THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Diffusive Mass Transport of Ions in Wood

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Gothenburg, Sweden 2016

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ISBN 978-91-7597-403-3

Doktorsavhandlingar vid Chalmers tekniska högskolan
Ny serie Nr 4084
ISSN 0346-718X

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Cover:

(a) Wood cell: The radial surface of a softwood tracheid, showing pits on the side walls and the lumen within the hollow cell
(b) Schematic diagram of the ion exchange and chemical complexation likely to occur during the sorption of metal ions onto wood material. (M^{n+} M: cation, n: valance)
(c) Schematic diagram of the transport of chemicals/ions in softwoods in the longitudinal direction.

Printed by Chalmers Reproservice

Gothenburg, Sweden 2016

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ABSTRACT

Understanding the conditions that control the mass transfer of various chemicals/ions in wood is of great importance when it is subjected to various processes. Homogeneous impregnation with chemicals/ions, for example, increases the uniformity of the treatments to which the wood is subjected, reduces reaction times and may increase the yield of the final products. Wood material is porous and anisotropic and the constituents of the cell wall (solid) are composed of a variety of functional groups, so the properties of the cell wall may influence not only the mass transport of chemicals through the pores in the wood but also how these chemicals interact with the cell wall's components. The mass transports involved when wood material is impregnated with chemicals are advective (penetration) and diffusive (diffusion). The latter is a complex mass transfer with several processes that may involve the diffusion of chemicals through the cell pores (lumen and pit pores) and through the cell walls at certain conditions, as well as sorption at solid surfaces. Although several concepts and theories currently exist, some aspects of this type of mass transfer remain unclear.

The aim of this work is to develop a methodology to investigate the diffusive mass transport of ions in wood, combining experimental and modelling work. Experiments were performed on Norway spruce in the form of wood flour, pieces of wood and isolated components of wood. An experimental methodology was developed to measure the concentration profiles of cations through the porous structure of a piece of wood that considered the effect of sorption of the ions onto the matrix of the solid wood. In order to differentiate the amount of ions distributed between the solid wood and the external solution located in the wood pores (partition coefficient), additional experimental methodology was developed, using wood flour samples, to investigate the sorption of ions onto wood. The diffusion accessible porosity of the wood material was estimated from the intrusion pore volume measured by mercury (Hg) porosimetry and the solid volume of the cell wall was determined using a helium pycnometer. The impregnation of Norway spruce wood with lithium chloride (LiCl) was investigated in this study. Spectroscopic analysis (XPS, FTIR and AAS) was employed to investigate the potential interactions that occur on the surfaces of the wood material upon LiCl treatment. Using the concentration profiles, the partition coefficients and porosities measured, the effective diffusion coefficients along with tortuosity factors were estimated, using a transport model which was developed in COMSOL® multiphysics modelling software.

The findings in this thesis showed that, for the experimental conditions chosen, the methods developed gave reasonable results. However, defects in the pieces of wood (micro-cracks) remained and were detectable. It was observed that the sorption of Li^+ ions in Norway spruce wood flour was a spontaneous process that probably involved several types of interaction/bonding between the various functional groups in the cell wall of the wood and the Li^+/Cl^- ions; interactions with functional groups containing oxygen, for example, are identified as Li-O interactions.

Keywords: diffusion, impregnation, mass transport, sorption, wood

List of publications

This thesis is based upon the studies presented in the following papers, referred to by Roman numerals in the text.

I. **Determination of the diffusion of monovalent cations into wood under isothermal conditions based on LiCl impregnation of Norway spruce**
Reddysuresh Kolavali and Hans Theliander
Holzforschung 2013; 67(5):559-565

II. **Experimental determination of the diffusion of monovalent cation into wood: Effects of micro-cracks, wood structure, impregnation time and temperature on local concentration profiles**
Reddysuresh Kolavali and Hans Theliander
J-FOR, Journal of Science & Technology for Forest Products and Processes 2014; 4(2): 29-35

III. **The sorption of monovalent cations onto Norway spruce: model studies using wood flour and LiCl solution**
Reddysuresh Kolavali, Merima Hasani and Hans Theliander
In manuscript

IV. **The sorption of monovalent cations onto Norway spruce wood flour: molecular interactions behind the LiCl impregnation**
Reddysuresh Kolavali and Merima Hasani
Submitted for publication in Holzforschung

V. **Solute sorption and diffusion in wood based on the LiCl impregnation of Norway spruce**
Reddysuresh Kolavali, Merima Hasani and Hans Theliander
In manuscript

Results relating to this work have also been presented at the following conferences:

1. **Experimental determination of the diffusion of monovalent cation into wood under isothermal conditions**
   Kolavali Reddysuresh and Hans Theliander
   (Poster presentation)
   In conference proceedings. EWLP 2012, 12th European Workshop on Lignocellulosics and Pulp, Espoo, Finland, August 27-30, 2012, pp 476-479
2. **Experimental determination of the diffusion of monovalent cation into wood: Effects of temperature and impregnation time on concentration profiles**
   Kolavali Reddysuresh and Hans Theliander
   (Oral presentation)
   In conference proceedings. ISWFPC 2013, 17th International Symposium on Wood, Fiber and Pulping Chemistry, Vancouver (BC), Canada, June 12-14, 2013, Process Chemistry Track, Chemistry of the fiber wall and its components

Contribution report

The author of the thesis is the main author of the papers below:

Paper I-II– The experiments were planned, and the results evaluated, together with Professor Hans Theliander. The author performed all of the experiments and analyses involved.

Paper III– The experiments were planned, and the results evaluated, together with Professor Hans Theliander and Dr. Merima Hasani. The author performed all of the experiments and analyses involved, with the exception of the analysis of the metal ion concentrations in wood flour, before and after acid treatment. The modelling work was also performed by the author.

Paper IV– The experiments were planned, and the results evaluated, together with Dr. Merima Hasani. The author performed all of the experiments and analyses involved, with the exception of the XPS experiments.

Paper V– The experiments were planned, and the results evaluated, together with Professor Hans Theliander and Dr. Merima Hasani. The author performed all of the experiments and analyses involved. The modelling work was also performed by the author.

Contents

1. INTRODUCTION AND OUTLINE

1.1 Introduction

Petroleum and other fossil reserves are considered as being non-renewable carbon resources because of their long geological recycling times (~ 200 million years) compared with biomass (~ <1 to 80 years) feedstocks, which are renewable and carbon-neutral resources (**Liu** *et al.,* 2006). Wood lignocelluloses are biomass that are seasonal-independent; they are also the most abundant biomass on Earth, accounting for an annual production of ~170 billion metric tons in the biosphere. In Sweden, wood biomass resources have been the basis of significant industrial activities for several centuries. The dominant use of wood raw material is for pulp, paper and sawn timber products, although its use for energy purposes has increased during recent decades. However, sharper competition from countries with fast-growing forests means that competitiveness needs to be improved, and new and highly-refined products be found that complement existing pulp-based products. In this context, the "biorefinery" is the suitable concept for converting biomass into fuels, power and chemicals (**Fernando** *et al.,* 2006). A biorefinery is, in many ways, analogous to a petroleum refinery, in that a single feedstock is fractionated into a multitude of commodity products, depending on societal necessity.

The pulping industry is the most developed chemical technology for processing wood. It is, to some extent, already a biorefinery in which energy, cellulosic fibres and minor amounts of turpentine and tall oil are produced from wood. Interest in the biorefinery concept in this area has increased significantly in recent years mainly due to: (a) the trend of increasing costs for wood and decreasing prices for pulp and paper, (b) greater competition from low cost producers of pulp and paper in South America and Asia and (c) higher energy prices and new policy instruments that affect the production of materials such as non-petroleum-based materials and chemicals.

It is not only in the production of paper pulp and in the fractionation of different wood components in wood-based biorefineries but also in operations in which solid wood is treated with different kinds of chemicals (e.g. preservatives, fire retardants and dimension-stabilizing chemicals) that chemicals must be transported into wood prior to a reaction. The wood has to be impregnated with the reactants, so an understanding of the conditions that control the mass transfer of various chemicals/ions in wood is of great importance in wood processing technology: homogeneous impregnation, for example, increases the uniformity of a treatment, reduces reaction times and may increase the yield of the final products.

Wood material can be impregnated with chemicals by means of either advective (penetration) or diffusive (diffusion) mass transport (**Akhtaruzzaman** and **Virkola**, 1979). Penetration is defined as the flow of liquor into the gas/vapour-filled voids of the pieces of wood under a pressure gradient, and diffusion as the transport of chemicals/ions through the liquid within the pieces of wood under the influence of concentration gradients. The former occurs very fast and at reasonable pressure gradients, whilst the latter is a much slower phenomenon. Diffusion is therefore the controlling mechanism in most (but not all) wood conversion processes. Little is known about diffusive mass transport, however, partly because of the difficulties in determining the relevant diffusivities for a given system. The phenomenon that occurs during the diffusion of chemicals in wood therefore needs to be understood better.

The transport of chemicals/ions in a heterogeneous, porous, hygroscopic, and anisotropic material such as wood is very complex; the diffusive transport of chemicals in it is restricted due to the reduced cross-sectional area available for transport and tortuous pathways. In addition, the cell walls of wood consist of functional groups associated with hemicelluloses, lignin and cellulose, and solutes (chemicals) may therefore be subjected to sorption interactions with these components that reduce their rate of transport further. A wood cell (fibre) may be described as a pipe that is closed at both ends. The cells overlap each other and, under normal conditions, the mass transport between the fibres is via "pit pores". The cell wall may be described as being a more or less swollen gel. When the fibres and the pit pores become filled with a liquid, the main diffusive mass transport of the solutes occurs through that liquid. The solutes may be sorbed onto the cell wall too, so there may also be mass transport at the cell wall (surface diffusion) and/or in the gel-like structure of the cell wall. The overall mass transport rate may thus be influenced by several different mass transport phenomena as well as by sorption phenomena (**Figure 1.1**).

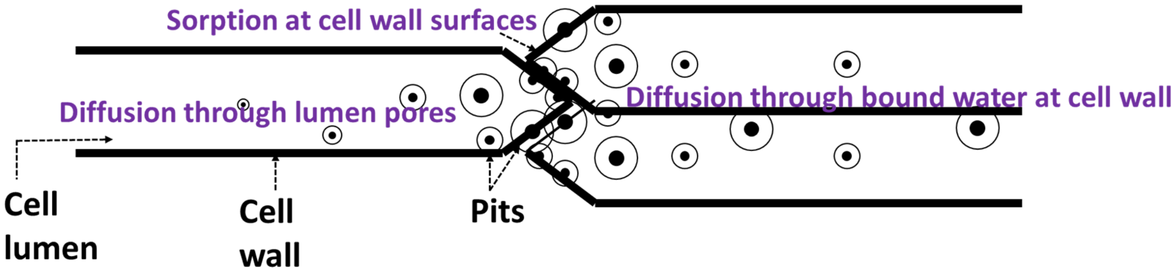


Figure 1.1 Schematic diagram of the transport of chemicals in softwood in the longitudinal direction.

1.2 Outline

This work is based on five papers, all of which can be found at the end of the thesis. The following chapter provides background information on the structure and composition of wood (Section 2.1) and its impregnation with chemicals (Section 2.2). It also provides some literature pertaining to existing methods, and the drawbacks associated with them, on the measurement of ion diffusion in wood. The objective of this thesis is stated in Chapter 3, with the focus being on the diffusive mass transport of ions in wood. The materials and methods used in this work, together with the theoretical model formulated for the determination of transport properties (effective diffusion coefficient and tortuosity factors) of ions in wood, are described in Chapter 4. This is followed by Chapter 5, which provides the important findings of the various investigations carried out, along with some discussion and interpretation of the results. Chapter 6 discusses the contributions made to this field of research. Finally, Chapter 7 summarizes the outcomes of the various investigations and the conclusions that are drawn.

2. Background

2.1 The structure and composition of wood

The classification of tree species as either "hardwoods" or "softwoods" is based on a botanical distinction. Softwoods (or "gymnosperms") are conifers: they are needle-bearing trees and are often evergreen. Hardwood trees (or "angiosperms"), on the other hand, are broad-leaved and mostly deciduous. Today, more than 90% of the world's trees are angiosperms. Gymnosperms includes species such as pine (*Pines*), spruce (*Picea*) and fir (*Abies*), and angiosperms include birch (*Betula*), beech (*Fraxinus*), oak (*Quercus*) and poplar (*Populus*). The wood species used most commonly in the Swedish forest industry are spruce (*Picea abies*), pine (*Pinus sylvestris*) and birch (*Betula verrucosa*) (**Henrikson** *et al.,* 2008).

The structure of wood

Wood is a heterogeneous, hygroscopic, anisotropic and porous material. There are large variations in structure both between and within individual trees. Many studies on the structure of wood can be found in the literature, e.g. **Fengel** and **Wegener**, 1984; **Sjöström**, 1993; **Miller**, 1999; **Rowell**, 2005; **Wiedenhoeft**, 2010. An understanding of the nature of the various capillary components of wood and the extent to which each influences the transport of liquids, dissolved materials and chemicals through wood is imperative. Wood is composed of different kinds of capillaries of variable size: from structures observable to the naked eye down to capillaries that approach molecular dimensions. In general, softwoods have a more uniform structure than hardwoods, with a fewer number of cell types. Since this study focuses on Norway spruce, only structural details of softwood are described.

Levels of structure in wood

The fundamental structure of wood, from the molecular to the cellular or anatomical level, determines its properties and behaviour. Four different levels of structure can be identified in wood:

Macroscopic structure

When a tree stem is cut transversely, a surface appears that is comprised of various annual growth rings presented in the form of concentric bands (**Figure 2.1**). A tree consists of several layers which, from the outside in, are known as the outer bark, inner bark, vascular cambium, sapwood (Sw), heartwood (Hw) and pith. The outer bark is a corky dead part, whereas the inner bark (phloem) is a thin living part through which sugars produced by photosynthesis are translocated from the leaves to the roots or parts of the tree that are growing. The outer bark not only provides mechanical support and protection to the softer inner bark, it also decreases the evaporative water loss (**Wiedenhoeft**, 2010).The cambium layer, located with the inner bark, forms cells of wood and bark; it can be seen only with the aid of a microscope. Growth in the thickness of the bark and wood is the result of cell division in the cambium.

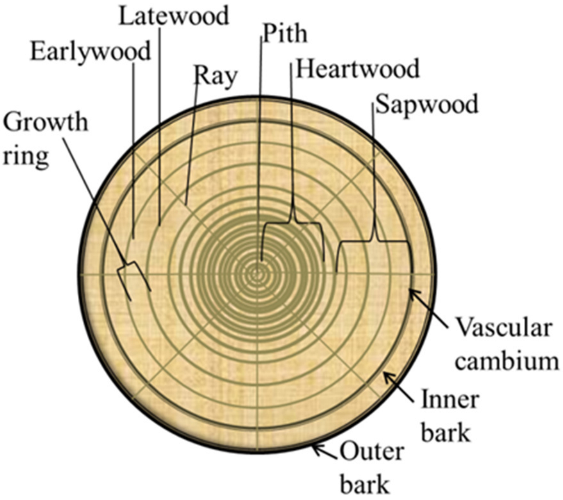


Figure 2.1 Macroscopic view of a transverse section of a tree stem.

Sapwood, which is next to the cambium, contains both living and dead cells. Its primary functions are to store photosynthate, provide mechanical support and handle the transport of sap, which consisting mainly of sugars and mineral salts dissolved in water. Heartwood is comprised of dead cells that have no function in either conducting water or storing nutrients/photosynthate. Hw has a lower moisture content than Sw. The transition from Sw to Hw is accompanied by an increase in the content of extractives; it is often these which darken the colour of the Hw. The extractives in Hw may also affect wood by reducing its permeability, thus making Hw slower to dry and more difficult to impregnate with chemical substances. The pith is a small core of tissue located at the centre (inner layer) of a tree stem, and comprises remnants of the early growth of the tree stem before the formation of wood. The inner part of the growth ring, formed first in the growing season, is called earlywood and the outer part, formed later on in the growing season, is called latewood (see **Figure 2.1**).

Microscopic structure

Softwoods consist mainly of longitudinal tracheids (90-95 % of cell volume) and a small number of ray cells (5-10 % of cell volume) (**Fengel** and **Wegener**, 1984; **Brändström** 2001). For the sake of simplicity, the longitudinal tracheids are hereafter referred to simply as “fibres”. All fibres are hollow, elongated tubes that are tapered and closed at both ends, with a cross-section that is something between rectangular and elliptical in shape. The hollow void in the fibres is called the lumen, and it is this which enables water to be transported within them. The distribution of fluids between adjacent cells is achieved through a system of pits that allows intercellular connection. The average length of Scandinavian softwood (Norwegian spruce and Scots pine) fibres is 2-4 mm and the average diameter is around 0.02-0.04 mm. The main function of earlywood, which is characterized by cells with relatively large cavities and thin walls, is to transport water and nutrition. Latewood cells serve more as mechanical support, as they have smaller cavities, thicker walls and are longer in length than earlywood cells. The average content of latewood in Norway spruce has been reported to be 20-25% on a volume basis. When growth rings are prominent, as is the case in most softwoods, earlywood differs markedly from latewood in its physical properties in that it is lighter in weight, softer and weaker than latewood (**Brändström**, 2001; **Miller**, 1999). The average thickness of cell walls of earlywood fibres is 2-4 μm whereas that of latewood fibres is 4-8 μm (**Sjöström**, 1993). The radial system is made up of ray cells, which run perpendicular to the fibres and across the void volume of the wood, and are known as wood rays (see **Figure 2.1**). Ray cells have an average length of 0.01-0.16 mm and diameter of 2-50 µm. The main functions of wood rays are to redistribute and store, for example, starch. A number of softwoods also contain vertical and horizontal resin ducts (channels), but these are usually filled with resin; their contribution to diffusion and flow is minor (**Burr** and **Stamm**, 1947). The other types of cells present in wood are epithelial cells (resin canals) and parenchyma (ray canals), the latter of which are involved in the transport of liquids in the horizontal direction (**Rowell**, 2005).

