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Parallel Diffusion of Moisture in Paper. Part 2: Transient Conditions

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A theoretical model describing the unsteady-state transport of moisture in the thickness direction of paper is formulated that accounts for the parallel diffusion of moisture in the pore and fiber phases, as well as external mass-transfer resistance. Using values of the effective water-vapor and bound-water diffusion coefficients of a bleached kraft paperboard (BKP), which were estimated from steady-state moisture flux measurements in the first part of our work (see the preceding article in this issue), and no fitting parameter, the predictions of the dynamic moisture-transport model are found to be in good agreement with measurements of the transient weight change and relative humidity (RH) profile of stacks of BKP sheets subjected to ramp changes of the external RH under a variety of experimental conditions.

Introduction

Moisture has a profound influence on the mechanical and electrical properties of paper. According to Anderson,[1] knowledge of the moisture content of paper and paperboard should help in producing a more dimensionally stable product. There is a marked loss in the strength properties of paper with increasing moisture content; e.g., the stiffness of paper decreases by 5−10% for each unit percentage change in moisture content.[2] Under high humidity, paper exhibits lower elastic modulus, yield stress, and tensile strength.[3] The strength of paper degrades rapidly, and accelerated creep intensifies under cyclic changes in the external relative humidity (RH), causing loaded paperboard boxes exposed to cyclic RH changes to fail earlier than similarly loaded boxes in a constant-RH environment.[4] The accelerated creep phenomenon is believed to result from the interaction of tensile loading with transient moisture gradients.[5] It is the main intent of the present work to address such gradients that occur in the thickness direction of paper (denoted by z) under ramp changes of the external RH.

In the first part of our work,[6] we presented a mathematical framework for describing the steady-state transport of moisture in the thickness direction of a stack of paper sheets contained inside a diffusion cup placed in a controlled-humidity chamber. The model accounted for mass-transfer resistances outside the paper stack and the parallel diffusion of water vapor in the pore space and bound water in the fiber phase in the z direction of the stack. By comparing the theoretical expression for the effective moisture diffusivity with experimental values measured over a wide range of conditions, the water-vapor and bound-water diffusion coefficients of a machine-made bleached kraft paperboard (BKP) were estimated. The transport model was then validated against additional measurements of the steady-state moisture transmission rate in the paperboard stack, RH and moisture profiles in the stack, and average moisture content of the stack under a variety of experimental conditions. In the present investigation, we extend the above work to the unsteady-state situation. Specifically, we present a theoretical model that describes the parallel diffusion of moisture in the thickness direction of paper sheets that are subjected to ramp changes of the external RH. This unsteady-state model utilizes values of the effective water-vapor and bound-water diffusion coefficients (D_p and D_q, respectively) in the BKP, which were estimated by steady-state moisture flux measurements reported earlier.[6] The predictions of the model are compared against experimental measurements of the transient uptake of moisture by BKP sheets and RH profiles in stacks of such sheets under ramp changes of the external RH. We note that Wadsö[7] found that moisture diffusion coefficients in wood derived from transient experimental data did not correspond with those derived from steady-state "cup" measurements. This could be because the single-phase unsteady-state diffusion model typically used in the wood field considers wood to be a homogeneous material without regard to its internal microscopic porous structure and, thus, its internal hygroscopicity. This approach, which does not capture the physics of the moisture-transport process adequately, can give rise to unrealistic results and contradictory trends of how the moisture diffusivity varies with moisture content, as evidenced by the work of Chen et al.[8]

For a brief review of the relevant work on moisture transport in paper under both steady and transient conditions, we refer the reader to our earlier paper.[6] Einstein[9] recommended two desirable features in a scientific theory: it should have the fewest possible logically independent elements (basic concepts and axioms), and it should enable the closest and most complete coordination of the totality of sense experiences. We made an effort to implement these suggestions in our earlier work,[6] where we assumed local equilibrium between the pore and fiber phases of paper and found that only two parameters (D_p and D_q) were

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sufficient in the conceptual framework to explain the steady-state experimental data (moisture transmission rate, RH and moisture profiles, average moisture content) under different experimental conditions. In the current work, we examine whether the values of D_p and D_q of the BKP that were estimated from the steady-state investigation[6] can also be used to predict the transient weight change and RH profile of BKP sheets undergoing ramp changes of the external RH without using any fitting parameter in the unsteady-state model.

Theoretical Development

Consider a single sheet or a stack of M paperboard sheets, initially in equilibrium with air at a relative humidity of $\mathrm{RH_i}$, subjected to a ramp change of the external or bulk RH ($\mathrm{RH_b}$), which changes linearly from $\mathrm{RH_i}$ at time $t = 0$ to $\mathrm{RH_f}$ at a rate of r. The time t_r of the duration of the ramp is then given by

$$t_r = \frac{\mathrm{RH_f} - \mathrm{RH_i}}{r} \tag{1}$$

For $t > t_r$, $\mathrm{RH_b}$ is maintained at a level equal to $\mathrm{RH_f}$. Therefore, $\mathrm{RH_b}$ can be described by

$$\begin{aligned}\mathrm{RH_b}(t) &= \left(\frac{\mathrm{RH_f} - \mathrm{RH_i}}{t_r}\right)t + \mathrm{RH_i} \qquad \text{for } 0 \le t \le t_r \\ &= \mathrm{RH_f} \qquad \text{for } t > t_r\end{aligned} \tag{2}$$

