Preferred citation: B.V. Ramarao and S.G. Chatterjee. Moisture sorption by paper materials under varying humidity conditions. In **The Fundametals of Papermaking Materials**, *Trans. of the XIth Fund. Res. Symp. Cambridge, 1997*, (C.F. Baker, ed.), pp 703–749, FRC, Manchester, 2018. DOI: 10.15376/frc.1997.2.703.

Moisture Sorption by Paper Materials Under Varying Humidity Conditions

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ABSTRACT

The uptake of moisture by paper sheets was analyzed as an adsorption process occurring in a porous medium. Water vapor was assumed to diffuse into the pore space and was subsequently adsorbed onto the surfaces of the fibers constituting the paper sheet. The response of the sheets to variations in relative humidity was investigated.

Since the transient moisture profiles inside paper sheets depend upon the moisture sorption equilibria for paper, the equilibrium behavior was investigated with special emphasis on a description of sorption hysteresis. It is necessary to follow equilibrium trajectories inside the hysteresis loop for paper sheets. Sorption equilibria inside the hysteresis loop for paper sheets (bleached kraft linerboard, 290 gsm) were evaluated experimentally. Complete sets of desorption and adsorption scanning trajectories were obtained. Further higher order loops were obtained experimentally. The theory of

independent domain complexions was applied to the hysteresis loop. By constructing a so-called moisture distribution function for the hysteresis, arbitrary trajectories representing equilibrium sorption behavior under cyclic humidity changes could be predicted.

An investigation of transient sorption was also undertaken. A model for moisture uptake based upon diffusion inside the pore space and the fibers in the sheet was set up. Experimental data on transient moisture uptake was obtained under ramped changes in humidity. It was found that the model for moisture uptake incorporating a linearized isotherm could describe the sorption response of paper sheets to ramped changes in humidity adequately. From the experimental data, a value for the intra-fiber mass transfer coefficient representing moisture diffusion through fibers was determined.

INTRODUCTION

The sorption of moisture by paper and its influence on the performance of paper products is an important phenomenon which has attracted much attention recently [1]. It is well known that humidity variations decrease the strength properties of paper drastically. In analyzing the performance of paper products when exposed to humidity variations, it becomes necessary to study the dynamic uptake and distribution of moisture within paper sheets and boards.

The sorption of moisture in paper sheets has two fundamental aspects. When a sheet is exposed to an environment of a definite relative humidity (RH), the moisture content it achieves is referred to as the equilibrium moisture content (EMC) when the sheet achieves thermodynamic equilibrium with its surroundings. A complicating feature of most paper and board materials is that the EMC is usually not a unique function of the RH level but depends upon the prior history of RH to which the sheet has been subjected.

With regard to the dynamic aspect of moisture sorption, a paper sheet can be considered as a fiber network. Thus, moisture distribution within the paper sheet can be affected by not only the external boundary layers in moisture diffusion but by resistance to diffusion inside the void space in the sheet and finally, the resistance to water transport within the fibers. All of these interact together and produce complex variations in the dynamics of moisture transport within the paper sheet.

In this paper, we present a study of the interaction of the various equilibrium and transport processes occurring during dynamic sorption of moisture in paper materials. A brief survey of the literature gives the background to our studies of both the equilibrium and transient aspects of moisture sorption in paper. The equilibrium sorption of moisture is examined with a focus specifically on the hysteresis region. Even though the EMC is a multivalued function of the RH, it is shown that it can be estimated by following the history of the turning points i.e. relative extrema in RH history. Representation of the hysteresis loop by means of a moisture density function allows us to predict the EMC for any given RH variation. A comparison with experimental EMC data for arbitrarily set RH regimens shows good agreement. In the next section we develop a moisture transport model incorporating three resistances to mass transfer to the transient moisture sorption process. The first is a surface resistance existing at the paper sheet's surface. This is caused by a concentration (humidity) boundary layer which interferes with vapor diffusion from the bulk of the air to the sheet's surface. The second resistance is that to vapor phase diffusion inside the void spaces of the sheet. The third is the diffusional resistance to moisture movement in the interior of the fibers. Our model is based on the application of the linear driving force (LDF) approximation to the intrafiber transport common in studies of adsorption in packed beds [2]. A brief parametric study indicates how each of these resistances influences the transient sorption process. A comparison of model predictions with experimental data is then presented.

BACKGROUND

MOISTURE SORPTION EQUILIBRIA

Moisture sorption equilibria for paper and other cellulosic materials (e.g. textiles materials, cotton, wood) have been widely investigated and reported in the literature. Common to all these materials are the facts that moisture sorption isotherms are generally of the high affinity type and usually show considerable hysteresis.

Moisture sorption by wood has been dealt with extensively in the early work of Barkas [3]. He attributed sorption hysteresis in wood systems primarily to the plastic deformation caused by gel expansion during sorption. Stamm [4] considered the adsorption of moisture by wood to be that of water dissolution in solid solution. Urquhart [5] and Urquhart and Williams [6] performed an intensive study of the moisture sorption characteristics of cotton. Based on these experimental findings, Urquhart [7] attributed sorption hysteresis of cellulose to the free secondary-valence bonds of the hydroxyl groups. It is thought that upon drying, all secondary-valence bonds which are hydrated under the wet state start to link with each other. Rehydration by subsequent absorption does not break all of these linkages thus reducing the sorption sites giving rise to hysteresis in sorption. Moisture sorption by paper and pulps has also been reported by Seborg and coworkers [8, 9, 10, 11, 12]. Careful measurements of EMCs were made for a variety of papermaking pulps by these investigators. Their results indicated that hysteresis was present and that it was independent of the rate of approach to equilibrium. Thus, it was true hysteresis and not a memory effect caused by rate limitations. They also found that processing of pulp by beating caused a small increase in moisture contents. The hygroscopicity measured by the increase in EMC changed by a maximum of about 6% due to beating. The EMC is more strongly affected by bleaching of the pulps and it was found that mild bleaching caused a significant reduction in the EMC. Subsequent bleaching caused smaller decreases in the hygroscopicity. An interesting feature of Seborg's results was that the ratio of the EMC during adsorption to the EMC during desorption was found to be approximately a constant over the majority of the RH range (specifically 12% to 88%). This constant did not seem to be affected by the processing conditions pulps had received nor even the origins of the pulps themselves. Moreover, the drying of saturated pulps resulted in a reduction of their hygroscopicity as long as drying was done over a range of RH limited to above 50%. When the pulps were dried below this range, the desorption isotherms coincided. Sorption isotherms at high humidities can be obtained by using a porous plate technique [13]. Two recent papers by Peralta [14] describe an investigation of the hysteresis behavior of moisture sorption by wood. Peralta used the theory of independent domains and the domain complexion function to follow paths within the main hysteresis loop.

A representation of the moisture sorption equilibrium for typical paper materials is provided in Figure 1. The lower isotherm is obtained when the material is equilibrated with progressively more humid environments starting from a perfectly dry state. If we start with an equilibrated sample at 100% RH and expose it to drier environments, the upper equilibrium curve is obtained. These curves are referred to as the boundary adsorption and desorption curves respectively. In general, the EMC of a given sheet will lie somewhere between these two bounding curves - the specific location depending upon the history of the RH - hence the term hysteresis. Curves on the EMC-RH diagram can be obtained by varying the RH according to a prescribed history, with sufficient time allowed in between each successive RH step for the paper sheet to reach equilibrium with its surroundings.

Thus the EMC vs. RH paths on this diagram represent trajectories as the EMC evolves with respect to RH. Note that such paths or trajectories are equilibrium paths. A trajectory corresponding to the EMC evolution when the sample is taken from the dry state to a certain RH and then subjected to decreasing RH back to the dry state is known as a desorption scanning curve. Similarly, when the sample is taken from a wet state to a low RH and then subsequently exposed to increasing RH the curve obtained is known as an adsorption scanning curve. Besides these, other complex paths such as spirals and interior trajectories are also possible within the hysteresis loop.

Hysteresis is found not only in sorption processes but also in the dewatering of porous media and the magnetization of ferromagnetic materials besides others. One fundamental requirement for hysteresis is that it should be rate independent [15]. Memory effects on certain variables can be represented by means of a memory integral (Volterra operator). Rate dependent history effects can be modeled as a composite of linear springs and dashpots generating viscoelastic behavior to describe the evolution of the variables. However, this is not so for true hysteresis phenomena which are equilibrium processes in the thermodynamic sense (cf.[16]). An elegant theory for equilibrium hysteresis has been put forward by Everett and coworkers (a description can be found in [16]). The material exhibiting sorption hysteresis is idealized as consisting of a large number of microscopic 'domains'[17]. Each such domain can exist in one of two states (I and II). A transition between the states (I to II) occurs as the RH is increased. Upon decreasing the RH from a high value, the reverse transition (i.e. II to I) does not occur at the same RH threshold but at a lower level giving rise to irreversible behavior of the domain. The behavior of a large assembly of these micro-domains whose transition characteristics are distributed according to some arbitrary probability distribution function will show hysteresis on the macroscale.