Ultra-structure

The wall of a mature wood cell consists of different layers (see **Figure 2.2 A**): a thin outer layer called the primary wall (P) and a thicker inner layer towards the cell cavity called the secondary wall (S). Three sub layers make up the secondary wall: the outer, or transition, layer (S_1), the central layer (S_2) and the inner layer or tertiary wall (S_3). Individual cells are connected together by the intercellular middle lamella region (ML).

Pits are characteristic to the structure of wood (see **Figure 2.2 B**). They represent canals that facilitate the transport of liquids both horizontally and vertically through the cell walls. Earlywood tracheids have more pits than latewood tracheids, which makes it easier to impregnate earlywood than latewood. Earlywood has approximately 50 to 300 pits per tracheid whereas latewood has only 10 to 50 (**Stamm**, 1946).

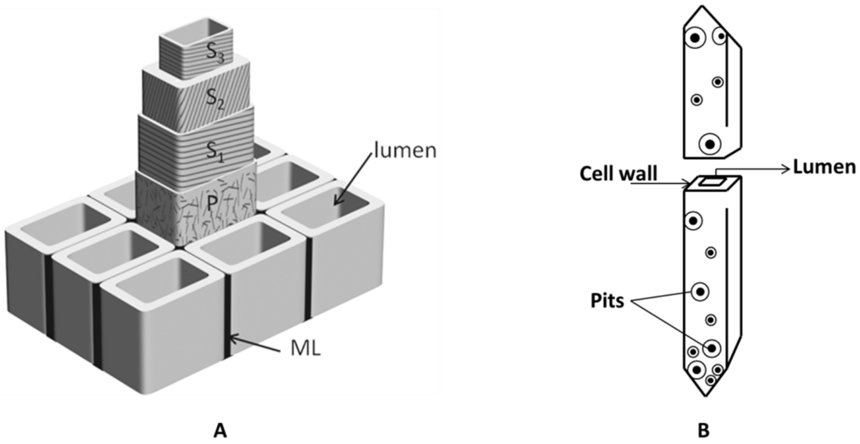


Figure 2.2 A. The different layers in the cell wall of wood. ML: middle lamella, P: primary cell wall, S1, S2, S3: secondary walls (from **Saltberg**, 2009). **B.** The radial surface of a softwood tracheid, showing pits on the side walls and the lumen within the hollow cell.

Pits of adjacent cells are normally paired off and form pit pairs, of which there are three common types: simple (link parenchyma cells together), bordered (in the radial walls of the tracheids and link tracheids to tracheids) and half-bordered (connect the vertical tracheids with horizontal ray parenchyma cells) (see **Figure 2.3**).

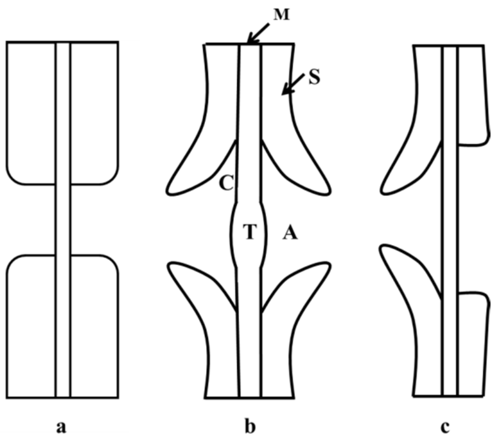


Figure 2.3 The three basic types of pit pairs: **a** simple, **b** bordered and **c** half-bordered. **A** aperture, **C** chamber, **M** middle lamella-primary wall, **S** secondary wall and **T** torus.

All pits have essentially two main components: a cavity and a membrane. The pit membrane consists of the primary wall and the middle lamella and, since pits occur in pairs, it is therefore composed of two primary walls and the middle lamella. Pits are localized exclusively on radial cell walls and are more frequent at the ends of tracheids than in the middle. The pit membranes of bordered pit pairs have a central thickened portion called the torus (T). This may be pushed against the opening of a cell wall and possibly become sealed in this position, thereby reducing the rate of material transport significantly: such pits are known as aspirated pits. Bordered pits on the tangential walls of longitudinal tracheids are always smaller than those on the radial walls (**Kazi**, 1996). The pit chamber is roughly in the form of a truncated cone, with the smaller end opening into the fibre cavity and the larger end closed by the pit membrane. The pit membrane is three to four times greater in diameter than the pit opening.

Molecular structure

Wood polymers can be classified into three major types: cellulose, hemicelluloses and lignin (**Sjöström**, 1993). The proportion of these three polymers varies between species. A typical composition of softwood is 40-50% cellulose, 20-30% hemicelluloses and 20-30% lignin, based on the weight of the extractive-free wood (**Kazi**, 1996).

Cellulose is a polysaccharide; its monomers, β-D-glucose units, are linked together by (1→4)-glycosidic bonds. The equatorial orientation of the hydroxyl groups in the structure of cellulose provides many opportunities for strong intra and intermolecular interactions, such as hydrogen bonds and hydrophobic interactions, to form. The cellulose chains show a tendency to self-order: they arrange themselves into so-called elementary fibrils that have regions with varying degrees of order. The elementary fibrils result in highly ordered crystalline structures, which have great tensile strength and low accessibility. Structures that are less ordered, on the other hand, are amorphous and easily degradable.

Hemicelluloses form a diverse group of polysaccharides that are substantially smaller in size than cellulose. The five main sugar monomers that can compose the chains of hemicelluloses are: D-glucose, D-mannose, D-galactose, D-xylose and L-arabinose (**Sjöström** 1993). Of these, L-arabinose and D-xylose are pentose (C_5) sugars while the rest are hexose (C_6) sugars. Hemicelluloses may also contain small amounts (as side chains) of L-rhamnose, D-glucuronic acid, 4-O-methyl-D-glucoronic acid and D-galacturonic acid. Three main types of hemicellulose occur in softwoods: (galacto) glucomannan, arabinoglucuronoxylan and arabinogalactans, although the latter is found primarily in larch wood.

Lignin is an amorphous and highly branched irregular complex polymer, predominantly constituted of three phenyl propane units that form the major building blocks, namely p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which give rise to a random sequence of p-hydroxyphenyl (H-lignin), guaicyl (G-lignin) and syringyl (S-lignin) sub-units, respectively, in the polymer. It has been identified that softwood lignins are mostly composed of G units, with the remainder being H units. The main function of lignin is to act as an adhesive between the cellulose fibrils and hemicelluloses, thereby providing the fibres and their structure with strength, hydrophobicity and resistance against microorganisms (**Sjöström** 1993).

There are other chemical compounds in wood, but these usually account for only a few percent of its total composition. One class of such compounds is called extractives; they include both water-soluble and organic-soluble extractives and form, on average, up to 10% of softwood. There are also inorganic compounds present in wood; as a group, they are generally known as ash. Metal ions such as calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn) and silicon (Si) are elements commonly found in wood (**Saltberg**, 2009).

Water in wood

Water has an inevitable effect on the properties of wood material (**Engelund**, 2011). The cell walls of wood are made of polymers that are more or less hydrophilic and can thus accommodate a substantial amount of water within the structure itself. Functional groups capable of attracting water molecules are termed as sorption sites. In wood, most of the sorption sites are found in the hemicelluloses, followed by cellulose and then lignin.

Shrinking and swelling in the structure of wood

Swelling and shrinking in wood occur as a result of changes in the moisture content. The moisture present in wood has two forms: bound or hygroscopic water, and free or capillary water. Bound water is found in the cell wall: it is believed to be hydrogen-bonded to the hydroxyl groups of primarily the cellulose and hemicelluloses and, to a lesser extent, to the hydroxyl groups of lignin too. The moisture content at which the cell walls are saturated with bound water, with no free water in the lumen cavities, is called the “fibre saturation point” (**Siau**, 1984). At saturated conditions, liquid water is available only in the cell walls: once the cell walls have been saturated, however, liquid water may also enter the cell cavities. The fibres in green (i.e. living) wood are always swollen. The moisture content in its structure may decrease when wood is cut; when it is reduced to below the fibre saturation point, the fibres shrink. This shrinking causes the cracking in the fibre walls that affects the mass transport of chemicals in wood, as an increased number of paths and/or smaller lumen develop. In most cases, wood pieces used in diffusion measurements have a moisture content that is higher than the fibre saturation point, which then leads to tangential swelling. Tangential swelling can easily be seen in the form of an increase in volume (**Skaar**, 1972); longitudinal swelling is much smaller than transversal swelling. Some electrolytes increase swelling by softening the cell walls (**Wallström** and **Lindberg**, 2000); they usually have a very high pH, e.g. NaOH (aq) and white liquor. This phenomenon may occur because the solution can penetrate the wood from the lumen, through the secondary wall layer S_3, and into the middle lamella.

2.2 Impregnating wood with chemicals

Impregnation is a method commonly used in the treatment of wood material whereby a variety of chemicals are employed to improve properties such as dimension stability, chemical and biological resistance, weathering and mechanical properties and resistance to fire (**Kazi**, 1996). Impregnation is also the first step in conventional pulping or wood conversion processes, followed by cooking, steam explosion and other processes. Proper impregnation of wood with chemicals is of great importance in attaining economically viable and efficient chemical pulping and biorefinery operations, because homogeneous impregnation not only increases the uniformity of the treatments but also reduces reaction times.

During impregnation, chemicals are transferred into the core of the wood by two entirely different primary mechanisms (**Stone** and **Förderreuther**, 1956). The first of these, liquor penetration, is the flow of liquor into the gas/vapour-filled voids of the wood material under the influence of a pressure gradient. The second, diffusion, refers to the movement of ions or other soluble matter through liquid present within the wood material under the influence of a concentration gradient. Both mechanisms occur simultaneously in fresh wood but, in certain cases (such as in Kraft cooking), most of the chemicals are transported into wood by diffusion. The role of penetration is to fill the fibre cavities with liquid, which enables a faster and more even diffusion of chemicals/ions into the wood (**Määttänen** and **Tikka**, 2012). Penetration occurs very rapidly initially if there are any gas/vapour-filled pores, whereas diffusion is the mechanism involved if the pores are completely filled with liquid, and is much slower.

In the conventional pulping process, a major portion of the cooking chemicals (white liquor) required may be added at the beginning of the process. The wood material contains water in the form of moisture from the beginning of the pulping process, which contributes to the dilution of the cooking liquor that penetrates into the interior of the wood chips. A concentration gradient (the driving force for the diffusion mechanism) is thus established between the bulk of the cooking liquor surrounding the wood chips and the liquor inside the fibre lumina. Following this initial penetration stage, the distribution of chemicals within the chips occurs mainly by diffusion, due to the chemicals (causing a decrease in concentration) present in the cooking liquor being consumed by various reactions that occur between lignin and polysaccharides, e.g. the neutralization of acidic groups present in wood or produced by the peeling of polysaccharides.

Diffusion in wood

Diffusion is a phenomenon involving the movement of constituents from one zone, with a high concentration, to another with a lower concentration (**Stamm**, 1967; **Siau**, 1984). The basic mechanism behind diffusion is random molecular motion. Diffusion in its simplest form is uni-dimensional diffusion, and can be expressed using Fick's first law of diffusion thus:

$$\mathrm{J} = -D_f \frac{\partial c}{\partial x} \qquad (2.1)$$

where J = mass flux, c = concentration of the solute in the liquid phase, x = direction of transport and D_f = diffusion coefficient of the "free-solution".

The diffusive transport of solutes in wood is influenced by tortuous pathways. There are lesser mass fluxes in wood than in free solution because some of the cross-sectional area in wood is occupied by solid portions. **Equation** (2.1) must therefore be modified for diffusion in wood as follows:

$$\mathrm{J} = -D_f \varphi \frac{\partial c}{\partial x} \qquad (2.2)$$

where c = concentration in the liquid phase of the wood pores and φ = volumetric water content, which is defined as:

$$\varphi = nS \qquad (2.3)$$

where n = total wood porosity and S = degree of saturation of the wood (0-1). The maximum flux for liquid phase diffusion will therefore occur when the wood is saturated (S = 1), all other conditions in **Equation** (2.2) being equal.
The tortuosity of the wood is usually accounted for by the inclusion of a tortuosity factor, τ, in the transport equation; in most of the cases, tortuosity factors cannot be measured independently. It is thus convenient to define an effective diffusion coefficient (**Saripalli** *et al.* 2002), D_e as:

$$D_e = \frac{D_f \phi \Theta}{\tau} \qquad (2.4)$$

where ɸ = effective, transport-through-porosity (porosity that is accessible to diffusion), ϴ = a constrictivity factor that accounts for the constricted transport paths caused by the small pores and pore throats in a porous medium (usually assumed ~ 1) and τ = tortuosity factor that accounts for the reduction in the diffusive flux caused by the tortuous path lengths traced by the solute molecules (in contrast to the straight paths in an unrestricted aqueous medium).
For time-dependent (transient) transport of non-reactive solutes in wood (i.e. solutes that are non-interactive with wood), Fick's second law is assumed to apply

$$\frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2} \qquad (2.5)$$

However, diffusion into, or from, a porous material such as wood is much more complicated than diffusion under steady-state conditions through a porous, inert material. The boundary conditions, for example, change continuously. Whilst wood is being impregnated with chemicals, it becomes swollen to varying degrees: in alkaline solutions, for example, the structure of the wood changes due to swelling. Reactions with various wood components also consume alkali and organic matter becomes dissolved which, in turn, affects the mass transport rate due to the increased permeability of the cell walls (**Gustafson**, 1988). Thus, for a given concentration of agent in solution, such as NaOH, the swollen wood matrix can be considered as having an irregular geometry with time.

A solute migrates faster through an open area (lumen) than through a partially-closed area (pit or pit membrane). Moreover, wood material has a variety of functional groups in its cell walls; the solutes are often subjected to chemical interactions with the components of cell walls, which also affects the rate of transport. Mass transport in wood is thus affected by both physical and chemical conditions. Under these dynamic conditions (e.g. to account for sorption interactions), **Equation** (2.5) may be modified thus:

$$\frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2} - \frac{\partial q'}{\partial t} \qquad (2.6)$$

where q' = sorbed concentration of the chemical species expressed in terms of the mass of sorbed species per unit volume of voids (i.e. occupied by the liquid phase), or thus:

$$q' = \frac{\rho_b}{\varphi} q \qquad (2.7)$$

where q = sorbed concentration expressed as the mass of solute sorbed per mass of dry wood; ρ_b = bulk density of the wood; and φ = volumetric water content.

The partition coefficient (k) is defined as:

$$k = \frac{q}{c} \qquad (2.8)$$

where q = sorbed concentration (mass of solute sorbed per mass of dry wood) and c = concentration of solute in the liquid phase of the wood pores. When the relationship of q versus c is linear, k is termed as the "distribution coefficient, k_d." Otherwise, k is a function of the equilibrium concentration of the liquid in the wood's pores. A plot of the mass of the solute sorbed per mass of wood, q, versus the concentration of the solute in solution, c, is called a "sorption isotherm".

Important factors that affect the mass transport of ions in wood

Properties of wood: Different types of wood (within the tree: Sw vs. Hw, juvenile vs. mature wood, reaction vs. compression wood, as well as different species) have different capillary structures, which influence the diffusion paths within the wood. This affects the rate of mass transport through wood, at least in the early stage of impregnation, where its permeability remains unchanged. **Törnqvist** *et al.,* (2001b) found significant differences in diffusion between different wood species: birch had a diffusion coefficient that was significantly higher than spruce and pine in the transversal (radial) direction due to their different capillary structures, but the differences were negligible in the longitudinal direction. The grain orientation also influences the rate of diffusion, and the rate of diffusion in different directions in wood generally follows the rule: longitudinal >> radial > tangential.

Degree of saturation: It is generally true that a higher moisture content facilitates diffusion, and that the diffusion rate varies depending on the uniformity of the water throughout the wood's matrix. In unsaturated pieces of wood, local barriers to diffusion are found in zones of gas or vapour that break up the water phase. This leads to a decrease in the number of pathways available for diffusion. The diffusion rate is at its maximum when the pore structure of a piece of wood is filled with water.

Temperature: The diffusion rate generally increases with an increase in temperature. Temperature affects the mobility of ions and thereby also diffusion and, consequently, the diffusion coefficient.

Properties of the chemical solution: The important factors that affect the mass transport rate of chemicals in wood with respect to the properties of the chemical solution are sorption, temperature, pH, concentration and viscosity (**Stone** and **Förderreuther**, 1956).

Sorption in wood

When a metal ion in solution interacts with a wood tissue, it can be sorbed by physisorption or chemisorption. An ion exchange takes place between the incoming cation and either the sorbed metal ions or the hydrogen ions of the functional groups at the surface of the wood material. The sorption of metal ions from the solution onto the wood's surface may also occur via the formation of surface complexes in which site-specific interactions take place between metal ions and functional groups at the wood surface (**Hubbe** *et al.,* 2011). Based on the behaviour of heavy metal sorption on sawdust, it has been speculated that an ion exchange and hydrogen bonding may be the principal mechanisms in the sorption of heavy metals (**Shukla** *et al.,* 2002). The sorption equilibrium is dependent on the pH of the aqueous solution. At pH values greater than the pK_a of most functional groups on wood surfaces, the sites are mainly in the dissociated form and can therefore bind with the ions in the solution. At pH values lower than the pKa of functional groups on wood, cations can, for example, bind to the sorption sites through the ion exchange mechanism of releasing protons (H^+).

