SORPTION OF MOISTURE BY WOOD WITHIN A LIMITED RANGE OF RELATIVE HUMIDITIES

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ABSTRACT

Information on wood sorption behavior provides desorption and adsorption curves from the green and fully dry initial conditions, respectively. Wood in service, however, is exposed to only a narrow range of relative humidities (RH) and, therefore, should exhibit intermediate isotherms that are different from those of the full isotherms. This paper presents the results of a study performed to establish the intermediate desorption curves at 30 C for yellow poplar wood samples subjected to RH ranges of 92% to 0%, 75% to 0%, 53% to 0%, and 32% to 0%. The desiccator method was used to establish the full desorption curve, while a high-vacuum system was employed to obtain the full adsorption and the four intermediate desorption curves. The desired relative humidities were maintained by saturated salt solutions.

The generated intermediate desorption curves all fall within the full adsorption and desorption isotherms, with the isotherms originating from 92%, 75%, 53%, and 32% RH tracing progressively lower curves. These isotherms exhibit relatively short crossovers; a 40% RH change being needed for an intermediate desorption curve to cross over from the full adsorption isotherm to the full desorption isotherm. The intermediate curve from 92% RH has the characteristic sigmoidal shape, but those from 75%, 53%, and 32% RH are concave towards the X-axis. All the intermediate curves exhibit hysteresis, even at low RH levels and narrow RH ranges.

Keywords: Sorption, adsorption, desorption, isotherm, hysteresis.

INTRODUCTION

Wood in use is constantly subjected to cyclic humidity changes. Being a hygroscopic material, it gains or loses moisture with the fluctuating atmospheric humidity. The curve relating the moisture content (MC) of wood with the relative humidity (RH) at a constant temperature is called the sorption isotherm. It is a well-known fact that the sorption curve obtained when wood is losing moisture (desorption isotherm) does not coincide with the curve when the wood is gaining moisture (adsorption isotherm)—that is, moisture sorption exhibits the phenomenon called hysteresis. At any given temperature and relative humidity, the adsorption equilibrium moisture content (EMC) is lower than the corresponding desorption EMC (Fig. 1).

Existing data on the sorption behavior of wood provide desorption and adsorption curves from the green and fully dry initial conditions, respectively. Wood in actual use, however, is exposed to only a very narrow range of relative humidities and, therefore, should exhibit isotherms different from the full cycle isotherms. Studies on hygroscopic materials other than wood show that intermediate sorption curves are formed between those for the full-cycle adsorption and desorption when the direction of sorption is reversed at points between 0 and 100% relative humidity. There is no abrupt jump from the full adsorption curve to the full desorption curve but rather a smooth crossover occurs. A representative intermediate isotherm for textile materials is given by curve C in Fig. 2. Morton and Hearle (1975) pointed out that the intermediate curves for cotton are very long, such that if adsorption is started from 10% RH on the desorption curve, the complete adsorption curve will not be

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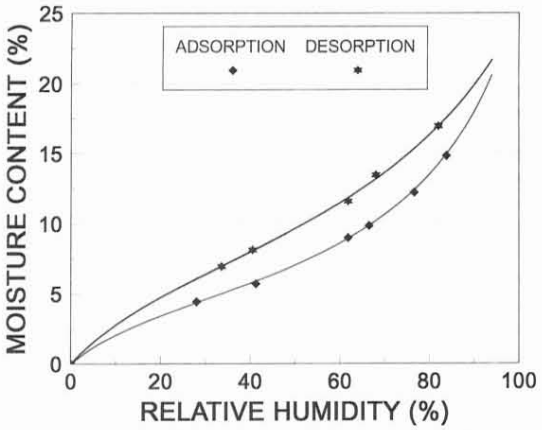

FIG. 1. Desorption and adsorption isotherms fitted to yellow poplar sorption data at 30 C. (From: Peralta 1990)

