# A MODEL TO EXPLAIN "ANOMALOUS" MOISTURE SORPTION IN WOOD UNDER STEP FUNCTION DRIVING FORCES

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## ABSTRACT

It has been hypothesized that "anomalous" transient moisture sorption in wood at high relative humidities is due to slow sorption of moisture in the cell walls. A mathematical model describing this phenomenon has been developed, which fits well the two-stage sorption (Fickian and non-Fickian) visible in experimental data and uses parameters with clear physical meaning. The values of these parameters can be derived by simple means. Thickness effects and other non-Fickian behavior are examined.

*Keywords:* Diffusion, water vapor, cell walls, adsorption, non-Fickian behavior.

## NOMENCLATURE

| | |
|---|---|
| a | proportion of moisture transfer governed by non-Fickian processes (dimensionless) |
| c | moisture concentration in the wood cavities (kg m$^{-3}$) |
| C | total moisture content in the wood cavities (kg) |
| $D_c$ | diffusion coefficient with wood cavity moisture concentration driving potential (m$^2$ sec$^{-1}$) |
| $D_\varphi$ | diffusion coefficient with driving potential $\varphi$ (units depend upon units of $\varphi$) |
| E | fraction of completed transient sorption (dimensionless) |
| h | lumped wood-cavities to cell-walls mass transfer coefficient (units depend upon units of $\varphi$) |
| k | coefficient connecting potential $\varphi$ and cell-wall moisture concentration (units depend upon units of $\varphi$) |
| l | coefficient connecting potential $\varphi$ and wood cavities moisture concentration (units depend upon units of $\varphi$) |
| L | half length (m) |
| m | total moisture concentration (cell wall plus wood cavities) (kg m$^{-3}$) |
| M | total moisture content (cell wall plus wood cavities) (kg) |
| t | time (sec) |
| $t_1$ | time constant for cavity diffusion (sec) |
| $t_2$ | time constant for cell-wall sorption (sec) |
| w | total cell-wall moisture concentration (kg m$^{-3}$) |
| W | total cell-wall moisture content (kg) |
| x | distance (m) |
| $\alpha$ | ratio of Fickian to non-Fickian time constants (dimensionless) |
| $\varphi$ | a generic potential (units depend upon the particulars of $\varphi$) |

### *Subscripts*

| | |
|---|---|
| 0 | at the initial time |
| 1 | at the final time |

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c with respect to moisture concentration of the wood cavities
w with respect to the total cell-wall moisture content
$\varphi$ with respect to potential $\varphi$

## INTRODUCTION

In a recent paper entitled "Unsteady-State Water Vapor Adsorption in Wood: An Experimental Study," Wadsö (1994) showed, with some very careful experimental work, that the adsorption of moisture in wood, subjected to relative humidity step functions, could not be explained by diffusive, or Fickian, processes alone. Other authors have also observed this effect earlier: Comstock (1963), Kelly and Hart (1970), and Skaar et al. (1970). The experimental evidence shows a component of non-Fickian behavior in wood moisture transfer, thought to be due to the slow adsorption of moisture in the cell walls (Wadsö 1994), such that there is not instantaneous equilibrium between the moisture content in the wood cavities and the surrounding cell walls. This slow sorption is thought to be due to the creation of sorption sites by molecular bond breaking or rearrangement (Skaar et al. 1970; Christensen 1960). The consequences of this hypothesis of the slow absorption of moisture in the cell walls are explored in this paper.

As well as being of interest to wood scientists and the timber drying community, this non-Fickian behavior is also of particular interest to the building physics community. In building physics, a number of mathematical models have been developed to explain the moisture performance of building structures under indoor and outdoor climate driving effects: Kohonen (1984), Kerestecioglu and Gu (1990), Yuill et al. (1990), Pedersen (1990), Burch and Thomas (1991), Cunningham (1990, 1994). None of the models cited consider non-Fickian behavior of moisture sorption in wood, but Wadsö's results show that, at higher humidities and for thinner pieces of timber, such behavior is important. It is under these very conditions that moisture problems are possible within a building structure—for example, within relatively thin sheathings towards the outside of a structure exposed to high humidities; see for example Burch and Thomas (1991).

In this paper, wood moisture transfer is modelled as a two-stage process—ordinary Fickian diffusion and a non-Fickian process of slow sorption of moisture in the cell wall. The resulting differential equations are solved for the boundary condition of a step change in the external driving potential. The nature of the solutions is examined, and some comparisons are made with Wadsö's experimental results.

Within this work, the term *transient sorption curve* describes the time plot of total moisture content in response to a step in external driving forces, while the term *equilibrium sorption curve* is used to describe the relative humidity equilibrium moisture content curve of the material at constant temperature.

## MODEL DETAILS

We will consider a length 2L of wood, essentially one-dimensional, bounded by parallel planes at $x = \pm L$, under the boundary condition of a step change of the external driving potential from $\varphi_0$ to $\varphi_1$. The potential $\varphi$ could be relative humidity, vapor pressure, moisture concentration, chemical potential, etc. The initial conditions are taken as the wood moisture content in equilibrium, both with the external potential and between the moisture content of the wood cavities and cell-wall moisture, i.e.,

$$\text{At } t = 0, \qquad \varphi_0 = \varphi_c = \varphi_w \qquad \text{independent of x.} \tag{1}$$

In this analysis it is assumed, in line with experimental conditions established by Wadsö, that external air velocities are high enough to give a large surface mass transfer coefficient, allowing surface effects to be ignored.

