

# A model for non-Fickian moisture transfer in wood\*

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## Abstract

A model for non-Fickian moisture transfer in wood is presented. The model considers the transfer of water vapour separate from the transfer of bound water. These two components are linked by an equation describing the sorption on the cell wall level. Hereby, a formulation capable of describing known non-Fickian effects, including the effects of step size, absolute moisture content, and sample length, is achieved. The sorption curves predicted by the model are compared with experimental results and good agreement is found.

## Keywords

Wood, non-Fickian, moisture, sorption, coupled transfer.

## 1 Introduction

The mathematical description of the transfer of moisture in wood below the fiber saturation point is often made using two basic assumptions. Firstly, that the moisture flux can be described by a Fickian type gradient law, and secondly that the bound water in the cell walls is at all times in equilibrium with the surrounding mixture of vapour and air as described by the sorption isotherm.

In one dimensional isothermal transfer the moisture flux  $j$  is given by

$$j = \mathcal{D}_m \frac{dm}{dx} \quad (1)$$

where  $m$  is the moisture content and  $\mathcal{D}_m$  a moisture dependent diffusion coefficient. Using the equilibrium assumption this expression can, alternatively, be formulated with the relative humidity  $r$  as potential

$$j = \mathcal{D}_m \frac{dm}{dx} = \mathcal{D}_m \left( \frac{dm}{dr} \right) \frac{dr}{dx} = \mathcal{D}_r \frac{dr}{dx} \quad (2)$$

where the diffusion coefficient with  $r$  as potential is given by

$$\mathcal{D}_r = \mathcal{D}_m \left( \frac{dm}{dr} \right) \quad (3)$$

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<b>Roman letters</b>	
$\mathcal{D}$	Diffusion coefficient
$E$	Fractional weight increase
$h$	Sorption term ( $\text{kg m}^{-3} \text{ s}^{-1} \text{ Pa}^{-1}$ )
$j$	Flux ( $\text{kg m}^{-2} \text{ s}^{-1}$ )
$m$	Moisture content (MC) ( $\text{kg m}^{-3}$ )
$\dot{m}$	Sorption term ( $\text{kg m}^{-3} \text{ s}^{-1}$ )
$p$	Pressure (Pa)
$r$	Relative humidity (RH)
$R$	Gas constant ( $\text{J mol}^{-1} \text{ K}^{-1}$ )
$T$	Temperature (K)
$w$	Bound water content ( $\text{kg m}^{-3}$ )
<b>Greek letters</b>	
$\varphi$	Porosity
$\rho$	Concentration ( $\text{kg/m}^3$ )
$\zeta$	Internal area/volume ratio ( $\text{m}^{-1}$ )
$\xi$	Vapour diffusivity reduction factor
<b>Sub- and superscripts</b>	
$a$	Air
eff	Effective
$g$	Gas – air + vapour
$L$	Longitudinal
$T$	Tangential
$v$	Vapour

Table 1: Nomenclature

By mass conservation considerations unsteady state conditions can then be described by either of the two following partial differential equations

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x} \left( \mathcal{D}_m \frac{\partial m}{\partial x} \right) \quad \text{or} \quad c \frac{\partial r}{\partial t} = \frac{\partial}{\partial x} \left( \mathcal{D}_r \frac{\partial r}{\partial x} \right) \quad (4)$$

where  $c = dm/dr$  is the slope of the sorption isotherm.

In the following, the shortcomings of this so-called Fickian model are discussed. An alternative model is then proposed and the capabilities of this model are demonstrated by comparison to experimental results.

## 2 Failure of Fickian models

As already discussed the Fickian models rely upon two basic assumptions, namely that the transfer of moisture is governed by a Fickian type gradient law and that within the wood there exists an equilibrium state such that the moisture content is at all times a unique function of the corresponding relative humidity as given by the sorption isotherm.

The first assumption that the flux of some quantity can be taken as being proportional to the gradient of this

quantity by some scalar  $\mathcal{D}$  is probably reasonable, at least as a first approximation and especially when dealing with a relatively slow transfer under isothermal conditions. However, the second assumption that there is instantaneous equilibrium between the bound water and the water vapour at all times is harder to justify.

Considering in more detail the mechanisms of moisture transfer in the hygroscopic range this must consist of a diffusive, and possibly convective, transfer of water vapour in the cellular structure with simultaneous sorption in the cell walls. In addition, bound water may be transferred within the cell walls by diffusion. Thus, in general the validity of the equilibrium assumption depends on the rate of the diffusive and convective processes in relation to the rate of sorption. If, for example, the resistance to vapour transfer within the wood is very small it is the rate of sorption that will govern the overall process. Conversely, in the case of a high vapour resistance it is the transport of vapour to the sorption sites which will be determining for the overall behaviour.

In many cases the latter scenario is predominant and either of the Fickian models (4) may be applied. There are, however, also cases where the results obtained with the diffusion equation can not be made to fit the experimental data. Such measurements have been made by Wadsö [1]. These experiments, which were conducted on one-dimensional samples with half lengths of 4.8 mm to 11.4 mm, show among others things a dimensional dependence such that if the moisture transfer is to be described by (4) the diffusion coefficient must be made to vary with the length of the sample. This is illustrated in Figure 1. In Figure 1 (a) the results of two sorption experiments with samples of different length are shown. The samples were initially in equilibrium with 54% relative humidity and then subjected to a step increase to 75% RH. In the figure the relative weight increase is shown as a function of the square root of time divided by the respective sample lengths. If diffusion was the dominant mechanism involved the two experimental curves should be superimposed on each other, *even in the case of a moisture dependent diffusion coefficient*, see e.g. Crank [2]. As is clearly seen this is not the case. If, nevertheless, diffusion is assumed valid this would imply a sample length dependent diffusion coefficient, which is clearly unacceptable from a physical point of view.

In Figure 1 (b) the results of the same type of experiment is shown, now for a step increase in relative humidity from 75% to 84% and, as can be seen, the situation becomes even more extreme in this case. Apart from the suggestion that the diffusion coefficient should be moisture dependent, the most commonly mentioned cause of the discrepancies is probably that there could be a finite surface resistance at

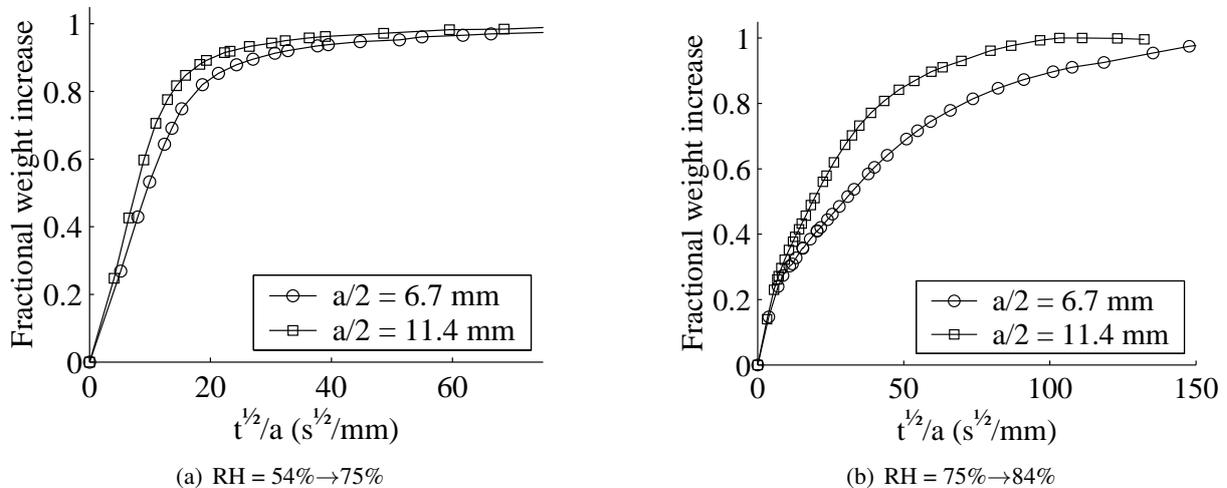


Figure 1: Failure of Fickian models by non-Fickian sample length dependence.

the ends of the sample. In general this is of course a valid point. However, the air velocity used by Wadsö was 3 m/s which by Rosen [3] has been shown experimentally to be close to the upper limit at which surface resistance has any effect. Furthermore, in a series of experiments conducted by Christensen [4] the atmospheric air was evacuated from the sorption chamber such that the samples were subjected to an environment of pure vapour. Under these conditions surface resistance can be assumed to be very close to zero, but still the results produced showed significant deviation from what one would expect on the basis of a diffusion model.

In addition to the obvious discrepancies involved when considering samples of different lengths, another and more fundamental concern is that the sorption curves produced experimentally look very different from what would be expected from Fickian diffusion. This is illustrated in Figure 2. In Figure 2 (a) the sorption curve is shown for a sample of half length equal to 11.4 mm. The sample was subjected to a step change in relative humidity from 75% RH to 84% RH. As can be seen the sorption curve displays an abrupt change in slope very early on around a fractional weight increase of  $E = 0.2$ . This is very uncharacteristic of Fickian process, again, even if the diffusivity varies with moisture content. Such Fickian processes are shown in Figure 2 (b) where the results of three different simulations with different moisture dependent diffusion coefficients were used. First a constant diffusion coefficient was used after which two simulations with exponentially increasing and decreasing coefficients were performed. In these nonlinear computations the coefficients were varied by a factor of 3 (even though this is much more than can be justified within the relatively small sorption step of 75%–84% RH). As can be seen these curves differ qualitatively only slightly from the results obtained by a constant diffusivity: up to approximately  $E = 0.6$  the slope of all three curves are approximately linear, after which the sorption rates decrease in a smooth manner.

Although this demonstration does not constitute a mathematical proof of the impossibility of sorption being a Fickian process, it does illustrate the difficulties involved with fitting experimental results to a Fickian model.

