

STUDY OF ANISOTROPIC MOISTURE DIFFUSION IN
PAPER MATERIAL

by

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Abstract

Study of Anisotropic Moisture Diffusion in Paper Material

The influence of moisture on the final use of paper has been a critical issue for papermakers. In this thesis, we studied transient and steady state moisture diffusion in paper under different humidity conditions and its relationship to sheet structure. Moisture transport through this medium occurs by a number of mechanisms, which the most important are: diffusion through the pores, diffusion of condensed water through the cell-wall of the fibers, surface diffusion and capillary transport. In the first part of this work, we investigated the sorption of moisture by paper sheets exposed to rapid changes in the external humidity. We found that transient moisture transported in paper material is Non-Fickian, most likely being caused by two sequential diffusion steps: the first being a rapid diffusion through the pores followed by a slow diffusion through the fibers/cell wall material. External boundary layers cause further departures from Fickian sorption.

The porous structure of paper significantly impacts its diffusion characteristics. At low to moderate moisture contents, it is the pore space that conducts water vapor by diffusion: transport is therefore proportional to the sheet porosity and is inversely proportional to the tortuosity. Pulp refining reduces the porosity and increases tortuosity, decreasing the moisture diffusivity. Since the pore structure is strongly anisotropic, reflecting the layered structure of paper, diffusion is also anisotropic and is usually greater in the lateral (in-plane or XY) dimensions as compared to the transverse (through plane or ZD) dimension. In machine made paper, there could be a weak dependence on

the in-plane fiber orientation giving rise to higher diffusion in the machine direction (MD) as compared to the cross machine direction, (CD). Parameters describing the moisture diffusivity in paper are necessary for calculating transport rates and moisture profiles. Therefore, we present diffusion parameters for moisture transport through the pore space (D_p) and the non-linear diffusivity of condensed phase moisture (D_{q_0} and m) for sheets made from bleached kraft softwood pulps refined to different levels. We demonstrate the utility of the diffusion parameters by estimating moisture profiles through a stack of sheets using a mathematical model for transient moisture transport. The model predictions agreed with our measurements of the moisture profiles showing the usefulness of these diffusion parameters.

Keywords: moisture diffusion, paper, water vapor, bound water.

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Introduction

The main structural component of wood fibers is cellulose, which has a particular relation with water due to its hydrophilic character. This characteristic is relevant for paper once its properties are greatly modified by moisture content. Therefore, the study of moisture diffusion in paper proposed by the present work demand, in first place, the understanding of the relationship between cellulose and water. This issue has been very much studied, although new approaches, methods and equipments could bring advances in near future. A discussion regarding to these latter developments is made as part of a chapter of this work. The present study identified the necessity of an investigation on the influence of the changes on the paper structure on moisture diffusion. A variety of mechanisms of diffusion have been proposed and two of them are well accepted, the moisture vapor diffusion on paper pores and the condensed water diffusion in the fiber wall. This investigation pursues to proof these mechanisms through changing the paper structure in order to benefit one mechanism in detriment of another and evaluating the effects.

The importance of moisture diffusion anisotropy is another important phenomenon covered in this work. Studies of moisture diffusion in paper have most frequently been focused on transverse direction transport, but with printing processes and with photographic, liquid containers and decorative papers the lateral moisture diffusion becomes more important. A couple of preliminary works have pointed to lateral diffusion as faster and more important in paper applications and even during paper manufacturing.

The main objective of the present work is to describe the phenomenon of moisture diffusion in paper using the approach of the lateral and transverse diffusion to explore the difference between the mechanisms on both directions. The use of refining and calendering allowed significant changes in paper tortuosity and drastic increases in fiber contact, which then were used to study the effectiveness of pore diffusion and fiber wall diffusion under these different conditions. Research on the model of diffusion presented through the approaches of diffusion described by Crank, in his book *Mathematics of Diffusion*, brings a conclusive point. The discussion shows experimentally that the Fickian diffusion model does not represent properly the phenomenon of moisture diffusion in paper. The characteristic of paper as a hydrophilic material with easy adsorption of moisture has to be represented by a non-Fickian model. The factor representative of this Non-Fickian characteristic in the model used in this work and described by Ramarao and Chatterjee is the fiber mass transfer coefficient.

PROBLEM STATEMENT

The objective of this doctoral research was to investigate the moisture diffusion inside of the paper structure in order to understand the mechanisms that control it, besides to effectively measure the diffusion coefficient of moisture in both direction XY and Z. Therefore is necessary to understand this phenomenon and for that was carried out experiments at steady state and unsteady state under different conditions of relative humidity. Only then was possible to characterize the behavior of moisture diffusion and

apply the mathematical model developed before by our study group in the Z-direction and XY-direction. Moreover, the conditions of paper structure modifications with pressing, refine and calendering was added to the study of moisture diffusion in both directions.

STUDY RELEVANCE

The anisotropy approach for moisture diffusion in paper is an important issue, mainly considering that moisture diffusion in paper has been most of the time focused on transverse direction (Z). However, with lately developments in printing, photography, liquid containers and decorative papers, the lateral moisture diffusion (XY) has become more important. Other properties, more evident lately with increasing of hardwood use, and that are closely related with moisture are dimensional stability and creep. Some preliminary works have pointed the lateral diffusion as faster and important in paper applications and even during paper manufacturing.

Therefore the present work describe the phenomenon of moisture diffusion in paper using the approach of lateral and transverse diffusion to explore the difference of mechanisms on both directions. The use of refine and calendering allowed us to change the paper tortuosity and increase the fiber contact drastically in order to measure the effectiveness of pore diffusion and fiber wall diffusion under these different conditions. The research on the model of diffusion presented through the approaches of diffusion described by Crank brings a conclusive point. The results show experimentally that the

Fickian diffusion model does not represent properly the phenomenon of moisture diffusion in paper. The characteristic of paper as a hydrophilic material with easy adsorption of moisture has to be represented by a Non-Fickian model. The factor representative of this Non-Fickian characteristic in the model used in this work and described by Ramarao and Chatterjee is the fiber mass transfer coefficient. The experimental set up allows to work with relative humidity as different as 5 % or 90 % and differentiate the behavior of paper under such conditions.

CHAPTER I

ASPECTS OF MOISTURE TRANSPORT IN PAPER

1.1. Introduction

Moisture transport in paper material involves the interaction of water with a complex composite material formed by components with different characteristics. The fiber walls are formed by different layers disposed with particular compositions. Moreover, fibers contain pores which contribute to transport phenomena according to their size. Cellulose is the key component to be studied in fiber wall due the higher amount present in most papers and its hydrophilic property. The formation of hydrogen bonds between cellulose molecules and water, as well as the fiber swelling characteristics and the importance of the moisture access in cellulose material, are part of the scope of this bibliographic research. The phenomenon of adsorption is very important and the specific aspects of cellulose sorption of water are discussed here.

This chapter will discuss the principal aspects of water and paper relationship to clarify, as much as possible, what is happening inside of a paper sheet when the ambient relative humidity is increased. Therefore, some known mechanisms of moisture sorption and the difference on water bond forces available inside of a paper sample are also to be considered. This is an introduction chapter for a study of moisture transport in paper. The knowledge of the current information in water and cellulose interactions is fundamental to develop further works, although several aspects of this process are still in debate.

1.2. Paper Influence

The importance of moisture transport in paper manufacturing is evident, but the moisture contribution in several properties of paper demand further research to be better understood. Paper mechanical properties, for example, are known to be directly related to the bonds among fibers, more specifically mechanical properties, are dependent on the amount of hydrogen bond between fibers and these can be harmed by water-fiber hydrogen bonds. Paper immersed in water can lose about 96% of its mechanical strength but regain a substantial fraction of that when dried again. Looking at the inverse process, during drying the fibers come together and shrink, immobilizing the paper sheet structure.

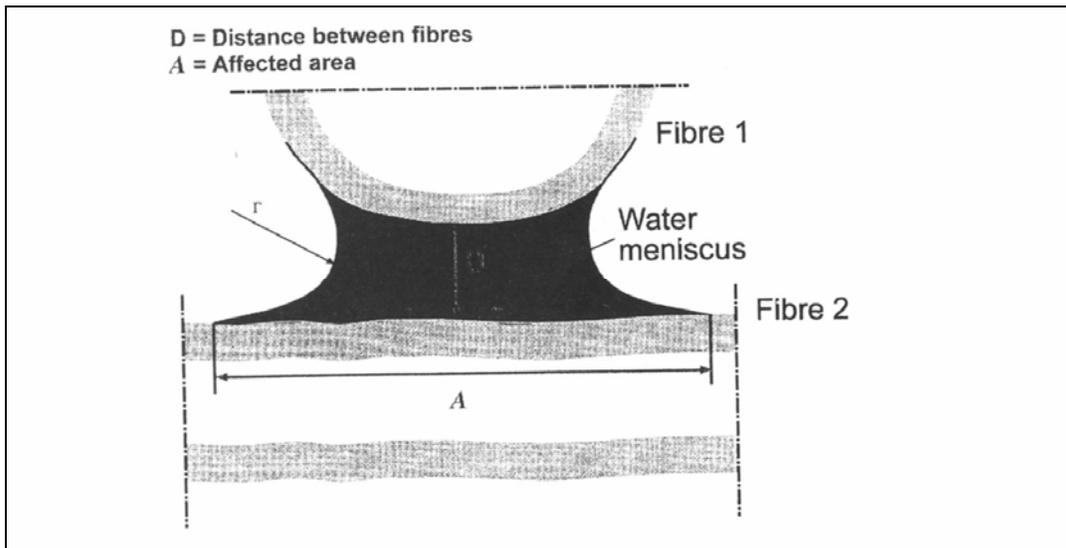


Fig 1.1. Scheme of water meniscus formation during paper drying. Physicochemical characterization of papermaking fibers, Wagberg L. and Annergren G., 11th Fundamental Research Symposium in held at Cambridge, 1997.

An important papermaking operation, which depends on water relations, is fiber refining. The fibrillation, which is the main consequence of refine, is achieved mainly because of the aqueous medium that is forced into the cellulosic structure and is able to change its glassy characteristic. The combination of water with the holocellulose makes it more elastic and flexible, which contributes for fiber entanglement and consequently paper formation. Moreover, the water drainage and the moisture removed to the end of the drying section contributes to fiber contacts and improve fiber bonding in the paper sheet. Robertson [1] developed an interesting work on the interaction of liquids and paper. He found that a loss of paper strength without a change in initial modulus was observed for non-swelling liquids, and speculated that it was because the number of bonds that remained constant although there was a loss in individual bond strength. Therefore, the strength lost with non-swelling liquids was much smaller than in swelling liquids. The tensile strength ratio MD/CD was found to be constant independent of the liquid used, showing that strength reduction is independent of direction. The author also found that the greater the shrinkage during drying of paper, the greater is the internal stresses and as consequence the greater is the swelling during moisture adsorption. In this work was also noted that liquid is entrapped in the fiber wall during desorption, as had been observed by several other authors. His work conclusions are supported by the experimental evidence that most liquids can be released by cellulose re-swelling, rapid drying give higher retention than slow drying, retention increases by repeating wet and drying process, and results varied for different cellulose content samples (cotton linter > kraft > hydroxyethylated linter > dissolved pulp > BHDKP). The apparent important liquid property highlighted in this work is molar volume, it was observed that liquids with

molar volumes greater than 100–110 cc (centimeter cubic) are relatively inactive in wood pulp. Liquids with molar volumes greater than 55-60 cc were reported to prevent the plasticization and weakening of viscose rayon that depends on liquid diffusion into the fiber. Thus, the author concluded that the interaction of liquids with fibers depends on the fiber structure and porosity and its relation with the molecular size of the liquid.

The relationship between moisture and paper also is important due to paper swelling and its effect on dimension stability. This property is important in printing and copy processes where paper moisture or temperature can change fast and drastically. Paper anisotropy is shown in experimental measurements where dimension during swelling could vary in the ratio 1 (machine direction): 2 (cross direction): 50 (thickness direction) as mentioned in several text books, depending of paper grade and refine intensity obviously. Swelling by moisture is a consequence of hydrogen bonds breaking and stress release, this is followed by an irreversible increase of paper volume, unless an additional operation such as calendering occurs to densify the paper again [2].

1.3. Cellulose Role

The participation of water in the process of paper manufacturing is remarkably important, and moisture content continues to influence paper applicability throughout its diverse areas of use. The principal raw material for paper industry is wood, a composite material formed mainly by cellulose, hemicelluloses, lignin and extractives. These wood constituents remain a significant part of paper composition, and our study on the relation

The pore data for these cellulose samples were measured by small angle X-ray scattering method [4]:

Table 1.I – Pore Characteristics Information on Cellulose Samples			
Sample	Volume of Pores (%)	Inner surface of Pores (m ² /g)	Parameter of Average Pore Size (nm)
Cotton Linter	1.7 – 1.8	5.3 – 6.0	11.6 – 13.1
Sulfite Dissolving Pulp	0.7 – 1.5	1.7 – 3.2	10.1 – 25.4
Sulfate Pulp Prehydrolyzed	1.2	3.7	13.1
Cellulose Powder from Spruce Sulfite	1.4	5.2	10.4
Cellulose Powder Mercerized	1.7	15.8	4.4
Cellulose Powder Enzyme Treated	2.5	6.2	15.9

From the data in the table, could be observed that cellulose enzyme enlarged the pores. Other important effect on pores is interfibrillar and intercrystalline swelling in the presence of liquids or when fiber is dried, a significant and partially irreversible reduction of pores occur due hornification. Stone and Scallan [5] studied water transport in fiber extensively and they claim that during the pulping of wood, large pores are progressively created by enlarging of micro pores through fiber degradation. The authors also accepted the idea that fiber walls consist of a gel of carbohydrates and lignin that can take water

and swell. Based on their model, the authors hypothesized that the multiple lamellas that form the fiber have cellulose rich as well as lignin and hemicelluloses rich layers. In the first layers cellulose is organized as micro fibrils which form sheets.

At around the 70% yield level during the pulping, layers of lignin and hemicelluloses are dissolved, increasing the pore size around cellulose. Following pulping, the cross linking effect of lignin is removed and cellulose networks are released, being able to move. Thus spaces between lamellas begin to close up and the macro pore volumes are lost and the fiber wall shrinks.

The shrinkage hypotheses are based on the assumption that lignin and hemicelluloses impose a strain on the system during fiber growing and expand the cellulose network and therefore when they are removed cellulose shrinks. However the authors recognized that the procedure of solvent exchange used in this work raised many questions and that structural studies on fiber swelling should be done when fibers are saturated with water.

The interactions with water changes with the degree of polymerization of glucose, such that solubility decreases above DP 6, and when the DP reaches 30 the polymer has the structure and properties of cellulose. Intermolecular hydrogen bonds are the links responsible for interchain cohesion, but this cohesion is not uniform through all the polymer chain. There are regions of low molecular organization called amorphous and regions of high molecular organization called crystalline.

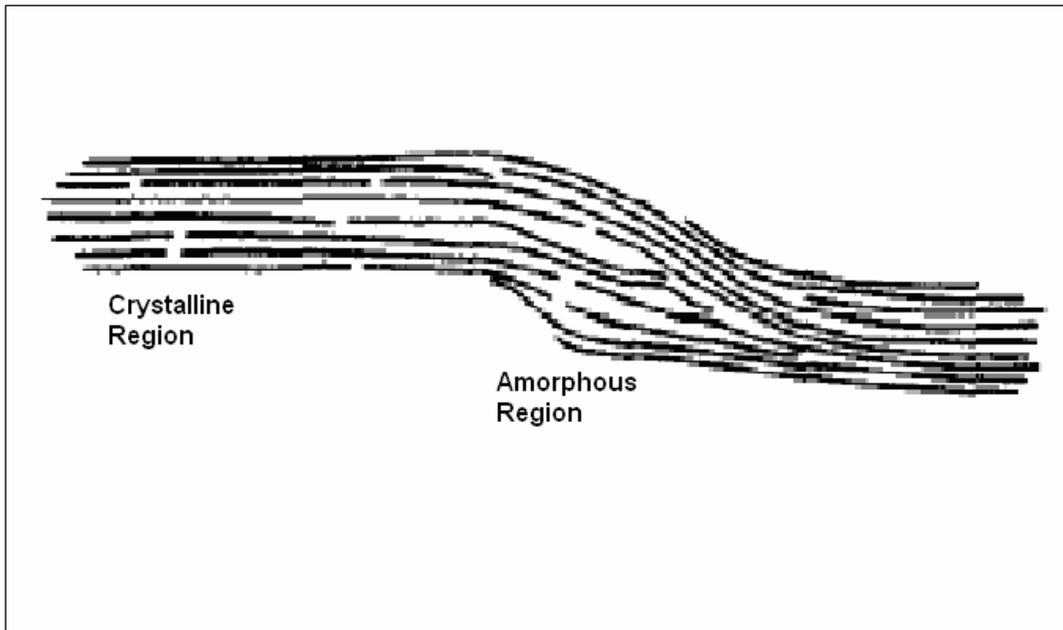


Fig 1.3. Representation of Cellulose chain regions, a more organized called Crystalline and a more dispersed called Amorphous. From the book, “Recent advances in the chemistry of cellulose and starch, J. Honeyman, 1959

When the concept of amorphous region is admitted, the glass transition temperature of cellulose and as consequence a transition to an elastic state is admissible too. However, in normal conditions, cellulose is in a glassy state and degradation conditions are higher than transition conditions. Therefore, this polymer would suffer degradation before become elastic. Nonetheless, in a water medium this condition changes and the glass transition temperature decreases to below room temperature. Moreover, in the presence of water the heat capacity of cellulose decreases and the molecular order of the crystalline region increases because water breaks the hydrogen bonds between cellulose and allows it to rearrange in a higher order [6].

An interesting and didactic study of glass transition temperature and its effects on polymers properties is shown as below:

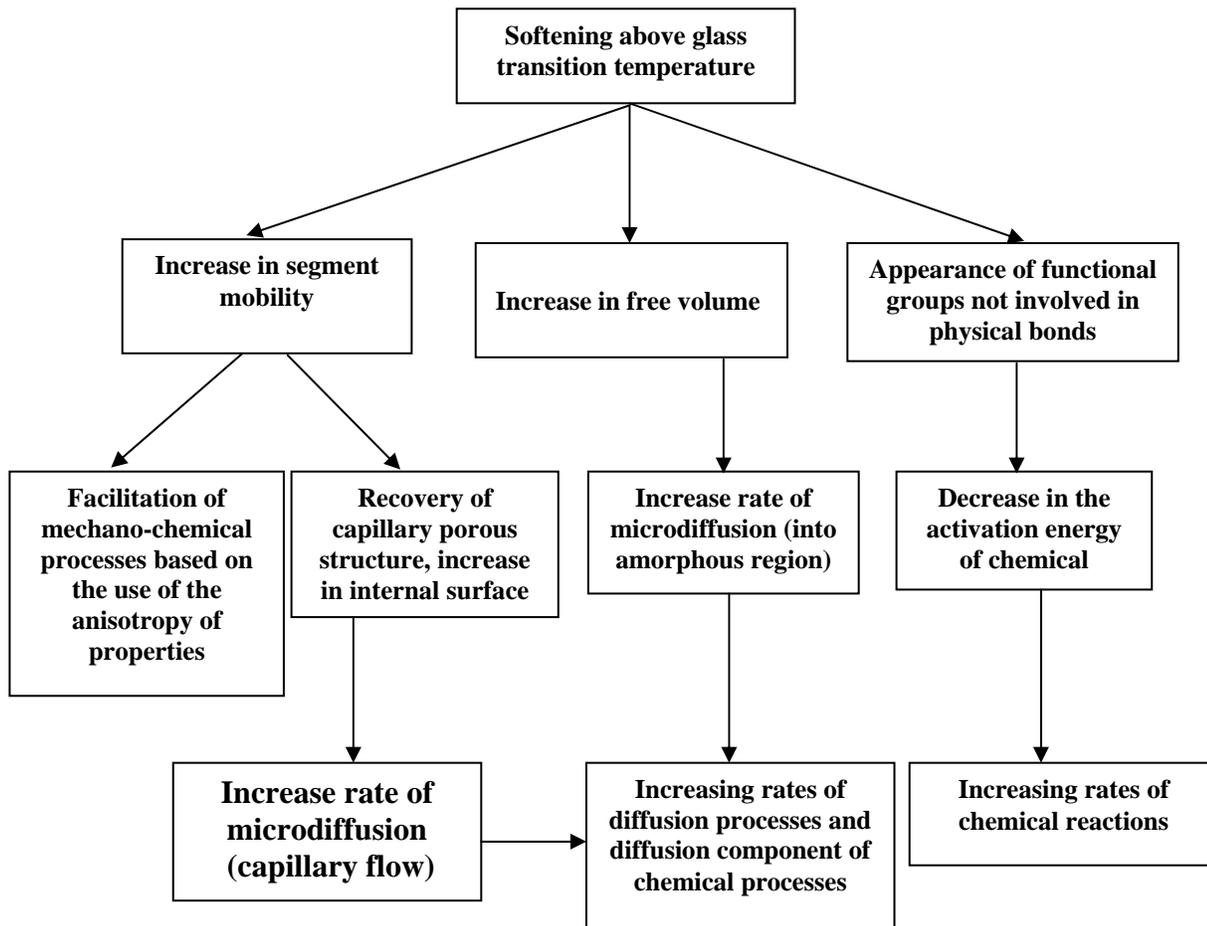


Table 1.II Effect of polymer transition from Glassy to a Elastic state on its behavior in chemical and other processes. E. L. Akim, Changes in cellulose structure during manufacture and converting of paper [7].

Akim [7] has investigated the transition of polymers from a glassy to a highly elastic state in the process of papermaking and converting. This change, called plasticization, is very important in cellulose aspects of paper engineering, but it is even

more important with hemicelluloses that plays an important role in mechanical properties of paper. However, due to the severe elimination of hemicelluloses during pulping and with the primary focus of this work being on moisture transport in paper, cellulose behavior is the more important issue here.

The interaction of cellulose with water is extremely important for several processes involving this polymer, but not all the cellulose structure allow an intimate contact with water. The degree of substitution (DS) is the average number of hydroxyl groups substituted in a glucose unit, and solubility and swelling are affected by DS. The presence of hydroxyl groups, which form hydrogen bonds within and between cellulose chains as well as with water, provide the highly hygroscopic character to cellulose molecule. This interaction of cellulose with moisture depends on the availability of the site of reaction, particularly the hydroxyl groups. This is called accessibility.

Studies with methylation of cellulose in cotton suggest that only 44 % of hydroxyl groups are accountable for the first rapid stage of reaction, while the other 56 % remain inaccessible [4]. It is estimated that 25% of the hydroxyl groups of the crystalline region are available for water adsorption, while in the amorphous region only a few hydroxyl groups are not available, once are bonded with others cellulose chains. The water is accessible to react with weaker hydrogen bonds on non-crystalline regions and on pores but cannot penetrate the regions that are more crystallized under normal conditions. Nevertheless, the intramolecular interactions with water make this relation irreversible after drying, because the last molecules of water remained are strongly bonded to the hydroxyl groups, with an enthalpy of 4.3 kcal/mol of water. The following figure illustrates the drying phenomena between two cellulose chains.

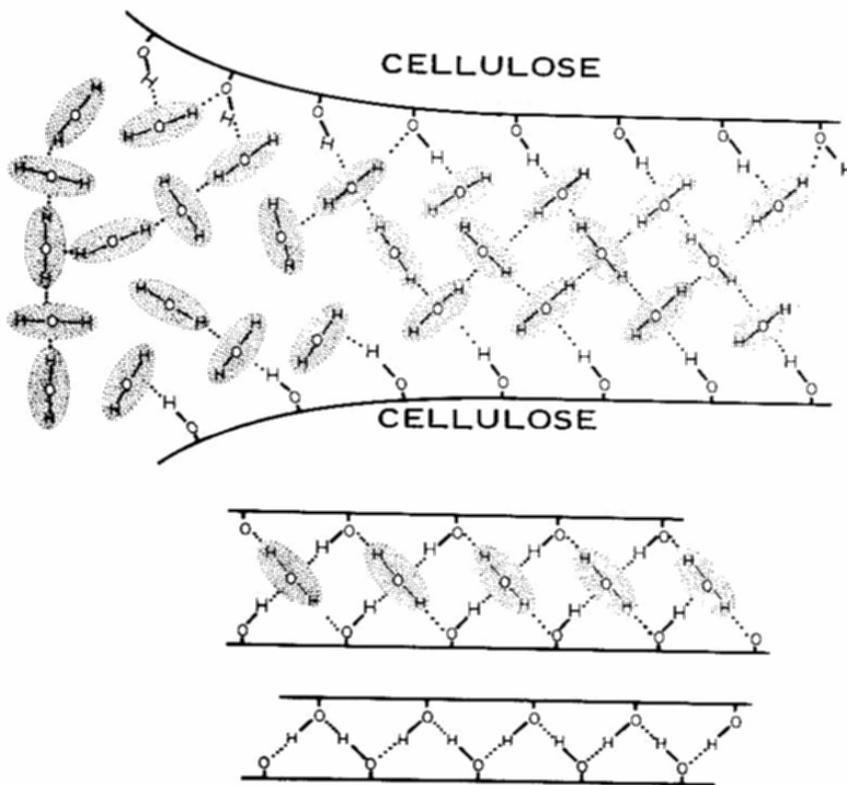


Fig 1.4. Interaction between Cellulose Molecules and Water during different levels of Hydrogen bond.

Hatakeyama and Yamamoto [8] studied the effect of cellulosic hollow fiber on the structural changes of water by differential scanning calorimetry and compare it with the water sorbed on cellulose films. Their results showed that cellulose hollow fiber has more

non-freezing water, what suggest that hydroxyl groups in these samples were freer to attach with water molecules.

The cellulose is the main interface with water in the fiber wall, thus in this chapter the process of interaction, swelling and the most acceptable mechanisms of adsorption as capillary condensation and plasticity with the cellulose will be discussed as preamble of the present work of moisture diffusion in paper material.