Based on the micro-domain concept, Everett and Smith [18] proposed a set of theorems governing the nature of the interior paths, loops and the shapes of the scanning curves inside the hysteresis loop. Everett [19, 20] developed a formal treatment of the domain model for hysteresis wherein he introduced the concept of the domain complexion function which serves as a memory of the system and tracks the evolution of the precise thermodynamic state of the material. The domain complexion function works as follows.

Consider the paper material to consist of a large population of micro-domains. Let h_{12} denote the humidity at which a domain undergoes a transition (i.e. fills up with moisture). Upon dehumidification, this domain undergoes desorption at a lower humidity level, h_{21}. Thus, there is a fundamental irreversibility in the sorption behavior associated with each micro-domain. The population of domains which are filled with moisture i.e. those that are in state II is reflected by the domain complexion function introduced by Everett. This population can be tracked by a two dimensional diagram (Figure 2a) where the humidity level h_{12} is plotted against the level h_{21} representing transitions of the domains from states I to II and II to I, respectively. At a certain RH, the paper material contains a distribution of domains of which some will be in state I and the remaining in state II. Since for any micro-domain, the filling up with moisture occurs at a higher RH as discussed above, h_{21} is always less than h_{12} and thus the permissible states of the entire system will be confined to the right side of the diagonal in this figure. Along the diagonal, the states are all reversible since for these domains, $h_{12} = h_{21}$. Figure 2b shows a representative diagram of the EMC against the RH along with a sample trajectory when the system is taken through a series of equilibrium adsorption and desorption processes. When the paper material is taken from a completely dry state to a certain RH, say h_{12}^0, all domains within the triangular region OCD in Figure 2a are filled i.e. in state II. When the RH is subsequently decreased to say h_{21}^1, domains represented parallel to the x-axis desorb i.e. transition from state II to state I. Thus, at the end of the desorption process at this point, the domains within the system which are in state II are represented by the quadrilateral area OCFJEO. Adsorption and desorption along the branches E'G' and G'H' in Figure 2b are represented by triangles EJH and GKH respectively in Figure 2a. Thus, at the end of the spiral trajectory, the domains in state II are given by the shaded area OCFJKHEO. The integral of the probability density of the domains over this area gives the total moisture content within the material in this state. These diagrams have been termed domain complexion diagrams by Everett and Smith [18]. A key assumption in this theory is that the probability density describing the domains during the various adsorption and desorption paths is a unique function of the material i.e. independent of the path itself. This is valid if the domains are independent of each other. Note that the domain theory provides a convenient way of following rate independent hysteresis effects if the material can be described by a population of independent domains.

The independent domain theory was successful in predicting paths and loops inside the main hysteresis loop besides the secondary adsorption or desorption curves. However, it was observed that the theory also failed in certain instances of adsorption and capillary-condensation caused hysteresis phenomena. An example is the adsorption of xenon on porous glass (quoted by Everett [16]). Thus, it appears that the independent domain theory may not be applicable universally and that for some systems at least, consideration of interactions between the domains needs to be taken into account. Alternate and equivalent formulations of the domain theory have been proposed e.g. for ferromagnetism (in which case the model is known as the Preisach model [15, 21]).

MOISTURE TRANSPORT

The transport of moisture through paper materials has been investigated to a limited extent in the past. Studies of moisture transport are generally of two types. Steady state transport of moisture has been studied with particular reference to the barrier properties of paper and board materials (see e.g. Liang et al. [22], Ahlen[23]). Steady state moisture flux across paper sheets is monitored under different humidity gradients with the objective of determining the water diffusivity. Ahlen indicated that the moisture diffusivity thus determined is independent of the moisture concentration within the sheets only at low RH values. Above this range, a strong dependence of the diffusivity on moisture content was found. Ahlen proposed that diffusion through the vapor space is dominant at the lower end of the humidity whereas at higher values, moisture transport in bound form through the fiber matrix dominated. Liang et al. [22] in their more recent report indicated that vapor phase transport is dominant over much of the humidity range at least for pulp mats and transport through the fiber matrix is significant only at the very high humidity regions.

Unsteady moisture transport is often analyzed by modeling the sorption process as a diffusion process of water through the fiber matrix of the paper sheet. At the sheet's surface, a convective mass transfer resistance is assumed; a mass transfer coefficient (also called the surface emission or transmission coefficient) is used to represent the transport through the boundary layer. Water vapor is assumed to adsorb at the sheet's surface and subsequent transport is assumed to occur by diffusion through the fiber matrix of the paper sheets. A study of unsteady state transport of moisture in paper based on this model has been reported by Lin [24] who considered the response of the moisture content of paper subjected to step changes in humidity variation. Numerical solutions to the unsteady diffusion equation were obtained and compared with experimental moisture concentration data published in the earlier work of Steele for kraft paper [25] and Ewart for oil soaked paper [26]. By obtaining best fitting model predictions to experimental data, the dependence of the diffusivity on the moisture content was determined. The use of a non-linear dependence of the diffusivity on the moisture content has been widely used in investigations of unsteady state moisture transport in wood and food materials.

In a recent paper by Lescanne et al. [27], diffusion mechanisms of water in a sheet of paper were investigated in detail. Firstly, they found that under steady state, water vapor diffusion through the sheets was dominant. Further, in the case of response to step changes in humidity, by modeling the process as diffusion through the vapor space followed by diffusion through the fibers, they could effectively describe the transient moisture uptake by the sheets. An important conclusion from their model is that moisture uptake can be considered as this two step diffusion process; each step can be described by Fick's law. On the macroscopic scale, diffusion seems non-Fickian though on account of the slow relaxation of the fibers' moisture content. This is in accordance with recent results on diffusion in multiphase polymeric materials where, it is found that unsteady state diffusion within these materials shows non-Fickian behavior which can indeed be modeled by Fickian diffusion within each of the phases of the polymeric composite (see [28]).

EXPERIMENTAL SYSTEM AND PROCEDURES

The experimental work reported in this paper is composed of experiments intended to study the equilibrium sorption behavior and the rate of approach to equilibrium. The equilibrium experiments were conducted to enable an in-depth study of the hysteresis loop, trajectories within it and to investigate the applicability of the independent domain complexions theory of hysteresis. The transient moisture experiments were conducted to provide experimental data for the confirmation of a diffusion model for moisture transport.

A schematic description of the humidity-control system is given in Figure 3. A more complete description of the experimental system has been provided by Chatterjee et al. [29]. The experimental system consists of a test chamber within which the humidity can be controlled to a prescribed variation. The test chamber is continuously swept with a mixture of dry and saturated air mixed in controlled proportions by a humidity control system. Prescribed variations of humidity such as step and ramp changes can be programmed into a computer connected to the control system. Paper samples are hung from a Mettler PM 200 recording balance so that their weights can be monitored continuously. Further, by obtaining the dry weight of the samples after conclusion of the experiments, the moisture content can be determined.

Paper samples 10 cm by 10 cm and approximately 0.29 mm thick were used. The samples were pre-conditioned successively at relative humidities of 50%, 90%, 15%, 90% and 15% for five hours at each RH level. The maximum deviation of the RH from its mean value was 1.04% (in the range of accuracy of the humidity probe) while that of the EMC from its mean was 0.06% at any RH level. The maximum and minimum differences in the EMC between two replicates at the same RH were about 0.35% and 0.02%, respectively.

Experimental measurements of the sorption isotherms and corresponding desorption scanning curves were obtained in the following manner. A dry sample of the paper board was taken (after preconditioning) from an RH of 15% through 80% in steps as shown in Table 1. Upon reaching 80%, the same sample was subjected to a decreasing RH from 80% to 15%. At each level, equilibrium was attained and the sample weight was determined. The sample was dried in a moisture analyzer after the completion of the experiment and its oven-dry (OD) weight was obtained. From the dry weight and the sample weight at each RH, the EMC could be determined. This gave the secondary or desorption scanning curve starting from 80% RH. Similarly, desorption scanning curves were obtained for starting points - 45%, 60%, 75% and 90%. The limiting desorption curve was established by choosing a completely wet sample and allowing it to attain equilibrium successively in various decreasing RH environments.

Transient moisture sorption experiments were conducted in the following manner. The paper sample was hung in the humidity chamber and preconditioned as described above. After preconditioning, the RH was brought to the lower level of the test and then was ramped according to the specifications. The sample weight was continuously monitored. After the ramping period was concluded, the sample was held within the chamber to allow attainment of equilibrium. After this, it was taken out and its O.D. weight was determined to allow calculation of the moisture contents. During the ramp process, the determined moisture contents are referred to as average moisture contents (AMC) in contrast to the equilibrium moisture content (EMC) which is used exclusively for moisture contents when the sample is in equilibrium with its surroundings.

EXPERIMENTAL RESULTS

The EMC values describing sorption equilibria (adsorption, desorption and desorption scanning) are shown in Table 2. Some of these data are also shown in Figure 4. The EMC increases sharply as RH increases above 80% where there is also a significant hysteresis between the boundary curves. This sudden increase in the EMC in the upper RH range has been attributed by some workers to capillary condensation. The observed hysteresis is quite large and distinct and cannot be attributed to experimental error in determining the EMC since the magnitude of the experimental error is much smaller than the magnitude of the hysteresis. The secondary desorption curves start on the boundary adsorption isotherm, lie in between the two boundary curves and exhibit much smaller hysteresis. They do not appear to cross over and join the boundary desorption curve (unlike that observed for yellow poplar wood by Peralta) except at RH values of 15% where questions of experimental precision become important.

