% caused by the fungi. Notably, mass losses of ethanol treated specimens were greater than 20%, similar to mass losses of virulence

specimens (Table 4.1). Among the fungi, *C. puteana* is the most aggressive against ethanol treated specimens, causing an average mass loss above 40%. Notably, *R. placenta* caused an average mass loss higher than 20% in ethanol treated specimens, which was not observed in virulence specimens. Thus, the strain was more active on ethanol treated specimens than on virulence specimens. Treatment with ethanol could have promoted swelling of wood, which after its evaporation caused cracks that opened sites for fungal colonization resulting in high mass losses. Ethylene glycol treated specimens also had mass losses higher than 20%. The average mass loss caused by *T. versicolor* to ethylene glycol treated specimens was similar to average mass loss of ethanol treated specimens. Therefore, it can be concluded that treating wood with either ethylene glycol or ethanol does not protect it from decay caused by fungi.

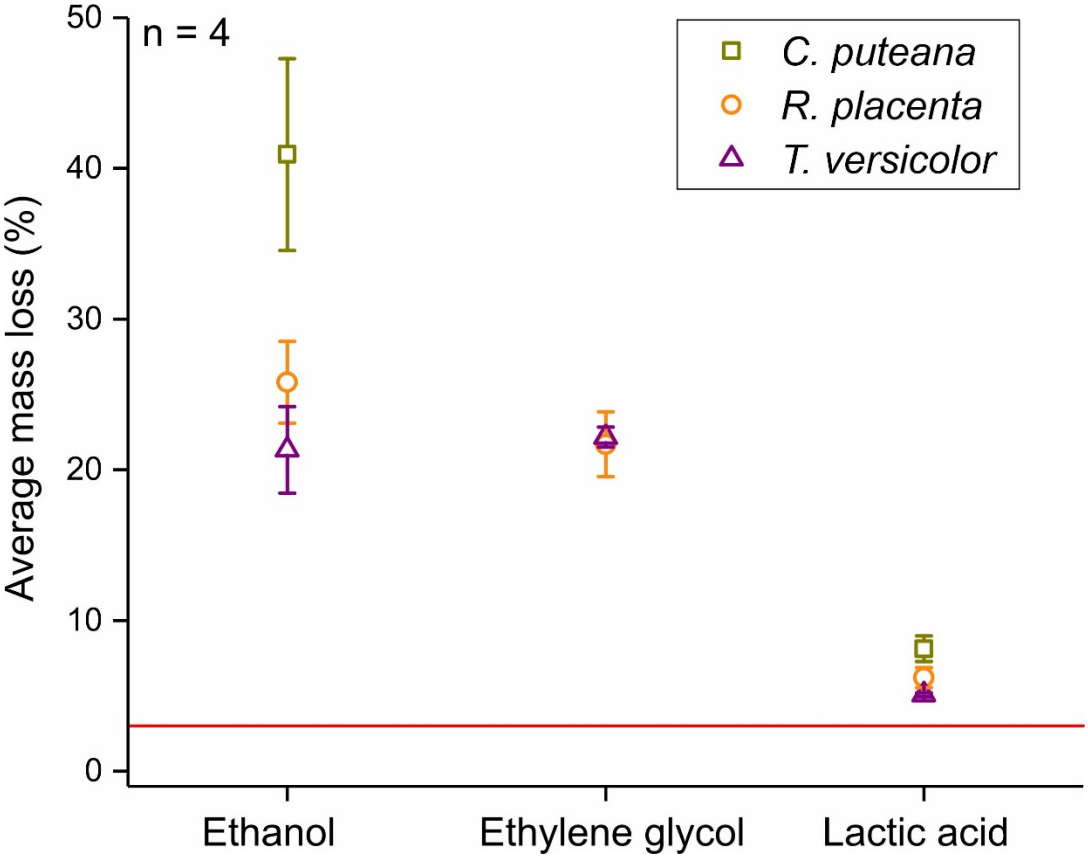


Fig.4.2 Mass loss (%) of solvent treated wood caused by fungi. The red line is the mass loss cut-off at 3% for durability classification.

Compared to ethylene glycol and ethanol treated specimens, the lactic acid treated specimens had lower mass losses (Fig.4.2). This is explained by the equilibrium moisture content (EMC) of over 70% in lactic acid treated specimens, as presented in the previous

chapter on the properties of treated wood (3.4). Their high EMC could have contributed to a slower growth of fungi on treated wood resulting in lower mass losses than those observed for ethanol and ethylene glycol treated specimens. Also, the acidity of lactic acid could have played a role in minimizing decay caused by fungi.[125] Nonetheless, lactic acid treated specimens did not have mass losses below 3%, the cut-off accepted for biocidal efficacy of a wood preservative.

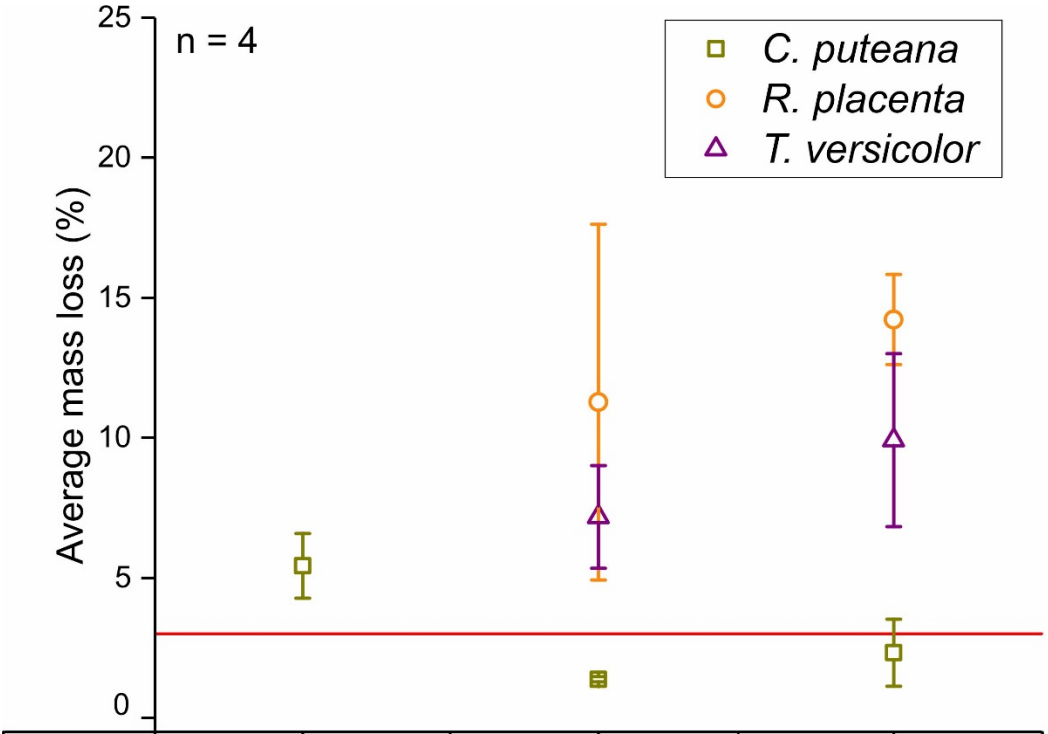
As described in the introduction, lactic acid oligomers were evaluated for biological resistance of wood by Grosse, et al. (2019).[58] In that study, wood was thermally cured at 160°C to initiate *in-situ* polymerization of lactic acid oligomers, which resulted in a mass loss of 2% caused by *T. versicolor* (formerly known as *Coriolus versicolor*).[58] The current study is different from that reported by Grosse et al. (2019), as here, lactic acid was combined with CaF_2 (without thermal treatment) to evaluate their synergistic efficacy against fungal activity in wood. The results of which are presented later in this chapter (4.4).

4.2.2 Efficacy of NMF treated wood

In the first set of fungal tests, MgF_2 and CaF_2 were tested in accordance with the EN 113 test for biocidal efficacy against two brown-rot fungi (*C. puteana*, *R. placenta*) and one white-rot fungus (*T. versicolor*), the results of which are shown in Fig.4.3. Mass losses caused by all three fungi were lower in MgF_2 treated wood than CaF_2 treated wood. This is expected as MgF_2 (130 mg/L)[91] is more soluble than CaF_2 (16 mg/L),[92] it releases more fluoride ions to counteract the fungal attack.

Treatment of wood with 0.1 M MgF_2 was not sufficient to protect it from decay by *C. puteana* as it resulted in an average mass loss above 5%. A higher concentration of NMF (0.4 M) was required in treated wood to reduce the mass losses to below 3% that were caused by *C. puteana*. In contrast, *R. placenta* had a higher tolerance to NMF as it resulted in wood mass losses greater than 10%. Likewise, *T. versicolor* had higher tolerance to NMF resulting in wood mass losses greater than 5% (Fig.4.3). Thus, treating wood with 0.4 M of either MgF_2 or CaF_2 was not sufficient to protect it from *R. placenta* and *T. versicolor*.

The first set of results demonstrate the efficacy of NMF treatment in wood against *C. puteana.* The next step was to improve the NMF formulation such that treated wood is protected from decay caused by *R. placenta* and *T. versicolor*, as well.



Treatment	MgF_2	MgF_2	CaF_2
M (mol/l)	0.1	0.4	0.4
Solvent	Ethylene glycol (EG)		

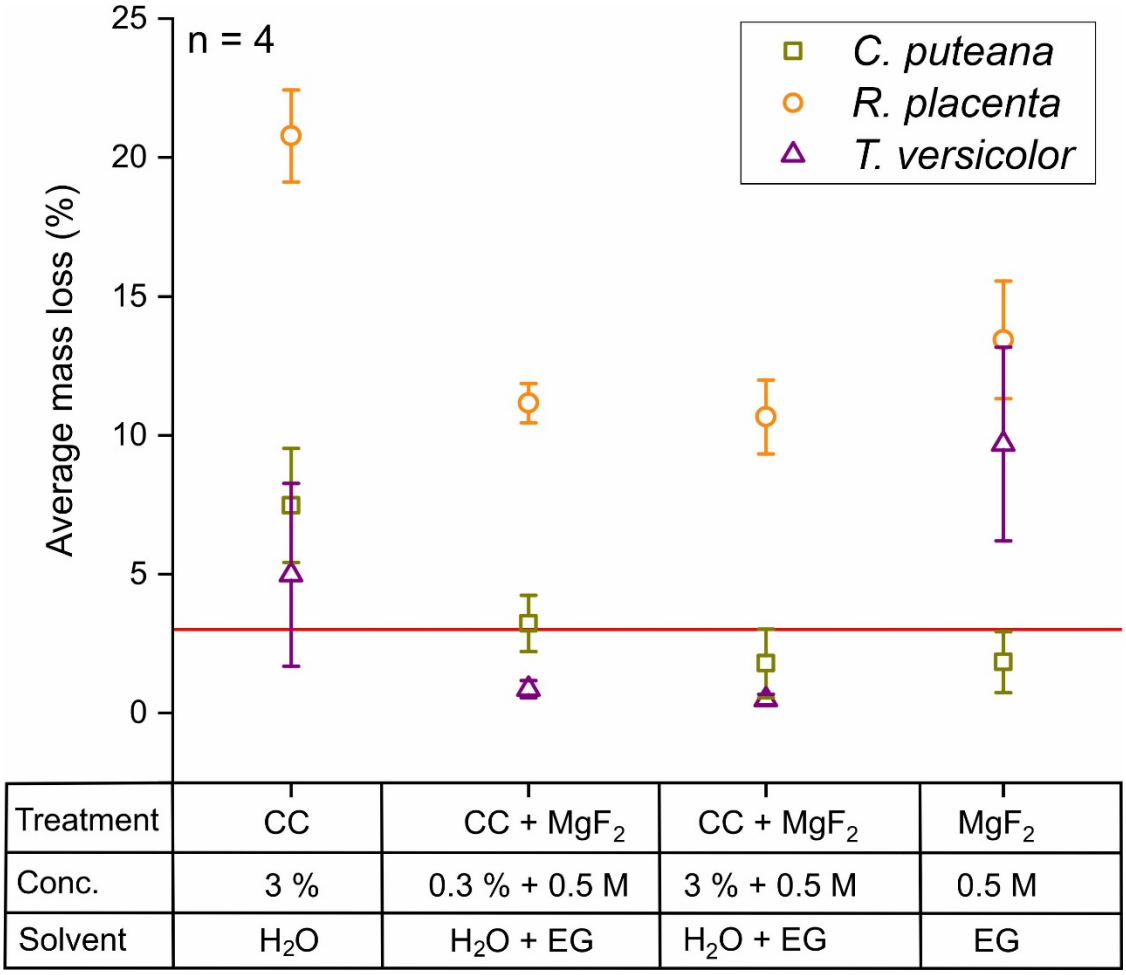
Fig.4.3 Mass loss of NMF treated wood caused by fungi. The red line is the mass loss cut-off at 3% for durability classification.

4.2.3 Addition of NMF to copper treated wood

In this section, MgF_2 was combined with copper (a commonly used active ingredient in wood preservative formulations) to evaluate if the resultant treatment in wood would protect it from decay caused by *R. placenta* and *T. versicolor*. In Fig.4.4, it is observed that the 3% formulation of copper chromate (CC) alone is not effective against the three fungi. However, with the addition of MgF_2 (0.5 M) to a 0.3% CC formulation for wood treatment, the mass loss caused by *T. versicolor* was reduced to below 3%. To protect against *T. versicolor*, increasing the concentration of CC from 0.3% to 3% was not needed as the mass loss was similar for both treatments.

Similarly, the addition of MgF_2 to CC formulation in treated wood reduced the mass loss caused by *C. puteana*. Here, there was a difference between the CC concentration for the combination treatment. Although the difference between the combination treatments was not significant, an increase in CC concentration from 0.3% to 3% in addition to MgF_2 (0.5 M) was needed to meet the mass loss cut-off of 3% for biocidal efficacy and durability.

Even though mass loss caused by *R. placenta* was reduced from 21% in only CC treated specimens to 11% in the specimens treated with the combination of CC (0.3%) and MgF_2 (0.5 M), it was still above the cut-off of 3%. This leads to the conclusion that the combination of CC and MgF_2 does not meet the durability requirement needed to protect wood from *R. placenta*. Therefore, the NMF formulation needs to be further optimized such that the treated wood has biological resistance against decay caused by *R. placenta*.