1.4. Adsorption Role

There are considerable amounts of work done in water-fiber relation, approaching different aspects of this interaction according with the author interest. The present search does not intend to discuss all variants in this theme, but to highlight the studies related with moisture diffusion through cellulosic fibers.

The study of water adsorption in fiber can be defined according to three different situations, as mentioned by Hoyland and Field [9]: the water of constitution, which is the water that remains even at zero relative vapor pressure and is estimated to be less than 1% of dry fiber; the free water, which is that held in the cell pores after the fiber saturation point, it is not bond at all with fiber and depending on the fiber treatment, the amount estimated is 200%; and the bound water, which is held in the fiber wall by hydrogen bonds with the sorption sites and some authors suggest that it is composed of several layers, the amount estimated is of 30% to 60% on dry basis. These sites are considered to hold up to seven layers of water molecules, although the bond force decreases with the number of layers. Obviously these three conditions of water have

different properties; the water present in intimate contact with cellulose does not freeze, for example. According to methods used to study relation of cellulose with water, the portion of water in the swollen fiber does not behave as solvent for salts or lower molecular weight compounds. Although it seems more probable for some authors that the water difficulty to act as solvent is more due to accessibility of solute and its ability to break the bond to free the water molecule so that it becomes available as solvent. Another definition of water related with cellulosic fiber is given by Froix and Nelson [10] on their study with cotton fibers using NMR. They named four types of water: primary bound up to 0.09g/g of cotton fibers, secondary bound between 0.09 and 0.20 g/g of cotton, free and bulk water. The first two are non freezing water and are defined in the transition of the plasticization point where cellulose swelling occurs and its chain mobility increases. The free water is related with freezing water and bulk water with the water that is not in the fiber wall.

The adsorption theories that involve most of discussions on adsorption isotherms could be simplified in three as follow: the monomolecular adsorption, the multilayer adsorption with heat of adsorption greater than vapor heat of condensation, and the multilayer adsorption with heat of adsorption equal or less than vapor heat of condensation. The Brunauer, Emmet, Teller (BET) is a well known theory applied to monolayer adsorption which describe sorption of moisture on cellulose satisfactorily at low relative humidity. This theory is criticized because neglect adsorbate self interactions and solid substrate heterogeneity. In regards with this isotherms Timmermann [11] shows that Guggenheim, Andersen, de Boer (GAB) isotherms are much superior, and effective

at a large range of applicability. The cellulose generally has a water vapor multilayer adsorption with the heat of adsorption greater than heat of condensation.

Another interesting theory is the formation of clusters where mathematical equations are defined to calculate number of water molecules that form a cluster. At low relative humidity the water molecules are isolated and strongly bonded to cellulose. As moisture increases the clusters also increase to a point when they form bridges among them. The increase of clusters as well as the formation of bridges brings to the percolation theory that facilitates the water transport in the solid support. As the cluster percolation as moisture increases, the water transport accelerates significantly and as a result the diffusivity increases what translate in diffusivity increases. This explains the greater gradients of diffusivity as paper samples come closer to saturation. The percolation theory is relatively recent with few applications in moisture transport in paper.

Stamm [12] studied the mechanisms of attachment between water and cellulose and its effect on bonding between fibers. According to the author, in 1929 Bateman and Beglinger used different methods to investigate water remove from wood. They found that drying for 24 hours at 105°C over phosphorus pentoxide removed 0.2% more water than without the oxide, but after seven days the difference was only 0.02%. When they dried at 105°C under a pressure of 55 mm of mercury, removed 0.3 % less moisture in 24 hours and 0.4% less in seven days than drying at atmospheric pressure over phosphorus pentoxide. Using distillation in toluene and xylene with boiling points of 111°C and 140°C respectively, for one and four hours resulted practically in the same moisture lost than in drying in oven over phosphorus pentoxide for five to seven days. Even when the

temperature is raised to 70°C above water boiling point, they found that only 0.3% more water is lost than in drying to constant weight in conventional temperature. The authors concluded that the bound water retained in regular drying is about less than 1 %. These simple experiments show the complexity of water relation with fibers. The fiber in suspension could take up to 300% of its dry weight in water, and at the fiber saturation point, where the fiber wall is saturated without fill the lumen, the fiber moisture content is generally less than 30% of dry weight at standard temperature. It is general opinion that below the fiber saturation point the fibers begin to shrink, therefore this is an important point for papermaking. Stamm [12] made an interesting review on sorbed water in fiber where he mentioned several works analyzing the moisture sorption curve. Certainly there are controversy among the conclusions, some authors say that is formed a monomolecular adsorption on fiber surface up to about 0.4 relative vapor pressure, others authors claim that this point is 0.3. Barkas is mentioned as defending that up to relative vapor pressure 0.70 there is a combination of adsorbed molecules and capillary condensation and beyond that just the last mechanism. It is opportune to remember the well known BET theory where around 0.30 relative vapor pressure is the transition point between monomolecular and polymolecular water adsorption. This polymolecular concept commented above reaches its maximum at 0.80 relative vapor pressure, with formation of the seven layers of water molecules.

1.5. Fiber Swelling

As it is known the walls of wood fibers are constructed of cellulose hemicelluloses and lignin basically. These fibers are constituted of primary and secondary walls, where the secondary is divided in three other layers S_1 , S_2 , S_3 . The layer S_2 is the thickest and most important due to its contribution to the fiber bulk. It also has the lower concentration of lignin and small angle of microfibrils with fiber axis. The microscopic and submicroscopic structures of cellulose are shown below.

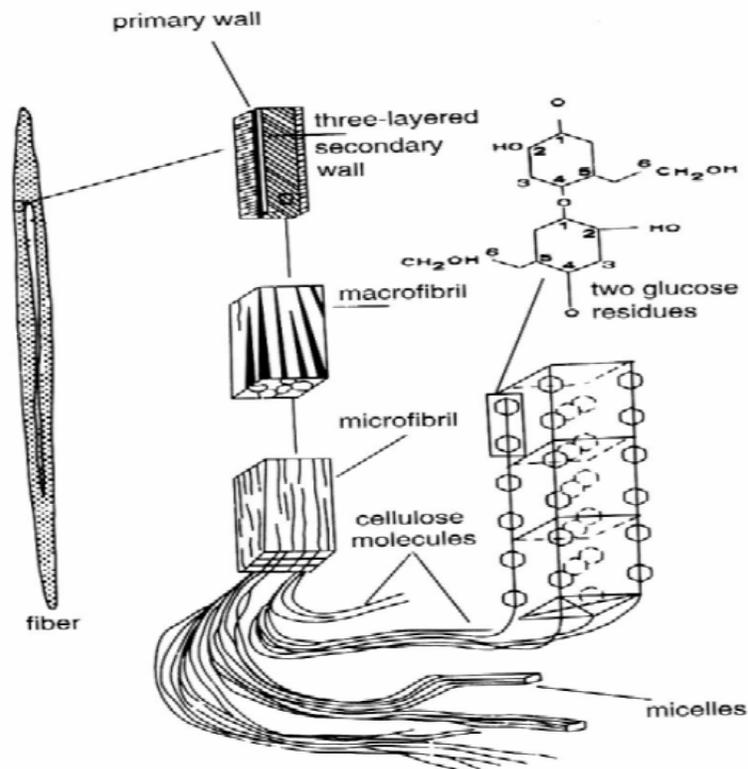


Fig 1.5. Schematic representation of cellulosic fiber from its walls to the cellulose molecules.

Pelton [13] proposed a model of fiber surface that consider roughness and the presence of a water soluble polymer. The author claims that surface of wood fibers are coated with a hydrated polymer layer creating a steric stabilization, which characteristic shows that polymer molecules on the surface are soluble in the dispersion medium. The pulping process is important for steric stabilization, and the microcrystalline cellulose that remains after a fully bleached pulp does not show the mentioned soluble surface. Thus the hemicelluloses would be the only component to possess this property, what has not been proved according to the author.

The fiber swelling in virtue of water adsorption is not uniform due to the disposition of its structure, being the lateral swelling much more pronounced than the longitudinal. The water retained as consequence of properties of the cellulosic material can be an advantage or a limitation depending on its destiny and process to be submitted. When fibers swell and dry repeatedly, the swelling effect decreases, probably due to a better alignment of microfibrils. The mentioned effect is known as hysteresis, and there are large amounts of investigations on this phenomenon. Zeronian and Kim [14] studied the water vapor sorption hystereses of viscose rayon in order to check out the hypotheses that this phenomena is caused by stress induced in cellulose when it dilates and constricts. They found a good correlation between hysteresis and stress relaxation of cellulose at low stresses.

When water is sorbed in wood fiber material, the displacement of molecules due to intermolecular hydrogen bond breaking cause the called mechano-sorptive

phenomenon, which is the relation between the moisture sorbed and the mechanical properties. Wang et al. [15] in their review, came to the conclusion that the water movement inside the fiber is due to free water molecules and that the number of water molecules have to change to induce the disruption. However, as they mention, this explanation does not explain the quantitative differences between materials and conditions. The review emphasized that cyclic in moisture conditions accelerates creep, as well as creep recovery and relaxation process.

Fiber swelling is a well known characteristic and has been measured by several ways, although the process description has important gaps. There is a general agreement that fiber swells in the order of 30% in width and about 1% in length.

Wood fiber swelling is directly related with inter-cellulose molecules hydrogen bonds breaking and rearranging between such molecules and water or another polar solvent. After breaking the hydrogen bonds the cellulose molecules move apart and several layers of water can intercalate between cellulose chains. From a macroscopic point of view we can say that when dried fiber structures adsorb water, its capillary channels are opened and become available to receive condensed water to the point of equilibrium saturation. This happens due to water polarity, which is function of an uneven electron density distribution on its molecule. The polarity gives the property to form hydrogen bonds with cellulose molecules, most specifically with hydroxyl groups.

The cellulose structure is an important influence on the swelling, for example, comparing cotton shows a lower swelling than wood pulp, it is understandable due to the high degree of polymerization presented by cotton.

Although cellulose swells in water and a number of organic liquids, it remains stable as a molecule at neutral pH and low temperature. However, obviously there is an increment on sample volume due to the incorporation of water molecules as well as changes of the physical properties due to the inclusion of weaker hydrogen bonds between cellulose molecules. The swelling could occur in the amorphous region of cellulose, of easier access, called intercrystalline swelling.

The swelling agent would fill the pores and breaking the interfibrillar bonds. The swelling also could be intracrystalline, where an increasing in lattice dimensions of the crystalline region is observed. The well known Water Retention Value (WRV) procedure described by Jayme and Rothamel could be used to determine swelling quantitatively. It determines the weight percentage of water that can be held within the water swollen cellulose substrate. Through this measurement, important information can be obtained such as variation of accessibility or effect of additives on swelling region.

The cellulose swelling is important in the sense that allow more effective interaction of cellulose with others chemical components, which otherwise would happen only on the available surface.

A physicochemical characteristic of cellulose with respect to water vapor is the great capacity of adsorption, at low relative humidity is assumed that water is adsorbed by chemical interactions with hydroxyl groups of cellulose forming a monolayer of water molecules, and when more water molecules are available, multilayers are formed. However, the later layers are adsorbed with less intensity to cellulose. The further increment of relative humidity cause capillary condensation of free water.

Meredith and Preston (3) measured separately the components of bound water and free water of the total water sorption, as showed in the graphic below. Around seven layers of water molecules sorbed on cellulose can be considered bound water.

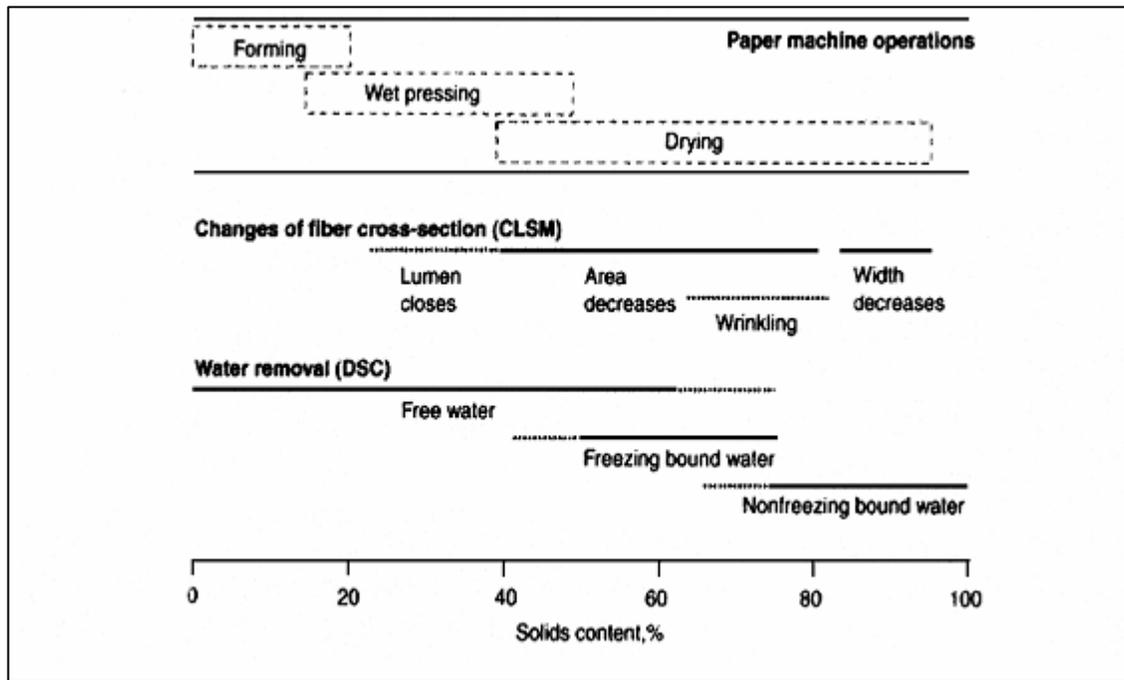


Fig 1.6. Relation among solid content, changes occurring with fiber and specific water removal during papermaking.

Merchant [16] claims that fiber surface area decreases 60% as consequence of been dried to negligible moisture with phosphorus pentoxide. He also observed that the amorphous region was still accessible after drying, but the fiber structure was brought

together and had less space to move. As consequence of that there were more fiber bonds and water trapped.

Stamm [17] refers to cellulose as swelling gel with respect to water because besides being adsorbed on the surface, it also forms a called solid solution in the fiber wall. He claims that adsorption on surface fiber could be neglected when compared with inside fiber wall adsorption, such is the importance of the late adsorption. Thus this detail seems to be an important point of consideration to a mathematical model that describes moisture relation with cellulosic material. Stamm concludes that water molecules layers adsorbed close to saturation is smaller for swelling systems due to the work necessary to open such system.

An important physicochemical variable in pulp and papermaking, already defined before in this chapter, is fiber accessibility. This theme was studied by Bendzalova et al. [18] in order to verify the changes on the porous structure of fiber when treated with swelling agents prior pulping. They found that pulps treated with more effective swelling agents, carbonates of univalent cations and amines, retain more water and have increased specific surface. The authors also claim that wood fibers surface are chemically modified during the swelling process exposing cellulose and hemicelluloses. This modification would improve the inter-fiber bond, what was determined by light scattering coefficient.

Alinec [19] measured density of cellulosic fibers as function of its moisture content by electromagnetic float method, and he found that the total volume was not equal to the sum of water and fiber. This phenomenon was understood as a contraction of the system, apparently associated with the degree of crystallinity, and is more accentuated during the first stage of adsorption. Maloney et al. [20] measured the amount of hydration

water and swelling of pulp fibers using the differential scanning calorimetry method based on isothermal melting of water. The measurement is based on the energy absorbed when the water in a frozen pulp sample is melted. In this particular case hydration is defined as the process in which water is absorbed in fiber wall and alters its thermodynamic properties. The method can calculate the freezing water and the non-freezing water which are the molecules that are suffering the interference of hydrogen bonds because they are closer to the fiber sorption sites. Several authors related the amount of non-freezing water with the number of hydroxyl groups accessible to water. The authors also call the attention for the melting temperature depression, a known phenomenon. This could have two basic reasons according to a thermodynamic analysis, due to the fiber porosity, once pressure increases within a small pore, or partial solubilization of fiber wall components, forming a mixture of polymer and water.

1.6. Mechanisms of Water Transport

The complexity of paper structure, involving the anisotropy in lateral and transversal directions, high range porosity of paper and fiber, and the affinity of cellulose for water as well as the different forms of water present in paper, make the analysis of water transport quite complicated. Nevertheless, various mechanisms have been proposed to explain these relationships. The most important are surface adsorption, capillary condensation and gel swelling, and there are authors defending each of these theories with the same determination.

Hoyland and Field [21] have an interesting retrospect of researches on water penetration in paper. The first concepts around the transport of water in paper was based on capillary penetration as the major process, then later fiber wall penetration was considered as being a slower process. Another approach defined that there was capillary flow through the pores and diffusion through the fibers simultaneously. One more accurate explanation of water interaction claims that there is vapor condensation as well as surface diffusion and the water adsorbed penetrates inside the fiber. Different authors found that fiber sorption plays an important role in moisture transport, and that it is not only function of capillarity. Hoyland and Field believe that the process appears to be controlled by liquid properties and paper porosity, although capillary flow path is responsible for most water transport. The authors concluded from their review that fiber surface sorption can occur and water penetration is a strong function of paper moisture content. At low values, below 5 % penetration is slow, and at high moisture content, above 15% based on dried support, penetration is fast with complete sample wetting. Another understandable conclusion is that at high moisture content the water uptake is lower as well as the fiber sorption capability during penetration. The authors remark that at this point penetration occurs quickly and water picked up is little. Probably the water sorption decreases because the attraction force is weaker due to the previous water accumulated on the sorption sites. The difference between water penetration, where the major mechanism is capillarity, and water uptake, where surface fiber sorption and diffusion, and capillarity are important, is highlighted. Thus, the final remark states that a different mechanism drives the moisture transport at these moisture content ranges, with an initial fast penetration due to the hydrophilic surface available, followed by a slower

capillary flow and by a last slowest fiber penetration. The analysis of this review is interesting because it involves the main possible processes of water transport, however further analysis are available currently.

During his result discussion Alince [17] disagree with some authors that defend that water increases density when adsorbed by cellulose. He considered that once there are strong bonds between water and cellulose hydroxyl groups, and formation of solid solution inside the amorphous region, then water would not form a separate phase and its density has not physical meaning.

The explorations of Nuclear Magnetic Resonance (NMR) techniques to help to understand the moisture and paper relation have brought light to this theme. Froix and Nelson [22] used this resource to study the free and bound water as function of relative humidity, and determined the plasticization point. They claim that free water is present even at low moisture content and that it increases significantly above the plasticization point. The experiments show that addition of water to dried cellulose changes the mobility on cellulose chain and bound water, although the effect changes according with moisture content. In the moisture range between 0.05g/g and 0.09g/g the sorbed water is directed to break cellulose hydroxyls and interfibril hydrogen bonds. At moisture content above 0.09g/g (dry base), the NMR results show the greater motion of bound water over cellulose chain, as well as the greatly restrict motion of bound water over free and bulk water. The authors remark that water sorption makes cellulose swells opening new hydroxyls to be bounded with water and allowing multiple layers of water. This work presents the point of plasticization as coincident with the second inflection point of the adsorption isotherm.

Nilsson et al. [23] used Magnetic Resonance Imaging (MRI) method to measure moisture distribution in pulp samples and found a linear relation between MRI signal and moisture, which can be measured up to 1.4 g water/g dry material.

Garvey et al. [24] used solid state Nuclear Magnetic Resonance (NMR) and Small Angle Neutron Scattering (SANS) methods to study hydration of paper. They found that diffraction peaks appeared at high humidity, what is interpreted as a structural unit of a cellulose crystallite surrounded by a layer of swollen cellulose and a layer of water. However they could not identify the widths of cellulose and water layers, although at high humidity the water layer is larger than the microfibril. Nonetheless, in order to study cellulose stiffness, Newman [25] discusses biosynthesis of cellulose as a bundle of molecules and remembers a model that corroborates the mentioned observation of Garvey et al. related with cellulose structure. This model mentioned by the interesting review of Delmer and Amor [26] is proposed for higher plants, where were found single rosettes of six globular particles with 8 nm in diameter. Each rosette extrudes 36 cellulose chains, which has rectangular cross section of 3.6x3.2nm, and just the chains exposed to the surface have hydroxyl groups available.

In Garvey et al. work, they state that dry fibers have pores due to the microfibrils packing and when humidity increases the pores are filled. Their model assumed that the first effect of moisture on the disordered layer around the microfibril is swelling, what appears to be affected by hemicelluloses and lignin. The NMR experiments show that effective surface area increases with amorphous regions swelling first. The authors argument that in some situations the effect could be opposite and moisture can result in a more dense structure, once amorphous cellulose has also tendency to recrystallize to

cellulose II. Another possible example of cellulose recrystallization with changes in macroscopic fiber properties is hornification. As could be seen the evolution in this field is slow but the modernization of equipments and methods are bringing light to explain with more details the interaction between water and cellulose in the full spectrum of humidity.

1.7. References

1. Robertson A.A., "Interactions of Liquids with Cellulose", Tappi Journal, vol 53(7), 1331-1339, 1970.
2. Ziegler G.A., "Water Vapor Sorption by Softwood Cell Wall Constituents" Doctoral thesis, Pennsylvania State University, 1974.
3. Rowland S.P., Bertoniere N.R., " Chemical Methods of Studying Supramolecular Structure", Cellulose Chemistry and its Applications, chapter 4, 112-137, John Willey and sons limited, New York, 1985.
4. Klemm D., Philipp B., Heinze T., Heinze U., Wagenknecht W., "Comprehensive Cellulose Chemistry. Vol 1 Fundamental and Analytical Methods, Willey-VCH, Germany, 1998.
5. Stone J.E., Scallan A.M., "The Effect of Component Removal upon the Pore Structure of the Cell Wall of wood. II Swelling in Water and the Fiber Saturation Point", Tappi Journal, vol50 (10), 1967.
- 6 . Prahl J.M., "Thermodynamics of Paper Fiber and Water Mixtures", Harvard University, Cambridge, 1968.

7. Akim E.L., "Changes in Cellulose Structure during Manufacture and Converting of Paper", Chapter 11- Manufacture and Converting of Paper, Cellulose chemistry and Technology, 153-171, Leningrad.
8. Hatakeyama T. and Yamamoto S., "Structural change of Water Restrained in Cellulose Hollow Fibres", Structural Change of Water, 431-445, ...
9. Hoyland R.W., Field R., "A Review of the Paper Transudation of Water into Paper – Part 2 The Cellulose-Water Relationship, Wetting & Cutting Angles", Paper Technology and Industry, 216-219, October, 1976.
10. Froix M.F., Nelson R., "The Interaction of Water with Cellulose from Nuclear Magnetic Resonance Relaxation Time", Macromolecules, 8, 726-730, 1975.
11. Timmermann E.O., " Multilayer Sorption Parameters: BET or GAB Values?", Colloids and surface A: Physicochem. Eng. Aspects, 200, 235-260, 2003.
12. Stamm A.J., "Bound Water and Hydration", Tappi Journal, vol 33(9), 435-439, 1950.
13. Pelton R., "A Model of the External Surface of Wood Pulp Fibers", Nordic Pulp and Paper Research Journal, no.1, 113-119, 1993.
14. Zeronian S.H., Kim M.S., "Studies of the Water Vapor Sorption Hysteresis of Viscose Rayon and of Chemically Modified Viscose Rayon", 325-341,
15. Wang J.Z., Dillard D.A., Kamke F.A., "Transient Moisture Effects in Materials – A Review", J. of Materials Science, 26, 5113-5126, 1991.
16. Merchant M.V., "Study of Water-Swollen Cellulose Fiber which have been Liquid-Exchanged and Dried from Hydrocarbons", Tappi Journal, vol 40(9), 1957.
17. Stamm A.J., "Adsorption in Swelling versus Non-swelling Systems", Tappi Journal, vol 40(9), 761-765, 1957.

18. Bendzalova M., Pekarovicova A., Kokta B.V., Chen R., "Accessibility of Swollen Cellulosic Fibers", *Cellulose Chem Technol.*, 30, 19-32, 1996.
19. Alinec B., "Volume Contraction of Cellulose-Water System", *Pulp and Paper Research Institute of Canada*, 379-387,
20. Maloney C., Paulapuro H., Stenius P., "Hydration and Swelling of Pulp fibers Measured with Differential Scanning Calorimetry", *Nordic Pulp and Paper Research Journal*, vol 13 (1), 1998.
21. Hoyland R.W., Field R., "A Review of the Transudation of Water in Paper – The Mechanism of Penetration & Conclusions", *Paper Technology and Industry*, 7-9, January, 1977.
22. Froix M., Nelson R., "NMR Relaxation Time Studies of Water in Cellulose", 269-273, *Webster*, New York.
23. Nilsson L., Mansson S., Stenstrom S., "Measuring moisture Gradients in Cellulose Fibre networks: An Application of the Magnetic resonance Imaging Method", *J. Pulp Paper Sci*, vol 20 (2), 48-52, 1996.
24. Garvey C.J., Parker I.H., Simon G.P., Whittaker A.K., Knott R.B., "An Experimental Study by NMR and SANS of the Ambient Hydration of Paper", 12th *Fundamental Research Symposium*, 359-392, Oxford, September, 2001.
25. Newman R., "How Stiff is an Individual Cellulose Microfibril?", Butterfield B.G. ed., *proc IAWA/IUFRO, International Workshop on Microfibril Angle in Wood*, 81-93, University of Canterbury.
26. Delmer D.P., Amor Y., "Cellulose Biosynthesis", *The Plant Cell*, vol 7, 987-1000, American Society of Plant Physiologists, 1995.

