PENETRATION OF WATER INTO HARDWOODS

Howard N. Rosen

Research Chemical Engineer, Forestry Sciences Laboratory, North Central Forest Experiment Station,[1] Forest Service, U.S. Department of Agriculture, Carbondale, IL 62901

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ABSTRACT

The longitudinal penetration of water into hardwoods was studied by continuously measuring swelling and uptake in a swelling cell apparatus. Mathematical equations were developed to relate swelling, bound moisture uptake, free moisture uptake, and time of penetration. The initial stages of bound moisture uptake and free moisture uptake were each shown to be linear when plotted against the square root of time.

Bound and free moisture penetration constants were calculated from swelling and uptake data for different wood species at different temperatures. The transport of bound water by vapor and water diffusion became more important than transport by capillarity as temperature increased, or when wood species with obstructed vessels were used. The relative amount of water uptake distributed between bound moisture and free moisture was shown to change with increasing temperature.

Additional keywords: Liriodendron tulipifera, Quercus shumardii, Juglans nigra, swelling, bound moisture, free moisture, diffusion, temperature.

NOTATION

D diffusion constant, cm^2/sec

D_{gL} longitudinal water-vapor diffusion coefficient of gross wood, cm^2/sec

E fraction of final moisture content

G specific gravity at M_i

G_S specific gravity of water

G_w specific gravity of wood substance

K coefficient of volumetric swelling

L specimen thickness, cm

M_B bound moisture uptake, percent

M_F free moisture uptake, percent

M_{fsp} fiber saturation point, percent

M_m maximum moisture content, percent

M_i initial moisture content, percent

M_T total moisture uptake, percent

N_B bound-moisture flux, g/cm^2-sec

N_F free-moisture flux, g/cm^2-sec

P_B bound-moisture penetration constant, cm^2/sec

$\overline{P}_B$ integral bound-moisture penetration constant, cm^2/sec

P_F free-moisture penetration constant, cm^2/sec

$\overline{P}_F$ integral free-moisture penetration constant, cm^2/sec

S volumetric swelling percentage relative to oven-dry conditions

S' volumetric swelling percentage relative to initial moisture of M_i

S_m maximum volumetric swelling percentage relative to oven-dry conditions

S_m' maximum volumetric swelling percentage relative to M_i

S_i volumetric swelling percentage at M_i relative to oven-dry conditions

t time, hours

V_L liquid volume

V_T wood volume at oven-dry conditions

V_w wood volume at M_i

x distance along the wood axis, cm

ρ_w wood density

σ differential swelling, cm^3

INTRODUCTION

Although considerable fundamental research has been done on the drying of green wood, little work has been done on the reverse process, the addition of liquid

[1] Laboratory maintained in cooperation with Southern Illinois University.

during treatment of dried wood. As liquid penetrates wood that has been dried below the fiber saturation point (fsp), the liquid is adsorbed by the cell walls (causing swelling of the wood), as it simultaneously fills the lumens or cell cavities. Before methods can be devised to control the swelling, uptake, and distribution of liquids in wood, a mechanism must be found to explain how liquids move in wood, the proportion of liquid uptake that contributes to swelling, and the effect of temperature, wood structure, etc. on liquid movement.

The objective of this study is to investigate the simultaneous uptake and swelling as water penetrates wood that has been previously dried below the fsp. Water is the liquid used because it causes considerable dimensional change in wood and because considerable data are available in the literature concerning this liquid and its interaction with wood. Longitudinal penetration is studied because this pathway offers the least resistance. Mathematical relationships will be developed through extension of previous theory to evaluate penetration constants related to the rate of bound and free water uptake.

BACKGROUND

The movement of liquids through the capillaries in wood is a complex process. Stamm (1959, 1960) showed that for the initial stages of diffusion the bound water diffusion constant as well as the combined bound water and vapor diffusion constant could be determined by the following relationship:

$$D = \frac{\Pi L^2 E^2}{16t}, \qquad (1)$$

where L is the specimen thickness, E is the fraction of final moisture content or final swelling, t is time, and D is the diffusion constant for either bound water or combined bound water and water vapor. This relationship was shown to be valid until $E = 0.667$.

The penetration of water along the fiber direction of Sitka spruce (*Picea sitchensis* (Bong.) Carr.) was observed by Stamm (1953). The swelling was shown to occur almost as fast as the water was distributed through the structure. Weight increased linearly with the square root of time up to 20% moisture content.

Stamm and Petering (1940) have suggested three steps for the uptake of a solution by wood: (1) wetting of the wood surfaces by the solution, (2) capillary rise of the solution in the capillary structure of the wood, and (3) diffusion of the solution into the cell walls of the wood. They concluded that except for the first few minutes, either capillary rise or diffusion through the cell walls controlled the rate of uptake of aqueous solutions by wood.

METHODS

Three species were used in this study—yellow poplar (*Liriodendron tulipifera*), red oak (*Quercus shumardii*), and black walnut (*Juglans nigra*). Sections 5 by 5 by 40 cm in the fiber direction were cut from the bolts of trees found locally in southern Illinois. The straight-grained and defect-free sections were kiln-dried to 8% moisture content. The square sections were then turned on a lathe into cylinders 3.6 cm in diameter and 10 cm in length along the grain. Cylindrical samples of yellow poplar heartwood (YPH), yellow poplar sapwood (YPS), red oak heartwood (ROH), and black walnut heartwood (BWH) were then stored in an environmental chamber controlled for 8% equilibrium moisture content until use in a swelling cell run.

