WOOD RESEARCH
57 (1): 2012
01-14

ASSESSMENT OF FLUID FLOW PATHS AND DISTRIBUTION IN CONIFERS

Katrin Zimmer
Norwegian University of Life Sciences, Department of Ecology and Natural Resource Management
Norwegian Forest and Landscape Institute, Section Wood Technology
Ås, Norway

Erik Larnøy
Norwegian Forest and Landscape Institute, Section Wood Technology
Ås, Norway

Olav Høibø
Norwegian University of Life Sciences, Department of Ecology and Natural Resource Management
Ås, Norway

(Received September 2011)

ABSTRACT

Wood in its natural condition is vulnerable to biological decay caused by fungi, insects and bacteria. To facilitate its outdoor application and enhance the durability, wood protection systems are applied ever since. Due to restrictions for established but hazardous wood protection treatments, newer systems are utilized. The protection agents´ uniform allocation within the wooden matrix is essential for successful performance of wood protection approaches. Hence a detailed knowledge about transport mechanisms and the different penetrating properties is essential for design and development of successful impregnation wood protectives. Both commercial wood protectives and other chemical solutions are used for the study of cavity sizes, distribution patterns, microdistribution and general flow paths of protective agents in wood. In principal, the tracing chemicals have to be aligned to the aim of the study. This review paper is prepared to give an overview of chemicals and methods utilized for studying cell wall accessibility, fluid flow and its inhibiting factors as well as the distribution of chemicals over the tissue and the microdistribution within the wood cell wall.

KEYWORDS: Cell wall accessibility, fluid flow, microdistribution, trace chemicals introduction.

INTRODUCTION

Wood is one of the world's most important building and construction materials. In outdoor applications the wooden structure is exposed to climate conditions that promote attack of fungi and insects. Depending on the natural durability of the wood species and the part of the tree employed, this vulnerability leads to a reduction in the material's service life. To enhance the use of wood in outdoor applications and to be able to better predict and improve its service life, wood protection is essential.

Wood protection in general includes every activity to protect the material properties both functionally and aesthetically (Willeitner 2003). Strictly speaking, wood protection is a generic term for activities preventing wood degradation caused by fungi and insects as well as marine organisms. One of the most important and effective protection systems utilized earlier was copper chrome arsenates. With a changing environmental focus and growing awareness of the responsibilities for human and environmental health and its importance, hazardous protection systems have been restricted or banned (Hill 2006). Accompanied by these changes, the research on developing alternative protection systems is enhanced tremendously during the last decades (Homan and Jorissen 2004). Today, research on a great number of protection systems for various applications is on-going. Except for only a few examples (Heat treatment (Rapp 2001)), all systems have in common that a fluid substance has to be transported into the wood and the cell wall structures.

An accurate knowledge about fluid pathways, penetration and microdistribution patterns of impregnation agents into the wooden structure are essential to design wood modification systems and wood protectives with the best performance possible. In contrast to ordinary wood preservation systems which often include a toxic component against fungi, wood modification systems take effect by altering wood cell wall properties without any production of toxic substances or residues in the material (Homan and Jorissen 2004). Pilgård et al. (2010) indicate that *Trametes versicolor* is present within the modified wooden substance without the fungi degrading the structure. Gradients in impregnation and modification as well as unmodified areas cause unprotected areas. Therefore are microdistribution and the uniform allocation of wood protection agents important factors for preservative performance (Chou et al. 1973, Matsunaga et al. 2004, Jusoh and Kamdem 2009, Matsunaga et al. 2009). For the industry, process conditions have to be adjusted to the material most difficult to treat in order to ensure impregnation qualities required (EN 350-2, 1994). Studying the fluid pathways and fluid flows inhibiting factors is of economic interest, too, as one can choose material more favourable to impregnate.