Most workers believe that slow sorption of moisture into the cell wall is governed by swelling pressure, the relaxation of which is determined by the rate of creation of sorption sites by molecular bond breaking or rearrangement, and by the formation of microvoids (Skaar et al. 1970; Christensen 1960).

The simplest relationship that could quantify this behavior is to assume that the rate of uptake of moisture, at least over a small driving potential range, is proportional to the local excess potential, i.e.,

$$\frac{\partial w}{\partial t} = h(\varphi_c - \varphi_w) \tag{2}$$

where $\varphi$ represents an appropriate driving potential and h is an effective mass transfer coefficient that lumps all microscopic processes such as stress relaxation and perhaps cell-wall diffusion processes, and also lumps all microscopic geometrical considerations such as cell-wall area involved in the exchange processes, at distance x from the middle of the specimen. In general, h will be dependent upon the level of the potential and temperature. It is assumed in this work that h is constant over the range of potential of interest, while the temperature effect is unimportant here as the analysis is isothermal.

Equation (2) can be rewritten as

$$\frac{\partial w}{\partial t} = h(lc - kw) \tag{3}$$

where

$$\varphi_c = lc$$

$$\varphi_w = kw \tag{4}$$

The relationships in Eq. (4) describe the equilibrium sorption functions for the potential $\varphi$ as a function of the moisture concentrations c, moisture content of the wood cavities, or w, cell-wall moisture content.

l and k will in general be functions of moisture content and perhaps of temperature.

In terms of c and w, the initial conditions, Eq. (1), can be rewritten as

$$\varphi_0 = lc_0 = kw_0 \tag{5}$$

Within the wood cavities, the standard assumption is made of moisture diffusion by potential gradient; however, conservation of moisture requires including both this diffusive term and a term for moisture transfer to the cell walls, i.e.,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D_\varphi \frac{\partial \varphi}{\partial x} + h(kw - lc) \tag{6}$$

This can be rewritten as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \frac{D_c}{l} \frac{\partial (lc)}{\partial x} + h(kw - lc) \tag{7}$$

where

$$D_c = lD_\varphi \tag{8}$$

In principle, a further diffusive term may exist for moisture movement from one cell wall to another (Yokota 1959). However, its magnitude must be small; otherwise cell-wall moisture would equilibrate quickly under conditions of a step in external driving potential, making cell-wall moisture sorption an unimportant mechanism, contrary to experimental evidence. Consequently, no term will be included in this model for cell-wall diffusion.

Equations (3) and (7) constitute a pair of coupled partial differential equations which, with the boundary and initial conditions given by Eq. (1), describe our model of moisture transfer within wood.

Key parameters in the model, viz., l, k, h, and $D_c$, are functions of moisture content and temperature. The model equations describe isothermal diffusion so that the temperature dependence of l, k, h, and $D_c$ does not affect the solution process. The mathematical approximation made is to take l, k, h, and $D_c$ as constant, independent of potential, and in particular independent of moisture concentration. The physical implication of taking l and k constant is to linearize the equilibrium sorption curve. Provided the step in external driving force is not large, these approximations are not too severe. Wadsö's published experimental data are for relatively small driving force steps of about 20% relative humidity.

Using these simplifications Eqs. (3) and (7) become

$$\frac{\partial w}{\partial t} = h(lc - kw) \tag{9}$$

$$\frac{\partial c}{\partial t} = D_c \frac{\partial^2 c}{\partial x^2} + h(kw - lc) \tag{10}$$

## MODEL SOLUTIONS

Equations (9) and (10) are now linear and in principle solvable by standard techniques. However, as they stand, solutions will be extremely complex, and consequently more progress can be made if appropriate simplifications are made.

An iterative approach to give an approximate solution is used: to begin the iteration the standard solution for c when h = 0 is taken to Eq. (10), i.e., the without cell-wall sorption case; this solution is substituted into Eq. (9) (h from this iteration onwards not necessarily zero), which is then solved for the cell-wall moisture content w; and the solution of c is reiterated by substituting this solution for w back into Eq. (10). The total moisture content M in the wood is then found by integrating the result for m = c + w through the length of the specimen, giving

$$M = M_1 - (W_1 - W_0)e^{-t/t_2} - (C_1 - C_0) \sum_{n=0}^{\infty} \frac{8e^{-b_n{}^2t/\pi^2t_1}}{b_n{}^2} \tag{11}$$

where

$$t_1 = \frac{4L^2}{\pi^2 lD_\varphi} = \frac{4L^2}{\pi^2 D_c} \tag{12}$$

$$t_2 = \frac{1}{hk} \tag{13}$$

$$b_n = (2n + 1)\pi \tag{14}$$

Mathematical details can be found in the appendix.