A swelling cell described by Rosen (1973) was used to measure simultaneously and continuously the volumetric swelling and liquid uptake in the longitudinal direction of the cylindrical samples (Fig. 1). After weights and dimensions of the sample were taken, a run was started by adding water through the liquid feed tube until the level was in the range of the scale. The scale was placed on a slight tilt so that the pressure created by the head of water in the feed tube was as small as possible, approximately 4 cm. An initial reading of liquid feed and swelling (level of glycerol tube) was taken.

A valve above the liquid collection flask was open to allow liquid to run through the wood. The valve was kept open until either 2 min elapsed or the first drop came through, whichever was first, and then was closed for the duration of the run. Readings were taken several times on the first day and then one or two times a day after that until about 350 hr had passed. Air that came out of the wood sample was periodically bled from the normally closed liquid air bleed valve to make sure that the liquid displaced in the feed tube was a true value of liquid taken into the wood sample. Samples were removed at the end of a run so that the weight could be taken and the dimensions measured.

Runs were made at least in triplicate in a temperature bath controlled to 0.2 C for temperatures of 0, 25, 50, and 75 C with yellow poplar sapwood. Additional runs were made with yellow poplar sapwood at room conditions, 22 ± 2 C. The scatter of data was not significantly affected, so other runs were made at room temperature. As there was only one temperature bath, this procedure allowed runs to be made simultaneously at different temperatures. Runs were made at 22 and 75 C for black walnut and red oak, and 22 C for yellow poplar heartwood. Runs were terminated at approximately 350 hr except for the 75 C runs, which were ended at about 200 hr.

Additional experiments were run at varying humidity conditions with thin wafers of red oak heartwood, yellow poplar sapwood, and yellow poplar heartwood to determine swelling-moisture curves. The wafers, 2.5 × 2.5 × 0.3 cm in the fiber direction, were initially oven-dried before being subjected to increasing relative humidity in steps of 13, 37, 59, 76, 86, 94, and 97% at 27 C. Dimensions and weights of the wafers were taken at each increase in humidity.

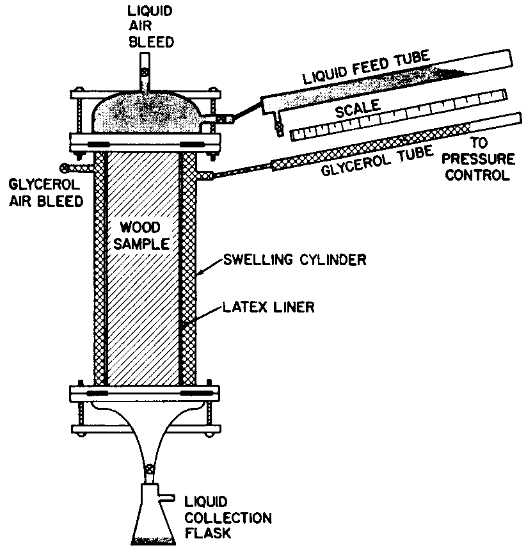

FIG. 1. Swelling cell assembly; the shaded areas are filled with penetrating liquid and the cross-hatched areas are filled with glycerol, which is displaced when the wood cylinder swells.

GENERAL EQUATIONS

According to the theory to be tested, water brought into contact with one surface of a wood specimen dried below the fsp will penetrate the wood fibers by diffusion, by capillarity, and, if the water is above the wood surface, by gravity. The water that penetrates the wood expressed on a percentage weight of water per weight of dry wood basis (total moisture uptake), M_T, can be proportioned into bound moisture uptake, M_B, and free moisture uptake, M_F:

$$M_T = M_F + M_B . \qquad (2)$$

The bound moisture uptake is the water that is absorbed by the cell walls, and the free moisture uptake is the water that fills the lumens or cavities of the cell.

As the water moves along a distance x from the surface ($x = 0$) toward the dry end of the wood ($x = L$), bound and free moisture simultaneously fills the wood structure. The amounts of free and bound moisture at a particular distance from the wood surface will change as time increases. Water reaching a differential element, dx, is assumed to satisfy the cell-wall requirements for bound moisture before filling the cavity with free water. Justification for this assumption is provided by Stamm (1953), who showed that wood that had been evacuated prior to soaking swelled several orders of magnitude faster than wood penetrated naturally. He showed that wood swelled almost as fast as water was distributed through the structure.

Although bound moisture is commonly thought to be transferred by cell wall and vapor diffusion, it can also be transferred by free moisture movement. Since free water is instantaneously incorporated into the cell wall, the free moisture must necessarily lag behind the bound moisture.

The uptake of bound moisture will therefore be that moisture adsorbed by the wood structure from the initial moisture content, M_i, to the fiber saturation point, M_{fsp}, and the uptake of free moisture will be that moisture from M_{fsp} to the maximum moisture content, M_m. In some cases the initial moisture content will be above the fsp. In this case, there is no bound moisture uptake ($M_B = 0$), and M_F is that free water from M_i (which is above M_{fsp}) to M_m.

Fick's first law of diffusion states that the mass flux (rate of transfer per unit area) is directly proportional to the concentration gradient. If, in using Fick's Law to develop the mathematical relationships, the volume change of wood with a change in moisture content is neglected, as is done in the literature for wood-moisture studies (Comstock 1963; Moschler and Martin 1968; and Hart 1964), then Fick's Law can be modified such that the mass flux is directly proportional to the moisture content gradient.

Although the penetration of water into wood is not completely a diffusional process, bound and free moisture gradients do occur in the wood structure. Fick's concepts are therefore applied to the penetration of water into wood. The bound moisture flux, N_B, and the free moisture flux, N_F, are assumed to occur simultaneously. The equations for the unidirectional cases are:

$$N_B = \frac{-P_B G \rho_w}{100} \frac{dM_B}{dx} \qquad (3)$$

$$N_F = \frac{-P_F G \rho_w}{100} \frac{dM_F}{dx}, \qquad (4)$$

where G is the specific gravity of the wood, ρ_w is the density of water, P_B is the bound moisture penetration constant, and P_F is the free moisture penetration constant. The initial moisture is assumed to be uniform throughout the sample. The constants P_B and P_F are used to gauge the penetration rate and are not to be confused with diffusion constants.

