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ADSORPTION RATE OF WOOD DURING MOISTURE SORPTION PROCESSES

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ABSTRACT

Moisture sorption processes carried out in successive steps in seven relative humidity environments between 11% and 92% at 20°C for Chinese fir (*Cunninghamia lanceolata* Hook.) and Sitka spruce (*Picea sitchensis* Carr.) were studied. A theoretical equation was developed to describe wood adsorption processes, either started from oven-dry condition or certain initial moisture content. The relation between adsorption rate constant in the equation and relative humidity was clarified as follows: with an increase in relative humidity, the adsorption rate constants for both species first decreased and then increased slightly with the minimum values falling into the relative humidity range between 60% and 70%. Further, an attempt was made to model the observed relation between the rate constant and relative humidity by applying the Hailwood-Horrobin sorption theory.

KEY WORDS: adsorption rate; moisture sorption; relative humidity

INTRODUCTION

Wood is a material with high hygroscopicity which is closely related to many other properties, such as mechanical properties, dimensional stability, environment-humidifying ability and so on. Since relative humidity in the atmosphere is rarely constant, wood is continually subject to moisture adsorption and desorption processes. Therefore, study on the effect of relative humidity on moisture sorption rate of wood is helpful for understanding and controlling the dimensional stability and environment-humidifying ability of wood products in service effectively. Furthermore, it could not only provide scientific information for wood processing carried out under high relative humidity condition, but also give important index to wood drying on controlling wood drying rate through the regulation of relative humidity.

Various theories have been developed to describe sorption rates in wood. Stamm (1959) explored Fick's diffusion law dealing with the sorption process for Sitka spruce. Although it has been assumed that rates of moisture change in wood are governed by Fick's laws of diffusion, studies showed that they do not adequatedly describe moisture movement in small wood specimens, other processes in addition to Fickian diffusion operate to limit the rates of moisture change in wood (Christensen and Kelsey 1959, Kelly and Hart 1969, Skaar et al. 1970; Nakano 1994 a and b, Zhang et al. 2007). Christensen and Kelsey (1959) studied the rate of water vapour adsorption by small specimens of Klinkii pine in the absence of air. They found the sorption rate decreased as the moisture content increased. Kelly and Hart (1969) measured the rate of water vapour adsorption and desorption of yellow poplar and white oak. An empirical equation was derived to fit the experimental data, but only limited success was achieved in relating the constant of the equation to the corresponding relative humidities. Nakano (1994 a, b) proposed a rate equation of non-steady state adsorption for wood, in which the process of water adsorption was regarded as an auto-catalyzed sorption reaction.

The work reported here was conducted to 1) develop a theoretical equation to predict wood adsorption and compare it with other study, and 2) find the relationship between and constant of the equation and relative humidity and try to give tentative explanation of the relationship by proposing a modeling equation.

MATERIAL AND METHODS

Wood specimens were prepared from Chinese fir (*Cunninghamia lanceolata* Hook.) and Sitka spruce (*Picea sitchensis* Carr.) with the dimensions of 4mm thick along the grain and 20mm in both tangential and radial directions.

Tab. 1: Relative humidities at 20°C maintained by the different salt solutions used in this study [a]

Relative humidity	Salt solution
11%	Lithium chloride
22%	Potassium acetate
33%	Magnesium chloride
47%	Lithium nitrate
62%	Sodium bromide
75%	Sodium chloride
92%	Lead (II) nitrate

[a] From Macromolecule Academy (1958).

The specimens were put into weighing bottles and dried at 105°C to the oven-dry state, after which their oven-dry weights were measured. They were then subjected to successive moisture adsorption processes by successively placing the weighing bottles into seven relative humidity conditions maintained inside different desiccators by saturated salt solutions. The different salt solutions used in this study, together with their corresponding relative humidity at 20°C are given in Tab. 1. The desiccators were kept in a climate-controlled conditioning room maintained at 20 ± 1°C where the specimens were weighed periodically in the weighing bottles during each adsorption process until there were no apparent weight changes. All the weight measurements were conducted with the weighing bottles being capped to prevent the specimens from exchanging moisture with the surrounding environment and the weights were determined to within 0.1 mg. During the adsorption processes, five replicates were used and their mean moisture content values were taken as the final results.