### PROPERTIES OF THE SOLUTION

It is in the evaluation of the diffusion coefficient by transient methods that the non-Fickian processes show most clearly. Wadsö proposes three tests for Fickian behavior, viz:

1. Transient sorption plots resulting from a step humidity change plotted against the square root of time should be linear initially, until the material has reached at least 60% of its new equilibrium content.
2. No thickness effect should show on a transient sorption versus square root of time divided by thickness plot, when the transient sorption curves of materials of different thicknesses are exposed to the same relative humidity step function.
3. Diffusion coefficients derived from transient measurements should be the same as those derived from steady-state measurements.

Each of these effects will be examined in turn.

1. *Initial linearity.*—For times small compared to $t_1$, Eq. (11) can be approximated as

$$M = M_1 - (W_1 - W_0)e^{-t/t_2} - (C_1 - C_0)\left(1 - 4\sqrt{\frac{2}{\pi^3 t_1}} + \dots\right. \tag{15}$$

using standard series expansions and approximations. (See Carslaw and Jaeger 1959 or Crank 1975.)

At $t = 0$ and $t = \infty$, since the system is in equilibrium, then using Eq. (4), we have

$$lC_0 = kW_0 \quad \text{and} \quad lC_1 = kW_1 \tag{16}$$

so that

$$\frac{W_1 - W_0}{M_1 - M_0} = \frac{1}{(W_1 + C_1 - W_0 - C_0)/(W_1 - W_0)} = \frac{1}{1 + k/l} \tag{17}$$

and

$$\frac{C_1 - C_0}{M_1 - M_0} = \frac{1}{(W_1 + C_1 - W_0 - C_0)/(C_1 - C_0)} = \frac{1}{1 + l/k} \tag{18}$$

Therefore, Eq. (15) becomes

$$\begin{aligned} E = \frac{M - M_0}{M_1 - M_0} &\cong 1 - \frac{W_1 - W_0}{M_1 - M_0}e^{-t/t_2} - \frac{C_1 - C_0}{M_1 - M_0}\left(1 - 4\sqrt{\frac{t}{\pi^3 t_1}}\right) \\ &= 1 - \frac{1}{1 + k/l}e^{-t/t_2} - \frac{1}{1 + l/k}\left(1 - 4\sqrt{\frac{t}{\pi^3 t_1}}\right) \quad t \ll t_1, t_2 \end{aligned} \tag{19}$$

Differentiating Eq. (19) with respect to $t^{1/2}$ gives

$$\frac{dE}{dt^{1/2}} = \frac{4}{(1 + l/k)}\sqrt{\frac{1}{\pi^3 t_1}} + \frac{2}{(1 + k/l)}\frac{\sqrt{t}}{t_2}e^{-t/t_2} \quad t \ll t_1, t_2 \tag{20}$$

When $t = 0$, Eq. (20) reduces to the standard equation used to evaluate the diffusion coefficient by measurement of the slope of the transient sorption curve plotted against $t^{1/2}$ (see Crank 1975), except for a factor $1/(1 + l/k)$, i.e.,