The unsteady-state equations derived from a mass balance on a differential element are:

$$\frac{\partial M_B}{\partial t} = \frac{\partial}{\partial x}\left(P_B \frac{\partial M_B}{\partial x}\right) \qquad (5)$$

$$\frac{\partial M_F}{\partial t} = \frac{\partial}{\partial x}\left(P_F \frac{\partial M_F}{\partial x}\right). \qquad (6)$$

Equations 5 and 6, with the appropriate boundary conditions, are similar to those used by a number of authors (Crank 1956; Stamm 1964; and Comstock 1963). The solutions for the initial stages of penetration in terms of the fraction of total moisture uptake for bound, E_B, and free, E_F, moisture are:

$$E_B = \frac{M_B}{M_{fsp} - M_i} = 2\left(\frac{\overline{P}_B t}{\pi L^2}\right)^{1/2} \qquad (7)$$

$$E_F = \frac{M_F}{M_m - M_{fsp}} = 2\left(\frac{\overline{P}_B t}{\pi L^2}\right)^{1/2}. \qquad (8)$$

The above equations assume that P_B and P_F are functions of moisture content, and thus can be defined as integral penetration constants:

$$\overline{P}_B = \frac{1}{M_{fsp} - M_i} \int_{M_i}^{M_{fsp}} P_B \, dM_B \qquad (9)$$

$$\overline{P}_F = \frac{1}{M_m - M_{fsp}} \int_{M_{fsp}}^{M_m} P_F \, dM_F \qquad (10)$$

The amount of bound moisture in the wood is reflected by the amount of swelling of the wood. Barkas (1949) has defined the differential swelling, σ, as the change in volume of the wood with a change in bound moisture content.

$$\sigma = \frac{dV}{dM_B} \times 100 \ . \qquad (11)$$

Both sides of Eq. 11 can be divided by the oven-dry wood volume V_T

$$K = \frac{\sigma}{V_T} = \frac{dS}{dM_B} \ , \qquad (12)$$

where S is the percentage swelling relative to oven-dry conditions, S_i is the swelling relative to oven-dry conditions at M_i, and K is defined as the coefficient of volumetric swelling.

Integration of Eq. 12 gives the relationship between swelling and moisture uptake:

$$S - S_i = \int_0^{M_B} K dM_B \ . \qquad (13)$$

Equations 7, 8, and 13 show that swelling, bound and free moisture uptake, and treatment time can be related to the physical parameters of the wood.

SPECIFIC EQUATIONS

Although the equations have been developed for relating swelling, moisture uptake, and time, more relationships must be derived to evaluate the physical parameters used in the equations.

The coefficient of volumetric swelling, K, is the slope of the volumetric swelling-moisture content curves. Since the slope of the volumetric shrinkage-moisture content curve has been shown to be linear over most of the bound-water range (Stamm 1964), a similar assumption of a linear relationship for volumetric swelling-moisture content is made. Data will be shown later to verify this assumption.

The following method was developed to evaluate K by using the physical data from the swelling cell. Since K will vary with temperature and specific gravity of the wood, a K must be evaluated independently for each run (Table 1).

Equation 13 integrates to yield:

$$K = \frac{S - S_i}{M_B} \ . \qquad (14)$$

A correction is made for measuring volumetric swelling relative to initial moisture contents other than oven-dry conditions:

$$S' = \frac{S - S_i}{1 + 0.01 S_i} \ , \qquad (15)$$

where S' is the volumetric swelling relative to wood at initial moisture, M_i. For maximum swelling, Eq. 15 is:

$$S'_m = \frac{S_m - S_i}{1 + 0.01 S_i} \ , \qquad (16)$$

Combining Eq. 14 at maximum swelling (i.e., $S = S_m$ at $M_B = M_{fsp} - M_i$) and Eq. 16 gives a direct relationship between S_m' and K:

$$K = \frac{S'_m \ (1 + 0.01 \ S_i)}{M_{fsp} - M_i} \ . \qquad (17)$$

Since S_i is not a measured parameter in this study, an approximation for S_i is used:

$$S_i \cong K \ M_i \ . \qquad (18)$$

Equation 18 will hold if swelling is linear with moisture content from oven-dry conditions to S_i with the same slope as from S_i to S_m. Since the effect of S_i in Eq. 17 is small, the approximation of Eq. 18 can be greatly in error and have a negligible effect on the value of K. Solving for K by substituting Eq. 18 into Eq. 17 yields

$$K = \frac{S'_m}{M_{fsp} - M_i(1 + 0.01 \ S'_M)} \ . \qquad (19)$$

Values of the maximum moisture content, M_m, are calculated as follows:

$$M_m = \frac{(1 - \frac{G}{G_w} + 0.01 \ S'_m) \ G_s \times 100}{G} \ , \qquad (20)$$

where G is the specific gravity of the wood based on M_i, G_w is the specific gravity of the wood substance determined in water (1.53) and G_S is the specific gravity of the water.