In addition to using single sheets of the BKP in our experimental work, we also used stacks of 4, 6, 8, 10, and 16 such sheets. As discussed in our previous work on steady-state moisture transport in paper,[6] we can make the following two extreme assumptions regarding the contact between any two adjacent sheets in the stack: (a) There is complete contact between any two adjacent paperboard sheets; the paper stack then becomes one continuous whole, i.e., there is zero contact resistance between the adjacent sheets. (b) There is an air gap that completely separates any two adjacent paper sheets of the stack. The actual situation lies somewhere between these two extremes. Even in the second case, we assume in this work that there is no resistance to mass transfer offered by the air gap between any two adjacent sheets in the stack. As indicated earlier, we also assume that water vapor and bound water are in equilibrium at every point in the paperboard (i.e., exchange of moisture between the pore and fiber phases is much faster than moisture diffusion in the z direction). This assumption and the assumption made earlier about negligible contact resistance between any two adjacent sheets in the stack reduces the two extreme cases of perfect contact and no contact between adjacent sheets into a single idealized case, thereby greatly simplifying the mathematical analysis.

We postulate that the transport of moisture in the paperboard occurs via two parallel pathways, i.e., by the diffusion of water vapor and bound water in the pore and fiber phases, respectively. The mass conservation equation for moisture, assuming Fick's law, is then given by

$$\rho_p \frac{\partial q}{\partial t} + \epsilon_p \frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(D_p \frac{\partial c}{\partial z}\right) + \rho_p \frac{\partial}{\partial z}\left(D_q \frac{\partial q}{\partial z}\right) \qquad \text{in } 0 < z < H \text{ for } t > 0 \tag{3}$$

where H is the half-thickness of the single sheet or stack under consideration. D_p and D_q are the effective diffusivities of water vapor and bound water respectively, in the paperboard; c is the water-vapor concentration at any location z in the stack where the bound-water concentration is q; ρ_p is the oven-dry density of the paperboard; and ϵ_p is the porosity of the paperboard. D_p is relatively independent of c,[10-12] but D_q is a strong function of q.[6,10,12-14] In the case of paper with moisture contents up to approximately 25%, $D_q(q)$ can be adequately represented by[6,12-14]

$$D_q(q) = D_1 e^{mq} \tag{4}$$

where D_1 and m are constants for the particular paper under consideration. A theoretical justification for eq 4 and estimated values of D_p, D_1, and m for the BKP used in this work were provided by us earlier.[6] Imposing the condition of equilibrium between c and q, we have

$$q = f(c) \qquad \text{in } 0 < z < H \tag{5}$$

where $f(c)$ is the sorption isotherm. We have used the GAB model[15,16] to represent the (boundary) sorption isotherm $f(c)$. This is given by

$$f(c) = \frac{q_m C_{\mathrm{GAB}} \dfrac{K_{\mathrm{GAB}} RT}{P_{\mathrm{sat}}} c}{18.016\left(1 - \dfrac{K_{\mathrm{GAB}} RT}{P_{\mathrm{sat}}} c\right)\left[1 + (C_{\mathrm{GAB}} - 1)\dfrac{K_{\mathrm{GAB}} RT}{P_{\mathrm{sat}}} c\right]} \tag{6}$$

where q_m (equilibrium moisture content corresponding to monolayer coverage), C_{GAB}, and K_{GAB} are parameters of the isotherm. These parameters for the BKP were also reported in our earlier work.[6]

The initial and boundary conditions for eq 3 are

$$c = c_i,\ q = q_i = f(c_i) \qquad \text{at } t = 0 \text{ in } 0 \le z \le H \tag{7}$$

$$k_f[c_b(t) - c] = -D_p \frac{\partial c}{\partial z} - \rho_p D_q \frac{\partial q}{\partial z} \quad \text{and} \quad q = f(c) \qquad \text{at } z = 0 \text{ for } t > 0 \tag{8}$$

$$\frac{\partial c}{\partial z} = 0 \quad \text{and} \quad q = f(c) \qquad \text{at } z = H \text{ for } t > 0 \tag{9}$$

Here, k_f is the mass-transfer coefficient at the surface of the paper sheet or stack (measured experimentally in this work); c_i and q_i are the initial water-vapor and bound-water concentrations, respectively, in the stack at $t = 0$; and $c_b(t)$ is the bulk concentration of water vapor in the humidity chamber. We note that all water-vapor concentrations, including c, c_i and c_b, can be related to the corresponding RH values via the ideal-gas law; e.g.

$$c_b(t) = \frac{\mathrm{RH_b}(t) P_{\mathrm{sat}}}{100RT} \tag{10}$$

where P_{sat} is the vapor pressure of water at the temperature of the experiment T and R is the universal gas constant.