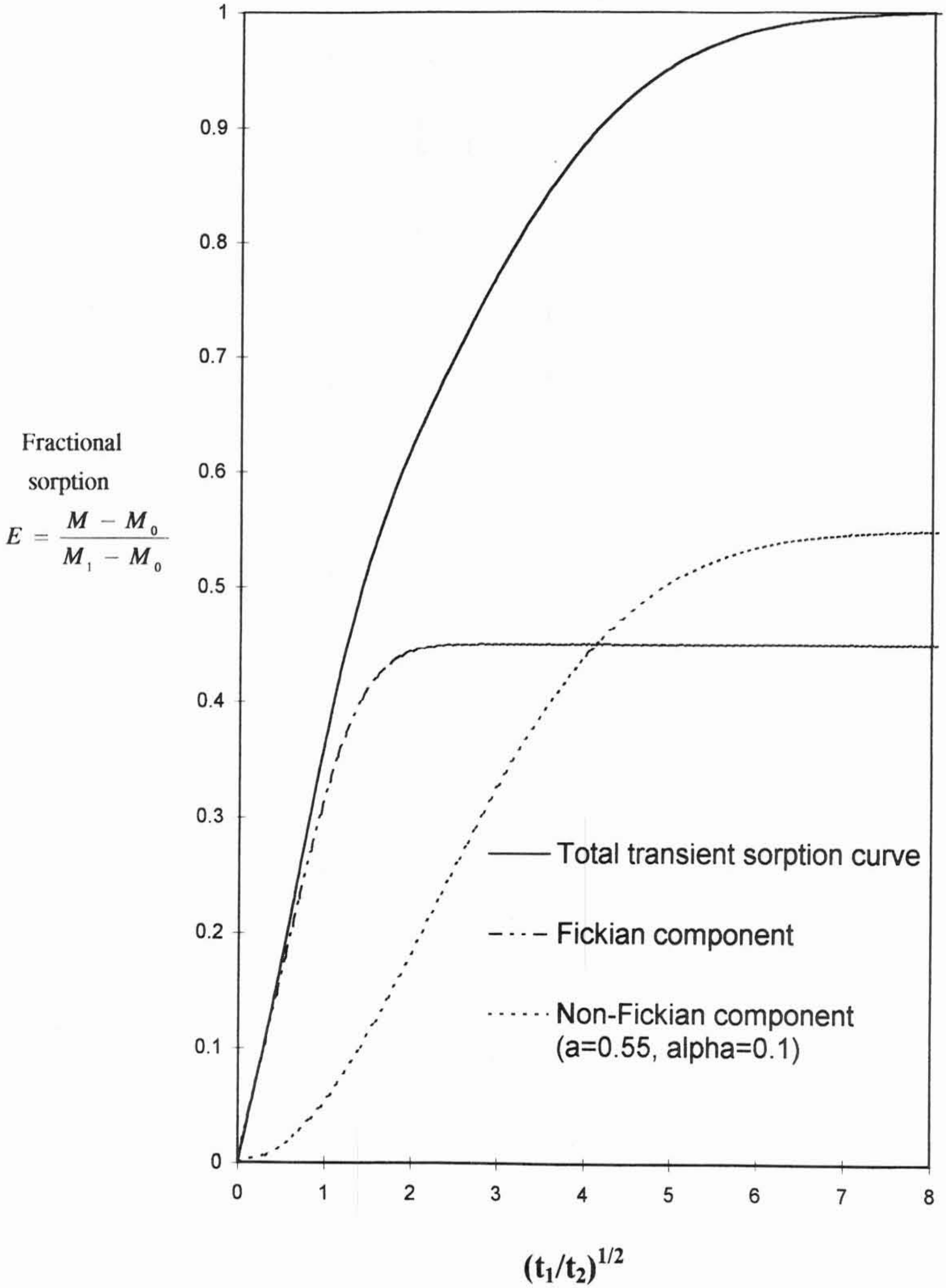

FIG. 1. Simulated transient sorption curve, showing Fickian and non-Fickian components. In this case the non-Fickian component represents 0.55 of the total moisture content (a = 0.55), and the ratio of the Fickian to non-Fickian time constants is 0.1 ($\alpha = t_1/t_2 = 0.1$).

$$\frac{dE}{dt^{1/2}} = \frac{1}{1 + l/k} \sqrt{\frac{4lD_\varphi}{\pi L^2}} = \frac{1}{1 + l/k} \sqrt{\frac{4D_c}{\pi L^2}} \tag{21}$$

However, in the case of $t_1 < t \ll t_2$ the terms due to diffusion have settled nearly to steady-state (Fig. 1), leaving the sorption of cell-wall moisture still in a transient state. Equation (19) becomes

$$E = 1 - \frac{1}{1 + k/l} e^{-t/t_2} \tag{22}$$

and this case

$$\frac{dE}{dt^{1/2}} = \frac{2}{1 + k/l} \frac{\sqrt{t}}{t_2} e^{-t/t_2} \tag{23}$$

This represents the second slope in the transient sorption curve observed by Wadsö and others.

Wadsö, in examining these two moisture transfer processes, separates the non-Fickian cell-wall sorption from the first fast Fickian sorption by using a, the fraction of the sorption governed by the slow non-Fickian cell-wall sorption mechanism. a is closely related to the coefficients l and k used here that govern the potential/moisture concentration equilibrium sorption relationships. A straightforward analysis considering the initial slope of the transient moisture sorption curves yields the required relationship, viz:

$$l/k = \frac{a}{1 - a} \tag{24}$$

Figure 1 illustrates how the Fickian and non-Fickian processes add together to give the overall transient sorption curve, while Fig. 2 shows the total transient sorption curve with different non-Fickian time constants, $t_2$ as measured by the ratio $\alpha = t_1/t_2$.

In this work all relaxation processes were lumped into one time constant; it is, however, feasible that more than one relaxation process exists. In the absence of experimental evidence as to the nature of these mechanisms, it would be premature to include these in the mathematical model.

2. *Thickness effects.*—Equation (20) can be re-expressed as

$$\frac{LdE}{dt^{1/2}} = \frac{1}{(1 + l/k)} \sqrt{\frac{4D_c}{\pi}} + \frac{1}{2(1 + k/l)} \frac{\pi^2 \alpha D_c \sqrt{t}}{L} e^{-t/t_2} \quad t \ll t_1, t_2 \tag{25}$$

This slope $LdE/dt^{1/2}$ is seen to fall into two terms, one thickness independent, due to Fickian sorption, and one thickness dependent, due to cell-wall sorption. Only if L is large will all transient sorption curves coincide when plotted against the square root of time divided by the thickness of the sample.

Note that, when plotted against time only, Fickian processes show a thickness effect and the non-Fickian relaxation processes do not, since, from Eq. (19)

$$\frac{dE}{dt} = \frac{1}{(1 + l/k)L} \sqrt{\frac{D_c}{\pi t}} + \frac{hk}{(1 + k/l)} e^{-t/t_2} \quad t \ll t_1, t_2 \tag{26}$$

3. *Transient and steady-state values.*—Values of the diffusion coefficient calculated by the standard formula