The total moisture uptake, M_T, can be determined from:

$$M_T = \frac{V_L \ G_L}{V_W \ G} \times 100 \ , \qquad (21)$$

TABLE 1. *Penetration data*[a]

Run	Temperature °C	S_m percent	M_m%	K	$\bar{P}_B$ cm ^{2}/sec x 10^4	$\bar{P}_F$ cm ^{2}/sec x 10^7
		Yellow poplar sapwood (G = 0.49)				
1	0	10.7	152	0.432	1.00	3.73
2	0	10.5	165	0.413	1.76	6.53
3	0	10.9	148	0.421	1.02	0.97
4	22	11.6	167	0.509	9.65	102.00
5	22	11.8	158	0.519	4.02	119.00
6	25	14.0	146	0.625	5.16	111.00
7	25	12.5	164	0.564	2.53	73.00
8	25	12.0	163	0.540	7.15	80.00
9	50	12.6	169	0.615	5.45	147.00
10	50	12.4	174	0.607	5.40	101.00
11	50	14.0	146	0.676	5.59	121.00
12	75	12.1	169	0.695	3.87	212.00
13	75	11.8	173	0.659	4.54	557.00
14	75	11.8	173	0.659	3.28	376.00
15	75	10.2	164	0.591	1.89	160.00
		Yellow poplar heartwood (G = 0.43)				
16	22	10.3	204	0.368	0.23	1.07
17	22	9.6	190	0.360	2.32	--
18	22	9.8	190	0.352	0.11	2.61
19	22	10.5	186	0.395	1.33	2.03
		Red oak heartwood (G = 0.74)				
20	22	14.0	93	0.694	0.293	13.90
21	22	15.7	85	0.700	0.353	29.60
22	22	14.5	90	0.692	1.20	30.50
23	75	18.4	101	1.09	1.70	229.00
24	75	18.9	97	1.08	4.94	276.00
25	75	20.9	95	1.25	46.1	329.00
26	75	20.5	91	1.20	19.3	375.00
		Black walnut heartwood (G = 0.54)				
27	22	10.0	146	0.435	0.119	7.46
28	22	11.0	144	0.471	0.213	6.95
29	22	9.9	134	0.434	0.201	10.40
30	22	11.7	146	0.538	0.242	7.00
31	22	10.8	140	0.495	0.296	11.90
32	75	13.9	140	0.761	0.272	5.10
33	75	13.5	134	0.760	0.262	3.93
34	75	14.6	126	0.822	0.199	--

a/ Samples averaged 8% initial moisture content.

where V_w is the initial volume of the wood at M_i and V_L is the volume of inlet water.

Volumetric changes in the samples are measured directly from the glycerol tube at different time intervals. Swelling relative to M_i is:

$$S' = \frac{\Delta V_w}{V_w} \times 100 \ , \qquad (22)$$

where ΔV_w is the volume of glycerol displaced, which is equal to the change in wood volume.

The bound moisture uptake is determined from the swelling measurements. Combination of Eqs. 14, 15, and 18 yields the relationship relating bound moisture uptake to swelling:

$$M_B = \frac{S' \ (1 + 0.01 \ KM_i)}{K} \ . \qquad (23)$$

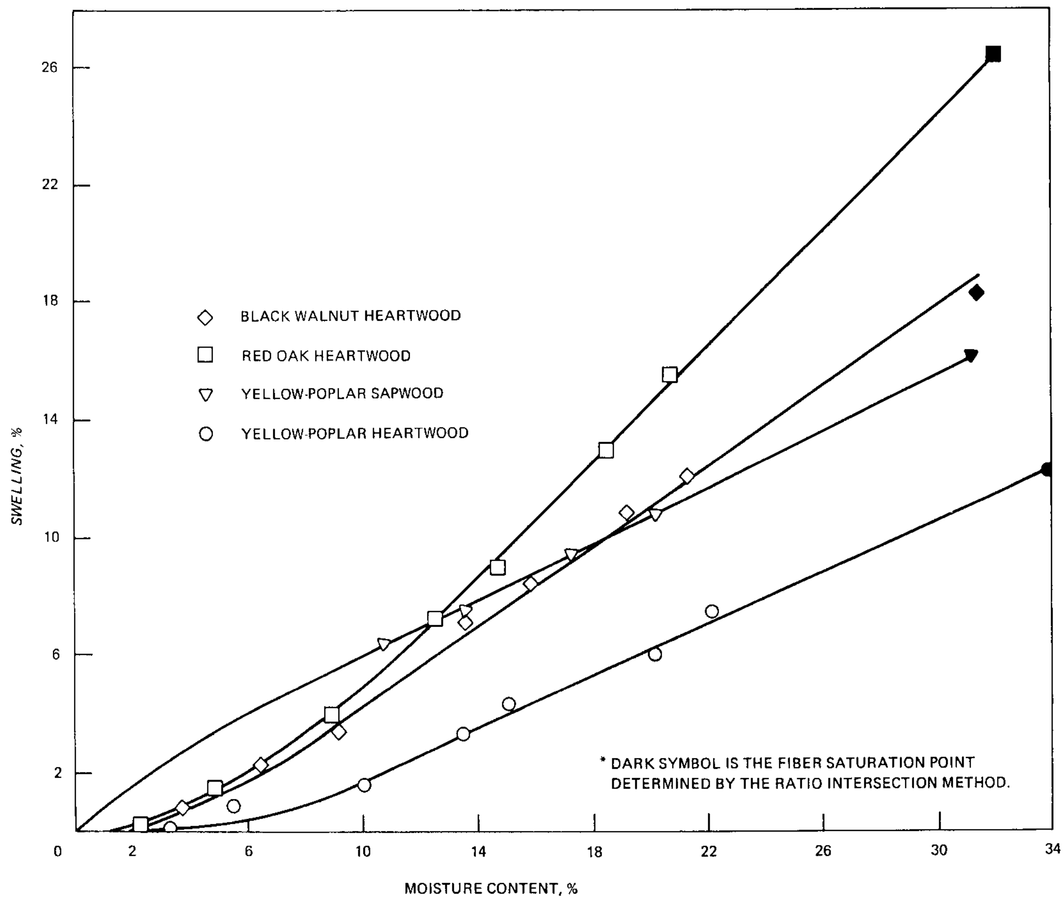

FIG. 2. Moisture content vs. swelling for once-dried specimens at 27 C.