We introduce the following dimensionless quantities

$$C = \frac{c}{c_i},\quad C_b = \frac{c_b}{c_i},\quad Z = \frac{z}{H},\quad \tau = \frac{t}{t_r}$$

$$Q = \frac{q}{q_i} = \frac{f(c)}{f(c_i)} = \frac{f(c_iC)}{f(c_i)} = F(C)$$

$$\alpha = \frac{D_p t_r c_i}{\rho_p q_i H^2},\quad \beta = \frac{D_1 t_r}{H^2},\quad \gamma = m q_i,\quad Bi = \frac{k_f H}{D_p}$$

We also introduce a variable Y related to Q by

$$Y = \frac{e^{\gamma Q}}{\gamma} = \frac{e^{\gamma F(C)}}{\gamma} \tag{11}$$

Noting that $\rho_p q \gg \epsilon_p c$, we can transform the governing equations to read

$$\frac{1}{\gamma Y}\frac{\partial Y}{\partial \tau} = \alpha \frac{\partial^2 C}{\partial Z^2} + \beta \frac{\partial^2 Y}{\partial Z^2} \qquad \text{in } 0 < Z < 1 \text{ for } \tau > 0 \tag{12}$$

with

$$C = 1,\ Y = \frac{e^{\gamma}}{\gamma} \qquad \text{at } \tau = 0 \text{ in } 0 \le Z \le 1 \tag{13}$$

$$Bi[C_b(\tau) - C] = -\frac{\partial C}{\partial Z} - \frac{\beta}{\alpha}\frac{\partial Y}{\partial Z} \quad \text{and} \quad Y = \frac{e^{\gamma F(C)}}{\gamma} \quad \text{at } Z = 0 \text{ for } \tau > 0 \tag{14}$$

$$\frac{\partial C}{\partial Z} = 0 \quad \text{and} \quad Y = \frac{e^{\gamma F(C)}}{\gamma} \qquad \text{at } Z = 1 \text{ for } \tau > 0 \tag{15}$$

Equation 2 becomes

$$\begin{aligned} C_b(\tau) &= B\tau + 1 \qquad \text{for } 0 \le \tau \le 1 \\ &= B + 1 \text{ for } \tau > 1 \end{aligned} \tag{16}$$

where

$$B = \frac{RH_f}{RH_i} - 1 \tag{17}$$

The average moisture content of the paperboard stack, q_{avg}, is given by

$$q_{avg} = \frac{1}{H}\int_0^H \left[\frac{\epsilon_p c(z)}{\rho_p} + q(z)\right] dz \approx \frac{1}{H}\int_0^H q(z)\, dz \tag{18}$$

The first term of the integrand in eq 18 is negligible compared to the second term. In dimensionless form, eq 18 becomes

$$Q_{avg} = \frac{q_{avg}}{q_i} \approx \int_0^1 Q(Z)\, dZ \tag{19}$$

To determine C and Q, eq 12 subject to eqs 11 and 13−17 was solved by the control-volume method.[17] The RH and bound-water (BW) profiles in the stack and the average moisture content of the stack (MC_{avg}) were calculated from the following equations

$$RH = (RH_i)C \tag{20}$$

$$BW = (18.016 \times 100 \times q_i)Q \tag{21}$$

$$MC_{avg} = (18.016 \times 100 \times q_i)Q_{avg} \tag{22}$$

The theoretical weight gain, ϕ_{theory}, of the sheet or stack is defined as

$$\phi_{theory} \equiv \frac{MC_{avg}(t) - MC_{avg,i}}{MC_{avg,i} + 100} \tag{23}$$

where $MC_{avg,i}$ is the initial average moisture content.

Experimental Procedures

In all of the experiments reported here, we used a machine-made BKP sample that was free of fillers and additives and consisted of approximately 80% southern pine and 20% hardwood pulp fibers beaten to 530 mL of CSF (Canadian standard freeness). The BKP had a mean basis weight of 230 g/m^2 and was preconditioned at approximately 50% RH and 23 °C in a controlled-humidity room. Single or multiple sheets of the BKP in a stack were used in the experiments; they were suspended from an electronic balance and subjected to RH ramps inside a controlled-humidity chamber, a description of which is available elsewhere.[18] A typical experimental RH ramp is shown in Figure 1. Before the actual ramp was begun, the RH of the chamber was maintained at RH_{start} (50% RH in this work) for 30 min. In the next stage, the chamber RH was lowered at a rate of 1% RH/min to RH_i and was held at that level for time periods ranging from 6 h (single sheet) to 20 h (stack of multiple sheets) so that the sample attained equilibrium. Thereafter, the RH in the chamber was changed at a constant rate (0.25, 0.5, or 1% RH/min) until a final desired RH value, RH_f, was attained in the chamber. This final RH level was then maintained for several more hours. The average temperature of the experiments reported in this work, which were carried out under atmospheric pressure, was generally in the range 23−24 °C. The experiments, which were performed to examine the predictive ability of the unsteady-state transport model, can be broadly categorized into the following two groups:

Experiments with Single Sheets. A single BKP sheet measuring 10 cm × 10 cm was suspended (from a balance) inside the humidity chamber and, after the preconditioning procedure described above, was subjected to an RH ramp (eq 2) varying from RH_i to RH_f. Values of RH_i of 10 and 20% and RH_f of 50, 60, 70, 80, and 90% were used. Ramp rates of 0.5 and 1% RH/min

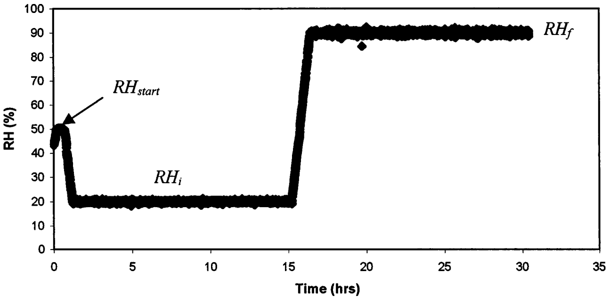

Figure 1. Typical experimental RH ramp (i.e., RH_b vs time).