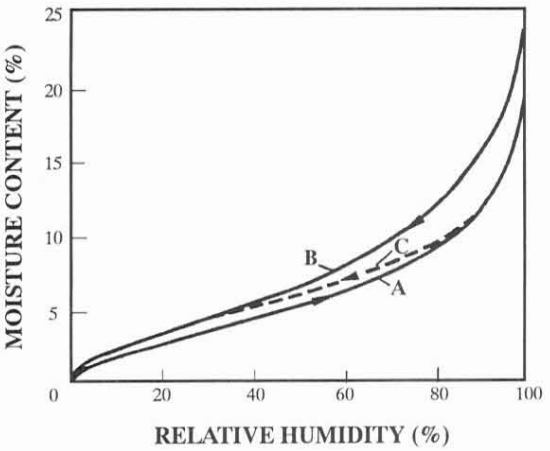

FIG. 2. Illustration of an intermediate isotherm (C) relative to the full adsorption (A) and desorption (B) curves. (From: Morton and Hearle 1975)

joined below 80% RH. In contrast, the intermediate curve for wool is shorter, a change of 18% RH being sufficient to pass between the complete sorption isotherms (Speakman and Cooper 1936). This phenomenon of "crossing over" of an intermediate curve has similarly been observed in food (Labuza 1984) and soil systems (Jury et al. 1991).

Although studies on the moisture sorption behavior of wood are quite extensive, literature search reveals that no investigation has ever been conducted to elucidate the nature and behavior of the intermediate sorption curves. Hence a study was designed and conducted to generate information on this particular area of wood-moisture relationship. In this paper, the results of experiments performed to establish the desorption curves for wood subjected to narrower relative humidity ranges are presented. The data will supplement available information provided by the complete sorption curves. It is expected that the results will be of practical importance to the wood products industry.

MATERIALS AND METHODS

Green 6/4-in. yellow poplar (*Liriodendron tulipifera* L.) boards were obtained from a local sawmill and stored in a cold chamber maintained at −20 C to keep the moisture content at the green condition until needed. From these boards, samples measuring 7 mm (L) × 50 mm (R) × 50 mm (T) were obtained for the full desorption experiments. Thirty-six such samples were partitioned randomly into nine sets of four samples, each set being allocated to one of nine different RH conditions maintained inside a desiccator by a saturated salt solution. The different salt solutions used in this study, together with their corresponding RH at 30 C, are given in Table 1. The samples were oven-dried at 103 ± 2 C for at least 24 hours, then allowed to gain moisture up to above the fiber saturation point by dipping them in water several times until the computed moisture content was above 50%. The rewetted samples were then introduced into the desiccators to obtain the full desorption curve. Two additional samples were likewise prepared and placed inside a bell jar where the relative humidity was maintained by a saturated lithium chloride solution. The desiccators and the bell jar were then kept inside a chamber maintained at 30 C for at least 30 days until the samples had attained equilibrium. Equilibrium was determined by monitoring the weights of the two samples inside the bell jar. Once equilibrium was attained, the equilibrium and oven-dry weights were determined to within 1 mg to allow calculation of the moisture contents.

Except for the full desorption studies, all

other sorption experiments were performed entirely in a vacuum system using samples with dimensions of 2 mm (L) × 15 mm (R) × 45 mm (T). If the experiments were performed exclusively using the desiccator method, it would have taken at least 6 years to complete the study. The vacuum-type setup allowed equilibration time to be reduced from 35 days to only 3 days, hence reducing the total experimental time to about a year.

The schematic diagram of the high-vacuum apparatus, which was designed and constructed for this study, is presented in Fig. 3. Except for the sorption cells and the salt solution flasks which are made of pyrex glass, the system components are all made of stainless steel of size NW16, with all fittings conforming to the KF (small flange) standard of the International Organization for Standardization (ISO). The O-rings in all junction flanges are of the viton type. Individual samples were suspended on a calibrated quartz helical spring whose extension was measured to within 0.01 mm by a cathetometer attached to a digital height gauge. Since the load-extension relationship for each of the springs was shown to be linear, the moisture content was calculated from the extension of the spring at the unknown moisture content and the extension at completely dry condition. The latter extension was the constant value attained on continuous evacuation at a pressure of less than 10^{-4} mm Hg at 30 C. The temperature inside the sorption cells was maintained to within ±0.1 C by circulating water through the cylindrical jackets of the sorption cells. Additional temperature control was provided by enclosing in a temperature-controlled chamber the part of the experimental setup bounded by the dashed box in Fig. 3. To minimize the disturbance of the chamber temperature, the heat-insulated chamber door was provided with a pair of gloved ports for manipulation of the valves and other items inside.