CHAPTER II

EXPERIMENTAL METHODS

2.1. Controlled humidity experiments.

The measurement of moisture transport dynamics and equilibrium needs an environment of controlled humidity and temperature according to prescribed regimens. For this purpose, we used a humidity chamber with flexibility for obtaining relative humidity variations and a precise control. The calibration of relative humidity, made several times with different sensors and as much as six sensors at a time, shows very satisfactory results. Although the temperature measurement is made by the system and there is a bath that could be attached to the humidity chamber to allow temperature changes, all the experiment were run at conditioning room temperature of 23 °C according with standard TAPPI methods. The experiments performed with this equipment do not have operator interference only the setup adjustment in the computer before the start up. The only operator task is to replace water in the wet line, drain the purged water, and do the maintenance to keep it working. The possibilities to work with this apparatus involve experiments that could have a relative humidity variation in a large range, variations of relative humidity at different time steps, countless numbers of steps and the flexibility to perform very long experiments with time variation among steps.

The following scheme shows the humidity chamber system used for the experimental work in the present dissertation. The figure 2.1 has the main components of the system, which are going to be commented in details.

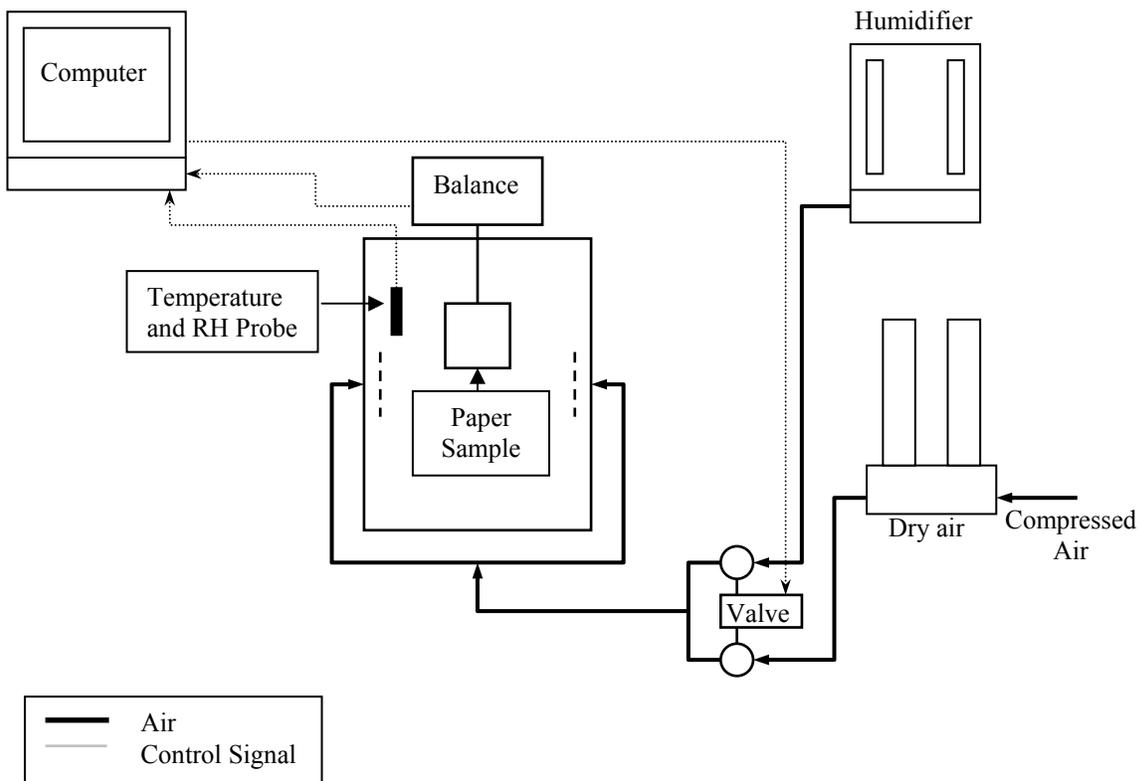


Fig 2.1. Scheme of the humidity chamber used in the experimental work.

The photography below shows the humidity chambers in the laboratory 106 in Walters Hall, Department of Paper Science and Engineering (PSE) in Syracuse, state of New York:

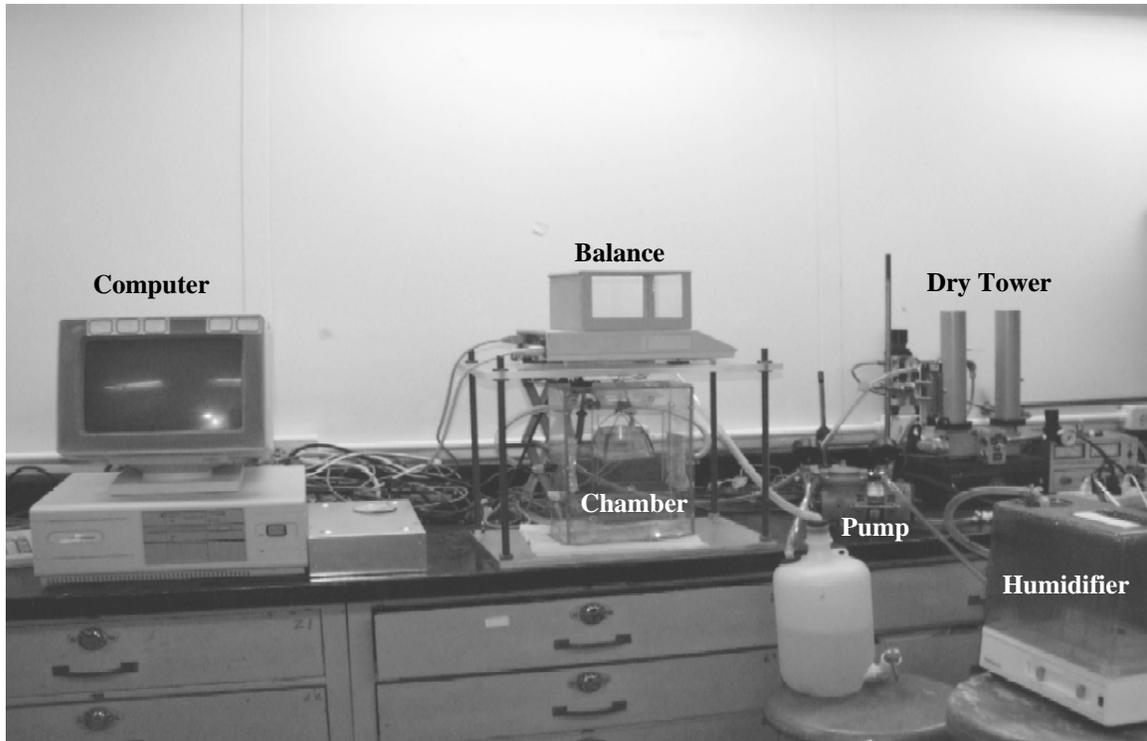


Fig 2.2- Relative Humidity Controlled system shows the main parts of the Dry and Wet lines, but the valve that connects the dry and wet lines is behind the balance.

Its dimensions are 17cm length, 11 cm breadth and 31 cm height.

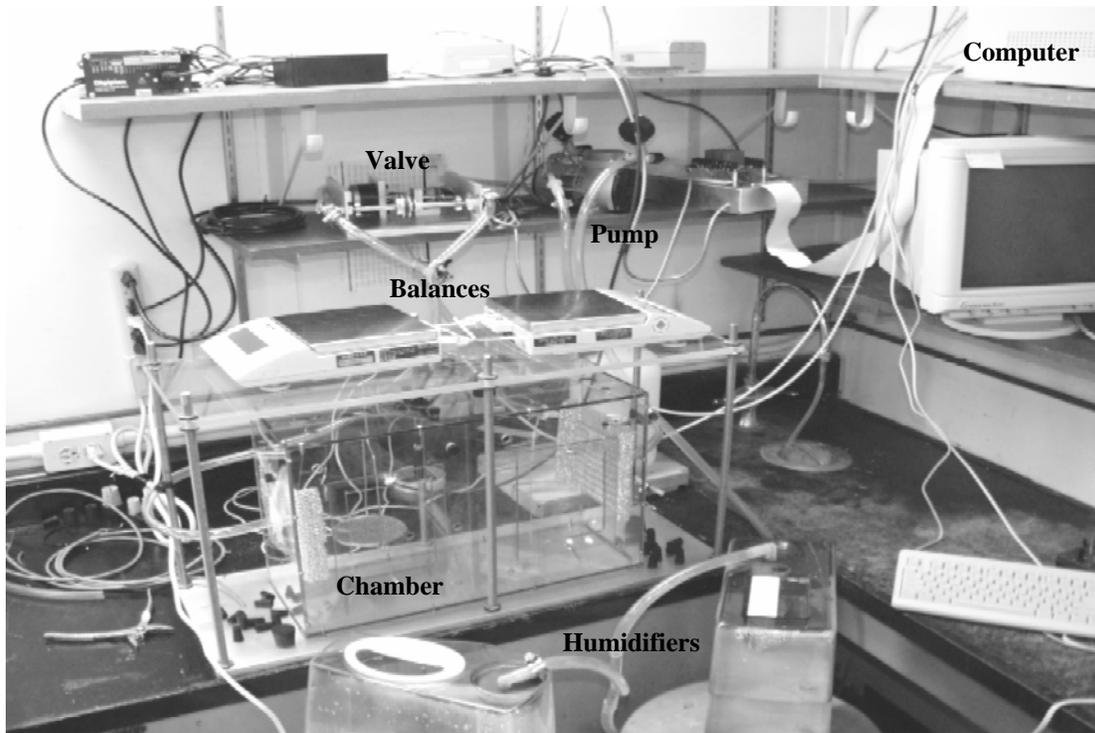


Fig 2.3 – Humidity chamber with two balances, and larger volume. Length 50 cm, breadth 19 cm, height 31 cm.

This chamber allows running replications simultaneously and its big volume prevents interference of one sample on another for most of the experiments. This chamber has easy control and is very sensitive to set up changes, showing that the size does not prejudice its performance.

The table 2.I shows the Specifications of the Relative Humidity Control [1], which were generated during the building of the first humidity controlled chamber.

Table 2.I. These are the Specifications of the Relative Humidity Control

RH Limit %	(Min., Max)	10,97
Response Time, min (40->93% RH, 93->40% RH)	Loop Interval = 2500msec Loop Interval = 7500msec Loop Interval = 12500msec	None, 12.5 35,22.5 37.5,32.5
Ramp Duration, min.	(Min., Max)	1,440
Hold Duration, min	(Min., Max)	1,440
Sine Profile Period, min	(Min., Max)	1,440
Sine Profile Duration, min	(Min., Max)	1,7200
Data Array Size, pts	Max.	9,600
Sampling Rate, Hz	0 to 24 hr +24hr	0.05 1.333/Test Duration,hr
Trend Plot on Screen	Display Update Frequency	Every 6 th Data Point Once Every 5 Data points
PID Control Values (Min., Max., Default)	Gain (P) Integral (I) Derivative (D) Loop Interval (LI),msec	-100,100,0.1 0,100,15 0,100,0.002 0,60000,5000
Input Signals, Scaled Range	Relative Humidity Temperature Valve Position	0-5Vdc, 0-100% 0-5Vdc, -20 to 80°C 0-5Vdc,0-2500 counts
Waveforms	Step Ramp Saw	Yes Yes Yes
PC Requirements	RAM, MB	64

These specifications are similar for all humidity chambers showed before and the eventual changes made in the chamber command program are minor. The referred

modifications involved addition of a balance as shown in the pictures and increasing the experiment time limit.

2.2. Description of the Relative Humidity Controlled System

The system is designed to provide relative humidity control at steady state and transient conditions, and to store important data through a data acquisition system. The relative humidity control is achieved by the simultaneous adjustment of the two ways valve that while the dry line opens, the wet line closes or vice-versa. The command of relative humidity is set up in the computer and reaches the stepping motor by regulating the amount of dry and wet air in the total flux. This system is able to make this adjustment automatically or manually according with the necessity. Although the same sensor reads relative humidity and temperature, this last variable is not controlled.

As mentioned before the system requires two lines, one with high relative humidity, approximately 99%, and another with low relative humidity air source (approximately 0.5%). The line with high relative humidity has as generator an ultrasonic humidifier that is available in regular stores. The system can have two apparatus in parallel in a chamber of bigger volume. This apparatus is connected to a diaphragm pump after what is the controlled valve. Due to the high accumulation of condensed water in this line, two containers that work as a purge are placed online, one after the humidifier and another after the diaphragm pump. An operational care for this system is to fill the humidifiers with water and drain the containers regularly. The main component in the dry

line is a dry tower that receives compressed air from a line, which is filled with a desiccant that has to be changed eventually. This line is connected directly to the controlled valve. The pressure adjusted in the compressed air line is such that the required relative humidity that ranges inside of the humidity chamber could change smoothly through all range. After the controlled valve, the lines converge to a single line mixing both flows, which enter in the humidity chamber from both lateral sides. The chamber has a relative humidity and temperature sensor that send signals to the computer.

2.3. The Salt Solution Alternative

The principle of the saturated salt solutions constant humidity is due to the affinity that these substances have with water, which regulates the water vapor pressure in the atmosphere surrounding the salt.

The salt solution is a largely used option to work with relative humidity, what is understandable once it is a cheap and easy to assemble alternative. However, several factors about the credibility of an experiment carried out with saturated salt solutions should be considered.

Our experience during the present work shows that the saturated salt solution in the cup without stirring can result in a much higher relative humidity than the ideal conditions are suppose to be. The verification of this problem was made by introducing a mini sensor inside of the cup while using the saturated salt solution of lithium chloride to maintain the relative humidity inside of the cup 11.3 %. The amount used in the cup was

about 200 ml, and although it had an excess of salt in the solution bottom, the relative humidity close to the solution was much higher than expected.

The work of Labuza [2] states that some conditions have a reliable saturated salt solution preparation and use:

- Solution preparation, starting with purity of salt and water, the salt has to be chemically pure and the water distilled.
- Slush, the called solution in truth has to be more a slush, or a solution with excess of salt undissolved. Excess of water increases the relative humidity, and excess of salt over the water surface reduces the relative humidity.
- Large slush surface area and small vapor space, the diffusion rate from a salt solution is exponential, with a slow approach to equilibrium. Thus these conditions are going to make the equilibrium easier to be reached.
- Temperature, is well known that temperature is fundamental for accuracy.

Besides the factors commented before, maybe the biggest problem is to maintain the ideal conditions during the entire experiment time, which can be relatively long. This also would require a constant measurement of relative humidity by a sensor in order to guarantee the expected values.

2.4. Conclusion

The conclusion is that the experiment with saturated salt solution is reliable and feasible since all the requirements commented here are accomplished in order to maintain

the slush at desired relative humidity during all the experiment. As mentioned before, the salt solution preparation is cheap and the experiment easy to assemble. However, the operator attention must be constant in order to detect any deviation of the ideal conditions during the entire experiment.

The humidity chamber nevertheless has several advantages and certainly a more reliable result because the operator's interference is very small once the variables are loaded. The chamber also shows good behavior following the ramps at different relative humidity rates, as well as working step by step through a large range of relative humidity, as in the case of the Isotherms calculation. The chamber either can keep the relative humidity constant for many hours without problem and with an excellent accuracy.

2.8. References

1. Gupta H., "Relative Humidity Chamber with two Weighing Balances. Instruction Manual", State University of New York, Department of Paper Science and Engineering, Syracuse, NY, 2001.
2. Labuza T., "Creation of Moisture Sorption Isotherms for Hygroscopic Materials", Published in internet with the address,
[HTTP://faculty.che.umn.edu/fscn/Ted_Labuza/PDF_files/papers/Creation_Moisture_Isotherms.pdf](http://faculty.che.umn.edu/fscn/Ted_Labuza/PDF_files/papers/Creation_Moisture_Isotherms.pdf).

Chapter III

Non-Fickian Behavior of Moisture Diffusion in Paper

3.1. Introduction

The analyses of recent publications on paper moisture transport have brought up to our group a concern. It is if the concepts of mass diffusion have been completely understood and duly discussed. This is because the moisture transport theory in hydrophilic material has followed a variety of approaches, many times without the necessary justification of the assumptions adopted .

The process of diffusion, in general, has been developed based on the classic Fickian concepts that introduced the definitions of mass transfer, which work very well for many situations. However, in more complex cases such as moisture diffusion in paper, where changes of penetrant phase and stress relaxations occur, other factors that are underestimated by the Fickian definition have to be considered. The peculiarities of this system should account with problems such as variation of mass transfer coefficient, dependence of thickness on diffusion, time of relative humidity step on transient adsorptions.

The present chapter has the objective of raise and discuss the influence of these variables on both Fickian and Anomalous approaches, specifically for moisture diffusion in paper. Experimental and theoretical results are presented in order to identify the differences between the two processes. The presentation of Fickian model shows that it could work as a drastic simplification of the moisture transport phenomenon. This model consider paper a homogeneous medium with fast local equilibrium between pore and fiber surface adsorbed water or even just one phase diffusion. However, an analysis of the experimental results of moisture sorption shows that the model for moisture diffusion in paper should be Non-Fickian, otherwise could not describe the transient diffusion of moisture in paper.

Diffusion of moisture in paper has been analyzed earlier neglecting important variables that affect significantly the results. The transient sorption of moisture in paper, was measured experimentally in the present paper. The effects considered were external convection conditions, speed of external humidity changes and the diffusion mechanisms through the pore space and fiber matrix phases. The transient sorption exhibited significant Non-Fickian behavior due to the interaction between these factors. The experimental results indicate that moisture transport is Non-Fickian even when the influence of external convection and rate of humidity change are eliminated. The hypothesis is that this behavior could arise from diffusion of moisture in sequential behavior through the pores and into the fiber matrix. Calculations of transient moisture sorption in paper were made using classical Fick's Law for overall moisture diffusion, and another modified model allowing serial diffusion through the pore and fiber matrix phases.

Analysis of the results shows that models that intend to represent moisture diffusion in paper should incorporate the ability to describe Non-Fickian behavior.

3.2. Literature Research

Many researchers have studied moisture adsorption and its mechanisms of transport in cellulosic materials, including wood fibers and paper. There are several approaches about moisture diffusion in paper material employed by researchers, but the intention is not to write a review here. Thus, the most important points of view closely related with the focus of this chapter will be brought to discussion, once there is assumptions in this field that need to be addressed.

Considering the porous and hygroscopic nature of paper, several mechanisms of moisture transport operate simultaneously leading to a complex interaction. A closely related research in moisture diffusion was earlier developed in polymer science, and the work developed in this field was the support for the present chapter.

In the work published in 1953, Crank [1] claimed that both mechanisms mentioned previously might be present in his polymer diffusion experiment. In the early sixties, studies on water vapor diffusion in polymers showed that this process, in most cases, does not correspond with the diffusion defined by Adolf Fick, although this model can be applied for some kind of polymers. Thus, was initiated the concern that some factors deviate the sorption process from this ideal behavior. These factors could be a response of the medium under diffusion internal stresses such as structural changes, stress

relaxation such as sorption, swelling, or yet variation on the substance diffusing such as changes of state. This question was largely studied in polymers diffusion where Crank [2] discussed the diffusion time factor related with the relaxation process on the characterization of a process as Fickian or Non-Fickian. The stress relief effects make the process of diffusion time dependent because diffusivity changes according with the experiment development and as consequence deviate the diffusion from the conditions initially established as Fickian.

In paper science there is a variety of models, but not an experimental study with paper samples and under variable conditions that help to figure out when and how to apply one or another model. A recent review by Ramarao et al. [3] contains a comprehensive description of moisture diffusion in paper literature as well as a comparison among the proposed models. Prior works on this theme indicates that two main model classes have been pleaded for moisture diffusion in paper. The first applies the classical Fickian Law considering paper a homogeneous material with moisture diffusivity been assumed as constant or a nonlinear function of moisture content. The models used by Lin [4], ten Donkelaar and Jeager [5], Roisum [6] and Rahmans et al. [7], Gupta [8] are examples of this class. The second class, that could be called Non-Fickian model because does not fit on Fick conditions, represents paper as a composite material with pores and a fiber matrix, where both interact and conduct moisture at different rates. The models used by Lescanne et al. [9], Foss et al. [10], Ramarao and Chatterjee [11], Bandyopadhyay et al. [12], Massoquete et al. [13], Liesen et al. [14], Lavrykov and Ramarao [15], are part of this class. A more elaborate version of these models which

pictures a specific pore-fiber geometry for the paper material has been proposed by Lavrykov and Ramarao [16].

However, there is a necessity of a more consistent work in order to show experimentally what are the implication of choose one or another class of model and under which circumstances they would work properly.

A brief comment about examples of the two classes of model mentioned before is expounded here in order to be more specific regards to the different perspectives on moisture diffusion in paper. These works were chosen because they present approaches that justify the development of this chapter.

Lin S. H. [4] studies with moisture adsorption on cellulosic materials assumed that diffusivity is exponentially dependent of moisture and equilibrium on the cellulosic material surface at a given temperature and relative humidity. The justification used by the author to assume surface equilibrium is that air surrounding the sample is not completely still and that moisture diffusion inside the cellulose is much slower than at the surface. Although assume equilibrium on the sample surface require appropriated experimental support for this decision. Regards to the exponential dependence of diffusivity with moisture content, several authors have shown that this dependence is real just beyond certain value of relative humidity, below this value diffusivity is independent of moisture content. Another particularity about the defined diffusivity equation is that it does not account with possible changes in structure characteristic of paper, such as porosity, tortuosity and density.

Gupta and Chatterjee [17,18] study of moisture transport in paper assume a parallel diffusion concept where the equilibrium is established between the water vapor

diffusion in the paper pores and the liquid water in the fiber walls. This model becomes a classical Fickian diffusion when the equilibrium is assumed. This model also assumed the external mass transfer coefficient resistance as important, but there are no quantification of its influence in the results.

Other paper related with the theme was the written by Lescanne et al. [9], which investigate transient and steady state moisture diffusion in paper. The authors claimed that at unsteady state the Fick's law can not describe the experimental results, and linear relaxation is considered in the proposed model. The model idealized paper as a cylindrical fiber surrounded by void space and establishes two diffusivities, one for solid phase and one for gas phase, which are not in equilibrium between them. The authors show surprise about the results on moisture adsorption in paper once it is independent of thickness. The model also assume moisture diffusivity through fiber as a constant however several works have found that at relatively high relative humidity condition, diffusivity is significantly dependent of moisture content.

Foss et.al [19], also do not use Fickian diffusion to explain moisture diffusion in paper. They admit diffusion in pores, in fibers and stress the importance of mass transfer coefficient during sorption of moisture in the transient regime. The authors even demonstrated the importance of mass transfer coefficient experimentally in the first reference. However, they did not consider its interference during the transient experiments. The diffusivity in the cell wall constant is also considered as in Lescanne et al. work. In general the transient sorption experiments are provoked by a relative humidity ramp. The large time for the relative humidity change causes the transient

sorption to vary nonlinearly and indicates falsely Non-Fickian diffusion. Therefore, this factor has to be investigated and its possible influence eliminated.

This literature comments justify the preparation of the present chapter, which is introductory to a broader study of anisotropic moisture transport in paper.

3.3. Fickian Diffusion

Certainly a major advance in diffusion theory was the contribution of Adolf Fick with his two fundamental laws of diffusion. In his paper about the theme in 1855, he states the similarity of diffusion with heat transfer and electrical conductivity. Thereafter, Fick developed the first law of diffusion by the equation of flux at on direction:

$$J = -D \frac{\partial q}{\partial z} \quad \text{eq. 3.1}$$

Where: J is flux in (g/m²s), q is concentration in (g/cm³), z is distance of diffusion in (cm) and D is the diffusion coefficient in (cm²/s), which was defined by Fick as “the constant depending of the nature of the substances”.

This equation establishes linearity between diffusion and concentration distribution of diffusing component when the area and flux are constant.

In another words, the process of diffusion is independent of time, because there is not alteration of the medium with the process neither the adjustment of the medium in presence of the diffusing substance is very fast. In addition, concentration is considered the only driving force present in the hypotheses.

The most general equation of Fick for unsteady state and one-dimensional diffusion is:

$$\frac{\partial q}{\partial t} = D \frac{\partial^2 q}{\partial z^2} \quad \text{eq 3.2}$$

The equation is better known as Fick's second law. This equation could be stated as, the rate of concentration change at any point of the sample is directly proportional to the space derivative of the gradient. Yet, another statement of the equation would be that the diffusivity is equal to the rate of concentration change at the point where the gradient changes by one concentration unit per length for each length unit in the flow direction. Fick demonstrated these laws experimentally through diffusion of sodium chloride in water. One important characteristic pointed by Frinch [20] is that Fickian diffusion is easily recognized experimentally, what we could prove in the present work.

Fick's laws apply to dilute solution or generalizing isotropic mediums, which is the simplest case, where no temperature or pressure gradients could cause any convection on the diffusion system, and diffusion is result only of concentration gradient. Another assumption is that in case of diffusion through a uniform flat surface, any change in the

ambient partial pressure would determine an instantaneous change in the surface under diffusion towards the equilibrium.

Although that his laws could apply to many concentrated solutions with considerable accuracy, when these laws are used for diffusion in diluted solutions the diffusivity D can be taken as a constant. However, in case of diffusion in high polymers as well as for moisture diffusion in paper material under determined conditions, (D) depends very much on concentration. In the case of moisture diffusion in paper material specifically, several authors such as Ahlen [21], Nilsson [22], Radhakrishnan [23], showed experimentally that diffusivity is significantly dependent of concentration after a certain level of relative humidity.

The classic laws were applied in a mathematical model to observe the possible Fickian behavior of moisture diffusion in paper. The assumptions are that diffusion is in one dimension, through a homogeneous medium and driven exclusively by concentration gradient. There is no variation of concentration in the center of the paper sample.