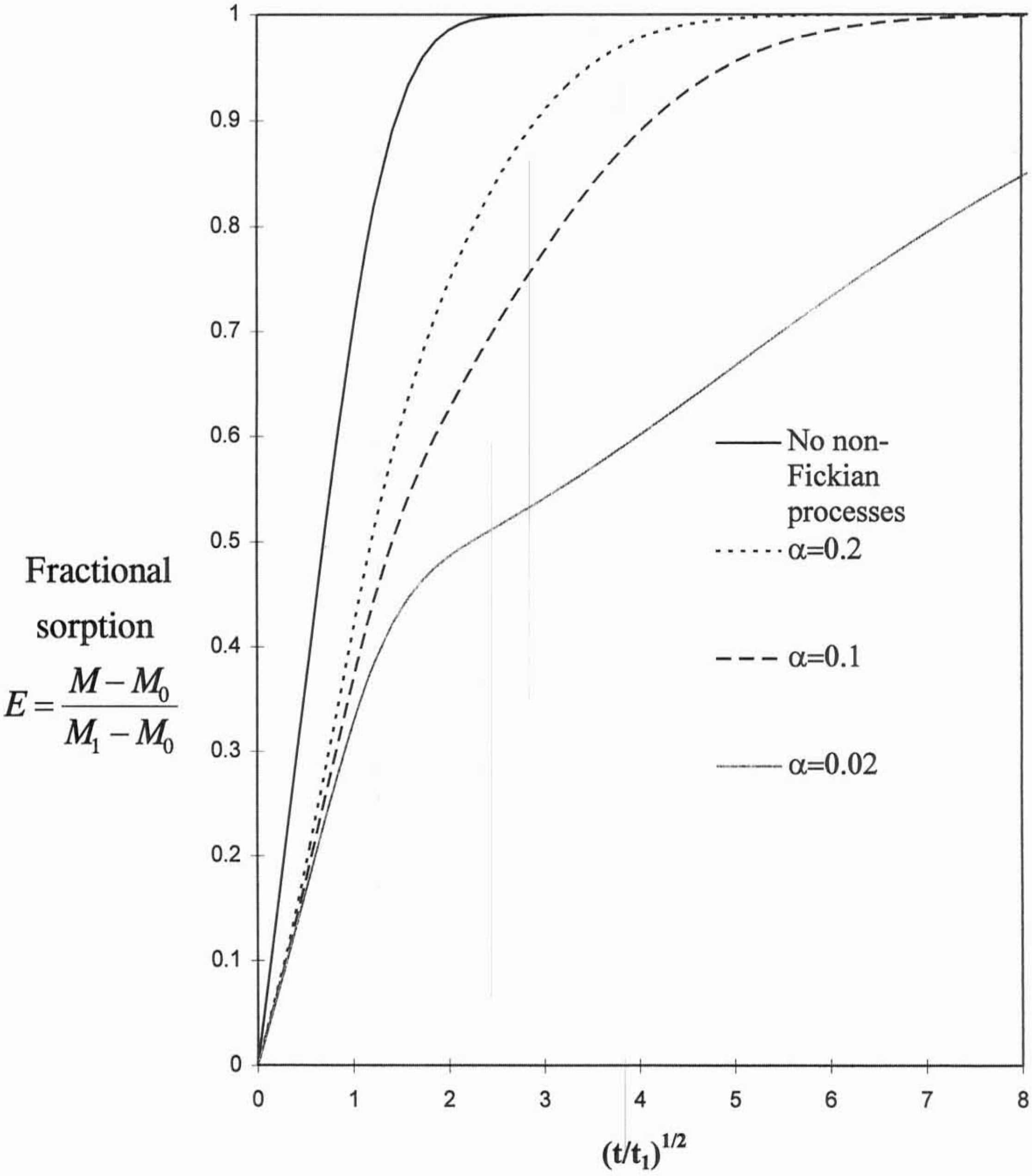

FIG. 2. Simulated transient sorption curves with different sized non-Fickian to Fickian time constant ratios, $t_1/t_2$. In this case the non-Fickian component represents 0.55 of the total moisture content (a = 0.55).