Treatment	CC	CC + MgF_2	CC + MgF_2	MgF_2
Conc.	3 %	0.3 % + 0.5 M	3 % + 0.5 M	0.5 M
Solvent	H_2O	H_2O + EG	H_2O + EG	EG

Fig.4.4 Mass loss of treated wood with addition of copper chromate (CC) caused by fungi. The red line is the mass loss cut-off at 3% for durability classification.

4.3 Optimization of NMF formulation: *In-vitro* agar test

An *in-vitro* agar test was done to determine the range of fluoride concentration that will be toxic to fungi. The time and resources required for an *in-vitro* test are significantly less than those required for an EN 113 test. Thus, an *in-vitro* test is a faster and cheaper way to estimate the optimal fluoride concentration and formulation needed for biocidal efficacy

against fungal activity. The fungal growth rate was calculated by measuring the radial growth of the fungi in centimeters on the *petri* dish over fourteen days, as shown in Fig.4.5. Besides the toxicity of stand-alone NMF, the synergistic biocidal efficacy of combining MgF_2 and CaF_2 against fungi was also evaluated with this test.

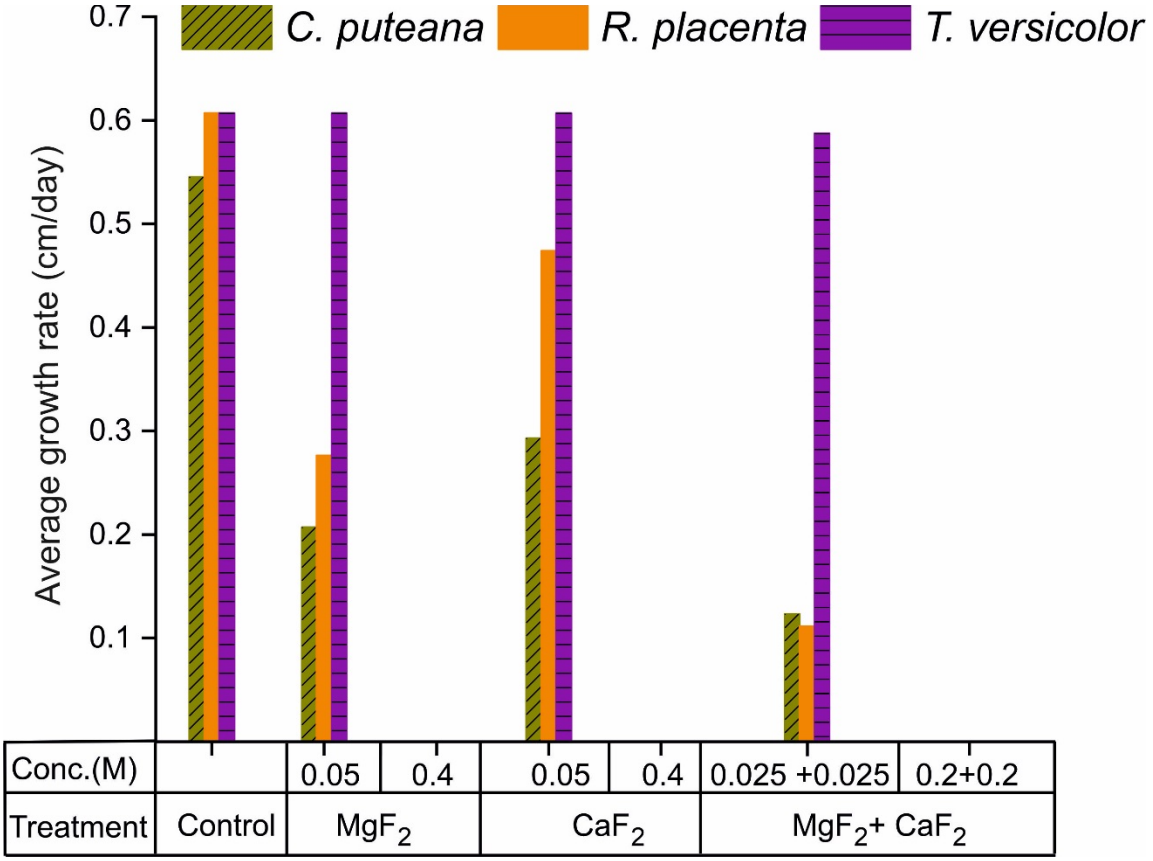


Fig.4.5 Growth rate of fungi in NMF treated medium. The measurements were done in triplicate. The standard deviations were in the range of 0.005 to 0.04. No growth was recorded for 0.4 M concentration for any NMF treatment.

In Fig.4.5, it is observed that the control showed the fastest growth for all three fungi. Comparing MgF_2 and CaF_2, the growth rate was slower for *C. puteana* and *R. placenta* in MgF_2-added medium than CaF_2-added medium (Fig.4.5). This result agrees with the first set of fungal tests where MgF_2 treated specimens had a lower average mass loss compared to CaF_2 treated wood (Fig.4.3). However, the medium with the combination of MgF_2 and CaF_2 performed better against *C. puteana* and *R. placenta* compared to the medium with formulation of either MgF_2 or CaF_2 alone. The growth rate of *C. puteana* in MgF_2-added medium (0.21 cm/day) was almost twice than the combination of MgF_2 and CaF_2 (0.12 cm/day). Likewise, against *R. placenta*, medium with the combination of MgF_2

and CaF_2 (0.1 cm/day) performed better than only MgF_2-added medium (0.27 cm/day). Based on these results, the efficacy of the NMF formulation at 0.05 M concentration against brown-rot fungi is ranked as follows.

$$MgF_2 + CaF_2 > MgF_2 > CaF_2$$

For white-rot fungus, *T. versicolor*, both the control and the NMF formulations at a concentration of 0.05 M had a similar growth rate. However, the growth rate of *T. versicolor* was slightly slower in the medium containing the NMF combination formulation than the stand-alone NMF, which proves the former has some resistance to *T. versicolor*.

In all NMF-mediums with a concentration of 0.4 M, no fungal growth was observed for any of the three fungi. This suggests that the concentration of NMF formulation needs to be increased for biocidal efficacy against the three fungi. Additionally, against brown-rot fungi, a formulation with a combination of MgF_2 and CaF_2 could have more efficacy than either MgF_2 or CaF_2 alone.

4.4 Second set of fungal tests

In the second set of tests, the average mass losses in the virulence specimens were lower than 20 % for all three fungi, as shown in Table 4.2. Thus, the activity levels of fungi were lower than optimal. If the standard deviation of virulence samples in Table 4.2 are considered, then they would be within optimal activity levels. Still, the following results are informative for fundamental research on the viability of NMF to protect wood from fungal decay.

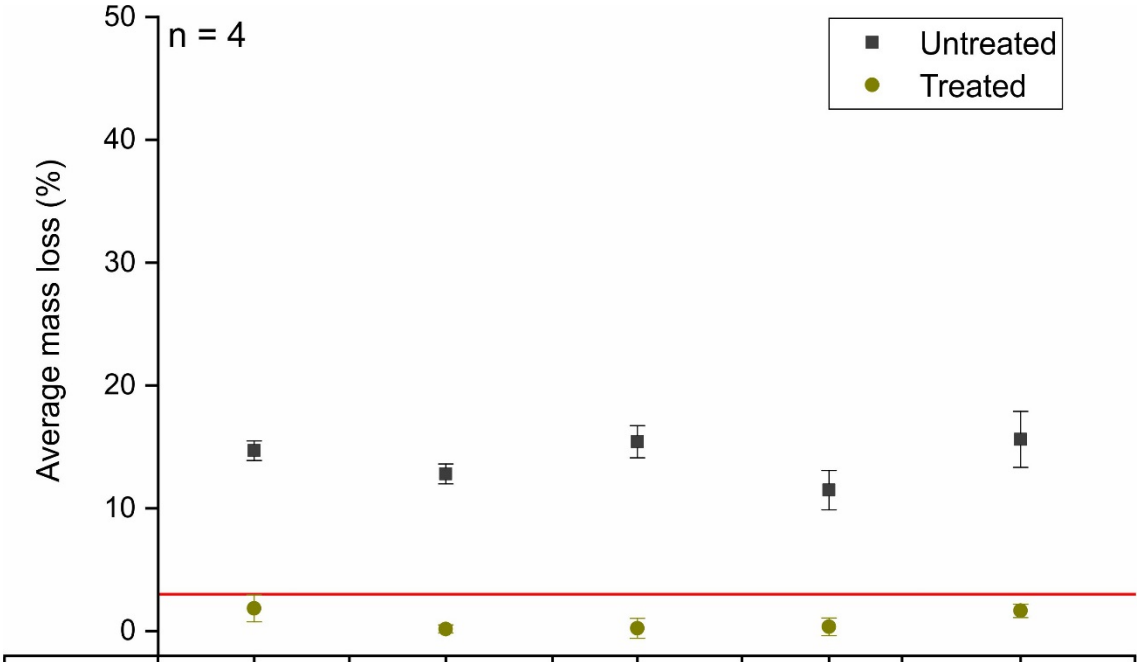
Table 4.2 Second set virulence

Fungi	Mass loss (%)	Standard deviation
C. puteana	15.7	5.1
R. placenta	18.4	2.3
T. versicolor	19.4	3.4

4.4.1 *Coniophora puteana*: NMF treated wood

The mass losses caused by *C. puteana* in the EN 113 test are compared in Fig.4.6. It is observed that mass losses in all untreated specimens were higher than 10%, while it was below 3% in all NMF treated specimens that were leached. The lowest average mass

loss of 0.17 ± 0.33% was measured in the specimens treated with the combination of MgF_2 and CaF_2 in ethylene glycol (EG). However, there was no significant difference in the mass losses among all treated specimens. Thus, all NMF treatments in wood reduced the mass loss caused by *C. puteana* relative to untreated specimens. This result agrees with the first set of fungal tests on *C. puteana* in section 4.2.2 of this chapter, where treatment of wood with NMF at 0.4 M also resulted in average mass losses below 3%.



Treatment	MgF_2	MgF_2 + CaF_2	MgF_2	CaF_2	CaF_2 + MgF_2
M (mol/l)	0.5	0.5	0.8	0.8	0.25 + 0.25
Solvent	Ethylene glycol (EG)			lactic	lactic + EG

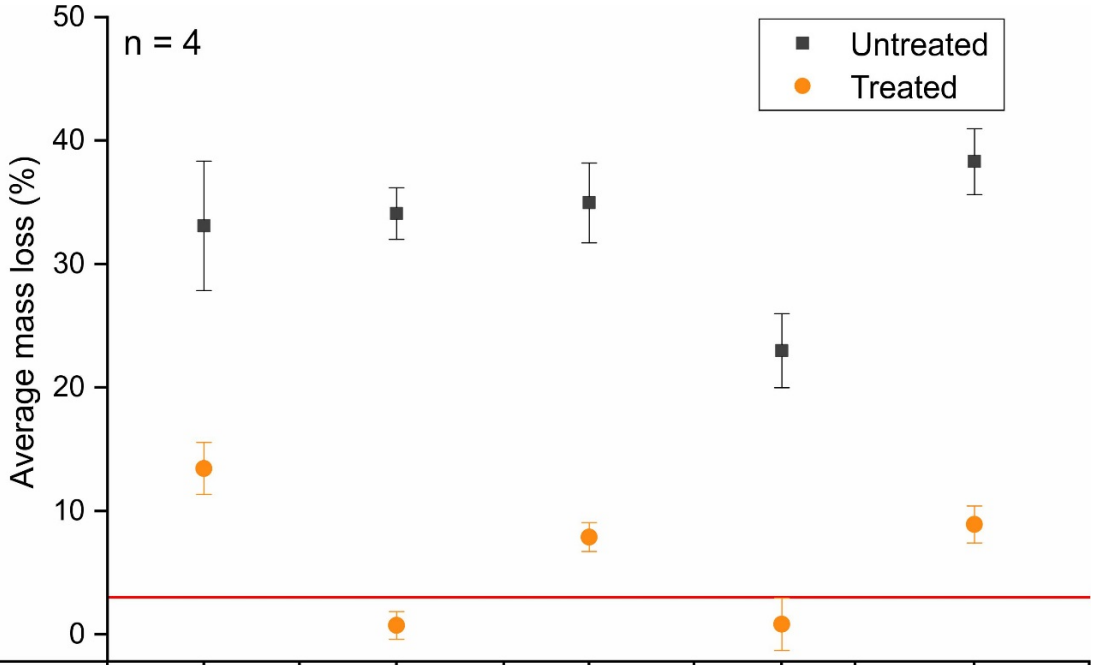
Fig.4.6 Mass loss of NMF treated wood caused by *Coniophora puteana*. The red line is the mass loss cut-off at 3% for durability classification.

Several studies have reported on the efficacy of nanoparticles to protect wood from decay caused by *C. puteana*. Unleached nano zinc oxide treated wood had a mass loss of 0.3% caused by *C. puteana*.[18] Similarly, unleached titanium alkoxide treated specimens had a mass loss of 0.8% caused by *C. puteana*.[76] One research group reported that *C. puteana* caused an average mass loss of 15% in Ag treated specimens that were leached.[126] Hence, Ag nanoparticles did not have efficacy against *C. puteana*. Another group reported that nano TiO_2/Ce treated spruce wood that was leached had efficacy against *C. puteana*.[81] However, they did not report the efficacy of the nano TiO_2/Ce treatment in wood against

white-rot fungi or termites. The next section presents results on the efficacy of NMF treated wood against *R. placenta*.

4.4.2 *Rhodonia placenta*: NMF treated wood

The mass losses in NMF treated specimens after exposure to *R. placenta* in the EN 113 test are compared in Fig.4.7. It is seen that the untreated specimens had high average mass losses (greater than 20%) compared to NMF treated specimens. Overall, the NMF treated wood specimens which had mass losses below 15% performed better than the untreated specimens.



Treatment	MgF_2	MgF_2 + CaF_2	MgF_2	CaF_2	CaF_2 + MgF_2
M (mol/l)	0.5	0.5	0.8	0.8	0.25 + 0.25
Solvent	Ethylene glycol (EG)			lactic	lactic + EG

Fig.4.7 Mass loss of NMF treated wood caused by *Rhodonia placenta*. The red line is the mass loss cut-off at 3% for durability classification.