RESULTS AND DISCUSSION

Acquirement of Adsorption Rate Constant

According to wood drying theory (Asano 1982), moisture sorption rates below the fiber saturation point can be described from the following equation:

$$\frac{dW}{dt} = Ak_p(p - p_b)\,, \tag{1}$$

where dW/dt is sorption rate (gh^{-1}), A is external sorption surface area (cm^2), k_p is sorption coefficient ($gh^{-1}cm^{-2}mmHg^{-1}$), p is vapour pressure for the surrounding atmosphere (mmHg), and p_b is vapour pressure for the surface of wood (mmHg). $p_b = p_w - p_r$, where p_w and p_r are saturated vapour pressure and evaporation resistance pressure for the surface of wood respectively (mmHg), and $p_r = p_w - p$ when equilibrium state is reached. Nakao's study (2002) indicated that calculation from atmospheric pressure, saturated vapour pressure and evaporation resistance pressure could give a good simulation to the adsorption process during the conditioning stage of wood drying.

Equation (1) can be written in terms of moisture content m (%) and relative humidity by being transformed into the following form:

$$\frac{dm}{dt} = \frac{Ak_p p_s}{W_0}(h - h_b) = a(h - h_b)\,, \tag{2}$$

where W_0 is oven-dry weight (g), p_s is saturated vapour pressure of the atmosphere (mmHg), h and h_b are relative humidity for the surrounding atmosphere and the surface of wood respectively (%). In equation (2), $a = Ak_p p_s / W_0$, defined as adsorption rate constant (h^{-1}), is dependent on relative humidity.

Rearranging equation (2) can be shown to yield:

$$m_i = m_{i-1} + a(h - h_b)_{i-1}\Delta t \quad (i \geq 1)\,, \tag{3}$$

where the subscript $i-1$, i are ordinal numbers of experimentally measured points.

Assuming that moisture content of a wood surface could reach equilibrium state with relative humidity for the surface of wood instantaneously, then the parameter h_b in equation (3) can be determined by the Bradley equation (Bramhall 1979).

$$h_b = \exp(K_2 K_1^{\,m} + K_3)\,, \tag{4}$$

$$K_1 = 1.0327 - 0.000674T\,, \tag{5}$$

$$K_2 = 17.884 - 0.1432T + 0.0002363T^2\,, \tag{6}$$

$$K_3 = -0.0251\,, \tag{7}$$

where T is temperature (K). The values of K_1, K_2 and K_3 calculated by equation (5)-(7) were validated by experimental isotherm curves, and K_3's values for Chinese fir and Sitka spruce were corrected to -0.040 and -0.049 respectively. In addition, it should be recognized that equation (4) provides mean value of adsorption and desorption isotherms. According to Bramhall (1979), it can be converted to the following equation for pure adsorption processes.

$$h_b = \exp(K_2 K_1^{1.087m} + K_3), \tag{8}$$

The starting moisture contents adopted in this study are zero for the initial 11% relative humidity exposure condition and the equilibrium moisture contents in the previous relative humidity environment for subsequent relative humidity conditions. Δt is taken as 1 h. Therefore, by use of equation (3) and (8), the theoretical curve between moisture content and time can be obtained for a certain value of a under every experimental relative humidity condition.

It is anticipated that moisture contents calculated with equation (3) and (8) should be values for the surface of wood, which neglects the effect of moisture content gradient. To transform the surface values into the corresponding ones for a whole piece of wood, a diffusion equation considering the Coulomb friction (Nakao and Kohara 2004), given by equation (9), is used here.

$$\frac{\partial m}{\partial t} = D\partial(dm/dx \pm f)/\partial x,$$

or

$$\frac{\partial m}{\partial t} = D\partial^2 m/\partial x^2 + \delta. \tag{9}$$

where D is moisture diffusion coefficient (cm^{2}h^{-1}), x is one-dimensional distance coordinate (cm), f is the Coulomb friction (%cm^{-1}) which is considered to reduce the moisture gradient dm/dx, then $dm/dx-f$ for $dm/dx>0$ and $dm/dx+f$ for $dm/dx<0$.δ is the Dirac's delta fuction (%h^{-1}). Equation (9) was solved by the finite difference method and the friction was considered by inserting the value of $2Df/\Delta x$ to a part corresponding to the position at which the sign of the moisture gradient changed.

Regarding the dependence of diffusion coefficient on moisture content, according to Nakao and Kohara (2004), D could be taken as a constant if the coulomb friction is considered in moisture diffusion. The value of D and $2Df/\Delta x$ adapted to the present test data are 0.0037cm^{2}h^{-1} and 0.008%h^{-1} respectively for both species. Accordingly, by taking the surface moisture contents calculated with equation (3) and (8) as the boundary condition for equation (9), the corresponding average values of all elements in the thickness direction can be obtained at different time points.