In Wadsö [5] different alternative models for predicting the above mentioned sorption response are reviewed. It is, however, concluded that none of the models are able to capture all of the effects which have been observed experimentally. We believe this in part be due to the fact that the resulting anomalous sorption behaviour is a result of anomalies on different levels. If the bound water–water vapour equilibrium

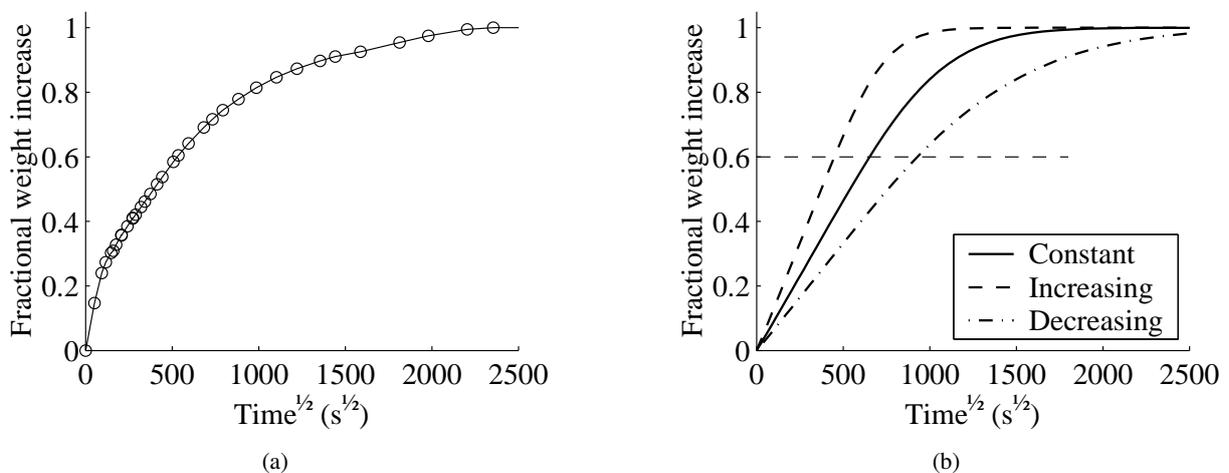


Figure 2: Failure of Fickian models. Experimental (a) and theoretical (b) sorption curves.

assumption is abandoned it is obvious that the overall behaviour will be influenced by the rate of vapour transfer to the rate of sorption. If vapour transfer is a faster process than sorption then the length of the sample will naturally influence the results in a way which is not predicted by a simple global diffusion equation. However, on the cell wall level a number of other anomalies have been observed. Christensen [4] performed adsorption measurements on single cell walls and found that large steps in relative humidity gave faster sorption rates than did smaller steps in a way which was inconsistent with what a diffusion model would predict. Furthermore, the sorption responses for cell walls of different thickness were almost identical indicating that diffusion is not the governing mechanism for cell wall sorption. Similar conclusions were drawn in [6, 7, 8, 9].

In the following, both the effects on the cell wall level and the effect of separating the water vapour from the bound water are considered. The result is a non-equilibrium Fickian model, that is, a model where the vapour pressure is not necessarily in equilibrium with the bound water content at all times, but where Fick's law is used throughout to describe diffusive transfer of both bound water within the cell walls and water vapour and air in the lumens.

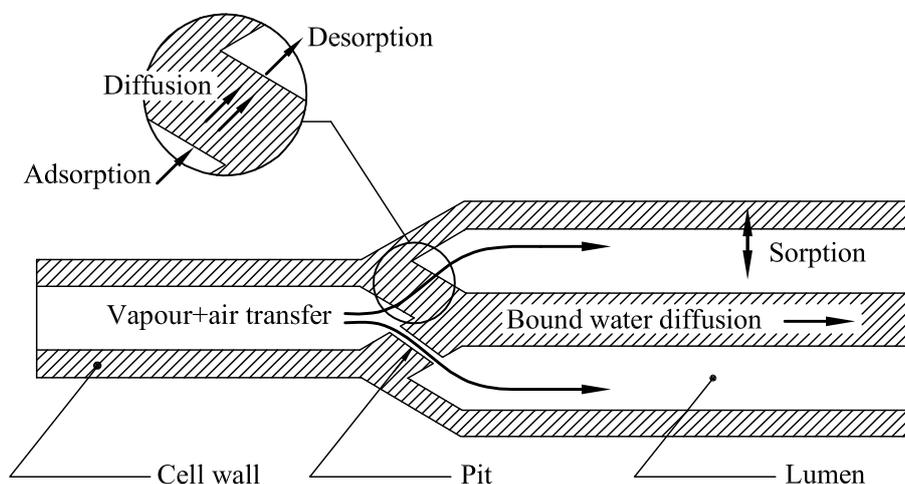


Figure 3: Moisture transfer model.

### 3 Non-equilibrium Fickian model

With the considerations of the previous section in mind a model has been formulated where the transfer of water vapour is considered independently from the transfer of bound water in the cell walls, see Figure 3. The cell wall moisture content is linked to the vapour pressure in the lumens by a term equivalent to that describing the transfer of vapour from a wet surface. Similar models have previously been formulated by Cunningham [10], Salin [11], and Absetz and Koponen [12].

The model presented here refers only to the one-dimensional isothermal case. However, inclusion of additional phases such as free water and dry air is straight forward, as is the extension to two and three spatial dimensions.

### 3.1 Bound water

The flow of bound water in the cell walls is assumed to be a diffusive process, Siau [13], governed by the following equation

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x} \left( \mathcal{D}_w \frac{\partial w}{\partial x} \right) + \dot{m} \quad (5)$$

where  $w$  is the mass of water per unit volume of gross wood ( $\text{kg/m}^3$ ),  $\mathcal{D}_w$  is the corresponding diffusion coefficient. The sorption term  $\dot{m}$  accounts for the interchange between bound water and water vapor, see Figure 3. This quantity will be positive in adsorption.

That the transfer of bound water within the cell walls is a diffusive process has been rendered probable by Stamm [11] who measured longitudinal bound water diffusion of *Picea Sitchensis* cell wall substance. Although several discrepancies have been reported, such as a difference between steady state and transient measurements, different values in adsorption and desorption and a possible influence of moisture induced stresses, Comstock [12], we shall make the assumption of the bound water transfer being a diffusive process with the diffusion coefficient depending solely on the moisture content and temperature.

### 3.2 Water vapour

The conservation equation for water vapour is given by

$$\varphi \frac{\partial \rho_v}{\partial t} = \frac{\partial j}{\partial x} - \dot{m} \quad (6)$$

where  $\rho_v$  is the vapour concentration,  $\varphi$  the porosity and  $j$  the flux. Since any bound water released from the cell walls will appear as water vapour, the sorption term  $\dot{m}$  is again included.

Using Fick's law the flux of vapour is given by

$$j = -\rho_g \mathcal{D}_{va}^{\text{eff}} \frac{d}{dx} \left( \frac{\rho_v}{\rho_g} \right) \quad (7)$$

where  $\rho_g$  is the concentration of total gas, i.e. water vapour and dry atmospheric air, and  $\mathcal{D}_{va}^{\text{eff}}$  is the effective vapour diffusivity which can be related to the diffusivity of water vapour in stall air as

$$\mathcal{D}_{va}^{\text{eff}} = \xi \mathcal{D}_{va}, \quad 0 \leq \xi \leq 1 \quad (8)$$

where the reduction factor  $\xi$  accounts for the resistance within the wood stemming from its porous structure. For  $\mathcal{D}_{va}$  several empirical expressions are available, e.g. Schirmer [14],

$$\mathcal{D}_{va} = 2.31 \times 10^{-5} \frac{p_a}{p_a + p_v} \left( \frac{T}{273.16} \right)^{1.81} \quad (9)$$

where  $p_a$  is the air pressure, in this case the atmospheric pressure, and  $T$  the absolute temperature.

If the concentration of vapour is much smaller than the concentration of total gas as is the case under moderate temperatures, Fick's law (7) reduces to the well-known form

$$j = -\mathcal{D}_{va}^{\text{eff}} \frac{d\rho_v}{dx} \quad (10)$$

By combining (6) and (10) and assuming isothermal conditions the governing equation for vapour transfer can be written in terms of pressure as

$$\varphi \frac{\partial p_v}{\partial t} = \frac{\partial}{\partial x} \left( \mathcal{D}_{va}^{\text{eff}} \frac{\partial p_v}{\partial x} \right) - \dot{m} \quad (11)$$

### 3.3 Cell wall sorption

As already mentioned the coupling between the bound water and the water vapour is assumed to follow a type of surface mass transfer relation. From the mass transfer of vapour from a saturated surface the following relation is known [15]

$$\dot{m} = h(p_v - p_w) \quad (12)$$

where  $p_w$  is the vapour pressure at the saturated surface,  $p_v$  is the vapour pressure in the surrounding air and  $h$  is the mass transfer coefficient. For the case of transfer between the lumens and the cell walls an analogous relation is assumed. In the works of Cunningham [10], Salin [11], and Absetz and Koponen [12],  $h$  was assumed constant within the RH-step in question. The assumption of a constant  $h$ , however, has some consequences which are in conflict with the findings of Christensen [4], who listed three major points:

1. For steps of identical magnitude in MC, e.g. 5% MC to 10% MC and 12% MC to 17% MC, the sorption rates were lower for steps in the higher MC-range.
2. For steps of different magnitude but with the same final MC, e.g. 5% MC to 10% MC and 8% MC to 10% MC, the sorption rates were lower for the smaller steps.
3. When starting from a completely dry sample the effect of step size was cancelled, such that a step from 0% MC to 5% gave the same qualitative response as a step from 0% MC to 10% MC.

These statements are also valid if RH is substituted for MC, i.e. the shape of the sorption isotherm does not help to explain the anomalies.

The first of the above points can be accommodated by making  $h$  depend on the moisture content, and assuming a constant  $h$  within steps of relatively small magnitude is thus reasonable. But the effect that larger steps should result in higher sorption rates than smaller steps cannot be captured by assuming a constant value of  $h$ . To see this, consider a sorption process governed by the equation

$$\dot{m} = \frac{dm}{dt} = h_0(m_\infty - m) \quad (13)$$

where  $m_\infty$  is the target moisture content. The solution is given by

$$m = m_\infty - c e^{-h_0 t} \quad (14)$$

where  $c$  is a constant of integration determined by the initial moisture content  $m_0$ . The relative moisture uptake is given by

$$E = \frac{m - m_0}{m_\infty - m_0} = 1 - \frac{c e^{-h_0 t}}{m_\infty - m} = 1 - e^{-h_0 t} \quad (15)$$

from which it is clearly seen that the step size effect cannot be modeled using a constant value of  $h$ .