Among the treatments, MgF_2 (0.5 M) specimens had an average mass loss higher than 10%, which is similar to the results of MgF_2 (0.4 M) treated wood from the first set of fungal tests (Fig.4.3). When wood was treated with a higher concentration of MgF_2 (0.8 M), the average mass loss was reduced to 7.8 ± 1.2%, although this was still above the 3% cut-off accepted for the efficacy of a preservative formulation. Wood treated with the

combination of MgF_2 (EG) and CaF_2 (lactic) had an average mass loss (8.9 ± 1.5%) similar to MgF_2 (0.8 M) treated wood. This suggests that the combination of MgF_2 (EG) and CaF_2 (lactic) was no better in biocidal efficacy against *R. placenta* than the stand-alone MgF_2 treatment.

In the second set of tests, only two treatments showed promise in protecting wood from *R. placenta* because they were the only NMF formulations that resulted in mass losses below 3%. The first one was wood treated with the combination of MgF_2 and CaF_2 synthesized in a single sol in EG, which resulted in the lowest average mass loss (0.71 ± 1.1%). The second formulation was CaF_2 (0.8 M) in lactic acid that led to an average mass loss of 0.81 ± 2.1%. Although wood treated with the combination of MgF_2 and CaF_2 in EG had the lowest mass loss, it was not significantly different to CaF_2 (0.8 M) treated wood (p-value – 0.37). Thus, both treatments imparted durability to wood against *R. placenta*. However, their mechanism for biological resistance against *R. placenta* may be different.

Unexpectedly, the two-step treatment of wood with CaF_2 (lactic) followed with MgF_2 (EG) did not result in similar mass losses relative to the treatment of wood with a single sol of MgF_2 and CaF_2 in EG. A comparison of their NMF formulation suggests that the solvent could have contributed to the difference observed in their mass losses.

Another unexpected observation from Fig.4.7 is that the wood specimens treated with CaF_2 (0.8 M) had lower mass loss than those treated with MgF_2 (0.8 M), as in the first set of tests, the latter treatment performed better. This is because in the first set, the CaF_2 formulation was in EG (Fig.4.3), while in the second, it was in lactic acid (Fig.4.7). Also, from Fig.4.7, it is observed that the untreated specimens associated with CaF_2 (0.8 M) treated specimens had average mass loss lower than 30%, which is in contrast to the higher average mass losses observed for the rest of the untreated specimens. In the EN 113 test, an untreated specimen is placed in the same Kolle flask along with the specific treated specimen for the duration of the experiment. This suggests that the fungal growth on the untreated specimen placed along with the CaF_2 (lac) specimen in the Kolle flask could have been affected by the lactic acid. The contribution of lactic acid to reduce wood decay caused by *R. placenta* is based on the results from sections 3.4 and 4.2.1. First, in section 3.4, it was shown that the equilibrium moisture content of CaF_2 (0.8 M) treated Scots pine wood was higher than 70% (Fig.3.4), which could have slowed down the fungal attack. Second, in section 4.2.1, it was shown that the lactic acid treated specimens had significantly higher

resistance to fungal attack compared to the ethylene glycol specimens (Fig.4.2). Thus, the inclusion of lactic acid in CaF_2 formulation for wood treatment improved its efficacy such that it was even better than the MgF_2 formulation in EG.

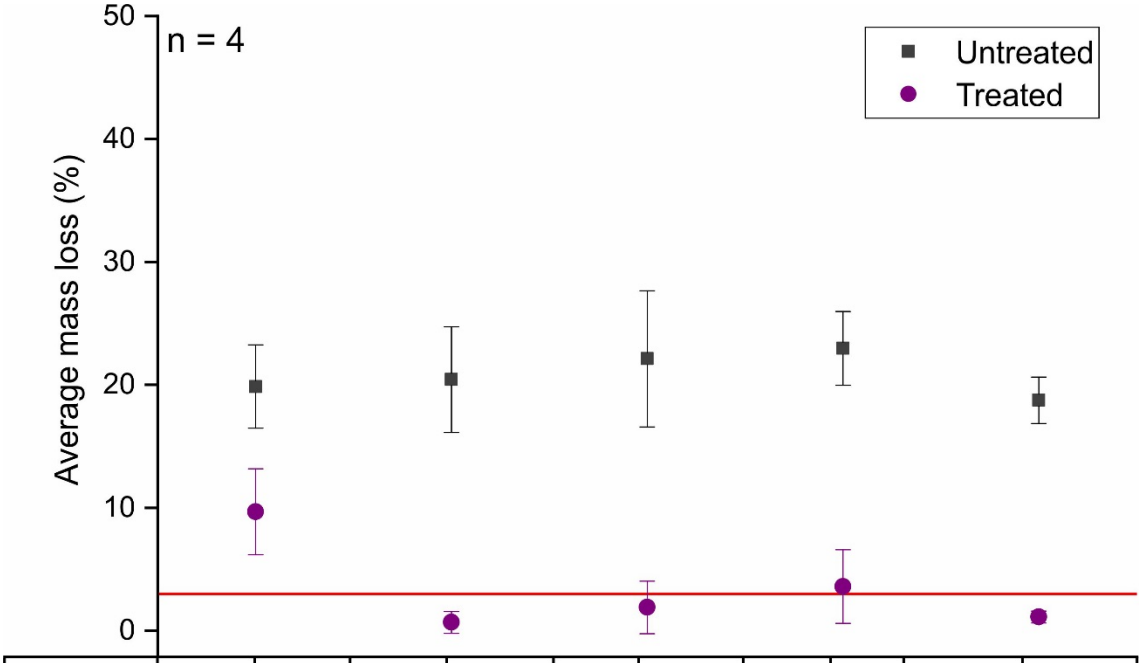
However, this is not the complete picture as in treated wood, the combination of MgF_2 and CaF_2 in EG at the lower concentration of 0.5 M was also found to have higher efficacy against *R. placenta* than the two-step combination of CaF_2 (lac, 0.25 M) and MgF_2 (EG, 0.25 M). It is likely that the concentration of lactic acid and fluoride in CaF_2 (lac, 0.25 M) was not sufficient to reduce fungal growth in wood treated with the two-step combination formulation. Nevertheless, more experiments need to be done to determine the role of lactic acid in combination with NMF on biocidal efficacy against *R. placenta*.

The present study demonstrates the biocidal efficacy against *R. placenta* for wood treated with a nano formulation of a well-known active ingredient, fluoride. Nanoparticles such as copper, silver, and zinc have also been tested for biocidal efficacy against *R. placenta* by several research groups. Lykidis, et al. (2016) showed that nano zinc oxide alone did not protect wood specimens from *R. placenta*.[19] However, wood specimens treated with a combination of nano zinc and borate that were unleached had 0.3% mass loss against *R. placenta*.[19] Unleached specimens treated with titanium alkoxide are also reported to be durable against *R. placenta*, although no results were included on treated specimens that were leached.[76] Another study reported results for unleached and leached specimens treated with copper (Cu) and silver (Ag) nanoparticles that were tested against *R. placenta*.[127] They found that durability was lost in both Cu and Ag treated specimens that were leached.[127] In comparison, the results on NMF treated specimens presented here have proven their durability against *R. placenta* even after leaching. Although weathered TiO_2/Ce specimens had anti-fungal resistance to *R. placenta*, their efficacy against white-rot fungi or termites has not been reported.[80] The next section presents results on the efficacy of NMF treated wood against *T. versicolor*.

4.4.3 *Trametes versicolor*: NMF treated wood

The mass losses in NMF treated wood specimens caused by the white-rot fungus, *T. versicolor* in the EN 113 test are compared in Fig.4.8. All the treatments resulted in mass losses lower than the untreated specimens. Among the treatments, the average mass loss was lowest for the combination of MgF_2 and CaF_2 (0.5 M). Similar to the results from *R. placenta*, wood treated with MgF_2 (0.5 M) had the highest average mass loss of

9.7 ± 3.5% among the NMF treated specimens. Wood treated with MgF_2 (0.8 M) performed better with an average mass loss below 3%. Although specimens treated with CaF_2 (0.8 M) had an average mass loss slightly higher than 3%, it was not significantly different to specimens treated with MgF_2 (0.8 M) (p-value – 0.19).



Treatment	MgF_2	MgF_2 + CaF_2	MgF_2	CaF_2	CaF_2 + MgF_2
M (mol/l)	0.5	0.5	0.8	0.8	0.25 + 0.25
Solvent	Ethylene glycol (EG)			lactic	lactic + EG

Fig.4.8 Mass loss of NMF treated wood caused by *Trametes versicolor*. The red line is the mass loss cut-off at 3% for durability classification.

The mass losses in the NMF treated specimens caused by *T. versicolor* in the second set of fungal tests are much lower than the first set of fungal tests (4.2.2). Thus, by increasing the NMF concentration to 0.8 M, it was shown that the MgF_2 treatment is sufficient alone and does not need to be combined with copper to improve its efficacy. This is an important result because it demonstrates that NMF treatment can be applied without additional fixatives, unlike the treatment of wood with copper. Therefore, NMFs have a smaller environmental footprint compared to conventional preservatives as less amount of chemicals will be needed to make durable wood products.

In contrast to efficacy results from *R. placenta* in the previous section, in this case, there was no difference in mass losses between the two NMF combination formulation

treatments in wood. Both, the treatments resulted in mass losses below 3%. Among all the NMF treatments, specimens treated with the combination formulation had the lowest mass losses caused by *T. versicolor*. Thus, the NMF combination formulation would be considered to have the most efficacy against *T. versicolor.*

Many studies have reported on nano-based wood treatments that have efficacy against *T. versicolor*. Most of these wood treatments were reported to lose their efficacy once they are leached. Unleached micronized zinc borate treated specimens had a mass loss of 2.1% caused by *T. versicolor*.[128] However, another study reported that nano zinc borate specimens that were leached had mass losses higher than 5% when tested against *T. versicolor*.[80] Likewise, specimens treated with Cu nanoparticles that were leached did not have high efficacy against *T. versicolor*.[127] In contrast to Cu and nano zinc borate treatments, both unleached and leached specimens treated with Ag were found to be sufficiently protected from decay caused by *T. versicolor*.[127] This was in agreement with findings from another group that reported leached specimens treated with Ag nanoparticles showed efficacy against *T. versicolor*.[80] However, Ag was shown to lose its efficacy against *C. puteana* and *R. placenta* after leaching.[80,127] In contrast to nanoparticle treatments of wood such as Ag and TiO_2/Ce mentioned earlier that have efficacy against only one type of fungi, the results of this study demonstrate that NMF treatment protects wood from brown-rot and white-rot fungi.

4.5 Summary

In this chapter, the biocidal efficacy of NMF treated wood was tested against brown-rot fungi (*Coniophora puteana* and *Rhodonia placenta*) and white-rot fungus (*Trametes versicolor*). Overall, this chapter demonstrates the steps from initial findings to optimization that finally led to NMF formulations, which protected treated wood from decay caused by all three fungi. The NMF treated specimens performed better than untreated specimens. All NMF formulations with a concentration of 0.4 M and higher reduced growth of *C. puteana* on wood. In contrast, *R. placenta* showed higher tolerance to nanoscopic metal fluoride particles. In this case, only two formulations in wood showed high efficacy, the sol of CaF_2 prepared in lactic acid and the sol of MgF_2 and CaF_2 prepared in ethylene glycol. Notably, biocidal efficacy against *T. versicolor* was highest in wood treated with the combination of MgF_2 and CaF_2. Also, NMFs are a better alternative for use as a preservative than NaF, which was found to lose its efficacy in wood after leaching. NMFs, on the other hand, were

present in treated wood even after leaching to protect it from fungal decay. Thus, to protect from both brown-rot and white-rot fungi, NMFs are a viable nano-based treatment for application in wood preservation.

5. Efficacy: Termites

Wood specimens treated with nano metal fluoride (NMF) that were unleached were tested against *Coptotermes formosanus* in accordance with the EN 117 (2012)[129] standard for termite test.

5.1 First set of termite tests

In the first round of the EN 117 test, wood treated with NMF formulations in the range of 0.1 M to 0.4 M were tested against *C. formosanus*. The following are results on termite mortality, mass loss, and visual rating of the treated specimens.

5.1.1 Termite mortality

Termite mortality shows how toxic the preservative treatment of wood is to termites. It can also indicate a possible mechanism for the efficacy of the preservative. In the EN 117 test, termites exposed to untreated controls should have a mortality of 50% or less to show that they are virulent and for the experiment to be considered valid.[129]

The Fig.5.1 shows the average termite mortality after the EN 117 test. The termite mortality was below 50% for control and ethanol treated specimens. Thus, the following results meet the validity requirement for the EN 117 test. The NMF treated specimens caused termite mortality higher than control and ethanol treated wood specimens. Among the treated specimens, the termite mortality was in the range of 60 to 80%. There was no significant difference in termite mortality among the treatments, although the lowest termite mortality was observed for CaF_2 (0.1 M) treated specimens. Notably, none of the NMF treatments in wood resulted in 100% termite mortality.