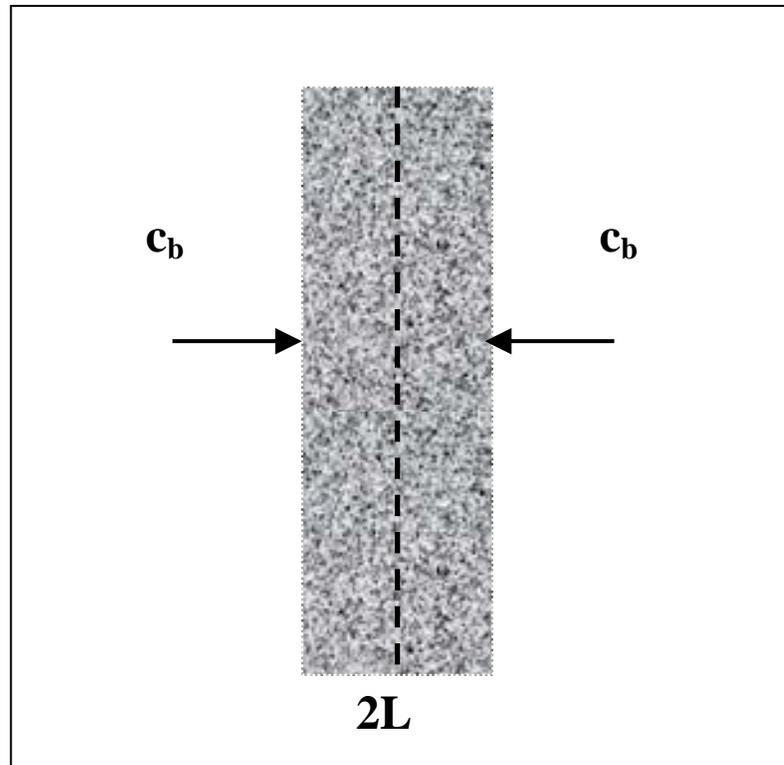


Fig 3.1- Representation of the Model assumed to calculate moisture diffusion in paper when the process is assumed Fickian.

This model does not admit variations in the medium nor on the penetrant that could interfere on the process. Thus, changes of water state, swelling, heat of adsorption, and internal fiber diffusion are ignored as process variables.

The alternative to have two diffusive medium also is restrict by the fact that vapor diffusion in pores and bound water diffusion in fiber wall must be in local equilibrium. The Fickian model also admits in the transient situation that diffusivity is an exponential function of moisture.

The initial and boundary conditions used to characterize this model are:

Initial condition

$$t = 0 \Rightarrow q = q_0, q_0 = q^*(c_0) \quad \text{eq 3.3}$$

Boundary conditions

$$Z = 0 \Rightarrow \frac{\partial q}{\partial Z} = 0 \quad \text{eq 3.4}$$

$$Z = L \Rightarrow k_f (q - q^*) = -\rho_p D_q \frac{\partial q}{\partial Z} \quad \text{eq 3.5}$$

and the dependence of (D_q) with paper moisture is:

$$D_q = \frac{D_p \alpha + \rho_p D_{q0} e^{mq}}{\epsilon \alpha + \rho_p} \quad \text{eq 3.6}$$

Where: L is the length of path diffusion in paper (cm), q is the moisture concentration in paper (g/cm^3), k_f is the mass transfer coefficient (cm/s), ρ_p is paper density (g/cm^3), Dq is water diffusivity in fiber (cm^2/s), m is a parameter, D_{q0} is initial diffusivity in fiber (cm^2/s), α is isotherm slope, ϵ is porosity (%).

Besides these conditions, the GAB isotherm equation also relate moisture concentration (c) with relative humidity (RH), and the parameter of the equation C_{GAB} , M_{GAB} , K_{GAB} . The equation is shown below:

$$q^*(c) = \frac{C_{GAB} M_{GAB} K_{GAB} RH}{(1 - K_{GAB}) [1 + (C_{GAB} - 1) K_{GAB} RH]} \quad \text{eg 3.7}$$

The experimental guarantee that the process is Fickian is given by the second boundary condition (eq 3.5) which implies that the mass transfer coefficient on the paper surface is infinity in order to maintain the flux gradient zero. The proof of this condition is approached later in the experimental comments. It is important to notice that a system have a Fickian diffusion if they obey the first and second laws of Fick with a history independence of time diffusivity and the boundary conditions also time independent.

In order to develop a reliable experimental set up to establish definitively if the process of moisture diffusion in paper is or not Fickian, we applied the successful experience on polymer studies. Fujita [24] claims that the most important experimental contribution to define the Fickian behavior was given by Crank and his group. They

studied the reduced sorption curves with polymers, which consist of a graphic with the q/q_{\max} in the ordinate axis and square root of time in the abscissa axis. Some of their observations are:

- Sorption curves are linear in the initial stage.
- After the linear stage, the curves are concave to the abscissa axis.
- The sorption curves are independent of thickness, or they superpose for different thickness.
- Absorption curves always lays above the correspondent desorption curves if diffusivity increase with concentration, however these curves are coincident when (D) is constant for the concentration interval considered.

The three first criteria are references to check if the diffusion process is Fickian, this is affirmative if all statements are observed experimentally.

An example of Fickian diffusion curve is shown in the figure 1 as follow, where experimental data obtained with paper sorption of water vapor under two different relative humidity step, the curves are plotted in the reduced sorption format. Although the graphic consider just one thickness the curve format characterize a Fickian behavior. In case of different thickness experiment, is very important that the interface conditions of

the paper sample are exactly the same for both experiments, thus is the most experimentally demanding proof of the referred diffusion process, nevertheless necessary.

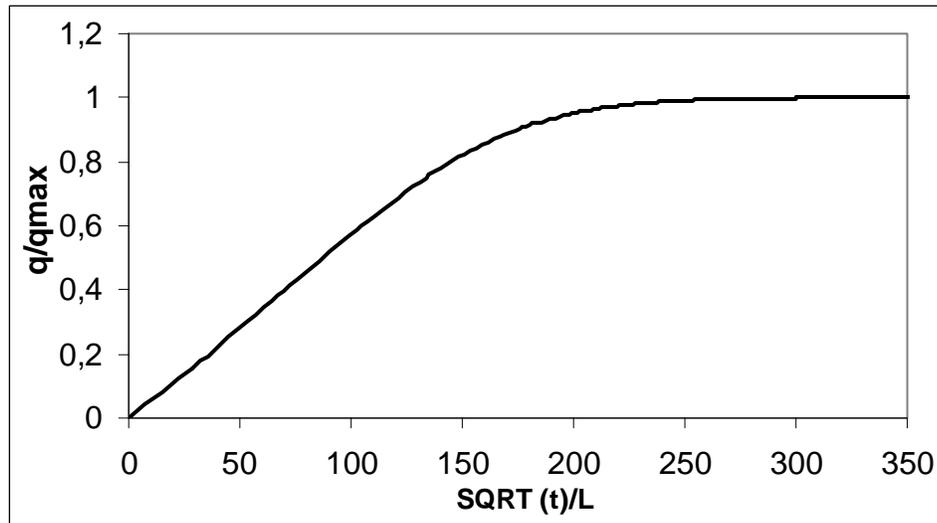


Fig 3.2 – Theoretical Fickian Behavior observed in the Reduced Humidity Sorption in Paper.

Another important characteristic of Fickian process is that the boundary conditions have to be constant, otherwise the variation of boundary conditions itself could state a Non-Fickian diffusion.

Therefore, the diffusion process can also be classified as Non-Fickian or anomalous. However, one fundamental condition to classify the process as Non-Fickian is that the relative rate of diffusion must be comparable with the rate of relaxation, neither significantly faster nor slower.

When diffusion is defined as Non-Fickian, obviously the process of diffusion as well as the relaxation has to be contemplated in the mathematical model in some way.

Thus, more parameters could be necessary to build the model as compared with a Fickian process.

3.4. Experimental Procedures

3.4.1. Samples

The approach of the experimental set up used in the present work referred to the reduced sorption curves used by Crank to study polymers. We used several samples during this investigation in order to reach the expected results.

The main characteristics of these samples are shown in table I below:

Table 3.I – Characterization of the Samples used on the Experiments				
Sample	Composition	CSF	Basis weight (g/m ²)	Thickness (mm)
BKP Machine Made	80 % Southern pine, 20% mixed hardwood	530	230	0.307
H0570 Handsheets	Bleached kraft softwood	570	347	0.451
H4001 Handsheets	Bleached kraft softwood	400	1275	2.591
H4002 Handsheets	Bleached kraft softwood	400	2134	4.007
H4003 Handsheets	Bleached kraft softwood	400	2588	4.757

Initially we used a bleached kraft paperboard (BKP) made on the 1.22 m Fourdrinier paper machine at the Paper Science & Engineering Department in State University of New York, Syracuse. This paper was made in 1984, and has been conditioned properly and used in several research works since then.

The H0570 handsheet samples (Ramaswamy et.al [25]), were sent from the Department of Wood and Paper Science in University of Minnesota, which are well characterized with moisture diffusion parameters through most of the works presented in this dissertation, and finally fiber pads, with different thickness, made on TAPPI sheet former. These pads (H4001, H4002, H4003) are also handsheets made in TAPPI standard laboratory sheet machine, but with significant thickness. The high thickness has as objective highlight the effect of moisture diffusion in the experiment.

The following table show some paper properties and parameters that are necessary for the theoretical calculation of data used to plot the reduced sorption graphics.

Table 3.II - Moisture Diffusion Parameters and Properties								
Sample	M_{GAB}	K_{GAB}	C_{GAB}	D_p	D_{q_0}	m	ρ	ε
H570 [11]	0.043	0.802	45.050	1.50E-2	1.49E-7	136.9	0.769	0.37
BKP [6]	0.051	0.749	56.417	5.24E-3	3.82E-8	398.0	0.663	0.44

The necessity to use several samples came because this work was carried out after many experiments with moisture diffusivity, and the similar results found with the experiments in such diversity of paper samples is a strong corroboration of this chapter conclusions.

3.4.2. Equipment

A humidity chamber with relative humidity control, weight and temperature registration was used to keep the desired environment conditions around the sample during the experiments. The diagram of system is shown in the next figure:

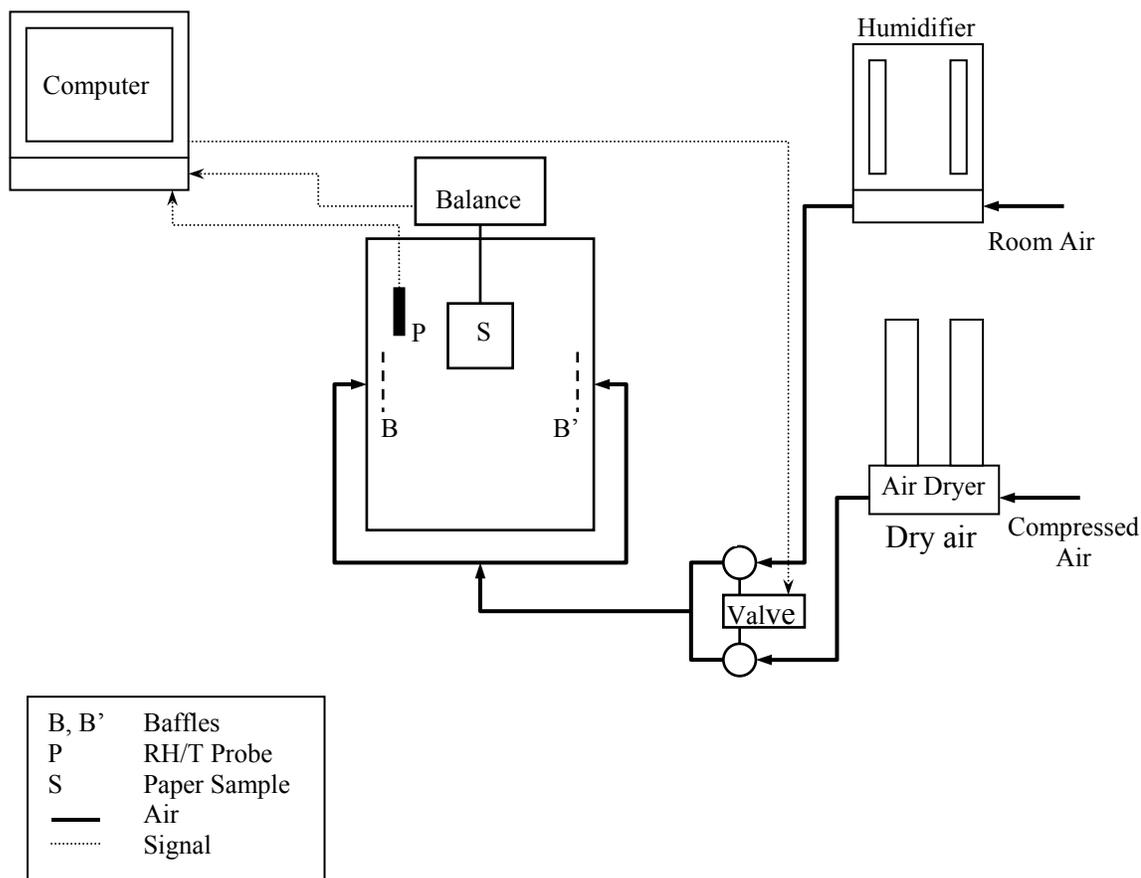


Fig 3.3 – Scheme of the humidity chamber used in the experiments, which make possible to vary relative humidity on paper surface from 5 to 95%.

A brief comment about the equipment is reported here because it was described in details in the chapter II. The ultrasonic humidifiers humidify the air in the room and send it to the mixing valve. A computer with specific software controls this valve. A dryer

column dries the compressed air, which goes to the mixing valve. The RH/Temperature probe measures the humidity inside the chamber and sends the signal to the computer. The computer compares the humidity inside the chamber with the set point and controls it by open or closing the dry and wet air entering the mixing assembly. The paper sample is placed inside the chamber, in a balance that has 1.0 mg of error, and the computer constantly monitors its weight. The data measured during an experimental run are, RH, temperature, weight of sample is output to a file as a function of time. The humidity chamber can be programmed to change relative humidity at certain rate of time. However, this facility is limited by the reaction time of the chamber. The particularities of these experiments obligated some modification in the chamber, such as place extra humidity sensors, addition of fans to increase convection inside, and fast change on relative humidity to pick up real response of paper sorption.

3.4.3. Experiments

The experiments consist in let the paper sample reaches equilibrium in the conditioning room at relative humidity of 50 % and temperature 23 °C. Then place it in the humidity chamber and let reach a new equilibrium at the desired initial relative humidity. The fast relative humidity step is set manually and triggers the moisture sorption of the paper sample until the final relative humidity equilibrium is reached. The change in this experiments were done manually because the relative humidity step has to be as fast as possible to avoid interference in the results. The relative humidity steps were in a relatively large step such as from 10% to 50%, 20% to 70% and 30% to 80%.

These values were chosen to make the chamber operation easier and less error in the sorption results.

The mass transfer coefficient (k_f) values presented in this chapter were measured by independent evaporation experiments. The paper sheet was first soaked with water and then allowed to dry under chosen conditions. The moisture flux was calculated from the initially constant weight loss measurements and used to determine the mass transfer coefficient. The large amount of moisture evaporating from the large soaked paper surface results in higher moisture flux and a probably overestimated variable. Therefore, the mass transfer coefficient values reported in this chapter are taken only for comparison purposes, indicating the power of the convection environment.

In the experiments where the use of fan were not required, the step is made manually and the temperature, weight and relative humidity data is read by computer until the final relative humidity equilibrium is reached. Some experiments require a fan be placed inside of the chamber directed to the sample; in this case the researcher has to make the readings. When reading weight, the fan is isolated from the humidity chamber by a Plexiglas plate to avoid convection disturbance on the balance. The readings are taken every one minute in the beginning and at increasing time as the weight variation become slower. The step change in relative humidity was accomplished by placing the sample inside a plastic bag before allowing the chamber to equilibrate at the higher relative humidity value. The convection level inside of the chamber was also measured using a portable anemometer that gives air velocity in m/s. This equipment permit to find out at which air velocity the convection have not further influence in the moisture

sorption. The results registered are weight, time, relative humidity and temperature. The weight and time are used to calculate the axis of the graphic plotted in the present work.

The plot of results is in the reduced moisture sorption format, where the relative moisture content increases, defined as the ratio of the moisture content gained at certain time and that gained at equilibrium at infinite time ($q/q_{\max} = (qt - q_{\min})/(q_{\max} - q_{\min})$), is in the Y axis; and the similarity variable ξ ($t^{1/2}/L$) is in the X axis. This reduced sorption graphic format is particularly important because show the diffusion process second the definition of the procedure used.

3.5. Theoretical Study of Fickian Diffusion

Considering a paper sample as described before, which is initially at equilibrium with an environmental relative humidity 50 % and temperature 23 °C. This sheet is exposed to a relative humidity 20 % until equilibrium and a sudden increase in the RH to 80 % at both surfaces. The moisture uptake is modeled by Fickian equations and subject to the respective initial and boundary conditions.

The relative moisture content increase defined as the ratio of the moisture content to that at equilibrium at infinite time (q/q_{\max}) is shown as a function of the similarity variable (ξ) in Figure 3.4. As described previously, the reduced transient sorption scales linearly with the variable ξ ($= t^{1/2}/L$) and is independent of the sheet's thickness L. This is a typical example of Fickian diffusion.

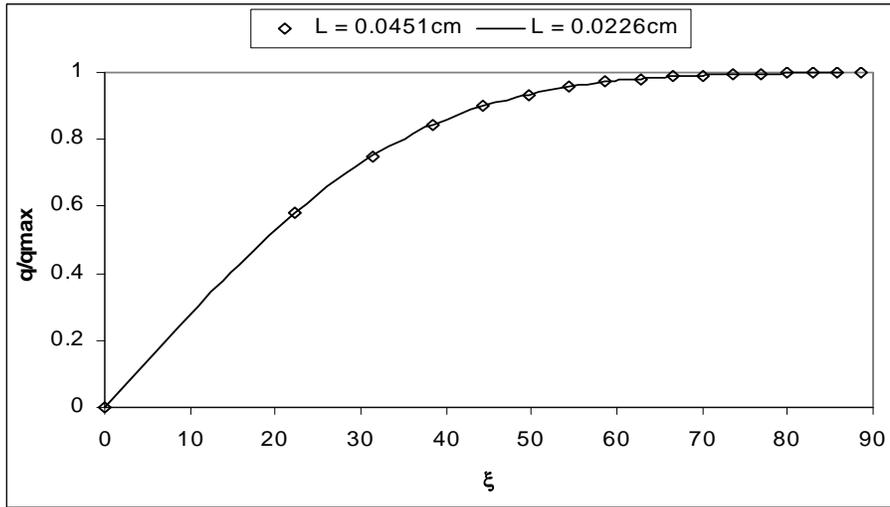


Fig 3.4- Reduced sorption transient (q/q_{max}) determined by solution of Fickian Model for H570 paper parameters shown for two different thicknesses conditions and properties are given in Table II. Relative humidity step from 20 % to 80 %.

Figure 3.5 shows the reduced moisture sorption transient when the external convective coefficient (k_f) is allowed to vary in order to affect a convective resistance at the boundary. In contrast to the curves represented in Figure 3.4, the curves for low mass transfer coefficient values ($k_f = 1.10^{-3}$, 1.10^{-4} and 1.10^{-5}) are no longer uniformly concave but have a sigmoid shape, showing a Non-Fickian behavior.

The external surface boundary layers pose a significant resistance to mass transport for these values of mass transfer coefficient, and result in a considerable deviation of the surface from the bulk humidity.

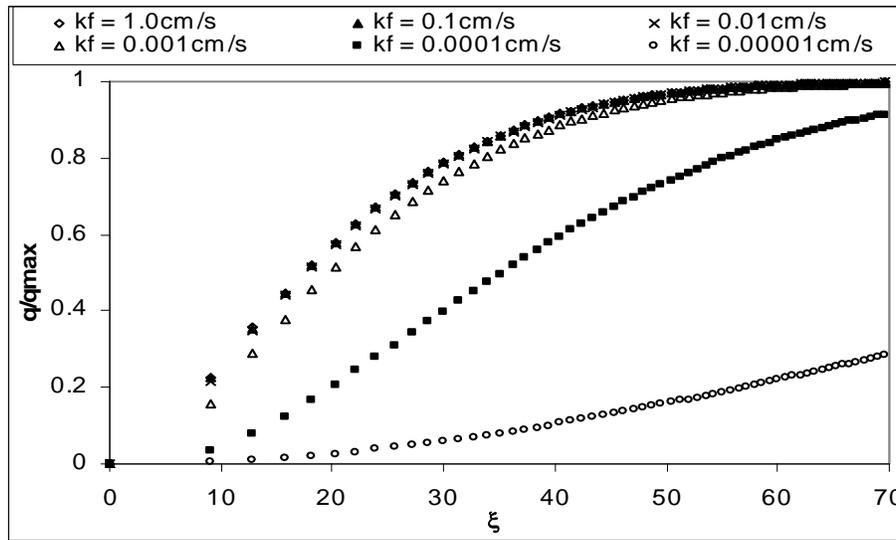


Fig 3.5- Sorption transient for H570 paper at different mass transfer coefficient values, applied on Fickian Model. Parameters and conditions described in Table II. Mass Transfer Coefficient k_f varies from 1.10^{-5} to 1.0 cm s^{-1} , and relative humidity step vary from 20% to 80%.

The Biot number ($Bi = k_f L / D_0$), which represents the ratio of the diffusion resistance to the convective resistance within the material, varies from 2.26×10^{-3} to 2.26×10^{-5} . At high (k_f), the external surface resistance is a much smaller component of the overall transport resistance and hence, the curves for higher values of (k_f) closely approximate Fickian behavior. The dynamics of internal diffusion determine the sorption transient in this case. Significant departure from Fickian behavior occurs when the mass transfer coefficient is quite small of the order of $10^{-3} \text{ cm s}^{-1}$ or lower, corresponding to Biot numbers of 2.26×10^{-3} . Experimental measurements of these coefficients were reported by Radhakrishnan et al., Bandyopadhyay et al., Gupta & Chatterjee using drying fluxes from a water-soaked paper sheet under similar conditions. Their values are in the

range of 0.1 cm s^{-1} through 1.0 cm s^{-1} corresponding to Biot numbers of 2.26×10^{-1} through 2.26. Since these Biot numbers are high, the diffusional resistance dominates sorption and the influence of external convection on sorption rates is negligible under their experimental conditions. This is reflected in the calculations shown in Figure 3.5 for high and low Biot numbers. Figure 3.6 shows sorption transients for the case where the external humidity change occurs as a linear ramp. The ramp times are given in the legend. The curves show that for sufficiently fast changes of the external humidity, with time for change less than 1.5 min, the sorption transients are Fickian. However, for slower changes, Non-Fickian behavior sets in. The Peclet number (P) represents the ratio of the diffusion time to that of the external change. For large (P), the sorption process tends to be Fickian whereas for small Peclet number, Non-Fickian behavior is observed due to the surface concentrations changing too slowly. Thus, ramp time could be a factor that makes a Fickian model to be interpreted as Non-Fickian.

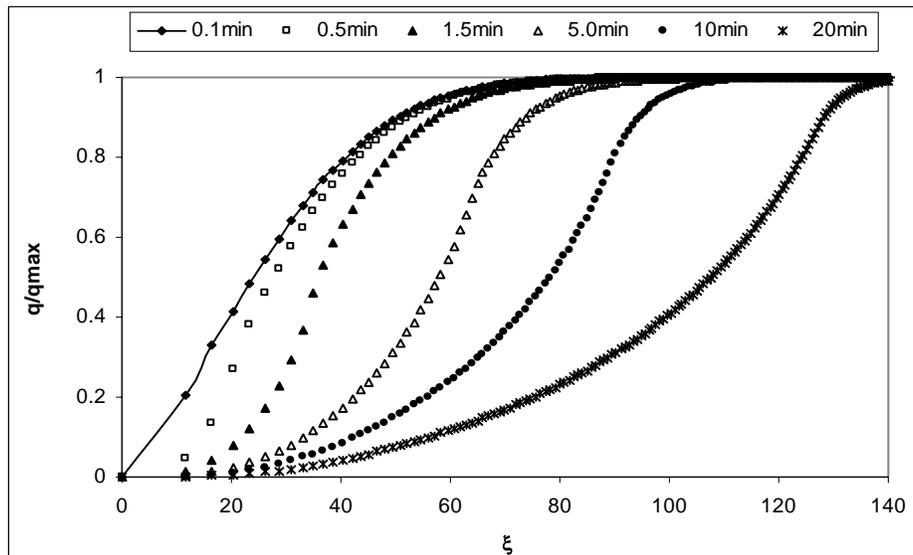


Fig 3.6- Reduced sorption transients – effect of ramp speed. Conditions for BKP paper shown in Table II. Ramp time denoted in legend. Relative humidity ramp from 20% to 80%, and k_f used 0.1 cm/s .

The effects of the convection layer and the rate of ramp change are external variables and are controllable in a laboratory situation. If the sorption dynamics continues to show significant deviation from Fickian behavior after these corrections, it should be due to the intrinsic physics of moisture diffusion.

We chose the linear relaxation model, which is going to be presented later, to demonstrate that internal relaxation processes also can cause Non-Fickian transients sorption. We determined the sorption transient for a paper sheet which parameters are as described in Table II.

Figure 3.7 shows the sorption transient as a function of the similarity variable for sheets of different thicknesses and mass transfer coefficients. The external humidity was assumed to undergo a step change and the humidity and moisture content at the surface were changed instantaneously to the final value (i.e. (k_f) is effectively infinite, $Bi \gg 1$ and $P \gg 1$).

It can be seen that Non-Fickian behavior as shown by the sorption transients depends on the value of the fiber mass transfer coefficient (k_i), present in the model. When the coefficient (k_i) increases to large values, local fiber relaxation towards equilibrium is rapid such that the overall diffusion becomes Fickian. Apart from that, when compared the behavior of this model with the Fickian model in relation with (k_f) , it is evident that mass transfer coefficient does not have the same effect on transient moisture sorption.