Table 1. Experimental Mass-Transfer Coefficient (k_f) at the Surface of a Single BKP Sheet Suspended in the Humidity Chamber at Three Different Bulk RH Levels

RH_b (%)	temperature (°C)	k_f (cm/s)
40	22.5	0.23
70	23.3	0.22
90	23.5	0.20
average	23.1	0.22

were utilized. The transient weight of the sample was continuously monitored and recorded by a computer as a function of time. The experimental weight gain, ϕ_{expt}, of the sheet was calculated from

$$\phi_{expt} = \frac{W(t) - W_i}{W_i} \tag{24}$$

where $W(t)$ and W_i are the weights of the sheet at any time t and at $t = 0$ (start of the RH ramp), respectively.

The mass-transfer coefficient, k_f, at the surface of the sheet was measured in a separate experiment. A sample of BKP (10 cm × 10 cm) was soaked in deionized water and suspended from the weighing balance inside the humidity chamber, which was maintained at a specified value of RH_b. The decrease in the weight of the sample due to water evaporation from its two surfaces was continuously monitored as a function of time for a period of 3 h. The sample weight versus time data over the first hour, which were observed to be linear, were used to calculate the weight loss or water evaporation rate dW/dt. Assuming that the RH at the surface of the wet sheet was 100% (we experimentally confirmed this assumption by placing a miniature RH probe on the surface), the expression used to calculate k_f was

$$\frac{dW}{dt} = \frac{k_f A P_{sat}}{100RT}(100 - RH_b) \tag{25}$$

where A is the total surface area of the exposed sheet (= 200 cm^2 because evaporation occurred from both surfaces of the sheet). Three different levels of RH_b (40, 70, and 90%) were used in the determination of k_f, the average value of which was used in the calculation of the theoretical weight gain by eq 23 (see Table 1).

Experiments with Multiple Sheets. Two types of experiments were performed with multiple sheets of BKP placed together in the form of a stack. The number of sheets in the stack was varied to examine the effect of stack basis weight (or stack thickness) on moisture transport. The dimensions of each sheet were 10.5 cm × 10.5 cm.

In the first type of experiment, a specific number of BKP sheets (M = 4, 6, 8, 10, and 16) were placed together as a stack whose edges were then sealed by scotch tape. Approximately 0.25 cm of tape overlapped on all four sides at both surfaces of the stack, so that the exposed area of the stack at its each surface was 10 cm × 10 cm. A schematic diagram of the paperboard stack, whose sheets were also stapled together at a few points along the edges that were sealed with tape, is shown in Figure 2. The sealed edges of the stack prevented any movement of water vapor through the sides, thus ensuring that moisture diffusion occurred in the stack through the two exposed surfaces predominantly in the thickness direction. As in the single-sheet experiments, the stack was subjected to an RH ramp, and its weight was continuously recorded as a function of time. Values of RH_i = 20%, RH_f = 80%, and a ramp rate of 1% RH/min were used. The experimental weight gain was calculated by eq 24 after discounting for the weight of the tape and staples. The mass-transfer coefficient in these experiments was assumed to be same as that measured for single sheets (Table 1). In the theoretical calculations for the weight gain of the stack containing multiple sheets (eq 23), an "effective" or "corrected" value of k_f was used. This value was calculated by multiplying the average value of k_f shown in Table 1 (0.22 cm/s) by 0.907 [=10 cm × 10 cm/(10.5 cm × 10.5 cm)] to account for the reduction in the area available for mass transfer due to the tape used to seal the edges of the stack.

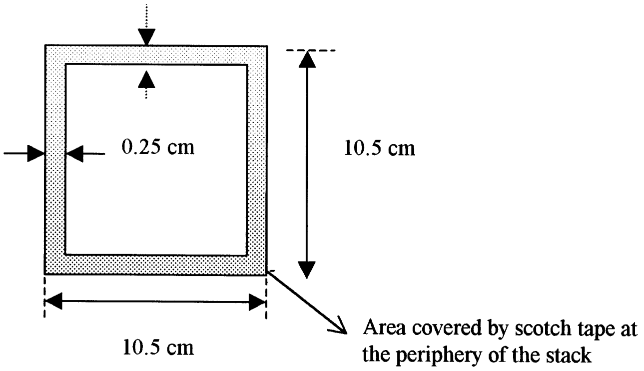

Figure 2. Schematic diagram of paperboard stack used in the weight-gain experiments with edges sealed with scotch tape on four sides.