The lower extreme point of the isotherms should pass through an EMC of zero at a zero value of RH (excluding the water of constitution of the cellulose). The other end of this isotherm should actually be determined at an RH of 100%. Since we were unable to achieve this experimentally, the average boundary adsorption data was fitted with the Guggenheim-Anderson-DeBoer (GAB) isotherm [30]. Similarly, the desorption isotherm was also fitted and the average of the adsorption and desorption isotherms at the 100% RH point was chosen to be the EMC.

The question of closure of the hysteresis loop at the upper end of the RH can only be resolved by taking accurate data in the range of 90-100% RH, especially along the boundary adsorption isotherm. Besides the issue of good RH control in this region (where the EMC is highly sensitive to the RH level) in a flow system such as the one used in this work, condensation processes can occur inside the humidity chamber at high humidities. Following Peralta [14], who used the Hailwood-Horrobin isotherm in the extrapolation of the boundary curves, the hysteresis loop was artificially closed at the upper end by taking the average of the extrapolated limiting adsorption and desorption EMCs at RH of 100% which gave a value 29.51% for the EMC. Thus, we assume that if an equilibrium adsorption process for the paper sample was begun at 0% RH and carried up to 100% RH after which the sample was desorbed back down to 0% RH, the EMC of the sample would trace the average boundary adsorption and desorption curves described above. This is an approximation to the true underlying surface.

Moisture distribution function & Prediction of EMC trajectories

From the data provided in Table 2, a discrete approximation to the moisture density function, $m\Delta h_{12}\Delta h_{21}$ was evaluated using a difference scheme [29]. Table 3 shows the moisture density function so constructed from the adsorption and desorption data. The differential moisture changes are larger along the diagonal of this table. Furthermore, the moisture changes are greater at higher humidities.

This moisture density function enables us to determine any EMC trajectory of a paper sample subjected to an arbitrary RH regimen by following the domain complexion function as discussed in the background section. Predicted secondary adsorption curves where the re-adsorption is begun from RHs of 45% and 60% are shown in Table 4. The predictions are also compared with experimental secondary adsorption isotherms from Table 2. Good agreement between Everett's theory of domain complexions and the experimental measurements is observed especially at RHs below 90%. The agreement at a RH of 90% is inferior. The relative errors in the EMC prediction at this RH are 7.23% and 7.53% for the RH 45% and 60% secondary adsorption curves, respectively.

Two sample spiral trajectories were also obtained experimentally. One trajectory started from the wet (saturated) sample and a desorption branch was followed by a sequence of adsorption and desorption steps, each decreasing in amplitude. A second trajectory starting from a dry sample equilibrated at 15% RH was also determined. The values of the moisture contents are given in Table 5. There is good agreement in general between the experimental data and the predictions obtained from the independent domain theory. Even at the highest relative humidity of 90%, the deviation between the predicted and experimental values is about 1.3%. The slightly larger error in the theoretical prediction at this point can be understood by recognizing that the moisture density function in this region was estimated by extrapolating the sorption isotherms. Between 90 and 100% relative humidities, the boundary adsorption and desorption isotherms were averaged in order to close the loop at 100% RH. This tends to skew the moisture density function and so results in a less accurate prediction of the moisture content at high humidities. Note that the prediction is consistently lower than the experimental data in this region. Since the experimental data were obtained from a completely wet sample, its desorption scanning curves are likely to be higher than the ones we have assumed in this region (by choosing to average the boundary adsorption and desorption values at 100% RH). Hence, we may expect the moisture densities in this region for the wet sample to be higher than the ones upon which the theoretical estimates were based. Thus, the theory can be expected to underestimate the moisture content in this region.

TRANSIENT MOISTURE TRANSPORT MODEL

The unsteady transport of moisture within paper sheets has hitherto been visualized as diffusion through the fiber medium, describable by a non-linear concentration dependent diffusivity. We generalize the transport process further by incorporating transport within the void spaces of the sheet in our model.

Consider a paper sheet as a structure composed of fibers and intervening voids as represented in Figure 5. In normal situations, we may visualize an external convective mass transfer resistance at the sheet's surface occurring due to a boundary layer. This has also been referred to as a surface emission coefficient [31, 32]. Moisture transport within the sheet occurs by diffusion within the voids and also within the fibers. Transport within the voids is in the form of vapor phase diffusion and is represented by D_p, the pore space water vapor diffusion coefficient. Transport within the fibers occurs by diffusion of the so-called bound water and is represented by the diffusion coefficient D_q. We consider this to be fiber-matrix diffusion. It is possible to approximate fiber-matrix diffusion by means of a linearized driving force approximation wherein the mass transport is assumed to be proportional to the difference in bound water concentration between the fiber matrix surface and that in the interior. The concentration within the interior is assumed to be the space averaged moisture content. This approximation is known as the Glueckauf approximation and its accuracy in representing the adsorption behavior in porous pellets has been studied [2].

Inter-fiber Transport

The diffusion of water vapor in the void space between the fibers in the paper sheet is described by

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho_p \frac{\partial \overline{q}}{\partial t} = D_p \frac{\partial^2 c}{\partial x^2} \qquad (1)$$

with

$$\begin{aligned} &c = c_o \quad \text{for} \quad 0 \le x \le L \quad \text{at} \quad t = 0 \\ &\frac{\partial c}{\partial x} = 0 \quad \text{at} \quad x = L \quad \text{for} \ t > 0 \\ &-D_p \frac{\partial c}{\partial x} = k_f \left[c_b(t) - c \right] \quad \text{at} \quad x = 0 \quad \text{for} \ t > 0 \end{aligned} \qquad (2)$$

In eq.(1), ε_p is the porosity (void volume) and ρ_p the density (g/cm^3) of the paper sheet, D_p is the diffusivity (cm^2/s) of water vapor in the inter-fiber void space, c is the water-vapor concentration (gmol/cm^3) in the inter-fiber void space at any location x (in the thickness direction of the sheet, cm), q is the adsorbed-phase moisture concentration (gmol/g), and t is the time (s). The first term on the left-hand side of eq.(1), $\varepsilon_p \partial c/\partial t$, which describes the accumulation of water vapor in the inter-fiber void space, is usually much smaller than the second term $\rho_p \partial q/\partial t$ which represents the uptake of water vapor by the fibers at a specific location x in the thickness direction of the sheet. The term on the right-hand side of eq. (1) is the net diffusive flux as given by Fick's Law.

The boundary conditions given by eq.(2) show that a symmetry condition is assumed on the sheet centerline (x = L; L is the half-thickness of the sheet) while a mass-transfer boundary condition describes the transport of water vapor from the bulk vapor [where the vapor concentration is any arbitrary function of time $c_b(t)$] to the surface of the paper board (x = 0), the mass transfer coefficient being denoted by k_f (cm/s).

Intra-fiber Transport

The moisture uptake by the fibers at any location x is described by the Glueckauf approximation . For our case, this can be written as

$$\frac{\partial \bar{q}}{\partial t} = k_i[q_s - \bar{q}] \tag{3}$$

with

$$\bar{q} = q_0 \quad \text{at} \quad t = 0 \quad \text{for} \quad 0 \le x \le L \tag{4}$$

In eq.(3), k_i denotes an intra-fiber mass-transfer coefficient (function of fiber properties) and q_s and $\bar{q}$ are the adsorbed moisture concentration (gmol/g) at the surface and in the bulk of the fiber, respectively at any location x. Next, we further assume that q_s is in equilibrium with the vapor-phase concentration of water vapor, c. This is given by the sorption isotherm represented symbolically as

$$q_s = f(c) \tag{5}$$

Initially, the sheet is at equilibrium with water vapor of concentration c_0 and thus

$$q_0 = f(c_0) \tag{6}$$

Dimensionless Formulation

The governing equations and boundary conditions described above can be cast into a non-dimensional form by defining the following dimensionless quantities:

$$C = \gamma\frac{c - c_0}{c_0},\quad C_b = \gamma\frac{c_b(t) - c_0}{c_0},\quad Q = \frac{\bar{q} - q_0}{q_0},\quad Q_s = \frac{q_s - q_0}{q_0},\quad X = \frac{x}{L},\quad \tau = \frac{D_p t}{L^2}$$

$$Bi = \frac{k_f L}{D_p},\quad \alpha = \frac{\rho_p q_0 \gamma}{c_0},\quad \beta = \frac{k_i L^2}{D_p}$$

where γ is a dimensionless parameter that will be defined later. Upon substitution of the above quantities, the governing equations (1)-(4) become

$$\varepsilon_p\frac{\partial C}{\partial \tau} + \alpha\frac{\partial Q}{\partial \tau} = \frac{\partial^2 C}{\partial X^2} \tag{7}$$

with

$$\begin{aligned} &C=0 \quad \text{for} \quad 0 \leq X \leq 1 \quad \text{at } \tau=0 \\ &\frac{\partial C}{\partial X}=0 \quad \text{at} \quad X=1 \quad \text{for } \tau>0 \\ &-\frac{\partial C}{\partial X}=\mathrm{Bi}\left[C_b(\tau)-C\right] \quad \text{at } X=0 \quad \text{for} \quad \tau>0 \end{aligned} \tag{8}$$

$$\frac{\partial Q}{\partial \tau}=\beta\left(Q_s-Q\right) \tag{9}$$

with

$$Q=0 \quad \text{for} \quad 0 \leq X \leq 1 \quad \text{at} \quad \tau=0 \tag{10}$$