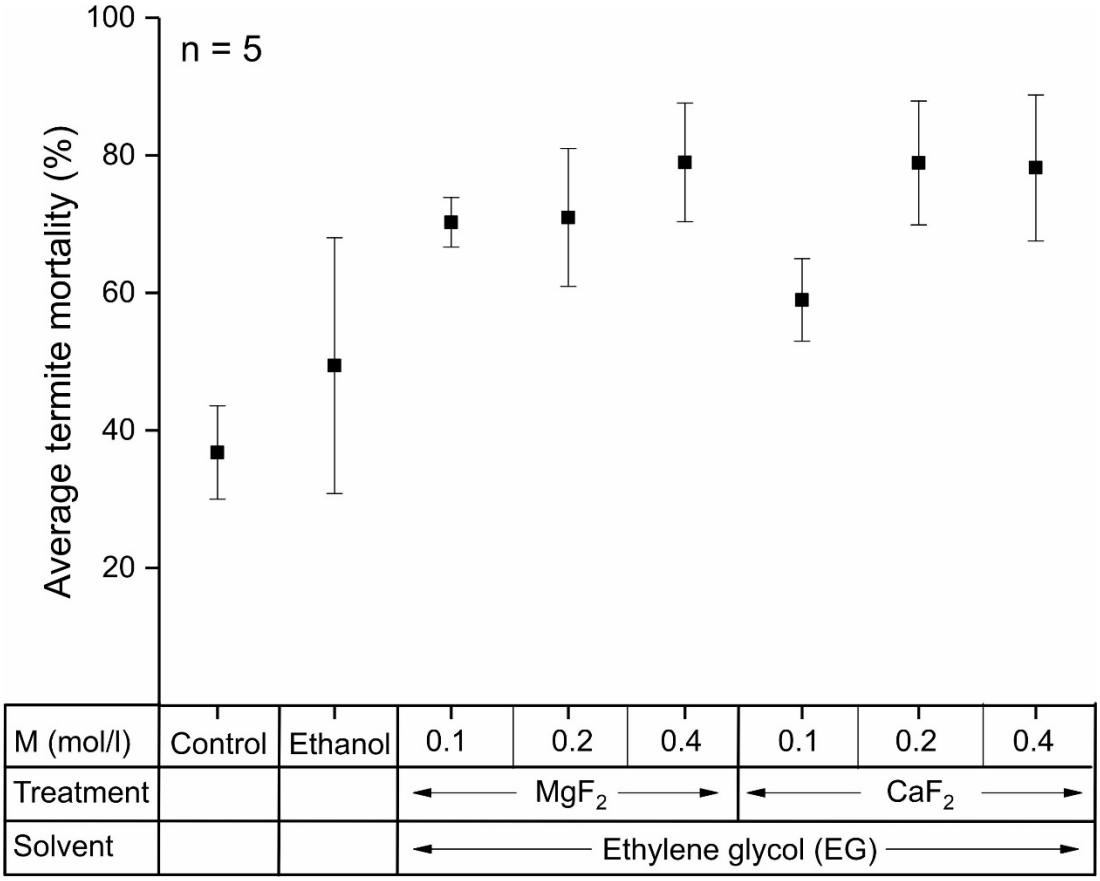


Fig.5.1 Termite mortality exposed to wood specimens.

5.1.2 Mass loss

The average mass loss in wood specimens due to termite attack is shown in Fig.5.2. The control and ethanol treated specimens had average mass losses above 10%. The high mass loss in ethanol treated specimens confirms that ethanol was not toxic to the termites. The mass loss in the NMF treated specimens was significantly lower than the control specimens. Increasing the NMF concentration from 0.1 M to 0.4 M did not result in a proportional decrease in mass loss, irrespective of either MgF_2 or CaF_2 treatment of wood. However, the average mass loss of MgF_2 treated specimens was lower than CaF_2 treated specimens. It is expected that MgF_2 treated specimens performed better than CaF_2 treated specimens as the former has higher solubility. This would result in more fluoride ions being released from MgF_2, which are biocidal to termites, and therefore fewer termites are available to attack the treated wood specimens leading to lower mass losses. Also, the higher efficacy of MgF_2 over CaF_2 is in agreement with the results from the first set of fungal tests (4.2.2).

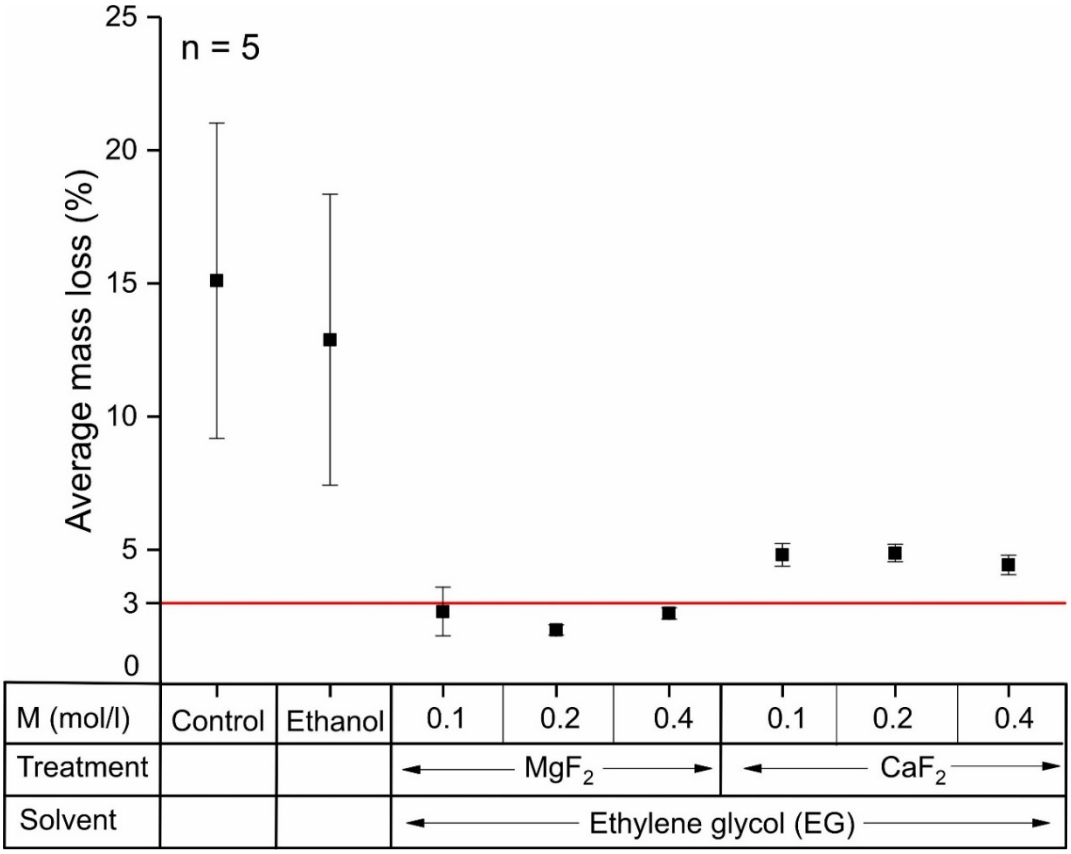


Fig.5.2 Mass loss of wood specimens against *Coptotermes formosanus.*

5.1.3 Visual assessment of specimens after EN 117 test

In the EN 117 test, *C. formosanus* caused severe damage to control and ethanol treated specimens which are presented in Fig.5.3. It is seen that the termites were able to create long and wide tunnels through these wood specimens.

Fig.5.3 Control and ethanol treated specimens after the EN 117 test.

In contrast to control and ethanol treated specimens, the NMF treated specimens were relatively less damaged, as shown in Fig.5.4. Most of the NMF treated specimens had surface erosion and tunnels that were created by termites. Even specimens treated with a higher NMF concentration of 0.4 M were as damaged as those treated with 0.1 M. This observation agrees with the mass loss trend discussed in the previous section (5.1.2), where there was no proportional decrease in mass loss with the increase in NMF concentration of treated wood. Thus, the higher NMF concentration of 0.4 M was insufficient to prevent damage to treated wood caused by *C. formosanus*.

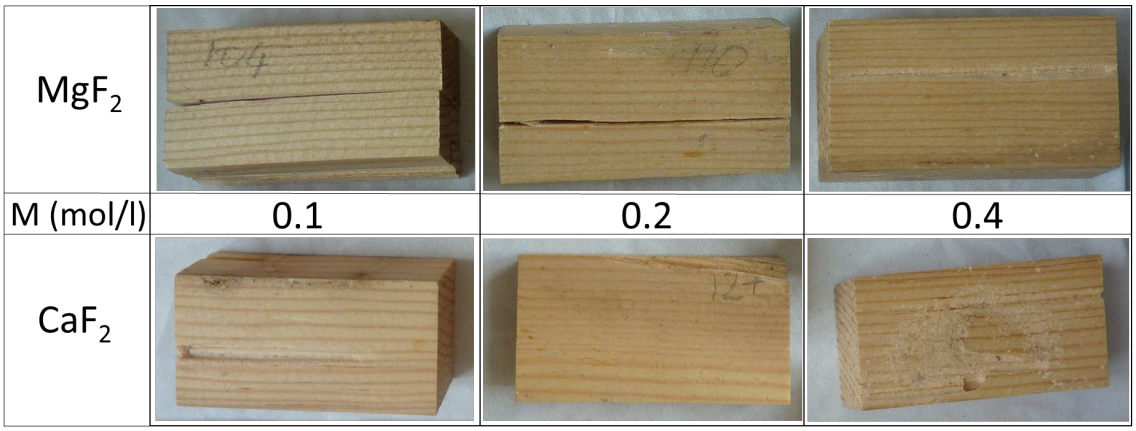


Fig.5.4 NMF treated wood specimens after the EN 117 test.

The damage to wood specimens was also assessed by rating them visually from 1 to 4, in accordance with the standard in EN 117 (2012).[129] The standard classifies treated wood specimens with an average visual rating of 1 as the cut-off for the efficacy of the preservative, while severely damaged wood specimens are given an average visual rating of 4.

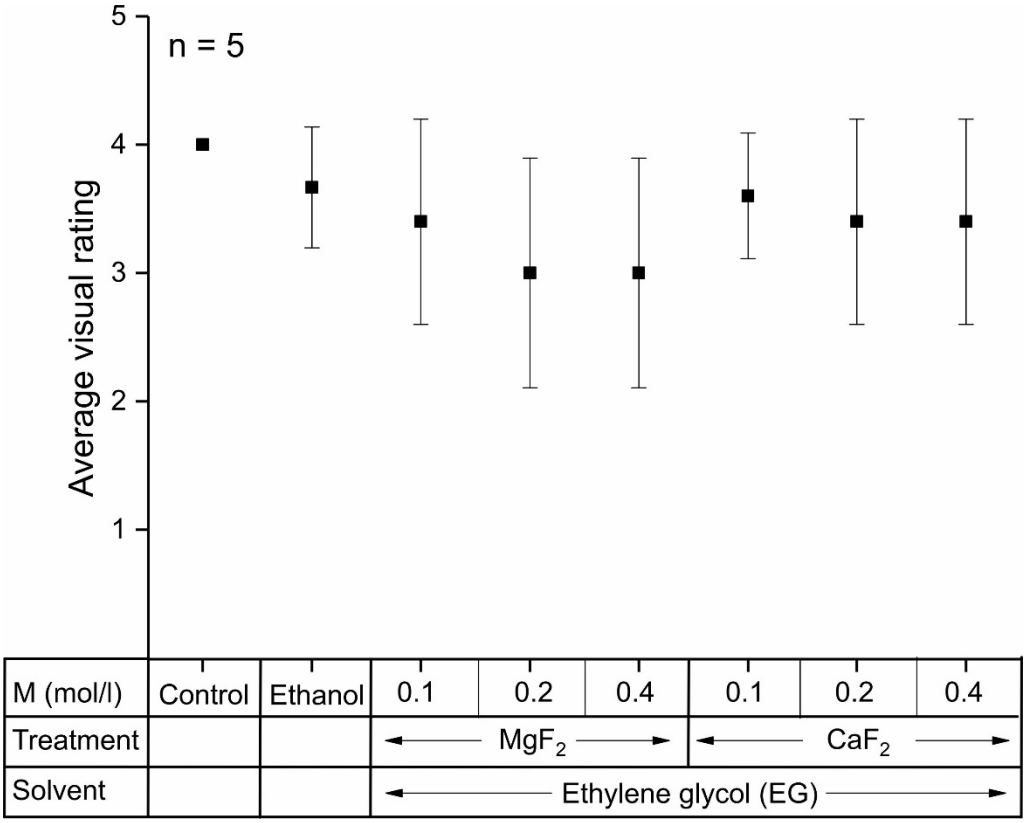


Fig.5.5 Visual rating of NMF treated wood after *C. formosanus* attack.

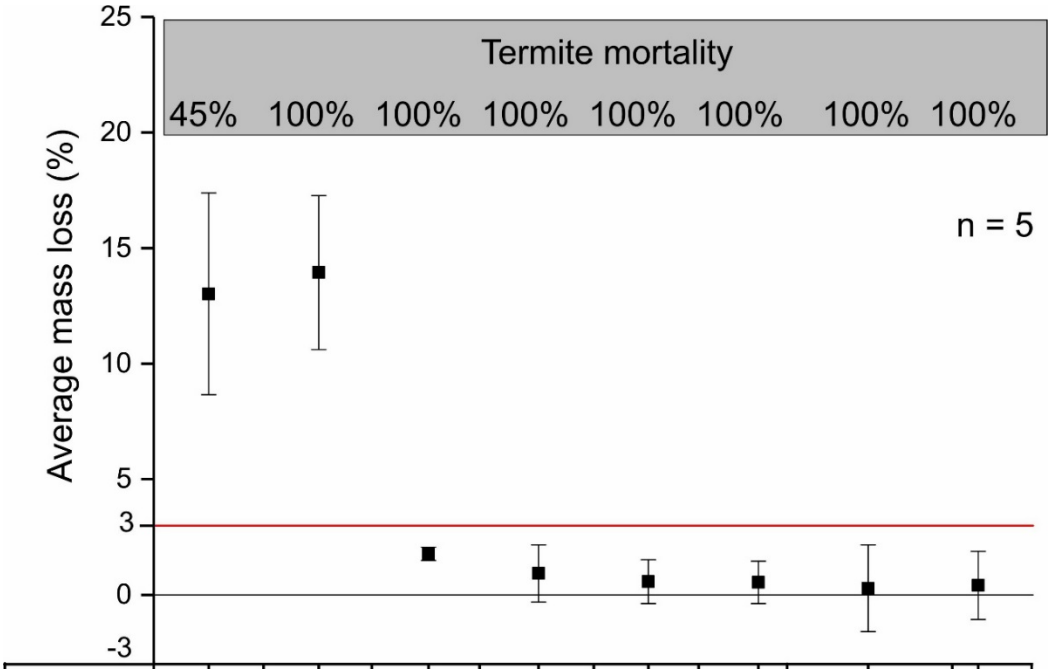
The control specimens were severely damaged with an average visual rating of 4, as shown in Fig.5.5. The average visual ratings of the NMF treated specimens were slightly lower than the control specimens. Results of the visual assessment of the treated specimens present a different picture when compared to their mass losses due to *C. formosanus* attack (Fig.5.2). Unlike the differences observed in their mass losses, there was no difference between the visual ratings of MgF_2 and CaF_2 treated specimens. Even though the treated specimens had lower mass losses than control, their average visual rating was higher than 2. Therefore, the lower mass losses in NMF treated specimens did not reflect the moderate damage caused by the termites. Like the fungal tests, in the second set of termite tests, higher NMF concentrations were evaluated to investigate if that would reduce the damage to wood specimens caused by *C. formosanus*.