2.3 Measurement of the diffusion of chemicals in wood

Methods for measuring the diffusion of chemicals in wood

Several methods are described in the literature for measuring liquid phase diffusion in wood, but there is none that is standard. A review of the literature showed that early research on molecular diffusion into wood was reported by **Cady** and **Williams** in 1935. It was inspired by experiments of diffusion across the interface between a moving liquid and a gel in a stirred bath, and was extended to conditions valid for wood. These authors studied the diffusion of urea, glycerol and lactose into several water-saturated softwoods. In 1947, another paper with the title “Diffusion in Wood” was published by **Burr** and **Stamm**. Most of the research during this period was related to developing the theoretical expression for the rates of transport of vapors, liquids and dissolved materials through softwoods in the three structural directions under various conditions of temperature and moisture content (**Stamm**, 1946; **Burr** and **Stamm**, 1947). In the early 1950s, the diffusion of salts, ions and organic molecules through green timbers was studied extensively (**Christensen** and **Williams**, 1951; **Christensen**, 1951a & b; **Narayanamurti** and **Ratra**, 1951; **Narayanamurti** and **Kumar**, 1953; **Behr** *et al.,* 1953), with a quantitative theory on diffusion in wood being provided by **Christensen** and **Williams** (1951). The effect of the wood’s structure on diffusion was studied in depth using electrical conductivity measurements made on impregnated blocks of wood. These measurements were then compared with the electrical conductivity of the solution. The ratio of the two conductivities was considered as being a direct measurement of the effective capillary cross-sectional area (ECCSA), defined as the ratio between the area available for diffusion and the total area (**Stone** 1957). **Stone** and **Green** (1959) used this method to study the effect of pH on the diffusion of KCl in the three structural directions of aspen wood. They found that, up to a pH of 12, the ECCSA in the longitudinal direction is approx. 5 times greater than in the transverse and radial directions. At a pH above 13, however, fibre swelling causes the ECCSAs to be about the same in all three directions.

Later on, in the 1980s, most of the research in this field was directed towards measurements of the diffusion of non-electrolytes (monohydric alcohols and polyethylene glycols) through wood (stika spruce Hw) filled with water using a highly sensitive, differential refractometer (**Fukuyama** and **Urakami**, 1980, 1982 and 1986). These studies emphasized the variation in the diffusion coefficient associated with the structure of wood. Tracer techniques using radioactive isotopes have been used to evaluate the impregnation of pulping chemicals during chemical and chemi-mechanical pulping (**Bengtsson** and **Simonson** 1984). After impregnation, the samples were sliced and the beta activity from the whole surface of a slice was used to provide an indication of the degree of diffusion.

One of the techniques frequently employed to measure the diffusion of ions in water-filled wood is based on the rate at which ions diffuse (a) through a slice of wood, the sides of which are in contact with a solution of different concentrations, or (b) in a water bath, into which a completely impregnated block of wood has been placed. **Robertsen** (1993) used this method to study the effects of concentration and temperature on the diffusion of NaOH in the radial direction of spruce wood. One of its limitations is that it gives only an average diffusivity, as it cannot differentiate between areas of varying diffusivity within a sample of wood. The Scanning Electron Microscopy/Energy Dispersive X-ray Analysis (SEM/EDXA) method was developed to measure liquor diffusion by measuring the concentration of a chemical at a defined area in a wood chip (**Bengtsson** *et al.,* 1988; **Sharareh** *et al.,* 1996). The advantage of this method is that it allows the concentration profile of the ion in the wood chip to be obtained, qualitatively and quantitatively, as the ion is transported from the edge of the chip inwards, towards its centre. **Sharareh** *et al.,* (1996) used this method to measure the concentration of sulphur in the three structural directions in an impregnated wood chip simultaneously. However, this method cannot differentiate between bound and free sulphur. In order to study the effect of the diffusion mechanism on the alcohol-based organosolv pulping process, unsteady-state diffusion experiments on methanol in Douglas fir Hw were conducted at high temperatures (**Meijer** *et al.,* 1996). Results from this research indicated that the diffusion mechanism was the same as for alkaline solution diffusion in kraft pulping, although a deviation from Fick's second law was also observed at low methanol concentrations. A diffusion model for the impregnation of lignocellulosic materials was developed in the same period of time to ensure a uniform chemical distribution within the lignocellulosic matrix prior to rapid steam treatment (**Kazi** 1996). During their impregnation experiments with NaOH, these authors also observed that a large fraction of the inorganics (e.g. ash) present in the lignocellulosic material (i.e. straw) could be removed. The quality of the fibre was thus improved and pure cellulose was produced. A new approach called "Drift speed" was proposed with the aim of studying the diffusion of ions in wood (**Törnqvist** *et al.,* 2001a). This research focused only on the effects of possible swelling during the transport of ions in the wood; this phenomenon is dependent only on the diffusion length and not the active area available for diffusion.

In order to improve a number of properties of wood, such as surface hardness and weathering resistance, some researchers have used UV microscopy to investigate the mass transport of resin in the cell walls of softwood (**Gindl** *et al.,* 2002; **Gindl** *et al.,* 2003). Results from such work have demonstrated that UV microscopy is a suitable technique for addressing the question of the possible transport of chemicals in the cell walls of wood. Much research has been conducted in the field of wood preservation to understand the diffusion mechanism in cell walls. Some researchers have studied extensively the effect of various factors, such as temperature, moisture content and pH, on the diffusion of wood preservatives (e.g. boron and copper) in pine wood (**Cooper**, 1998; **Ra** *et al.,* 2001). Fourier Transform Near-Infrared Transmission spectroscopy (FT-NIR) was applied to monitor the diffusion of deuterium-labeled molecules in beech wood by **Tsuchikawa** and **Siesler** (2003). Two of the important conclusions drawn from this particular work were that, independent of the wood species, the diffusion of the penetrant into the amorphous region was faster than into the semi-crystalline region, and the size effect of the diffusants (^{o}A) plays an important role in the diffusion process in wood. Recently, tritiated water (a conservative tracer for water) was used to understand the mass transfer phenomenon in water-filled wood particles of pine and aspen wood (**Jacobson** and **Banerjee**, 2006). The authors of that study calculated the diffusion coefficient as a function of tortuosity, porosity and the self-diffusion coefficient. They concluded that mass transfer in wood was more than a simple Fickian mechanism, and introduced the concepts of size exclusion and charge exclusion. However, this method must be tested for different chemical species and wood species, and for the effects of their structures, to gain greater knowledge and insight.

A model that describes the leaching of calcium ions from softwood chips, and also takes into account cracks, rough surfaces and the size distribution of the wood chips, has been developed (**Saltberg** 2009). Leaching experiments with hand-sawn pieces of spruce wood were conducted to determine the diffusion coefficient for calcium. However, this method cannot differentiate the concentration profiles at various locations within a single wood piece. It just calculates the effective diffusion coefficient and, unfortunately, the natural content of calcium ions (which for softwoods is 600 to 1200 mg/kg wood) aggravates the measurements. Recently, the free diffusion of ions through the secondary walls and middle lamellae of wood was investigated as a function of moisture content (MC) using synchrotron-based X-ray fluorescence microscopy (XFM) (**Zelinka** *et al.,* 2015). For the ions investigated in this study (i.e. K, Cl, Zn and Cu), a threshold MC was identified below which ion transport did not occur. It was also observed that the threshold for ion transport depends upon the ion species, cell wall layer and anatomical direction in the wood.

Drawbacks associated with existing methods

- It is clear from the literature review that three different methodologies are commonly used to measure the diffusion of solute ions in wood. The first measures either the rate at which ions diffuse through a wood block the sides of which are in contact with solutions of different concentration, or the change in the ion concentration in a water bath in which a completely impregnated block of wood has been placed. The second method measures the electrical conductivity of the impregnated wood block and compares it with that of the impregnating chemical solution; the ratio of the two conductivities gives a direct measurement of the ECCSA. The third method employs tracer techniques using radioactive isotopes, whereby samples are sliced and the radiation activity from the whole surface of a slice is used as an indication of the degree of diffusion. It is, however, these methodologies have limitations: the first and second methods give only an average diffusivity, and cannot be used for measuring concentration profiles, and the third is limited to mapping concentration profiles in only one direction at a time, since the whole surface of each wood slice is used to measure the concentration.
- Most of the investigations involving the measurement of cation diffusion in wood have been conducted using diffusing substances such as NaCl (sodium chloride), KCl (potassium chloride) and NaOH (sodium hydroxide). If NaCl or KCl are used, there is the possibility of inaccuracy occurring in determining the diffusion of cations into the wood: Na^+/ K^+ ions (in the form of alkali metal ions) are present naturally in wood. In the case of NaOH, reactions between the OH^- ions and the wood's components influence the properties, and thus the mass transport, of the Na^+ ions.
- Some observations indicate clearly that almost all wood pieces have micro-cracks that may be too small for direct visual detection, but they can change the capillarity of the surface layer, thereby influencing its interaction with the surrounding liquor, and/or also re-open the aspirated pits, making the layer more open in structure. These micro-cracks are the result of a damaged surface layer caused by the mechanical preparation of the pieces of wood, e.g. sawing (**Salin**, 2008), and influence the behaviour of the wood pieces when diffusion measurements are made.
- Wood material has a variety of chemical compositions (e.g. polymers) in its cell walls; interactions between diffusing solute ions and these components (e.g. via sorption) affect the measurement of concentration profiles, so these factors affect the determination of the diffusivities in the system.

- Native Norway spruce wood contains small amounts of metal ions (typically 1-5 g/kg wood), the main ones being Ca^{2+} , Mg^{2+} , Mn^{2+} , Na^{+} and K^{+} . Although these ions are present in small quantities, they may participate in the sorption mechanism induced by ion-exchange, and thus aggravate the measurements. Therefore, prior to the concentration profile measurements being made, the sample of wood can be treated with a dilute acid solution (e.g. sulphuric acid: pH=0.5/0.31 M H_2SO_4), to remove native metal ions, air and any floating fines present.
- In most of the methods, at the end of the impregnation time, the impregnated samples were either immediately processed in the diffusion measurement procedures or stored in a refrigerator (e.g. **Kazi** and **Chornet**, 1998) at freezing temperature to stop any further diffusion. These slow freezing rates may lead to incorrect measurements being made so, in order to minimize this effect, the impregnated pieces of wood may be placed in liquid nitrogen (-180°C), which has a very rapid freezing rate. The effect of inward migration of chemicals into the impregnated samples of wood can thus be minimized.

3. Research Objectives

The aim of this thesis is to develop knowledge of the diffusive mass transport of ions in wood. With the focus placed on developing a methodology for investigating the diffusive mass transport of ions in wood, using both experimental and modelling approaches, the objectives of this thesis are:

- To develop a method for measuring the concentration profiles of ions passing through the porous structure of the wood matrix.
- To develop a method that is suitable for differentiating the amount of ions that are sorbed onto the surface of the cell walls of solid wood from those that are dissolved in the solution in its pores.
- To develop a model that describes the diffusion of ions into a liquid-filled porous medium and quantifies the transport properties, such as the effective diffusion coefficients and tortuosity factors of the ions in a piece of wood.
- To investigate potential interactions during the sorption of ions from an aqueous bulk solution onto the surface of wood material.

4. Materials and Methods

4.1 Materials and chemicals

Materials

The wood materials investigated in this study were: wood flour and pieces of wood (both Sw and Hw), MCC (Avicel PH-101; particle size ~50 µm; SIGMA-ALDRICH Co., Germany), Xylan from beech wood (SIGMA-ALDRICH Co., Germany) and Kraft lignin (a softwood lignin, extracted from black liquor using the LignoBoost process at the Bäckhammar Mill, Sweden), along with isolated wood fractions from Sw flour: holocellulose fractions with varying contents of lignin and lignin carbohydrate complex (LCC).

Chemicals

Dilute sulphuric acid solution (0.31 M) was prepared by dissolving reagent grade (95-97%) sulfuric acid (Scharlau, Scharlab S.L., Spain) in deionized water. Stock solutions of different Li^+ ion concentrations were prepared by dissolving LiCl salt (≥ 99 %) (Merck KGaA, Darmstadt, Germany) in deionized water. 2 wt. % nitric acid solution was prepared by dissolving trace analysis grade (69 %) nitric acid (ARISTAR, VWR® PROLABO®, Leuven) in deionized water. Peracetic acid (39 wt. %), sodium (meta) periodate (≥ 99.8 %), acetone (≥ 99.8 %), cyclohexane (≥ 99.5 %), Ethylene glycol (≥ 99 %) and potassium bromide (FTIR grade; ≥ 99 %) were purchased from Sigma-Aldrich, and used as received. Sodium chloride (min. 99.5 %) were purchased from Scharlau, and used as received. NaOH (ACS, Reag, Ph Eur) and NaAc (Solution 50%) purchased from Merck, and used as received.

Preparation of wood pieces and wood flour

A stemwood disc 23 cm in diameter (free from bark) taken from a 31±1 year-old Norway spruce (*Picea abies* L) was investigated. Samples of both Sw and Hw were prepared carefully using a vertical band saw (Mossner Rekord, August Mössner KG, D-7075 Mutlangen, Germany and a metal cutting band saw : L.S. Starrett Company Ltd., Jedburgh, Scotland with 14 teeth per inch) and were kept preliminarily in an airtight polyethylene (PE) bag at 1°C. It was assumed that a stemwood disc contains 50% Sw, 30% Hw and that the remaining 20% is an intermediate between Sw and Hw (**Sandberg** and **Sterley**, 2009). In this study, both Sw and Hw were investigated. Only samples free from rot and other deformations were selected and cut into rectangular prototype pieces using the same vertical band saw mentioned above. The dimensions of the prepared pieces of wood were 100 × 25 × 7.5 mm^3 (L × R × T). The radial dimension was chosen to be approx. 3 times larger than the tangential dimension in order to minimize the effect of mass transport through the radial direction on the measurements of mass transport in the tangential direction. The material was then stored in an airtight PE bag in a freezer at -18°C. Defrosting the pieces took 24 h at ambient temperature.

For the study in which the concentration profiles were measured, surface damage to the wood caused by rough sawing was minimized by planing all four vertical surfaces of the pieces carefully (parallel to the longitudinal fibre direction) with a hand plane (Stanley Hand Tools, Stanley Canada, Mississauga, ON) to remove a surface layer of approx. 1-1.5 mm in thickness thus wood pieces used in the actual experiments had dimensions of 100 × 23 × 6.5 mm^3 (L × R × T). A similar approach of minimizing the surface damage to the wood caused by rough sawing, was not possible for the two surfaces perpendicular to the longitudinal direction of the fibres, so they can be expected to have a substantial number of micro-cracks e.g.in middle lamella.

In the case of the equilibrium sorption studies, the pieces of wood were ground in a Wiley-type mill (< 1 mm). The resulting wood flour was stored in an airtight PE bag until further use.

Isolating the components of the wood

Peracetic acid (PAA) delignification: Preparing holocellulose fractions with varying contents of lignin from Sw flour

Holocellulose fractions with varying contents of lignin were prepared from the Sw flour using PAA. The delignifying procedure, reported in detail by **Kumar** *et al.,* (2013), was performed at room temperature with 5 wt. % Sw flour samples and reaction times between 6 and 72 h (namely 6, 24, 51 and 72 h). PAA loadings of 5.5 g/g dry Sw flour were used.

Periodate oxidation: Preparation of lignin/LCC fraction from Sw flour

The lignin/LCC fraction was prepared by oxidizing the Sw flour with sodium periodate, employing a procedure reported in detail by **Alam** and **Van De Ven**, (2014). The oxidation procedure was carried out in a glass beaker equipped with an overhead stirrer, and the reaction mixture (Sw flour, sodium metaperiodate and sodium chloride) was stirred continuously in the dark, at room temperature, for 6 days. At the end of the reaction, ethylene glycol (~ 4 ml) was added to the reaction mixture to quench the residual periodate and the mixture was washed repeatedly with deionized water. A purified and oxidized suspension of Sw flour was then stirred gently at 80-90 °C in an oil bath for 6 hours. The sample was cooled to room temperature and the non-dissolved, brown, solid material (lignin/LCC fraction) was separated off by vacuum filtration.

Analysis of the composition of the wood

The untreated and delignified solids were dried in an oven at 50 °C for several days. The following methods were then used to analyse their contents of structural carbohydrates and acid-soluble and insoluble (Klason) lignin.

Analysis of Klason lignin

The method used was based on the procedure presented by **Theander** and **Westerlund** (1986), whereby Klason lignin is measured gravimetrically after complete acid hydrolysis with 72% H_2SO_4. In the present study, a 200 mg oven-dried sample was weighed before 3 ml of 72% H_2SO_4 was added. The sample was evacuated for 15 min and placed in a water bath at 30 °C for 1 h. Then 84 g of deionized water was added before it was heated to 125 °C in an autoclave for 1 h. Afterwards the sample was filtered off, and the solid residue collected was referred to as Klason lignin. The filtrate from the hydrolysis process was used later to measure the content of acid-soluble lignin and for analysis of carbohydrates.