In the second type of experiment, a specific number of BKP sheets (M = 4, 6, 8, and 10) of dimensions 10.5 cm × 10.5 cm were stacked together, and miniature RH sensors, described in the first part of our work,[6] were placed at the interfaces between the sheets of the stack, which was then secured by means of screws in a square plastic frame (13.9 cm × 13.9 cm), as shown in Figure 3. Each of the two exposed areas of the paperboard stack contained inside the frame measured 10 cm × 10 cm. The edges of the frame were sealed with scotch tape to prevent any lateral transport of moisture through the sides of the stack. The entire assembly was suspended inside the humidity chamber and subjected to an RH ramp. The voltage readings from the sensors at different locations in the stack were recorded manually at periodic intervals (generally every 5 or 10 min) after the ramp had started. The voltage was subsequently converted to the corresponding RH by a calibration curve supplied by the manufacturer. Values of RH_i = 10 and 20%, RH_f = 80 and 90%, and ramp rates of 0.25 and 1% RH/min were used in these experiments.

The mass-transfer coefficient, k_f, at the surface of the stack during the RH profile measurements was determined by placing a single 10.5 cm × 10.5 cm BKP sheet soaked in deionized water in the plastic frame, suspending the frame from a balance inside the humidity chamber maintained at a definite RH_b, and monitoring the weight loss of the assembly over the first hour. The same procedure as described earlier in the case of a single sheet was used to calculate k_f, the values are reported in Table 2 for four different levels of RH_b (50, 60, 70, and 90%). In the theoretical simulations of the RH and moisture profiles in the stack, the average value of k_f listed in Table 2 (0.31 cm/s) was corrected by multiplying it by the factor 0.907 to account for the reduction in the area available for mass transfer due to the frame. The difference in the average k_f values in Tables 1 and 2 might be a reflection of an alteration of

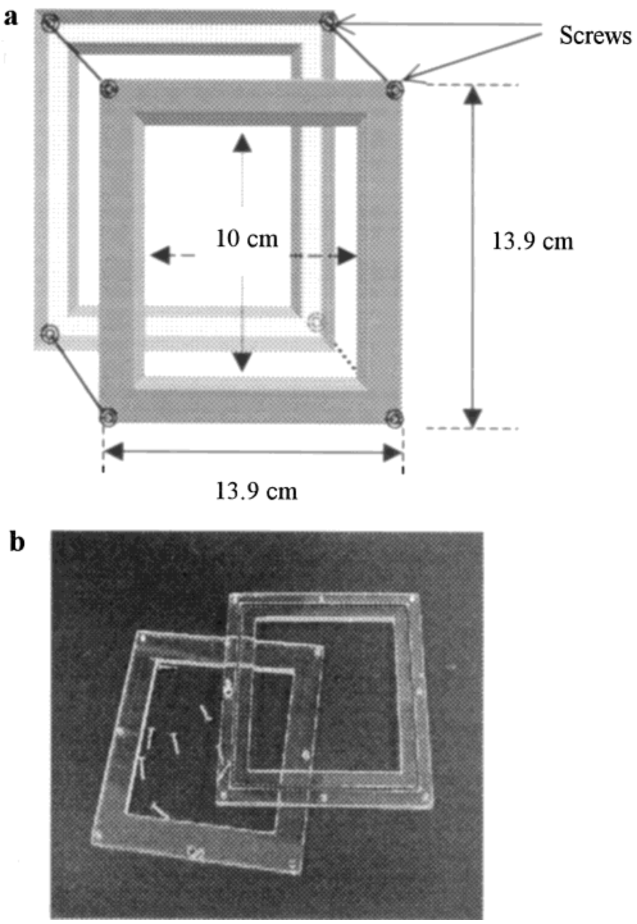

Figure 3. (a) Schematic diagram and (b) photograph of the frame in which a square stack of BKP sheets was placed for the RH profile measurements.

Table 2. Experimental Mass-Transfer Coefficient (k_f) at the Surface of a BKP Sheet Suspended in the Frame in the Humidity Chamber at Four Different Bulk RH Levels

RH_b (%)	temperature (°C)	k_f (cm/s)
50	22.2	0.32
60	22.5	0.30
70	23.3	0.32
90	23.6	0.30
average	22.9	0.31

the air flow pattern in the humidity chamber after the introduction of the frame.

Results and Discussion

In Figures 4−9, theoretical predictions of the transient weight gain of single sheets of BKP and the weight gain and RH profile of stacks of such sheets subjected to RH ramps are compared with their corresponding experimental measurements. The isotherm and diffusion parameters of the BKP are reported in Table 3; as mentioned earlier, they were determined from our previous study of steady-state moisture transport in paper.[6]