Weights of the specimens measured at different stages of adsorption were transformed into absolute moisture content which was plotted against adsorption time and therefore, the experimental curves of moisture content in relation to time during the adsorption processes under various humidifying conditions for Chinese fir and Sitka spruce were worked out.

Curve-fitting procedures were then carried out to fit the theoretical curves to the experimental ones for the two species by adjusting parameter a to an appropriate value for each relative humidity. Accordingly, the adsorption rate constant a in different relative humidity environments for Chinese fir and Sitka spruce were acquired.

Fig. 1 displays the comparison of theoretical curves with experimental results at various relative humidities for the adsorption of Chinese fir and Sitka spruce. It can be found from this figure that, on the whole, the theoretical curves agree satisfactorily with the experimental results except the initial stage of adsorption process at 11% relative humidity. This results primarily from the fact that wood usually has a moisture content of 0.5% or less even under oven-dry condition (Stamm 1964), while the starting moisture content value adopted in this study is zero.

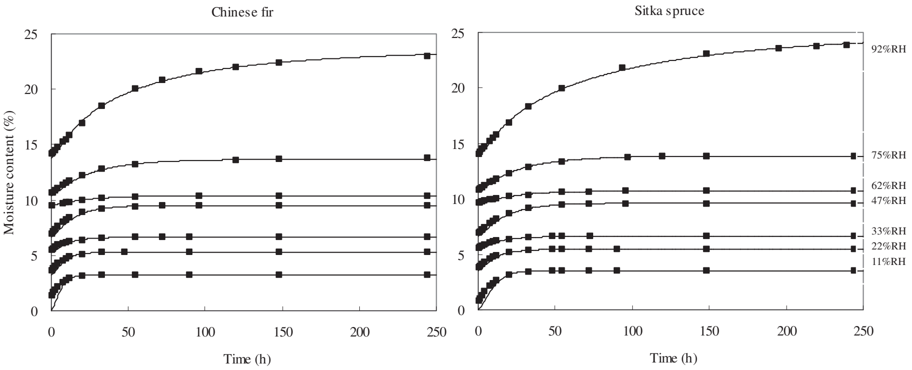

Fig. 1: Comparison of theoretical curves with experimental results for the adsorption of Chinese fir and Sitka spruce. Legend: ■ experimental results — theoretical curves

Tab. 2: Values of adsorption rate constant under different relative humidity conditions for Chinese fir and Sitka spruce

Relative humidity (%)	Adsorption rate constant (h^{-1})					
	From drying theory		From drying theory and diffusion theory		From Nakano's theory	
	Chinese fir	Sitka spruce	Chinese fir	Sitka spruce	Chinese fir	Sitka spruce
11	4.2	2.3	5	2.6	2.5	2.3
22	2	1.4	2.2	1.4	2	2
33	1.2	1.1	1.5	1.1	1.8	1.8
47	1.1	0.9	1.1	0.9	1.7	1.7
62	0.6	0.65	0.75	0.8	1.6	1.6
75	0.8	0.8	0.9	0.9	1.7	1.7
92	1.5	1.2	1.5	1.3	1.8	1.8

Values of adsorption rate constant used for curve-fitting based on analysis with drying theory and a combination of diffusion theory for Chinese fir and Sitka spruce are listed in Tab. 2. It suggests that a consideration of diffusion effect generally gives bigger values of adsorption rate constants than those calculated only with drying theory, and both analysis methods show the same tendency that with an increase in relative humidity, the adsorption rate constants for the two species first decrease and then increase slightly with the minimum values falling into the relative humidity range between 60% and 70%. This relative humidity range, which is close to our daily condition, indicates that moisture sorption of wood products in service usually occurs with the minimum adsorption rate constant. This is favourable from a dimensional stability viewpoint. The non-monotone relationship between adsorption rate constant and relative humidity for Chinese fir and Sitka spruce is also shown in Fig. 2.