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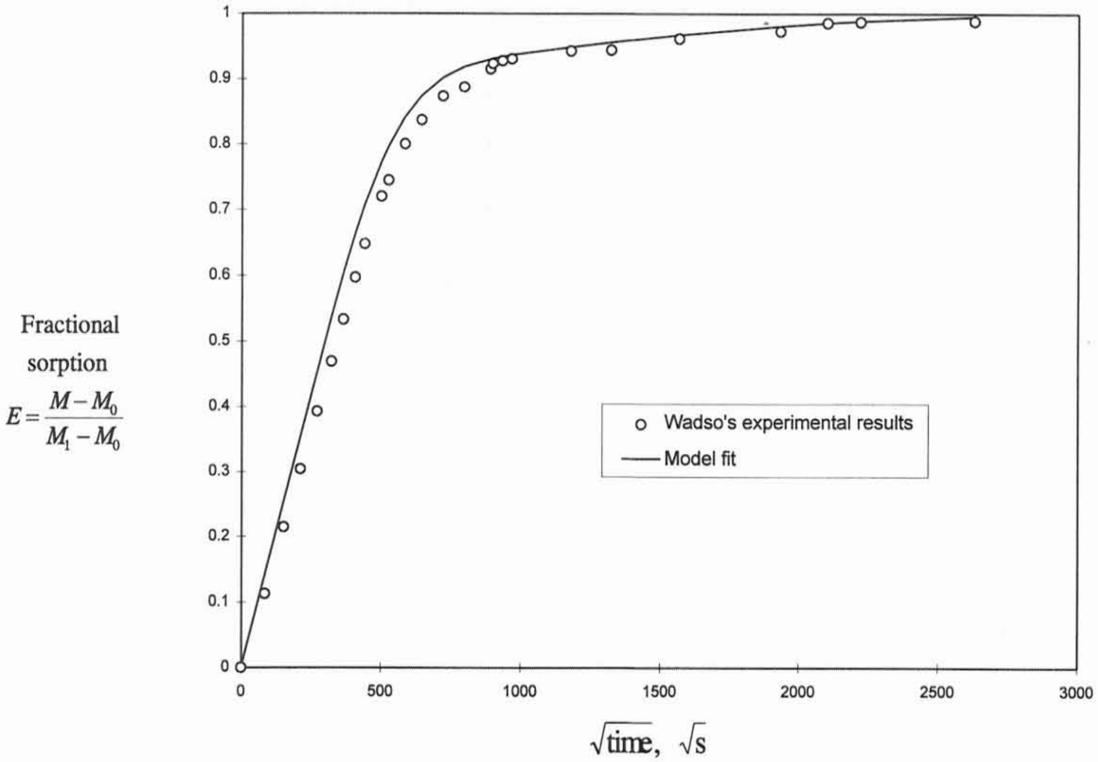
FIG. 3. A comparison between Wadsö's experimental data and the model developed in this work, using model parameters shown in Table 1. (Illustrative only, as the experimental data are measured off published graphs, rather than from the original raw data.) (a) Specimen 1. (b) Specimen 2.


Fractional sorption
$E=\frac{M-M_0}{M_1-M_0}$
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
500
1000
1500
2000
2500
3000
$\sqrt{\text{time}}$, $\sqrt{\text{s}}$
Wadso's experimental results
Model fit

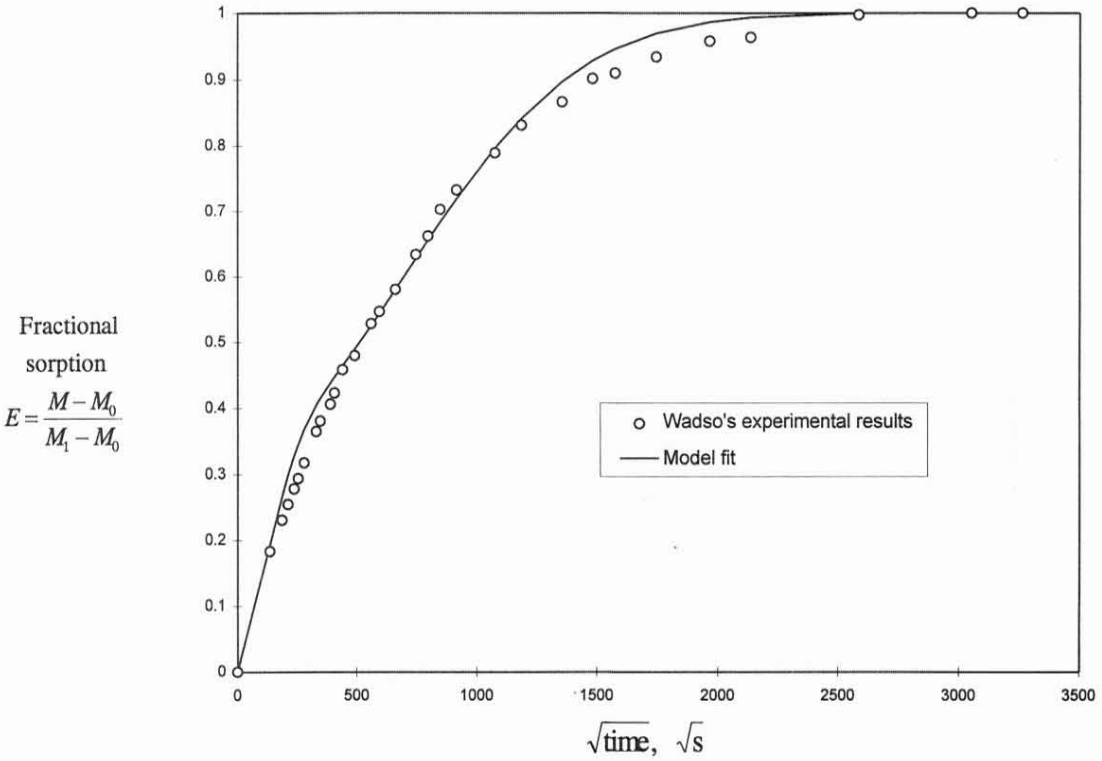

Fractional sorption
$E=\frac{M-M_0}{M_1-M_0}$
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
500
1000
1500
2000
2500
3000
3500
$\sqrt{\text{time}}$, $\sqrt{\text{s}}$
Wadso's experimental results
Model fit