Figure 4 shows the transient weight gain of single sheets of BKP subjected to RH ramps from 20 to 60, 70, and 80% at ramp rates of 0.5 and 1% RH/min. There is good agreement between theory and experiment, with the rate of moisture uptake at 0.5% RH/min being smaller than that at 1% RH/min. It can be seen that the sheets almost attained equilibrium some time after the conclusion of the ramp, and the small disagreement between the theoretical and experimental weight gains thereafter can be attributed to the discrepancy between the actual experimental equilibrium moisture content and the theoretical value predicted with the GAB isotherm (eq 6). In most of the previous work on transient moisture transport in paper,[19−23] bound-water diffusion in the z (thickness) direction of the paper was neglected, and the transport process was conceptualized as consisting of water-vapor diffusion in the z direction (represented by an effective water-vapor diffusion coefficient, D_p) and intrafiber diffusion of moisture (represented by an intrafiber mass-transfer coefficient, k_{fib}). Ramarao and Chatterjee[20] and Bandyopadhyay et al.,[23] using an approximate value of D_p (0.0063 cm^2/s), found that a value of $k_{fib} = 0.0035$ s^{-1} was able to fit the dynamic response of the average moisture content of single BKP sheets subjected to RH ramps. We emphasize that k_{fib} was used by these authors as a fitting parameter for their transient experiments and was not measured independently. In contrast, the theoretical curves in Figure 4, as well as those presented in Figures 5−9, contain no fitting parameter. The two parameters D_p and D_q of our present model were estimated by independent steady-state moisture flux measurements in a diffusion cup,[6] and in our opinion, this (D_p, D_q) model is more realistic than the earlier (D_p, k_{fib}) model given that it can explain both steady-state and unsteady-state data of moisture transport in paper that we have obtained in more recent times.

Figure 5 displays the transient weight gain of stacks of 4, 6, 8, 10, and 16 BKP sheets that were subjected to RH ramps from 20 to 80% at a ramp rate of 1% RH/min. The importance of diffusional resistances to moisture transport can be inferred from the fact that all of the experimental weight gains are substantially below

Table 3. Properties of Bleached Kraft Paperboard Used in the Present Work

parameter	value
mean basis weight of paperboard	230 g/m^2
paperboard sheet thickness (at ~50% RH)[a]	0.035 cm
oven-dry density of paperboard (ρ_p)	0.663 g/cm^3
moisture diffusion constants of paperboard[b]	
D_p	5.238×10^{-3} cm^2/s
D_1	3.821×10^{-8} cm^2/s
m	398 g/mol
GAB isotherm constants of paperboard[b] (boundary adsorption isotherm)	
q_m	0.051 g/g
K_{GAB}	0.749
C_{GAB}	56.417

[a] Used as a representative value in all calculations. [b] At 23.9 °C and atmospheric pressure.[6]

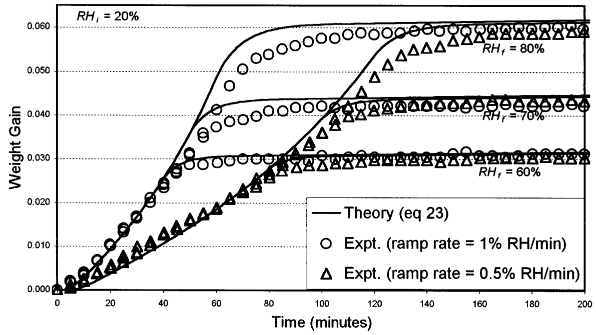

Figure 4. Experimental and theoretical weight gains of a single BKP sheet. The average temperature of the experimental runs was in the range 23.8−24 °C.

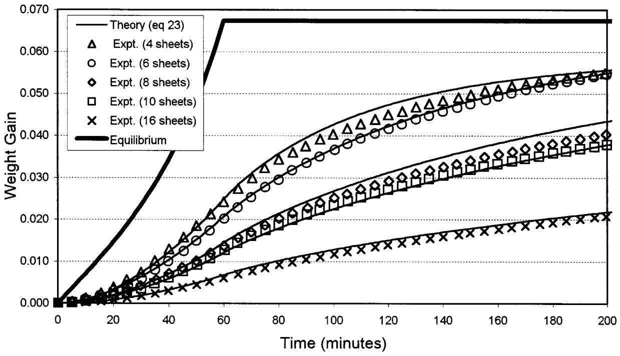

Figure 5. Experimental and theoretical weight gains of multiple BKP sheets in a stack. The average temperature of the experimental runs was in the range 23.1−23.9 °C. $RH_i = 20\%$, $RH_f = 80\%$, and ramp rate = 1% RH/min.

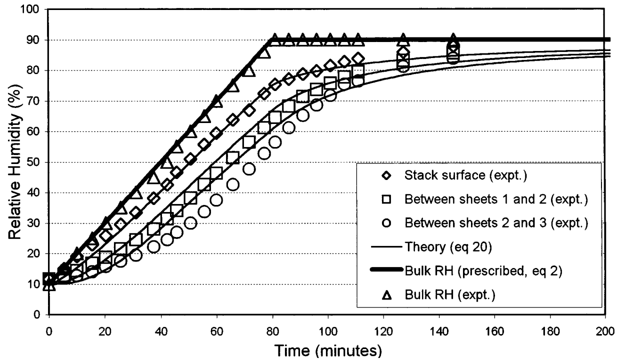

Figure 6. Experimental and theoretical RH profiles in a stack of four BKP sheets in the frame. The average temperature of the experimental run was 24.2 °C. $RH_i = 10\%$, $RH_f = 90\%$, and ramp rate = 1% RH/min.