A possible interpretation of the step size effect is that close to equilibrium there is an additional resistance to moisture uptake. This is the possibility explored in the following. As a measure of the proximity to equilibrium some function of the ratio of the actual moisture content to the target moisture content may be used. Thus, one possibility of including the increased resistance close to equilibrium would be

$$\frac{dm}{dt} = h(m_\infty - m) \quad \text{in adsorption } (m_\infty > m) \quad (16)$$

where

$$h = \begin{cases} h_0 (1 - m/m_\infty) & \text{in adsorption } (m_\infty > m) \\ h_0 (1 - m_\infty/m) & \text{in desorption } (m_\infty < m) \end{cases} \quad (17)$$

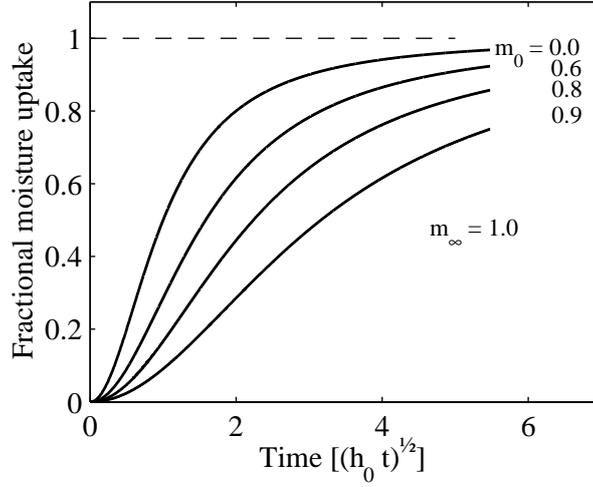


Figure 4: Sorption curves for steps of different magnitude.

and  $h_0$  is a constant. Considering the case of adsorption the solution to (16) is

$$m = \frac{h_0 t (m_\infty - m_0) m_\infty + m_0 m_\infty}{h_0 t (m_\infty - m_0) + m_\infty} \quad (18)$$

or in terms of fractional moisture uptake

$$E = \frac{(1 - m_0/m_\infty) h_0 t}{1 + (1 - m_0/m_\infty) h_0 t} \quad (19)$$

Clearly, the closer  $m_0$  is to  $m_\infty$  the slower the sorption will be. This is illustrated in Figure 4. More interestingly, however, is that when  $m_0 = 0$ , i.e. when starting from a completely dry sample, the fractional weight increase reduces to

$$E = \frac{h_0 t}{1 + h_0 t} \quad (20)$$

which is independent of the final moisture content and thereby the step size. This will generally be the case for all relations of the type

$$\frac{dm}{dt} = f(m/m_\infty) (m_\infty - m) \quad (21)$$

and thus, using  $m/m_\infty$  as a measure of the proximity to equilibrium has the obvious advantage that the observed behaviour of the canceling of step size effects when starting from completely dry conditions is included directly in the expression for  $h$ .

### 3.3.1 Relation of adsorption to swelling

In the above, the equilibrium proximity measure was introduced on the grounds of mathematical arguments. There are, however, also indications that this variable has a deeper physical significance. In the works of Christensen, and later also by Skaar et al. [16], it was argued that the only plausible explanation for the behaviour was to be found in the swelling which accompanies adsorption. That is, as the wood takes up moisture it swells which, until a stress relaxation has taken place, slows down the sorption of additional water molecules. In analogy with the osmotic pressure equation, Katz [17] originally proposed

that the maximum swelling pressure exerted by an elastic gel when the surrounding vapour pressure is raised from some value  $p_0$  to the saturation vapour pressure of the gel  $p_{\text{sat}}$  would be

$$\Pi = -\frac{\rho_w RT}{M_w} \ln \left( \frac{p_0}{p_{\text{sat}}} \right) \quad (22)$$

where  $\rho_w$  is the density of water and  $M_w$  the molecular weight. Later Barkas [18] extended this equation to be valid for any pair of vapour pressures  $p_i$  and  $p_f$

$$\Pi = -\frac{\rho_w RT}{M_w} \ln \left( \frac{p_i}{p_f} \right) \quad (23)$$

where subscripts i and f indicate the initial and final states respectively. Christensen [4] further explored experimentally the possibility of a relation between sorption and swelling and found that the half-time to sorption was approximately inversely proportional to  $\ln(p_i/p_f)$ , i.e.

$$\sqrt{t_{0.5}} \simeq \frac{a}{-\ln \left( \frac{p_i}{p_f} \right)} \quad (24)$$

where  $a$  is a constant. This result was interpreted such that the higher potential swelling pressure available the faster the relaxation, and thereby the sorption, will be.

As also admitted by Christensen, the choice of using the half-time to sorption is somewhat arbitrary and not particularly representative of the whole sorption process. However, the results do indicate that the variable  $\ln(p_i/p_f)$  could be of vital importance in describing the sorption process.

### 3.3.2 Application to wood

In the particular case of wood, a similar expression may be used. The equilibrium proximity measure can be taken as the ratio between the equilibrium vapour pressure  $p_w(w)$  corresponding to a given moisture content  $w$  as defined by the sorption isotherm and the actual vapour pressure  $p_v$ . Thus, the term  $\dot{m}$  in (5) has the following principal appearance

$$\dot{m} = h \left( \frac{p_w}{p_v}, w, \frac{\partial w}{\partial t}, T, \dots \right) (p_w - p_v) \quad (25)$$

where the influence of the absolute magnitude of the moisture content and temperature have been included. Also, the expressions for  $h$  should be different in adsorption and desorption as already discussed. Concerning the expression for  $h$  in adsorption it can be deduced from the results published by Christensen [4] and Wadsö [1] the  $h$  should be relatively large in the beginning of the sorption process, i.e. when far from equilibrium. This is followed by a rapid decrease as equilibrium is approached, where the point at which  $h$  begins to decrease abruptly is determined by the absolute moisture content. An analytical expression able to describe these characteristics is given by

$$h = c_1 \exp \left( -c_2 \left( \frac{p_w}{p_v} \right)^{c_3} \right) + c_4 \quad (26)$$

Whereas this expression contains four parameters which may be adjusted independently we have found that only the parameter  $c_2$  needs to be made dependent on the moisture content in order to fit the experimental results of Wadsö [1] satisfactorily. By varying  $c_2$  a family of curves as shown in Figure 5 is obtained.

As indicated in the figure the maximum value of  $h$  is approximately  $h = 2 \times 10^{-6} \text{ kg m}^{-3} \text{ s}^{-1} \text{ Pa}^{-1}$ .

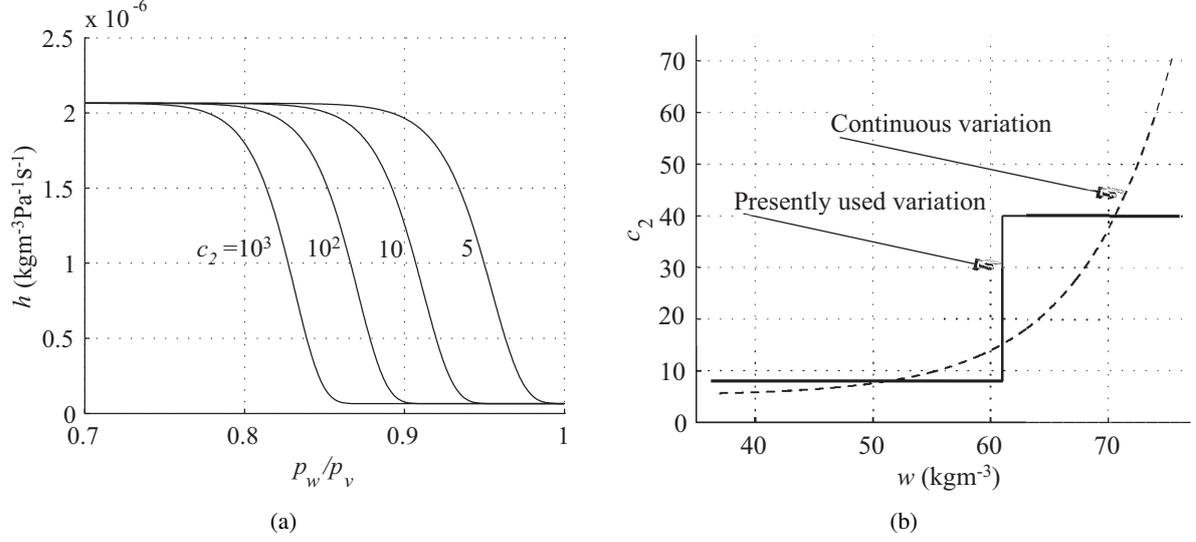


Figure 5: Variation of  $h$  with  $c_2$  and  $p_w/p_v$  (a) and variation of  $c_2$  with absolute moisture content  $w$  (b).

This value may be compared to the value of the surface evaporation coefficient  $k_p$  which has a typical value of around  $k_p = 5 \times 10^{-8} \text{ kg m}^{-3}\text{s}^{-1}\text{Pa}^{-1}$  [15]. The evaporation per unit volume of internal surface should then be at most  $\zeta k_p (p_w - p_v)$  where  $\zeta$  is the internal surface area per unit volume. For typical softwoods this may be taken as approximately  $\zeta = 10^5 \text{ m}^{-1}$  giving a maximum value of  $h$  of  $h_{\text{max}} = \zeta k_p \simeq 5 \times 10^{-3} \text{ kg m}^{-3}\text{s}^{-1}\text{Pa}^{-1}$ . This is well above the maximum value actually used, suggesting that the process of sorption is more complicated and involves other mechanism with much higher times scales than evaporation/condensation.

Since the approach to equilibrium should be slower with higher moisture contents,  $c_2$  has to increase with increasing  $w$ . As seen the curves have been constructed such that  $h$  is near constant for low values of  $p_w/p_v$ . Whether this can be experimentally justified is of course an open question. It is, however, an attractive feature to be able to recover the basic surface evaporation equation in the limit of small values of  $p_w/p_v$ .

## 4 Results

In the following a number of sorption simulations are performed and the results compared to those of Wadsö [1].