5.2 Second set of termite tests

In the second set of termite tests, NMF formulations with a concentration of 0.5 M and higher were evaluated for protection of wood from *C. formosanus*.

5.2.1 Termite mortality and mass loss

The Fig.5.6 shows the average mass loss and termite mortality from the second EN 117 test. The results from this test are valid because the control specimens had a termite mortality of 45%. All treated specimens including the lactic acid treated specimens had 100% termite mortality. Even though lactic acid treated specimens had 100% termite mortality, their average mass loss was similar to control specimens. This could be due to a delayed response from the micro-organisms present in the termite gut to the acidic lactic acid.[125] Due to a delayed toxic response, the termites were probably eating wood resulting in their 100% mortality during the last week of the test. This explanation needs to be investigated in the future by periodically recording the number of live termites in the test jar during the duration of the experiment.



Treatment	Control	Lactic acid (lac)	NaF	MgF_2	MgF_2	MgF_2 + CaF_2	MgF_2+CaF_2	CaF_2
M (mol/l)			0.1	0.5	0.8	0.5	0.25 + 0.25	0.8
Solvent			H_2O	Ethylene glycol (EG)			EG + lac	lac

Fig.5.6 Mass loss and termite mortality of NMF treated wood.

Notably, in the second set, the higher concentration of the NMF formulations caused 100% termite mortality, which was not observed in the first set of termite tests (5.1.1). Also, the average mass losses for treated specimens were below 3%. The NMF treated specimens

had lower average mass loss than the NaF treated specimens, although the difference was not statistically significant. Therefore, the durability of NMF treated wood is on the level with NaF treated wood against *C. formosanus*. Furthermore, NMFs could be considered as a viable low-water soluble alternative to highly soluble NaF in reducing damage caused by termites to wood products. In the present study, the treated specimens were not leached prior to the EN 117 test. In future research, NMF and NaF treated specimens that have been leached can be evaluated for their durability against termite attack.

5.2.2 Visual assessment of wood specimens

In the second set, the control specimens were severely damaged as shown in Fig.5.7. The severity of their damage was similar to control specimens from the first set of EN 117 test (Fig.5.3).

Fig.5.7 Control specimens after second round of EN 117 test.

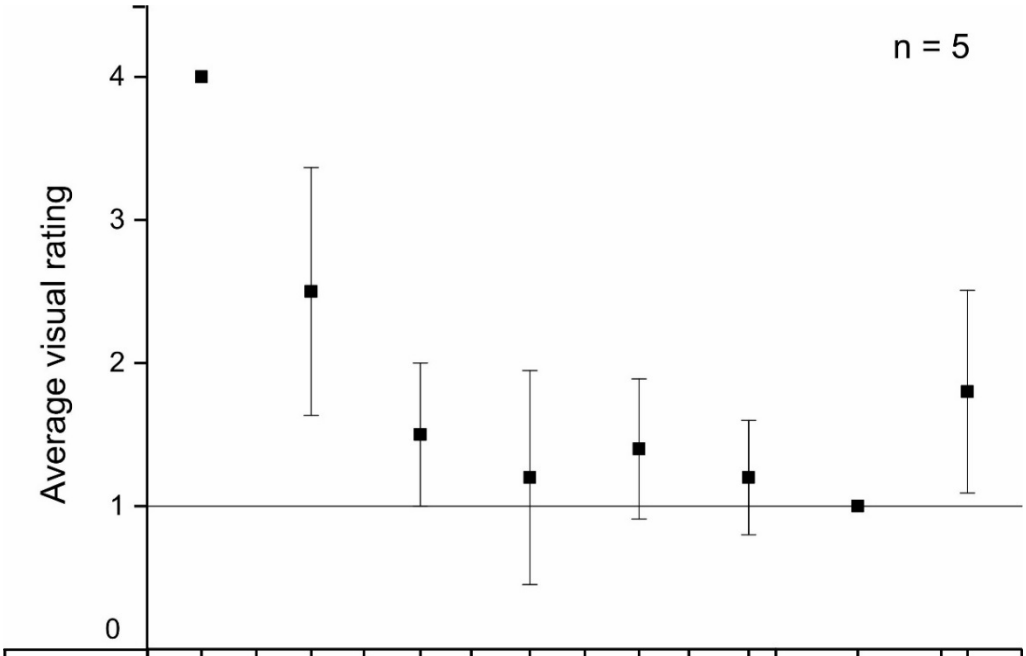
Unlike the control specimens, the treated specimens shown in Fig.5.8 are relatively less damaged. The most damage was seen in lactic acid treated specimens where termites caused surface erosion of more than 1 mm in depth (Fig.5.8). The NMF treated specimens have relatively minimal signs of termite attack. It is shown in Fig.5.8 that termites chipped the CaF_2 treated wood specimen (1 mm in depth) at its right edge corner. Both NaF and MgF_2 treated specimens show marks of attempted attack by termites, albeit with no deep erosion. In contrast to stand-alone NaF and MgF_2 treated wood, the signs of attack by *C. formosanus* on wood specimens treated with the NMF combination formulations are hardly visible.

Treatment	Lactic acid	NaF	MgF_2	MgF_2	MgF_2+ CaF_2	MgF_2+ CaF_2	CaF_2
M (mol/l)		0.1	0.5	0.8	0.5	0.25 0.25	0.8
Solvent	ET	H_2O	EG	EG	EG	EG lac	lac

Fig.5.8 Lactic acid, NaF, and NMF (different formulations) treated specimens after second round of EN 117 test.

The visual ratings of the specimens are shown in Fig.5.9. The control specimens were the most damaged, with the highest average visual rating of 4. Lactic acid treated specimens had a visual rating higher than 2, which fits with their higher average mass loss (Fig.5.6). In the second set, optimized NMF formulations for treated specimens resulted in relatively less damage caused by termites. This is evident in their average visual ratings, which were all below 2 (Fig.5.9). There was no significant difference in the visual ratings of the treated specimens, although the highest visual rating was for wood treated with CaF_2 (lac) and the lowest was for wood treated with the combination of MgF_2 (EG) and CaF_2 (lac). Among the wood treatments, the NMF combination formulation can be considered to be the most durable against *C. formosanus*.

In literature, nano-based wood treatments have shown promising results in termite resistance tests. Mass losses of less than 3% were reported for nano-borate and nano tin oxide treated wood against *C. formosanus* in a test done over three weeks.[79] Similarly, Mantanis et al. (2014) showed that nano zinc borate was resistant to termite attack in a four-week test. In comparison, the termite resistance results for NMF treated wood were done over a longer duration of eight weeks. Therefore, in the current study NMFs have proven their efficacy against *C. formosanus* under more aggressive testing conditions and consequently demonstrate their potential to provide long-term durability to wood products.



Treatment	Control	Lactic acid (lac)	NaF	MgF_2	MgF_2	MgF_2 + CaF_2	MgF_2+CaF_2	CaF_2
M (mol/l)			0.1	0.5	0.8	0.5	0.25 + 0.25	0.8
Solvent			H_2O	Ethylene glycol (EG)			EG + lac	lac

Fig.5.9 Visual rating of NMF treated wood exposed to *Coptotermes formosanus.*

5.3 Toxicity of NMFs to protists in termite gut

In the introduction, it was described how the protists present in the gut assist termites in the digestion of cellulose (1.4.4). To understand the efficacy mechanism of NMFs on termites, a short experiment was done to evaluate their impact on the protist population. During the exposure of termites to treated wood specimens, the number of protists present in their termite gut was counted over 16 days. The estimated number of protists present in the termite gut was then calculated and is shown in Fig.5.10.

From Fig.5.10, it is observed that there was a steep decline in the number of protists for all specimens including the control. This is expected as the termites' surroundings underwent a sudden change from the developed colony that they were raised in, to the vermiculite in a glass jar. On Day 4, it is observed that the number of protists in the termites exposed to lactic acid and CaF_2 treated specimens were similar to the control. In contrast, lower numbers of protists were found in termites exposed to specimens treated with stand-alone MgF_2 and the NMF combination formulation. This trend remained the same over the duration of the experiment.

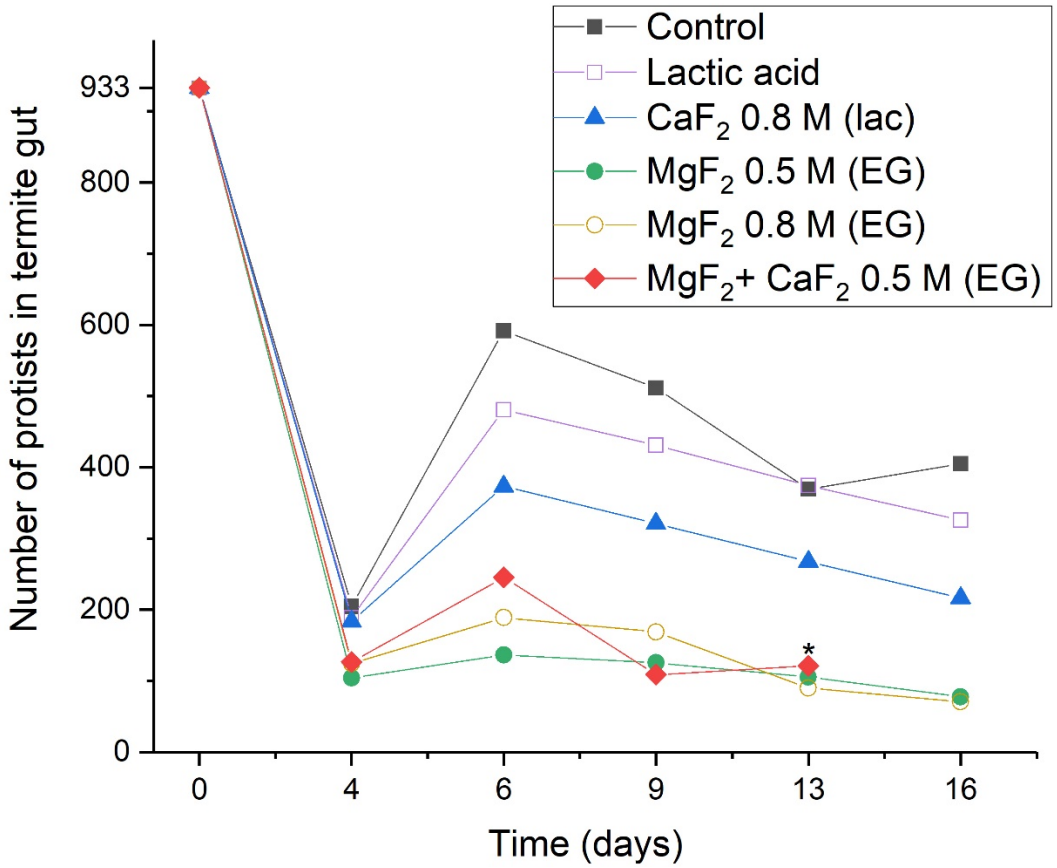


Fig.5.10 Protists found in the gut of the termites exposed to treated specimens. The asterisk is to note that there were no alive termites in the jars with the MgF_2+CaF_2 treated specimens after Day 13.

The number of protists in the lactic acid treated specimens decreased gradually, which might explain its delayed toxicity effect on the termites resulting in their 100% mortality (Fig.5.6) in the EN 117 test. Although a similar trend in the decrease of protists population is observed for termites exposed to CaF_2 and lactic acid treated specimens, the number of protists in the former was lower compared to the latter. It is likely that the CaF_2 (lac) treated specimens accelerated termite mortality by exacerbating the deleterious effect of the lactic acid on the gut protists. This potential synergistic role between CaF_2 and lactic acid could be explored in future experiments.

In contrast to the CaF_2 treated specimens, the number of protists present in termites exposed to the MgF_2 treated specimens was lower which is due to the differences in their solubility. MgF_2 has a higher solubility and therefore releases a higher concentration of fluoride compared to CaF_2, which can be biocidal to the protists as well. More importantly, the NMF combination formulation of MgF_2 and CaF_2 is even more toxic to the gut protists, as after Day 13, no termites were alive in the glass jars containing these NMF treated

specimens. Therefore, the NMF combination formulation seems to be the most promising as it releases an optimal concentration of “free” fluoride ions in wood that are toxic to protists present in the termite gut.

5.4 Summary

In this chapter, all NMF formulations with a concentration of 0.5 M and higher resulted in 100% termite mortality of *C. formosanus*. Even though all NMF treatments had some efficacy, the NMF combination formulation showed the highest efficacy in terms of mass loss and visual damage. Moreover, the NMF combination formulation was also the most toxic to the protists found in the termite gut. Similar to the results from the fungal tests, wood treated with the combination of MgF_2 and CaF_2 had the highest durability against termites. The reason for this would be that the NMF combination treatment in wood regulates the release of fluoride for optimal biocidal efficacy, which is discussed in the next chapter.

6. Fluoride concentration in sols

A short experiment was conducted after the biological tests to investigate how biocidal efficacy depends on the composition of NMF formulation. NMF sols of 5 mM were prepared in distilled water and the amount of fluoride was measured using ion chromatography. The nominal concentration of fluoride measured in the NMF sols is shown in Fig.6.1.

In the 5 mM NMF sols, the nominal fluoride concentration is lowest in the CaF_2 sol (Fig.6.1). The fluoride concentration of stand-alone NMF sols measured in this study are similar to the literature values for their solubility data, which are 130 mg/L for MgF_2 and 16 mg/L for CaF_2.[92] In the combined sol of MgF_2 and CaF_2, the measured fluoride concentration is a bit higher than the stand-alone MgF_2, although the difference is not statistically significant. Since the concentration of fluoride in the combination sol is similar to the stand-alone MgF_2 sol, the role of CaF_2 in the combination formulation on biocidal efficacy is not clear. In an earlier chapter (2.2.2), solid-state ^{19}F MAS NMR spectra of wood treated with the NMF combination showed that the signal intensity of CaF_2 was much higher than MgF_2. This higher signal intensity of CaF_2 suggests that it could have an indirect influence on biocidal efficacy.