Analysis of acid-soluble lignin

The content of acid-soluble lignin was calculated in relation to the absorbance value measured with UV at a wavelength of 205 nm in a Specord 205 (Analytik Jena); an absorptivity constant of 110 $dm^3g^{-1}cm^{-1}$ was assumed (**Lin** and **Dence**, 1992).

Analysis of carbohydrates

The filtrate resulting from the acid hydrolysis was diluted to 100 ml in a volumetric flask. This solution was diluted a further 5 times before being filtered through a 0.45 µm PVDF filter. The monomeric sugars were analysed using the Dionex ICS-5000 HPLC system equipped with CarboPac PA1 columns and run using NaOH, NaOH/NaAc (0.2 M) as the eluents; fucose was used as the internal standard. An electrochemical detector was used for detection, and the software used was Chromeleon 7, Chromatography Data System, Version 7.1.0.898. The amounts of cellulose, (galacto) glucomannan and xylan were calculated from the carbohydrate analysis using the assumptions and corrections described by **Jedvert** *et al.,* (2012).

4.2 Measurement of density and porosity

The mass of air-dried (at normal conditions i.e. room temperature (R T)) samples divided by their volume gives the bulk density (ρ_b). The volume of the samples was determined by simply measuring their dimensions.

The AccuPyc 1330 helium pycnometer (MICROMETRICS) was used to determine the volume of the cell walls of the solid wood. Helium gas was used as the displacement medium to fill as small pores as possible; for these measurements, wood flour (< 1 mm sieve) was used to have as many pores as possible open to the displacement medium. The density of the cell wall (ρ_p) was then calculated with the solid volume that was measured for the cell walls and the weight of the sample.

Using the normal bulk density (ρ_b) and the solid density of the cell wall (ρ_p), the total porosity can be calculated as:

$$Total\ Porosity = 1 - \frac{\rho_b}{\rho_p} \tag{4.1}$$

This total porosity includes all of the pores, regardless of whether they are open or closed. Hg porosimetry was carried out with a Micrometrics AutoPore IV Mercury Porosimeter and analysed using the software AutoPore IV 9500, Version 1.09. The porosity determined by mercury intrusion porosimetry (Hg porosimetry) only determines the percentage of pores that are accessible to Hg. Specimens of about 0.2 g in size were cut perpendicular in the dimensions of about 2.5 (L) x 24 (R) x 7.5 (T) mm. Specimens approx. 2.5 mm in length were the smallest practical length that could be prepared. This length is nonetheless small enough to cut most of the fibres (the average fibre length is about 3 mm) and means that, in most cases, mercury can enter the lumen of the fibre without passing through a pit pore. Consequently, the intrusion volume and the diameters of the lumen could be measured in a satisfactory way. Several duplicates were prepared from two different pieces of wood and they were all analyzed.

The porosity (Hg porosimetry) can be calculated from the intrusion pore volume, determined using Hg porosimetry, and the solid volume of the cell wall, determined using helium pycnometer, thus:

$$Porosity\ (Hg\ porosimetry) = \frac{Intrusion\ pore\ volume/mass}{Intrusion\ pore\ volume/mass + cell\ wall\ solid\ volume/mass} \tag{4.2}$$

In this study, the intrusion volume of a pore was measured using Hg-porosimetry divided into 2 parts: (i) the total intrusion volume of a pore, which applies to the whole range that the instrument is able to measure (i.e. diameters 0 - 330 µm), and (ii) the effective transport-through-intrusion (diffusion-accessible) volume of a pore (i.e. diameters 0 - 41 µm).

4.3 Studies of equilibrium sorption

Sorption experiments

Batch sorption experiments were conducted on flour samples of both Sw and Hw at various temperatures and using different concentrations of bulk aqueous LiCl solution in order to determine the amount of Li^+ ions that are sorbed onto the surfaces of solid wood at equilibrium conditions ($q_{wood,e}$). The experimental procedure for studying sorption is reported in detail in Paper **III**. Wood flour was placed in polypropylene (PP) beakers containing a bulk aqueous LiCl solution of the desired concentration, with a ratio of liquor to wood flour of 100:1(400:4 (g/g)). This mixture was shaken sporadically during the course of the experiment and, at the end of the specified residence time for each particular temperature, it was centrifuged (SERIE 130; F.I.E.M.M.E., Establishments Couprie 7, Quai Clande Bernard, Lyon, France) at approx. 2960 rpm for 5 minutes to separate the wood flour from the solution. Samples of wood flour treated with LiCl were then lyophilized (Labconco, Kanas City, MO, USA) for 5 days. The freeze-dried sample of wood flour treated with LiCl was then acid leached at room temperature with 2 wt. % HNO_3 for ~ 24 h. The leaching liquor was analyzed for its concentration of Li^+ ions using Flame Atomic Emission Spectroscopy (FAES).

4.4 Measurement of the concentration profiles

Figure 4.1 illustrates the steps in the experimental procedure followed in this study, a detailed description of which is reported in Papers **II** and **V**.

The wood pieces were pre-impregnated with either water or dilute acid solution in a vacuum-pressure cycle, which removed air and any metal ions that may present in the wood. During the preliminary study (Papers **I** and **II**), in which experiments were carried out for treatment times of 4 and 12 h at the specified temperature (R T, 40 and 60°C), the pieces of wood were pre-impregnated with water. In the later chemical impregnation experiments (Paper **V**) at 40 °C and for treatment times of 36, 72 and 168 h, the pieces were pre-impregnated with a dilute acid solution (pH=0.5/0.31 M H_2SO_4). In the experiments using samples of wood flour, only traces of major metal ions (Ca^{2+}, Mg^{2+}, Mn^{2+}, Na^+ and K^+) were observed after dilute acid treatment (Paper **III**). The effect of these metal ions on mass transport of Li^+ in wood is thus negligible.

Impregnation experiments - Impregnation with LiCl

The pieces of wood pre-impregnated with either water or dilute acid were first dabbed with filter paper before being immersed in a LiCl solution. During the preliminary study (Paper **II**), with samples of both Sw and Hw, the pieces were immersed in a 1 M LiCl solution with a wood-to-liquor ratio of 1:125. In the later experiments, the samples of Sw (Paper **V)** were immersed in a 1 M LiCl solution and Hw in a 0.5 M, at a wood-to-liquor ratio of 1:75. After chemical impregnation at the time intervals specified and at each particular temperature, the pieces were removed and placed in liquid N_2 (-180°C) to minimize the further migration of any ions. Finally, these frozen pieces were lyophilized (LABCONCO®, Kansas City, MO, USA) for about 2 weeks to avoid secondary thermal diffusion.

In preparation for measuring the concentration of Li^+ ions, each of the impregnated pieces of wood was cut into small cubes (**Figure 4.2**) with dimensions of approx. 6 x 6 x 6.5 mm^3. Each cube was microtomed in the tangential direction into slices ~ 0.3 mm thick and then oven-dried at 105°C for 1 h to remove any moisture accumulated during the microtoming process. The slices of wood were placed in desiccators containing blue gel salt and left at R T until constant mass was reached. Each slice was then acid leached at R T with 2 wt. % HNO_3 for ~ 24 h. The leaching liquor was analysed for its concentration of Li^+ ions using Flame Atomic Emission Spectroscopy (FAES).

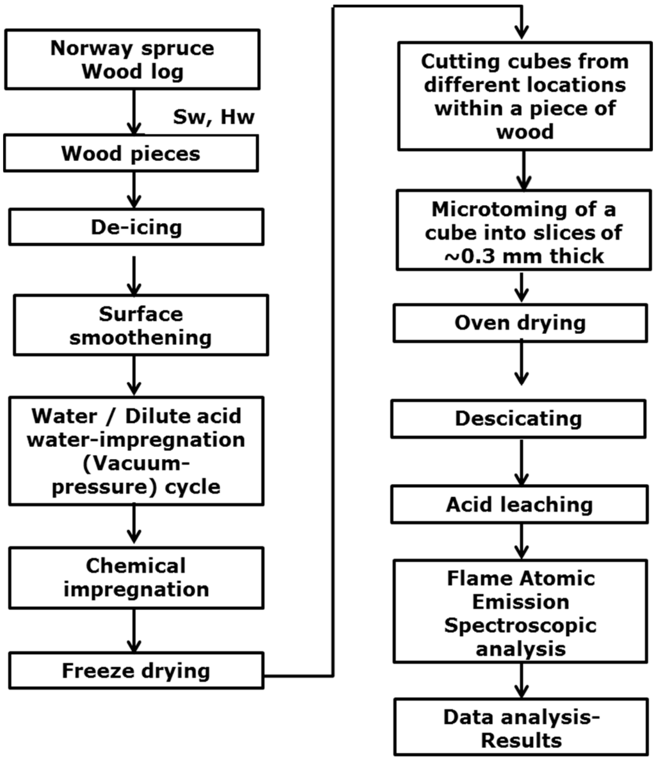


Figure 4.1 The steps in the experimental procedure used to measure the concentration profiles.

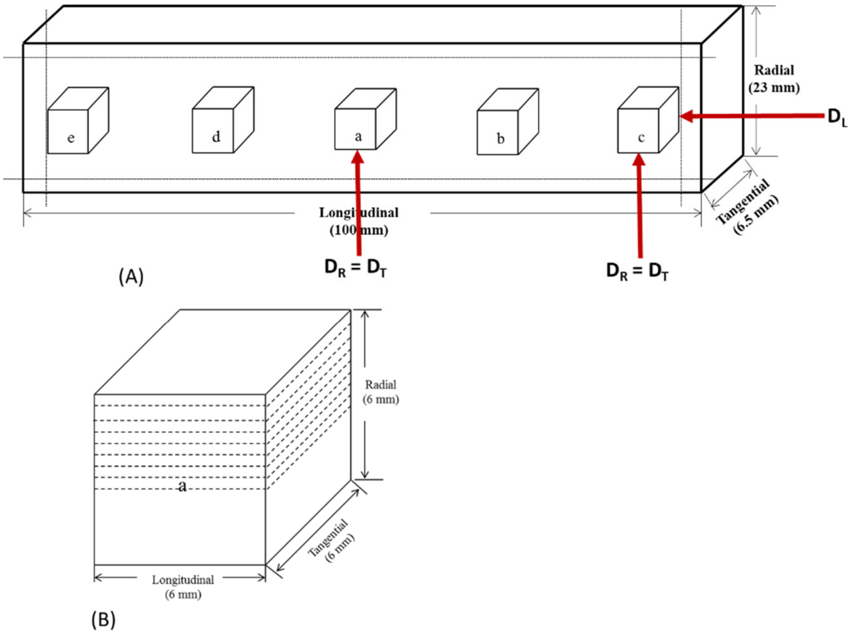


Figure 4.2 (A) Locations of the small cube samples in an idealized piece of impregnated wood. (B) Microtoming a small cube into slices of thickness ~0.3 mm for use in measuring the concentration profile of Li^+ ions. D_L and D_T (= D_R) are the diffusion coefficients of the Li^+ ions from the aqueous bulk solution to the wood in the longitudinal, tangential and radial directions, respectively.

4.5 Characterization of the material

Flame Atomic Emission Spectroscopy (FAES)

The leaching liquor was analyzed for Li^+ ion concentration at the end of the leaching period using Flame Atomic Emission Spectroscopy (Thermo Scientific, iCE 3000 series, AA spectrometer, Cambridge, United Kingdom). An air-acetylene torch was used as the source of the flame; the emission was measured at a wavelength of 670.8 nm. The concentration of Li^+ ions was kept at an optimum working concentration range of 0.02 - 5 µg/ml. The average deviation from the mean values of these measurements was ~8%.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded in a Fourier Transform Infrared Spectrophotometer (Perkin Elmer, Spectrum One, FTIR-Spectrometer) using the KBr discs technique. Each spectrum was collected 16 times in the range of 4000 - 400 cm^{-1} with a resolution of 4 cm^{-1} and corrected for background noise. Each spectrum was collected 16 times in the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} and corrected for background noise. The spectra were normalized using a peak at 1424 cm^{-1}, which corresponds to the CH_2 contributed by the cellulose.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were collected using a Quantum 2000 scanning Electron Spectroscopy for Chemical Analysis (ESCA) microprobe from Physical Electronics (Chanhassen, Mn, USA) with a monochromatic Al Kα source (1486.6 eV). The samples were analyzed at a take-off angle of 45°, with the area under analysis being about 400 x 500 µm in size and 4-5 nm in depth. The pressure in the chamber during XPS analysis was lower than 10^{-9} torr, making it an ultra-high vacuum regime. An overall survey spectrum (i.e. low-resolution) from 0 to 1100 eV binding energy, and a high resolution spectrum of the C1s region from 280 to 300 eV and O1s region from 525 to 535 eV, were collected. Analyses of the chemical bonds of carbon and oxygen were made by fitting the curves of the C1s and O1s peaks from the high resolution spectra and deconvoluting them into sub-peaks using ESCA tools (MultiPak Vers. 6.1).

BET measurements of surface area

The specific surface area of both untreated and LiCl treated samples were measured according to the BET theory (Brunauer–Emmett–Teller) from measurements of nitrogen adsorption using a Micrometrics TriStar 3000 instrument. Hornification whilst the samples are being dried is avoided by performing a solvent exchange and replacing water with cyclohexane. This was done through a solvent exchange procedure in which the water was replaced initially with dry acetone which, in turn, was replaced with cyclohexane (**Palme** *et al.,* 2014). The samples were then dried overnight in a stream of nitrogen.

4.6 Theoretical model formulation: Estimating the transport properties of ions in wood

The model used to determine the transport properties of Norway spruce wood, such as the effective diffusion coefficients and tortuosity factors of Li^+ ions, is based on the theory of the transport of diluted species in porous media (**Paper V**). The model is solved using COMSOL® multiphysics modelling software (Vers. 5.0, COMSOL, Stockholm, Sweden). Equation (4.3) describes the transport of solutes in a porous media saturated with liquid (The Transport of Diluted Species in Porous Media Interface, COMSOL®, Vers, 5.0) thus:

$$(\phi + \rho_b k)\frac{\partial C_i}{\partial t} + \left(C_i - \rho_P C_{P,i}\right)\frac{\partial \phi}{\partial t} = \nabla \cdot \left[\left(D_{e,i}\right)\nabla C_i\right] \tag{4.3}$$

where C_i is the concentration of the species i in the liquid located in the porous media (g/l), $C_{P,i}$ is the amount sorbed onto the solid particles (g/kg), k is the wood-Li^+ ion equilibrium partition coefficient (l/kg), $D_{e,i}$ is the effective diffusion coefficient of species in the porous medium (m^2/s), ϕ is the effective transport-through-porosity calculated using **Equation** (4.2), and ρ_b and ρ_P are the densities of the bulk and solid phases, respectively, of the wood (kg/m^3). The two terms on the left-hand side of **Equation** (4.3) describe the accumulation of the species within the liquid and the solid, respectively, whilst the term the right-hand side introduces the transport of the species due to diffusion.

The initial condition (I.C) and boundary condition (B.C) are:

I.C: time t = 0, Concentration $C_i = 0$ g/l for all domains of the geometry

B.C: for all times t, Concentration $C_i = 1$ M = 6.941 g/l for all surfaces of the geometry.

The effective diffusion coefficient (D_e) for the transport of a solute in a porous medium saturated with a liquid is significantly lower than the free-water diffusion coefficient (D_f) because of the constricted and elongated (tortuous) transport paths. In a saturated porous medium, D_e is related to D_f as (**Saripalli** *et al.,* 2002):

$$D_e = \frac{D_f \phi \Theta}{\tau} \tag{4.4}$$

where ϕ is the porosity of the piece of wood that is accessible to diffusion, Θ is a constrictivity factor to account for the constricted transport paths (caused by the small pores and pore throats in a porous medium and usually assumed to be ~1) and τ is a tortuosity factor. The latter accounts for the reduction in diffusive flux caused by the tortuous path lengths formed by the solute molecules, which can be compared to the straight paths in an unrestricted aqueous medium. The estimation procedure used to determine the self-diffusion coefficient of Li^+ ions in a free solution (D_f) can be found in **Appendix A1**.

5. Results and Discussion

5.1. Development of an experimental procedure: Concentration profiles of ions in pieces of wood

One finding of this work is that the preparation of samples is of the utmost importance. Our results indicate that even if the surface seems to be smooth from visual inspection, this is not in fact the case. The following abbreviations are used in the text below: NWP (Normal Wood Pieces) refers to pieces of wood that were prepared carefully from a disc of stemwood using a vertical band sawing machine and SsWP (Surface smoothed Wood Pieces) refers to pieces that were planed carefully on all 4 vertical surfaces (four surfaces parallel to the longitudinal fibre direction) to a depth of about 1 - 1.5 mm with a hand plane in order to peel off the damaged surface layer from the NWP.

The concentration of ions (i.e. moles of Li^+ /kg dried wood) is plotted against the thickness of the impregnated pieces of wood to describe the effects of various factors on the concentration profiles. It should be kept in mind that this concentration, which is measured experimentally, is the total concentration of the Li^+ ions: it is the sum of the Li^+ ions that are sorbed onto the surfaces of the wood's cell walls and dissolved in the solution located in the pores.

Figure 5.1 provides an example of how damaged surface layers influence the concentration profiles of Li^+ ions in samples of Norway spruce. The figure shows that there is a higher concentration of Li^+ ions in the outer surface layers (< 1.5 mm depth) of the NWP compared with SsWP. This is a clear indication that the rough surface layers, which were formed during the rough sawing process, may have affected the mass transport of Li^+ ions in wood. It therefore seems that the formation and behaviour of the damaged surface layers depends on the method of preparation the pieces of wood have been subjected to. So, in the sections discussed below, SsWP are used in order to minimize the effects of such damaged surface layers (micro-cracks) on the measurement of concentration profiles of Li^+ ions in wood.