The source of water vapor for the sorption experiments was a flask of the desired saturated salt solution connected through a series of valves to the sorption cells. To assure saturation, the solution was continuously agitated by a teflon-coated magnetic bar driven by a magnetic stirrer. The first salt solution was held through several cycles of vacuum to remove any dissolved gases by opening the valve (#2) leading to the vacuum pumps while keeping valves #1, #3, #4, and #5 closed. Next, valve #2 was closed and the sorption cells were evacuated to less than 10^{-4} mm Hg by opening valve #1. After the sorption system was isolated from the vacuum pumps (by closing valve #1), the valve (#4) connecting the first salt solution to the sorption cells was opened. While the sample was equilibrating at the first relative humidity condition, the salt solution that would supply the water vapor for the next RH level was placed under vacuum to remove dissolved gases by opening valve #3. Once the second salt solution was fully evacuated and the sample had attained equilibrium at the first RH level, valves #3 and #4 were closed and valve #5 was opened to establish the next RH value. The whole process was repeated for the other salt solutions in the series. In all experiments, the relative humidity was changed at intervals of approximately 10% using the saturated salt solutions shown in Table 1. At a given RH level, at least 3 days were allowed for the attainment of equilibrium, in each case equilibrium being assumed when the moisture content remained constant overnight.

Evacuation was accomplished by an oil-diffusion pump backed by a rotary-vane roughing pump. These pumps form a two-stage arrange-

TABLE 1. *Relative humidities at 30 C maintained by the different salt solutions used in this study.*[a]

Salt solution	Relative humidity at 30 C
Lithium chloride	11%
Potassium acetate	22%
Magnesium chloride	32%
Potassium carbonate	43%
Sodium bromide	53%
Sodium nitrite	63%
Sodium chloride	75%
Potassium chloride	84%
Potassium nitrate	92%

[a] From Labuza (1984).