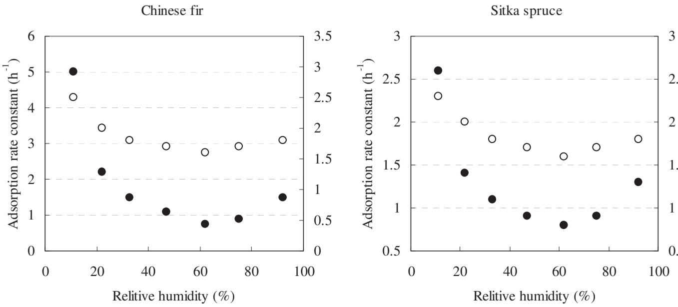

Fig. 2: Relationship between adsorption rate constant and relative humidity for Chinese fir and Sitka spruce. Legend: ●(main Y axis) from drying theory and diffusion theory ○(secondary Y axis) from Nakano's adsorption equation

Comparison with Nakano's adsorption equation

Combining equation (3) with equation (8) gives

$$m_i = m_{i-1} + a(h - \exp(K_2 K_1^{1.087 m_{i-1}} + K_3))\Delta t \quad (i \geq 1)\,. \tag{10}$$

Equation (10) derives from external surface sorption of wood, while the adsorption process studied by Nakano (1994a, b) considered internal surface sorption, from which adsorption equation was proposed in the following form:

$$\frac{m}{m_e} = \frac{1}{1 + \exp(-a(\ln t - b))}\ , \tag{11}$$

where m and a are defined as above, m_e is moisture content at equilibrium state (%), t is time and b is taken as a constant. Since the values of m and m_e should be moisture contents of adsorption started from oven-dry condition, in the case of adsorption from certain initial moisture content m_b (%), the value of m_b should be subtracted from m and m_e respectively. Then

$$m = (m_e - m_b)/[1 + \exp(-a(\ln t - b))] + m_b\,. \tag{12}$$

When m_b=0, equation (12) becomes equation (11) which describes adsorption processes from oven-dry condition. It can be found that there are two constants, a and b, in equation (11) or (12), while only one constant a involved in equation (10).

The adsorption data in this study were analyzed by equation (12) as well and comparison of theoretical curves with experimental results for Chinese fir and Sitka spruce is shown in Fig. 3. Tab. 2 and Fig. 2 also indicate values of adsorption rate constant calculated with Nakano's equation under various relative humidity conditions for Chinese fir and Sitka spruce. It is apparent that the relation between adsorption rate constant and relative humidity obtained from Nakano's equation is consistent with that acquired from drying theory and diffusion theory. Therefore, though these two approaches derive from different theoretical backgrounds, internal or external surface sorption, or different sorption processes, adsorption or desorption, the analyses from both equations presents the same result.

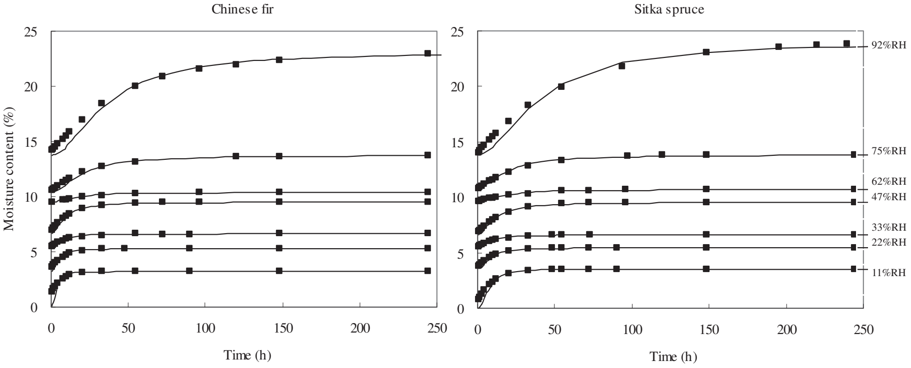

Fig. 3: Comparison of theoretical curves calculated with Nakano's equation with experimental results for the adsorption of Chinese fir and Sitka spruce. Legend: ■ *experimental results — theoretical curves*

Modelling the relation between adsorption rate constant and relative humidity

As indicated in Fig. 1, adsorption rate of wood is higher at the initial stage of moisture adsorption and it decreases as the adsorption proceeds until equilibrium state is reached. Therefore, it is convenient in this discussion to consider that the adsorption rate is directly proportional to the amount of unoccupied sorption space available for moisture adsorption. In the Hailwood-Horrobin sorption theory (Hailwood and Horrobin 1946), water is presumed to exist in two forms. These are "hydrated water" which forms a hydrate with the wood, and "dissolved water" which forms a solid solution in the cell wall. Assume m_h and m_d are the quantities of unoccupied sorption space for hydrated and dissolved water in terms of moisture content (%), according to the sorption model, their values can be determined by,

$$m_h = m_0 - m_1, \tag{13}$$

$$m_d = m_s - m_0 - m_2, \tag{14}$$

where m_0 is an moisture content corresponding to complete hydration of all of the available sorption sites (%), m_s is moisture content of wood at fiber saturation point (%), and m_1 , m_2 are moisture content of hydrated water and dissolved water (%), respectively.