During biocidal action, as the "free" fluoride ions keep being disbursed, more of them would be needed to resist a severe fungal attack on wood. It could be speculated that the role of CaF_2 is to keep releasing a constant low flow of "free" fluoride ions such that the fungi are not given any respite. A metastable phase of $MgCaF_4$, the formation of which is reported in literature,[98] could provide the necessary bridge between MgF_2 and CaF_2 for such an arrangement. The role of CaF_2 in the combination formulation to replenish and regulate the "free" fluoride supply through the $MgCaF_4$ complex would need to be confirmed in a future experiment. This would need to reflect the dynamics in fluoride concentration inside the wood matrix during leaching and the subsequent fungal attack. One option could be to monitor the changes in nominal concentration of fluoride over a set time. In such an experiment, specific aliquots of the NMF solution can be removed and replaced with distilled water to determine if and when the fluoride concentration returns to the level before removal. Another aspect is to understand the interaction of NMF aggregates distributed in the wood matrix with the fluctuating moisture content. One possibility could be to determine if there are any changes in the mass of NMF treated wood specimens due to different humidity conditions.

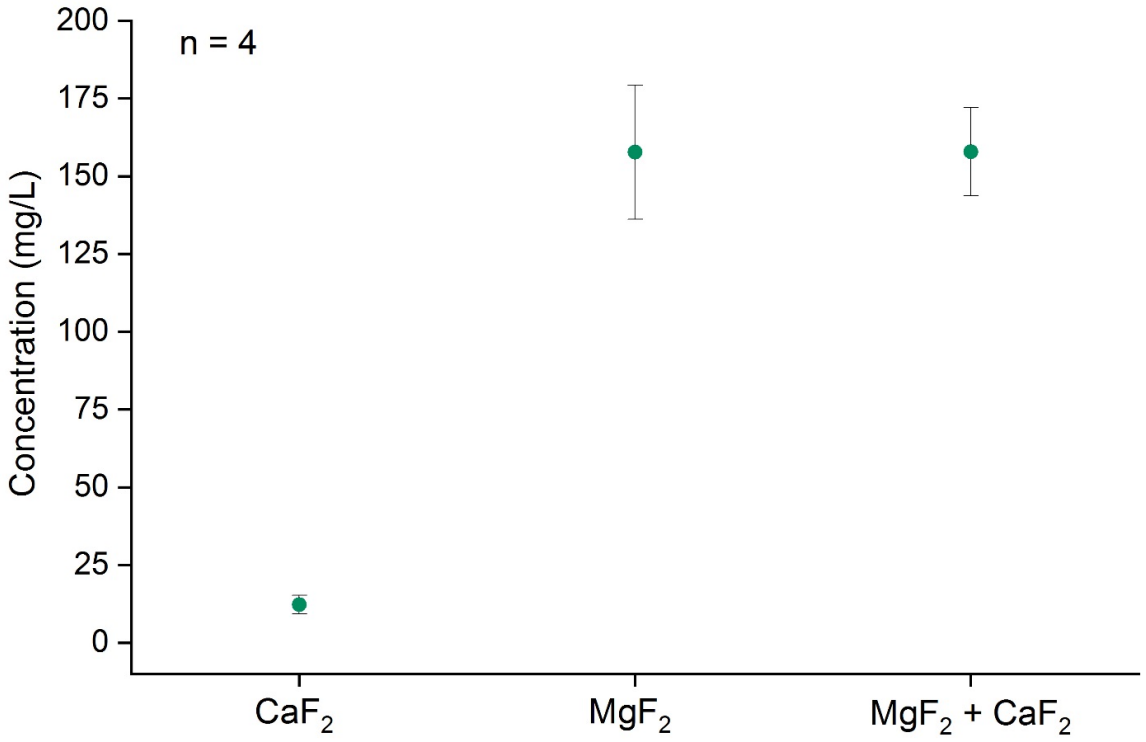


Fig.6.1 Nominal concentration of fluoride measured in NMF sols.

A schematic is presented in Fig.6.2, to illustrate how the NMF treated wood specimens would resist fungal attack. When wood is treated with NMF sols, the initial nominal fluoride concentration is high. After leaching some fluoride is lost, although most of it remains in wood in the form of aggregates due to the low solubility of NMFs. These remaining NMF aggregates in the wood matrix act as a reservoir from which "free" fluoride ions are released for biocidal action.

The amount of fluoride released from NMF is important for biocidal efficacy, albeit dependent on the tolerance level of the specific fungi to fluoride. The results from the fungal tests in this study show that against *C. puteana*, most NMF treated wood released sufficient "free" fluoride ions to keep mass losses below 3%. Thus, *C. puteana* has a low tolerance level to fluoride. Compared to *C. puteana*, the tolerance level of *R. placenta* to fluoride is higher as only two treatments in wood resulted in mass losses below 3%. One of those treatments was the combination of MgF_2 and CaF_2. The tolerance level of *T. versicolor* to fluoride is also high. In this case, the NMF combination formulation treatment of wood resulted in the lowest mass loss. It can be speculated that the solubility of the NMF combination formulation in treated wood was optimized, such that the amount of "free" fluoride ions released was at the level needed to protect it from all three fungi.

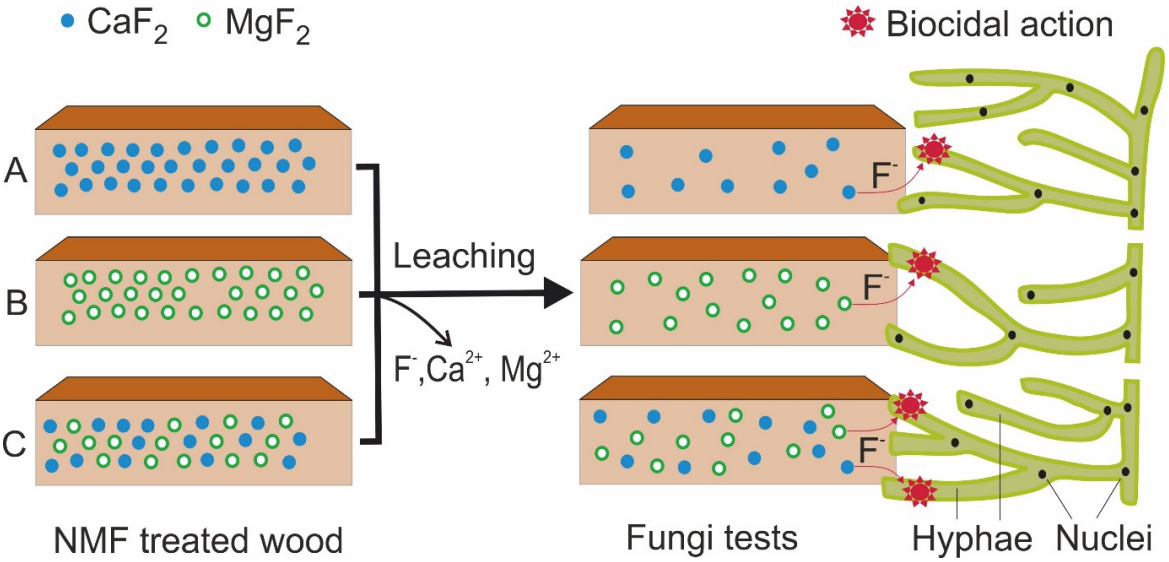


Fig.6.2 Schematic showing the cross-cut section of treated wood with changes in NMF concentration leading up to fungal testing. Three NMF wood treatments are shown, A – CaF_2, B - MgF_2, and C – MgF_2 and CaF_2. Image created by S. M. Usmani.

To summarize, fluoride needs to be released from NMFs for it to be biocidal to the attacking fungi and termites, although their release needs to be optimized for high efficacy. More "free" fluoride ions are needed to resist decay caused by *R. placenta* and *T. versicolor*, as they have a higher tolerance level to fluoride. In the present study, this was achieved by treating wood with MgF_2 and CaF_2. The NMF combination formulation demonstrated biocidal efficacy against brown-rot fungi, white-rot fungus, and termites.

$$Biocidal\ action$$
$$MgF_2 + CaF_2 > MgF_2 > CaF_2$$

This study can explain to some extent the variations in efficacy of different NMF treatments in wood. However, still more research is needed to explain the role of lactic acid in combination with NMF on biocidal efficacy. ENV 807 (2001)[130] is a longer duration test (32 weeks), which could be done in the future to substantiate the durability results of NMF treated wood observed in the current study.

7. Conclusion

This project assessed the durability of wood treated with sparingly soluble fluoride compounds in their nanoscopic form.

Historically, fluoride compounds were widely used as wood preservatives. Over time, the use of these conventional fluoride compounds in treated wood products declined because of their high susceptibility to leaching. One approach to overcome this limitation is to use sparingly soluble fluorides. Then, the challenge is to impregnate these low-water soluble fluorides into wood. Advances in materials science have been used to improve the distribution of active ingredients into wood for preservation. Recently, nanoparticles of copper, zinc, silver, and titanium dioxide were studied for their efficacy against wood-degrading fungi and termites. Yet, no studies have reported on the durability of wood treated with metal fluoride nanoparticles.

In the present study, formulations of sparingly soluble fluoride compounds in the form of nanoparticles were investigated for their potential to improve the durability of wood. The following objectives were set.

- Characterization of nano metal fluorides (NMFs) and the resultant treated wood.
- Material properties of wood treated with NMFs.
- The durability of NMF treated wood against wood-degrading fungi and termites.
- The possible mechanism of biocidal efficacy of NMFs.

The nanoscopic synthesis of sparingly soluble fluorides such MgF_2 and CaF_2 using the fluorolytic sol-gel synthesis is already established. In this research, this synthesis route was used to prepare a novel and stable combination of MgF_2 and CaF_2 particles in one colloidal sol.

There were several steps involved in the evaluation of NMFs as wood preservatives. Firstly, the composition and the size of the nanoparticles were characterized by X-ray diffraction (XRD), dynamic light scattering (DLS), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX). From the characterization methods, it was shown that the sizes of metal fluoride nanoparticles in different combination formulations were smaller than 10 nm. The nanoscopic size of sparingly soluble fluorides enabled their impregnation into the wood matrix. In addition, solid-state ^{19}F MAS nuclear magnetic resonance (NMR) spectra showed that the fluorides were present inside the treated

wood specimens even after leaching. Thus, the novel results of this study provide evidence of successful treatment of wood with sparingly soluble fluorides.

Secondly, high-resolution electron imaging was used to determine the distribution of NMFs inside wood. Back-scattered electron images combined with energy-dispersive X-ray spectroscopy maps revealed that the NMFs had aggregated in the bordered pits and cell lumina. In addition, the images proved that NMFs were uniformly distributed throughout the wood matrix all along the flow path from longitudinal tracheids to ray tracheids. Moreover, X-ray micro-CT images showed that the NMF aggregates were present in the resin canals even in NMF treated wood that was leached. Therefore, it was shown that the nanoscopic form of sparingly soluble fluorides facilitated their distribution throughout the wood matrix.

Thirdly, the properties of NMF treated wood were evaluated such as retention, equilibrium moisture content (EMC), dimensional stability, and hydrophobicity. Compared to untreated specimens, NMF treatment of wood specimens lowered their EMC and increased their dimensional stability. Among the NMF formulations, it was found that wood treated with the combination of MgF_2 and CaF_2 in ethylene glycol had the most hydrophobic surface. Therefore, the NMF composition and the type of solvent are important determinants of the properties of the resultant treated wood.

After characterization and evaluation of the physical properties of NMF treated wood, their efficacy against fungi and termites was tested. The tests were done in accordance with EN 113 (1996) and EN 117 (2012), respectively. Prior to testing against fungi, the treated specimens were leached according to EN 84 (1997). Although NMFs significantly lowered mass losses of treated specimens compared to untreated specimens in the biological tests, their efficacy varied depending on their composition and formulation.

The first set of tests determined the viability of sparingly soluble fluorides to protect wood from fungal attack. Although both MgF_2 and CaF_2 treated wood minimized decay caused by *C. puteana*, the average mass loss was lower in the former than the latter. This is because MgF_2 has a higher solubility than CaF_2. Following the first set of tests, an *in-vitro* agar test was done to determine the NMF concentration and formulation that will also resist the growth of *R. placenta* and *T. versicolor*. The results indicated that combining MgF_2 and CaF_2 would have more efficacy against *R. placenta* than the use of either MgF_2 or CaF_2 as a stand-alone treatment in wood. In addition, it was observed that a higher NMF concentration in treated wood would also resist growth of *T. versicolor*. Based on the results

from the *in-vitro* agar test, NMF formulations for the second set of fungal tests were prepared.

In the second set of tests, all NMF treated wood specimens were protected from decay caused by *C. puteana* compared to severely decayed untreated specimens. However, only two NMF formulation treatments in wood had biocidal efficacy against *R. placenta*, a CaF_2 sol with lactic acid as solvent and a sol of MgF_2 and CaF_2 with ethylene glycol as solvent. Against *T. versicolor*, the lowest mass loss (below 2%) was observed for wood treated with the combined formulation of MgF_2 and CaF_2.

For the tests against termites, *Coptotermes formosanus*, the treated specimens were evaluated based on termite mortality, mass loss, and visual assessment of the damage. NMF formulations of 0.5 M and higher were highly toxic to termites resulting in their 100% mortality. In addition, these NMF treatments in wood specimens reduced mass losses to less than 3%. Also, these NMF treated specimens had minimal damage due to termite attack, with visual ratings of 2 and lower. Among NMF treated specimens, the specimens treated with the combined formulation of MgF_2 and CaF_2 had the least damage, reflected in their average visual rating of 1.