Linear Isotherm

In this work we will be concerned with small variations of RH over which the adsorption isotherm can be considered to be essentially linear, i.e.,

$$q_s-q_0=K\left(c-c_0\right) \tag{5A}$$

where K is the slope of the isotherm. For this special case of a linear isotherm, we choose

$$\gamma=\frac{Kc_0}{q_0}$$

and therefore we get

$$\alpha=\rho_p K, \qquad Q_s=C$$

and eq.(9) reduces to

$$\frac{\partial Q}{\partial \tau} = \beta(C - Q) \tag{9A}$$

Solution of Moisture Uptake Model for Linear Adsorption Isotherm

The governing equations presented above are amenable to an analytical solution for the case of a linear adsorption isotherm. Below, we present solutions for the case where the bulk water-vapor concentration $c_b(t)$ is described by a ramp function, i.e.,

$$\begin{aligned} c_b(t) &= a\,t + c_0 \quad \text{for} \quad 0 \le t \le t_r \\ c_b &= c_{br} = a\,t_r + c_0 \quad \text{for} \quad t > t_r \end{aligned} \tag{11}$$

where a is the slope of the ramp and t_r is the ramp time. In dimensionless form

$$C_b = A\,\tau + B \tag{12}$$

where

$$A=\gamma\frac{aL^2}{c_0D_p}=\frac{\gamma\left(\frac{c_{br}}{c_0}-1\right)}{t_r}\frac{L^2}{D_p}\quad,\quad B=0\qquad \text{for } 0\leq\tau\leq\tau_r$$

$$A=0\quad,\quad B=\gamma\left(\frac{c_{br}}{c_0}-1\right)\qquad \text{for } \tau>\tau_r \tag{13}$$

where $\tau_r = D_pt_r/L^2$. Further, $\varepsilon_p\partial C/\partial\tau << \alpha\partial Q/\partial\tau$, and hence the first term on the left-hand side of eq. (7) can be neglected in comparison with the second. This is because the adsorbed-phase moisture is much greater than that held in vapor form in the inter-fiber void space of the sheet.

The solution of eqs.(7) and (9A) subject to the initial and boundary conditions represented by eqs.(8), (10) and (12) was obtained by the method of integral transforms. The partial differential equations (7) and (9A) were converted to ordinary differential equations in the time domain by taking the finite-region Fourier transforms. These ordinary differential equations were then solved by the Laplace transform technique
after which C and Q were recovered by applying the inversion formula for Fourier transforms. This method of first applying the integral transform to transform the space coordinate instead of the transforming the time variable as in the Laplace transform method avoids algebraic and inversion problems of the latter technique since both the integral transform and the inversion formula are defined at the beginning of the problem.

Stage 1: $0 \leq \tau \leq \tau_r$

The solution for C(X, τ) and Q(X, τ) are given as follows:

$$C(X,\ \tau) = \sum_{m=1}^{\infty} L_m \cos\beta_m (1 - X)\ f_{1m}(\tau) \tag{14}$$

$$Q(X,\ \tau) = \beta \sum_{m=1}^{\infty} L_m \cos\beta_m (1 - X)\ g_{1m}(\tau) \tag{15}$$

with

$$f_{1m}(\tau) = N_m + O_m \tau + P_m e^{-K_m \tau} \tag{16}$$

$$g_{1m}(\tau) = N_m \left[\frac{\left(1 - e^{-\beta\tau}\right)}{\beta} \right] + O_m \left[\frac{\tau}{\beta} - \frac{\left(1 - e^{-\beta\tau}\right)}{\beta^2} \right] + \frac{P_m}{\beta - K_m} \left[e^{-K_m \tau} - e^{-\beta\tau} \right] \tag{17}$$

The β_m's are the roots of the transcendental equation

$$\beta_m \tan\beta_m = Bi \tag{18}$$

while the coefficients L_m, N_m, O_m and P_m are given by

$$L_m = \sqrt{\frac{2\left(\beta_m^{\ 2} + Bi^2\right)}{\beta_m^{\ 2} + Bi^2 + Bi}} \tag{19}$$

$$N_m = \frac{J_m (A + \beta B)}{K_m} - \frac{J_m \beta A}{K_m^{\ 2}} \tag{20}$$

$$O_m = \frac{J_m \beta A}{K_m} \tag{21}$$

$$P_m = I_m + J_m B - N_m \tag{22}$$

where the appropriate values of A and B are obtained from eq.(13) for $0 \leq \tau \leq \tau_r$. The coefficients I_m, J_m and K_m are in turn obtained from

$$I_m = \frac{\alpha \beta R_m}{\alpha \beta + \beta_m^2} \tag{23}$$

$$J_m = \frac{(L_m \cos \beta_m) Bi}{\alpha \beta + \beta_m^2} \tag{24}$$

$$K_m = \frac{\beta \beta_m^2}{\alpha \beta + \beta_m^2} \tag{25}$$

and

$$R_m = 0 \tag{26}$$

The dimensionless average moisture content of the sheet ,$Q_{ave}(\tau)$, is given by

$$Q_{ave}(\tau) = \frac{q_{ave}(t) - q_0}{q_0} \approx \int_0^1 Q(X, \tau) dX \tag{27}$$

where $q_{ave}(t)$ is the average moisture content (or simply, moisture content) of the sheet at any time, t. Substituting eq.(15) for $Q(X, \tau)$ into eq.(27), we obtain

$$Q_{ave}(\tau) = \beta \sum_{m=1}^{\infty} \frac{L_m \sin\beta_m}{\beta_m} g_{1m}(\tau) \tag{28}$$

Stage 2: $\tau > \tau_r$

During this stage, the concentration of water-vapor in the bulk gas is a constant equal to c_{br}. The solutions for C(X, τ) and Q(X, τ) are given by

$$C(X,\ \tau) = \sum_{m=1}^{\infty} L_m \cos\beta_m(1-X)\ f_{2m}(\tau) \tag{29}$$

$$Q(X,\ \tau) = \beta \sum_{m=1}^{\infty} L_m \cos\beta_m(1-X)\, g_{2m}(\tau) \quad + Q(X,\ \tau_r)\, e^{-\beta(\tau-\tau_r)} \tag{30}$$

where $Q(X, \tau_r)$ is the moisture profile at the end of stage 1 and is obtained from eq.(15) by setting $\tau = \tau_r$. The functions $f_{2m}(\tau)$ and $g_{2m}(\tau)$ are given by

$$f_{2m}(\tau) = N_m + P_m e^{-K_m(\tau-\tau_r)} \tag{31}$$

$$g_{2m}(\tau) = N_m \left[\frac{\left(1 - e^{-\beta(\tau-\tau_r)}\right)}{\beta} \right] + \frac{P_m}{\beta - K_m} \left[e^{-K_m(\tau-\tau_r)} - e^{-\beta(\tau-\tau_r)} \right] \tag{32}$$

The β_m's and L_m are defined by eqs.(18) and (19) while N_m and P_m are now obtained from

$$N_m = \frac{J_m \beta B}{K_m} \tag{33}$$

$$P_m = I_m + J_m B - N_m \tag{34}$$

where B is obtained from eq.(13) for $\tau > \tau_r$. I_m, J_m and K_m are defined by eqs.(23)-(25) but R_m is now given as

$$R_m = \beta \sum_{n=1}^{\infty} L_m L_n \, S(\beta_m, \beta_n) \, g_{1n}(\tau_r) \tag{35}$$

where $S(\beta_m, \beta_n)$ is obtained from

$$\begin{aligned} S(\beta_m, \beta_n) &= \frac{1}{2}\left[\frac{\sin(\beta_m - \beta_n)}{\beta_m - \beta_n} + \frac{\sin(\beta_m + \beta_n)}{\beta_m + \beta_n}\right] && \text{for } m \neq n \\ &= \frac{1}{2}\left[1 + \frac{\sin(2\beta_m)}{2\beta_m}\right] && \text{for } m = n \end{aligned} \tag{36}$$

The dimensionless average moisture content of the sheet, $Q_{ave}(\tau)$, can be calculated from

$$Q_{ave}(\tau) = \left[Q_{ave}(\tau_r)\right] e^{-\beta(\tau - \tau_r)} + \beta \sum_{m=1}^{\infty} \frac{L_m \sin \beta_m}{\beta_m} \, g_{2m}(\tau) \tag{37}$$

where $Q_{ave}(\tau_r)$ is obtained from eq.(28) by setting $\tau = \tau_r$.