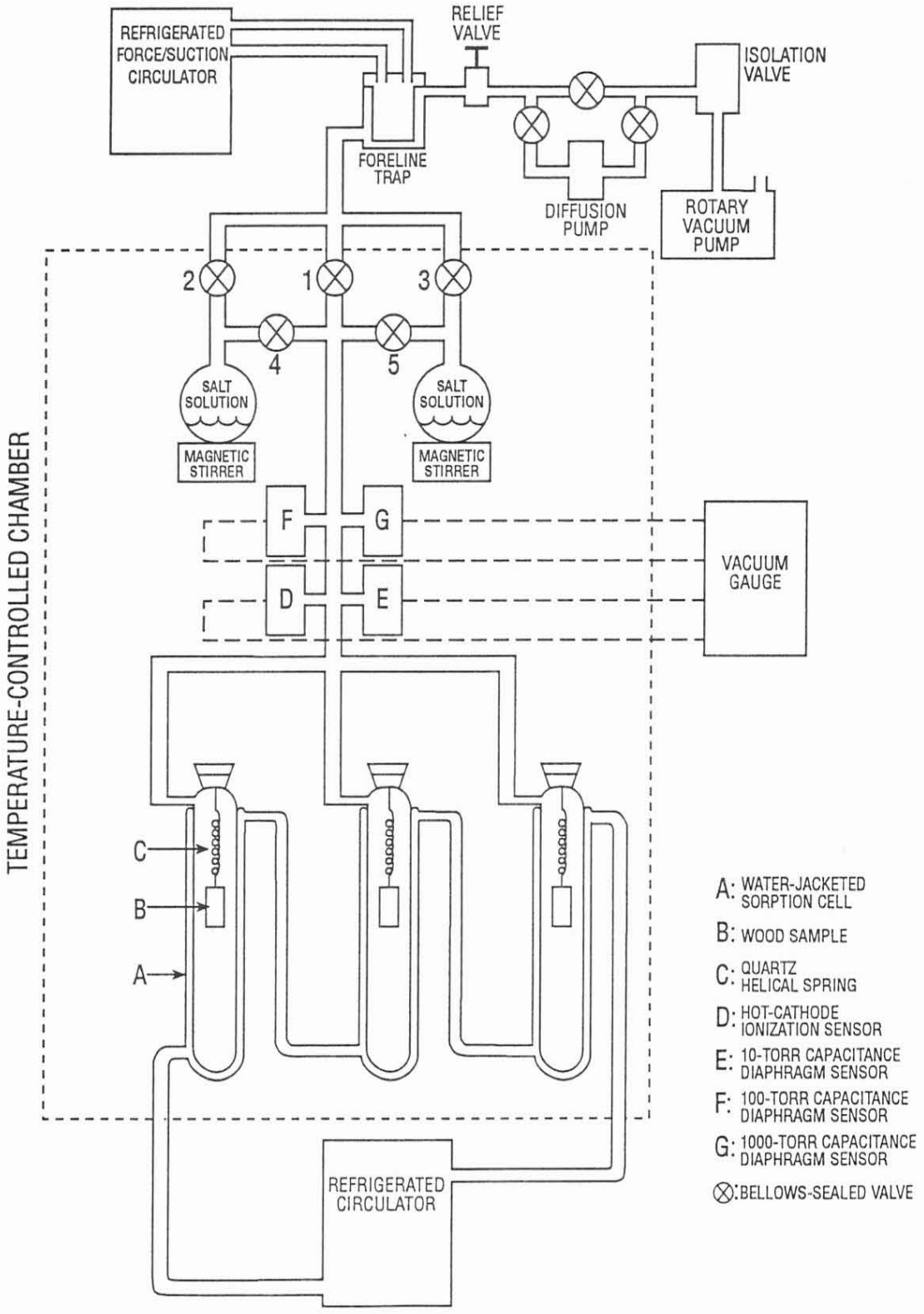

FIG. 3. Schematic diagram of the high-vacuum sorption system used in the study.

ment providing an ultimate vacuum of 10^{-6} mm Hg. A foreline trap maintained at −15 C by a refrigerated bath circulator prevented condensable vapors from entering the pump and acted as a safeguard against backstreaming of the pump oil into the sorption apparatus. Measurements of the magnitude of the vacuum established in the system and of the vapor pressure maintained by the various salt solutions were provided by four different sensors connected to a vacuum gauge. A glass-tubulated hot-cathode ionization sensor covered the range from 10^{-10} to 10^{-2} mm Hg; while the 10-torr, 100-torr, and 1,000-torr capacitance diaphragm manometers covered the range from 10^{-3} to 10^{+1} mm Hg, 10^{-2} to 10^{+2} mm Hg, and 10^{-1} to 10^{+3} mm Hg, respectively.

The first step in the determination of isotherms using the vacuum method was to subject the samples loaded in the sorption cells to a vacuum of less than 10^{-4} mm Hg to completely dry the samples. The full adsorption curve was established by exposing the dried samples to successively increasing RH values of about 10% increments from 0 to 92%. The intermediate desorption curves were obtained by preconditioning different sets of the dried samples to different initial moisture contents corresponding to relative humidities of 92%, 75%, 53%, and 32% on the full adsorption curve—that is, the dried samples were allowed to reabsorb moisture stepwise until the desired initial EMC was attained. Then, the sorption process was reversed by exposing the samples to successively reduced humidity stages of about 10% decrement down to 11% RH. Finally, the vapor supply was cut off while the vacuum was sustained to get the dry weights of the samples. Four replicates were used in each of the equilibrium conditions. The samples were allocated randomly among the different experimental treatments. In all, a total of 53 equilibrium RH conditions at 30 C were established.