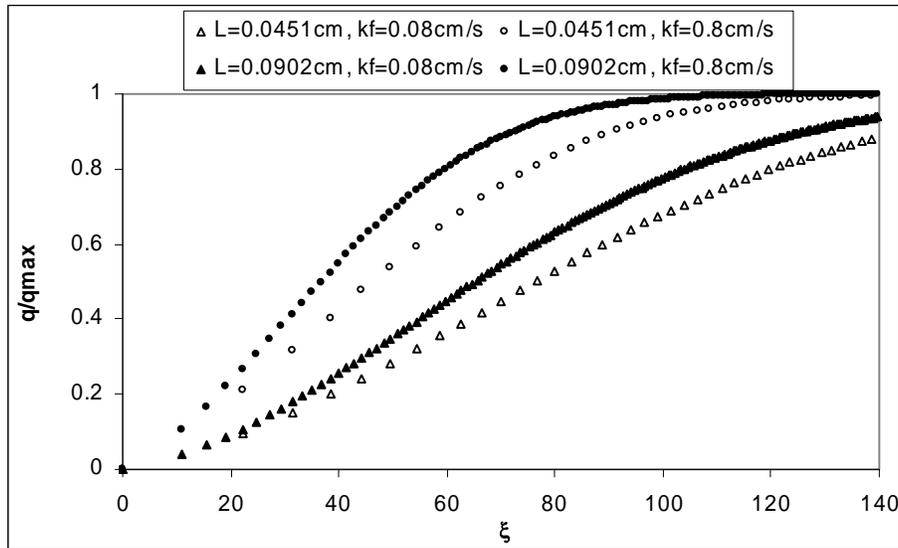


Fig 3.7- Sorption transients effect of internal relaxation (fiber diffusion following pore diffusion) for H570 paper. Non-Fickian behavior is shown even with influences of k_f and t_R eliminated. Fiber mass transfer coefficient $1.0E-3 \text{ s}^{-1}$ and step time 0.1 min.

From this previous theoretical analysis moisture sorption in paper is shown to be Non-Fickian due to two types of causes. The first contribution could be external conditions such as the convective boundary resistances in the environment or the rate of external change, provoking Non-Fickian behavior. The second category of causes is internal relaxation processes in the sheet where the condition of local equilibrium is not attained. Local diffusion of moisture into fiber phases from the pores could be one portion of this cause, as well as localized swelling and adsorption or desorption kinetics. Thus, in any chosen experimental situation, it is important to control the external causes and only then draw inferences regarding the physics of transport internal to the sheets.

3.6. Experimental Aspects of Transient Moisture Diffusion in Paper

The initial test on the experiment set up of the present chapter was in regards of the necessity to establish the Fickian conditions as shown previously. The initial figures show the first studies with equipment and conditions used here.

The samples used in the following experiments have relatively high basis weight and known diffusion characteristics. One of the mentioned samples is a bleached kraft paperboard refined to 570 CSF, with thickness 0.451mm and basis weight 347 g/m². This sample was part of the development of our moisture diffusivity work. The experiments results in Figure 3.8 are concern with the influence of the mass transfer coefficient (kf) when a step from 30% to 80% relative humidity was applied in the humidity chamber.

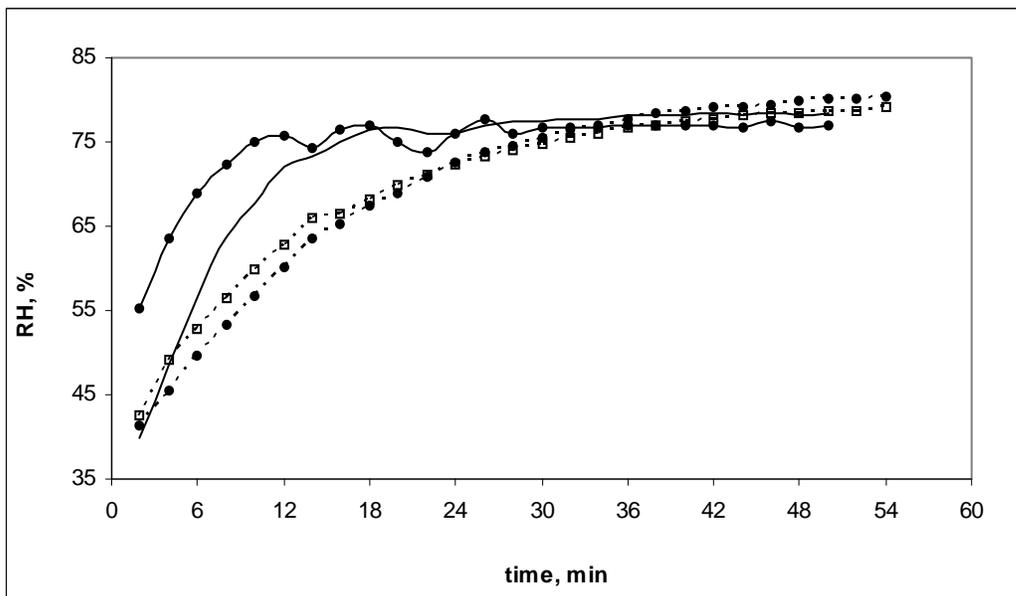


Fig 3.8- Effect of mass transfer coefficient on adsorption of moisture in sample 570 CSF placing RH sensors on its surface. The full line represent data obtained with fan, and the dot lines without fan inside chamber, each experiment have two sensors for RH.

This picture shows the relative difference between the mass transfer coefficient in both experiments where the presence of fan inside of the chamber increase this coefficient and as consequence decreasing the resistance of the limit layer resulting in a faster adsorption. This experiment also shows the difference of relative humidity registered by two sensors placed at short distances from paper sample, but at different positions. As shown, convection uniformity on both sides of the sample could be critical. The addition of fans can result in differences in sorption on both sides.

The first reduced moisture sorption result with experiment with a moisture step sorption is shown in figure 3.9, where the inclusion of convection inside of the chamber improves moisture adsorption significantly. Another important aspect of this figure is the Non-Fickian shape of the curves, which is more visible when no fan is used, for reasons that will be explained later with the theoretical results.

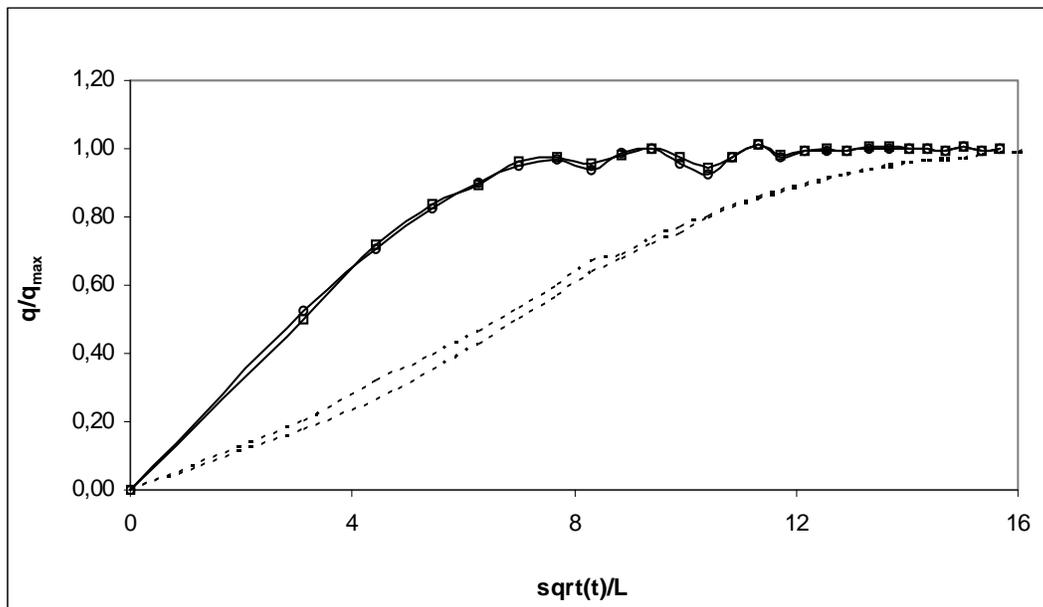


Fig 3.9- Relative Moisture gain variation with square root of time for BKP sample at 570 CSF with and without use of fan inside chamber. The step used in this experiment is from 30% to 80%. Each condition was measured with two sensors simultaneously.

Once the experimental set up was figured out and some preliminary experiments were run, some variables have to be evaluated. Among the most important variables, we decided to explore the effect of sample thickness, convection in chamber and step time. Therefore, handsheets we made with fibers from disintegrated blotter paper in order to form really thick sheets, which would permit to make the necessary measurements more appropriately.

In the attempt to study the Fickian theory applied to paper moisture diffusion several experiments we carried out under different conditions and with different samples. The conditions employed in the experimental research presented in this chapter are described in the table 3.III shown below.

Table 3.III – Variables and Sample Properties Related with the Experiments				
Condition	Thickness, L (mm)	Convection	Air velocity, v (m/s)	Mass Trans Coef, k_f (cm/s)
#1	2.591	No	-	0.41
#2	2.591	Low	0.94	0.51
#3	4.007	Low	0.94	0.51
#4	2.591	High	1.91	0.62
#5	4.007	High	1.91	0.62
#6	4.757	High	1.91	0.62
#7	4.757	Highest	3.02	0.69

The mass transfer coefficient is an important boundary condition in our mathematical model for moisture diffusion through paper plane. Its effects on the experiments, mainly in the transient conditions, are an obligatory subject to be investigated with the purpose to guarantee that the effects experimentally measured were effectively moisture diffusion.

Theoretical simulations have showed that this variable can affect significantly moisture sorption in paper. Thus, the objective was to make the mass transfer coefficient infinity experimentally in order to neglect the mass transfer resistance on the surface of the paper sample.

We accomplished this objective by increasing the convection inside of the humidity chamber to the point that the mass transfer coefficient had no more influence in the moisture sorption on paper.

This was obtained by the introduction of fans inside humidity chamber with increasing air velocity and uniform convection through both paper surfaces. The successful accomplishment of this objective is shown in the figure 3.10 as follow.

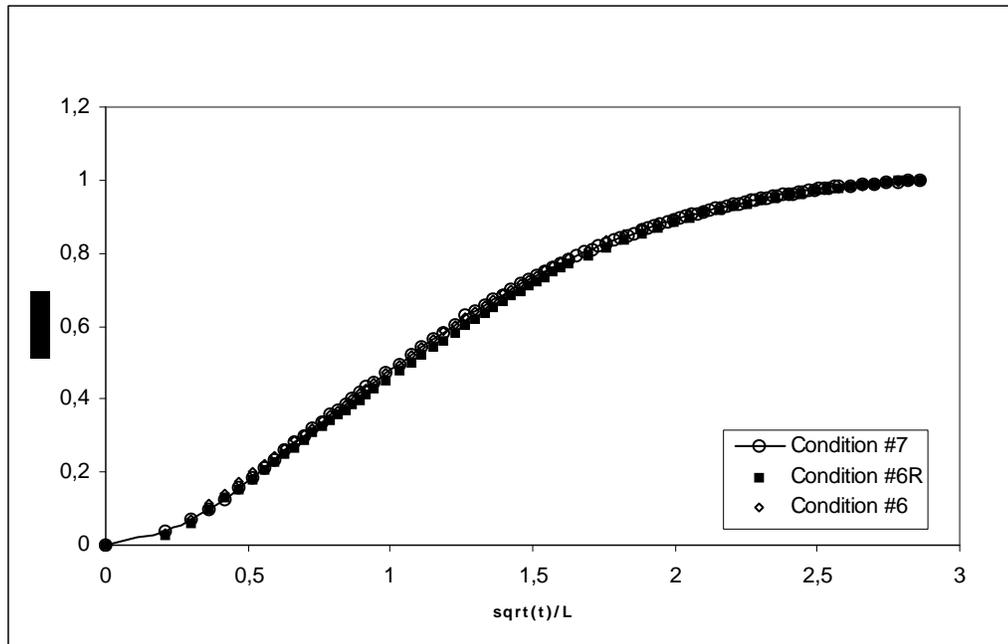


Fig 3.10- Reduced moisture adsorption applied to the same paper sample but with increasing convection from condition #6 and its replication #6R to condition #7.

Figure 3.10 shows the sorption transient (q/q_{\max}) measured experimentally as a function of ξ for a single sheet of paper (H570). We exposed it to a humidity change from 10 % to 50 % achieved within 1 min. Curves under conditions #6 and #7 correspond to experiments which were conducted at different convection levels ($v = 1.91 \text{ ms}^{-1}$ and 3.02 ms^{-1} , $k_f = 0.62 \text{ cms}^{-1}$ and 0.69 cms^{-1}). Curve under condition #6R is from a replicate experiment and indicates repeatability of the experiments.

Note that the moisture uptake rate is not affected by air velocity, showing that the effect of external convective resistances could be neglected under these conditions. Any further increases in the fan speed or convection within the chamber beyond this value do

not enhance moisture sorption. It is interesting to note that the sorption curves remain sigmoid indicating Non-Fickian behavior.

The following figure refers to the samples under conditions #2 and #3, where a less powerful fan was used to provoke convection movement inside the humidity chamber. The relative humidity step in this case was from 30 % to 80 %.

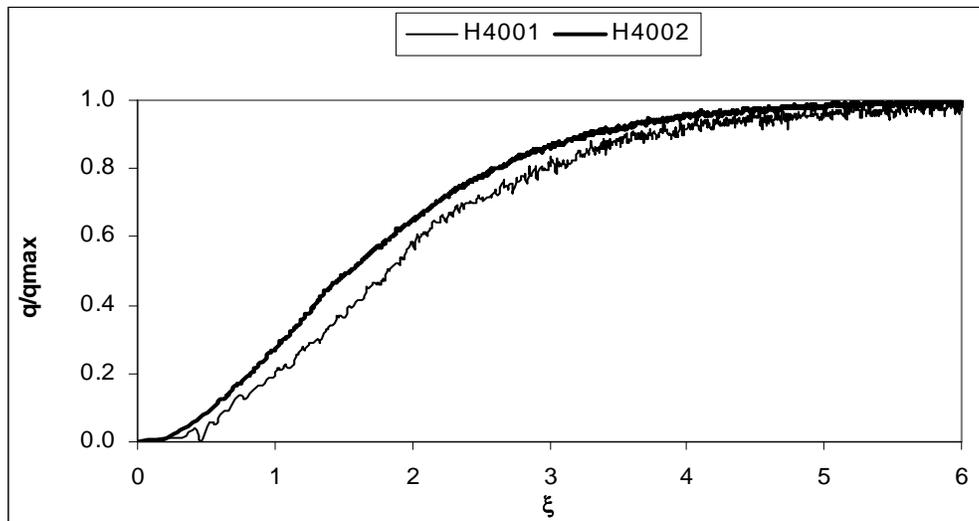


Fig 3.11- Experimental reduced moisture sorption. Curves represent samples with different thicknesses. H4001, $L = 2.591\text{mm}$, and H4002, $L = 4.007\text{mm}$.

Figure 3.11 shows experimental transient sorption data for two samples, one of which had nearly double the thickness of the other. Although the air velocity was not high enough to eliminate the convection resistance, these experiments were conducted with thick sheets with the objective to decrease experimental error. The curves are clearly

sigmoid in shape and are different for the two thicknesses indicating Non-Fickian behavior.

The figure 3.12 shows the sample H4002 under condition of air velocity increasing from 0.94 m/s to 1.91 m/s and the relative humidity is raised to 70 % after remain in equilibrium for long time at 20 %.

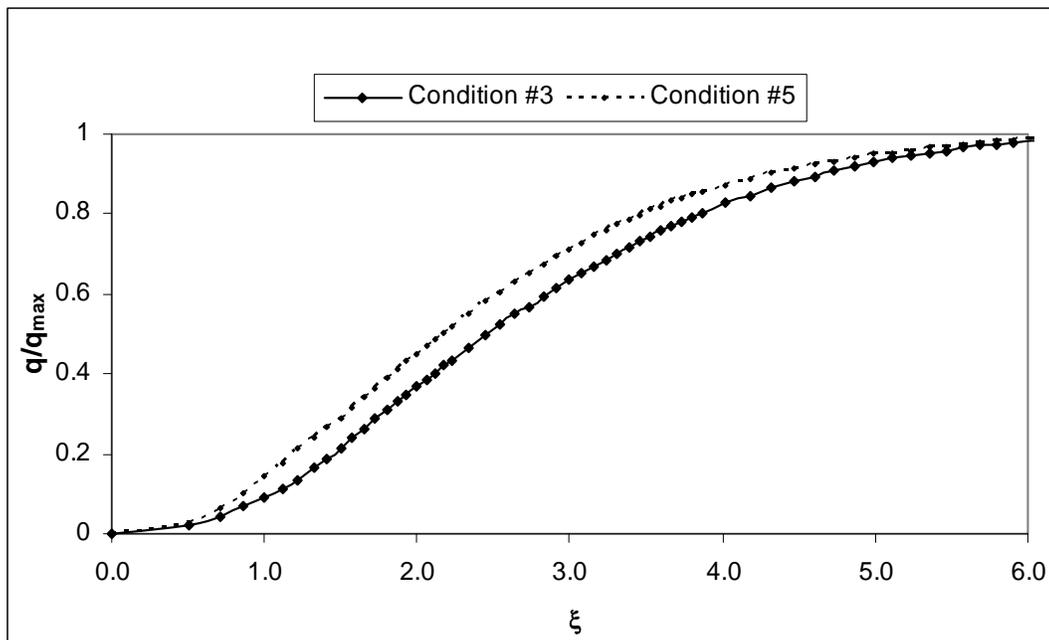


Fig 3.12- Moisture adsorption of the same sample under two different air velocity, therefore two conditions of mass transfer coefficient.

The figure shows a similar Non-Fickian behavior with same thickness sample but under different air velocity.

The next figure represent the weight gain of the samples at three different thickness, under the same chamber condition and with the relative humidity starting from

equilibrium at 10 % and reaching 50 % at the end of the experiment. The convection velocity (v) in this case was 1.91 ms^{-1} . The clear separation of the moisture gain curves and their sigmoid shape leave no doubts as to the Non-Fickian nature of diffusion in paper sheets.

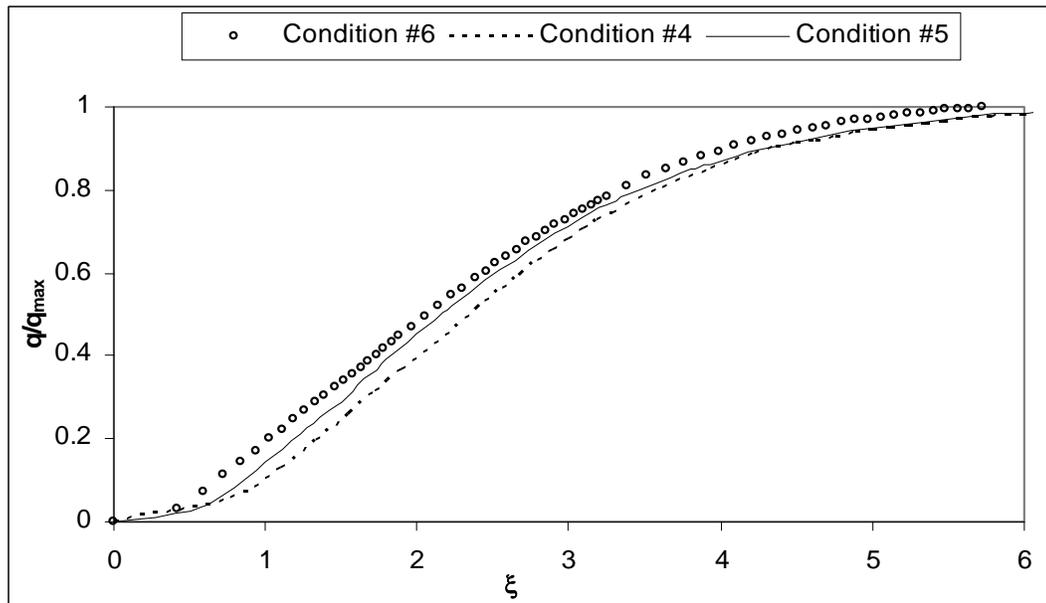


Fig 3.13- Experimental moisture sorption with samples properties described on table I. Condition # 4, $L = 2.591 \text{ mm}$; condition # 5, $L = 4.007 \text{ mm}$; condition # 6, $L = 4.757 \text{ mm}$. Air velocity is 1.91 m/s for all conditions. RH step 10% to 50%.

This experiment clearly shows the dependence of thickness in the moisture diffusion process. Although the sample in condition #6 has just around 20 % difference in thickness from the sample in condition #5, the graphic still presents this influence.

In Figure 3.14 we plotted some experimental results redrawn from earlier investigators. Lescanne et al.'s measurements for the moisture sorption transients are for

two different thicknesses and show clear Non-Fickian behavior. Foss et al. [8, 19] conducted sorption measurements under high and low air velocity conditions. Niskanen et al. [26] data are relative transients strain, which are proportional to the sorption transients. The general sigmoid shapes and Non-Fickian behavior displayed by these transients experiments, together with the experiments presented in this work leaves no doubts about the complex interaction between mass transfer mechanisms in paper.

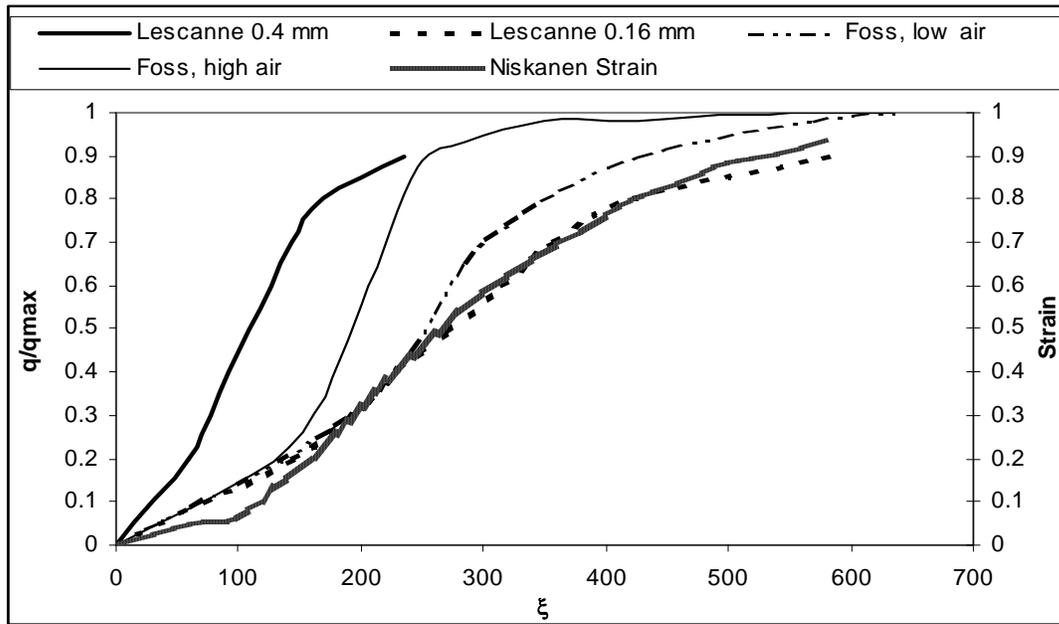


Fig 3.14- Moisture sorption data of Lescanne et al. [9] for two different thicknesses and Foss et al. [18] for two convection conditions, transformed in reduced sorption moisture. Niskanen et al. [26] data of Strain.

3.7. Non-Fickian Theoretical Approach

The simulations used in this study were very helpful to predict the behavior of the Fickian and Non-Fickian process as well as the effect of the variables that play an important role in moisture sorption. Several authors have used Fickian models to describe moisture transport in fibers or similar materials. As well, several of them have questioned Fickian definition with the phenomena of internal relaxation and experimental results. Cai L.W. and Weitsman Y.[27], studying fiber polymeric composites, made the interesting statement that in some circumstances the Non-Fickian moisture profile differ by about 25 % from predictions based on classical diffusion.

Another model under investigation was the Non-Fickian, and the model chosen was obviously the proposed by Ramarao and Chatterjee [28], which has been studied by our group in the past years. Its assumption predicts that the moisture transport in paper occurs in function of three distinct mechanisms:

- Water vapor diffusion through paper pores.
- Condensed water through the z direction of the fiber matrix.
- Condensed water through the cross direction of the fiber wall.

Considering moisture diffusion in one direction and two phases, according with the hypothesized mechanisms, the equations defining the process are shown below:

$$\varepsilon \frac{\partial C}{\partial t} = D_p \frac{\partial^2 C}{\partial z^2} - \rho k_i [q^* - q] \quad \text{eq 3.8}$$

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial z} [D_q \frac{\partial q}{\partial z}] + k_i (q^* - q) \quad \text{eq 3.9}$$

where: (ε) is the paper porosity, (C) water vapor concentration, (D_p) moisture diffusivity in paper pores, (ρ) paper density, (k_i) fiber mass transfer coefficient, (q) moisture content, (q^*) saturated moisture content, (D_q) moisture diffusivity in fiber.

The two equations above represent the continuity of the vapor water (C) and bound water (q) inside of the paper sample. The second term on the right side of both equations represents the exchange of moisture between the fibers and the adjacent water vapor in the pore space. This term is the responsible by the Non-Fickian characteristic of this model, and assumes that the rate of increasing local moisture content is linearly proportional to the deviation of the moisture content from its equilibrium.

The diffusivity of condensed water in this case is defined second the equation 6 and the initial and boundary conditions are the following:

$$C(z,0) = C_{init} \Rightarrow z > 0 \quad \text{eq 3.10}$$

$$q(z,0) = q_{init} = q_{sat}(C_{init}) \Rightarrow H \leq z \leq L + H \quad \text{eq 3.11}$$

$$c(0,t) = C_0 \Rightarrow t > 0 \quad \text{eq 3.12}$$

$$-D_w \frac{\partial C}{\partial z} = D_p \frac{\partial C}{\partial z} - \rho D_q \frac{\partial q}{\partial z} \Rightarrow z = H, t > 0 \quad \text{eq 3.13}$$

$$k_f (C - C_b) = -D_p \frac{\partial C}{\partial z} - \rho D_q \frac{\partial q}{\partial z} \Rightarrow z = L + H \quad \text{eq 3.14}$$

This model is also idealized for complex paper material once assumes that all variation in the plane direction of the paper sheet dimension is averaged. In another words, the paper is homogenized in this direction, and its variables can be represented by a suitable value. A more specific discussion of this model is going to be presented in the next chapters with a study of moisture diffusion in lateral and transversal direction.