The results of this study show that the solubility of fluoride can be tuned to increase its biocidal efficacy against fungi and termites. Overall, the combined formulation of MgF_2 and CaF_2 was found to have biocidal efficacy against all three fungi and termites, which is a promising result for improving the durability of wood. The higher efficacy of the combination treatment compared to the stand-alone treatment is not entirely clear. It could be a result of the formation of $MgCaF_4$ complex, which regulates an optimal release of fluoride ions against attack from fungi and termites. Alternatively, it could be that the combination of higher soluble, MgF_2 and lower soluble, CaF_2 results in a long-term availability of fluoride for biocidal efficacy. Still, the solubility of MgF_2 (130 mg/L) and CaF_2 (16 mg/L) remains much lower compared to conventional fluoride compounds used in wood preservative formulations such as NaF (40 g/L), which is an advantage. Due to their low-water solubility, NMFs in treated wood will remain as a reservoir in the porous wood matrix even after leaching. From this reservoir, “free” fluoride ions will be released in a controlled manner to provide long-term protection to NMF treated wood from fungi and termites.

The physical barrier posed by the nanoparticle aggregates, which were shown to be well distributed inside the wood matrix, also play an important role in improving the

durability of NMF treated wood. The NMF aggregates in the matrix decreased the flow path for water absorption into wood and blocked the entry points for fungal hyphae. Therefore, in addition to their biocidal efficacy, the NMF aggregates reduced the moisture content and voids in wood to minimize the likelihood of a fungal attack.

Unlike conventional fluorides, such as NaF, it is shown here that NMFs provide protection to wood from fungal decay even after it has been leached. Also, unlike widely used active ingredients in wood preservative formulations such as copper, a significant finding of this work is that NMF treated wood is durable without additional fixatives. This is important for several reasons, the primary being that fewer chemicals are needed to protect wood, and therefore NMF treated wood products have a smaller environmental footprint. In particular, NMFs do not provide evidence for higher health and environmental risks than the ones posed by conventional wood preservatives. Even more, when compared to other wood preservatives, NMFs constitute a safer alternative due to their low-water solubility. The resultant NMF treated wood can have multipurpose use, both in Use Class 3.1 (limited wetting conditions) and Use Class 3.2 (prolonged wetting conditions), according to EN 335 (2013). In summary, the findings demonstrate that NMFs are a viable alternative to conventional preservatives used in wood products. The high biocidal efficacy and low leachability of nano-sized metal fluoride particles shown in the present study provide strong arguments for the revival of fluoride compounds in wood preservation.

8. Outlook

Based on the research presented in this work, several avenues are now opened to further monitor the use of nano metal fluorides (NMFs) in wood protection in terms of formulation, type of treatment, distribution in wood matrix, and organisms.

In subsequent tests, it can be examined if anti-swelling efficiency of specimens treated with CaF_2 sol prepared in lactic acid can be improved. Even though the NMF treated specimens that were leached had biocidal efficacy against fungi, some fluoride was lost during leaching. In future experiments, the proportion of solvent in the formulation can be optimized, and an additional thermal curing step can be added to NMF treated wood to evaluate the possibility of further reducing fluoride leaching and increasing its dimensional stability. Also, efficacy of NMF treated specimens that are leached can be evaluated against *C. formosanus.*

Two types of wood were used in the biological tests; Scots pine (*Pinus sylvestris)* and beech (*Fagus sylvatica)*. Due to their nanoscopic size, attempts can be made to treat species with lower permeability such as Norway spruce and white Fir with NMFs. Wood specimens in this study were dried under low pressure before treatment with NMF. The efficacy of NMF formulation applied via brushing or dipping wood in it can be evaluated in future research. If this treatment is proven to result in similar efficacy compared to treatment used in the present study, it can simplify the processing of resultant wood products.

The analytical methods used in the current study to characterize NMF treated wood proved to be comprehensive tools. However, X-ray micro-CT can be done at an even higher resolution to get more information on the localization of NMFs in treated wood. In addition to X-ray micro-CT, a new technique known as electron ptychography can be applied to resolve the interaction between nanoparticles and a single wood cell in NMF treated wood.

In this study, material properties of NMF treated wood such as hydrophobicity were evaluated. More information on NMF treated wood can be determined by characterizing their mechanical properties such as modulus of elasticity (MOE) and Brinell hardness. In addition, natural weathering tests can assess the change in the physical appearance of NMF treated wood. If NMF treated wood is proven to be weather resistant, it may increase their commercial value as well.

Nano-sized particles of MgF_2 and CaF_2 were proven to have efficacy against brown-rot fungi, white-rot fungus, and termites. It will be informative to determine their efficacy

against blue-stain fungi in accordance with EN 152 (2012).[131] In the current study, the efficacy of NMF treated wood was proven over 16 weeks, making them promising candidates for evaluation in ENV 807 (2001),[130] a longer duration field stake test of 32 weeks to determine efficacy against soft-rot fungi and other soil organisms. These tests can provide more information on the mechanism behind their efficacy. Instead of searching for tailor-made wood preservatives, NMFs can be shown to be treatable in many wood species with improved mechanical properties, and which has resistance against soft-rot and blue-stain fungi as well. Thereby, NMFs as a wood preservative can have broad applications in various built products made from non-durable wood to provide them with long-lasting protection from decay. In this way, NMFs can play a role in increasing the service-life of a sustainable material and reduce the rate at which trees are cut-down specifically to replace decayed and damaged wood products.

9. Experimental

The following chapter provides details for the chemicals used in synthesis and biological tests, followed with the steps in fluorolytic sol-gel synthesis of nano metal fluorides (NMFs), and then the procedure for the biological tests. Lastly, a brief overview is given of the analytical methods used in the present study to characterize NMFs and the resultant treated wood.

9.1 Chemicals, purities, and suppliers

The chemicals used for synthesis of NMFs are listed in Table 9.1.

Table 9.1 Chemicals used in synthesis and wood treatment

Compound	Purity	Supplier
Magnesium ethoxide, $Mg(OEt)_2$	99.8%	Evonik Industries
Calcium chloride, $CaCl_2$	anhydrous, ≥ 98%	Sigma Aldrich
Calcium oxide, CaO	96-100.5%, FCC	Sigma Aldrich
Calcium lactate pentahydrate, $Ca(OLac)\cdot 5H_2O$	98%	AppliChem
Hydrogen fluoride, HF (aqueous)	39.24 M, puriss p.a., ACS reagent, ≥72%	Steinebach Chemie
L-lactic acid (lac)	85%, FCC	Sigma Aldrich
Ethylene glycol (EG)	≥ 99% for synthesis	Roth
Ethanol	≥ 99.8% for synthesis	Roth
Copper sulfate pentahydrate, $CuSO_4\cdot 5H_2O$	≥ 98%	Sigma Aldrich
Potassium dichromate, $K_2Cr_2O_7$	≥ 99%	Sigma Aldrich
Chromium trioxide, CrO_3	≥ 98%	Sigma Aldrich

Table 9.2 lists the materials used for the preparation of media for EN 113 (1996)[124] and vermiculite for EN 117 (2012).[129]

Table 9.2 Materials used in biological tests

Standard	Purity	Supplier
EN 113 – Per kolle flask 5% malt 3% agar	Malt extract for microbiology	Merck
	Agar-Agar	Roth
EN 117 – Per container had 30 g vermiculite, 70 ml distilled H_2O	Vermiculite K0-K4, Granulation 2 (3 mm)	Klein Marken-Dämmstoffe

9.2 Fluorolytic sol-gel synthesis

The NMFs were prepared from the corresponding alkoxides or oxides dissolved in an aqueous solvent, to which stoichiometric amount of aqueous HF was added slowly. This suspension was stirred overnight for formation of a clear colloidal solution (sol). The synthesis was optimized to prevent the sol from turning into a wet gel. Following are the specific details for each NMF sol.

(1) CaF_2 sol (1.25 M, ethylene glycol)
1188 mmol of CaO and 62 mmol of $CaCl_2$ were suspended in 850 ml of ethylene glycol (EG) followed by fluorination with 2500 mmol of aqueous HF. A clear colloidal sol was obtained after one day of stirring.

(2) MgF_2 sol (1.25 M, ethylene glycol)
1250 mmol of $Mg(OEt)_2$ was suspended in 850 ml of ethylene glycol followed by fluorination with 2500 mmol of aqueous HF. A clear colloidal sol was obtained after one day of stirring.

(3) MgF_2 and CaF_2 sol (1.25 M, ethylene glycol)
In the first step, 337.5 mmol of CaO and 37.5 mmol $CaCl_2$ was dissolved in 530 ml ethylene glycol, followed by fluorination with 750 mmol of aqueous HF. To this suspension 375 mmol of $Mg(OEt)_2$ was added, followed by fluorination of $Mg(OEt)_2$ with 750 mmol of aqueous HF. A clear colloidal sol of MgF_2 and CaF_2 was obtained after two days of stirring.

(4) CaF_2 sol (0.8 M, lactic acid)
In 350 ml of L-lactic acid, 800 mmol of $Ca(OLac)\cdot 5H_2O$ was suspended. To this suspension 350 ml of ethanol was added, followed by fluorination with 1600 mmol of aqueous HF. A clear sol was obtained the following day after stirring.

(5) MgF_2 (0.25 M, ethylene glycol) and CaF_2 (0.25 M, lactic acid)
Another MgF_2 and CaF_2 combination formulation was prepared by combining sols of MgF_2 in ethylene glycol from synthesis (1) and CaF_2 in lactic acid from synthesis (4). This was different from the MgF_2 and CaF_2 formulation in (3), which was a single sol prepared in ethylene glycol.

9.3 Wood treatment

Wood was treated with nano metal fluoride (NMF) sols and conditioned for the subsequent biological tests as follows.

9.3.1 Impregnation of nano metal fluorides into wood

Scots pine (*Pinus sylvestris*) sapwood specimens were used to test for efficacy against brown-rot fungi (*C. puteana* and *R. placenta*) and termites (*C. formosanus*). Beech (*Fagus sylvatica*) specimens were used for efficacy tests against white-rot fungus (*T. versicolor*). The specimen dimensions for both types of wood species were; 15 mm x 25 mm x 50 mm (radial x tangential x longitudinal). Wood quality was according to the standards EN 113 (1996)[124] and EN 117 (2012).[129]

The sols were diluted in ethanol to prepare the final concentration for impregnating into the wood specimens. Also, a chromated copper (CC) formulation composed of 50% w/w copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), 48% w/w potassium dichromate ($K_2Cr_2O_7$), and 2% w/w chromium trioxide (CrO_3) was prepared for wood treatment.

The specimens were oven-dried at 103 ± 2°C for 18 h to remove any remaining water inside wood for better penetration of the treatment solutions. Then, the specimens were cooled down to room temperature in a desiccator after which their dry mass (M_1) was recorded and they were put back in the desiccator. Before impregnation with the treatment solution, the specimens were removed from the desiccator and placed in a glass vessel under low pressure at 0.4 ± 0.2 kPa for 1 h to remove the air from the wood cells. This step is to improve the uptake of the treatment solution into the wood specimens. After 1 h of evacuation, the treatment solution was introduced into the glass vessel and the specimens were soaked in it for 2 h at ambient pressure and room temperature.

The wet mass (M_2) of each specimen was recorded and then they were placed in the conditioning chamber at 20 ± 2°C with a relative humidity (RH) of 65 ± 5% for 4 weeks to achieve moisture equilibration. The weight percentage gain (WPG) was calculated using the dry mass before treatment and wet mass after treatment with the following formula.

$$\text{WPG}\ (\%) = \frac{(M_2 - M_1)}{M_1} \times 100$$

where,

M_2 – wet mass of the impregnated specimen

M_1 – dry mass of the specimen before impregnation

The retention (R) of NMFs in wood after treatment was calculated by the following formula.

$$\text{R}\ (\text{kg/m}^3) = \frac{(M_2 - M_1)C}{V}$$

where,

C – grams of preservative in 100 g of treatment solution

V – volume of the specimen

The specimen volumes were used to determine their volumetric swelling (S) and anti-swelling efficiency (ASE). The treated specimens were immersed in distilled water for 24 h followed with oven-drying (103 ± 2°C for 18 h) and their dimensions were measured with a digital caliper (0.01 mm accuracy). The equations for their measurements are as follows.

$$\text{S}\ (\%) = \frac{(V_2 - V_1)}{V_1} \times 100$$

where,

V_2 – volume of the dried impregnated specimen after water immersion

V_1 – initial volume of the specimen before impregnation

$$\text{ASE}\ (\%) = \frac{(S_U - S_T)}{S_U} \times 100$$

where,

S_U – volumetric swelling of untreated wood

S_T – volumetric swelling of treated wood

9.3.2 EN 84 - Leaching of treated wood specimens

The nano metal fluoride (NMF) treated wood specimens were leached before the EN 113 (1996) biological tests. The leaching procedure was performed in accordance with the EN 84 (1997) standard.[122] Subsequently, specimens were submerged in distilled water, exposed to low pressure at 4 kPa for 20 min, and then kept in distilled water for 2 h. The water was changed and collected nine times during a period of 14 days beginning with the 1st day. This collected water (leachate) was analyzed for the amount of active ingredients that were leached from the NMF treated wood.

The chemical analysis of leachates was done as follows. A Dionex 320 device equipped with an AS 40 autosampler, an ASRS 300 suppressor, an AS 9-HS column with thermostat and an electrical conductivity detector was used for the determination of fluoride according to DIN EN ISO 10304-1 (2009).[132] From the leachate specimen, 25 µl was injected and separated on a AS 9-HS column with carbonate (8 mM)/bicarbonate (1 mM) aqueous solution as an eluent at a flow rate of 0.35 ml/min in isocratic mode. If necessary, the specimens were diluted using ultrapure water prior to the measurement. An external calibration was used.

9.4 Biological tests

Wood specimens treated with NMF were tested in accordance with EN 113 (1996) and EN 117 (2012), respectively.

9.4.1 EN 113 - Efficacy against wood-destroying basidiomycetes

To evaluate the efficacy of NMF treated wood, four replicates were used per treatment as outlined in EN 113 (1996).[124] After NMF treatment and conditioning, the specimens were autoclaved at 121°C for 30 min. The wood specimens were tested against *Coniophora puteana* (BAM Ebw. 15), *Rhodonia placenta* (FPRL 280), and *Trametes versicolor* (CTB 863 A). One NMF treated specimen and an untreated specimen were introduced in a Kolle flask and then exposed to the selected fungi for 16 weeks. Additionally, treated specimens were put only on malt-agar medium to determine the mass loss not due to fungal decay at the end of the test, this is known as the correction value. At the end of testing, the mycelium adherent to the surface of the wood specimens was gently removed and their mass (M_3) was recorded. Then, all specimens were oven-dried (103 ± 2°C for 18 h) and their final mass (M_4) was recorded. The mass loss was calculated

as the difference between the initial and final mass. The formula for calculating the mass loss (ML) is presented below.

$$\mathrm{ML}(\%) = \frac{(\mathrm{M_1} - \mathrm{M_4})}{\mathrm{M_1}} \times 100$$

where,

M_1 – oven-dried mass of specimen before wood treatment

M_4 – oven-dried mass of treated specimen after EN 113 test

Correction values were used where high uptake of the NMF formulation during treatment resulted in final mass losses to be negative NMF treated wood specimens that had an average mass loss of 3% or below after the EN 113 test were classified as durable.