In all the simulations we use  $c_1 = 2.6 \times 10^{-6} \text{ kg m}^{-3}\text{s}^{-1}\text{Pa}^{-1}$ ,  $c_3 = 50$ , and  $c_4 = 8.0 \times 10^{-8} \text{ kg m}^{-3}\text{s}^{-1}\text{Pa}^{-1}$ . The coefficient  $c_2$  should in principle increase continuously with increasing moisture content in a manner similar to what is shown in Figure 5 (b). However, at this point there is not sufficient experimental data available to establish such a curve and we have therefore chosen to keep  $c_2$  constant within the two moisture ranges considered. In the first series of experiments the relative humidity is changed from 54% to 75%, whereas in the second series it is varied from 75% to 84%. The corresponding values of  $c_2$  that have been used are  $c_2 = 8.0$  and  $c_2 = 40.0$  respectively.

Also the water vapour diffusion coefficients are kept constant within each MC-range. In Table 2 the values used in the simulations are compared to values found by Siau [13] on the basis of a geometrical model of the cellular structure of a typical softwood. The latter values have been converted into equivalent diffusion coefficients with vapour pressure as potential. As can be seen, the values used in the simulations are in

all cases within the ranges determined by Siau [13]. In the model of Siau the resistance to vapour flow

RH (%)	Transverse		Longitudinal	
	$\xi$ (Siau [13])	$\xi$ (Present)	$\xi$ (Siau [13])	$\xi$ (Present)
54–75	156–56	130	2.8–1.7	1.7
75–84	56–28	30	1.7–1.5	1.7

Table 2: Values of  $\xi = \mathcal{D}_{va}/\mathcal{D}_{va}^{\text{eff}}$  of Siau and values used in the present simulations.

comprises cell lumens as well as cell walls. Thus, strictly speaking, the coefficients can only be regarded as apparent vapour diffusion coefficients, as in reality vapour is assumed to pass through the cell walls by being sorped on one side and subsequently released on the other side. This is, however, but one theory of the mechanism of vapour transfer. According to Dinwoodie [19] the principal pathway is through the pits of the cell walls. A diffusion coefficient independent of the moisture content should then be expected. This is not supported by the experimental results presented in the following and we have therefore chosen to adopt the model of Siau.

For the longitudinal bound water diffusion coefficients at a temperature of 23°C we use

$$\mathcal{D}_w^L = 3 \times 10^{-11} \text{ m}^2/\text{s} \text{ for RH in the range of 54\% to 75\%} \quad (27)$$

and

$$\mathcal{D}_w^L = 12 \times 10^{-11} \text{ m}^2/\text{s} \text{ for RH in the range of 75\% to 84\%} \quad (28)$$

The tangential bound water coefficient is related to that in the longitudinal direction by  $D_w^L = 3D_w^T$ . These values correspond to what is given in [20].

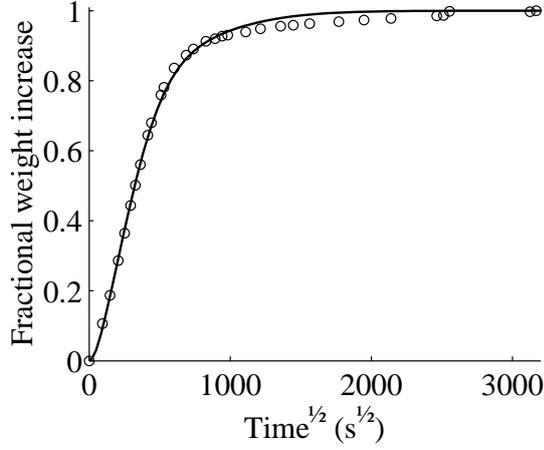
The air velocity reported by Wadsö (3m/s) is assumed to be so high that boundary effects in the layer between the sample and the surrounding air can be ignored. The computed and experimentally determined sorption curves are shown in Figures 6 and 7. As can be seen from Figures 6 and 7 all eight sets of sorption experiments are fitted quite well. For all the simulations the qualitative effect of a sudden change in sorption rate is clearly seen and thus, all in all the results suggest that it may be fruitful to consider sorption, or sorption rates, in relation to two variables, namely the moisture content and the proximity to equilibrium, where especially the last quantity is of importance. Especially, the results for transfer in the tangential direction are satisfactory as the overall response is here governed by a combination of vapour transfer and sorption, whereas for the longitudinal samples the response is governed mainly by sorption.

## 5 Future experimental work

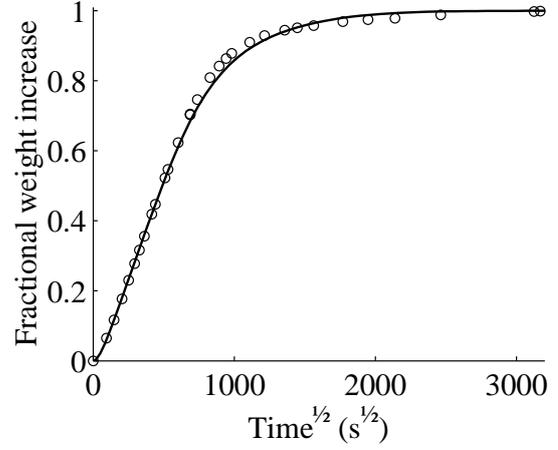
Clearly, experimental verification of the model presented here is needed. Concerning the sorption terms, the experiments should be conducted on very thin slices of wood such that the diffusion of vapour does not need to be considered. Step increments of varying magnitude in vapour pressure should be applied similarly to what was done by Christensen [4]. As in most mass transfer processes it must be expected that a boundary layer exists on the cell wall surface. To separate this resistance from the non-Fickian effects it would be necessary to conduct the experiments at different air velocities.

In practice the variation of  $h$  with  $w$  and  $p_w/p_v$  should be rather straight forward to determine, namely as

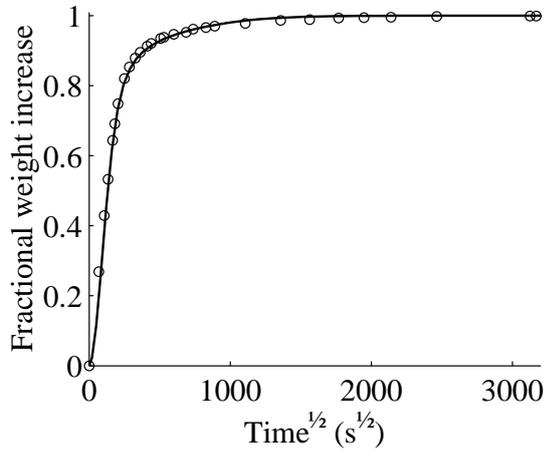
$$h(w, p_w/p_v) = \left( \frac{\partial w}{\partial t} \right) (p_v - p_w)^{-1} \quad (29)$$



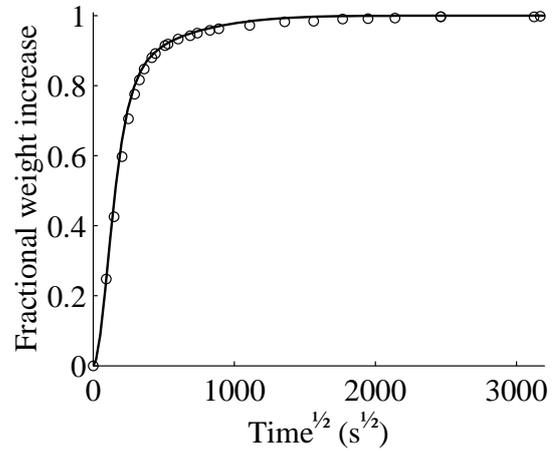
(a)  $a/2 = 4.8$  mm, tangential.



(b)  $a/2 = 8.1$  mm, tangential.



(c)  $a/2 = 6.7$  mm, longitudinal.



(d)  $a/2 = 11.4$  mm, longitudinal.

Figure 6: Computed (—) and experimental [1] sorption curves (◦) for series 1: 54% to 75% RH.

or in discrete form as

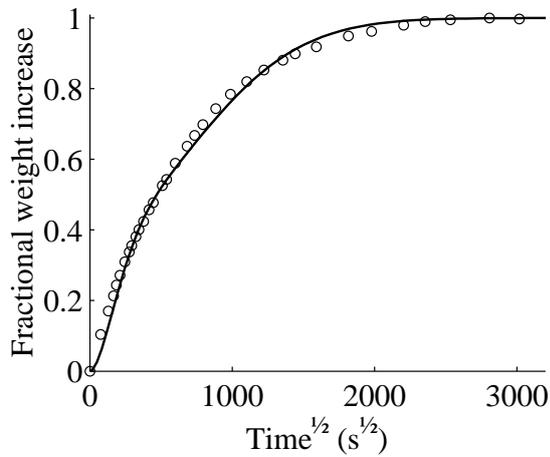
$$h(w_{n+1}, (p_w/p_v)_{n+1}) = \left( \frac{w_{n+1} - w_n}{t_{n+1} - t_n} \right) (p_{v,n+1} - p_{w,n+1})^{-1} \quad (30)$$

where  $n$  and  $n + 1$  refer to two consecutive measurement points. A complication, however, is that towards the end of the sorption process both  $p_v - p_w$  and  $\partial w/\partial t$  (or its discrete approximation) tend to zero, and thus the results may become inaccurate.

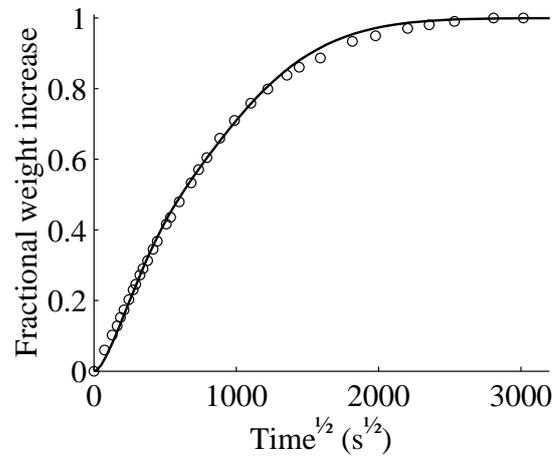
An interesting extension of the current application to wood is the application to other biological materials such as plant fibers where similar anomalous effects have recently been observed in an ongoing experimental study conducted at the Technical University of Denmark.