The water vapor concentration c, is related to the percentage RH by the following equation.

$$c = \frac{(RH)\, P_{sat}}{100\, RT} \tag{38}$$

where P_{sat} is the vapor pressure of water at the absolute temperature T of the system and R is the universal gas constant. Eq. (5A) can be rewritten in terms of the percentage moisture content MC as

$$EMC - EMC_0 = K_{RH}[RH - RH_0] \tag{39}$$

where

$$K_{RH} = \frac{18KP_{sat}}{RT} \tag{40}$$

RESULTS

We conducted a parametric study of the transient moisture sorption problem using the model and the solution developed above. Table 6 shows the various baseline parameters used for this investigation including the corresponding values of the dimensionless quantities. Ramp changes in RH from 15% to 45% were considered. The mass transfer coefficient k_f was obtained experimentally in the humidity chamber by monitoring the drying rate of a completely wet sheet of paper. The diffusion coefficient D_p for the bleached kraft paperboard sample was measured experimentally by the 'cup' method and was found to be the similar to that reported by Nilsson et al. [33] for a paperboard sample of similar density. The slope of the adsorption isotherm was determined from equilibrium data over the RH range of 15-45%. The thickness of the sample was measured. Representative values of the intra-fiber mass transfer coefficient k_i were chosen.

Figure 6 shows a plot of the calculated average moisture content according to Eqs. (28) and (37) for the parameters given in Table 6. The dimensionless moisture content is shown as a function of dimensionless time in this and subsequent figures. The solid line in this (and also Figures 7-10) represents the equilibrium moisture content obtained from the isotherm corresponding to each RH value during the ramp change. This curve thus represents the limiting value of the moisture content if the sheet were allowed to reach equilibrium at each time during the ramp change in RH. The deviation from equilibrium is caused by the presence of finite pore diffusion and external mass transfer resistances in this case. Figure 6 shows the predicted average moisture content as a function of time for various external mass transfer coefficient values. Figure 7 shows the moisture content development for various values of the inter-fiber i.e. pore diffusion coefficient of the water vapor. Observe that as the resistance is increased from an effective zero value ($k_f = 2.5$ cm/s for the external surface boundary layer) the transient moisture content moves away from the equilibrium value to increasing extents. Even when one of these resistances is effectively zero, the transient moisture content does not track the equilibrium curve. Figure 8 is a plot of the moisture content as a function of time for a set of four different ramp inputs in RH. The duration (and thus the slope) of the ramps was changed from a low value of 30 min through 120 min at the highest value. When the ramp duration is long, the slope of the RH change is small. This allows more time for equilibration of the sorption process to occur and thus the difference between the equilibrium moisture content and the transient values decreases. The sheet will then be able to track the imposed RH changes more closely when the RH change is slow. In the limit, one would expect the sheet to be entirely at equilibrium for sufficiently slow changes in RH.

Figure 9 shows the transient moisture content evolution for a ramp change in humidity. The data denoted by the crosses in this figure are experimental data obtained from the weight measurement of a paper sample in the humidity chamber. Model predictions for a variety of intra-fiber mass transfer coefficient values, k_i (from 0.001 through 1.0) are also shown on this figure as the continuous curves. Notice that for a value k_i of 0.0035 s^{-1}, the predicted moisture content agrees quite well with the experimental data of both the replicates. Also, increasing the k_i value to higher than 0.01 results in a negligible change in the moisture pick up indicating that beyond this value, intra-fiber moisture diffusion contributes little to the overall dynamics of the sorption. The fibers can be effectively assumed to be at equilibrium at this condition. In Figure 10 we show the evolution of moisture content of the sheet for a ramped humidity change of a different duration. Predictions from the transient diffusion model using a k_i value of 0.0035 s^{-1} are also shown. Good agreement between the experimental data and the model prediction indicates that the intra-fiber mass transfer coefficient we have obtained from prior experimental data (i.e. those in Figure 9) can indeed describe the new ramp data also.

CONCLUSIONS

The effects of moisture on the properties of paper are often drastic and significant. Thus, it is important to understand the sorption of moisture by paper materials exposed to conditions of varying humidity. Since even the equilibrium moisture sorption by a paper sheet is history-dependent (although not rate dependent), knowledge of the hysteresis behavior is important. Therefore, in the first part of this paper we have focused attention on the interior of the hysteresis loops and how the moisture density function could be developed from a knowledge of the boundary and some (minimal) data set consisting of either the adsorption or desorption scanning curves. The application of Everett's theory of independent domain complexions then allows us to predict the equilibrium moisture content of a paper sheet even when it is subjected to arbitrary (though equilibrium) cycles of humidity.

In order to gain a better understanding of paper materials and the effect of humidity on their behavior, we must obtain insight into the dynamics of moisture sorption also. The dynamic moisture sorption process inside paper sheets is controlled by rate limiting transport resistances and also by the equilibrium sorption behavior. Thus, it is necessary to develop models which can represent the resistance to moisture transport effectively. In this paper, we have modeled moisture sorption dynamics by considering transport to be describable by a sequence of three resistances to moisture sorption in a series. The first resistance is furnished by the external boundary layer which leads to humidity changes in the bulk being modulated at the surface of the sheet. The second is the inter-fiber diffusional resistance to the transport of water vapor. This inhibits the transport of water vapor into the void space within the sheets. Finally, the intra-fiber matrix of cellulose and other fiber components sorbs moisture and a diffusional resistance can be associated with the sorption equilibration process. We have idealized these three as serial resistances, neglecting the parallel direct intra-fiber diffusional pathway to moisture transport. This is justifiable since diffusivity inside solids is usually orders of magnitude smaller than corresponding diffusivity inside the vapor phase. Furthermore, since the diffusion path length across the sheet thickness is also much greater than the average fiber diameter, although moisture equilibrates along the cross section rapidly, the contribution of moisture diffusion along the sheet thickness is negligible to the overall transport. Thus, we find that in the overall sorption response to ramped humidity variations, the surface boundary layer and the pore diffusional resistance dominate the transport process with cross-fiber diffusion making a much smaller contribution.

It is important to note that the mathematical model for sorption presented in this paper is only preliminary and glosses over a number of important effects which could come into play under different conditions. Specifically, for larger humidity variations at the higher end, the sorption hysteresis of the sheet plays an important role in determining the dynamics. As was explained in an earlier work [34], sorption hysteresis implies that different portions within the sheet are constrained by differing equilibrium cycles within the overall hysteresis loop. In this case, recourse to a more complete model incorporating a hysteresis model (such as Everett's) has to be made. Furthermore, we have assumed isothermal conditions during the transport process. This is usually justified on the grounds that thermal diffusion is much greater than molecular transport and thus temperature gradients tend to equilibrate faster than concentration gradients in such porous media. The validity of this assumption needs to be examined experimentally and we expect that for faster and larger changes in humidity this may be invalidated.

Acknowledgments

We thank Mr. H. Radhakrishnan for help with some of the experimental measurements. Prof. Chi Tien is also gratefully acknowledged for many useful discussions.

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Replicate 1		Replicate 2	
RH ± s.d.	EMC ± s.d.	RH ± s.d.	EMC ± s.d.
15.02 ± 0.80	4.77 ± 0.06	14.95 ± 0.66	4.79 ± 0.04
30.01 ± 0.82	6.17 ± 0.06	30.01 ± 0.74	6.24 ± 0.05
45.01 ± 0.85	7.67 ± 0.06	44.89 ± 1.04	7.75 ± 0.05
59.93 ± 0.58	9.59 ± 0.05	59.94 ± 0.73	9.68 ± 0.04
75.03 ± 0.63	11.84 ± 0.05	74.99 ± 0.71	12.09 ± 0.04
79.97 ± 0.79	12.72 ± 0.06	79.91 ± 0.98	12.97 ±0.05
74.95 ± 0.75	12.24 ± 0.05	75.13 ± 0.65	12.46 ± 0.05
60.02 ± 0.68	10.26 ± 0.06	59.98 ± 0.91	10.41 ± 0.06
45.12 ± 0.86	8.35 ± 0.05	45.01 ± 0.77	8.45 ± 0.06
30.03 ± 0.85	6.59 ± 0.06	30.00 ± 0.72	6.70 ± 0.06
14.93 ± 0.74	4.87 ± 0.06	14.96 ± 0.53	4.92 ± 0.06

Table 1. Relative humidity and equilibrium moisture content data for two replicates.

RH, %	Bound. Ads.	Secondary Desorption Isotherms starting at RH, %							
		100	90	80	75	60	45	30	15
		Equilibrium Moisture Content EMC, %							
15	4.84	5.04	4.97[d]	4.9	4.87	4.86[d]	4.85[d]	4.847[d]	4.84
30	6.23	6.89	6.82	6.65	6.58	6.55[d]	6.33[d]	6.23	
45	7.74	8.79	8.58	8.40	8.28	8.25	7.74		
60	9.67	11.20	10.63	10.34	10.20	9.67			
75	12.00	14.80	13.19	12.35	12.0				
80	12.90	16.25	14.10	12.9					
90	17.23	25.11	17.23						
100	29.51	29.51							

Table 2. Sorption equilibria data. Boundary adsorption, desorption and secondary desorption data.

[d] Interpolated from neighboring values.