Transport processes mainly take place through the same pathways as in the living tree (Nicholas and Siau 1973). In softwoods this system includes tracheids in longitudinal and radial direction, the ray parenchyma cells, the resin canal system, intercellular spaces as well as the pits connecting the structures and small cavities within cell wall structures (Bellmann 1955). Strong contributors to permeability of wood are the pits in terms of presence, number, structure and aspiration state (Stamm 1946, Buro and Buro 1959, Liese and Bauch 1967). Diffusion of impregnation agents occurs through the pit chambers into the middle lamella (Wardrop and Davies 1961) and the S_2-layer (Wallström and Lindberg 2000b). Submicroscopic spaces within cell wall fibrils work as diffusion pathways (Bellmann 1955, Wardrop and Davies 1961). Within the cell wall, in the S_2 layer, spaces between microfibrils are filled with lignin; but this filling is incomplete. These spaces have a size in the nanometer range but are often found in literature as micropores and microvoids. The maximum size for micropores in the cell wall is approximately 2-4 nm, whereas particles bigger than this can penetrate the cell wall in its swollen state (Hill 2006). The characteristics of these cavities delimit maximum particle sizes of the impregnation agent.

Physical and chemical interactions appear for certain treatment fluids and wood species combinations dependent on the specific characteristics as e.g. viscosity, solution concentration, polarity, and ion diameters (Hackbarth and Liese 1975, Rapp and Peek 1994). Due to this, the distribution of laboratory impregnation fluids like silver nitrate does not reflect the real distribution of a wood preservative under the same process conditions (Pendlebury et al. 1991). Rapp and Peek (1994) suggested therefore the use of at least two wood preservatives with different characteristics for testing permeability. When testing the permeability, the penetration depth, not the retention of impregnation fluids is crucial (EN 350-2, 1994).

Industry and researchers are faced by the varying permeability of Scots pine sapwood (*Pinus sylvestris*), (Lebow et al. 2006, Larnøy et al. 2008, Lande et al. 2010), even though the material is characterized as class 1 (easy to treat) according to the EU standard EN 350-2, 1994. This variation is yet not fully understood. The general penetration patterns as well as structural and chemical properties need to be analysed. In addition, impregnation with trace molecules in different molecule sizes should be performed to reconstruct fluid pathways and their microdistribution within the tissue. For analysing the structural properties and fluid pathways within the material and to investigate structural differences between permeable and less permeable material, microscopic techniques should be applied.

The question is what are the suitable molecules for comparing permeability of wooden samples with different background? To gain a better understanding the permeability of the wooden matrix, trace chemicals and wood protectives are utilized to study particle distribution and fluid flow within the wooden tissue and structures that inhibit fluid and particle flow.

This review paper is prepared to give an overview of chemicals utilized for studying the microdistribution and permeability of wood.

MATERIAL AND METHODS

For the study of cavity sizes, distribution patterns, microdistribution and general flow paths of preservatives in wood, commercial wood preservatives and other chemical solutions are used. Generally, the trace chemical has to be adapted to the purpose of the study and it is highly dependent on the field to be studied such as general flow paths of the impregnation agent or the accessibility of the cell wall to different molecules. Different trace chemicals will be needed when investigating the general distribution of an impregnation agent over the tissue or the microdistribution within the cell wall.

RESULTS AND DISCUSSION

Cell wall accessibility

Solute exclusion is a way to measure the accessibility of the cell wall structures to molecules of different sizes in a water-swollen state. (Tarkow et al. 1966, Hill et al. 2005). Measuring the features of the cell wall cavity system enables the selection of impregnation solutions from the outset that are capable of diffusing into the cell wall and impregnating it entirely. Conditional features for the molecules to be used are a large range in molecular sizes, inertness, monodispersity and a spherical shape (Hill et al. 2005).