Following from Eq. 2, the free moisture is the difference between M_T and M_B.

For determination of penetration constants, Eqs. 7 and 8 are rearranged:

$$\bar{P}_B = \pi \left[\frac{L}{2(M_{fsp} - M_i)}\right]^2 \frac{M_B^2}{t} \qquad (24)$$

$$\bar{P}_F = \pi \left[\frac{L}{2(M_m - M_{fsp})}\right]^2 \frac{M_F^2}{t} . \qquad (25)$$

RESULTS AND DISCUSSION

Justification for the assumption of a linear relationship between volumetric swelling and moisture content using the thin wafers is shown in Fig. 2. Each point is the average of eight replicates. The curve for black walnut was determined by Cooper (1974). Except for the initial portion of the curves (0 to 6% moisture content), there is a linear relationship between swelling and moisture content. Since the samples observed during water penetration in this study are about 8% initial moisture content, K can be assumed a constant for each run.

The fiber saturation point of once-dried wood is determined by the extension of the adsorption/swelling ratio to unit vapor pressure as described by Cooper (1974). The values for 27 C are given in Table 2 and shown plotted in Fig. 2. The fiber saturation point is know to decrease with temperature at approximately 0.1%/°C (Stamm 1935). This correction has been applied to the M_{fsp} for calculation of P_B and P_F in Table 1.

TABLE 2. *Fiber saturation point for once-dried woods at 27 C by the ratio intersection method*

Species and type	Fiber saturation point
Yellow poplar sapwood	31.2
Yellow poplar heartwood	33.9
Black walnut heartwood	31.3[a/]
Red oak heartwood	32.0

a/ Determined by Cooper (1974)

The normal method for determining the value of maximum swelling (S_m in Table 1) is to determine that value of swelling when no further volume change takes place as more water penetrates the wood. In some runs where the maximum swelling had not been reached by the end of a run, the values were obtained by extrapolation of the swelling data.

Following from Eqs. 7 and 8, plots of the square root of time versus M_B and M_F should each yield a straight line. Values of $\overline{P}_B$ and $\overline{P}_F$ have been calculated from Eqs. 24 and 25 using M_B^2/t or M_F^2/t as

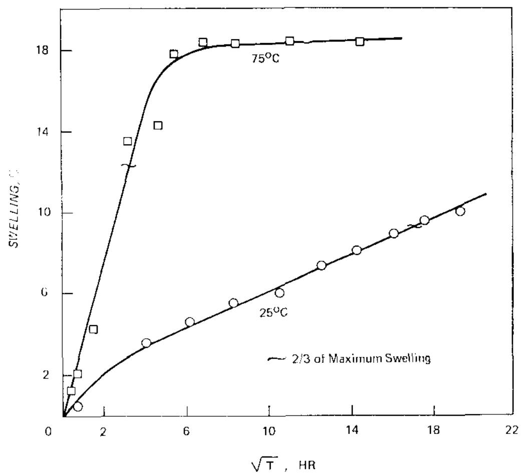

FIG. 4. Red oak heartwood swelling data at various temperatures (G = 0.73 at 9% initial moisture content).

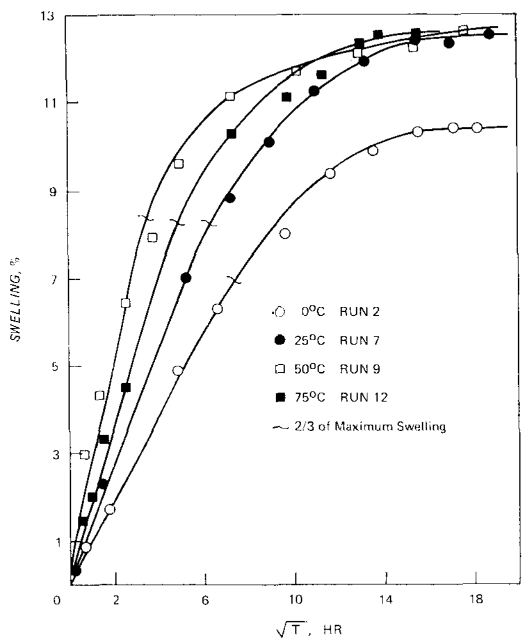

FIG. 3. Yellow poplar sapwood swelling data at various temperatures (G = 0.48 at 8% initial moisture content).

equal to the square of the slope of the line up to two-thirds of the maximum values of M_B or M_F. Rather than show average values for $\overline{P}_B$ and $\overline{P}_F$ at each set of conditions, the results have been presented for all runs (Table 1).

The penetration Eqs. 7 and 8 for bound and free moisture fit the data very well for penetration of water into the wood specimens used in this study. The regressions of liquid uptake on the square root of time up to two-thirds of the maximum uptake were all significant at the 5% level. The percentage of the data accounted for by variation about the regression line (R^2) was above 90% in all but a few cases. In the case of the few lower R^2 values, experimental difficulties such as a drop in pressure of the glycerol air bleed could have caused the increased scatter in the data.

Equation 23 predicts linearity between swelling and bound moisture untake. It follows from Eq. 7 that a plot of the square root of time versus swelling should initially yield a straight line. Sample plots of swelling, M_B, M_F, and M_T, against the square root of time are shown in Figs. 3 to 6.