RESULTS AND DISCUSSION

The average moisture contents of the four replicates at the different relative humidities and sorption histories are shown in Table 2. Figure 4 presents the curves fitted to these experimental data points. For its simplicity and proven good performance when applied to the full sorption data (Okoh 1976; Simpson 1980), the Hailwood-Horrobin single-hydrate model was used in fitting the curves to the full sorption points and to the 92–0% RH intermediate desorption data. This was accomplished by performing nonlinear regression analyses using the Marquardt option of the NLIN procedure in the Statistical Analysis System package (SAS 1990). The same statistical software was employed in performing linear regression analyses to fit equations of a quadratic form to the other intermediate isotherms.

Figure 4 shows that the intermediate desorption curves all fall within the full adsorption and desorption isotherms, with the intermediate isotherms originating from 92%, 75%, 53%, and 32% relative humidity tracing progressively lower curves. The data indicate, as Urquhart (1960) has concluded for textile materials, that at a particular temperature, the full curves define the limiting equilibrium values and thus may be viewed not as equilibrium loci but as borders that outline the hysteresis area. Hence, the full cycle isotherms should be aptly referred to as boundary isotherms. Any point within the hysteresis region may be reached depending upon the condition to which the material is initially subjected. The temperature and relative humidity to which a piece of wood is exposed do not uniquely define the equilibrium moisture content of the material. It is also necessary to specify the sorption history of the wood specimen.

It is evident in Fig. 4, that wood exhibits a relatively short crossover of the intermediate curves from the boundary adsorption isotherm to the boundary desorption isotherm. It takes about a 40% RH change before the intermediate desorption isotherms join the boundary desorption curve. This crossover for wood is much shorter than that for cotton (70% RH change) but longer than that for wool (18% RH change). Just as in the above textile fibers, the length of the crossover for wood is indepen-

TABLE 2. *Average moisture contents of four replicates at the different relative humidities and sorption histories.*[a] *Also included are the Hailwood-Horrobin and quadratic equation parameters for the sorption curves.*[b]

	Full adsorption	Full desorption	Intermediate			
			92	75	53	32
Relative humidity						
11	2.61	3.19	3.16	3.11	3.06	2.98
22	4.19	5.18	5.14	5.00	4.83	4.62
32	5.39	6.67	6.62	6.50	6.17	5.39
43	6.86	8.48	8.41	8.19	7.54	—
53	8.27	10.19	10.11	9.73	8.27	—
63	9.77	11.96	11.84	11.00	—	—
75	12.44	14.81	14.46	12.44	—	—
84	15.88	18.68	17.25	—	—	—
92	20.91	23.69	20.91	—	—	—
Equation parameter						
M_p	362.677	271.887	241.798	—	—	—
K_1	8.538	7.913	6.497	—	—	—
K_2	0.828	0.793	0.722	—	—	—
A	—	—	—	0.3243	0.1577	0.0226
B	—	—	—	0.2233	0.2573	0.3120
C	—	—	—	−0.0084	−0.0020	−0.0045

[a] Intermediate 92, 75, 53, and 32 refer to the intermediate desorption curves whose reversal points correspond to relative humidities of 92, 75, 53, and 32%, respectively.
[b] M_p, K_1, and K_2 are the Hailwood-Horrobin parameters in Eq. (1); A, B, and C refer to the parameters in Eq. (2).

dent of the reversal point on the adsorption curve. Beyond the 40% RH range, the deviation of the intermediate desorption EMC from the boundary desorption EMC is less than 0.2% for all four intermediate curves. The significance of these results lies in the fact that if the immediate history of a piece of wood is not known, it is imperative to precondition the sample in an atmosphere at least 40% RH higher than the desired value. This is done in order to obtain a final moisture content that would fall on either of the two boundary curves, the most easily repeatable and well-documented points of the hysteresis region. For instance, if it is desired to study the mechanical property at 30 C and 65% RH of two pieces of wood of unknown history, substantial error in moisture content may be introduced if the samples are immediately conditioned at 65% RH. If one sample is initially in equilibrium with an atmosphere at 30 C and 75% RH on the adsorption curve and the other sample is green, conditioning them at 30 C and 65% RH will yield an EMC of 11.15% and 12.4%, respectively (see Fig. 4). Comparison of the strength properties of the two samples will be erroneous because of the difference in moisture content. In this example, since 65% + 40% is higher than 100%, the samples must first be presoaked in water.