In this context both polyethylene glycols (PEG) in different molecular weights as well as sugars and cross-linked dextrans have been used to identify the limiting size of molecules

penetrating into the cell wall in its swollen state. Tarkow et al. (1966) impregnated wood with polyethylene glycols in varying molecular weights from PEG-200 up to PEG-20000. They found the PEG-3000 to limit the voids at 22°C. Results from a test where the accessibility of the cell wall voids to sugars and cross-linked dextrans in different molecular weights was performed, indicated that the maximal accessible micropore diameter is 4 nm (40 Å) (Hill et al. 2005). Within this study there is a large gap between the molecules sizes 12 and 38 Å making the characterization of this micropore size area challenging. These molecules with a rather spherical shape have molecular weights of 504 and 6000 Dalton. The PEG-3000 limiting the voids in the test described earlier (Tarkow et al. 1966) had a molecular weight of 3000 Dalton, but was not as spherically shaped. This makes it more difficult for the molecule to penetrate the cell wall cavities. The data corresponds, but are difficult are to compare directly as the molecules are shaped differently and hence may have different penetration behaviour.

With the help of solute exclusion, differences in cell wall accessibility can be obtained. For accurate data, monodispers chemical solutions with comparable properties are necessary.

Flow paths

The way an impregnation agent penetrates a wooden structure reveals interesting aspects of the material properties in terms of extractive concentrations and allocations, as well as anatomical properties like interconnections between adjacent cells and tissues. Studying the flow paths is an important way of looking at these material features. These techniques reveal tissues transporting impregnation chemicals and it gives the possibility to compare ways of fluid flow and penetration depth, learn about inhibiting factors and reasons for deceleration of fluid transportation in both longitudinal and transversal direction.

The use of dyes can be a valuable tool for studying the flow paths in wood by using light microscopy. Although easily applicable, one needs to keep in mind that the molecular size and chemical properties can give a false positive or false negative when comparing to the impregnation fluids used for wood.

Mehrtens (1999) used Lugol´s solution to stain chitosan and used it to see the lateral penetration of the reactant, a thereby describing the penetration of chitosan in Scots pine. The penetration occurred only in the outermost tracheids, which can be caused by the very high molecular weight, which is difficult to bring into the wood matrix.

In a study accomplished by Singh et al. (2010) Radiata pine was impregnated with a low molecular weight chitosan solution. Toluidine blue as well as 1 % aqueous osmium tetroxide (OsO_4) solution was used to visualize the chitosan impregnated into the tissue. In unstained but chitosan impregnated sections, the chitosan filling the cell lumen was visible, but changes within the cell wall remained invisible (Fig. 1, left). Toluidine blue is a dye used to enhance contrast in lignified plant cell tissues (O'Brien and McCully 1969). This dye enables the observer to distinguish between cell walls impregnated with chitosan (orange colour) and unchanged cell walls (blue colour) (Fig. 1, middle) as the dye is incapable of penetrating chitosan impregnated cell wall regions. Singh et al. (2010) also used OsO_4 to enhance the contrast of impregnated and unchanged cell wall areas of the tissue. OsO_4 is a chelating agent with chitosan involving the amino groups of chitosan (Huang et al. 2003). Chitosan filled cell lumen appeared black after staining with OsO_4 and some of the cell walls also appeared darker when located close to the filled cells (Fig. 1, right). Those changes in colour are due to the chitosan impregnation (Singh et al. 2010).

Matsumara et al. (1998) describe a method where a combination of impregnating wood

samples with toluidine blue and fluorescein with vacuum and confocal microscopy is applied. An advantage of this method is that it is an effective way to visualize flow in tissue. Microtome damage of the specimen can be avoided as thick sections can be analysed and dry material can be studied, as the use of a fixation medium is not necessary. This avoids the redistribution of the dye in the material already treated.