TABLE 1. *Moisture transfer parameters calculated by the techniques developed in this work, compared to those calculated by Wadsö (illustrative only).*

| | Wadsö's results | | | | This work | | | |
|---|---|---|---|---|---|---|---|---|
| | $D_c$ $10^{-10}$ $m^2/sec$ | $a$ | $t_2$ $10^6$ sec | $\alpha$ | $D_c$ $10^{-10}$ $m^2/sec$ | $a$ | $t_2$ $10^6$ sec | $\alpha$ |
| Specimen 1 | 1.83 | 0.62 | 1.06 | 0.025 | 2.73 | 0.65 | 0.90 | 0.034 |
| Specimen 2 | 0.65 | 0.16 | 0.98 | 0.077 | 0.63 | 0.09 | 2.40 | 0.064 |

$$D_c = \frac{\pi L^2}{4}\left(\frac{dE}{dt^{1/2}}\right)^2\Bigg|_{t=0} \tag{27}$$

can only give correct values for $D_c$ if cell-wall sorption processes are negligible. For the case that includes cell-wall sorption, the time constant $t_2$ must be first found by examining the slope in the $t > t_1$ region, a calculated, and formula (12) used to calculate $D_c$.

This process has been carried out using data from two of Wadsö's results, as shown in Table 1 and Fig. 3. Comparison with Wadsö's values of a and $\tau$ (corresponding to $t_2$), derived by curve fitting, shows reasonable agreement with those derived using the algorithm above. This comparison is meant for illustration only, since data points and slopes were derived by measurements from the published graphs and not from the raw data.

## DISCUSSION

Wadsö's work shows that more than just Fickian diffusive mechanisms are taking place during moisture transport in wood. Using a model that considers diffusion alone can yield quite erroneous values for the diffusion coefficient if this is extracted from transient experiments. There are two classes of error that will be made: first, the value of the diffusion coefficient could be substantially different from the steady-state value; and second, although this incorrect value of the diffusion coefficient may fit well the initial part of the transient sorption curve from which it was derived, the agreement becomes poor at longer time intervals.

Poor prediction of moisture transfer as a consequence of these errors has probably been avoided until now in part by the use of a diffusion coefficient dependent upon moisture content. It should be possible to fit any transient sorption curve by appropriate adjustment of the diffusion coefficient. This, of course, is unsatisfactory if the underlying mechanism of slow sorption is being ignored, and indeed degenerates to a parameter fitting exercise with limited physical meaning. Furthermore, diffusion coefficients fitted in this fashion can only correctly describe the transient sorption curve from which they were derived. Reproduction of moisture transfer under other conditions, e.g., cyclic or steady-state conditions, will be inferior.

Whether the slow cell-wall diffusion hypothesis will be finally accepted as the explanation for Wadsö's "anomalous" results is not yet certain. However, Wadsö's results may necessitate a reexamination of those literature values for diffusion coefficients that were derived by transient means, including their moisture concentration dependence.

Each of the parameters $t_1$, $t_2$, and a (or l/k) derived here has clear physical meaning (viz., time constants for Fickian and non-Fickian transport, and proportion of non-Fickian transport, respectively) and can be calculated from the transient sorption curve by measurement of appropriate slopes. Wadsö used curve-fitting techniques to derive his parameters, effectively treating them as free parameters and thus loosening somewhat the connection between the parameter value and its underlying physical meaning. At this stage there is no physical justification for including more than one relaxation term, although doing so provides Wadsö with a better fit to his experimental data; this is always so if a larger number of free parameters are included in a model.

## CONCLUSIONS

This work has examined the consequences of including the non-Fickian relaxation mechanism of slow cell-wall sorption on the moisture transfer behavior of wood, subjected to a step change in external conditions. It is found that such a model describes well the two-slope experimental results derived by Wadsö. The parameters required for this model have clear physical meaning, whose size should help quantify the underlying mechanisms. Measurement of appropriate slopes is all that is required to derive these parameters.

However, a deeper understanding of these mechanisms and their consequences requires much future work. The details of slow sorption into the cell wall are not well understood: it is not clear how many mechanisms are operating; the temperature and moisture concentration dependence of these mechanisms are not known; and the consequences of these mechanisms on moisture transfer under different boundary conditions have not been worked out.

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## APPENDIX—MATHEMATICAL DETAILS OF AN ITERATIVE SOLUTION TO THE MOISTURE MODEL DIFFERENTIAL EQUATIONS

The coupled partial differential equations describing the moisture model are given by Eqs. (9) and (10) as

$$\frac{\partial w}{\partial t} = h(lc - kw) \tag{A1}$$

$$\frac{\partial c}{\partial t} = D_c \frac{\partial^2 c}{\partial x^2} + h(kw - lc) \tag{A2}$$

The initial conditions are given by Eq. (1) as the wood moisture content in equilibrium, both with the external potential and between the moisture content of the wood cavities and cell-wall moisture, i.e.,

$$\text{At } t = 0, \qquad \varphi_0 = \varphi_c = \varphi_w \qquad \text{independent of } x. \tag{A3}$$

An iterative approach to give an approximate solution is used: to begin the iteration the standard solution when $h = 0$ is taken to Eq. (A2), i.e., the without cell-wall sorption case; this solution is substituted into Eq. (A1) (h from this iteration onwards not necessarily zero) which is then solved for the cell-wall moisture content w; and the solution for c is reiterated by substituting this solution for w back into Eq. (A2).