The penetration rate of water both in different hardwood species and in different types of wood within the same species is

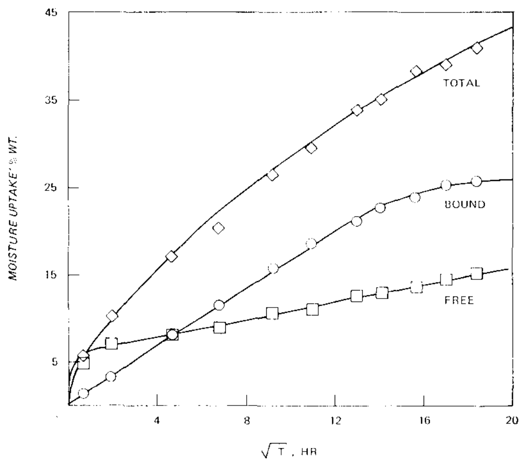

FIG. 5. Penetration of water in yellow poplar sapwood at 0 C (G = 0.51 at 8% initial moisture content).

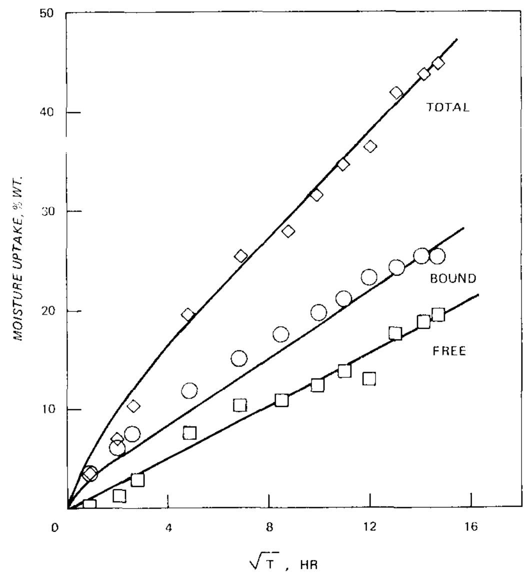

FIG. 6. Penetration of water into black walnut heartwood at 75 C (G = 0.55 at 8% initial moisture content).

widely variable. For example, although the specific gravities for YPS and BWH are similar, there is a large difference in $\overline{P}_B$ and $\overline{P}_F$ (Table 1). There is a marked difference in the penetration of water, especially free water, in the sapwood as compared to the heartwood of yellow poplar (Table 1, 22 C). Free water penetration is considerably faster in the sapwood. These results agree with permeability studies that show the heartwood in many woods to be much less permeable than the sapwood (Stamm 1964).

The vessels in hardwood provide a large canal for water to penetrate the wood rapidly. Water was observed at the bottom of a 10-cm sample in many runs with ROH and YPS within seconds after a run was initiated. The initial surge of water in YPS, as seen by the initial jump in free moisture (Fig. 5), is not as pronounced in black walnut (Fig. 6). The reason for this difference is that ROH and YPS have large interconnecting vessels without obstructions to block the direct flow of liquids. Tyloses are present in BWH to block the flow (Panshin and de Zeeuw 1964). The initial uptake surge does not add appreciably to the overall moisture content, but does provide avenues for easier penetration throughout the wood specimen.

The results of this study confirm the initial linear proportionality of total water uptake with the square root of time as found by Stamm (1953) when studying the softwood, Sitka spruce. The softwoods have no vessels, and thus the initial surge of water uptake would be minimal as in black walnut. The proportionality of water uptake with the square root of time will hold until two-thirds of the volumetric swelling (which is the same as two-thirds of the bound moisture uptake) is complete. Since the total moisture is the sum of the bound moisture and free moisture and both uptakes are linear with the square root of time, it follows that the total moisture uptake is also linear.

The effect of temperature on $\overline{P}_B$ and $\overline{P}_F$ appears complicated and generalities for one species do not hold for others. Only the penetration of YPS was observed at more than two temperatures.

The values of $\overline{P}_B$ seem to reach a peak at about 50 C and then fall back slightly as the temperature is increased (Fig. 7). The values of $\overline{P}_F$ increase with increasing temperature. The surprising decrease in $\overline{P}_B$ above 50 C may possibly be explained by

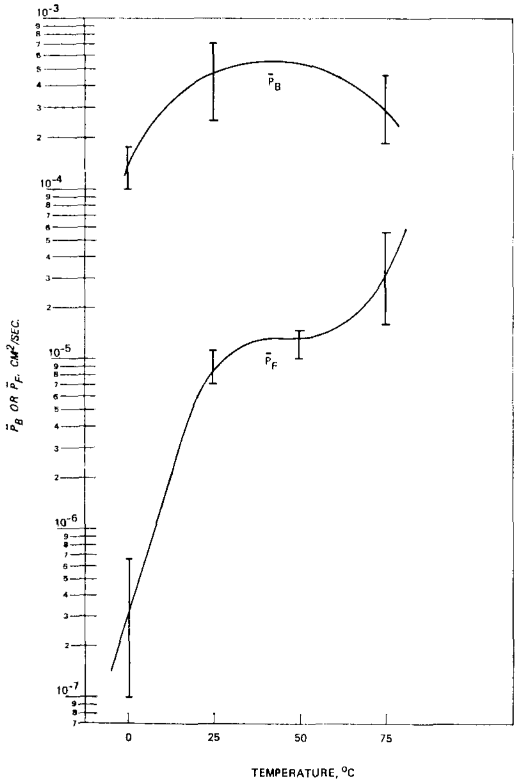

FIG. 7. Temperature dependence of $\bar{P}_B$ and $\bar{P}_F$ for yellow poplar sapwood.