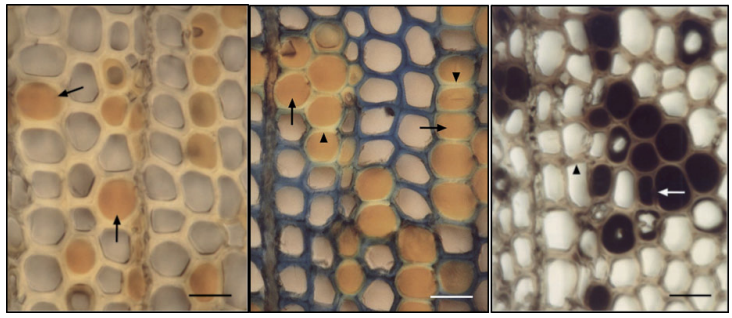

Fig. 1: Left: unstained wood section impregnated with chitosan. Chitosan fills the lumen, no differences in cell wall colour obtainable. Middle: Light micrograph of a toluidine blue stained section. Differentiation between chitosan (orange colour) and wood cell walls (blue colour) is possible. Right: Light micrograph of a section stained with osmium tetroxide. Cell walls around lumens that are filled with chitosan (black coloured regions) appear darker and more sharply defined (arrow) than those associated with empty lumens (arrowhead). Bar = 30 µm. (Singh et al. 2010).

In this study, the axial and radial resin canals were stained and claimed to be the main conductive pathways in Radiata pine (*Pinus radiata*), but uniserate and fusiform rays in radiate sapwood transported the dye material, too. For sapwood the fluid flow was determined by using a conventional light microscope. For the study of pathways within heartwood, a combination of detection of toluidine blue with conventional light microscopy and fluorescein with confocal microscopy was applied. The fluorescein dye was not found within the ray cells for unsteamed Radiata pine heartwood. Very limited amounts of dye were found in tracheids, but still within the resin canal system.

In another approach to study the transverse movement of liquids within the general pathways of wood, Olsson et al. (2001) applied an impregnation of both Scots pine and Spruce sapwood and heartwood with low-viscous epoxy resin. Fluid flow was studied in main cavities such as cell lumens. Penetration of cell wall cavities was of minor interest in this study. This work focused on revealing the role of rays and especially in the cross-fields between ray cells and longitudinal tracheids. Appearance and distribution of the cured epoxy resin were studied using SEM. The SEM observations revealed that liquid flow of low-viscous epoxy resin in Scots pine sapwood is enabled through damaged membranes of cross-field pits dividing longitudinal tracheids and the parenchymatic ray cells. The fluid pathways in Scots pine heartwood were blocked due to a deposition of extractives on the cell wall surfaces and within the parenchymatic ray cells. The liquid flow of both spruce sap and heartwood was reduced compared to Scots pine. Generally, the use of epoxy can give an overview of fluid pathways.

Important information about dispersion and extension pathways and the way a solute spreads within the wooden tissue can be revealed by studying the fluid pathways. Especially dyes can be supportive enhancing the contrast of specific components.

Distribution

Learning about the distribution behaviour of an impregnation fluid is an important step in ensuring and designing a reliable wood protection agent. Different techniques and chemicals are applied to disclose distribution patterns within the wood and to highlight differences within the different cell types.

In this context, De Vetter et al. (2006) impregnated both beech (*Fagus sylvatica*) and Scots pine sapwood sample material with a siloxane, a hydroxiterminated polydimethylsiloxane with a silicone concentration of 5 %. A combination of scanning electron microscopy with an energy dispersive X-ray spectrometer and an X-ray micro-computed tomography was applied to visualize the distribution. For the micro CT analysis, the siloxane was doped with a bromine functional silane and the impregnation went on with an aqueous mixture of 5 % siloxane and 20 % 3-bromopropyltrimethoxysilane to enhance the contrast.

3-D reconstruction after CT-micro scanning is a non-destructive technique based on an X-ray micro computed tomography and visualises the internal microstructure. Samples are scanned twice, once before and once after treatment (De Vetter et al. 2006). The siloxane/silanes mixture was found all through the sample (Fig. 2), and, as the cell lumen stood mostly free, it penetrates the cell walls. The rays of Scots pine seem to contain more siloxane/silane than the rest of the tissue. Differences is material concentration can be distinguished by changes in grey shades.