Total	4.84	1.39	1.51	1.93	2.33	0.9	4.33	12.3	29.51
100-90								4.40	4.40
90-80							3.13	5.73	8.86
80-75						0.55	0.36	0.54	1.45
75-60					1.80	0.21	0.55	1.04	3.60
60-45				1.42	0.50	0.02	0.11	0.36	2.41
45-30			1.41	0.29	0.00	0.05	0.01	0.14	1.90
30-15		1.383	0.097	0.21	0.02	0.04	0.10	0.00	1.85
15-0	4.84	0.007	0.003	0.01	0.01	0.03	0.07	0.07	5.04
h_{21} h_{12}	0-15	15-30	30-45	45-60	60-75	75-80	80-90	90-100	Total
↑ →									

(Note: The top row and the extreme right column represent totals of the percentage moisture changes along each column and each row, respectively.)

Table 3. Moisture Distribution Function $m(h_{12}, h_{21})\ \Delta h_{12} \Delta h_{21}$ of Bleached-Kraft Paper Board at 23.82 C (average percentage values shown in each grid cell)

Relative Humidity, %		45	60	75	80	90
Secondary Isotherm 45%-90%	Experimental EMC (%)	8.72	10.37	12.75	13.74	18.80
	Everett and Smith (1953)	8.79	10.21	12.51	13.29	17.44
Secondary Isotherm 60%-90%	Experimental EMC (%)		11.13	13.28	14.21	19.25
	Everett and Smith (1953)		11.20	13.00	13.76	17.80

Table 4. Experimental Secondary Adsorption Data of Bleached-Kraft Paper Board and comparison with predictions from Everett's theory.

RH, %	Spiral from wet state		RH, %	Spiral from dry state	
	Experiment	Everett		Experiment	Everett
90	25.50	25.11	15	4.77	4.84
45	8.72	8.79	90	17.69	17.23
90	19.42	17.44	30	6.57	6.82
60	10.92	10.84	75	12.21	12.24
75	13.01	12.64	45	8.32	8.52
80	13.98	13.40	60	9.90	9.94
75	13.29	12.85			

Table 5. Comparison of moisture content predictions using Everett and Smith's independent domain complexions theory with experimental data. Spiral trajectories starting from wet saturated state of paper sheet and also from dry state. Experimental data represent averages of at least two replicates which agreed with each other to at least within 0.05%.

Parameter		
Temperature	T, C	23.7
External mass transfer coefficient*	k_f, cm/s	0.25
Pore diffusivity#	D_p, cm^2/s	0.0063
Intra-fiber mass transfer coefficient	k_i, s^{-1}	0.0035
Ramp time*	min	60
Total time*	min	120
Sheet thickness*	2L, mm	0.325
Sample size*	cm	10 x 10
Paper Density	ρ_p, g/cm^3	0.839
RH_0		15%
MC_0		0.0484

Table 6. Parameters governing transient moisture sorption. Baseline values for parametric study. * denotes experimental values obtained independently. # Value estimated from diffusion cup experiments which also agrees with Nilsson et al. [33] for a sheet of similar density.

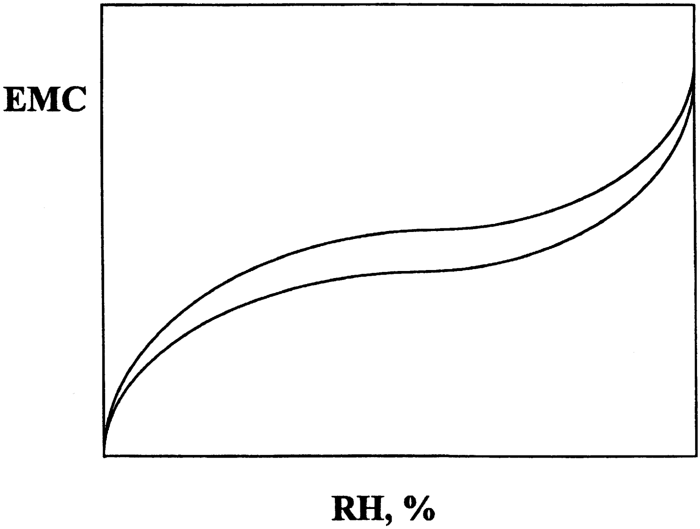

Figure 1. Representative equilibrium diagram for moisture in paper materials.

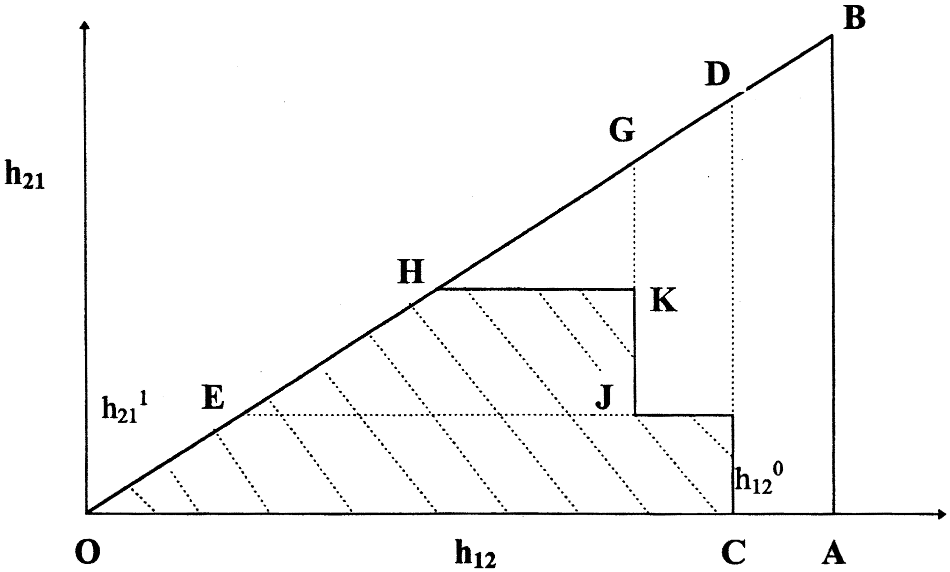

Figure 2a. Domain complexion diagram for a spiral trajectory. Points on this figure A, C,… correspond to points labeled A',C',… in Figure 2b.

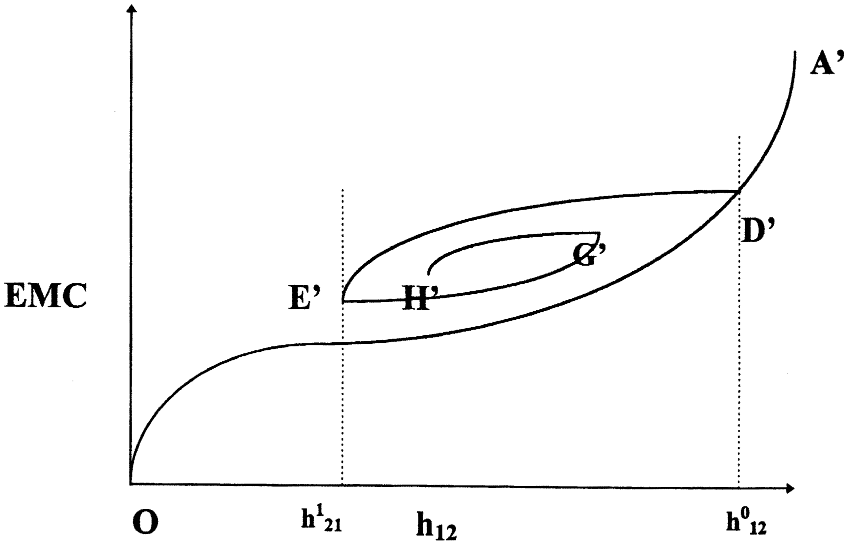

Figure 2b. Spiral trajectory on EMC-RH plane.

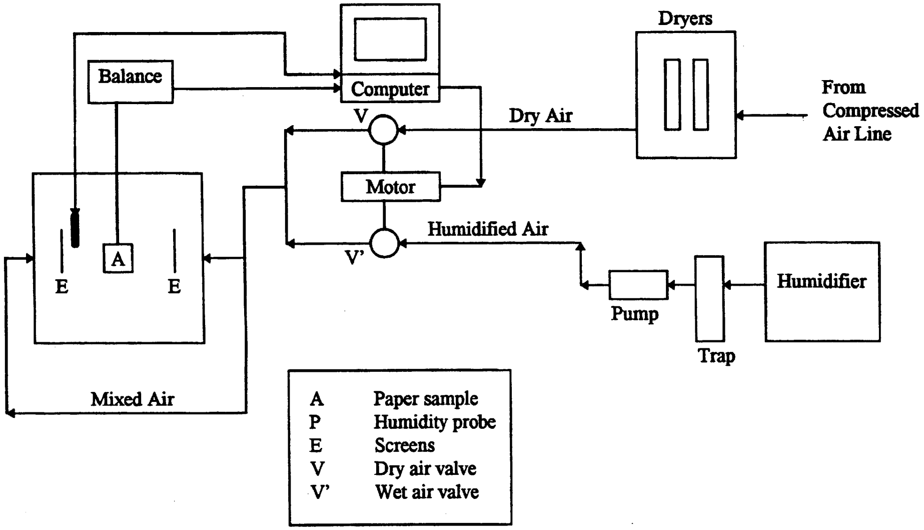

Figure 3. Schematic of experimental set-up for determining moisture uptake under varying RH conditions.