## 6 Conclusions

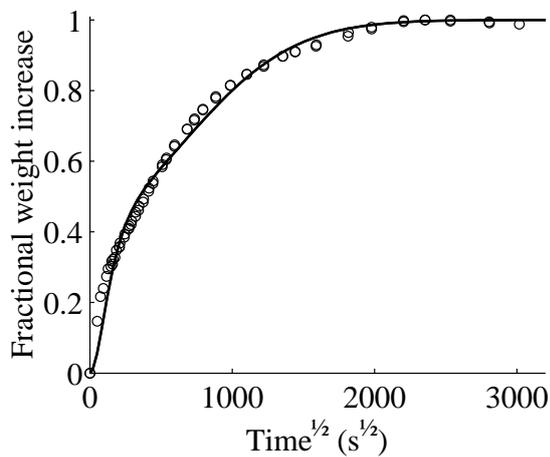
A new model for the transfer of moisture in wood in the hygroscopic range has been formulated. With this model all the common non-Fickian effects reported in the literature can be explained. This is demonstrated



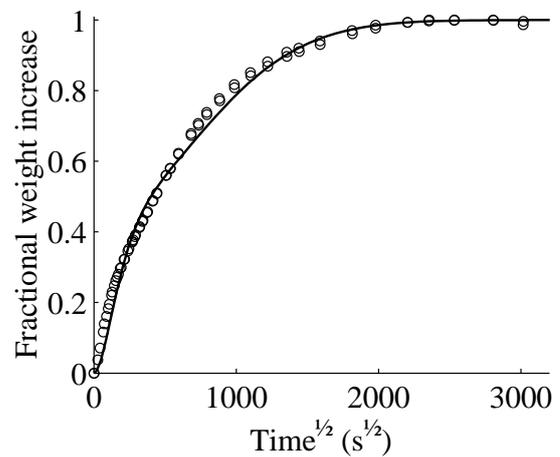
(a)  $a/2 = 4.8$  mm, tangential.



(b)  $a/2 = 8.1$  mm, tangential.



(c)  $a/2 = 6.7$  mm, longitudinal.



(d)  $a/2 = 11.4$  mm, longitudinal.

Figure 7: Computed (—) and experimental [1] sorption curves (○) for series 2: 75% to 84% RH.

by reproducing a set of eight different sorption experiments. The model has been implemented in a general finite element framework where the extension to multiple spatial dimensions is straight forward. Further experimentation is still necessary, both in order to verify the model presented here as well as to study the influences of temperature and the response in desorption in relation to the response in adsorption.

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# A model for non-Fickian moisture transfer in wood

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## ABSTRACT

A model for non-Fickian moisture transfer in wood is presented. The model considers the transfer of water vapour separate from the transfer of bound water. These two components are linked by an equation describing the sorption on the cell wall level. Hereby, a formulation capable of describing known non-Fickian effects, including the effects of step size, absolute moisture content, and sample length, is achieved. The sorption curves predicted by the model are compared with experimental results and good agreement is found.

## RÉSUMÉ

*Un modèle pour le transfert non-Fickien d'humidité dans le bois est présenté. Le modèle considère le transfert de la vapeur d'eau séparé pour le transfert de l'eau liée. Ces deux composants sont liés par une équation décrivant la sorption au niveau de mur de cellules. Par ceci, une formulation capable de décrire des effets non-Fickian connus, comprenant les effets de la taille d'étape, le contenu d'humidité absolu, et la longueur d'échantillon, est réalisée. Les courbes de sorption prévues par le modèle sont comparées aux résultats expérimentaux et une bonne concordance est trouvée.*

## 1. INTRODUCTION

The mathematical description of the transfer of moisture in wood below the fiber saturation point is often made using two basic assumptions. Firstly, that the moisture flux can be described by a Fickian type gradient law, and secondly that the bound water in the cell walls is at all times in equilibrium with the surrounding mixture of vapour and air as described by the sorption isotherm.

In one dimensional isothermal transfer the moisture flux  $j$  is given by

$$j = D_m \frac{dm}{dx} \quad (1)$$

where  $m$  is the moisture content and  $D_m$  a moisture dependent diffusion coefficient. Using the equilibrium assumption this expression can, alternatively, be formulated with the relative humidity  $r$  as potential as

$$j = D_m \frac{dm}{dx} = D_m \left( \frac{dm}{dr} \right) \frac{dr}{dx} = D_r \frac{dr}{dx} \quad (2)$$

where the diffusion coefficient with  $r$  as potential is given by

$$D_r = D_m \left( \frac{dm}{dr} \right) \quad (3)$$

By mass conservation considerations unsteady state conditions can then be described by either of the two following partial differential equations

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x} \left( D_m \frac{\partial m}{\partial x} \right) \quad \text{or} \quad c \frac{\partial r}{\partial t} = \frac{\partial}{\partial x} \left( D_r \frac{\partial r}{\partial x} \right) \quad (4)$$

where  $c = dm/dr$  is the slope of the sorption isotherm.

In the following, the shortcomings of this so-called Fickian model are discussed. An alternative model is then proposed and the capabilities of this model are demonstrated by comparison to experimental results.

## 2. FAILURE OF FICKIAN MODELS

As already discussed the Fickian models rely upon two basic assumptions, namely that the transfer of moisture is governed by a Fickian type gradient law and that within the wood there exists an equilibrium state such that the moisture content is at all times a unique function of the corresponding relative humidity as given by the sorption isotherm.

The first assumption that the flux of some quantity can be taken as being proportional to the gradient of this quantity by some scalar  $D$  is probably reasonable, at least as a first approximation and especially when dealing with a relatively slow transfer under isothermal conditions. However, the second assumption that there is instantaneous equilibrium between the bound water and the water vapour at all times is harder to justify.

Considering in more detail the mechanisms of moisture transfer in the hygroscopic range this must consist of a diffusive, and possibly convective, transfer of water vapour in the cellular structure with simultaneous sorption in the cell walls. In addition, bound water may be transferred within the cell walls by diffusion. Thus, in general the validity of the equilibrium assumption depends on the rate of the diffusive and convective processes in relation to the rate of sorption. If, for example, the resistance to vapour transfer within the wood is very small it is the rate of sorption that will govern the overall process. Conversely, in the case of a high vapour resistance it is the transport of vapour to the sorption sites which will be determining for the overall behaviour.

In many cases the latter scenario is predominant and either of the Fickian models (4) may be applied. There are, however, also cases where the results obtained with the diffusion equation can not be made to fit the experimental data. Such measurements have been made by Wadsö [1]. These experiments, which were conducted on one-dimensional samples with half lengths of 4.8 mm to 11.4 mm, show among others things a dimensional dependence such that if the moisture transfer is to be described by (4) the diffusion coefficient must be made to vary with the length of the sample. This is illustrated in Fig. 1. In Fig. 1 (a) the results of two sorption experiments with samples of different length are shown. The samples were initially in equilibrium with 54% relative humidity and then subjected to a step increase to 75% RH. In the figure the relative weight increase is shown as function of the square root of time divided by the respective sample lengths. If diffusion was the dominant mechanism involved the two experimental curves should be superimposed on each other, *even in the case of a moisture dependent diffusion coefficient*, see e.g. Crank [2]. As is clearly seen this is not the case. If, nevertheless, diffusion is assumed valid this would imply a sample length dependent diffusion coefficient, which is clearly unacceptable from a physical point of view.

In Fig. 1 (b) the results of the same type of experiment is shown, now for a step increase in relative humidity from 75% to 84% and, as can be seen, the situation becomes even more extreme in this case.

Apart from the suggestion that the diffusion coefficient should be moisture dependent, the most commonly mentioned cause of the discrepancies is probably that there could be a finite surface resistance at the ends of the sample. In general this is of course a valid point. However, the air velocity used by Wadsö was 3 m/s, which by Rosen [3] has been shown experimentally to be close to the upper limit at which surface resistance has any effect. Furthermore, in a series of experiments conducted by Christensen [4] the atmospheric air was evacuated from the sorption chamber such that the samples were subjected to an

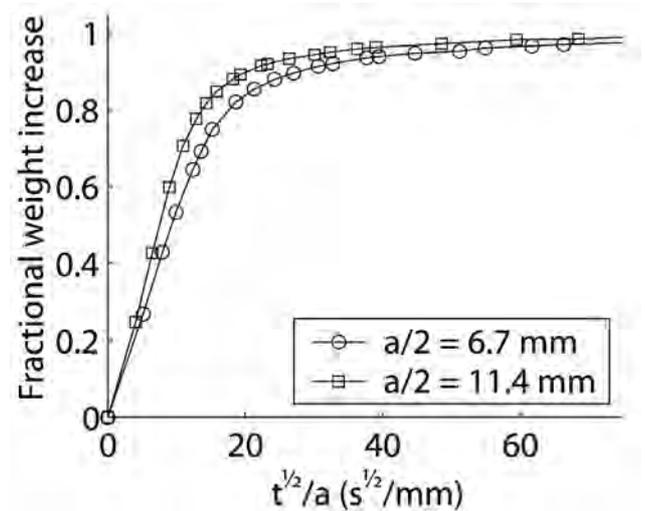


Fig. 1 (a) - Failure by non-Fickian length dependence.

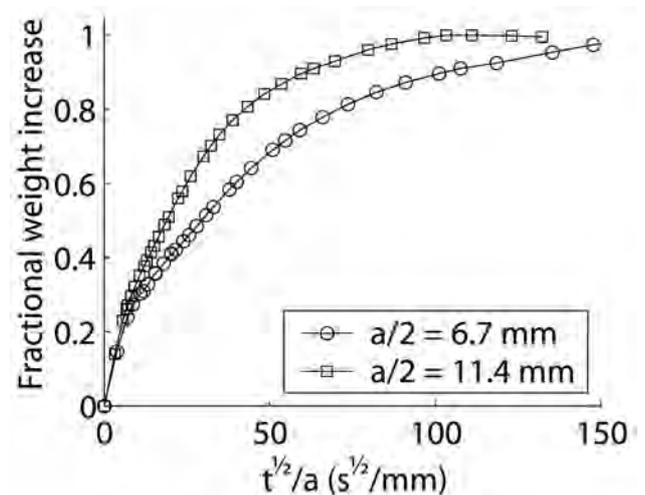


Fig. 1 (b) - Failure by non-Fickian length dependence.

environment of pure vapour. Under these conditions surface resistance can be assumed to be very close to zero, but still the results showed significant deviation from what one would expect on the basis of a diffusion model.