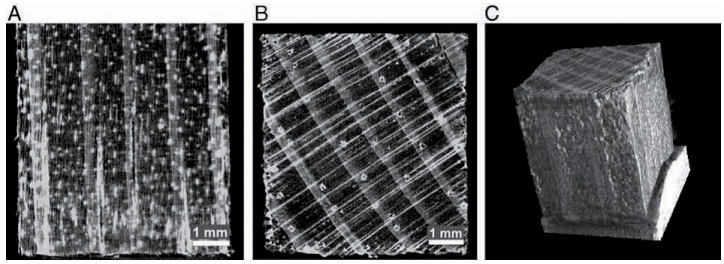

Fig. 2: Reconstruction of siloxane/silane impregnated Scots pine: A) longitudinal image, B) transverse view and C) 3D view. (De Vetter et al. 2006)

The micro-CT does not offer the same resolution as the SEM analysis, but it provides the user with a good overview of the distribution (De Vetter et al. 2006). Later developments in nanotom technologies have increased the resolution making the detection and distributing of trace chemicals much easier. Although this methods gives results with high 3D resolution, the apparatus is not general available and the scanning are laborious.

In Fig. 3 the authors have scanned a beech (*Fagus sylvatica*) sample impregnated with a copper based solution and linseed oil at the facilities of Phoenix x-ray in Germany, using a nanotom with sub-micron resolution (voxel size). In Fig. 3 left, a 3D rendering of the sample was produced, indicating the presence of linseed oil in the vessels. By making a virtual cut in the density, different substances can be filtered out. In Fig. 3 right, a three way cross section is shown visualizing an un-impregnated vessel.

Confocal microscopy is an optical imaging technique used to enhance image contrast by using a spatial pinhole to eliminate out-of-focus fluorescence in specimens that are thicker than the focal plane. As this technique allows examinations beneath the specimen's surface, studies on whole elements in the wooden structure are possible. A 3D image or expression of cells and the penetrating substances can be obtained without destroying the sample.

Thygesen et al. (2010) used confocal microscopy to localize furfuryl alcohol in different polymerisations within the wood (Fig. 4). Furfuryl alcohol is also known as 2-furanmethanol; furfural alcohol; alpha-furylcarbinol and FA. This molecule is an organic compound that consists of a furan ring with an attached methoxyl group. It is soluble with water and stable under these conditions, whereas it is insoluble in general organic solvents. Upon treatment with acids and under heat impact, it forms a linear polycondensate (Choura et al. 1997).

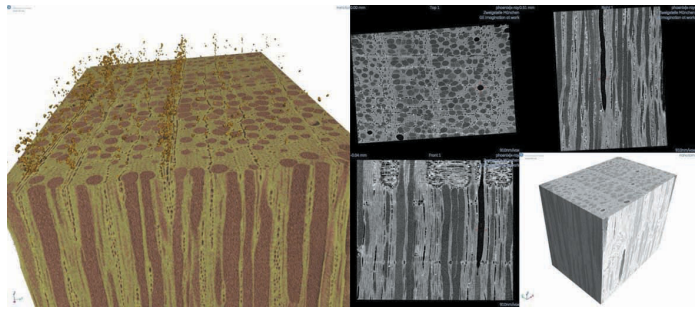

Fig. 3: Left side: a 3D rendering of a beech sample, indicating the presents of linseed oil in the vessels. By making a virtual cut in the density, one can filter out different substances. Right side: A three way cross section is shown visualizing an un-impregnated vessel.