Of the intermediate curves generated, only the one traced upon sorption reversal at 92% RH showed the characteristic sigmoidal shape of the complete boundary isotherm. The Hailwood-Horrobin equation was successfully fitted to these data points, achieving convergence in less than 10 iterations. Table 2 gives the parameters for the Hailwood-Horrobin equation shown below:

$$MC = \frac{1{,}800}{M_p}\left(\frac{K_1K_2RH}{100 + K_1K_2RH} + \frac{K_2RH}{100 - K_2RH}\right) \quad (1)$$

where M_p is the molecular weight of wood per mole of sorption sites, K_1 the equilibrium constant between the reaction product (hydrated wood) and the two reactants (water and dry wood), and K_2 the equilibrium constant between water vapor and dissolved water. The

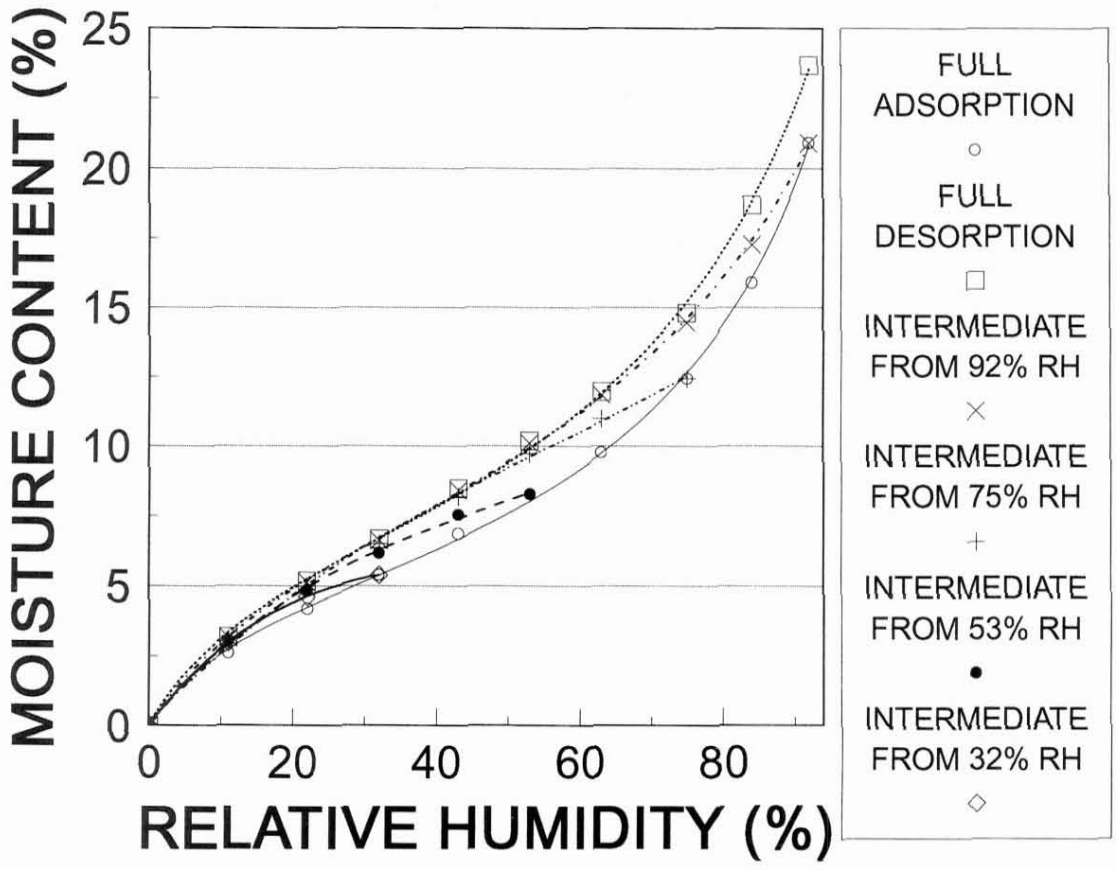

FIG. 4. Graphical representation of the average data points and of the sorption curves which were fitted using the equation parameters in Table 2.