9.4.2 Equilibrium moisture content (EMC)

Moisture content of wood depends on the relative humidity and temperature of the surrounding environment. Wood reaches an equilibrium moisture content when it is neither gaining nor losing moisture. The equilibrium moisture content (EMC) of specimens was calculated after the end of the EN 113 test as follows.

$$\mathrm{EMC}\ (\%) = \frac{(\mathrm{M_3} - \mathrm{M_4})}{\mathrm{M_3}} \times 100$$

where,

M_3 – mass of specimen after EN 113 test

M_4 – oven-dried mass of specimen after EN 113 test

9.4.3 *In-vitro* agar test

An *in-vitro* agar test was done after the first set of biological tests to determine the optimum NMF concentration and formulation for biocidal efficacy against fungi. The test was done on three fungal species, *C. puteana* (BAM Ebw. 15), *R. placenta* (FPRL 280), and *T. versicolor* (CTB 863 A). Two concentrations of NMF were tested; 0.05 M and 0.4 M, in three formulations; MgF_2, CaF_2, MgF_2+CaF_2. For each formulation, three *Petri* dishes with their respective medium were prepared. To a 20 mL medium of 5% malt extract

and 3% agar, NMF sols were added in different amounts to get the respective final concentration of 0.05 M and 0.4 M and then sterilized. After the medium solidified, an inoculum from a fungal culture was placed in each *Petri* dish. The *Petri* dishes were incubated at 20 ± 2°C and 65% RH. The anti-fungal efficacy was assessed by measuring the size of the fungal colony diameter in centimeters over the duration of the experiment (14 days) to calculate the fungal growth rate. The formula for growth rate is shown below.

$$\text{Growth rate (cm/day)} = \frac{\text{Fungal diameter in cm}}{\text{Number of days}}$$

9.4.4 EN 117- Efficacy against termites

The testing against termite species, *Coptotermes formosanus* was done in accordance with EN 117 (2012)[129] in a glass jar. Each jar comprised of 30 g of vermiculite, 10 ml of H_2O, and 1 cm^3 of untreated wood specimen. To each jar, 250 termite workers and 30 termite soldiers were introduced. The termites were given three days to start settling in their new environment indicated by their active movement in the jar. Then, unleached treated wood specimens were introduced into the jar. After 8 weeks, the test specimens were removed from the jar and termite mortality was calculated by counting the number of alive termites with the formula shown below.

$$\text{Termite mortality (\%)} = \frac{(250 - \text{Number of alive termites})}{250} \times 100$$

Then, the specimens were dried at 103°C for 18 h and weighed to record their final oven-dried mass. The mass loss (%) due to termite attack was calculated as the difference between the initial oven-dried mass of the specimen before NMF treatment and final oven-dried mass of the specimen after the end of the EN 117 test. These specimens were also visually examined to classify the severity of termite attack with an assessment scheme provided in EN 117 and shown in Table 9.3. Based on the visual rating and according to EN 350 (2016),[133] the treated specimens can be assigned to Durability Classes ("Durable" if the visual rating was 0 or 1, "Moderately Durable" if less than 50% test specimens had a visual rating of 3 or 4, and "Not Durable" if more than 50% had a visual rating of 3 or 4).

Table 9.3 Visual rating assessment scheme from EN 117 (2012)

Rating	Description
0	No attack;
1	Attempted attack – Surface erosion (less than 0,5 mm in depth);
2	Slight attack – erosion of wood surface (less than 1 mm in depth) and/or single tunneling (less than 3 mm in depth);
3	Average attack – erosion between 1 mm to 3 mm in depth and/or single tunneling (greater than 3 mm in depth) without cavities;
4	Strong attack – tunneling greater than 3 mm in depth with formation of large cavities;

The number of protists in the termite gut were also measured according to the method described by Lewis and Forschler.[134] The termite gut was gently removed using fine-tipped forceps. The gut contents of three termites were pooled in a phosphate buffered saline (PBS) solution (500 µl) with a pH of 7.4. Then, the solution was gently agitated with a pipette tip. From this solution, 50 µl aliquot was added to a counting chamber (Nageotte, Bioanalytic, GmbH), which was then placed under a microscope to count the number (#) of protists. The protist population in the termite gut was estimated using the following formula.

$$\text{Protists} = \frac{\#\ \text{Counted protists} \times \text{Original volume (500 µl)}}{\text{Chamber volume (50 µl)} \times \#\ \text{Termites per sample}}$$

9.5 Analytical methods

The NMF sols and the resultant NMF treated wood specimens were characterized. The following is a brief explanation of the analytical techniques used for their characterization.

9.5.1 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive technique to characterize materials. It is based on constructive interference between scattered beams diffracted from the lattice planes of the material. The periodic arrangement of atoms in a given material gives rise to

an X-ray diffraction pattern characteristic to the material. The diffracted beams are measured by the goniometer at specific angles 2θ satisfying the Bragg's law shown below.

$$n\lambda = 2d\sin\theta$$

where, n – integer, λ – X-ray wavelength, d – interplanar spacing, θ – diffraction angle

In this study, XRD measurements were performed using the Seifert XRD 3003 TT with a rotating specimen holder (Rich, Seiffert & Co., Freiberg) and Cu Kα radiation (Cu $K\alpha_{1,2}$, λ = 1.542 Å, V = 40 kV, I = 40 mA, 2θ range - 5° < 2θ < 90°, step scan - 0.05°, step time - 5 s). All specimens were measured in Bragg-Brentano geometry and the diffraction patterns were compared to powder diffraction files (PDF) in the ICDD powder database.[109]

9.5.2 Dynamic light scattering

Dynamic light scattering (DLS) is used to determine the hydrodynamic diameter of the nanoparticles. In this technique, laser light is shined on the clear colloidal suspension of nanoparticles. The light interacts with the nanoparticles causing it to be scattered. The intensity of the scattered light depends on various characteristics of the nanoparticle. This scattered light is analyzed and information about the nanoparticle is extracted from the data using a light scattering model.

In this study, DLS was done with Malvern Instruments Zeta-sizer Nano using a He-Ne Laser (λ = 633 nm, 4 mW). The scattered light was detected at an angle of 173° to minimize the scattering effects. Three measurements were recorded for each sample to determine the average hydrodynamic size of the nanoparticle.

9.5.3 Transmission electron microscopy

In transmission electron microscopy (TEM), the sample is irradiated with an electron beam. Instead of secondary electrons, the transmitted electrons from the sample are detected. Only the elastic electrons contribute in TEM imaging. Therefore, large number of electrons with a small energy distribution are needed to reach the detector for characterization. As a result, the specimen thickness should not exceed 100 nm otherwise not enough transmitted electrons would reach the detector.

For TEM and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) measurement, the NMF sol was dispersed in ethanol and 10 µl of it was transferred on a conventional carbon hole film with a thickness of 20 nm

supported on a copper grid. After complete evaporation of the ethanol from the grid, the particles were studied on a JEOL 2200 FS (S)TEM that was operated at an acceleration voltage of 200 kV. In high-resolution mode TEM (HR-TEM), the point-to-point resolution is 0.19 nm and the information limit for the visualization of crystal lattice planes is 0.14 nm.

9.5.4 Scanning electron microscopy

Scanning electron microscopy (SEM) is a method that provides information about the surface topography and morphology of a given sample in the nanometer range. The sample is scanned with a finely focused electron beam. Typical energy range of the electron beam in SEM is from 5 to 20 kV. The irradiation stimulates the atoms in the sample and generates secondary electrons, which together with the back-scattered electrons are collected in a detector. A photomultiplier transforms the energy of the collected electrons into an electrical signal that is transferred to the screen of a monitor to visualize the sample.

In SEM, the wood specimens are prepared as follows. The wood specimens were cut using a sledge microtome and sputtered with carbon (15 nm). The SEM images were acquired on Leo 1530 VP (Zeiss) at 15 kV in variable pressure (5−10 Pa) with a working distance of 10 mm.

The composition contrast between the wood specimen and the NMFs in a back-scattered electron (BSE) image is due to the back-scattered electrons. The energy of back-scattered electrons reflected from wood is lower than NMFs. Therefore, the higher energy from the NMF aggregates is associated with the lighter regions in the back-scattered electron image. Thus, BSE provides information about the spatial distribution of NMFs in treated wood.

9.5.5 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDX) is used to determine the elemental composition of the specimen. A finely focused electron beam incident on the specimen causes an electron in the atom to be excited and ejected from the inner shell creating an electron hole. Another electron from an outer, higher energy shell fills up that hole. The energy difference between the higher energy shell and the inner energy shell is released as an X-ray, which is characteristic of each element. An energy-dispersive spectrometer is used to measure the number and energy of the X-rays emitted from a representative area of the specimen and thus provide its elemental composition map.

Elemental distributions of calcium, magnesium, and fluorine on the wood surface were mapped with EDX Bruker Esprit at 15 kV, in variable pressure (5−10 Pa), at a working distance of 10 mm, and an acquisition time of 600 s.

9.5.6 X-ray micro-computed tomography

Non-destructive analysis of the whole wood specimen was done with X-ray micro-computed tomography (X-ray micro-CT). The advantage of this technique is that there is no sample preparation required. The measurement is done under ambient conditions by directing X-rays at the wood specimen from multiple orientations. The chemical composition (atomic number) and density of wood changes the X-ray intensity.[135] These changes in intensity are recorded and then algorithms are used to reconstruct the internal structure. The voids in wood appear black as they do not change the X-ray intensity. In contrast, the X-ray intensity changes when it encounters aggregates of NMFs in wood which appear white. In such an analysis, location of NMFs in the whole wood specimen can be determined.

X-ray micro-CT was performed on a Phoenix v|tome|x L 300/180. The specimen was scanned using an open type microfocus transmission X-ray tube at 60 kV, 170 µA, 3000 projections, and 6000 ms exposure time per projection. Reconstructions were performed with the datos|x reconstruction software package, a tomography reconstruction package for cone-beam from GE Sensing & Inspection Technologies GmbH phoenix|x-ray, resulting in reconstructed data with a voxel size of 12 µm. The reconstructed volumes were analyzed using 3D Imaging software, CT Viewer, licensed by BAM.

9.5.7 Nuclear magnetic resonance spectroscopy

Solid-state MAS (magic angle spinning) NMR spectra were recorded on a Bruker AVANCE 400 spectrometer at room temperature. A 2.5 mm rotor was filled with grounded wood and then ^{19}F (Larmor frequency of 376.4 MHz) was measured using rotation frequency of 20 kHz. All ^{19}F MAS spectra of wood specimens were recorded using a $\pi/2$ pulse length of 4.4 µs, a spectrum width of 400 kHz, a recycle delay of 5 s, and an accumulation number of 2048.

Solid-state MAS ^{1}H-^{13}C NMR spectra was performed at 10 kHz using a 4 mm rotor filled with grounded wood. NMR spectra were acquired with a cross-polarization (CP) pulse sequence under the following conditions:^{13}C frequency of 100.62 MHz, $\pi/2$ pulse

length of 5 µs, ^{1}H decoupling pulse power of 11 dB, recycle delay 5 s, contact time of 1000 µs, time domain of 1796, and line broadening of 40 Hz. A TPPM15 pulse sequence was used for ^{1}H decoupling. The acquisition time was 0.019 seconds and the sweep-width was 45 kHz. The number of scans was 2194.

9.5.8 Contact angle

Contact angle is used to characterize the surface wettability of a given material. The angle between the liquid surface and the contact surface is called the contact angle (CA). The water contact angle depends on the chemical composition of the substrate material. At an angle of 0°, the surface becomes completely wet as the water droplet spreads. An angle between 0° and 90° means that wetting the surface is possible. When the angle is over 90° the surface is poorly wettable as the surface tension of the liquid is greater than the substrate to be wetted. For this reason, a substrate with a CA above 90° is characterized as hydrophobic and if CA is below 90°, then it is characterized as hydrophilic. A substrate with an angle of over 150° has super hydrophobic properties.[116]

CA measurements were performed with a drop-shaped analyzer (Kruss, DSA100). The syringe above the specimen stage was set to dispense 0.5 µl amount of distilled water on the wood surface. The CA values were recorded immediately after droplet deposition on the wood specimen surface until complete wetting of the surface with a time interval of 30 s. The CA was measured on three different locations for each specimen.

9.5.9 Fluoride concentration in sols

Four replicates of each NMF sols at 0.5 mM were prepared with distilled water. The amount of fluoride in NMF formulations was measured using ion chromatography as follows. A Dionex 320 device equipped with an AS 40 autosampler, an ASRS 300 suppressor, an AS 9-HS column with a thermostat and an electrical conductivity detector was used for the determination of fluoride concentration. From the NMF sol, 25 µl was injected and separated on a AS 9-HS column with carbonate (8 mM)/bicarbonate (1 mM) aqueous solution as an eluent at a flow rate of 0.35 ml/min in isocratic mode. An external calibration was used.

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Shirin M. Usmani, September 2020

Selbständigkeitserklärung

According to the regulations for the award of a doctoral degree of the Faculty of Mathematics and Natural Sciences 2018:

Declaration of Independent work for inclusion in the thesis (see § 7/4)

Declaration: "I declare that I have completed the thesis independently using only the aids and tools specified. I have not applied for a doctor's degree in the doctoral subject elsewhere and do not hold a corresponding doctor's degree. I have taken due note of the Faculty of Mathematics and Natural Sciences PhD Regulations, published in the Official Gazette of Humboldt-Universität zu Berlin no. 42/2018 on 11/07/2018."

Shirin M. Usmani Berlin, 01.09.2020