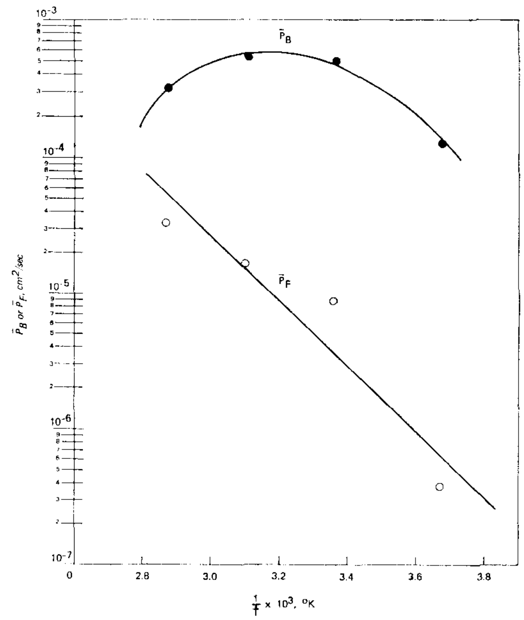

FIG. 8. Logarithm of bound and free moisture penetration constants against reciprocal temperature for yellow poplar sapwood.

the occurrence of localized stresses as temperature increases and the moisture gradient steepens. The contribution to $\bar{P}_B$ of increasing diffusion rates with increasing temperature might be more than offset by localized stresses above 50 C. Barkas (1949) has shown that equilibrium moisture content can be decreased by application of mechanical stress. Evidence that uneven moisture gradients in wood can cause internal stresses that affect diffusion rates has been presented by Comstock (1963). Thus, internal stresses, such as those observed by Comstock, slow the movement of bound moisture in the wood until the stresses are relieved and thus retard the overall movement of bound moisture.

The values of $\bar{P}_B$ and $\bar{P}_F$ are averaged for each temperature and plotted against the reciprocal of the absolute temperature in Fig. 8. The $\bar{P}_B$ values clearly do not give a straight line, indicating that bound liquid penetration is not an activated process. Conversely, the free liquid penetration gives a straight line with an activation energy of 10,900 cal/mole. This value is similar to the activation energy of 8,400 cal/mole found by Stamm (1967) investigating drying diffusion constants for a number of wood species.

As seen in Table 1, ROH shows a significant increase in both $\bar{P}_B$ and $\bar{P}_F$ as temperature is increased from 22 to 75 C; whereas BWH showed very little change in $\bar{P}_B$ and a slight decrease in $\bar{P}_F$. Different penetration phenomena than that of YPS appear to be controlling for BWH.

By showing that at different temperatures the ratio of vapor pressures of water was approximately equal to the ratio of adsorption times for a fixed percentage of moisture uptake, Stamm (1953) concluded that the uptake of water in Sitka spruce heartwood was controlled by diffusion. Similar calculations from the data of this study show that although ROH behaves much like Sitka spruce, BWH and YPS do not. The

TABLE 3. *Comparison of experimental bound moisture penetration constant with theoretical combined water-vapor diffusion constant*

Run	Temperature °C	Wood[a]	$\bar{P}_B$ cm ^{2}/sec x 10^4	D_{gL}[b] cm ^{2}/sec x 10^4	Ratio $\bar{P}_B/D_{gL}$
1	0	YPS	1.0	0.044	23
7	25	YPS	2.5	0.11	23
9	50	YPS	5.5	0.34	16
14	75	YPS	3.3	1.1	3
18	22	YPH	0.11	0.13	1
20	22	ROH	0.29	0.047	6
23	75	ROH	1.7	0.71	2
27	22	BWH	0.12	0.11	1
33	75	BWH	0.26	0.51	1

a/ YPS = yellow poplar sapwood, YPH = yellow poplar heartwood, ROH = red oak heartwood, BWH = black walnut heartwood.
b/ Calculated from Equation 6.20, p. 94, Siau (1971).

ratios of adsorption times for a fixed percentage of moisture uptake are lower than the ratio of vapor pressures at different temperatures for BWH and YPS. It cannot be concluded that diffusion controls the rate of water uptake for BWH and YPS.

The swelling in wood is affected to varying degrees in the different species by a change in temperature (Table 4). The swelling of each species has been corrected for specific gravity and initial moisture content in each case. Each swelling value is an average of the corrected values in Table 1 for each temperature. The greatest change was observed for ROH—over 20% increase in maximum swelling from 22 to 75 C.

The contribution of the combined diffusion of water and water vapor through both wood substance and void space to the bound water uptake is shown in Table 3. A theoretical longitudinal bound water-vapor diffusion coefficient, D_{gL}, is calculated from an equation derived by Siau (1971). A sample run from each set of conditions is used to compare D_{gL} with $\bar{P}_B$. The lowest value of $\bar{P}_B$ is chosen to give the lowest ratio of P_B/D_{gL}. For a fixed temperature of 22 C, the $\bar{P}_B$ for YPH and BWH appear to be controlled by D_{gL}; whereas for YPS and ROH, D_{gL} contributes only a small portion to the overall bound water movement. The results are consistent with the earlier findings. ROH and YPS are more accessible to water because of the open vessel elements. In this case the movement of bound water by capillarity is more important than the contribution of combined bound water-vapor diffusion. As the temperature is increased, the relative contribution of capillarity decreases as can be seen for YPS. At 75 C more of the bound liquid movement is explained by D_{gL} than at 0 C. The D_{gL} values are only approximate, so the ratios P_B/D_{gL} are rounded to the nearest whole number.

There have been several papers in the literature with data of direct relevance to the longitudinal penetration of water in wood. These are summarized in Table 5. Values of $\bar{P}_B$ were calculated from swelling data (Table 5). Statistical fit for all data was significant at the 5% level with all R^2 greater than 85%. Values of $\bar{P}_F$ could not be calculated in that either uptake data was not reported or it was not taken on the same sample as the swelling data.