In addition to the obvious discrepancies involved when considering samples of different lengths, another and more fundamental concern is that the sorption curves produced experimentally look very different from what would be expected from Fickian diffusion. This is illustrated in Fig. 2. In Fig. 2 (a) the sorption curve is shown for a sample of half length equal to 11.4 mm. The sample was subjected to a step change in relative humidity from 75% RH to 84% RH. As can be seen the sorption curve displays an abrupt change in slope very early on around a fractional weight increase of  $E = 0.2$ . This is very uncharacteristic of Fickian process, again, even if the diffusivity varies with moisture content. Such Fickian processes are shown in Fig. 2 (b) where the results of three different simulations with different moisture dependent diffusion coefficients were used. First a constant diffusion coefficient was used after which two simulations with exponentially increasing and decreasing coefficients were performed. In these nonlinear computations the coefficients were varied by a factor of 3 (even though this is much more than can be justified within

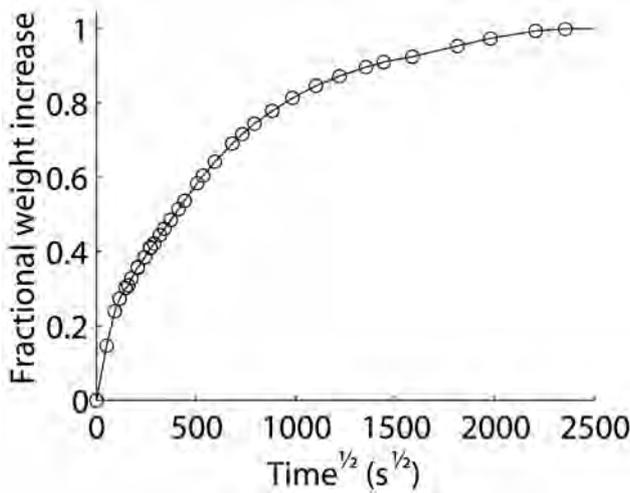


Fig. 2 (a) - Failure of Fickian models. Experimental curve.

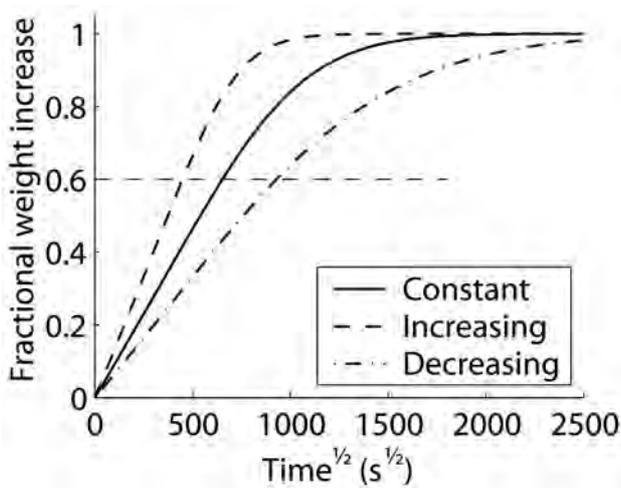


Fig. 2 (b) - Failure of Fickian models. Theoretical curves.

the relatively small sorption step of 75% to 84% RH). As can be seen these curves differ qualitatively only slightly from the results obtained by a constant diffusivity: up to approximately  $E = 0.6$  the slope of all three curves are approximately linear, after which the sorption rates decrease in a smooth manner.

Although this demonstration does not constitute a mathematical proof of the impossibility of sorption being a Fickian process, it does illustrate the difficulties involved with fitting experimental results to a Fickian model.

In Wadsö [5] different alternative models for predicting the above mentioned sorption response are reviewed. It is, however, concluded that none of the models are able to capture all of the effects which have been observed experimentally. We believe this in part be due to the fact that the resulting anomalous sorption behaviour is a result of anomalies on different levels. If the bound water-water vapour equilibrium assumption is abandoned it is obvious that the overall behaviour will be influenced by the rate of vapour transfer to the rate of sorption. If vapour transfer is a faster process than sorption then the length of the sample will naturally influence the results in a way which is not predicted by a simple global diffusion equation. However, on the cell wall level a number of other anomalies have been observed.

Christensen [4] performed adsorption measurements on single cell walls and found that large steps in relative humidity gave faster sorption rates than did smaller steps in a way, which was inconsistent with what a diffusion model would predict. Furthermore, the sorption responses for cell walls of different thickness were almost identical indicating that diffusion is not the governing mechanism for cell wall sorption. Similar conclusions were drawn in [6-9].

In the following, both the effects on the cell wall level and the effect of separating the water vapour from the bound water are considered. The result is a non-equilibrium Fickian model, that is, a model where the vapour pressure is not necessarily in equilibrium with the bound water content at all times, but where Fick's law is used throughout to describe diffusive transfer of both bound water within the cell walls and water vapour and air in the lumens.

### 3. NON-EQUILIBRIUM FICKIAN MODEL

With the considerations of the previous section in mind a model has been formulated where the transfer of water vapour is considered independently from the transfer of bound water in the cell walls, see Fig. 3. The cell wall moisture content is linked to the vapour pressure in the lumens by a term equivalent to that describing the transfer of vapour from a wet surface. Similar models have previously been formulated by Cunningham [10], Salin [11], and Absetz and Koponen [12].

The model presented here refers only to the one-dimensional isothermal case. However, inclusion of additional phases such as free water and dry air is straight forward, as is the extension to two and three spatial dimensions.

#### 3.1 Bound water

The flow of bound water in the cell walls is assumed to be a diffusive process, Siau [13], governed by the following equation

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x} \left( D_w \frac{\partial w}{\partial x} \right) + \dot{m} \quad (5)$$

where  $w$  is the mass of water per unit volume of gross wood ( $\text{kg}/\text{m}^3$ ),  $D_w$  is the corresponding diffusion coefficient. The sorption term  $\dot{m}$  accounts for the interchange between bound water and water vapour, see Fig. 3. This quantity will be positive in adsorption.

That the transfer of bound water within the cell walls is a diffusive process has been rendered probable by Stamm [11] who measured longitudinal bound water diffusion of

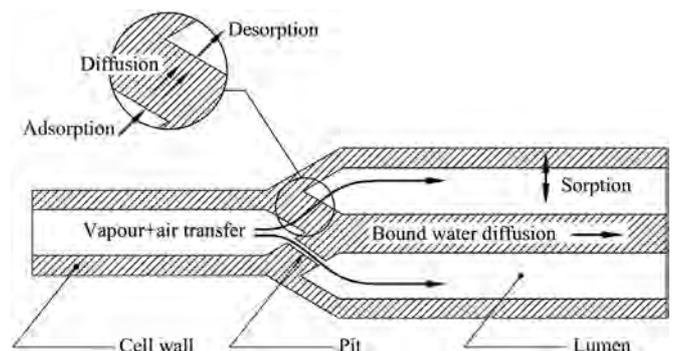


Fig. 3 - Moisture transfer model.

*Picea Sitchensis* cell wall substance. Although several discrepancies have been reported, such as a difference between steady state and transient measurements, different values in adsorption and desorption and a possible influence of moisture induced stresses, Comstock [12], we shall make the assumption of the bound water transfer being a diffusive process with the diffusion coefficient depending solely on the moisture content and temperature.

### 3.2 Water vapour

The conservation equation for water vapour is given by

$$\varphi \frac{\partial \rho_v}{\partial t} = -\frac{\partial j}{\partial x} - \dot{m} \quad (6)$$

where  $\rho_v$  is the vapour concentration,  $\varphi$  the porosity and  $j$  the flux. Since any bound water released from the cell walls will appear as water vapour, the sorption term  $\dot{m}$  is again included.

Using Fick's law the flux of vapour is given by

$$j = -\rho_g D_{va}^{eff} \frac{d}{dx} \left( \frac{\rho_v}{\rho_g} \right) \quad (7)$$

where  $\rho_g$  is the concentration of total gas, *i.e.* water vapour and dry atmospheric air, and  $D_{va}^{eff}$  is the effective vapour diffusivity which can be related to the diffusivity of water vapour in stall air as

$$D_{va}^{eff} = \tau D_{va} \quad (8)$$

where the reduction factor  $\tau$  accounts for the the resistance within the wood stemming from its porous structure. For  $D_{va}^{eff}$  several empirical expressions are available, *e.g.* Schirmer [14],

$$D_{va} = 2.31 \times 10^{-5} \frac{p_a}{p_a + p_v} \left( \frac{T}{273.16} \right)^{1.81} \quad (9)$$

where  $p_a$  is the air pressure, in this case the atmospheric pressure, and  $T$  the absolute temperature.

If the concentration of vapour is much smaller than the concentration of total gas as is the case under moderate temperatures, Fick's law (7) reduces to the well-known form

$$j = -D_{va}^{eff} \frac{d\rho_v}{dx} \quad (10)$$

By combining (6) and (10) and assuming isothermal conditions the governing equation for vapour transfer can be written in terms of pressure as

$$\varphi \frac{\partial p_v}{\partial t} = \frac{\partial}{\partial x} \left( D_{va}^{eff} \frac{\partial p_v}{\partial x} \right) - \dot{m} \quad (11)$$

### 3.3 Cell wall sorption

As already mentioned the coupling between the bound water and the water vapour is assumed to follow a type of surface mass transfer relation. From the mass transfer of

vapour from a saturated surface the following relation is known [15]

$$\dot{m} = h(p_v - p_w) \quad (12)$$

where  $p_w$  is the vapour pressure at the saturated surface,  $p_v$  is the vapour pressure in the surrounding air and  $h$  is the mass transfer coefficient. For the case of transfer between the lumens and the cell walls an analogous relation is assumed. In the works of Cunningham [10], Salin [11], and Absetz and Koponen [12],  $h$  was assumed constant within the RH-step in question. If the non-Fickian behaviour was solely the result of an internal boundary layer this would probably be reasonable, and these models are then equivalent to the model introduced by Choong and Skaar [16]. The assumption of a constant  $h$ , however, has some consequences which are in conflict with the findings of Christensen [4], who listed three major points:

1. For steps of different magnitude but with the same final MC, *e.g.* 5% MC to 10% MC and 8% MC to 10% MC, the sorption rates were lower for the smaller steps.
2. For steps of different magnitude but with the same final MC, *e.g.* 5% MC to 10% MC and 8% MC to 10% MC, the sorption rates were lower for the smaller steps.
3. When starting from a completely dry sample the effect of step size was cancelled, such that a step from 0% MC to 5% gave the same qualitative response as a step from 0% MC to 10% MC.