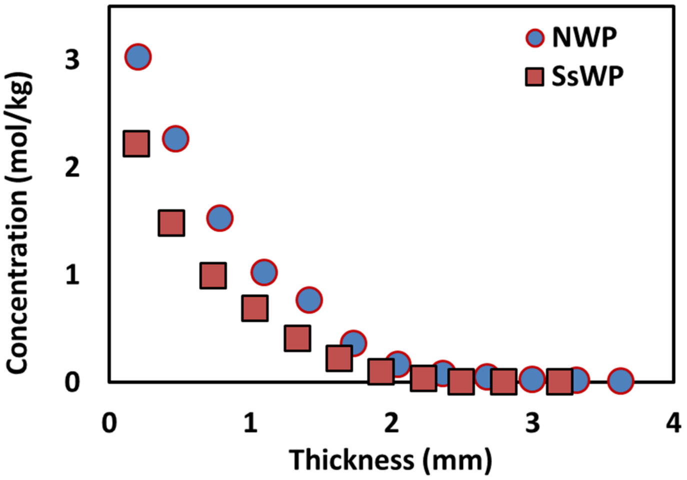


Figure 5.1 Concentration profiles of Li^+ ions measured in a piece of Norway spruce Sw treated with 1 M LiCl solution at room temperature for 4 h residence time: NWP vs. SsWP for Cube a (see Figure 4.2 (A)).

Concentration profiles at various locations in a piece of wood

Figure 5.2 shows the concentration profiles at different locations in a single piece of LiCl (aq.) impregnated wood. The differences between the profiles are due to the fact that mass transport properties are strongly influenced by the anisotropy of the samples of wood. It is evident here that the concentration profiles of Cubes a (taken from the middle of the piece) and c (taken from the edge) (see **Figure 4.2** (A)) differ. In the case of Cube a, this is because the diffusion of Li^+ ions was mainly influenced by mass transport in the transversal direction alone, whereas in the case of Cube c, diffusion was influenced by mass transport in both the longitudinal and the transversal directions. Moreover, as shown in **Figure 5.2**, the concentration profiles observed for Cubes a and b were within the experimental error: it is therefore reasonable to assume that, in the case of Cube a, the concentration is not affected by longitudinal mass transport due to the diffusion distance, which is relatively long compared to mass transport in the radial and tangential directions. However, the behaviour seen at the outer layers (< 1 mm depth) and the edge (Cube c) may be attributed to micro-cracks caused by the mechanical preparation of the pieces (e.g. sawing). The four surfaces parallel to the longitudinal fibre direction were planed using a hand plane, which eliminated a large fraction of the micro-cracks. It was not possible to use a similar approach with the two surfaces perpendicular to the longitudinal fibre directions, however, so a substantial amount of micro-cracks can be expected at these two surfaces, e.g. in the middle lamella.

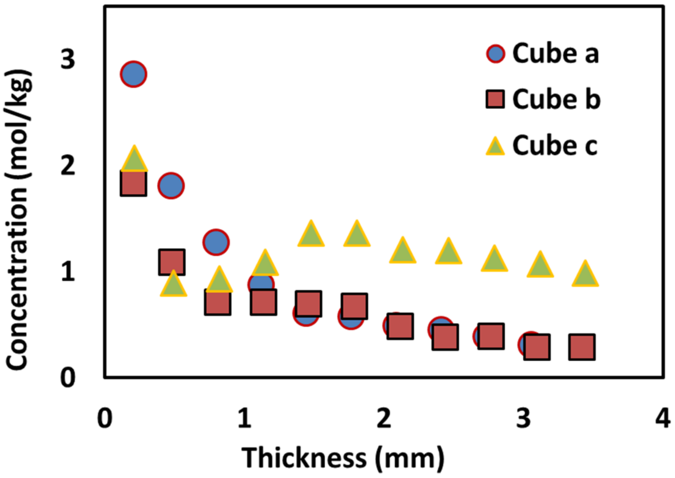


Figure 5.2 Concentration profiles of Li^+ ions measured in a piece of Norway spruce Sw treated with 1 M bulk LiCl solution at 60 °C for 4 h residence time. Cubes a, b and c refer to the position within the piece of wood from where the samples originate (see **Figure 4.2** (A)).

For the experimental conditions studied (i.e. relatively neutral or low pH), it was the carboxylic sites (pKa 3-4) that were predominantly ionized (**Sjöström** 1993): they therefore exist in anionic forms, and the Li^+ cations can bind to the carboxylic sites. However, the concentrations of Li^+ ions observed at the outer layers (< 1 mm depth) and the edge (Cube c), were much higher than those of the carboxylic acid groups (0.086±0.007 mol/kg) (**Werkelin** *et al.,* 2010) present in the samples of native Norway spruce. This result suggests that, in addition to the carboxylic sites, other functional groups of the components of the wood's cell walls (such as carbonyl and hydroxyl) might also be involved in the interactions with the Li^+/Cl^- ions. It is therefore evident that the transport of Li^+ ions in wood may be influenced by other phenomena, such as surface diffusion, adsorption/desorption and Donnan equilibrium.

5.2. Investigation of possible interactions between Norway spruce wood and aqueous LiCl solution

XPS characterization

The XPS survey spectra of the samples of Sw flour before and after treatment with aqueous LiCl solution reveal the presence of Li and Cl ions in the samples treated with LiCl, thus indicating sorption onto their surfaces. Wide-scan XPS spectra are presented in **Figure 5.3**, and the composition of the surface of the elements detected, estimated using the atomic sensitivity factor and the area under each peak, is presented in **Table 5.1**. In general, the theoretical value of the O/C ratio for carbohydrates (0.83 for cellulose and 0.8 for hemicelluloses) is higher than the corresponding value for lignin (0.33) (**Sernek**, 2002), which reflects the abundance of the hydroxyl groups present in carbohydrates. In this case, although the O/C values measured were significantly lower than those estimated from the chemical composition and elemental analysis, they are in good agreement with values reported previously for wood material by **Sinn** *et al.,* 2001 and **Inari** *et al.,* 2006. Whilst this difference reflects the restriction of the XPS analysis to the surface layer, it may also be an effect of the adaptation of cellulose surfaces which, upon drying, expose more hydrophobic structural motifs, as reported previously (**Johansson** *et al.,* (2012)). According to previous findings, the high vacuum released during XPS analysis, which allows for vaporization of the residual water contained in the material, can also contribute to the low O/C values observed (**Inari** *et al.,* 2006). A slight decrease in the O/C ratio was observed for Sw flour upon LiCl treatment, as shown in **Table 5.1**. As mentioned above, this result is likely to be associated with the rearrangement of cellulose fibrils during drying, leading to the reduced accessibility of –OH groups and a more pronounced hydrophobic surface. The indication here is that this rearrangement seems to be promoted by LiCl treatment.

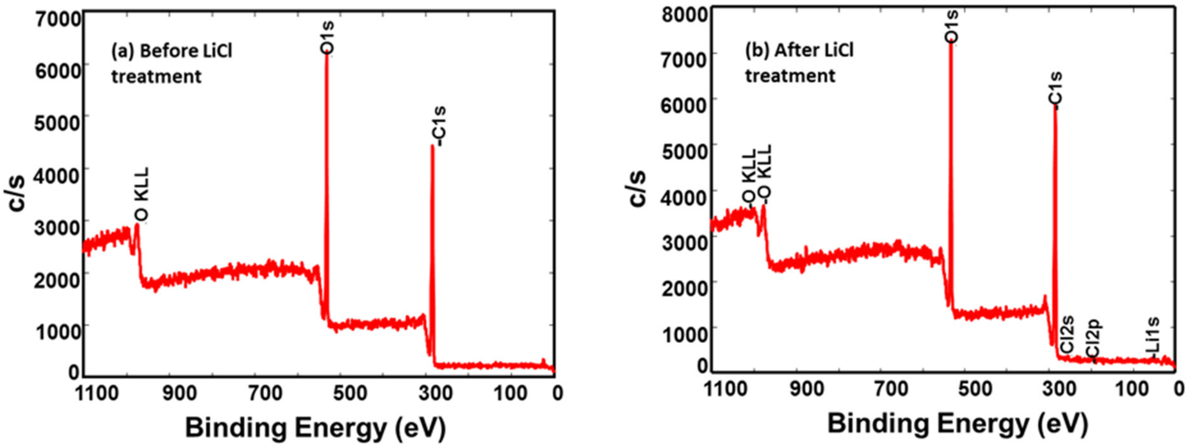


Figure 5.3 Survey spectra of Norway spruce Sw flour (a) before and (b) after treatment with 1 M LiCl aqueous solution for 3 h at room temperature (R T).

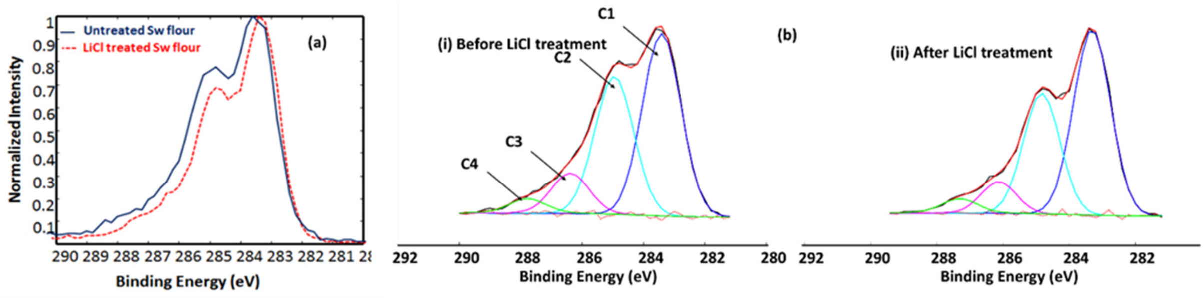
Table 5.1

Surface composition of the elements on samples of Sw flour before and after treatment with 1M LiCl for a residence time of 3 h at R T, as detected by XPS.

Sample	**Element**				
	C1s	O1s	Li1s	Cl2p	O/C
Untreated Sw flour	73.96	26.04	-	-	0.35
LiCl treated Sw flour	73.12	24.29	2.06	0.53	0.33

Deconvolution of the carbon (C1s) and oxygen (O1s) signals observed could provide further insight into these changes. The C1s signal was deconvoluted into four sub-peaks corresponding to (i) C1- carbon atoms bonded only to hydrogen or other carbon atoms (C-C or C-H), appearing at a binding energy (BE) of 283.4±0.11 eV and arising predominately from the lignin and extractive constituents of the wood (**Nzokou** and **Pascal Kamdem**, 2005), (ii) C2 - carbon atoms bonded to a single, non-carbonyl, oxygen atom (C-O or C-OH), at a BE of 285.0±0.13 eV, arising from both the carbohydrate and lignin constituents (**Sernek**, 2002), (iii) C3 - carbon atoms bonded to one carbonyl (mostly lignin) or two non-carbonyl oxygen atoms of polysaccharides (C=O or O-C-O), with a BE of 286.5±0.18 eV, and (iv) C4 - carbon bonded to one carbonyl and one non-carbonyl oxygen (O-C=O) at a BE of 287.7±0.17 eV (**Dorris** and **Gray**, 1978). The O1s signals were deconvoluted into two sub-peaks: O1 (at a BE of 531.3±0.13 eV), corresponding to oxygen atoms bonded to carbon with a double bond (O-C=O), and the O2 (at a BE of 532.4±0.11 eV) arising from oxygen atoms bonded to carbon with a single bond (C-O) (**Inari** *et al.,* 2006; **Nzokou** and **Pascal Kamdem**, 2005). **Figure 5.4** shows the high resolution and deconvoluted spectra of the C1s and O1s signals from the Sw samples before and after treatment with LiCl.

(A) Sw flour-C1s



(B) Sw flour-O1s

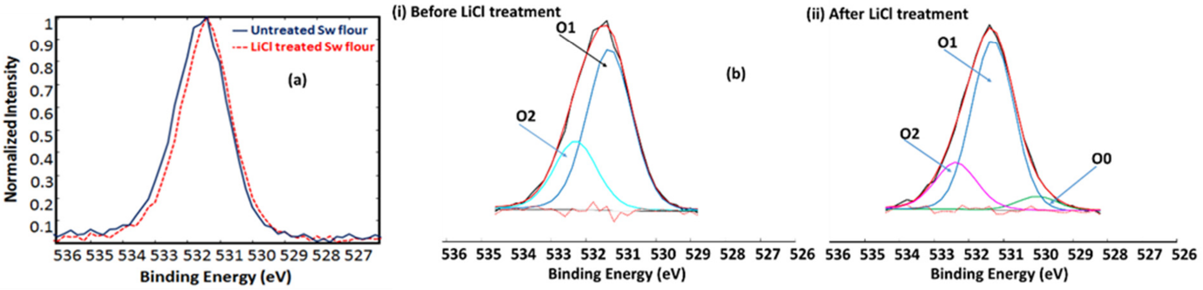


Figure 5.4 Spectra of carbon (C1s) (A) and oxygen (O1s) (B) signals from Norway spruce Sw flour (a) at high resolution and (b) deconvoluted. (i) Before and (ii) after treatment with 1 M LiCl aqueous solution for 3 h residence time at R T (as indicated).

It is evident from **Figure 5.4** (A)-(a) that the changes in the C1s signal observed upon LiCl treatment are associated with a slight increase in the contribution from the C1 (C-C/C-H) component as well as a decrease in that from the C2 (C-O/C-OH) and C3 (C=O/O-C-O) components. This indicates, once again, an enrichment of the more hydrophobic C-C/C-H structures on the surface that are a result of the rearrangement of the wood matrix discussed above. Corresponding analyses of the O1s signals confirmed the same trend: the contribution of the O2 component (C-O structures) decreased, indicating the withdrawal of C-O structures from the surface and thus giving rise to a simultaneous relative increase in the O1 (C=O) signal. More importantly, a new signal (O0) at 530.1±0.01 eV was observed (**Figure 5.4** (B)-(b)). This signal, which is generally assigned to metal oxides (**Chastain** and **King**, 1992), can be attributed to interactions between the functional groups of the wood material that contain oxygen and the Li^+ ions (Li-O interactions). **Harilal** *et al.* (2009) assigned this signal to lithium oxides and peroxides (Li2O, Li2O2) and other species containing lithium and oxygen (Li2CO3, LiOH).

In order to explore these observations further, samples of Sw flour were fractionated into its constituent fractions: holocelluloses with high and low lignin contents and lignin/LCC fractions. The resulting fractions were treated individually with LiCl and analysed using XPS (**Paper IV**). The same decreasing trend observed for the Sw samples was also observed for holocelluloses in the samples with high and low contents of lignin in the values of the O/C ratios upon LiCl treatment, which indicates the rearrangement of the cellulose fibrillary structures (as mentioned above). It is evident that this rearrangement is probably facilitated by the LiCl treatment step: it could possibly be explained by the fact that LiCl disrupts the stabilizing H-bonding and thereby promotes mobility within the fibre's matrix. Enhanced mobility in the more delignified fraction makes this rearrangement even more pronounced and results in the O/C ratio being decreased further.

The deconvoluted C1s spectra of the holocellulose fractions, in line with the observations above, show an accumulation of C1 class carbon on the surface, with a simultaneous decrease in the C2 contribution upon LiCl treatment; the effect is much more pronounced for the more delignified samples (holocelluloses with low lignin content) with enhanced matrix mobility. This indicates that the rearrangement at the surface (leading to the accumulation of the C-C/C-H motifs at the surface) is facilitated by the action of the LiCl. The action of LiCl is more noticeable in the more delignified samples with enhanced accessibility: matrix mobility could therefore be attributed to the disruption of the H-bonds.

The corresponding analysis of the deconvoluted O1s spectra indicates, once again, the occurrence of Li-O interactions (the appearance of an O0 signal), with increased intensity upon lignin removal, when compared to the original Sw samples. Furthermore, the deconvoluted oxygen spectra reveal a decrease in the O1 signal upon LiCl treatment, being more pronounced for more delignified samples. This could indicate the withdrawal of the carbonyl functionalities (C=O) from the surface of the holocellulose samples as a part of the rearrangement promoted by the LiCl, and facilitated by the improved mobility in the more delignified samples. On the other hand, it could also indicate the removal of hemicellulose acetyl groups during LiCl treatment. Moreover, changes in carbonyl signals may also be associated with the removal of oxidized shortened chains formed as side products during PAA delignification. However, no significant oxidative effects on carbohydrates are expected under the mild conditions applied in this study (**Jääskeläinen** *et al.,* 2000), so the losses observed in carboxyl signals are indicative instead of the enhanced removal of hemicellulose carbonyls (deacetylation) from the more accessible matrix. The variations observed in the O2 signal (C-O) also concur with this explanation. In the original Sw sample, the O2 portion on the surface was reduced significantly upon LiCl treatment, which can be understood as being the surface hydrophobization mentioned above that occurs upon rearrangement. As delignification proceeds, water-soluble oxidized carbohydrates become more accessible. Some of these are washed out during LiCl treatment, giving rise to a reduction of O1 and the simultaneous relative increase of O2, as observed. It should be pointed out here that, when changes in O2 are considered, the gradual removal of lignin (in Sw, from holocelluloses with a high lignin content to those with a low lignin content) makes it increasingly difficult to "hide" C-O motifs from the surface upon rearrangement, which may affect the variations observed.