Confocal microscopy was able to show the location of poly(FA) within the wood, while the red shift in the fluorescence was able to show the areas with highest poly(FA) concentration. Fig. 4 shows colour coded images of Scots pine, after FA modification, with different excitation wavelengths and emission ranges. These images suggest that the cell walls, not the lumen show fluorescence. This indicates the poly(FA) as a fluorescent reaction product being present within the cell walls. Moreover, the compound middle lamella appears in a brighter colour, hence more fluorescence is emitted from this area, indicating higher concentrations of poly(FA) located there. A comparison of the emission intensities at excitation intensities of 488 nm and 633 nm indicates rather short conjugation length of the FA polymer.

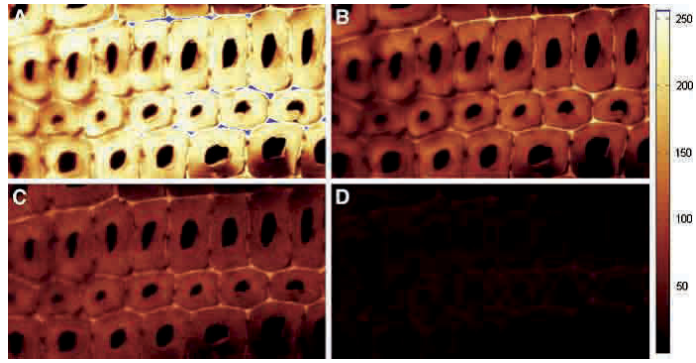

Fig. 4: Colour coded CLSM images of the fluorescence from a furfurylated Scots pine sample (data set3). Each image shows a 187 mm x 103 mm area. Excitation wavelengths and emission ranges: A) 488 nm/500–550 nm, B) 488 nm/550–600 nm, C) 633 nm/650–700 nm, D) 633 nm/700–750 nm (Thygesen et al. 2010).

By investigating the distribution of an impregnation or modification agent within the wood material, one can gain a good overview about the mode of penetration and patterns of its distribution. The techniques described above promote on understanding of possible variations within the tissue as well as the localization within the lumen or especially the cell walls. Those techniques however, are not capable of visualizing the microdistribution of impregnation chemicals within the cell wall structures.

Microdistribution

The distribution of chemicals or wood modification monomers diffusing into the cell wall structures is of great importance for the subsequent performance of the protective in service. Hence studying either the microdistribution of a specific impregnation agent into a wood material as well as investigations of the impregnation behaviour of a specific agent penetrating a variety of materials is gaining important knowledge to improve the predictability of service life in outdoor applications.

The microdistribution of copper and copper containing preservatives has been studied intensively. Numerous investigations have been performed with waterborne copper chromium arsenates (CCA) or copper chromium borate (CCB) applying scanning or transmission electron microscopy in combination with X-ray analysis (Petty and Preston 1968, Chou et al. 1973, Dickinson 1974, Greaves 1974). A Cu^{2+}-ion has an ionic radius of 0.073 nm and from literature it is known that this can penetrate the wood cell wall and bind to its components (Petty and Preston 1968, Greaves 1974, Petrič et al. 2000). Copper sulphate, the main substance to provide the solution with copper in CCA, is associated with 5 water molecules in solvent state. Depending on the wood species, and structures observed, different results were obtained. Even distribution along the cell wall as well as an enhanced copper occurrence in the middle lamella was reported (Petrič et al. 2000). The microdistribution of copper and other metals seems to follow those of lignin as phenolic hydroxyls of lignin and some extractives react with copper (Lebow 1996, Daniel and Nilsson 1987).

Petrič et al. (2000) also used an organic borne copper carboxylate and compared its deposition to wood treated with ammoniac copper or zinc containing formulations and to aqueous copper (II) chloride. The authors applied TEM with X-ray microanalysis and found a heterogeneous distribution of water and oil borne preservatives containing zinc and copper within the layers of the cell wall. The cell corners and middle lamella, the areas with highest lignin content, showed en enhanced copper content. A peak in copper concentration can also be seen within the torus (Fig. 5), a structure which usually does not contain lignin when they are in the sapwood, but mainly pectins (Bauch and Berndt 1973).