3.8. Transient Moisture Sorption In-plane

3.8.1 Introduction

After conclude the study of reduced moisture sorption through the paper sheet thickness, we used a similar approach for investigate the transient moisture sorption In-plane. The objective is to search whether there is any change when sorption is allowed just on this direction of paper sheet, once in this case the superficial sorption is smaller than in transversal direction.

As pointed by Crank, the stress relaxation make the diffusion process time dependent once diffusivity changes according with the progress of the transient experiment. In case of moisture change, this condition changes the mechanism of transport significantly, and deviate the diffusion process from the established by Fick. However, a fundamental condition to characterize a process as Non-Fickian is that the relative rate of diffusion must be comparable with the rate of relaxation.

In case of one of them has significant different velocity, than there is predominance of only one diffusion process making the system Fickian.

As in case of in-plane experiments, the set up is very different, we suspect that a change in diffusion also could happen.

3.8.2. In-plane Experimental Setup

These experiments used samples of the bleached kraft paperboard, machine made, mentioned in the table 3.I. The hydrophobic poly-isobutylene (PIB) resin was also used as moisture insulator, which permit just diffusion in lateral direction. The samples were cut in strips which dimensions used were 15.0cm x 1.0cm or 15.0cm x 2.0cm, such that the length is in machine direction. Groups of six strips are assembled together forming a sandwich with PIB, such that just the lateral surface is exposed to moisture sorption. The top and bottom of the samples also are sealed to avoid bi-dimensional diffusion, although experiments and simulation with this borders opened did not show significant difference.

The experiment procedure changes in this case due to particularities of this moisture diffusion process. The samples are hanging up in a balance inside humidity chamber until reach the initial equilibrium, and then they are placed in a plastic bag duly sealed. After that, the relative humidity inside the chamber is increased to the desired value and the sample is replaced inside. This procedure has showed more effective for In-plane experiments.

3.8.3. In-plane Results

As was done before with through plane experiments, the possibilities of In-plane variations were simulated in order to find out the most important variables, as well as, the expected behavior of the experimental results.

The simulations presented in the following figure take in consideration three experimental condition variations. These possibilities are, first if the top and bottom of the sample are closed (Cl) or opened (Op), the second variable is the mass transfer coefficient in the surface (k_f), which the values tested are 0.1 cm/s and 2.1 cm/s. The third variable considered is diffusion path length, which the values used are 1L and 2L.

As shown in the figure 3.14, the fact that the top and bottom of the samples are opened does not change the moisture sorption significantly, probably because the sample length (15 cm) is much bigger than the sample wide (1.0 or 2.0 cm). However, the mass transfer coefficient in the surface and the diffusion thickness path are important variables to determine the moisture sorption in paper samples In-plane. The relative humidity step projected was from 10 % to 50 %, and the step time very short.

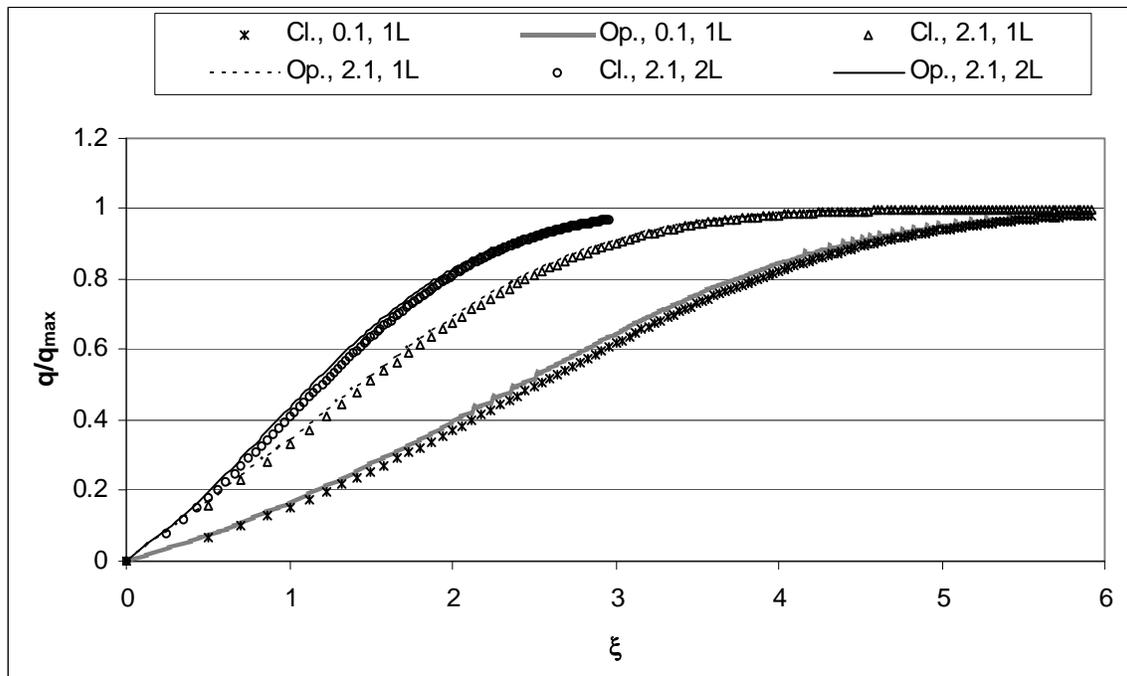


Fig 3.15- Reduced moisture sorption in paper sample simulation considering changes in the following variables: top and bottom closed or opened, k_f variation of 0.1 cm/s or 2.1 cm/s, diffusion path 1L or 2L. The model used is Non-Fickian.

This figure show the behavior of moisture sorption In-plane in the beginning of the process probably where the surface mass transfer coefficient play a important role, and the Non-Fickian characteristic sorption can be noticed.

Afterwards, the first experiment which check the equilibrium points were carried out with relative humidity step from 10 % to 50 % and air velocity 3.02 m/s. The plot of reduced moisture sorption In-plane for 2.0 cm wide and 15.0 cm length sample with top and bottom edge closed is shown as follow.

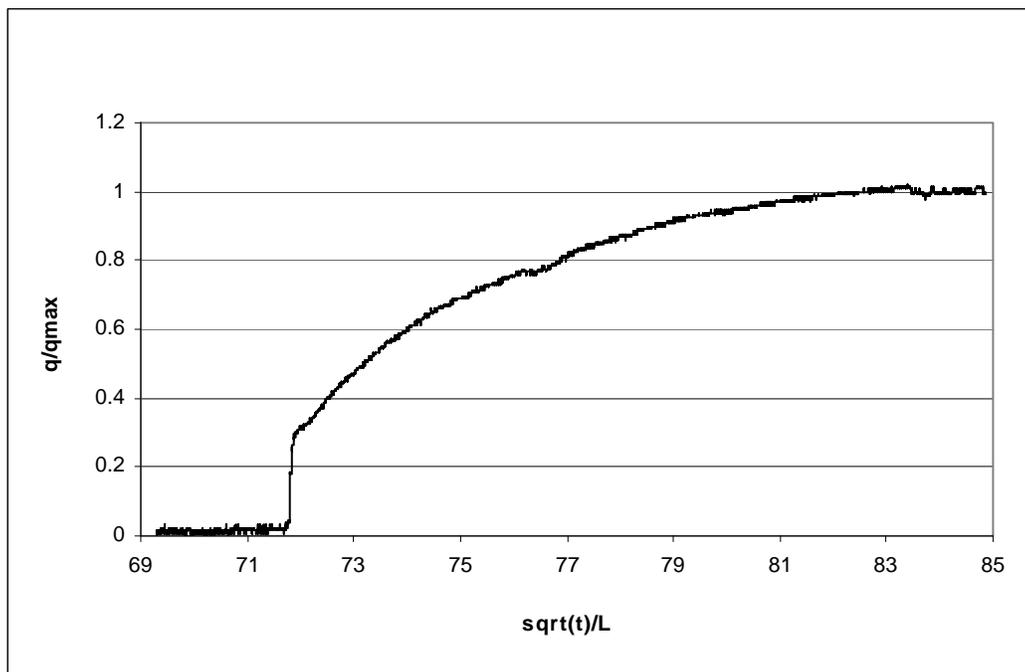


Fig 3.16- Moisture reduced sorption in-plane for BKP sample, machine made, with six layers of sheets of 15.0 cm x 2.0 cm. Air velocity 3.02 cm/s and relative humidity step from 10% to 50%.

The figure shows the effect of the relative humidity step on the In-plane moisture sorption and the time to reach the approximated equilibrium. As the isotherm of this paper was calculated before using the GAB model, the final sorption under determined relative humidity and temperature can be predicted.

The next figure shows experimental results that compare moisture sorption In-plane for different convection conditions. One curve show initial sorption of moisture when the relative humidity step is applied without convection and the air velocity inside the chamber could not be measured with the portable anemometer, another curve show initial sorption when fans were used and the air velocity was 3.02 m/s.

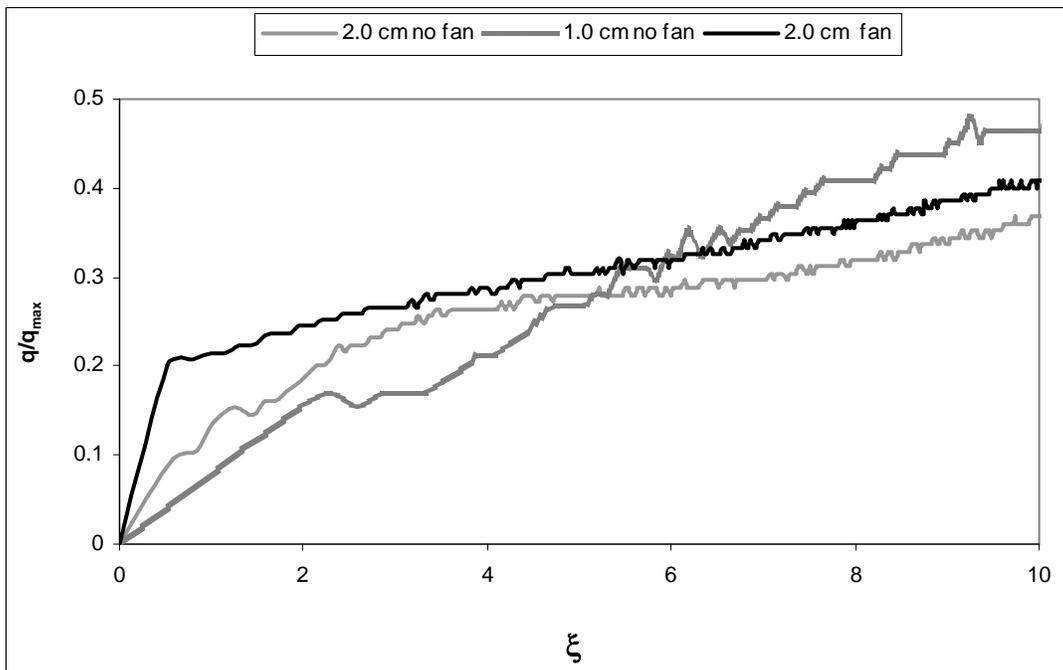


Fig 3.17- Initial reduced moisture sorption for a BKP paper sample 15.0cmx 2.0cm submitted to RH step from 10% to 50%. Air velocity using fan 3.02 m/s.

In order to compare and understand the transient diffusion In-plane, the figure 3.16 shows only the beginning of the moisture sorption, and in this threshold, the effect of mass transfer coefficient in the surface is noticeable. After this initial difference, both curves come together until reach the final equilibrium. The effect is similar to that found for moisture sorption through thickness, but also correspondent to the material area exposed to adsorption and the restriction imposed by the path of diffusion. Due to this reason, it is important focus in the initial portion of the experiment.

The next figure shows this aspect of surface mass transfer coefficient as well as the influence of thickness in a graphic build with much more data. Thus, the behaviors of these variables are presented after the initial sorption, and the effect of thickness and surface mass transfer coefficient compared.

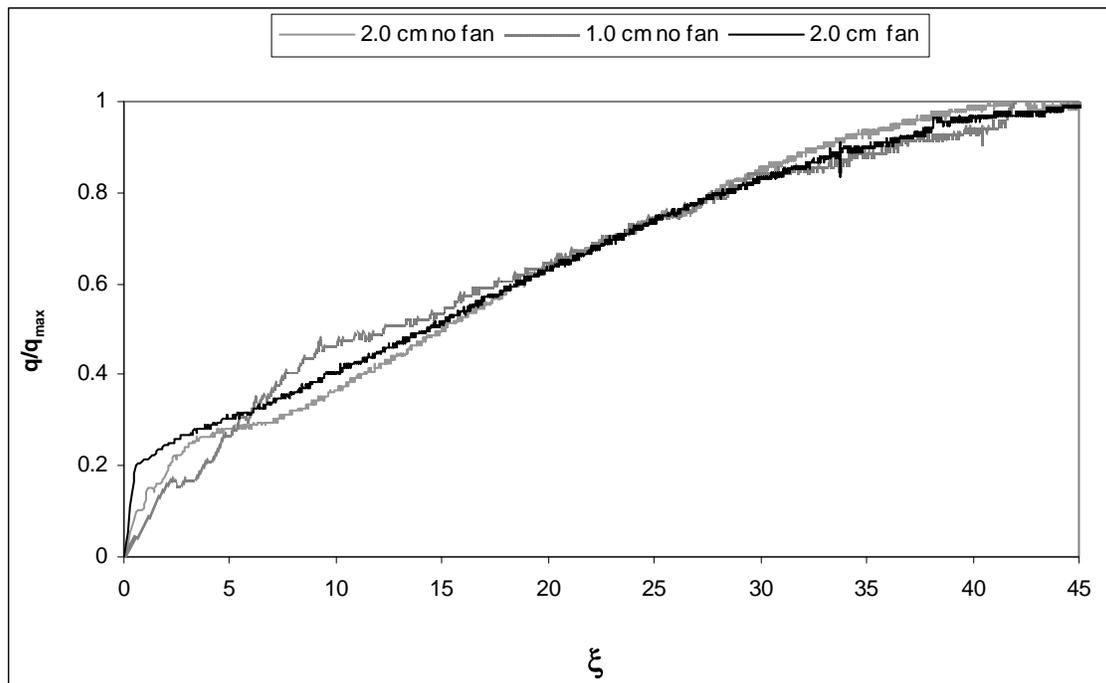


Fig 3.18- Reduced moisture sorption for bleached kraft paperboard (BKP) using as variables the surface mass transfer coefficient and diffusion path length. Air velocity inside chamber with fan 3.02 m/s and diffusion length 1.0 and 2.0 cm.

As shown in the figure, after an initial variation on the curves where the studied variables make difference, it reaches a stage where there is only one mechanism dominant in moisture sorption. Considering the extremely long and discontinuous path of water vapor diffusion in the pores through In-plane diffusion, the increasing tortuosity, we assume that this diffusion become slower inside the pores. Therefore, the adsorption of water by fibers is more effective and the bound water diffusion becomes the dominant mechanism of transport. As the mechanisms of moisture diffusion and relaxation become unique due to pore diffusion slow down, the process tend to approximate to a Fickian diffusion. The oscillations on these experiments are frequent. Probably because the sample weight and the weight gain are small.

The variation on the curve correspondent to the (1.0 cm No fan) is exaggerated, although we understand that the portion disturbed does not change the analysis of the graphic. As expected the restriction in the area of sorption and the extremely long diffusion path would highlight the bound fiber diffusion and restrict the pore diffusion, making the process approximate to Fickian model. This relation changes between the two mechanisms show the importance of the fiber mass transfer coefficient (k_f) in the moisture diffusion in paper, which in this case overcome the surface mass transfer coefficient (k_f). Nevertheless, physically the relaxation and swelling phenomena as well as the water state change are present in the moisture transport, what in our opinion still define the process as Non-Fickian.

3.9. Conclusion

The general agreement that paper is a complex heterogeneous material and the evolution of the mathematical models generated to describe the moisture diffusion is evident. However, some important questions about the behavior of the paper and experimental procedures regards to moisture diffusion still can be raised. The present work brings up some of these questions and answer them showing experimental and theoretical results, which we understand clarify every point of our approach.

The results show that moisture diffusion in paper is definitely Non-Fickian due to the material characteristics such as internal relaxation that imply in the formation of hydrogen bonds with water and swelling, the vapor and bound water mechanisms of diffusion which occur respectively in the pores and in the fiber wall. The results of moisture reduced sorption through lateral and transversal direction show a typical Non-Fickian graphic, with a sigmoidal shape curve and a clear dependence of sample thickness. Nevertheless, the reduced moisture sorption In-plane shows this characteristic only in the beginning of the sorption, loosing the thickness and surface mass transfer coefficient differentiation as the diffusion progress.

Non-Fickian behavior in moisture diffusion in paper can arise from external agents either, such as convective boundary resistances or sufficiently slow humidity changes. The Biot and Peclet numbers may be calculated to obtain the relevance of these parameters in transport. Therefore, their influences must first be minimized if not altogether eliminated before conclusions about mechanisms of diffusion can be made.

In order to prevent that the mass transfer coefficient (k_f) was brought to infinity, such that the resistance of mass transfer on the surface of the paper sample was approximately zero. As shown, even with the mass transfer coefficient being infinity, still the behavior of moisture diffusion in paper is absolutely Non-Fickian.

An important conclusion is that the mass transfer coefficient (k_f) of a transient moisture diffusion experiment through the paper thickness is important and when neglected can change the results significantly, as well a mathematical model have to consider this variable carefully. The results show this variation experimentally under different convection conditions and theoretically using a Fickian model.

Maybe the most consistent evidence of a Non-Fickian process is its sensitivity to sample thickness when plotted the reduced moisture sorption graphic, which is absent in a Fickian model as shown in a simulation. Mathematical manipulations allow making a Fickian model thickness independent, which is not possible with Non-Fickian model.

Another important experimental aspect questioned is the time used to design the transient paper sorption experiments. From the works investigated, this variable is consistently neglected. However, our experimental and theoretical results show that variation in data could be significant, and sorption could be much faster that expected. The times used in the present experiments are the faster possible with the equipment available, and seems to be reasonable according with simulated results.

The reduced moisture sorption graphics for In-plane diffusion show a peculiar behavior, because the beginning is characterized by Non-Fickian behavior showing differences with thickness and surface mass transfer coefficient, besides of the nonlinear curve shape. After that, due to emphasis on bond water diffusion in fiber the behavior

approximated to the Fickian diffusion. Although, in the authors opinion, physically the diffusion is Non-Fickian once the relaxation and swelling phenomena as well as the water state change are present in the process. The graphic, moreover is not linear but a smooth concave curve.

3.10. References

1. Crank J., "A Theoretical Investigation of the Influence of Molecular Relaxation and Internal Stress on Diffusion in Polymers", *J. of Polymer Science*, XI(2):151-168, 1953.
2. Crank J., "The Mathematics of Diffusion", Second Edition, Clarendon Press, Oxford, England, 1975.
3. Ramarao B.V., Massoquete A., Lavrykov S., Ramaswamy S., "Moisture Diffusion Inside Paper Materials in the Hygroscopic Range and Characteristics of Diffusivity Parameters", *Drying Technology* 21(10): 2007-2056, 2003.
4. Lin S.H., "Moisture Adsorption in Cellulosic Materials", *Int. J. Engng. Sci.*, 28(11): 1151-1156, 1990.
5. Donkelaar J.R., and S. Jaeger, "Transport and Sorption of Water Vapour in Corrugated Board", 4th International Symposium on Moisture and Creep Effects on Paper, Boards and Containers, EFPG, France, 1999.
6. Roisum D. R., "Moisture Effects on Webs and Rolls", *TAPPI Journal*, vol 76 (6), 1993.

7. Rahman A.A., Urbanik T.J., Mahamid M., “Moisture Diffusion Through a Corrugated Fiberboard under Compressive Loading: its Deformation and Stiffness Response”, Progress in Paper Physics Seminar, 8 – 13 september, Syracuse, NY, 2002.
8. Gupta H., “Moisture Transport in Paper under Steady and Unsteady Conditions Investigated with a Parallel Diffusion Concept”, PhD Thesis, Paper Science and Engineering Department, SUNY-ESF, Syracuse, New York, 2003.
9. Lescanne Y., Moyne C., Perre P., “Diffusion Mechanisms in a Sheet of Paper”, Drying 92: 1017-1026, 1992.
10. Foss W.R., Bronkhorst C.A., Bennett K.A., “Simultaneous Heat and Mass Transport in Paper Sheets During Moisture Sorption from Humid Air”, Fundamental Advances in the Pulp and Paper Industry AICHE, 322(95): 80-88, 1999.
11. Ramarao B.V. and Chatterjee S.G., “Moisture Sorption by Paper Materials under Varying Humidity Conditions”, Trans. 11th Fund. Res. Symp. Cambridge, UK (2):703-749, 1997.
12. Bandyopadhyay A., Ramarao B. V., Ramaswamy S., “Transient moisture diffusion through paperboard materials.” Colloids and Surfaces, A: Physicochemical and engineering aspects 206, 455-467. 2002.
13. Massoquete A., Lavrykov S., Ramarao B.V., Goel A., Ramaswamy S., “Anisotropic Moisture Diffusion Study on Refined Paper”, International Paper Physics Conference, Victoria, British Columbia, 2003.
14. Liesen J., Hottajie B., Coffin D.W., Lavrykov S.A., Ramarao B.V., Beckham H.W., “Through-Plane Diffusion of Moisture in Paper Detected by Magnetic Resonance Imaging”, Ind. Eng. Chem. Res., (41), 6555-6565, 2002.

15. Lavrykov S. and Ramarao B.V., "Models for Generalized Transport in Paper Materials: Comparison of the Linear Driving Force Approximation with a Periodic Array of Pores Model." Empire State Paper Research Institute, Res. Report 117:39-58, 2002.
16. Lavrykov S. and Ramarao B.V., "An Axisymmetric Pore-Fiber Cell Model for Moisture Transport in Paper Materials", Nordic Pulp Paper Res., 2004.
17. Gupta H. and Chatterjee S.G., "Steady State Moisture Transport in Paper Investigated with a Parallel Diffusion Concept", ESPRA Res. Report, SUNY-ESF, Syracuse, 117, 83-104, 2002.
18. Gupta H. and Chatterjee S.G., "Parallel Diffusion of Moisture in Paper under Transient Conditions", ESPRA Res. Report, SUNY-ESF, Syracuse, 118, 14-36, 2003.
19. Foss W.R., Bronkhorst C.A., Bennet K.A., Riedemann J.R., "Transient Moisture Transport in Paper in the Hygroscopic Range and its Role in the Mechano-sorptive Effect", Proceeding of the Third International Symposium on Moisture and Creep Effects on Paper, Board and Containers, 221-236, Rotorua, NZ, 1997.
20. Frisch H.L., "Sorption and Transport in Glassy Polymer – A Review", Polymer Eng. and Sci., Mid-January, 20(1): 2-13, 1980.
21. Ahlen, A.T., "Diffusion of Sorbed Water Vapor through Paper and Cellulose Film", TAPPI J., 53(7):1320-1326, 1970.
22. Nilsson L. Wilhelmsson B., Stenström S., "The Diffusion of Water Vapour through Pulp and Paper", Drying Technology, 11(6):1205-1225, 1993.
23. Radhakrishnan H., Chatterjee S.G., Ramarao B.V., "Steady-state Moisture Transport in a Bleached Kraft Paperboard Stack", J. Pulp Paper Science, 26(4):140-144, 2000.

24. Fujita H., "Organic Vapors above the Glass Transition Temperature", Diffusion of Polymers, Chapter 3, Academic Press, London, 1968.
25. Ramaswamy S., Huang S., Goel A., Cooper A., Choi D., Bandyopadhyay A., Ramarao B.V., "The 3D Structure of Paper and its Relationship to Moisture Transport in Liquid and Vapor Forms", 12th Fundamental Research Symposium, 1289-1311, Oxford, September, 2001.
26. Niskanen K.J., Kuskowski S.J., Bronkhorst C.A., "Dynamic Hygroexpansion of Paperboards", Nordic Pulp and Paper Research, 12(2), 103-110, 1997.
27. Cai L.W. and Weitsman Y., "Non-Fickian Moisture Diffusion in Polymeric Composites", Journal of Composite Materials, 28(2): 130-154, 1994.
28. Ramarao B.V. and Chatterjee S.G., "Moisture Sorption by Paper Materials under Varying Humidity Conditions", Trans. 11th Fund. Res. Symp. Cambridge, UK (2):703-749, 1997.

CHAPTER IV

MOISTURE DIFFUSION ON PAPER

TRANSVERSE DIRECTION

4.1. Introduction

Moisture diffusion has significant impact on the performance of various paper materials and products. Moreover, it is an important participant on the pulp and paper manufacturing process as well. Due to the heterogeneity of this porous material, moisture diffusion occurs via two pathways: the void spaces and the fiber matrix. The interaction of moisture transport along these two pathways can be quite complex and modify according with the moisture content and paper structure.

Since the void structure in paper and the fiber matrix are anisotropic, diffusion as well as other transport properties such as permeability and thermal conductivity are also anisotropic. Therefore, the definition of Lateral diffusion in the plane of the paper sheet (xy) and Transversal diffusion in the thickness direction (z) is perfectly acceptable to differentiate the moisture transport.