These statements are also valid if RH is substituted for MC, *i.e.* the shape of the sorption isotherm does not help to explain the anomalies.

The first of the above points can be accommodated by making  $h$  depend on the moisture content, and assuming a constant  $h$  within steps of relatively small magnitude is thus reasonable.

But the effect that larger steps should result in higher sorption rates than smaller steps cannot be captured by assuming a constant value of  $h$ . To see this, consider a sorption process governed by the equation

$$\dot{m} = \frac{dm}{dt} = h_0(m_\infty - m) \quad (13)$$

where  $m_\infty$  is the target moisture content. The solution is given by

$$m = m_\infty - ce^{h_0 t} \quad (14)$$

where  $c$  is a constant of integration determined by the initial moisture content  $m_0$ . The relative moisture uptake is given by

$$E = \frac{m - m_0}{m_\infty - m_0} = 1 - \frac{ce^{-h_0 t}}{m_\infty - m} = 1 - e^{-h_0 t} \quad (15)$$

from which it is clearly seen that the step size effect cannot be modeled using a constant value of  $h$ .

A possible interpretation of the step size effect is that close to equilibrium there is an additional 'resistance' to moisture uptake. This is the possibility explored in the following. As a measure of the proximity to equilibrium some function of the ratio of the actual moisture content to

the target moisture content may be used. Thus, one possibility of including the increased resistance close to equilibrium would be

$$\frac{dm}{dt} = h(m_\infty - m) \quad (16)$$

where

$$h = \begin{cases} h_0(1 - m/m_\infty) & \text{in adsorption } (m_\infty > m) \\ h_0(1 - m_\infty/m) & \text{in desorption } (m_\infty < m) \end{cases} \quad (17)$$

and  $h_0$  is a constant.

Considering the case of adsorption the solution to (16) is

$$m = \frac{h_0 t (m_\infty - m) m_\infty + m_0 m_\infty}{h_0 t (m_\infty - m) + m_\infty} \quad (18)$$

or in terms of the fractional moisture uptake

$$E = \frac{(1 - m_0/m_\infty) h_0 t}{1 + (1 - m_0/m_\infty) h_0 t} \quad (19)$$

Clearly, the closer  $m_0$  is to  $m_\infty$  the slower the sorption will be. This is illustrated in Fig. 4. More interestingly, however, is that when  $m_0 = 0$ , *i.e.* when starting from a completely dry sample, the fractional weight increase reduces to

$$E = \frac{h_0 t}{1 + h_0 t} \quad (20)$$

which is independent of the final moisture content and thereby the step size. This will generally be the case for all relations of the type

$$\frac{dm}{dt} = f(m/m_\infty)(m_\infty - m) \quad (21)$$

and thus, using  $m/m_\infty$  as a measure of the proximity to equilibrium has the obvious advantage that the observed behaviour of the canceling of step size effects when starting from completely dry conditions is included directly in the expression for  $h$ .

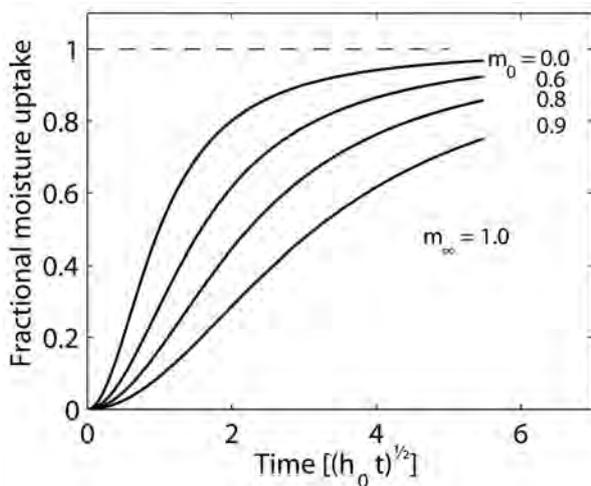


Fig. 4 - Sorption curves for steps of different magnitude.

### 3.3.1 Relation of adsorption to swelling

In the above, the equilibrium proximity measure was introduced on the grounds of mathematical arguments. There are, however, also indications that this variable has a deeper physical significance. In the works of Christensen, and later also by Skaar *et al.* [17], it was argued that the only plausible explanation for the behaviour was to be found in the swelling which accompanies adsorption. That is, as the wood takes up moisture it swells which, until a stress relaxation has taken place, slows down the sorption of additional water molecules. In analogy with the osmotic pressure equation, Katz [18] originally proposed that the maximum swelling pressure exerted by an elastic gel when the surrounding vapour pressure is raised from some value  $p_0$  to the saturation vapour pressure of the gel  $p_{sat}$  would be:

$$\Pi = -\frac{\rho_w RT}{M_w} \ln\left(\frac{p_0}{p_{sat}}\right) \quad (22)$$

where  $\rho_w$  is the density of water and  $M_w$  the molecular weight. Later Barkas [19] extended this equation to be valid for any pair of vapour pressures  $p_i$  and  $p_f$

$$\Pi = -\frac{\rho_w RT}{M_w} \ln\left(\frac{p_i}{p_f}\right) \quad (23)$$

where subscripts *i* and *f* indicate the initial and final states respectively. Christensen [4] further explored experimentally the possibility of a relation between sorption and swelling and found that the half-time to sorption was approximately inversely proportional to  $\ln(p_i/p_f)$ , *i.e.*

$$\sqrt{t_{0.5}} \approx \frac{a}{-\ln(p_i/p_f)} \quad (24)$$

where  $a$  is a constant. This result was interpreted such that the higher potential swelling pressure available the faster the relaxation, and thereby the sorption, will be.

As also admitted by Christensen, the choice of using the half-time to sorption is somewhat arbitrary and not particularly representative of the whole sorption process. However, the results do indicate that the variable  $\ln(p_i/p_f)$  could be of vital importance in describing the sorption process.

### 3.3.2 Application to wood

In the particular case of wood, a similar expression may be used. The equilibrium proximity measure can be taken as the ratio between the equilibrium vapour pressure  $p_w(w)$  corresponding to a given moisture content  $w$  as defined by the sorption isotherm and the actual vapour pressure  $p_v$ . Thus, the term  $\dot{m}$  in (5) has the following principal appearance

$$\dot{m} = h\left(\frac{p_w}{p_v}, w, \frac{\partial w}{\partial t}, T, \dots\right)(p_w - p_v) \quad (25)$$

where the influence of the absolute magnitude of the moisture content and temperature have been included. Also, the expressions for  $h$  should be different in adsorption and desorption as already discussed. Concerning the expression

for  $h$  in adsorption it can be deduced from the results published by Christensen [4] and Wadsö [1] the  $h$  should be relatively large in the beginning of the sorption process, *i.e.* when far from equilibrium. This is followed by a rapid decrease as equilibrium is approached, where the point at which  $h$  begins to decrease abruptly is determined by the absolute moisture content. An analytical expression able to describe these characteristics is given by

$$h = c_1 \exp \left[ -c_2 \left( \frac{p_w}{p_v} \right)^{c_3} \right] + c_4 \quad (26)$$

Whereas this expression contains four parameters which may be adjusted independently we have found that only the parameter  $c_2$  needs to be made dependent on the moisture content in order to fit the experimental results of Wadsö [1] satisfactorily. By varying  $c_2$  a family of curves as shown in Fig. 5 is obtained.

As indicated in the figure the maximum value of  $h$  is approximately  $h = 2 \times 10^{-6} \text{ kgm}^{-3}\text{s}^{-1}\text{Pa}^{-1}$ . This value may be compared to the value of the surface evaporation coefficient  $k_p$ , which has a typical value of around  $k_p = 5 \times 10^{-8} \text{ kgm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$  [15]. The evaporation per unit volume of internal surface should then be at most  $\zeta k_p (p_w - p_v)$  where  $\zeta$  is the internal surface area per unit volume. For typical softwoods this may be taken as approximately  $\zeta = 10^5 \text{ m}^{-1}$  giving a maximum value of  $h$  of  $h_{\max} = 5 \times 10^{-3} \text{ kgm}^{-3}\text{s}^{-1}\text{Pa}^{-1}$ . This is well above the maximum value actually used, suggesting that the process of sorption is more complicated and involves other mechanism with much higher times scales than evaporation/condensation.

Since the approach to equilibrium should be slower with higher moisture contents,  $c_2$  has to increase with increasing  $w$ . As seen the curves have been constructed such that  $h$  is near constant for low values of  $p_w = p_v$ . Whether this can be experimentally justified is of course an open question. It is, however, an attractive feature to be able to recover the basic surface evaporation equation in the limit of small values of  $p_w = p_v$ .

In the following the non-Fickian behaviour is described via the sorption term described in the above. Thus, the physical mechanisms responsible for the sorption behaviour are lumped into this one term. This includes also the boundary layer resistance in the lumens. Although this is probably oversimplified, it appears at the current time to be a satisfactory compromise. In a more complete model, however, each of the physical mechanisms contained in the sorption term should be considered separately.

#### 4. RESULTS

In the following a number of sorption simulations are performed and the results compared to those of Wadsö [1].

In all the simulations we use  $c_1 = 5 \times 10^{-3} \text{ kgm}^{-3}\text{s}^{-1}\text{Pa}^{-1}$ ,  $c_3 = 50.0$ , and  $c_4 = 8 \times 10^{-8} \text{ kgm}^{-3}\text{s}^{-1}\text{Pa}^{-1}$ . The coefficient  $c_2$  should in principle increase continuously with increasing moisture content in a manner similar to what is shown in Fig. 5 (b). However, at this point there is not sufficient experimental data available to establish such a curve and we have therefore chosen to keep  $c_2$  constant within the two

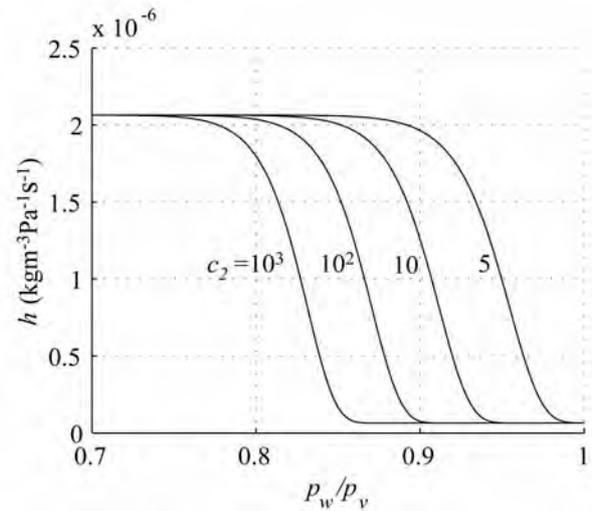


Fig. 5 (a) - Variation of  $h$  with  $c_2$  and  $p_w/p_v$ .