The standard solution to Eq. (A2) when $h = 0$, i.e., the without cell-wall sorption case, is (Crank 1975; Carslaw and Jaeger 1959),

$$\begin{aligned} c &= c_1 - (c_1 - c_0)\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\{-D_c(2n+1)^2\pi^2 t/4L^2\}\cos\{(2n+1)\pi x/2L\} \\ &= c_1 - (c_1 - c_0)\sum_{n=0}^{\infty} u_n \exp(-b_n^2\, t/\pi^2 t_1)\cos(b_n x/2L) \end{aligned} \tag{A4}$$

where

$$t_1 = \frac{4L^2}{\pi^2 l D_\varphi} = \frac{4L^2}{\pi^2 D_c} \tag{A5}$$

and

$$\begin{aligned} b_n &= (2n+1)\pi \\ u_n &= \frac{4(-1)^n}{\pi(2n+1)} = \frac{4(-1)^n}{b_n} \end{aligned} \tag{A6}$$

$t_1$ is a time constant associated with diffusion and sorption in the wood cavities. Under a step change, total moisture content within the wood cavities undergoes half its total change in a time of about $\frac{1}{2}t_1$ (Crank 1975).

Substituting this solution, Eq. (A4), into Eq. (A1) gives the following first-order linear equation in w

$$hl\left\{c_1 - (c_1 - c_0)\sum_{n=0}^{\infty} u_n \exp(-b_n^2 t/\pi^2 t_1)\cos(b_n x/2L)\right\} - hkw = \frac{\partial w}{\partial t} \tag{A7}$$

which, under the specified initial and boundary conditions, has the solution of

$$w = w_1 - (w_1 - w_0)\left\{\exp(-t/t_2)\sum_{n=0}^{\infty}\frac{u_n}{1-\epsilon_n}\cos(b_n x/2L) - \sum_{n=0}^{\infty}\frac{\epsilon_n u_n}{(1-\epsilon_n)}\exp(-b_n^2 t/\pi^2 t_1)\cos(b_n x/2L)\right\} \tag{A8}$$

where

$$t_2 = \frac{1}{hk} \tag{A9}$$

$$\alpha = \frac{t_1}{t_2} \tag{A10}$$

$$\epsilon_n = \frac{\pi^2 t_1}{b_n^2 t_2} = \frac{\alpha\pi^2}{b_n^2} \tag{A11}$$

$t_2$ is the exponential time constant governing the rate of sorption in the cell wall.

Equation (A2) is rewritten as

$$D_c\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} + \frac{\partial w}{\partial t} \tag{A12}$$

and (A4) and (A8) differentiated with respect to t and substituted into Eq. (A12). This results in an expression for $\partial^2 c/\partial x^2$ which, when integrated twice, taking into account the boundary and initial conditions, gives

$$c = c_1 - (c_1 - c_0)\left\{\sum_{n=0}^{\infty} u_n\left(1 + \frac{\epsilon_n l}{k(1-\epsilon_n)}\right)\exp(-b_n^2 t/\pi^2 t_1)\cos(b_n x/2L) - \frac{1}{k}\exp(-t/t_2)\sum_{n=0}^{\infty} u_n\frac{\epsilon_n}{1-\epsilon_n}\cos(b_n x/2L)\right\} \tag{A13}$$

Total moisture concentration, $m = c + w$, is the quantity of most interest. This can be calculated by adding together Eqs. (A8) and (A13), yielding

$$m = m_1 - \sum_{n=0}^{\infty} u_n\left\{c_1 - c_0 - \frac{\epsilon_n}{(1-\epsilon_n)}\left(w_1 - w_0 - \frac{1}{k}(c_1 - c_0)\right)\right\}\exp(-b_n^2 t/\pi^2 t_1)\cos(b_n x/2L)$$

$$- \exp(-t/t_2) \sum_{n=0}^{\infty} u_n \left\{ \frac{1}{(1 - \epsilon_n)} \left( w_1 - w_0 + \frac{\epsilon_n l}{k}(c_1 - c_0) \right) \right\} \cos(b_n x/2L) \tag{A14}$$

The mechanism under investigation is slow sorption into the cell walls, which implies that $t_2 \gg t_1$, i.e., $\alpha \cong 0$ and $\epsilon_n \cong 0$. This allows Eq. (A14) to be simplified to

$$m \cong m_1 - (w_1 - w_0)e^{-t/t_2} \sum_{n=0}^{\infty} u_n \cos(b_n x/2L) - (c_1 - c_0) \sum_{n=0}^{\infty} e^{-b_n{}^2 t/\pi^2 t_1} u_n \cos(b_n x/2L) \tag{A15}$$

The total moisture content M in the wood is found by integrating Eq. (A15) through the length of the specimen, giving

$$M = M_1 - (W_1 - W_0)e^{-t/t_2} - (C_1 - C_0) \sum_{n=0}^{\infty} \frac{8e^{-b_n{}^2 t/\pi^2 t_1}}{b_n{}^2} \tag{A16}$$

utilizing the fact that

$$\sum_{n=0}^{\infty} \frac{8}{b_n{}^2} = 1 \tag{A17}$$

At this limit of slow sorption in the cell walls, the moisture content of the wood cavities and the cell-wall moisture content are uncoupled.