TABLE 4. *Relationship between maximum swelling and temperature*

Species	G[a]	Temperature °C	Swelling %[b]
YPS	0.50	0	10.7
	0.50	22	12.0
	0.50	25	12.5
	0.50	50	12.7
	0.50	75	12.4
ROH	0.75	22	16.1
	0.75	75	20.6
BWH	0.55	22	12.0
	0.55	75	13.2

a/ Corrected to 8% initial moisture and deviations from G.
b/ Average values.

TABLE 5. *Comparative penetration data*

Type of heartwood	Temperature °C	M_{fsp} % weight[a]	M_i	$\bar{P}_B$ cm ^{2}/sec x 10^4	D_{gL} cm ^{2}/sec x 10^4[b]
Sitka spruce [c]					
(G = 0.42, L = 1.90 cm)	4	32.8	0	0.206	0.09
	30	30.2	0	0.840	0.31
	64	26.8	0	2.78	1.6
	90	24.2	0	5.32	4.9
Western white pine[d]					
(G = 0.40, L = 0.6 cm)	25	28.7	0	0.781	0.32
Englemann spruce[e]					
(G = 0.29, L = 0.3 cm)	20	30.0	0	1.62	0.32
	20	30.0	5	1.12	0.28
	20	30.0	9	1.30	0.25
	20	30.0	14	1.27	0.21
	20	30.0	18	1.05	0.19
	20	30.0	25	0.177	0.15

a/ Values obtained from Stamm (1964) and corrected for temperature.
b/ Calculated from Equation 6.20, p. 94, Siau (1971).
c/ Stamm (1953).
d/ Stamm and Petering (1940).
e/ Hittmeier (1967).

The literature results summarized in Table 5 confirm many of the findings in this study. The values of $\bar{P}_B$ are all more than the theoretical values of D_{gL} calculated for each set of conditions; thus, capillarity is significant for the transport of bound moisture in these woods. As the temperature is increased, the values of D_{gL} more closely approach $\bar{P}_B$, indicating that capillarity becomes less significant for bound moisture transfer at higher temperatures. The value of $\bar{P}_B$ at 0% initial moisture content and 20 C for the less dense Engelmann spruce is greater than the more dense white pine at 25 C—just the opposite would be predicted from theory if the combined water-vapor diffusion controlled the penetration.

Insight into the dependence of initial moisture content on $\bar{P}_B$ can be obtained from Hittmeier's data (1967). The value is high at low moisture content, relatively constant from 5 to 18% moisture content, and then lower at higher moisture content (Table 5). The value of $\bar{P}_B$ is almost equal to D_{gL} at the highest moisture content, indicating that capillarity is less significant for the transfer of bound moisture at higher moisture content.

CONCLUSIONS

The mathematical relationships and theory developed for the penetration of water into wood are applicable to the longitudinal penetration of water into once-dried wood. Bound and free moisture penetration constants can be evaluated directly from water uptake and swelling data obtained from a swelling cell at various time intervals. The bound moisture uptake is found to be proportional to the square root of the time it takes for bound moisture to rise from the initial moisture content to two-thirds of the fsp. Similarly, free moisture uptake is found to be proportional to the square root of the time free moisture takes to rise from the fsp to the maximum moisture content.

An increase in temperature will not necessarily increase the rate of penetration of water into some hardwoods, such as BWH.

In comparing theoretical values of combined bound vapor-water diffusion constants with bound moisture penetration constants, it has been observed that:

1. The influence of capillarity as the means of bound water transport decreases with increasing temperature; at higher temperatures combined bound vapor-water

diffusion is the principal means of bound water movement.

2. In wood with obstructed vessels as in BWH and YPH, the combined vapor-water diffusion is the principal means of bound water movement. Capillarity becomes more important for the transport of bound water when the vessels are unobstructed as in YPS and ROH.

REFERENCES

Barkas, W. W. 1949. The swelling of wood under stress. Her Majesty's Stationery Office, London.

Comstock, G. L. 1963. Moisture diffusion coefficients in wood as calculated from adsorption, desorption, and steady state data. For. Prod. J. 13(3):97–103.

Cooper, G. A. 1974. The effect of black walnut extractives on sorption, shrinkage, and swelling. Wood Sci. 6(4):380–388.

Crank, J. 1956. The mathematics of diffusion. Clarendon Press, London.

Hart, C. A. 1964. Principles of moisture movement in wood. For. Prod. J. 14(5):207–214.

Hittmeier, M. E. 1967. Effect of structural direction and initial moisture content on swelling rate of wood. Wood Sci. Technol. 1(2): 109–121.

Moschler, W. W., and R. E. Martin. 1968. Diffusion equation solutions in experimental wood drying. Wood Sci. 1(1):47–57.

Panshin, A. J., and C. de Zeeuw. 1964. Textbook of wood technology. 1, 3rd ed. McGraw-Hill Book Co., New York.

Rosen, H. N. 1973. Continuous measurement of the swelling of wood. For. Prod. J. 23(3): 55–57.

Siau, J. F. 1971. Flow in wood. Syracuse Univ. Press, Syracuse, N. Y.

Stamm, A. J. 1935. Thermodynamics of the swelling of wood. J. Phys. Chem. 39(1): 121–132.

———. 1953. Diffusion and penetration mechanism of liquids into wood. Pulp Paper Mag. Can. 54(2):54–63.

———. 1959. Bound-water diffusion into wood in the fiber direction. For. Prod. J. 9(1): 27–32.

———. 1960. Combined bound-water and water vapor diffusion into Sitka spruce. For. Prod. J. 10(12):644–648.

———. 1964. Wood and celluose science. Ronald Press, New York. 549 pp.

———. 1967. Movement of fluids in wood. Part II. Diffusion. Wood Sci. Technol. 1(3): 205–229.

Stamm, A. J., and W. H. Petering. 1940. Treatment of wood with aqueous solutions: effect of wetting agents. Ind. Eng. Chem. 32: 809–813.