Furthermore, several other studies deal with copper in different solutions (Wardrop and Davies 1961, Fengel and Wolfsgruber 1971, Lebow et al. 2006,). Matsunaga et al. (2004) applied copper amine complexes (CuAZ) for studying the relationship of wood anatomical properties to the distribution of copper (Fig. 5). For analysing the microdistribution, a scanning electron microscope equipped with an Energy Dispersive X-ray Analyser (SEM-EDX) was applied. They found that the copper microdistribution in CuAz treated material is comparable to this impregnated with CCA.

When Wallström and Lindberg (2000a) studied the distribution of silver particles in green wood, they used a two-step impregnation. In the first steps green material was impregnated with K-glycerate as precipitant and later reimpregnated with an aqueous solution of glycerol and silver nitrate. The silver nitrate is easily soluble in water and a single silver ion has a size of 113 pm in this solution. Bailey and Preston (1969) earlier used hydrazine hydrochloride to precipitate the silver into the wood.

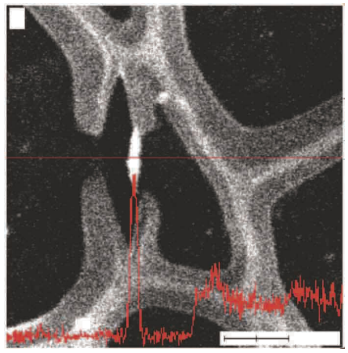

Fig. 5: Image obtained by superpositioning of the backscattered electron image and Cu-Ka X-ray line profile. Copper is more abundant in the torus, the compound middle lamellae including the cell corner, and secondary wall (Matsunaga et al. 2004).

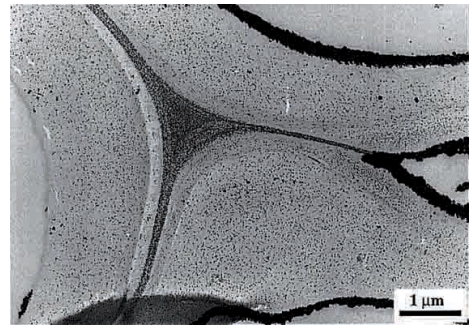

Fig. 6: Microdistribution of silver particles within cell walls (Wallström and Lindberg 2000b).

The silver is observable using transmission electron microscopy, where it becomes apparent as black dots which provide good electron contrast (Fig. 6). TEM is an electron microscopy technique, where electrons are transmitted through ultra-thin sections. Those electrons interact with the specimen under investigation. These interactions form a focused and magnified image. Resolution maximum up to 0.05 nm can be obtained. A disadvantage of this method is that sample preparation is very time consuming and only small numbers of samples can be studied. The diameter of the silver particles found precipitated in the green wood was between 2-20 nm and up to 1000 nm in the dried material. The most common particle size was in the S_2 2-4 nm with an additional peak at 13 nm. Within the S_1 and S_3, particles are of a size of 2-5 nm, whereas the size of the particles in the middle lamella ranges from 6-20 nm with most of them around 15 nm (Wallström and Lindberg 2000b). The distribution of silver in high temperature dried material is much more uneven due to damage in the form of microcracks. However, Wallström and Lindberg (2000b) state that the silver particles that attach to the glycerine molecules in this work do not reflect the real distribution of sizes.

Nanotechnology has no unified definition (Clausen 2007) but in general particles with a size of 1-100 nm are collected under this label (Siegel et al. 1999). With a controlled particle size, a homogeneous distribution within the wooden tissue is easily achievable.

A difference between soluble copper based protection systems for example, where the Cu^{2+} ion is supposed to bind to the cell wall structures, and micronized copper or other nanoparticle systems is the physical deposition of particles in the wood structure (Freeman and McIntyre 2008).

Matsunaga et al. (2009) studied the microdistribution of copper carbonate and iron oxide nanoparticles in treated wood (Fig. 7). The commercially purchased nano-Cu particles were present in a distribution from 1-25.000 nm with a mean size of 190 nm. The nanoparticles they found in the pit chambers of bordered pits varied in size from 50-700 nm.