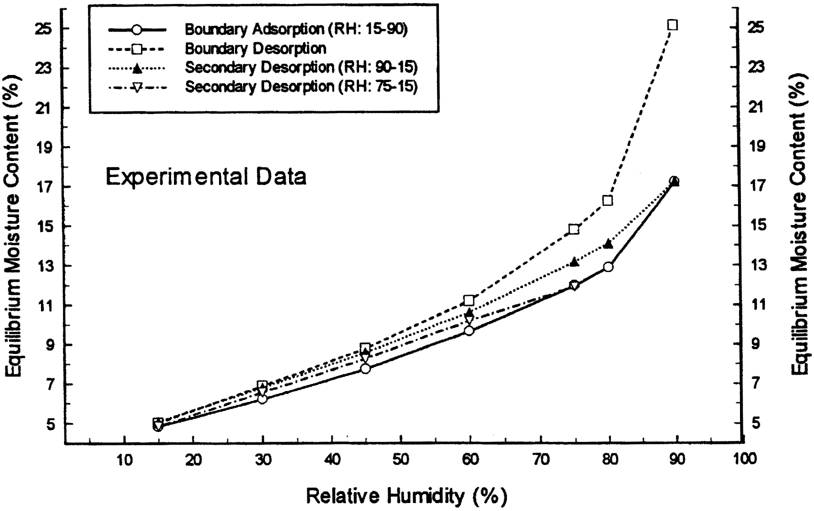

Figure 4. Equilibrium moisture content values at various RHs. Adsorption, desorption and some scanning experimental data are shown.

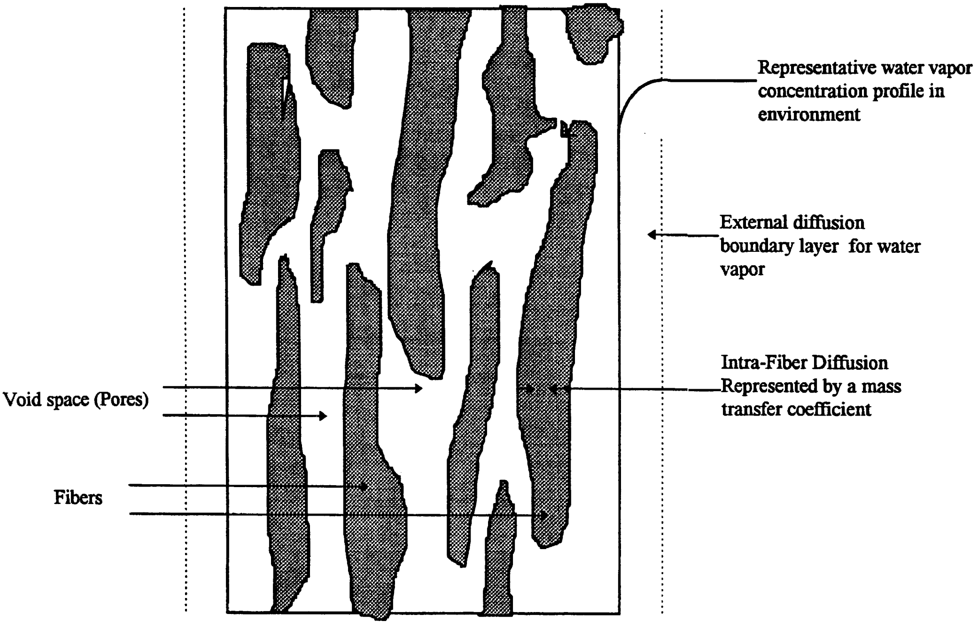

Figure 5. Representation of a paper sheet for modeling moisture transport.

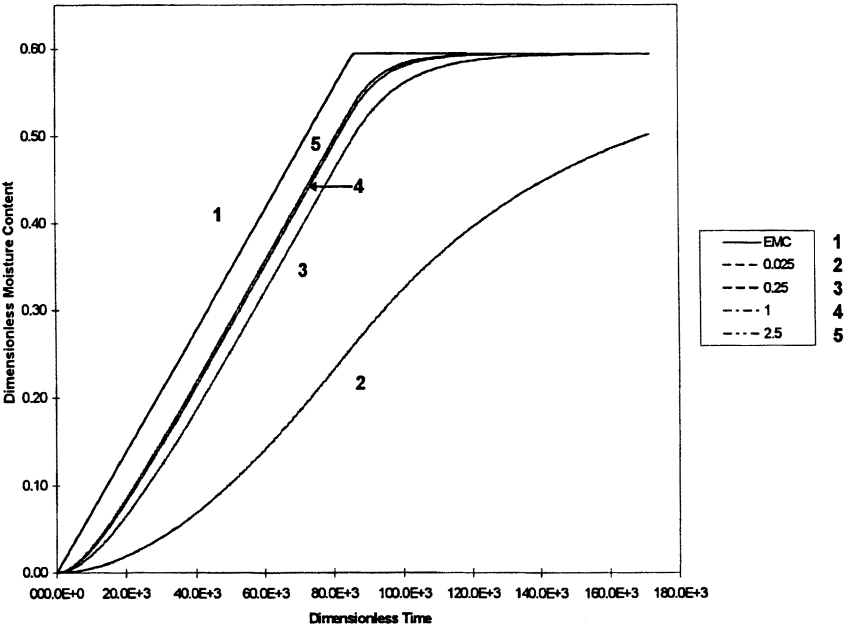

Figure 6. Moisture content model calculations. Variation of average moisture content with time. Effect of external mass transfer coefficient, k_f (cms^{-1})

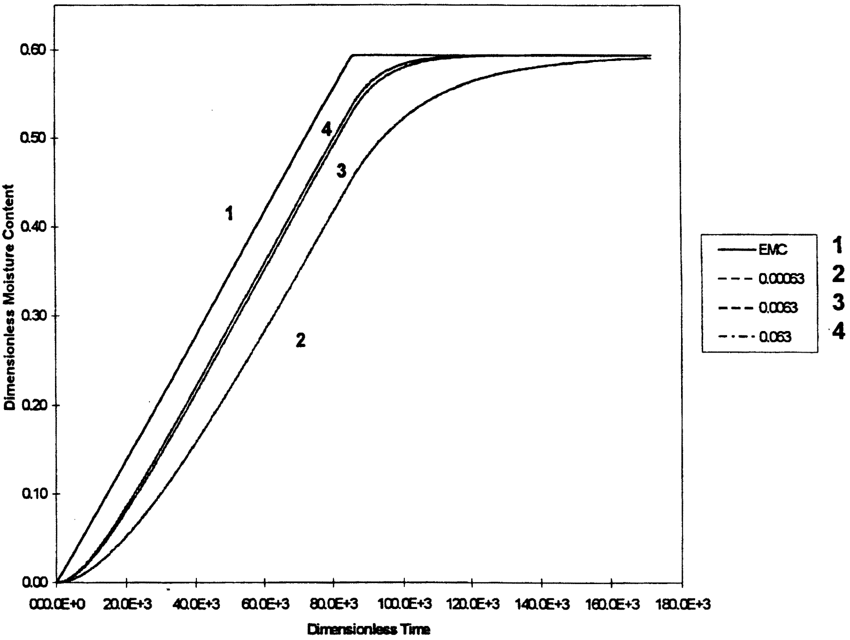

Figure 7. Moisture content calculations. Average moisture content variation with time. Effect of pore space diffusivity, D_p (cm^2s^{-1}).

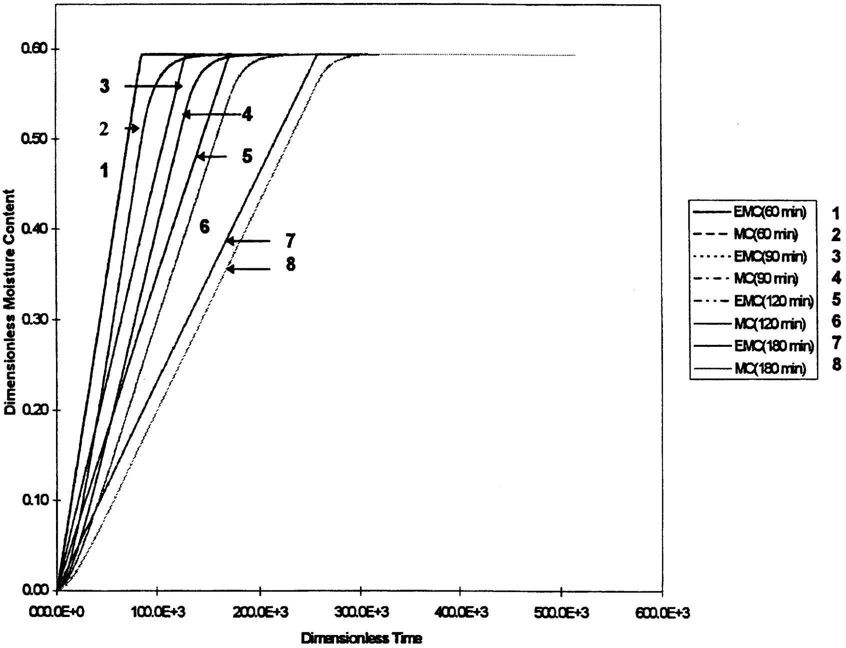

Figure 8. Moisture content model calculations. Average moisture content with time. Effect of different ramp profiles and times.