The lignin fraction in the Sw sample was isolated and included in the XPS analysis for the purpose of comparison (**Paper IV**). No rearrangement leading to the accumulation of C-C on the surface could be observed. Here, it is likely that the structure created during drying after LiCl treatment is determined by hydrophobic interactions of the lignin motifs, leading to the exposure of more hydrophilic groups on the surface. It was even more interesting to observe that there were no indications of Li-O interactions either. It is obvious that both of these phenomena seem to be characteristic of the carbohydrate fibrillar network that is capable of causing surface adaptation and interactions with Li^+/Cl^- ions. Nevertheless, the lignin fraction seems to retain a considerable amount of LiCl, probably through non-specific interactions between the surfaces of the lignin/LCC and the aqueous LiCl solution.

BET measurements of surface area

In order to investigate the rearrangements that were observed as being promoted by LiCl further, variations were monitored in the surface area of samples with holocelluloses with high and low contents of lignin before and after LiCl treatment. Upon LiCl treatment, the BET specific surface area increased from 1.5±0.0 m^2/g to 2.4±0.1 m^2/g for holocelluloses with a high lignin content, and from 1.6±0.03 m^2/g to 2.7±0.6 m^2/g for those with low a lignin content. LiCl treatment promoted an increase in surface area, with the effect being more pronounced as the content of carbohydrate increased, i.e. there is an increase in both the matrix mobility and the accessibility of the carbohydrate components. The increase observed in the surface area may be an effect of the aforementioned disruption of the stabilizing H-bonding, which promotes rearrangement of the fibrillar structure on the surface caused by the action of the Li^+/Cl^- ions. The literature (**Nada** *et al.,* 2009) reports that the crystallinity of the cellulose materials decreases upon LiCl treatment, allowing an increased surface area to be observed. However, the increased surface area of the cellulose-rich samples can also be affected by the removal of soluble components during LiCl treatment.

FTIR characterization

FTIR characterization of Sw flour samples (untreated, acid treated, and after acid treatment, followed by LiCl treatment) was carried out to identify the functional groups that are affected by the interactions between the Sw flour and the Li^+/Cl^- ions, and thus probably play an important role in the sorption of ions (**Figure 5.5**). The relevant functional groups and their tentative band assignments are in agreement with those reported in the literature for softwoods (**Schwanninger** *et al.,* 2004; **Pandey**, 1999). Comparing the spectra of the original wood with those of wood treated with LiCl, it is clear that there are differences in the absorbance signals originating from the groups containing –OH (e.g. alcohols, phenols and absorbed water) and carbonyl (C=O) and C-H functionalities. The differences observed in the absorption bands suggest that these functional groups are affected by the interactions of Li^+/Cl^- ions with Norway spruce Sw flour.

Changes in the stretching vibrations of the –OH detected within a broad range of frequencies (3700-3100 cm^{-1}) indicate interactions between the Li^+/Cl^- ions and the –OH groups. The changes in the signals corresponding to the C=O stretch in carbonyls (e.g. acetyl groups) present in hemicelluloses (1738-1709 cm^{-1}) and C-H deformations in carbohydrates (1470-1300 cm^{-1}) were also observed upon LiCl treatment (**Figure 5.5** (ii)). Corresponding bands shown a clear decrease in intensity, thus indicating the partial removal of acetyl groups during the treatment, which is in agreement with the XPS findings. Furthermore, signals originating from the sorbed water (1650-1635 cm^{-1}) were enhanced significantly in the LiCl treated samples, implying that the enhanced interaction with water is an effect of LiCl treatment.

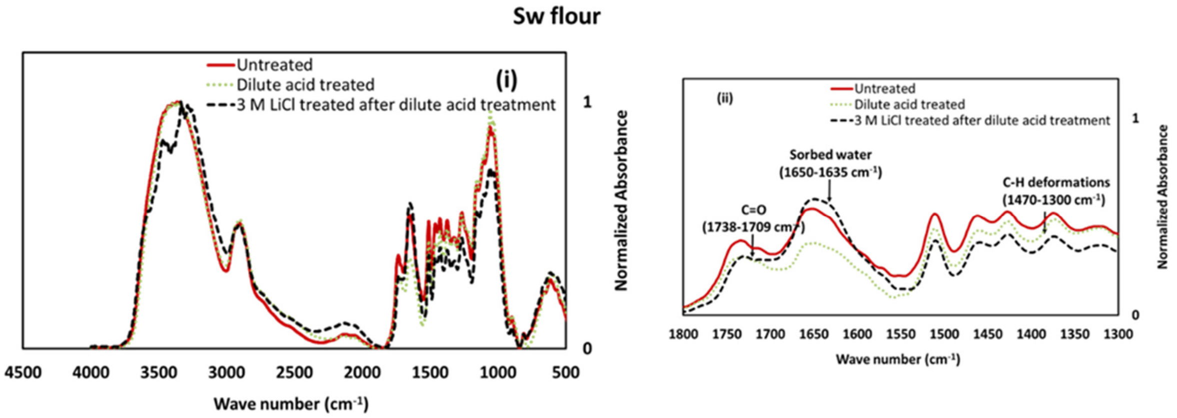


Figure 5.5 FTIR spectra of the Sw flour samples: untreated (native), treated with dilute acid and treated with 3 M LiCl after acid treatment at room temperature: (i) Overall spectra and (ii) magnified spectra between 1800 and 1300 cm^{-1}.

It was not possible to draw any conclusions from the results described above as to which functional groups of the individual wood constituents are involved in the sorption of ions. Therefore FTIR spectroscopy was also used to study the behaviour of the individual model components of wood: cellulose (Micro Crystalline Cellulose (MCC)), hemicelluloses (beechwood xylan) and lignin (Kraft lignin) (**Paper III**) as well as isolated fractions of Sw flour: holocelluloses with high and low contents of lignin and lignin/LCC fractions (**Paper IV**), and before and after 3 M LiCl treatment at room temperature. It is evident from this study that the bands assigned to the –OH groups of cellulose, xylan and lignin show changes upon LiCl-treatment, thus indicating their participation. The partial removal of acetyl groups assumed during aqueous LiCl treatment was supported further by a decrease in the intensity of the signals corresponding to C=O and the C-H of carbohydrates.

As the lignin was removed gradually from the Sw flour, and upon LiCl treatment, the spectral changes in these wave number intervals were even more pronounced, implying that the removal of acetyl groups was even more extensive. Furthermore, signals originating from the sorbed water (1652-1630 cm^{-1}) were enhanced significantly in delignified samples, implying an enhanced interaction with water during LiCl treatment. Moreover, significant changes in the -OH signals were also detected in the more delignified samples, implying the participation of these functional groups in interactions with LiCl: this might be due to changes in the H-bonding patterns, as already indicated by the XPS results. The lignin/LCC samples showed even more pronounced changes in the signals originating from these groups (i.e. -OH, C=O and sorbed water). According to **Alam** and **Van De Ven**, (2014), the softwood lignin isolated by the procedure employed in this study is rich in both phenolic groups and carbonyls originating from the oxidized carbohydrate residues in lignin-carbohydrate complexes. Drastic changes in the -OH region of this sample are indicative of the altered interactions of the phenolic groups due to the presence of LiCl and/or enhanced interactions with water.

FAES measurements

The effect the composition of the wood had on the amount of Li^+ ions sorbed onto samples of Norway spruce was measured quantitatively using Flame Atomic Emission Spectroscopy (FAES). The results revealed that the amount of Li^+ ions sorbed increased as the amount of lignin decreased in the sample (**Paper IV**). The highest concentration of Li^+ ion was observed in the carbohydrate-rich portion (i.e. holocelluloses with a low lignin content) and the lowest concentration in the lignin/LCC fraction. It is evident from this study that samples with more OH groups show higher amounts of Li^+ ions sorbed, suggesting that OH functional groups have significant interactions with Li^+ ions, as was observed in the FTIR studies. Moreover, this result also indicates that there is an increase in the number of interactions the functional groups make with the LiCl solution, which is due to the increased accessibility of the carbohydrate network upon delignification.

Effect of pH during the sorption experiments

The sorption experiments were performed in a closed-batch system in this study, without any adjustment of the pH. It was observed that the pH of the liquid phase decreased, and also that the drop in pH increased with increasing concentration of the Li^+ ion in the bulk solution (**Figure 5.6**). Similar results were observed for the samples of wood flour that were not acid treated prior to LiCl treatment. The pH drop observed was, however, more pronounced for acid treated than for non-acid treated samples prior to LiCl treatment (**Figure 5.6**). It was estimated that a drop in pH of approximately 1.9 units was due to acid liquor in the wood pores: the remaining drop must therefore have been caused by either the exchange of ions between the wood components and the Li^+/Cl^- ions or other structural changes in the wood that might have occurred upon LiCl treatment (such as deacetylation). Only a small part of the remaining decrease in pH can be explained by carboxylic groups; at these low pH values it is unlikely that phenolic groups are involved. The remaining drop in pH may therefore be due to deacetylation of carbohydrates upon treatment of wood samples with LiCl, as observed above in the FTIR and XPS studies.

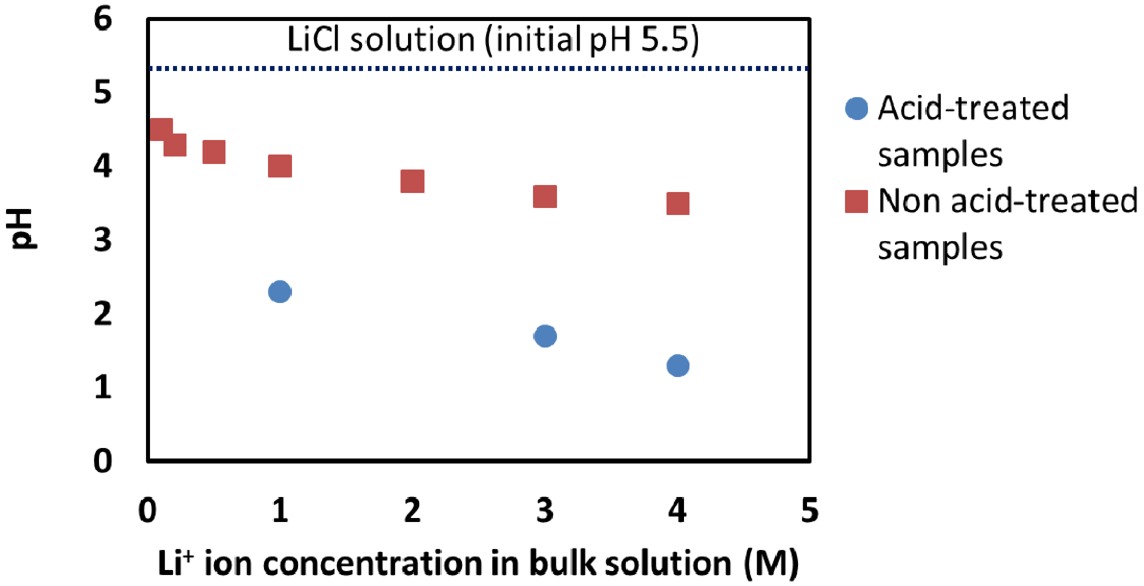


Figure 5.6 Decrease in pH vs concentration of Li^+ ions in bulk LiCl aqueous solution during the sorption experiments with Sw flour at room temperature.

5.3. Density and porosity measurements of Norway spruce wood

Data pertaining to the porosity and volume of pores that are accessible for the diffusion of ions in samples of wood pieces and wood flour is required in order to (a) measure the concentration profiles of the ions in the porous structure of wood and (b) estimate the amount of ions sorbed onto the surfaces of wood cell walls at equilibrium conditions. Measurements of density and porosity are therefore described first.

The densities measured (i.e. of the normal bulk and the cell walls) and the total porosities of Norway spruce wood are consistent with previous findings (**Plötze** and **Niemz**, 2011) (**Table 5.2**). In this table, the values of the intrusion volume and porosity of the pore determined by mercury intrusion porosimetry are also reported. **Figure 5.7** shows the incremental intrusion volume and pore size distribution of pores of diameter 0 - 41 µm (these diameters refer to pores accessible to diffusion) for untreated samples of both Sw and Hw of Norway spruce. In softwood, pores with a diameter larger than 20 µm may represent the resin canals and earlywood tracheids, and those between 20 and 6 µm represent the latewood tracheids (**Zauer** *et al.,* 2014), although there is a relatively large overlap between earlywood and latewood tracheids. Both of these pore classes are termed as macrovoids: pore diameters smaller than 6 µm (microvoids) represent the pointed ends of all cell elements as well as of the pit pores (**Thygesen** *et al.,* 2010).

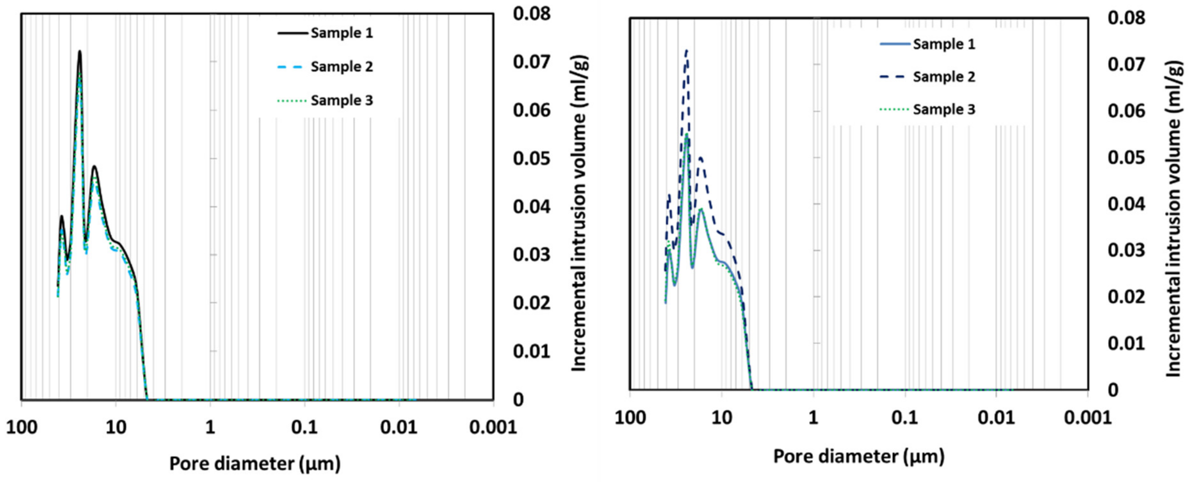
Sw vs. Hw

Significant differences in porosity and intrusion pore volume were observed between Sw and Hw pieces of Norway spruce (**Figure 5.7** (B)). The results show that Hw piece has lower porosity and intrusion pore volume than Sw piece. These differences in Sw and Hw piece are most likely due to differences in the structure of Sw and Hw, e.g. Hw is usually much less permeable than Sw due to pit aspiration and incrustation. But in the case of wood flour samples, similar intrusion pore volume and porosity were observed for both Sw and Hw flour samples (**Figure 5.7** (A)). In the determination of concentration profiles and estimation of transport properties discussed in the following sections, constant porosity (57.8±8.9 %) and intrusion pore volume (0.99±0.3 ml/g) are used for both Sw and Hw pieces.

Figure 5.7

Table 5.2

(A) Samples of wood flour



(B) Samples of wood pieces

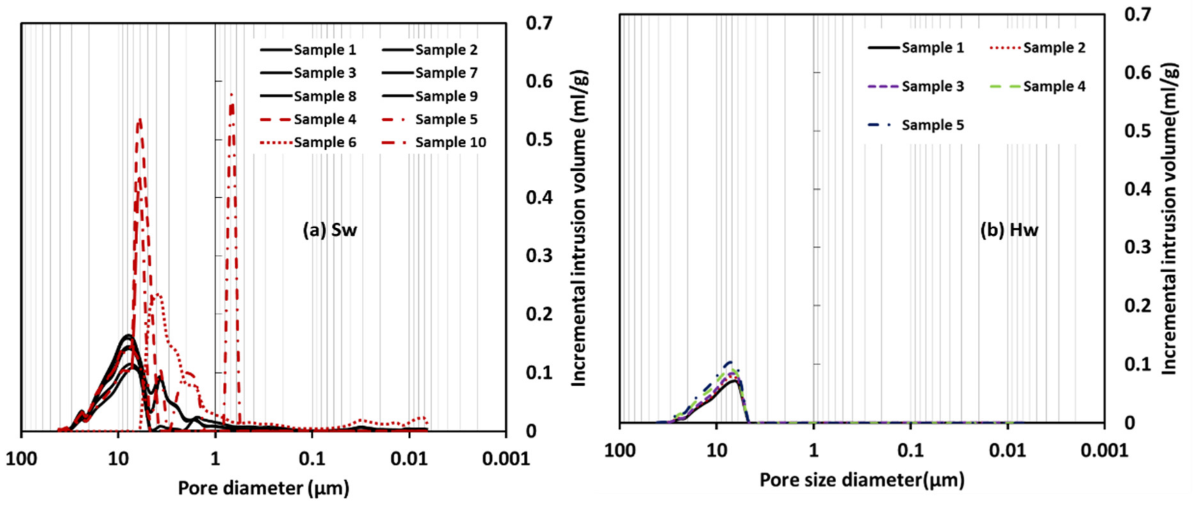


Figure 5.7 Pore size distribution of untreated Norway spruce (a) Sw and (b) Hw samples of wood flour (A) and wood piece (B) samples (as indicated); sample 1, sample 2…are replicates that were prepared from 2 different wood pieces.

Table 5.2 Normal bulk density, specific cell wall density, total porosity, intrusion pore volume and porosity (Hg porosimetry) of Norway spruce wood.