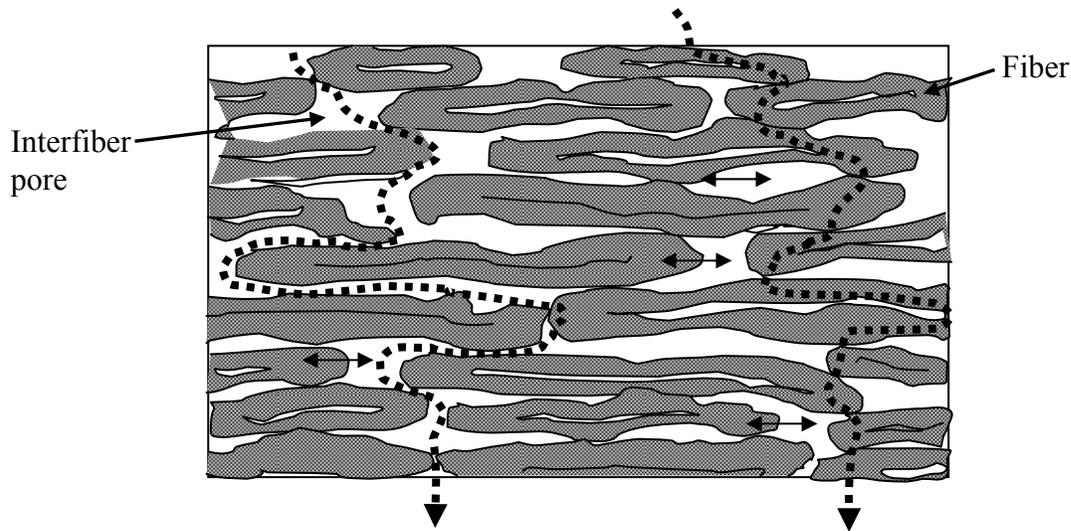


Fig 4.1- Schematic representation of the paper sheet structure showing the pore space and fiber matrix details. Moisture transport occurring through void space and through the fibers is traced, and local exchange of moisture due is represented by the horizontal double headed arrow.

The present chapter however is going to focus on transversal moisture diffusion which has been studied by several authors through time, with different perspectives. In this research, one of the objectives was to work on experimental determination of the diffusivity for handsheets made from bleached kraft softwood refined to different levels. An effective diffusivity was determined from gravimetric measurements of moisture flux through paper sheets. The moisture profile was also obtained experimentally and important parameters for the moisture diffusion model were calculated from that. As presented in the chapter VI, from these data, the moisture transport parameters consisting of diffusivities in the pores (D_p) and diffusivity in fiber matrix (D_o) were estimated using a non-linear parameter estimation algorithm.

Another objective of the present chapter is to relate structural modifications on paper such as refining, density and porosity with moisture diffusion. The diffusivity in the void space (D_p) shows a uniform decrease with increased refining levels of the pulps in the thickness direction. Nevertheless, were not found significant effects of the moisture diffusivity in the fiber matrix regards to the sorption isotherms due to refining effects. The effect of swelling is shown on pore diffusion through experiments carried out with n-propanol as diffuser through large part of the relative humidity range. The experiments with n-propanol diffusivity also help to show the effect of density variation on bound water diffusion in the fiber matrix.

The expectations are that the variety of experiments and approaches shown in this chapter could bring some important contribution in the moisture diffusion in transversal direction, mainly with respect to changes occurring in the paper structure provoked by refining. The intention also is to improve the understanding on the mechanisms of moisture transport with regards to vapor pore diffusion and bound water fiber diffusion.

4.2. Literature Review

Moisture is an important variable, which affects the physical properties of paper such as stiffness, elastic modulus and electrical resistance very significantly. The role of moisture in the performance of paper products is critical. Paper dimensions are also strongly affected by moisture and its dynamics. Koponen, [1] investigating microstructure of wood found that moisture decreases transverse shear properties of fibers and reduce the stiffness of cross-banded wood composites. He claims that variation

in the S2 microfibril angle, in fiber, cause variation of properties between different veneers and inside individual veneer in the structure of plywood.

Crook and Bennet [2] documented extensively results on the equilibrium moisture sorption, hysteresis effect and the mechanical properties behavior in a variety of paper materials. They concluded that humidity affect most properties of paper significantly. Moreover, the absolute moisture content of paper, the rate of moisture change also can significantly decrease the tensile or compressive strength of paper materials by large magnitudes and leads to damage of the products. The Benson [3] study investigated the effect of relative humidity from 22 % to 90 % or most specifically equilibrium moisture content (EMC), and temperature from 15.5 to 48.9 °C, on kraft linerboard. He found that tensile strength and modulus of elasticity appear to be linear between 4 and 13 % EMC, whereas properties like strain to failure, proportional limit stress and strain have linear behavior from 4 to 10 % EMC. The temperature effect was not conclusive and the author advises to explore interrelationships between temperature and moisture and its effect on tensile strain. However, was noticed that accuracy in temperature of at least 2 °C is desired, and this need was more important for 50 % than 65 % RH, the relative humidity tested then. Back et al. [4] related the effect of transient moisture sorption on mechanical properties of paper, and found reduction of elastic modulus comparable with woolen fibers, as well noticeable reduction on strain to failure and tensile energy absorption, on kraft sack paper. They suggest two means to reduce the transient effects on mechanical properties, which are auto cross linking of cellulose, that improve dimensional stability, and increase hydrophobation. The transient effects were larger in paper containing recycled fibers, although creep rates are not different. Wang et al. [5] present a review in

transient moisture effect with emphasis on viscoelastic properties and durability of materials like wood, plywood, particleboard, fiberboard, paper and fibers. Among their conclusions the statements are that changes in moisture content accelerate creep, creep recovery and relaxation processes, as well as reduce creep rupture life and dynamic modulus. The factors that influence the mechano-sorptive effects of the materials are history, direction, magnitude and rates of moisture changes, second concluded the authors.

Recently, Habeger and Coffin [6] and Alfthan [7], have proposed that moisture distributions due to transient humidity variations could be one cause for the accelerated creep response of paper and paper containers. Many paper and board materials show accelerated creep under transient moisture content changes. Therefore, in order to control these effects and design better paper products, it is necessary to understand and accurately model the mechanisms of moisture diffusion inside the paper structure.

Moisture transport in the thickness dimension of paperboards has been investigated under many aspects in the past. Gurnagul and Gray [8] used inverse gas chromatography to study surface changes in bleached kraft handsheets, refined at different grades, with variation of relative humidity. They show that there is irreversible loss of surface area when handsheets are exposed to high relative humidity, and suggest that it is due to fiber swelling and bond relaxation. The authors show decrease of n-decane adsorption with refine and claim that it is due to decrease of surface area.

Rahman et al. [9] studied the commercial corrugated fiberboard by applying induced moisture on one side and analyzing its behavior using a finite element model. Their objective was to predict change in paperboard characteristics like deformation, loss

of stiffness and swelling development. Niskanen et al. [10], analyzed strain of paperboards to determine the dynamic hygroexpansion by relative humidity changes. They showed that strain changes on cross direction are slower on adsorption than desorption, and that they are slower than machine direction in both situations. However their transient experiments have long ramps, what could make some differences as discussed in the chapter III. The authors also claim that due to the moisture diffusion time the hygroscopic strain of the paper or board can change as fast as or faster than relative humidity. It is interesting that during desorption, moisture content changes at the same rate as strain, but during adsorption moisture content lagged behind even the slower cross direction strain. Nevertheless, the authors used 60 min as ramp time, which is excessively long second our transient experiments exposed in the chapter III.

Another change caused by moisture is on surface properties, mostly in roughness, which is obviously important for printing quality. Enomae and Lepoutre [11] reported the simultaneous measurement of gloss and moisture content of paper samples with a new instrument as the relative humidity is changed. The results show that gloss decrease as moisture content increases, but also shows that gloss lags behind moisture content after the relative humidity ramp. Nonetheless this is explained by the slower relaxation due to fiber wall diffusion and fiber rearrangement in paper structure.

Han and Matters [12] studied transport of water vapor in a fiber mat during drying process and claim that normal diffusion accounts for about 40 % of the drying rate. However, they highlight that vapor surface transport add some complexity to vapor transport and that paper small pores bring vapor diffusion close to Knudsen regime. Water vapor diffusion through paper and cellulose film was also searched by Ahlen [13],

that reported an elaborate experimental investigation of the steady moisture flux, and determined the effective diffusivity. He found that it varied with the average paper sheets relative humidity, and suggested two simultaneous pathways for the transmission of moisture: through the void spaces and the fiber matrix. At low RH values, the void space was thought to be the dominant pathway for moisture transmission. At higher average RH values, above approximately 30 %, he found that the effective diffusivities increased with relative humidity indicating that transport was being enhanced possibly by conduction through the fiber matrix. Another important observation is that for less porous paper the bound water could become more important mechanism of moisture transport.

Rounsley [14] measured water vapor transmission rates through paper and expressed the diffusivity in terms of a permeability commonly used as a measure of mass conductance in membranes. Based on the fact that the measured permeability was a significant function of moisture content, he suggested surface diffusion as one mechanism of moisture migration. Surface diffusion was thought to dominate only after the fiber surface was covered with a monolayer of adsorbed molecules since the molecules constituting this monolayer are thought to be chemically bound and cannot diffuse easily. The demarcation for surface diffusion to be prominent was suggested to be at relative humidity close to 25 %. The author provided an equation for the surface diffusion flux based on a consideration of the driving force as the gradient of the chemical potential of the adsorbed molecules and the resistance.

As model simplification to describe moisture absorption and desorption in cellulosic materials, Lin [15,16] have idealized a paper sheet as a homogeneous material within which moisture diffusion is described by a single diffusivity parameter which

varies depending on the local moisture content. The equation used by Lin for unsteady moisture transport is:

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial z} \left[D_0 e^{k_L q} \frac{\partial q}{\partial z} \right] \quad \text{eq 4.1}$$

Notice that the moisture diffusivity is exponentially dependent on the moisture content (q) and the base diffusion coefficient (D_0) depend on type of material and conditions. This model implies that moisture transport within paper is governed by a single diffusion mechanism or at most, by a collection of physical processes, all of which occur together on the same time scale. It also assumes that the material surface is in equilibrium conditions during moisture absorption, and supported the equilibrium because the moist air surrounding the cellulose is not completely still. Although, our experience results tells that surface resistance is high and not easily disregarded. The model can not account for two or more diffusive processes occurring on different time scales and in series. However, this model has been used to describe transient diffusion in paper quite often. Recent work includes transient transport through corrugated boards by Donkelaar [17], who want to predict moisture content as function of time and profiles in thickness direction using a developed model, and by Ahmad et al. [18].

Transient moisture diffusion in paper rolls has been analyzed by Roisum [19] using this model, by comparing the rate of moisture uptake with model predictions. His

analyses involve weight variation, geometrical stability, strength properties, and converting runnability. This model of transient diffusion suffers from an important shortcoming. Usually, the parameters in the diffusivity equation are not constant but dependent on experimental conditions such as humidity ranges and sample thicknesses. Moreover, the diffusivity determined in unsteady state experimentation is different usually from that obtained from steady state experiments.

Nilsson et al. [20, 21] published another interesting works on water vapor diffusion through pulp and paper. In this work, they first measured effective diffusivity of water vapor in a diversity of samples of pulp and paper and showed some concern about the mechanisms that dominated the process.

The measurements were at two temperatures and relative humidity, and the resistances of mass transfer equations consider evaporation from the salt solution, paper surface resistance in film, paper resistance itself, water vapor diffusion through stagnant air and adsorption and diffusion in sieve pores. They questioned the reliability of salt solution and did not find dependence of diffusivity with relative humidity at the range studied.

At the second work, they defined the possible mechanisms of moisture transport through porous media as shown in the following table:

Transport Mechanism	Transported Phase	Place of Transport	Transport Coefficient	
			Dependence on Temperature	Dependence on RH
Gas Diffusion	Gas Phase	Pores	Proportional $T^{1.75}$	Independent (just swelling)
Knudsen Diffusion	Gas Phase	Pores <100A	Proportional $T^{0.5}$	Independent (just swelling)
Surface Diffusion	Adsorbed Phase	Fibers Surface		Increases with RH
Bulk solid Diffusion	Adsorbed Phase	Within Fibers		Increases with RH
Cappillary Trasnport	Condensed Phase	Pores		Only with filled pores

Table 4.I- Possible mechanisms for moisture transport through porous media. Nilsson et al. [20].

They also found a direct relation between paper density and diffusivity. Although, the differences among their samples involve also other components such as fibers, fillers, coating, chemicals, and morphology, which interfere in moisture transport. The final result showed that diffusivity was independent of relative humidity in the range studied, which was up to 58 %, although the authors advice that it should be investigated further.

The model assuming the cellulosic medium as homogeneous and moisture transport described by classic Fickian law has been found to be unsatisfactory to describe the moisture transport in these materials, as shown in the chapter III.

Lescanne et al. [22] have investigate the steady and transient state of moisture diffusion in a large range of relative humidity. By using a stack of sheets they neglected the mass transfer resistance of air layer between sheets. The theory assume two Fickian

diffusion paths without equilibrium between them, therefore the process is considered Non-Fickian. Their model idealizes a cylindrical fiber surrounded by void, where accumulation of moisture in pores is neglected and moisture diffusivity through fiber is considered constant, although it seems to be moisture dependent at high relative humidity. Hellen et al. [23] studied gaseous compound diffusion through paper and board using random walk simulations which were found consistent with steady state experimental results. The simulation of transient diffusion with one-dimensional diffusion has not good agreement at low porosities and thickness. The authors suggest that the cause of this discrepancy could be due to fluctuations in paper structure or sorption phenomena.

The work of Wadso [24] with water sorption in wood present a Non-Fickian model to describe the process, because his experiments also showed evidences of Non-Fickian behavior when steady and transient results are compared. The author used high air velocity in the transient experiments, but he is not clear how fast the relative humidity conditions were changed. The model assumed vapor transport in two serial stages, first to the lumen and then in the fiber wall, with the wood being considered a high porosity material with interconnected lumens.

Foss et al. [25, 26, 27] published several works on moisture transport in paper. In the first reference the approach is to understand the transient moisture transport regards to its sorption and transport mechanisms in paper in order to find out its effect on mechanical properties of paper. Thus they propose a model for moisture transport that consider paper as a composite material and found that water diffusivity through fiber wall is of the order of 10^{-12} m²/s, while effective diffusivity through handsheets was

approximately 2.10^{-6} m²/s. They concluded that almost all the steady state moisture transport through the paper is due to vapor diffusion through pores. They also proposed the Flory-Huggins theory to explain the sorption at high relative humidity, and rejected the theory of moisture movement through vapor filled fiber micro pores. The second and third references involve heat and mass transport in transient state, basically due to temperature increasing during moisture sorption, which could reach 6 °C second measurements done with infrared sensors. The maximum temperature increased depends on the rate of moisture sorption in the paper. During experimental moisture sorption the authors claimed that the nonlinearity in the isotherm and the differential in adsorption heat are the responsible to the two stage rise of sheet surface temperature. The first slope is assumed to be due to the large heat of adsorption from low moisture paper and the second slope due to rapid increase of moisture content at high humidity.

Our group in the Department of Paper Science and Engineering in SUNY, Syracuse, has been working in moisture transport for several years, and Ramarao et al. [28] has presented a comprehensive review recently covering many aspects of moisture diffusion in paper, such as models particularities, mechanisms of moisture transport, and experimental aspects of transient moisture sorption. The referred group work goes back to the study presented by Ramarao et al. [29] where paper moisture sorption and transport mechanisms are evaluated under cyclic variation of relative humidity. They assume that moisture diffuse through the paper pores, then it is sorbed to the fiber surface, and they also neglected the hysteresis phenomena once it has a maximum difference of 1 to 3 % in moisture content between adsorption and desorption. Nonetheless, they found some pseudo hysteresis when submitted the paper to cyclic relative humidity conditions, but

they also predicted that hysteresis due to mass transfer effect would vanish if paper diffusivity is sufficiently high. Besides this factor, the mass transfer induced hysteresis also depends on external mass transfer coefficient and frequency of the cyclic relative humidity fluctuations. Chatterjee et al. [30] studied the hysteresis region in bleached kraft paperboard more specifically using the Everett theory of independent domain, and had good agreement with experiments.

The work of Ramarao and Chatterjee [31] added the study of mechanisms of moisture transport and presented a model that assumes three resistances to mass transfer: first the resistance on the paper surface in the boundary layer, second the resistance of the vapor phase to diffuse in the paper pores, and third the resistance to the moisture diffusion inside of paper fibers. The authors also considered diffusion inside fiber and define an intra fiber mass transfer coefficient that is function of fiber properties. Their conclusion was that in the sorption transient conditions the surface boundary layer and the pore diffusion resistances dominate the moisture transport process through paper sheet, and the cross fiber diffusion have a small contribution to the process. Bandyopadhyay et al. [32] studied moisture transport in paper subjected to ramp changes of relative humidity using a model that consider paper a porous medium. The comparison with experimental results shows that a single value of fiber mass transfer coefficient can give good prediction of transient data.

Radhakrishnan et al. [33] explore the moisture transport through a stack of bleached kraft paperboard sheets using a gravimetric method. They found that diffusivity was constant until 65 % relative humidity but increase significantly after this value, what was interpreted as vapor diffusion in paper pores domination at lower relative humidity

and bound water diffusion in paper fibers domination at higher relative humidity. The paper stack was composed of eight paperboard sheet to ensure that paper resistance was dominant in the experiment. The model also consider the three resistances mentioned in the last reference, and explore more the intra fiber mass transfer coefficient which is inversely proportional to sorption time and minimum flux through paper at a relative humidity gradient.

Ramaswamy et al. [34] used a three dimensional approach to study moisture transport in paper structure, the refined samples used in this work are the same presented in this chapter as Minnesota samples. The paper structure is built by a digital image processing technique using images captured in x-ray microtomography at each 2 μm intervals. Then the structure is analyzed by measuring properties like pore size distribution, specific surface area. Different pore characteristics were found for pores lateral direction and transverse direction, the transverse pore size distribution is broader than in other directions, which support the anisotropic diffusion in paper. Therefore, the flow in the transverse direction encounters a much more open pore structure than in In-plane direction, second their results. When compared refined grades, the most refined the paper smaller the overall pore volume of the sheet. Measurements of network nodal density and bond coordination number distribution allowed determining pores transport properties such as water permeability and vapor diffusion. The authors however mentioned the low resolution of the x-ray technique that reach 3 to 4 microns and unable to visualize the smaller pores.

Lavrykov and Ramarao [35] have compared some models of diffusion transport in paper with emphasis on determination of fiber mass transfer coefficient and its

dependence on defined system parameters. Further comments on this work will be made in the chapter VI.

In the Gupta [36] thesis, as well as in the work of Gupta and Chatterjee [37] the steady state moisture diffusion through paper is interpreted as a parallel process between the water vapor diffusion on the paper pores and bound water diffusion in the fiber walls. They also assumed that exchange between water vapor in the paper pores and bound water in the fiber surface is much faster than moisture diffusion in the thickness direction, what establish the local equilibrium between these two phases. This assumption makes the diffusion process Fickian by relate vapor concentration with moisture content. The authors claim a good between model and experiments, thus water vapor and bound water diffusion coefficients are determined. They found water vapor diffusivity in paper pores 48 times smaller than in air what is attributed to paper tortuosity in the thickness direction. The transient part of Gupta and Chatterjee [38] work is a continuation of the last reference, and presented a model to describe the parallel diffusion of moisture in the transversal direction of sheet during ramp changes of relative humidity in the ambient. Values of effective water vapor and bound water diffusivity estimated in steady state work are compared with transient results. Good agreements were found between model and experiments, and the discrepancy on relative humidity profiles using sensors were attributed to accumulation of water vapor in the air gap between the paper sheets.

Massoquete et al. [39], in they work, studied moisture diffusion in paper considering it a composite with pore space and fiber matrix. The lateral and transverse diffusion were determined considering density variation obtained by changing refining grades. In general, lateral diffusivity was found higher than transversal diffusivity, and

water vapor diffusivity in pores was inversely proportional to refining levels. Either, no significant effect was found for bound water diffusivity in fiber or sorption isotherms. In a comparison of n-propanol with moisture diffusion in paper, was found that water diffuse faster in denser sheets than n-propanol. This fact call attention to bound water diffusion mechanisms under this conditions once pores are closer and fiber matrix diffusion become more important.

Massoquete et al. [40] worked in transient reduced moisture sorption experiments in order to establish whether or not this process behave according with classical Fick laws. After eliminate important interferences in the experimental set up such as surface mass transfer coefficient and step time, was found that moisture sorption is Non-Fickian exclusively due to the mechanisms of diffusion in paper.

In this chapter, we report relation of the diffusion parameters for paper sheets to the structure of the pore and fiber space. Another explored point is how the pulp refining process affects this relationship. Seborg and Stamm [41] reported that hydration is not affected by refining, and later Seborg et al. [42] reported the moisture sorption response related with the electrical conductivity, and concluded that refining had little effect on the equilibrium moisture content of pulp. Thereafter, with new equipment, they found that for severe beating unbleached pulp hygroscopicity could increase up to 6 % at high relative humidity. For instance, Lennholm and Iversen [43] using NMR analysis, reported that laboratory beating have no effect on chemical composition of cellulose polymorphs in pulp. Qiang et al. [44] also working with NMR, state that for bleached kraft pulp there is no influence of beating on the water-cellulose interactions. Maybe the most understandable explanation is given by Stamm [45] who affirm that beating has

insignificant effect in water absorption because adsorption within the fiber is much greater than superficial adsorption and internal adsorption occur without refine anyway. The equilibrium sorption isotherms for moisture for paper also do not seem to depend upon refining levels.

4.3. EXPERIMENTAL METHODS AND CALCULATIONS

4.3.1. Experimental Set Up for Transverse Moisture Transport

The experimental part of this chapter involves the measurement of diffusion variables in transverse directions of the paper sheet, which contribute to understand better the mechanisms of moisture transport under the entire range of relative humidity. Although there are more studies published in this direction, the present experiments bring contributions by changing fiber morphology and by measuring lateral and transversal diffusion on the same conditions. The humidity chamber described in the chapter II is a versatile equipment with considerable good variable control and data acquisition. A major part of experiments are carried out in a Plexiglas cup that allow moisture to flow mainly through thickness direction, and the diverged flow nominated leaking is determined apart and subtracted. The Plexiglas cup, which is shown in the Figure 4.2, support a stack of paper, create a humidity concentration gradient, and has its dimension carefully determined for necessary calculations.

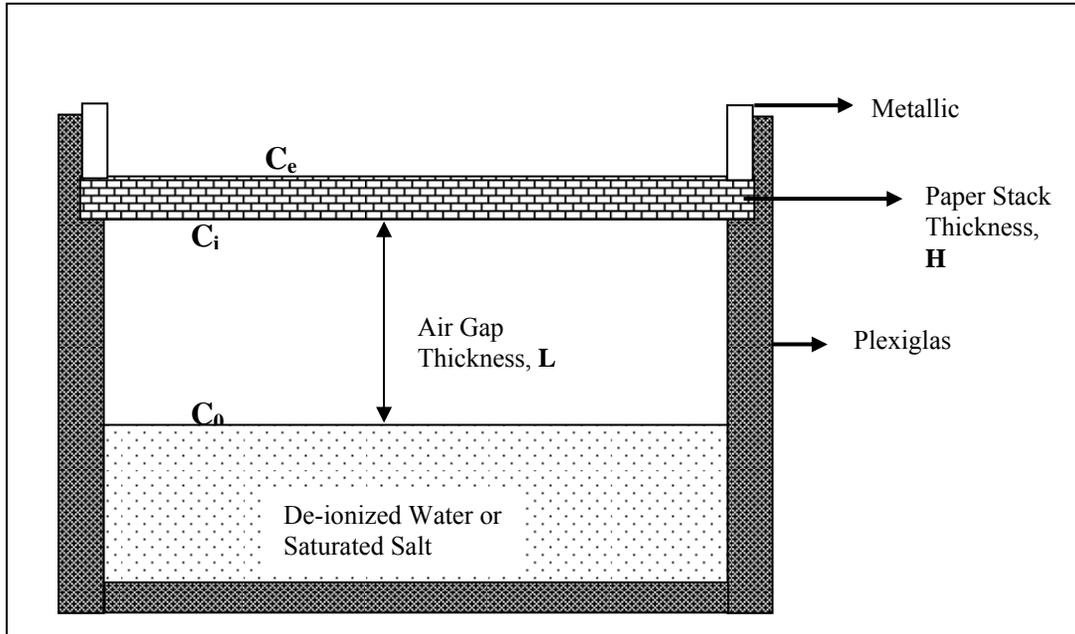


Fig 4.2- Schematic of the diffusion cup that is used for measuring diffusivity in the transverse (z) dimension of paper sheets. When suspended in a chamber which RH is controlled, gravimetric measurements provide transient and steady state moisture fluxes.

The cup is of 8.20 cm diameter and 4.50 cm height. It is provided with a step machined into the wall so that paper sheets of diameter 7.60 cm can be cut and placed on it, and held in place by a metallic ring. The ring is pressed against the paper stack by four springs attached to the bottom of the cup. The cup is filled partially with water or a saturated salt solution and a stack of paper sheets cut into circular shape is placed on top of it. The most important resistances to mass transfer considered in this experiment are: (i) the stagnant air layer between the water or solution level and the paper stack, (ii) the

paper stack resistance itself, (iii) the resistance from the air boundary layer at the top of the stack. Therefore, the main concentrations to be considered as shown in Figure 1 are, (C_0) the water vapor concentration adjacent to the liquid surface, (C_i) the water vapor concentration at the inner paper stack face, (C_e) the water vapor concentration at the outer paper stack face, and (C_b) the water vapor concentration in the bulk condition of the humidity chamber.

4.3.2. Steady State Experiments

The steady state experiments in transverse direction reported here were carried out with 6 samples of paper, which are conditioned to constant moisture content by placing them in environment of constant relative humidity of 50 % and at 23 °C for at least 48 hours prior to the experiment. The entire assembly is then hung from a bottom loading balance in a humidity controlled chamber, described in chapter II. After the experiment reaches steady state the samples are individually placed in plastic bags, sealed and weighed. Sometimes the set was weighed several times to check weight loss through the plastic bag, which did not occur. The dry weight of each sample is determined automatically in an infrared balance, model Mark 2, from Denver Instrument, at 105 °C until constant weight.