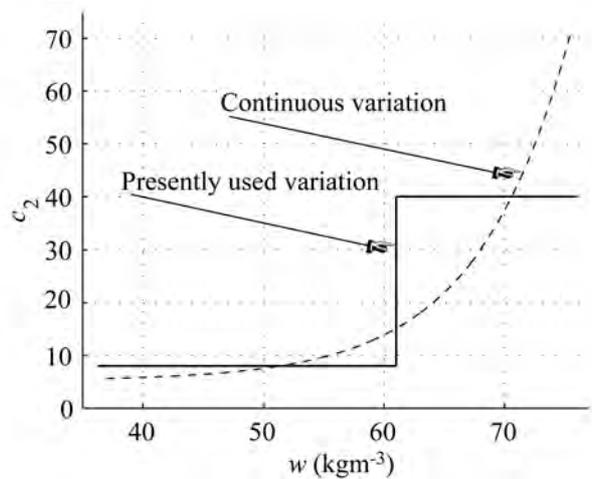


Fig. 5 (b) - Variation of  $c_2$  with absolute moisture content  $w$ .

moisture ranges considered. In the first series of experiments the relative humidity is changed from 54% to 75%, whereas in the second series it is varied from 75% to 84%. The corresponding values of  $c_2$  that have been used are  $c_2 = 8.0$  and  $c_2 = 40.0$  respectively.

Also the water vapour diffusion coefficients are kept constant within each MC-range. In Table 1 the values used in the simulations are compared to values found by Siau [13] on the basis of a geometrical model of the cellular structure of a typical softwood. The latter values have been converted into equivalent diffusion coefficients with vapour pressure as potential. As can be seen, the values used in the simulations are in all cases within the ranges determined by Siau [13].

In the model of Siau the resistance to vapour flow comprises cell lumens as well as cell walls. Thus, strictly speaking, the coefficients can only be regarded as apparent

	Trans.	Trans.	Long.	Long.
RH (%)	$\tau$ (Siau [13])	$\tau$ (Present)	$\tau$ (Siau [13])	$\tau$ (Present)
54-75	156-56	130	2.8-1.7	1.7
75-84	56-28	30	1.7-1.5	1.7

vapour diffusion coefficients, as in reality vapour is assumed to pass through the cell walls by being sorbed on one side and subsequently released on the other side. This is, however, but one theory of the mechanism of vapour transfer. According to Dinwoodie [20] the principal pathway is through the pits of the cell walls. A diffusion coefficient independent of the moisture content should then be expected. This is not supported by the experimental results presented in the following and we have therefore chosen to adopt the model of Siau.

For the longitudinal bound water diffusion coefficients at a temperature of 23°C we use

$$D_w^L = 3 \times 10^{-11} \text{ m}^2/\text{s} \text{ for } 54\% \leq \text{RH} \leq 75\% \quad (27)$$

and

$$D_w^L = 12 \times 10^{-11} \text{ m}^2/\text{s} \text{ for } 75\% < \text{RH} \leq 75\% \quad (28)$$

The tangential bound water coefficient is related to that in the longitudinal direction by  $D_w^T = 3D_w^L$ . These values correspond to what is given in [21].

The air velocity reported by Wadsö (3m/s) is assumed to be so high that boundary effects in the layer between the sample and the surrounding air can be ignored. The computed and experimentally determined sorption curves are shown in Figs. 6 and 7. As can be seen from Figs. 6 and 7 all eight sets of sorption experiments are fitted quite well. For all the simulations the qualitative effect of a sudden change in sorption rate is clearly seen and thus, all in all the results suggest that it may be fruitful to consider sorption, or sorption rates, in relation to two variables, namely the moisture content and the proximity to equilibrium, where particularly the last quantity is of importance. Especially, the results for transfer in the tangential direction are satisfactory as the overall response is here governed by a combination of vapour transfer and sorption, whereas for the longitudinal samples the response is governed mainly by sorption.

### 5. FUTURE EXPERIMENTAL WORK

Clearly, experimental verification of the model presented here is needed. Concerning the sorption terms, the experiments should be conducted on very thin slices of wood such that the diffusion of vapour does not need to be considered. Step increments of varying magnitude in vapour pressure should be applied similarly to what was done by Christensen [4].

As in most mass transfer processes it must be expected that a boundary layer exists on the cell wall surface. To separate this resistance from the non-Fickian effects it would be necessary to conduct the experiments at different air velocities.

In practice the variation of  $h$  with  $w$  and  $p_w = p_v$  should be rather straight forward to determine, namely as

$$h(w, p_w / p_v) = \left( \frac{\partial w}{\partial t} \right) (p_v - p_w)^{-1} \quad (29)$$

or in discrete form as

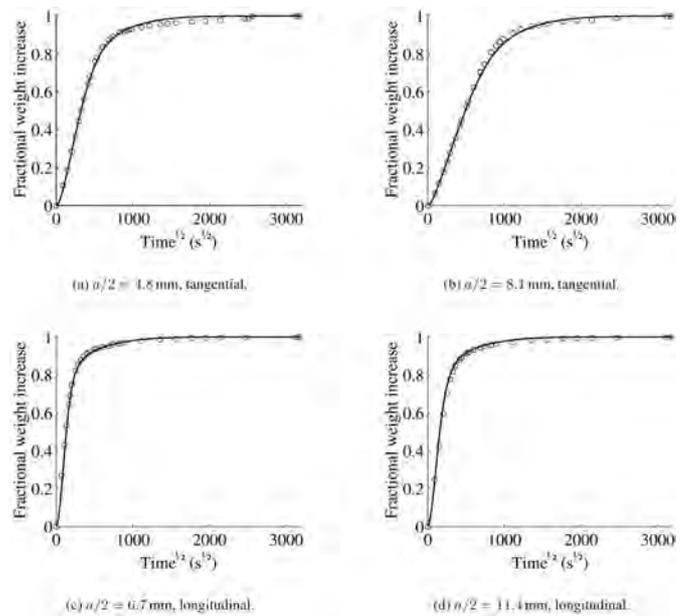


Fig. 6 - Computed and experimental sorption curves for series 1: 54-75% RH.

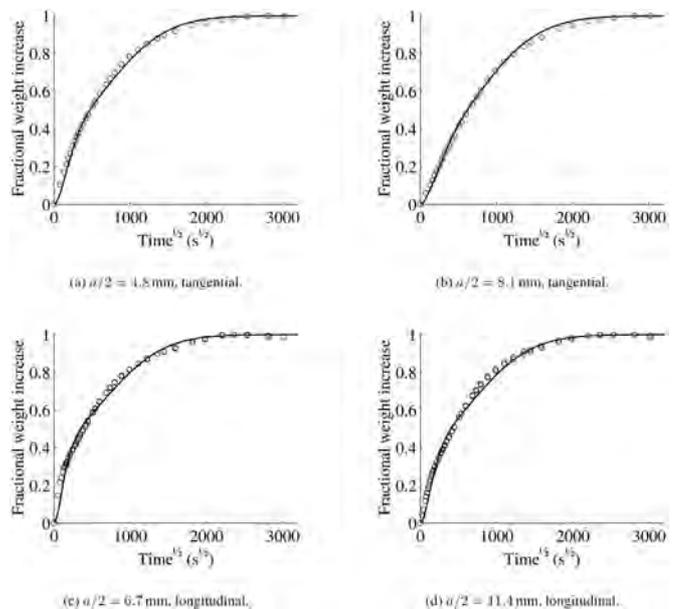


Fig. 7 - Computed and experimental sorption curves for series 2: 75-84% RH.

$$h(w_{n+1}, (p_w / p_v)_{n+1}) = \left( \frac{w_{n+1} - w_n}{t_{n+1} - t_n} \right) (p_{w,n+1} - p_{w,n+1})^{-1} \quad (30)$$

where  $n$  and  $n+1$  refer to two consecutive measurement points. A complication, however, is that towards the end of the sorption process both  $p_v - p_w$  and  $\partial w / \partial t$  (or its discrete approximation) tend to zero, and thus the results may become inaccurate.

An interesting extension of the current application to wood is the application to other biological materials such as plant fibers where similar anomalous effect have recently been observed in an ongoing experimental study conducted at the Technical University of Denmark.

## 6. CONCLUSIONS

A new model for the transfer of moisture in wood in the hygroscopic range has been formulated. With this model all the common non-Fickian effects reported in the literature can be explained. This is demonstrated by reproducing a set of eight different sorption experiments. The model has been implemented in a general finite element framework where the extension to multiple spatial dimensions is straight forward, see e.g. [22].

Further experimentation is still necessary, both in order to verify the model presented here as well as to study the influences of temperature and the response in desorption in relation to the response in adsorption.

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## NOMENCLATURE

### Roman letters

$D$	Diffusion coefficient
$E$	Fractional weight increase
$h$	Sorption constant ( $\text{kgm}^{-3}\text{s}^{-1}\text{Pa}^{-1}$ )
$j$	Flux ( $\text{kgm}^{-2}\text{s}^{-1}$ )
$m$	Moisture content (kg/kg)
$\dot{m}$	Sorption term ( $\text{kgm}^{-3}\text{s}^{-1}$ )
$p$	Pressure (Pa)
$r$	Relative humidity (RH)
$R$	Gas constant ( $8.31 \text{ Jmol}^{-1}\text{K}^{-1}$ )
$T$	Temperature (K)
$w$	Moisture content ( $\text{kgm}^{-3}$ )

### Greek letters

$\varphi$	Porosity
$\rho$	Density ( $\text{kgm}^{-3}$ )
$\zeta$	Internal area/volume ration ( $\text{m}^{-1}$ )
$\tau$	Vapour diffusivity reduction factor

### Sub- and superscripts

$a$	air
$eff$	effective
$g$	gas – vapour+air
$L$	longitudinal
$T$	tangential
$v$	vapour

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