This study	**Sample**	**Cell wall density (ρ_p) (g/cm^3)**	**Normal bulk density (ρ_b) (g/cm^3)**	**Total porosity n = 1-(ρ_b/ ρ_p) %**	**Total intrusion pore volume (mL/g) (0 to 330 µm)**	**Total porosity (Hg Porosimetry) % (0 to 330 µm)**	**Effective transport-through intrusion pore volume (mL/g) (0 to 41 µm)**	**Effective transport-through porosity (Hg Porosimetry) % (0 to 41 µm)**
	Sw flour	1.48±0.002(n*=3)			2.9±0.1(n=3)	81.5±0.7(n=3)	0.45±0.0(n=3)	39.9±1(n=3)
	Hw flour	1.48±0.006(n=3)			2.6±0.3(n=3)	79.5±1.6(n=3)	0.41±0.06(n=3)	37.7±3.5(n=3)
	Sw piece		0.41±0.01(n=3)	72.4±0.34(n=3)	1.1±0.4(n=10)	59.7±8.6(n=10)	0.99±0.3(n=10)	57.8±8.9(n=10)
	Hw piece		0.49±0.01(n=3)	66.7±0.97(n=3)	0.4±0.1(n=5)	38.3±4(n=5)	0.4±0.1(n=5)	36.1±4(n=5)
Reference **(Plötze and Niemz,** 2011**)**	Norway spruce Wood piece	1.524	0.401	73.68		68.39		

*n = number of samples prepared from the two different pieces of wood

5.4. Sorption equilibrium of ions onto solid portions of wood flour

The amount of Li^+ ions sorbed per unit weight of (dry) Norway spruce wood flour that is measured experimentally is the total amount of Li^+ ions sorbed by the wood (q_{total}), i.e. the quantity of Li^+ ions that is sorbed onto the surfaces of the cell walls of the solid wood (q_{wood}) and dissolved in the solution within the wood pores (q_{pores}). The measurements are aimed at steady state, so it is reasonable to assume that the concentration of Li^+ ions in the liquid in the wood pores is equal to that of the bulk liquor. Using **Equations** (5.1) and (5.2) below, it is thus possible to estimate the amount of Li^+ ions sorbed onto the solid wood. All of the results reported in this section were based on the amount of Li^+ ions sorbed onto the solid wood (q_{wood}).

$$q_{total} = q_{wood} + q_{pores} \tag{5.1}$$

$$q_{pores} = C_{Li^+, bulk} * V_{pores} \tag{5.2}$$

where $C_{Li^+, bulk}$ and V_{pores} are the concentrations of Li^+ ions in the bulk solution (mg/ml) and the volume of the pores in the wood flour (ml/g), respectively. The volume of the pores in the samples of wood flour was determined by the mercury porosimetry technique mentioned previously. V_{pores} was calculated as the total incremental intrusion volume of the pores in the wood flour, with the pores having a diameter of between 0 and 41 μm. The wood-Li^+ ion equilibrium partition coefficient (k), is defined as:

$$k = \frac{q_{wood,e}}{C_{Li^+}} \tag{5.3}$$

where $q_{wood,\,e}$ is the amount of Li^+ ions sorbed onto the solid wood (mg/g) and C_{Li^+} is the Li^+ ion concentration in the solution located in the porous structure of the wood matrix (mg/ml) at an apparent equilibrium condition. In this study, the surface area (sorption sites) available in the wood flour and samples of wood piece was also assumed to be constant.

In order to determine the residence time needed to obtain an apparent equilibrium (i.e. the time at which there is no change in the amount of Li^+ ion sorbed to wood flour), the experimental data (q_{wood}) was measured at several contact times ranging between 30 minutes and 30 days. The changes observed in the q_{wood} values as the residence time was varied were small, and indeed almost within the experimental error. Furthermore, the results indicated that, for all the experiments, there is a rapid initial rise in the sorption of Li^+ ions and steady state is almost reached within 8 h (**Figure 5.8**). However, the experimental data measured at 24 h was used as the amount of ions sorbed at a condition of apparent equilibrium ($q_{wood,e}$). Similar results were also observed for Hw flour samples.

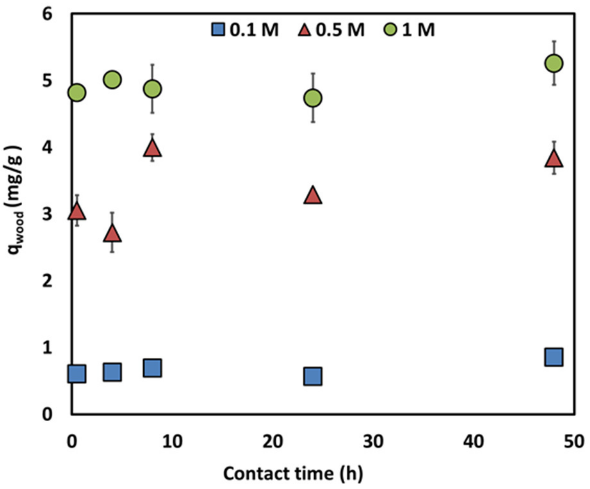


Figure 5.8 Variations in the amount of Li^+ sorbed onto Norway spruce Sw flour with time, at R T. The contact time varied between (a) 30 min and 30 days, and (b) 0.5 and 48 h.

The wood-Li^+ ion equilibrium partition coefficients (k) for both Sw and Hw, calculated using Equation (5.3) for experiments with 1 M LiCl aqueous solution at different temperatures, are reported in **Table 5.3**. The plot of $q_{wood,\ e}$ versus the concentration of Li^+ in bulk LiCl solution (C_e) is called sorption isotherm. In this study, at lower concentrations of bulk LiCl solutions (up to 1 M i.e. 6.941 mg/ml), the relationship $q_{wood,\ e}$ vs. C_e observed is linear (**Figure 5.9**): the slope of the linear curve is thus considered as being the distribution coefficient. The values of k obtained using **Equation** (5.3) (**Table 5.3**) and the value of the slope obtained from the linear sorption isotherm (**Figure 5.9**) agreed well. The results indicate that the equilibrium partition coefficient is almost constant with respect to temperature and concentration up to 1 M bulk LiCl solution for samples of both Sw and Hw flours. However, as the temperature increased from R T to 60 ^oC, the value of k decreased slightly for Sw flour, while the value of k increased slightly for Hw flour. This may be due to the structural and/or chemical changes that might have occurred in the wood at higher temperatures, although the differences are within the estimated experimental errors.

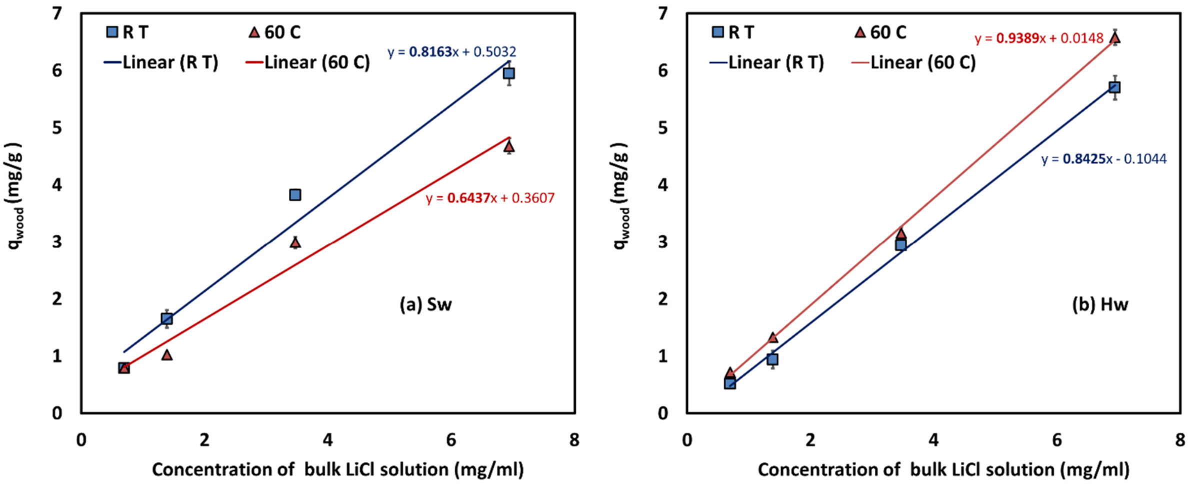


Figure 5.9 Experimental sorption isotherm of Li^+ ions onto Norway spruce wood in experiments with lower concentration of bulk LiCl solution (Upto 1 M i.e. 6.941 mg/ml) at different temperatures: (a) Sapwood (Sw) and (b) Heartwood (Hw) (as indicated).

Table 5.3
The values of $q_{wood,\,e}$ and k measured for samples of Norway spruce Sw and Hw in experiments using 1 M LiCl aqueous solution at various temperatures.

Temperature	**Sw**		**Hw**	
	$q_{wood,\,e}$ (mg/g)	k (ml/g)	$q_{wood,\,e}$ (mg/g)	k (ml/g)
R T	5.9±0.2	0.8±0.0	5.7±0.4	0.8±0.0
40 °C	5.6±0.5	0.8±0.1	5.6±0.0	0.8±0.0
60 °C	5.3±0.7	0.7±0.1	6.5±1.2	0.9±0.2

Effects of temperature and wood structure on equilibrium sorption isotherms

In **Figure 5.10**, $q_{wood,\,e}$ is plotted against the concentration of the Li^+ ions in the bulk liquid (C_e) at R T and 60 °C for samples of both Sw and Hw flour. Only a weak dependence on temperature can be observed for both samples. Approximately the same quantities were sorbed for bulk LiCl solutions of concentrations up to 1 M; above 1 M, these quantities increased slightly with temperature, which may be due to changes in the properties of the wood (e.g. a large surface becomes accessible) that, in turn, may result in slight changes in the interactions with Li^+ ions. Furthermore, for concentrations above 1 M, the sorbed quantities increased more for Hw than for Sw. These differences in the sorbed quantities of Sw and Hw may be attributed to differences in the structural and chemical compositions of Sw and Hw: the extractive content in Hw is, for example, higher than in Sw, and has a broader variety of functional groups available for Li^+ ion interactions (**Siau**, 1984). However, the differences are small: in most cases they are within, or almost within, the experimental errors estimated.

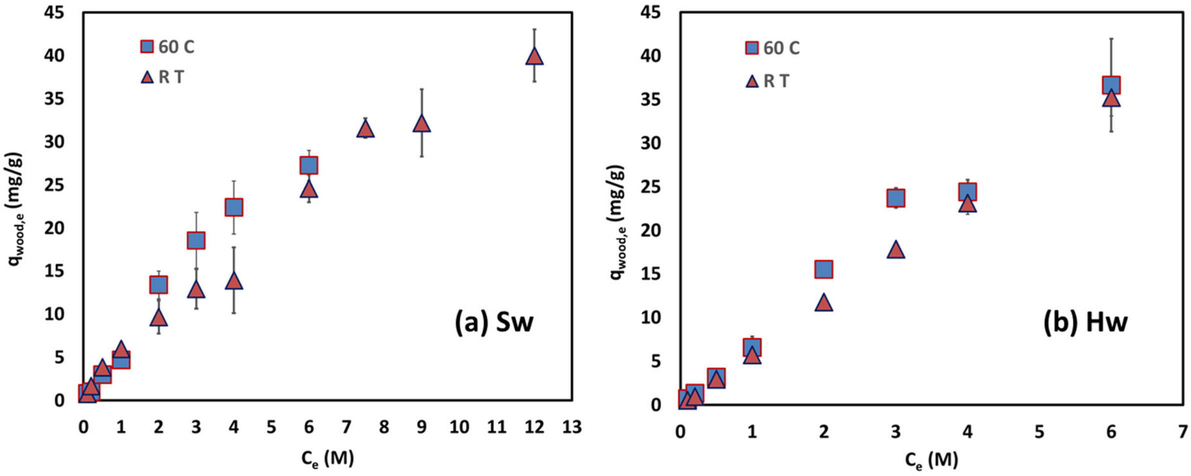


Figure 5.10 Effect of wood type (Sw and Hw) and temperature on the equilibrium sorption isotherms of Li^+ ions onto Norway spruce wood flour at different temperatures. (a) Sw and (b) Hw.

Study of sorption isotherms

An initial investigation was made into the possibility of fitting the Langmuir sorption isotherm model to the individual sorption isotherms described above (**Paper III**). It was, however, found that there was a very strong correlation between the two parameters ($q_{wood,max}$ and b) fitted and no stable results were obtained. Furthermore, as discussed above, there were only small differences between the four different sorption isotherms (Sw at R T, Sw at 60 °C, Hw at R T and Hw at 60 °C). It was decided therefore that all the data from the 4 sorption isotherms should be used to estimate the parameters in both the Langmuir and Freundlich models: both of these models fitted the experimental data reasonably good ($R^2 > 0.9$). The parameters estimated are thus valid for both Sw and Hw for the temperature range between R T and 60 °C, and for the concentrations range of Li^+ ions between 0 and 6 M.

Langmuir isotherm

The $q_{wood,max}$ and b values for Li^+ ions on Norway spruce wood were found to be approx. 132 mg/g and 0.05 l/mol, respectively. The estimated $q_{wood,max}$ value (approx. 132 mg/g or 19 mmol/g) is much higher than the concentration of the carboxylic acid groups (COOH) (0.086±0.007 mmol/g) (**Werkelin** *et al.,* 2010) and the theoretical OH groups (12.7 mmol/g) (see **Appendix A2**) for the estimation procedure) in wood samples of native Norway spruce. This result therefore suggests that, apart from the interactions of carboxyl, hydroxyl and other groups (e.g. C-H), as shown in the FTIR study and in XPS study (visible as Li-O interactions), a non-site-specific retention of ions might also have occurred during the sorption of Li^+ ions onto Norway spruce wood flour under the experimental conditions studied.

Freundlich isotherm

The Freundlich isotherm constants k_F and 1/n were found to be approx. 6.5 $(mg/g)\ (l/mol)^{1/n}$ and 0.87 (dimensionless), respectively. A value for 1/n below one implies chemisorption processes, whereas above one indicates co-operative sorption (**Foo** and **Hameed**, 2010). In this study, the value of 1/n was below one (1/n =0.87), so it is most likely that the sorption process for the experimental conditions studied includes chemisorption.

5.5. Concentration profiles of ions in the porous structure of pieces of wood

Native Norway spruce wood contains small amounts of metal ions (typically 1-5 g/kg wood). These may participate in the sorption mechanism induced by the exchange of ions and thus may aggravate the measurement of concentration profiles. So, prior to the LiCl impregnation experiments being carried out, the samples of wood pieces were treated in a dilute sulphuric acid solution (pH=0.5/0.31 M H_2SO_4) until no floating wood could be observed, in order to remove native metal ions and the air present in the wood material (**Paper V**). The concentration of Li^+ ions measured experimentally was the total concentration of Li^+ ions (q_{total}), i.e. the sum of the Li^+ ions sorbed onto the surfaces of the cell walls of the wood and those present in the solution located in the pores. The concentration of Li^+ ions in the solution in the pores (C_{Li^+}) was calculated using **Equation** (5.4), which is based on mass balance.

For each slice (i.e. thickness level), the q_{total} is defined as:

$$q_{total} = (C_{Li^+} * k) + \left(C_{Li^+} * V_{wood\,piece}\right) \tag{5.4}$$

where, C_{Li^+} is the concentration of Li^+ ions available in the solution located in the porous structure of the wood matrix (g/l) and k is the wood-Li^+ ion equilibrium partition coefficient (l/kg). $V_{wood\ piece}$ is the effective pore volume of the transport-through-intrusion (diffusion-accessible) of the piece of wood (0.99±0.27 l/kg). From this section onwards, all the results reported were based on the concentration of Li^+ ions in the solution located in the porous structure of the wood matrix, which was calculated by using **Equation** (5.4).

Effect of impregnation (residence) time

An increase in the concentration of Li^+ ions was observed at the corresponding positions in the pieces of wood as the impregnation time increased. In **Figure 5.11**, which shows an example at 40ºC, it can be observed that a shift occurred in the concentration profiles of the Li^+ ions towards the centre of the piece of wood as the duration of the treatment increased from 36 to 168 h. In the eluate of slices taken from the outermost surface layer, a concentration of Li^+ ions greater than in the bulk solution (6.941 g/l) was observed at extended residence times (i.e. 168 h). It appears that the micro-cracks continue to affect the concentration profiles to some extent, and thereby contribute to the different shapes of the concentration profiles at extended residence times.

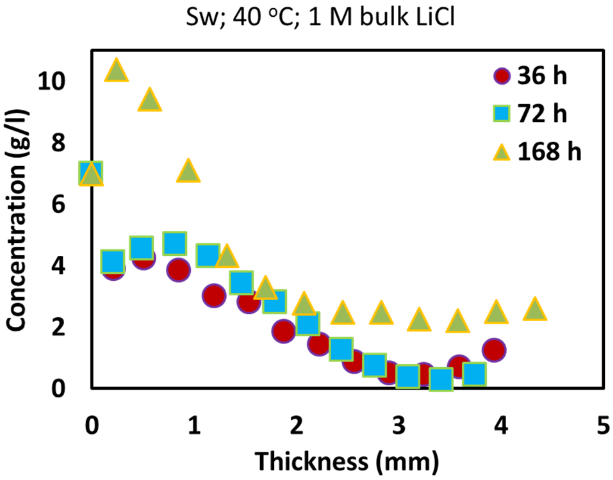


Figure 5.11 Concentration profiles measured for Li^+ ions (present in the wood pore solution) in SsWP Norway spruce Sw after residence times of 36, 72 and 168 h, at 40 ºC for Cube a.