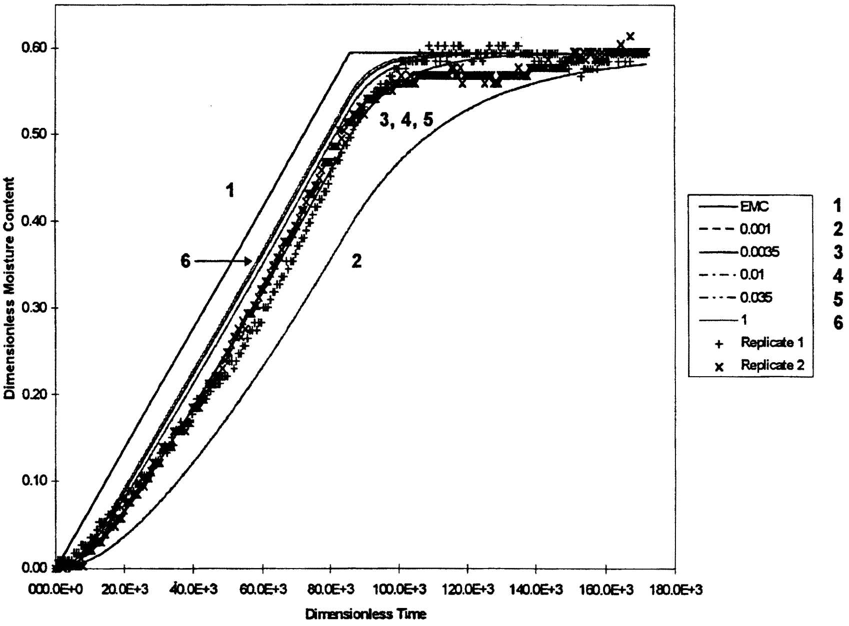

Figure 9. Comparison of model predictions with experimental data. Moisture content during transient sorption model calculations. Variation of moisture content with different values of the intra-fiber mass transfer coefficient, k_i (s^{-1}).

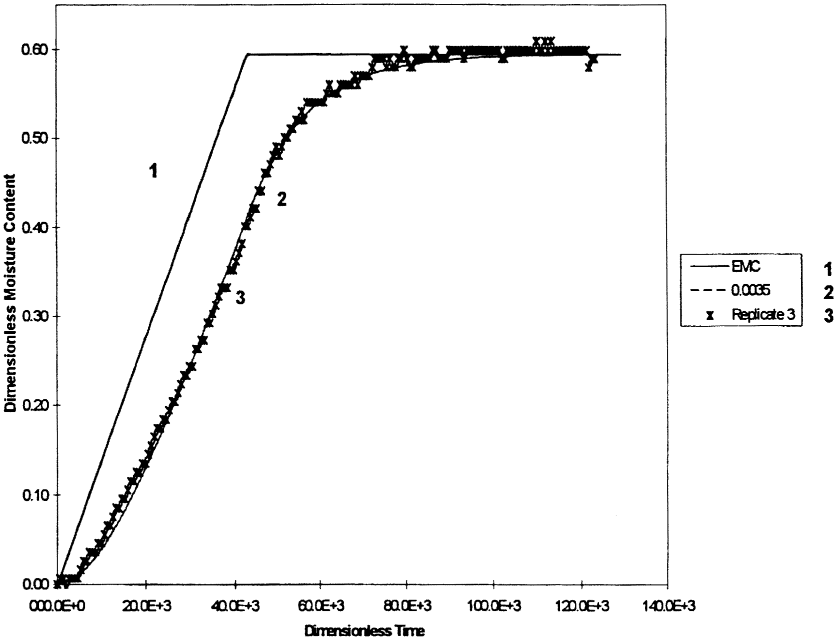

Figure 10. Moisture content evolution for a ramped RH change. Comparison of model predictions with experimental data ($k_i = 0.0035\ s^{-1}$).

Transcription of Discussion

Moisture Sorption by Paper Materials under varying humidity conditions

Siddharth Chatterjee, Assistant Professor, Syracuse University, USA

Anthony M Scallan, Principal Scientist, Paprican, Canada

The model that you use to explain your work seems a strange one. There is a much simpler model and this is that, during the first desorption, the surfaces in the fibre progressively come together until, at zero relative humidity there are no pores and the surfaces are all bonded. Then, when you re-expose to humidity, the pores are progressively opened but, since all the surfaces do not debond, adsorption is less. This is the usual explanation for hysteresis in a gel and usually the hysteresis is greatest during the first desorption-adsorption cycle. In your work you never see this properly because you cycle your sample before you begin the 'serious' measurements.

Siddharth Chatterjee

Yes, we recycle our samples, we precondition them. So you are saying that we don't see them.

Tony Scallan

The first desorption-adsorption is most important and results in what is called hornification. Pulp when first used to make paper is called 'never dried'. Once it's been dried, it hornifies and is not the same when recycled.

Siddharth Chatterjee

If you look at the papers by Seborg et al in the 1930s where the hysteresis group was found to be repeatable and it didn't change from cycle to cycle and said that it was something to do with the paper structure and not this availability of -OH sites with this different adsorption and desorption but you ask why, what is happening inside this fibre which is giving this non-availability of -OH sites. In our experiment we have also found that this hysteresis loop is repeatable. You have to eliminate those first histories.

Tony Scallan

You are getting your reproducible hysteresis because of your cycling of the sample before you start your proper measurements.

Siddharth Chatterjee

No, the purpose of the initial cycling is to get rid of the history of the paper. After that was done, when we did the experiments, we found that hysteresis loop was repeatable. Hysteresis is not a time dependent phenomenon. It is a time independent phenomenon.

Dr Richard Bown, Director, ECC, UK

As probably the only representative of Douglas Everett's research group I feel I ought to make a comment. In the later years of Everett's work we developed that theory to try and describe the pore structures and the surface chemistry within the samples and most of this work was done in fact with solid silica samples with things like ink bottle pores in them. Have you tried to use any of your data to describe the pore structure in the pulp and perhaps, if you know the pore structure to use it to try and describe the surface chemistry of the pulp.

Siddharth Chatterjee

This is the first step because in the future we will be trying to look at what is physically happening inside the structure as you said.

Richard Bown

When you start to do that you have to work at very high humidity, well above 90%. Reliable temperature control then becomes a very serious problem. You could find a difficulty there in taking this kind of work to a conclusion.

Prof Bandaru Ramarao, ESPRI, USA

If I may make a comment for clarification on this question. These kind of hysteresis theories are currently being used in adsorption in order to find out connectivity between pores. When you are trying to find the connectivity between pores you cannot use this theory directly - you have to do something like a Monte Carlo network modelling.

Siddharth Chatterjee

The point we were trying to make here is that the connectivity between these elements does not seem to be describable in terms of the hysteresis so the independence of these domains seems to be valid here. I think that's the key to what we're trying to do.

Murray Douglas, McGill University, Canada

You noted that you could not get data in the region above 90% RH and in your final presentation of the results at the high end you never started from the condition of above 90% RH. I don't know if you have future plans to extend the research but to leave out that region above 90% is a very important omission One of the important uses for experimental data such as you are developing is in the drying of paper, for which one starts in the soaking wet condition where the fibres are in the state Derek Page described in the discussion of the previous paper. So the desorption of water from saturated fibres is a condition of great importance and one which is not yet properly defined.

Siddharth Chatterjee

Yes you are absolutely correct. 90% RH is a very important region. There are very big changes happening in that region. We could do 95% but our controls are not very good but we are working on that to get data in that region.

Juha Mentu, Microbiologist & Laboratory Manager, Enso Group Oy, Finland

I have an extra point of view to present here. The loss of strength of paper due to moisture content is the most important problem indeed. Paper and board microbiologists, like myself. are also very interested in the moisture intake into paper and board because of additional risks of microbiological biodeterioration and decrease of hygienic quality of some sensitive products like liquid packaging board. These unfavourable events will take place whenever there is a certain level of 'active water' (p/po) present. So, my first question will be: is there a relationship between these variables you mentioned, RH and EMC, and water activity which is the relationship of vapour pressures above the product and in standard state. Secondly, do additives like internal sizes and fillers have any effects on the water intake phenomenon?

Siddharth Chatterjee

The experiments we have done so far have been with a bleached kraft there were no fillers in that just some cellulose, hemicellulose. We have tried to establish what is happening in the fibre putting in fillers will complete the picture but we can do that in the future. I do not have any data for that.

Theo van de Ven

Your vapour transport theory is in essence a one-dimensional theory of the z direction. Obviously there are other variations in the x-y plane. Can you say something about how they would affect the transport of moisture?

Siddharth Chatterjee

I have explained that in our system they were hanging vertically and in through circulation of air so the primary uptake is in the z direction. If you had x-y transport then you have to solve in more directions.

Theo van de Ven

Since paper is heterogeneous, you don't have the same moisture profile everywhere at the same distance z.

Siddharth Chatterjee

This is a wrong representation. We have 10cm x 10cm samples and for our case we think this is good.