The equation for the isotherm predicted by the Hailwood-Horrobin model is of the form

$$\frac{h}{m} = \frac{1}{m_0 b_2 (b_1 + 1)} + \frac{b_1 - 1}{m_0 (b_1 + 1)} h - \frac{b_1 b_2}{m_0 (b_1 + 1)} h^2, \tag{15}$$

where m is the total moisture content of wood (%), b_1 is the equilibrium constant where the hydrate is formed from the dissolved water and dry wood, and b_2 is the equilibrium constant between dissolved water and water vapour. The values of b_1, b_2 and m_0 can be evaluated by the nonlinear regression technique, from which m_s can be worked out when relative humidity is 100% in equation (15).

Further, moisture content of hydrated water and dissolved water can be calculated by the following equations,

$$m_1 = \frac{b_1 b_2 h m_0}{1 + b_1 b_2 h}, \tag{16}$$

$$m_2 = \frac{b_2 h m_0}{1 - b_2 h}, \tag{17}$$

Having calculated m_h and m_d, a modelling equation was proposed based on the assumption that the adsorption rate constant of wood is the weighted average of unoccupied sorption spaces for hydrated and dissolved water, given by the following form:

$$a = \frac{a_h m_h + a_d m_d}{m_h + m_d}, \tag{18}$$

where a_h and a_d are the adsorption rate constants for hydrated and dissolved water (h^{-1}), and they are independent of relative humidity. Equation (18) gives some insight that the rate of adsorption is limited by the rate at which sorption spaces can be made accessible to water molecules rather than strictly by diffusion rate.

Tab. 3: Values of the constants used for modelling

Constants	Chinese fir	Sitka spruce
b_1	14.30	11.09
b_2	0.81	0.82
m_0 (%)	5.74	5.61
m_S (%)	30.06	28.5
a_h (h^{-1})[a]	35	15
a_d (h^{-1}) [a]	0.1	0.1
a_h (h^{-1}) [b]	17	10
a_d (h^{-1}) [b]	1.15	1.2

[a] For observed result obtained from drying and diffusion theory .
[b] For observed result obtained from Nakano's equation.

Tab. 3 lists the values of the constants used for the modelling of Chinese fir and Sitka spruce, and a_h, a_d were determined when they gave the best fit to the observed relation between relative humidity and adsorption rate constant. The comparison of observed relations with modelling curves for Chinese fir and Sitka spruce are shown in Fig. 4 which suggests that, on the whole, the modelling curves agree well with the observed results obtained from both drying and diffusion theory and Nakano's adsorption equation. However, the modelling seem to break down at 11% relative humidity for the curves calculated from drying theory and diffusion theory. No satisfactory explanation is given for this failure, possibly it is related to the fact that low relative humidity region is a tough area for both experiment technique and theoretical analysis. Therefore, an introduction of the third phase of adsorbed water in wood will be considered in future work for further improving the modelling.

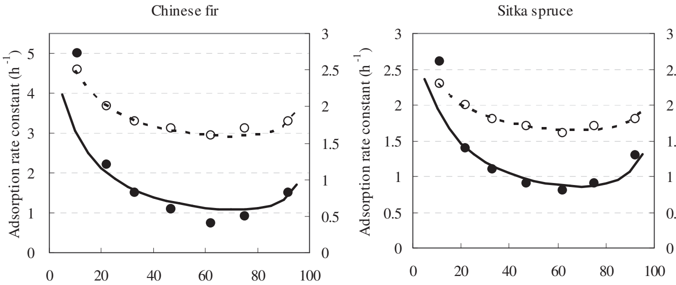

Fig. 4: Comparison of observed relation between adsorption rate constant and relative humidity with modelling curves for Chinese fir and Sitka spruce. Legend: ●(main Y axis) observed relation from drying theory and diffusion theory ○(secondary Y axis) observed relation from Nakano's adsorption equation — (main Y axis) modelling curves for observed relation from drying theory and diffusion theory --- (secondary Y axis) modelling curves for observed relation from Nakano's adsorption equation

CONCLUSIONS

Moisture adsorption over time in wood follows an exponential function. The adsorption rate constant has been shown to first decrease and then increase slightly with an increase in relative humidity. The model proposed in this study suggested that wood adsorption rate is related to the rate at which sorption spaces can be made accessible to water molecules rather than the classical Fickian behavior. Further work is needed to improve the present model by introducing a third phase of adsorbed water in wood.

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