A disadvantage of using nanoparticles for permeability testing is certainly their large size distribution.

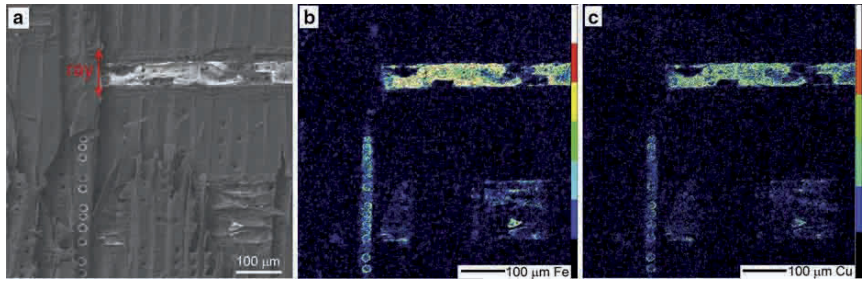

Fig. 7: Conventional SEM-EDX colour mapping of a radial section of southern pine treated with copper and iron nanoparticles and microparticles; A) Backscattered electron image, B) Fe-Ka X-ray image; C) Cu-Ka X-ray image (Matsunaga et al. 2009).

Investigations into the microdistribution behavior of specific molecules within the wood cell wall are important tools in designing wood protections with desirable features. Techniques such as SEM-EDX and TEM are sufficient contributors in disclosing particle allocation and microdistribution behavior.

CONCLUSIONS

The chemicals utilized for research on differences of the permeability, fluid flow in general, the distribution of a chemical within the tissue or the microdistribution within the cell wall have to be adapted to the aim of the study. Different chemicals and techniques are favourable for the various utilizations.

Differences in cell wall accessibility can be obtained by means of solute exclusion by employment of poly ethylene glycols (PEG) in different molecular weights as well as sugars and cross-linked dextrans. Important information about dispersion and extension pathways and the way a solute is spreading within the wooden tissue can be revealed by picturing the fluid pathways. Especially dyes can be supportive enhancing the contrast of specific components. Confocal microscopy as well can be a helpful tool tracing fluid pathways. By investigating the distribution of an impregnation or modification agent within the wood material, one can gain a good overview about the mode of penetration and patterns of its distribution. Here, a low viscous epoxy resin and furfurylalcohol as penetration agents were presented. With the aid of 3-D reconstruction after CT-micro scanning a nondestructive image of the wooden microstructure and the allocation of the chemical within can be revealed. Also Confocal microscopy enables the user to find differences in distribution and polymerization states of the fluorescent polymer within the tissue. However, to be able to see differences in microdistribution or the capability of a chemical diffusing into the cell wall, SEM-EDX and TEM are sufficient contributors in disclosing particle allocation and microdistribution behavior. Metallic ion particles such as copper or silver, zinc and iron are often utilized for these studies. Generally, the microdistribution of copper and copper containing preservatives has been studied intensively.

With the possibility of employing nanoparticles in monodispers solutions, these particle solutions provide an interesting tool for the study of material properties with for example different background. Cell wall accessibility as well as distribution and microdistribution in the cell walls swollen state could be analysed by applying different molecule sizes successively.

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Katrin Zimmer
Norwegian University of Life Sciences
Department of Ecology and Natural Resource Management
Norwegian Forest and Landscape Institute
Section Wood Technology
P.O.Box 5003
1432 Ås
Norway
Corresponding author: katrin.zimmer@skogoglandskap.no

Erik Larnøy
Norwegian Forest and Landscape Institute
Section Wood Technology
P.O.Box 115
1431 Ås
Norway

Olav Høibø
Norwegian University of Life Sciences
Department of Ecology and Natural Resource Management
P.O.Box 5003
1432 Ås
Norway