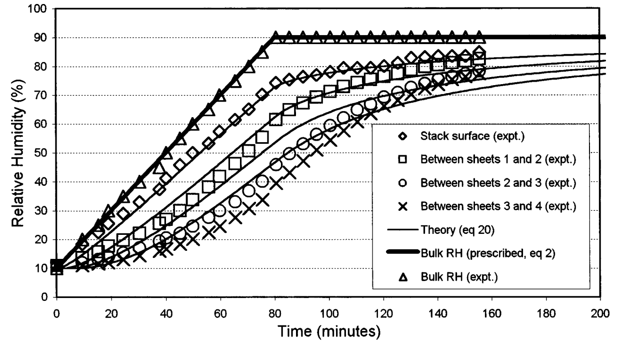

Figure 7. Experimental and theoretical RH profiles in a stack of six BKP sheets in the frame. The average temperature of the experimental run was 24.1 °C. $RH_i = 10\%$, $RH_f = 90\%$, and ramp rate = 1% RH/min.

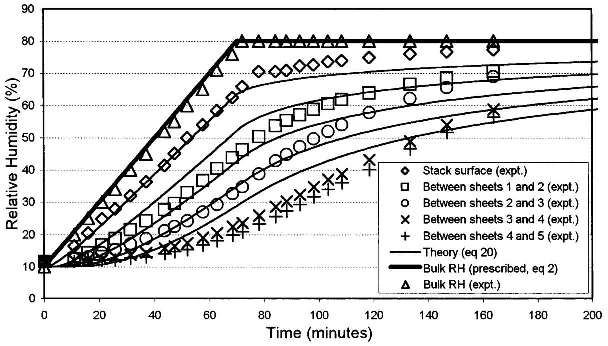

Figure 8. Experimental and theoretical RH profiles in a stack of eight BKP sheets in the frame. The average temperature of the experimental run was 24.1 °C. $RH_i = 10\%$, $RH_f = 80\%$, and ramp rate = 1% RH/min.

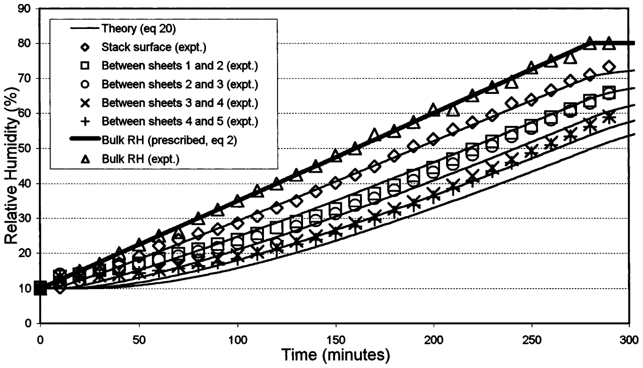

Figure 9. Experimental and theoretical RH profiles in a stack of eight BKP sheets in the frame. The average temperature of the experimental run was 24.1 °C. $RH_i = 10\%$, $RH_f = 80\%$, and ramp rate = 0.25% RH/min.

the theoretical equilibrium weight gain (i.e., no internal diffusional or external mass-transfer resistances) calculated using eq 6. There is good agreement between the experimental and theoretical weight gains, and as expected, the rate of weight gain of the stack decreases with increasing number of sheets in the stack.

Figures 6−8 show transient experimental RH profiles, measured with the miniature sensors mentioned earlier, in stacks of BKP sheets subjected to RH ramps from 10 to 90% (four- and six-sheet stacks) and from 10 to 80% (eight-sheet stack) using a ramp rate of 1% RH/min. The figures also include the corresponding theoretical predictions of the RH profile (eq 20) and the bulk RH in the chamber, which was measured by a Vaisala probe. It can be seen that there is very good agreement between the prescribed bulk RH (i.e., RH_b as given by eq 2) and the value measured in the experiments. It can also be observed from these figures that, in general, there is fair correspondence between the theoretical and experimental RH profiles in the stack. As one proceeds from the surface of the stack inward toward the center, the corresponding RH profiles lie below one another, indicating that RH changes occur at lower rates at greater stack depths, which, in turn, indicates the presence of diffusional resistances in the stack. It can also be observed that there is some divergence between the theoretical and experimental RH values as the interior of the stack is approached; this is especially evident for the eight-sheet stack (see Figure 8). However, this discrepancy appears to be transient, and the experimental and theoretical RH curves approach one another some time after the RH ramp has ended. We postulate that this disagreement between theory and experiment is due to the accumulation of water vapor in the air gap between adjacent sheets in the stack, which was not taken into account in our theoretical model. This air gap between adjacent sheets was chiefly due to the presence of the miniature RH sensors, which had dimensions of 12 mm × 15 mm × 4.5 mm. This effect of the air gaps becomes cumulative and, thus, increasingly important as the center of the stack is approached and appears empirically in the form of a 'resistance" offered by the gaps. To check this hypothesis, we repeated the eight-sheet-stack experiment at the lower ramp rate of 0.25% RH/min as this would lessen the effect of the accumulation of water vapor in the gaps. As seen in Figure 9, the experimental RH profiles in this case are much closer to their theoretical counterparts throughout the duration of the experiment.