5.6. Effective diffusion coefficients and tortuosity factors of ions in wood

The symbols and lines in **Figure 5.12** represent the experimental concentration profiles and the best fit of the model, respectively. Although the model fits these profiles reasonably well for Cube a (**Figure 5.12** (A)), as can be seen, it was not satisfactory for Cube c, especially at residence times of 36 and 72 h (**Figure 5.12** (B)-(a) and (b)). This behaviour is most likely due to micro-cracks caused by the mechanical preparation of the pieces of wood (e.g. during sawing), as mentioned previously. Regardless of the fact that it was not possible to verify the concentration profiles at shorter times (36 and 72 h) for the edge portions (Cube c) of the piece of wood in this work, rough estimations of the longitudinal diffusion coefficients and tortuosity factors have been made. Similar results were also observed for the samples of Hw (**Figure 5.13**). The estimated $D_{e,T(=R)}$ and $D_{e,L}$ are listed in **Table 5.4**, where it can be seen that, for samples of both Sw and Hw and for the experimental conditions studied, the predicted $D_{e,T(=R)}$ is about two orders of magnitude less than the $D_{e,L}$. This result is reasonable since the diffusion of chemicals/ions in the transversal direction takes place mainly through the cell walls and pits whereas in the longitudinal direction, it is mainly through the liquid in the fibre lumen.

Tortuosity factors for both samples (Sw and Hw) were calculated using **Equation** (4.4) in two diffusional directions, i.e. the longitudinal and transversal, and are given in **Table 5.4**. As expected, the tortuousness is smaller in the longitudinal direction than in the transversal direction for samples of both Sw and Hw. This result is understandable because the transport of ions in the longitudinal direction occurs mainly through the lumen openings in the tracheids and the distances through the pit pores are short. Sawing may also have caused some fibre separation in longitudinal direction at the edge part of the piece of wood, causing the formation of some micro-cracks between the fibres which may, in turn, enhance longitudinal mass transport. In the transverse direction, however, the ions are transported mainly through pit pores, which have rather small areas and their positions along the fibre wall cause the tortuosity.

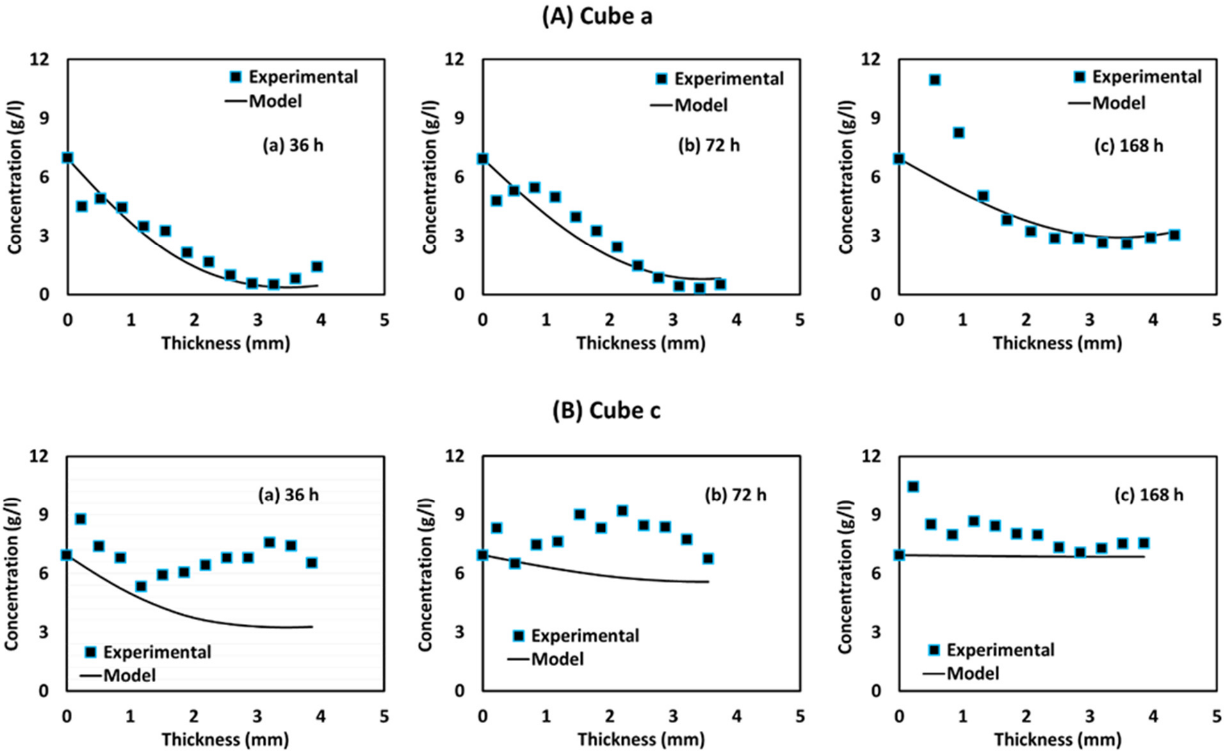
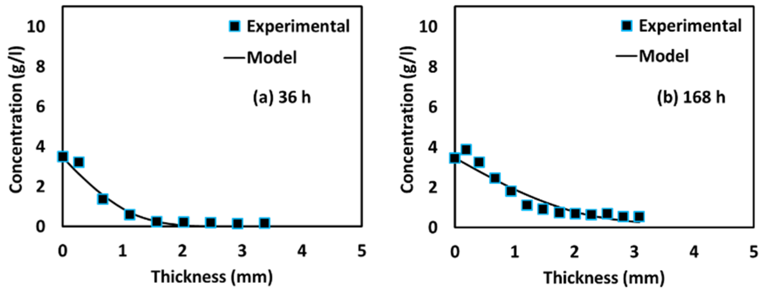
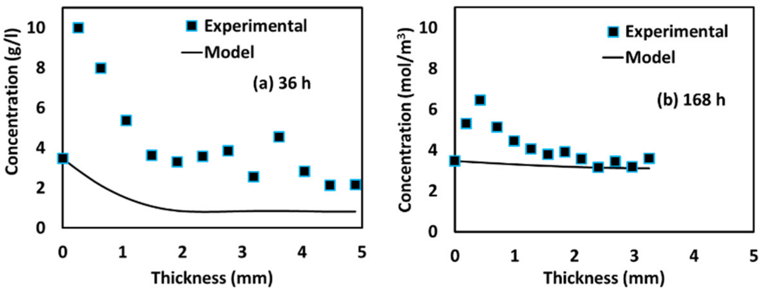


Figure 5.12 Measured and calculated concentration profiles of Li^+ ions in Norway spruce Sw at 40 °C for (A) Cube a (middle portion) and (B) Cube c (edge portion) of the impregnated piece of wood in the experiments with 1 M bulk LiCl solution after the residence times (a) 36, (b) 72 and (c) 168 h.



(A) Cube a



(B) Cube c

Figure 5.13 Measured and calculated concentration profiles of Li^+ ions in Norway spruce Hw at 40 °C for (A) Cube a (middle portion) and (B) Cube c (edge portion) of the impregnated piece of wood in the experiments with 0.5 M bulk LiCl solution after the residence times (a) 36, (b) 72 and (c) 168 h.

Table 5.4
Diffusive resistance and tortuosity factors of Li^+ ions in samples of Norway spruce Sw in the longitudinal and transversal (Radial & Tangential) directions at 40 °C.

Sample	Concentration of bulk LiCl solution (M)	Direction of diffusion	Effective diffusion coefficient (m^2/s)	Tortuosity factor
Sw	1	Longitudinal	Approx.1×10^{-9}	1.2
		Transversal	$1.7 \pm 0.7 \times 10^{-11}$	76 ± 35
Hw	0.5	Longitudinal	Approx. 6.5×10^{-10}	1.9
		Transversal	$4.7 \pm 2 \times 10^{-12}$	305 ± 159

6. Contributions made to this field of research

- The methods employed to prepare the samples used in this study are suitable for elucidating reasonably good measurements of the concentration profiles of ions in the porous structure of wood in the transversal direction. The diffusion of ions in the central part of a piece of wood is affected mainly by mass transport in the transversal direction, which has much shorter diffusional distances than the longitudinal direction. However, the method proposed is unable to explain the concentration profiles at the edge part of the wood piece, where the diffusion of ions is affected by mass transport in both longitudinal and transversal directions. This is probably due to the structural damage that might have occurred during the mechanical preparation of the wood pieces at the edge part of the wood piece; sawing, for example, may also cause some separation of fibres in the longitudinal direction, thus allowing micro-cracks between the fibres may to be formed.

- The chemical groups involved in the interactions between the Li^+/Cl^- ions and wood are partly identified. A decrease in the carbonyl content of the wood samples upon LiCl treatment indicates the deacetylation of hemicelluloses.

- The method employed to measure the sorption equilibrium is suitable for differentiating the amount of ions that is sorbed onto the surfaces of the cell walls of the wood from that dissolved in the solution within its pores. The sorption equilibrium of Norway spruce wood-Li^+ ions from LiCl solution is partially understood. At lower concentrations of LiCl solution, the major part of the sorption of Li^+ ions onto the wood can be explained by the ion exchange that occurs between the carboxylic groups in the wood's components and the Li^+/Cl^-. However, at higher concentration of LiCl, other interactions/bondings might be involved in the sorption process.

- Considering both the diffusive mass transport of ions through liquid-saturated wood pores and the sorption of ions onto the matrix of the solid wood, the transport model adopted provided reasonably good results for the transport properties (i.e. effective diffusion coefficients and tortuosity factors) in the transversal direction.

7. Conclusions

7.1. Sorption equilibrium experiments: development of the method

- The experimental methodology proposed was found to be suitable for determining the concentration of the ions sorbed onto the matrix of the solid wood.
- The results show that Norway spruce wood has a considerable affinity towards Li^+ ions.

7.2. Sorption isotherm models

- Both the Langmuir and Freundlich sorption isotherm models described the sorption of Li^+ ions onto Norway spruce wood flour reasonably good for the conditions investigated.

7.4. Changes in surface chemistry during sorption

- The introduction of Li^+ and Cl^- ions from an aqueous LiCl solution into the matrix of Norway spruce Sw is associated with the disruption of H-bonding and the accompanying enhanced mobility, which were demonstrated by an enhanced adaptation of the surface of the fibrillar structure upon drying and an enlarged surface area.
- Spectroscopic analysis of the wood material before and after LiCl treatment indicated clearly that the elements Li and Cl participated in interactions with the constituents of wood: the hydroxyl, carboxylic and carbonyl groups in the wood involved in the interactions and the amounts of Li^+ ions sorbed onto carbohydrate-rich fractions were higher than for the lignin fractions.

7.5. Measurement of the concentration profiles: development of the method

- An experimental methodology for determining concentration profiles of chemicals in porous structure has been adapted to wood.
- The method gave reasonable results, although defects (i.e. micro-cracks) in the pieces of wood remained and were detectable.

7.6. Transport properties of ions in wood

- The effective diffusion coefficient of Li^+ ions in samples of Norway spruce Sw and Hw is about two orders of magnitude less in the transversal direction than in the longitudinal direction for the conditions used in this study.
- The tortuousness is longer in the transversal direction than in the longitudinal direction for both the Sw and Hw: the tortuousness was calculated as being 63±29 and 160±83 times longer in the transversal direction for Sw and Hw, respectively, for the conditions used in this study.

8. Acknowledgements

I would like to thank:

My examiner and main supervisor **Professor Hans Theliander** for giving me this opportunity to be a Ph.D. student in his research group. I am grateful for his contributions of time, tremendous support, ideas and valuable guidance which were vital for the outcome of the research work presented in this thesis.

Dr. Merima Hasani, my advisor and co-author, for excellent collaboration. I am grateful for her support, commitment and guidance.

The **Chalmers Energy Initiative (CEI)** for financial support.

Kurt Löfgren and **Torbjörn Jönsson** for their help with carpentry: preparing samples of wood pieces from logs and then small cubes from the pieces.

Ms. Anne Wendel for her help with XPS measurements, and for answering many of my immature questions and providing input to help me understand the results obtained.

Mr. Tommy Friberg for his skillful help with smoothing the wood pieces.

Ms. Joanna Wojtasz for her help with analysing Klason lignin and carbohydrates and **Mr. Jonas Wetterling** for his help with BET surface area and Density (Pycnometer) measurements.

Professor Per Lincoln, for interesting discussions.

Ms. Eva Kristenson, **Ms. Malin Larsson** and **Ms. Carina Pettersson** for their assistance with administrative tasks.

Linguistic advisors: **Ms. Deborah Fronko,** for linguistic review of Paper II and Licentiate thesis, and **Ms. Maureen Sondell** for a much valued linguistic review of the three manuscripts (Papers III, IV and V) and the Ph.D. thesis.

Dr. Seshendra Karamchedu for listening to, and providing support for, many of my thoughts concerning my personal as well as my professional life over the course of these years.

My former and present colleagues and friends at the Division of Forest Products and Chemical Engineering and Chemical Environmental Science for a fascinating and enjoyable working environment with people from different cultures from all over the world.

All of my friends from India who reside in Gothenburg region, some of whom also work at Chalmers University, for sharing many enjoyable weekend breaks during my time here.

All of my teachers, past and present, for their guidance, support and encouragement. I would especially like to thank **Dr. P. Dinesh Sankar Reddy**, **Prof. Pallab Ghosh** and **Dr. Tamal Banerjee** for their valuable suggestions and support. I also thank a special teachers from my school, **Mr. B. Rajasekhar Rahul** and his wife **N. K. Saraswathi**, for it was them who also encouraged me to continue on to higher studies. This teacher's family is special to me, since I married to their daughter **Sumahitha Rahul.** Their support has been essential to me during these years in taking care of my wife and son (**Rituparan**), who reside in India.

My dear family, for all their constant support. Many thanks for understanding, and being with me through some tough times, and especially to my parents: mother (**Kolavali Subba Lakshmi**) and father (**Kolavali Aswartha Narayana**), who understand the importance of education and worked hard to provide the many things I needed to reach this level in my life. My mother never went to school at all and my father had only basic education, having had only 4 years of schooling during childhood. I am truly greatful for all their great support and encouragement, and for allowing me to realize my own potential.

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Appendices

Appendix A1

Estimation of the diffusion coefficient of Li^+ ion in an aqueous medium (free solution)

The diffusion coefficient of Li^+ ion in an aqueous medium (free water) (D_f) with a concentration of C_{aq} (M) and at temperature T (ºC) can be estimated from the following correlation, using viscosity data of the aqueous medium at a corresponding temperature and concentration (Poling *et al.,* 2001), Equation (A1):

$$D_{f,Li^+}^{T^{\circ}C} = D_{f,Li^+}^{25^{\circ}C} * \left(\frac{T^{\circ}C}{25^{\circ}C}\right) * \left(\frac{\mu_{C_{aq}}^{25^{\circ}C}}{\mu_{C_{aq}}^{T^{\circ}C}}\right) \quad \text{(A1)}$$

where $D_{f,Li^+}^{T^{\circ}C}$ and $D_{f,Li^+}^{25^{\circ}C}$ are the diffusion coefficients of Li^+ ions in an aqueous medium at temperature T (ºC) and 25 ºC, respectively, and $\mu_{C_{aq}}^{ToC}$ and $\mu_{C_{aq}}^{25oC}$ are the viscosities of an aqueous solution at concentration C, temperature T (ºC) and 25 ºC, respectively. $D_{f,Li}{}^+$ in an aqueous solution of concentration C at 40 ºC has been estimated using Equation A1 and the literature data presented in Table 2. $D_{f,Li}{}^+$ at 40 ºC in 1 M and 0.5 M aqueous solutions was found to be 2.0×10^{-9} m^2/s and 2.1×10^{-9} m^2/s, respectively.

Table A1

Viscosity of a 1 M LiCl solution and the self-diffusivity of Li^+ ions in 1 M LiCl solution at different temperatures.

Bulk LiCl solution concentration (M)	Temperature (ºC)	Viscosity **(Melinder 2007)** (μ) (mPa.s)	Self-diffusivity **(Braun and Weingärtner 1988)** (D_{f,Li^+}) (m^2/s)
1	25	1.023	0.924×10^{-9}
	40	0.753	-
0.5	25	0.965	0.95×10^{-9}
	40	0.69	-

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Appendix A2

Estimation of the number of theoretical OH groups in the sample of Norway spruce Sw wood flour

The number of theoretical OH groups in moles per gram (mol/g) can be estimated using Equation A2, as proposed by Rowell [1] and Hill [2]:

$$\frac{3A}{162}+\frac{3B}{162}+\frac{2C}{132}+\frac{D}{180} \qquad \text{(A2)}$$

where A is cellulose, B the hemicellulose hexosan, C the hemicellulose pentosan and D lignin. Analyses of the composition of Norway spruce Sw flour were performed using the procedure described by Jedvert *et al.,* 2012 [3] and found to be: 36.9% cellulose (A), 17.2% the hemicellulose hexosan (B) and 5.8% pentosan (C), and 33% lignin (both soluble and insoluble in acid). Based on this composition, the number of theoretical OH groups that were estimated was found to be 12.72 mmol/g. Since hydroxyl groups made inaccessible through binding between wood polymers or steric hindrance are not considered, this estimate expresses a theoretical upper limit. Also, two-thirds of the hydroxyl groups of cellulose are known to be inaccessible to water due to the crystalline part of cellulose. Moreover, the accessibility of the hydroxyl groups in a sample (e.g. drying) is also influenced by its history.

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