quality of the fit is very good, with the absolute residual not exceeding 0.42% MC, 0.29% MC, and 0.21% MC for the boundary desorption, boundary adsorption, and intermediate desorption at 92% RH, respectively. The model adequately shows the sigmoidal form of the isotherm and the expected moisture content corresponding to complete monolayer coverage of all available sorption sites ($1{,}800/M_p$). The intermediate curves whose reversal points corresponded to relative humidities of 75%, 53%, and 32% are concave towards the X-axis. Quadratic-type equations of the form

$$MC = A + B(RH) + C(RH^2) \qquad (2)$$

describe the data adequately, with the regression analyses yielding R^2 values of 0.997, 0.996, and 0.999 for the intermediate curves with reversal points at 75% RH, 53% RH, and 32% RH, respectively. The quadratic-equation parameters A, B, and C are also shown in Table 2. The shape of the last three intermediate curves is similar to those obtained by Speakman and Cooper (1936) for wool, but differs from what was observed for cotton by Urquhart (1960), who reported that the intermediate curves are of similar sigmoidal shape as the boundary curves.

A general criterion for the extent of sorption hysteresis on hygroscopic materials involves the ratio of the boundary adsorption moisture content to the boundary desorption moisture content (A/D ratio) at a given relative humidity. Figure 5 shows that this ratio ranges from 0.81 to 0.88, values that are slightly higher than, but of comparable magnitude to, the 0.68