This appears to indicate that the accumulation of water vapor in the air gaps was responsible for the discrepancy between theory and experiment at the higher ramp rate of 1% RH/min.

Conclusions

A theoretical model describing the unsteady-state transport of moisture in the thickness direction of paper that accounts for the parallel diffusion of moisture in the pore and fiber phases of paper and external mass-transfer resistance was formulated. Using values of the effective water-vapor and bound-water diffusion coefficients of a BKP sample, which were estimated from steady-state moisture flux measurements in the first part of our work,[6] and no fitting parameter, the predictions of the dynamic moisture-transport model were found to be in good agreement with measurements of the transient uptake of moisture by BKP sheets and the RH profiles in stacks of such sheets under ramp changes of the external RH for a variety of experimental conditions. Our investigation of steady and transient transport of moisture in paper indicates that the transport process can be conceptualized as one of parallel diffusion of water vapor in the pore space and bound water in the fiber phase of paper. Our work is one component of the knowledge base of moisture transport in cellulosic materials that should be useful in understanding the phenomena of accelerated creep of paperboard products under RH cycling; moisture transport in food, wood, and building materials; and drying of wood and paper.

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Nomenclature

A = total surface area of exposed sheet in eq 25 (cm^2)
B = defined by eq 17
Bi = Biot number, $k_f H/D_p$
BW = bound-water concentration at any specific location in a paperboard sheet or stack (%)
c = water-vapor concentration at any location z in a paperboard sheet or stack (mol/cm^3)
c_b = water-vapor concentration in the bulk air of the humidity chamber (mol/cm^3)
c_i = initial water-vapor concentration of a paperboard sheet or stack (mol/cm^3)
C = dimensionless water-vapor concentration in a paperboard sheet or stack, c/c_i
C_b = dimensionless water-vapor concentration in the bulk air of the humidity chamber, c_b/c_i
C_{GAB} = parameter of the GAB isotherm (eq 6)
dW/dt = weight-loss rate of a wet paperboard sheet (eq 25, g/s)
D_p = diffusion coefficient of water vapor in the paperboard (cm^2/s)
D_q = diffusion coefficient of bound water in the paperboard (cm^2/s)
D_1 = constant in eq 4 (cm^2/s)
$f(c)$ = bound-water concentration in equilibrium with a water-vapor concentration of c (mol/g of dry fiber)
$F(C)$ = dimensionless equilibrium bound-water concentration, $f(c)/f(c_i)$
H = half-thickness of a paperboard sheet or stack (cm)
k_f = mass-transfer coefficient at the surface of a paperboard sheet or stack (cm/s)
k_{fib} = intrafiber mass-transfer coefficient (s^{-1})
K_{GAB} = parameter of the GAB isotherm (eq 6)
m = constant in eq 4 (g/mol)
M = number of sheets in a paperboard stack
MC_{avg} = average moisture content of a paperboard sheet or stack (%)
$MC_{avg,i}$ = initial average moisture content of a paperboard sheet or stack (%)
P_{sat} = vapor pressure of water at temperature T (MPa)
q = bound-water concentration at any location z in a paperboard sheet or stack (mol/g of dry fiber)
q_{avg} = average moisture content of a paperboard sheet or stack (mol/g of dry fiber)
$q_i = f(c_i)$ = initial bound-water concentration of a paperboard sheet or stack (mol/g of dry fiber)
q_m = equilibrium moisture content corresponding to monolayer coverage in eq 6 (g/g of dry fiber)
Q = dimensionless bound-water concentration in a paperboard sheet or stack, q/q_i
Q_{avg} = dimensionless average moisture content of a paperboard sheet or stack, q_{avg}/q_i
r = rate of RH change (% RH/s)
R = universal gas constant [8.3144 cm^3 MPa/(mol K)]
RH = relative humidity at any specific location in a paperboard sheet or stack (%)
RH_b = relative humidity of the bulk air in the humidity chamber (%)
RH_f = final relative humidity of the bulk air in the humidity chamber (%)
RH_i = initial relative humidity of the bulk air in the humidity chamber at $t = 0$ (%)
RH_{start} = starting value of relative humidity of the bulk air in the humidity chamber (%)
t = time elapsed from the start of the ramp (s)
t_r = time duration of the ramp (s)
T = experimental temperature (K)
W = transient weight of a paperboard sheet or stack at any time t (g)
W_i = weight of a paperboard sheet or stack at $t = 0$ (g)
Y = dimensionless variable defined by eq 11
z = distance into a paperboard sheet or stack measured from its surface (cm)
Z = dimensionless distance into a paperboard sheet or stack (z/H)
$\alpha = D_p t_r c_i/(\rho_p q_i H^2)$
$\beta = D_1 t_r/H^2$
$\gamma = m q_i$
τ = dimensionless time, t/t_r
ϕ_{expt} = experimental weight gain of a paperboard sheet or stack defined by eq 24
ϕ_{theory} = theoretical weight gain of a paperboard sheet or stack defined by eq 23
ρ_p = oven-dry density of the paperboard (g of dry fiber/cm^3)
ϵ_p = porosity of the paperboard

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