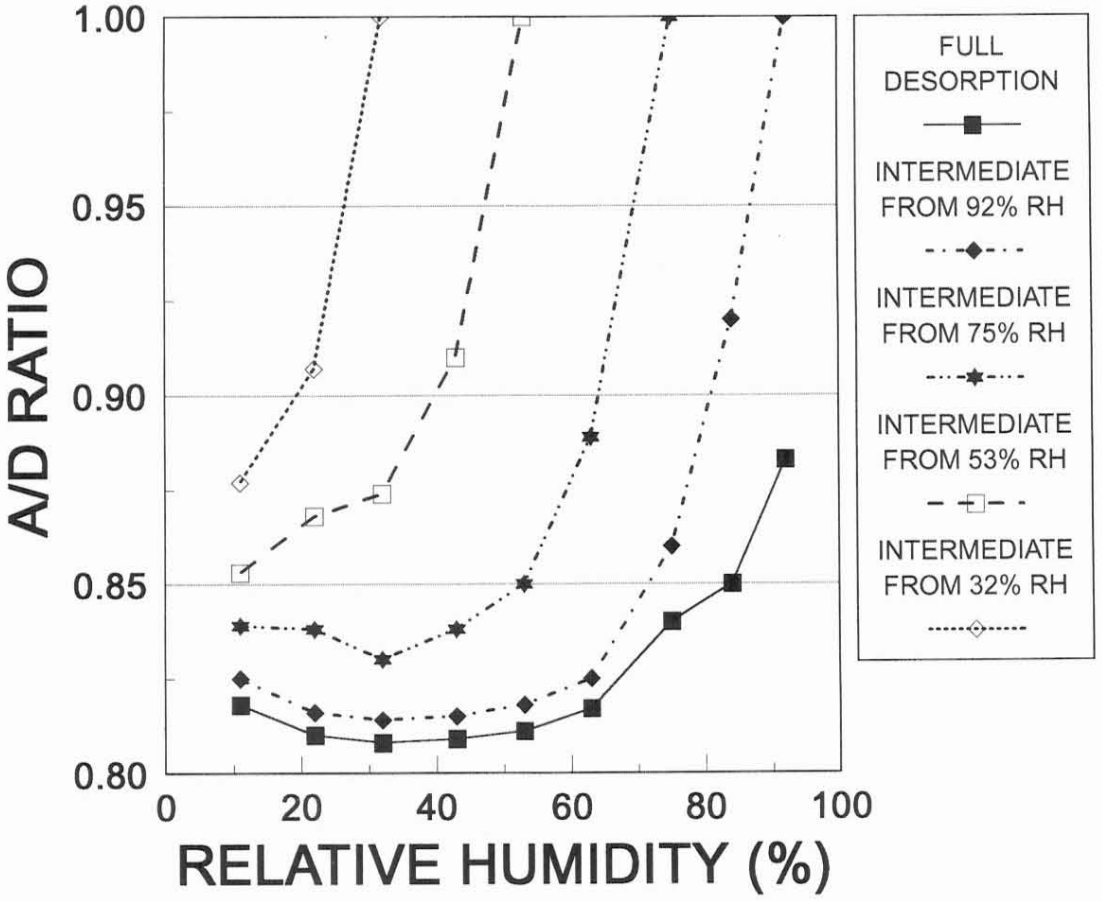

FIG. 5. Graphs of the ratio of the adsorption moisture content to the desorption moisture content at different relative humidity values for the full and intermediate desorption curves.

to 0.84, 0.79 to 0.83, and 0.76 to 0.85 obtained by Avramidis (1986) for western white pine, by Okoh and Skaar (1980) for 10 U.S. hardwoods, and by Spalt (1958) for basswood, respectively. The various intermediate curves also exhibited the sorption hysteresis phenomenon. At the lowest relative humidity level (11%), the intermediate curves corresponding to reversal points of 92%, 75%, 53%, and 32% RH have A/D ratios of 0.83, 0.84, 0.85, and 0.88, respectively. The value for the last intermediate curve is especially important because it shows that hysteresis occurs even at low levels and narrow ranges of relative humidity.

SUMMARY AND CONCLUSIONS

The sorption behavior of wood has been shown to be influenced not only by temperature and relative humidity but also by its immediate history. The full or boundary desorption and adsorption isotherms simply define the delimiting loop that encloses a hysteresis region, and any point within this region may be reached through a given intermediate curve by subjecting wood to an appropriate initial condition. These intermediate curves also exhibited hysteresis even at low RH levels and narrow RH ranges. They have relatively short crossovers, the knowledge of which could prove

useful in the characterization of wood of unknown seasoning history. The results of this study supplement available information on the full sorption curves and provide a better understanding of the interaction of wood with water. Future work will involve establishing more intermediate curves especially on the adsorption phase, evaluating the effect of temperature on the intermediate curves, and mathematical modelling of the sorption phenomenon.

REFERENCES

AVRAMIDIS, S. 1986. Nonisothermal diffusion of moisture in wood and sorption studies. Ph.D. thesis, SUNY College of Environmental Science and Forestry, Syracuse, NY.

JURY, W. A., W. R. GARDNER, AND W. H. GARDNER. 1991. Soil physics, 5th ed. John Wiley, New York, NY. 328 pp.

LABUZA, T. P. 1984. Moisture sorption: Practical aspects of isotherm measurement and use. American Association of Cereal Chemists, St. Paul, MN. 150 pp.

MORTON, W. E., AND J. W. S. HEARLE. 1975. Physical properties of textile fibers, 2nd ed. John Wiley, New York, NY. 660 pp.

OKOH, K. I. A. 1976. Moisture sorption and electrical resistivity of some woods and barks. Ph.D. thesis, SUNY College of Environmental Science and Forestry, Syracuse, NY.

———, AND C. SKAAR. 1980. Moisture sorption isotherms of the wood and inner bark of 10 southern US hardwoods. Wood Fiber 12(1):98–111.

PERALTA, P. N. 1990. Nonisothermal moisture transport in wood. Ph.D. dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA.

SAS. 1990. SAS/STAT User's guide, Version 6, 4th ed., vol. 2. SAS Institute, Inc., Cary, NC.

SIMPSON, W. T. 1980. Sorption theories applied to wood. Wood Fiber 12(3):183–195.

SPALT, H. A. 1958. The fundamentals of water vapor sorption by wood. Forest Prod. J. 8:288–295.

SPEAKMAN, J. B., AND C. A. COOPER. 1936. The adsorption of water by wool. I. Adsorption hysteresis. J. Textile Inst. 27:T183–T185.

URQUHART, A. R. 1960. Sorption isotherms. Pages 14–32 *in* J. W. S. Hearle and R. H. Peters, eds. Moisture in textiles. Wiley Interscience, New York, NY.