Data on the instantaneous weight of the cup, relative humidity and temperature is recorded in a computer every 22 seconds. Figure 4.3 shows a typical sample data set of the cup's weight as a function of time. The weight is monitored typically for 44 hours at

which time steady state is judged to have been attained by the fact that the slope of the weight curve is reasonably constant over a period of time.

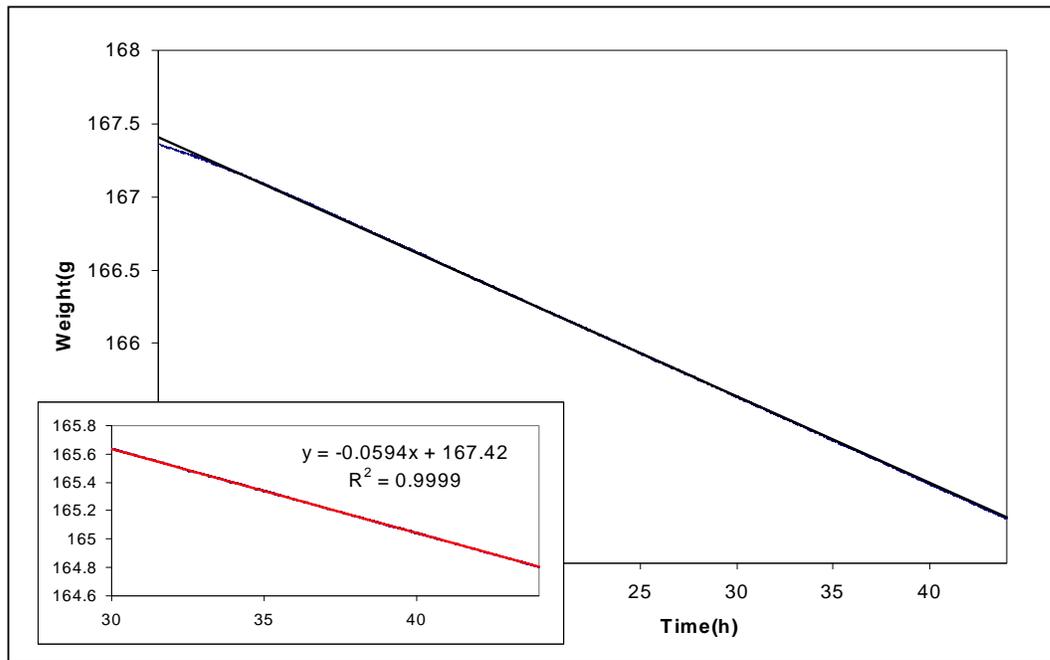


Fig 4.3- Weight Loss Plot for 570 CSF Through plane with 6 Samples at 23.86 °C and 30 RH %

The final portion of the curve is used to determine weight loss (dW/dt), and from it the mass flux (j_{tot}) once area (A) is known, as follows.

$$j_{tot} = \frac{1}{A} \frac{dW}{dt} \quad \text{eq 4.2}$$

The following equation for determining effective diffusivity (D_{eff}) was given for the above system by Radhakrishnan et al. [33], which is based on the three resistances obtained in the experiment set up and where all variables are known:

$$j_{tot} = \frac{(c_0 - c_b)}{\frac{1}{k_f} + \frac{H}{D_{eff}} + \frac{L}{D_w}} \quad \text{eq 4.3}$$

The diffusivity of moisture in air (D_w) is found in tables and the paper surface mass transfer coefficient (k_f) was estimated based in the moisture profile, measured at the end of each experiment. The moisture content of each paper sheet is really an average through the sample thickness. Thus, the value measured is assumed to be in the center of the paper sheet and using extrapolation to the top and bottom faces of the paper stack, the respective moisture content was estimated. An example of the moisture content profile is shown in figure 4.4.

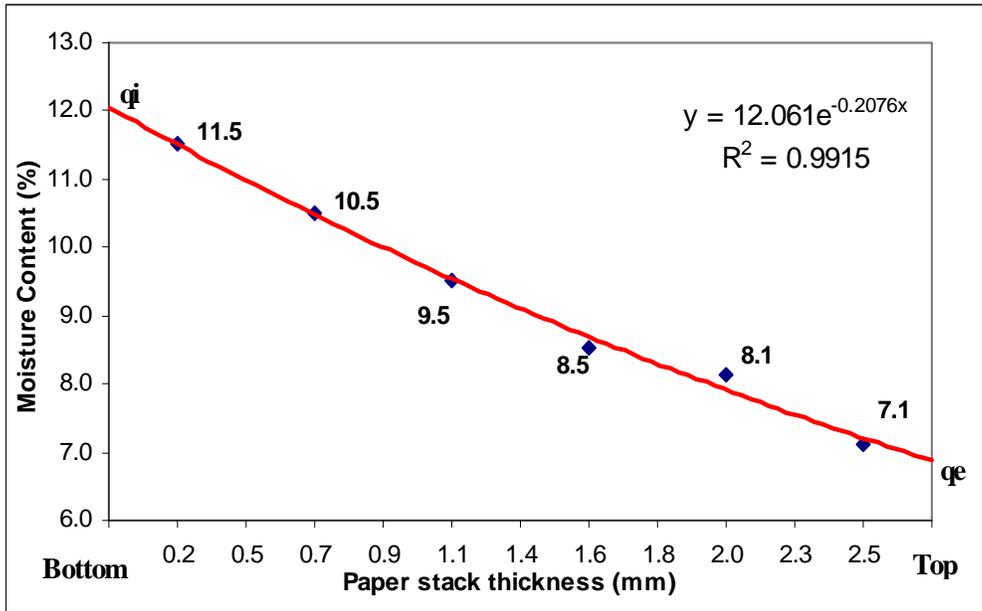


Fig 4.4- Moisture profile through paper stack in transverse direction for 570 CSF paper at 30/100% RH.

The moisture content is then used to calculate the relative humidity on the two faces of the paper stack by applying the GAB isotherm equation. The GAB isotherm was chosen due to its great versatility in a large range of application. The equation used in this calculation is the follow:

$$q^*(c) = \frac{C_{GAB} M_{GAB} K_{GAB} RH}{(1 - K_{GAB}) [1 + (C_{GAB} - 1) K_{GAB} RH]} \quad \text{eq 4.4}$$

Thereafter, vapor concentrations for top and bottom of the paper stack are calculated to finally obtain diffusivity. These vapor concentrations are calculated with the following relation with relative humidity:

$$C_j = \frac{RH_j P_{sat}}{100RT} \quad \text{eq 4.5}$$

Where: (R) is the universal gas constant 82.0567 in cm³atm/gmol K, and (P_{sat}) is the vapor pressure of vapor at certain temperature, calculated by the next shown equation.

$$P_{sat} = \frac{\exp[51.29 - \frac{6651}{(T + 273.15)} - 4.531 \ln(T + 273.15)]}{760} \quad \text{eq 4.6}$$

As the graphic extrapolation give the water concentration on the two surfaces of paper stack, the concentration on both sides are also calculated, and from these finally diffusivity is determined.

As a check on this procedure, we calculated the moisture concentration at the lower surface of the stack (C_i) by the following equation derivate from equation 3.

$$C_i = C_0 - j_{tot} \frac{L}{D_w} \quad \text{eq 4.7}$$

Then the result of this equation is compared with the value of vapor concentration on bottom of the paper stack calculated through the moisture content graphically extrapolated. The agreement between the procedures is very good.

A complete set of experimental conditions, data and calculated parameters are shown in Table 4.2 as follow:

Table 4.II- Variables calculations, results of diffusivity and mass transfer coefficient for transport in transverse dimension of the paper sheet.

Variable	Symbol	Value
Paper refining level (CSF)		570
Chamber Humidity	H_b	30%
Cup Humidity	H_0	100%
Temperature (°C)	T	23.66
Saturated Pressure (atm)	P_{sat}	0.0288
Diffusion area (cm ²)	A	37.37
Steady state weight Loss (g/h)	dW/dt	0.0606
Flux (g/cm ² .s)	j_{tot}	4.505E-7
Pad Thickness (cm)	H	0.2706
Moisture top (g/g dry fiber)	q_e	0.0691
Moisture Bottom (g/g dry fiber)	q_i	0.1206
GAB parameter	M_{GAB}	0.043198
GAB parameter	K_{GAB}	0.8021
GAB parameter	C_{GAB}	45.05025
Relative humidity top (%)	RHe	0.4909
Relative humidity bottom (%)	RHi	0.8021
Vapor conc. top (gmol/cm ³)	C_e	5.807E-7
Vapor conc. bottom (gmol/cm ³)	C_i	9.489E-7
Vapor conc. chamber (gmol/cm ³)	C_b	3.548E-7
Mass transfer coeffic. (cm/s)	kf	0.1107
Effective diffusivity (cm ² /s)	Deff	1.837E-2

4.3.3. Paper Samples Studied

The bleached softwood kraft refined handsheet samples came from the Department of Bio-based Products of University of Minnesota, through a common work with our group in order to study the three dimensional structure of paper and its relation with moisture transport. These samples are handsheets refined at six levels of Canadian Standard Freeness and formed according with the Tappi standard methods, such that changes in paper structure represent changes in paper density. Thus, the binarized x-ray images of the handsheets were taken for each paper and are shown below:

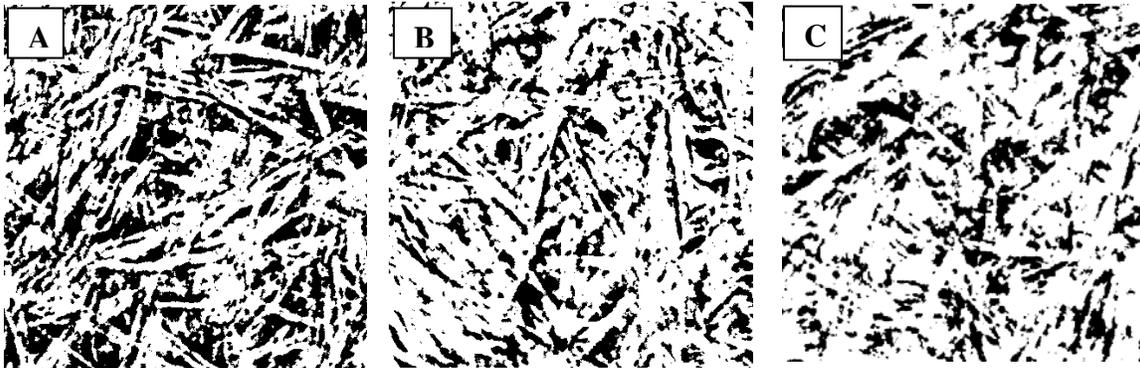


Fig 4.5- Binarized x-ray images of refined papers in XY plane with fibers in white and pores in black, A = 670 CSF, B = 480 CSF, C= 220 CSF. A courtesy of Dr Sri Ramaswamy, Department of Bio-based Products, University of Minnesota.

Some of the refined samples were photographed in the SEM microscopy on the N. C. Brown Center for Ultrastructure Studies in State University of New York in Syracuse. The photography represent a cross direction cut through the paper sample thickness, and

intend to show the difference in density between the slightly refined and the most refined fibers.

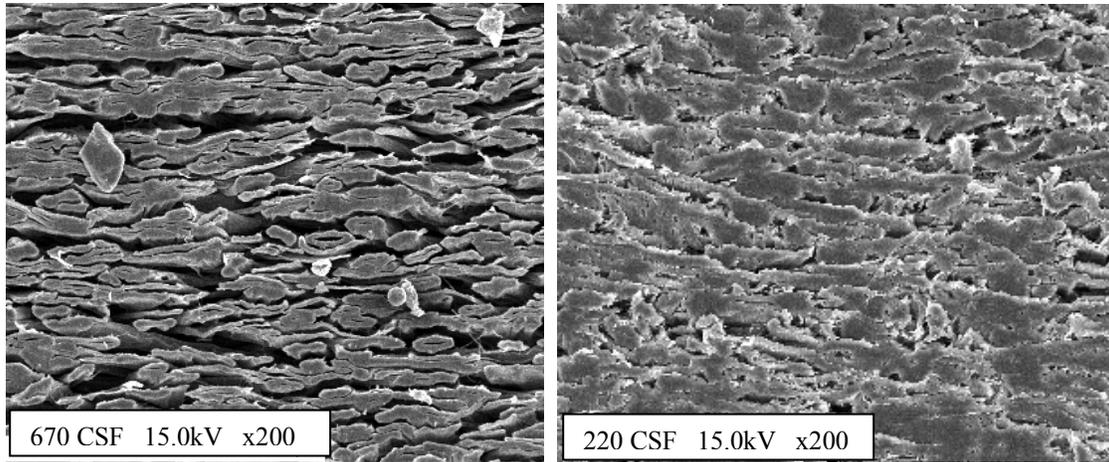


Fig 4.6- SEM microphotography of the least (670 CSF) and most refined (220 CSF) fibers in transversal cut through paper thickness. A courtesy of Dr Robert Hanna, Director of N. C. Brown Center for Ultrastructure Studies, SUNY ESF.

The structure information on x-ray pictures were used to obtain properties of these papers and the SEM pictures could also give a good idea of samples porosity and density.

CSF	Grammage	Thickness	Density	Permeability -1
670	390	0.729	0.535	5.23
570	347	0.451	0.769	31.67
460	389	0.447	0.870	121.36
330	333	0.369	0.902	221.03
280	354	0.391	0.905	360.83
220	399	0.424	0.941	973.44

Table 4.III- Properties of the refined paper most considered to related with moisture diffusion in this chapter.

4.3.4. Experimental Results

We conducted experiments to determine the equilibrium moisture content of the paper sheets at different relative humidity levels in order to establish their sorption isotherms. The experiment consists in let the paper sample reach moisture equilibrium at a sequence conditions over the largest range possible of relative humidity. Thus, a 10 x 10 cm paper sample was hung in the humidity chamber, with its weight, temperature and relative humidity monitored. The relative humidity varies on about ten steps over its range and equilibrium was reached at every step. The final results of the experimental moisture content data are shown in Figure 4.7.

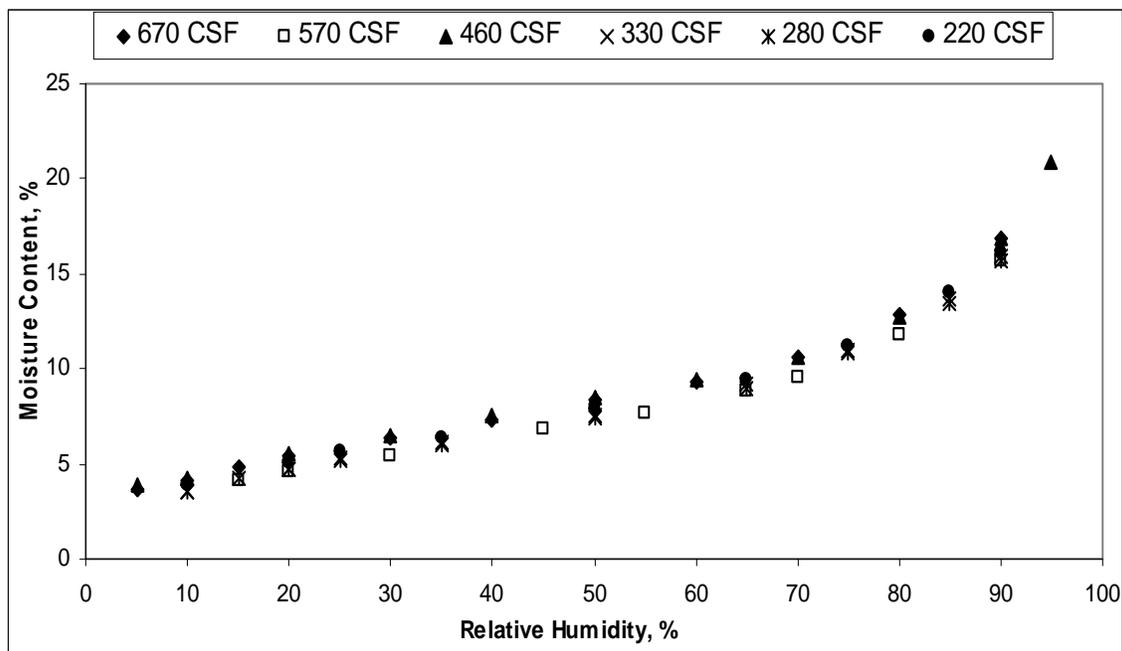


Fig 4.7- Final result of the experimental Isotherms obtained for the six refine grades of the bleached kratf softwood in a large range of relative humidity.

As the picture shows, there is no considerable difference in moisture sorption among the refined sheets. This indicates that the sorption isotherm is invariant with refining of the pulp at least for the bleached kraft softwood pulp in the range of humidity studied. This is in agreement with some authors mentioned in the literature review, such as Lennholm and Iversen [43] that using NMR analysis, reported that laboratory beating have no effect on chemical composition of cellulose polymorphs in pulp. Another work developed by Qiang et al. [44] with NMR, state that for bleached kraft pulp there is no influence of beating on the water-cellulose interactions.

The present situation seems to reinforce the concept that part of cellulose fiber is solvated by moisture mostly adsorbed in hydrophilic sites, which are more exposed by swelling. This phenomenon increases the possible reactive areas accessible by moisture significantly and the supposed capillarity increased by refining becomes negligible. Thus, the results and this mechanism make the refining influence on moisture adsorption insignificant. This statement is relate particularly to the moisture equilibrium at different relative humidity used to obtain the moisture isotherms.

The effect of refining on moisture diffusivity is known to be significant once other variables are in question in this case. The pore size distribution, the bond area and the exposed morphology of fiber are important factors that influence changes on diffusivity magnitude.

The next experimental results presented here consist primarily of effective diffusivity data in the transverse direction of paper sheets (D_{zz}) for different refining levels as a function of the average humidity, across the stack of paper sheets.

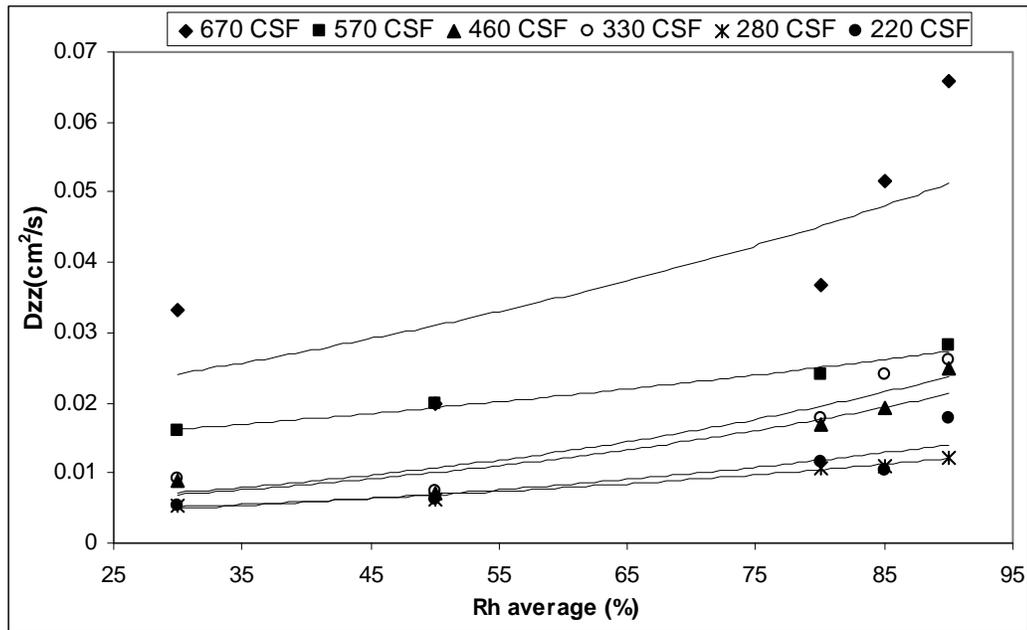


Fig 4.8- Moisture diffusivity variation through bleached kraft softwood paperboard thickness with average relative humidity in the paper stack with six samples, for six different refine grades.

We observe that the general behavior of the curve is similar to the curves of (D_{zz}), reported by Radhakrishnan et al. and others authors. The diffusivity seems to reach a constant value asymptotically at small average humidity and increases significantly as the humidity increases towards saturation. Probably more results would be necessary at lower humidity, however the experimental conditions were not the most appropriate to use salt solutions due to lack of a constant solution homogenization in the experiment set up. Thus, we preferred not to rely too much in salt solution experiments while using this cup and humidity chamber. Nevertheless, the results show that the increase seems to be uniform and repeated for all sheets and refining levels considered.

Furthermore, the dry end asymptotic value can be observed to decrease with freeness levels uniformly. This indicates that the pore diffusion coefficient (D_p), representing the diffusivity of water vapor through the void space, decreases uniformly with refining as the paper become more dense and close the pores. It is well known that porosity of paper decreases with higher refining levels, once the main fibers consequences are shortage by cut in some extent and rendered more flexible and conformable due to fibrillation. Therefore, decreasing sheet thicknesses and increasing the densities are expected results. Apparently the densification of the paper, that could have as consequence the improvement of bound water diffusivity and even effective diffusivity, is not sufficient to increase the water movement inside of fiber matrix under these circumstances. A possible explanation is that the effect of refine densification is counteracted by the fact that formation of fines and fibrillation disrupt the moisture transport inside fiber walls by creating tortuosity in a naturally ordered path for water migration, what slow down bound water diffusivity.

Figure 4.9 shows the moisture diffusivity in paper through transversal direction as a function of sheet density for different humidity levels inside of humidity chamber, considering that relative humidity inside the diffusion cup is approximately 100 %, once it contains liquid water. The data clearly indicate the decreasing in effective diffusivity with increasing density, displaying the strong role of the vapor diffusion mechanism through the paper pores, and its proportional variation with relative humidity, under these experimental procedure and conditions. At low density, moisture is probably carried out through the pores and proportional with relative humidity. At high relative humidity the bond water diffusion become more important and dominate the process progressively

because density is allowing a closer fiber contact. Even though the pore diffusion is slow down by increasing of tortuosity. For most humidity levels, vapor diffusion as a mechanism dominates moisture transport and is strongly affected by sheet density. Nilsson and Stenstrom [46] also found a similar dependence on sheet density.

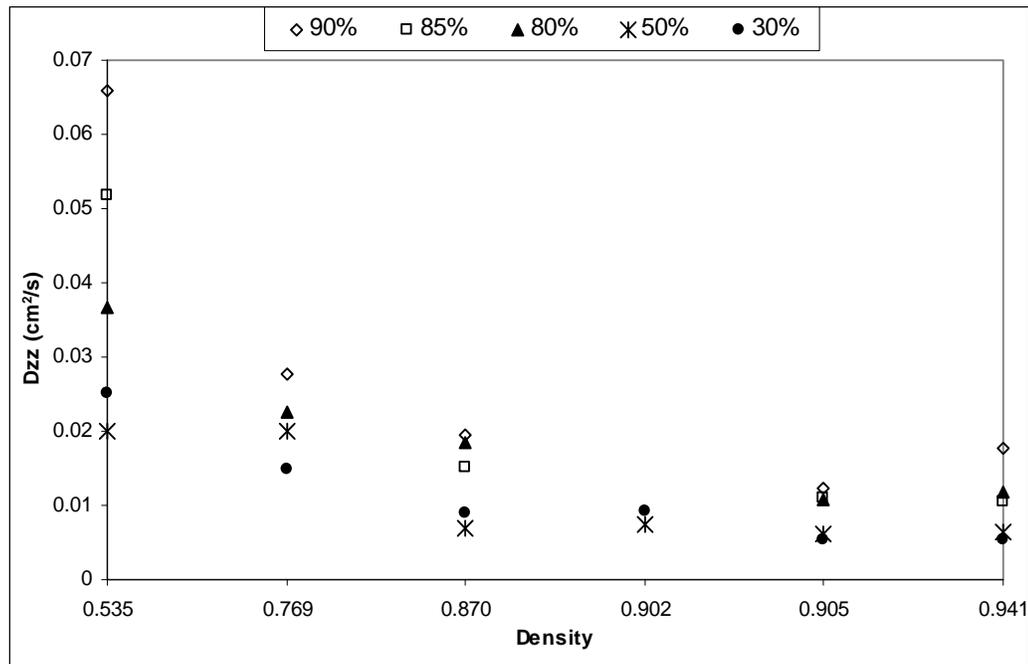


Fig 4.9 – Moisture diffusivity through paper thickness variation with density at several conditions of relative humidity in humidity chamber and with water inside the cup.

As the present work involves anisotropic analysis, the lateral diffusivity was found to be more appropriated to approach the argument about density claimed before. Thus, this question will be discussed on the next chapter again, where the argument used will be justified experimentally.

Goel et al. [30] have measured the tortuosity of the pore structure in these sheets using reconstructions of the three dimensional structure from X-Ray Micro-Tomographed sections. Their results indicate that lateral tortuosities are smaller than transverse tortuosities for these same pulp sheets. It appears that the lower tortuosities in the lateral dimension compared to the transverse, combined with the fiber laying in the lateral direction with fibrils directed in favor of moisture diffusion, are part of possible explanation for the higher lateral diffusivities. This discussion will be more elaborated with the presentation of the lateral diffusion results, and comparison between lateral and transversal diffusion.

The next figure shows the profile of moisture content for all refine set of paper sheets under steady moisture transport in the transverse dimension using the cup described in the figure 4.2. These data were measured after the steady state experiments ended, when each sample was quickly placed in a plastic bag and weighted, in order to obtain the most accurate moisture content of the samples in the end of the experiment. These procedures are important because they are experimentally reliable, and once profiles can be simulated from experimental diffusivity data either.

We observed that the moisture content profiles are steeper for the highly refined or denser sheets. The slope of the moisture content curve is inversely proportional to the effective diffusivity. Since the diffusivity is smaller for the denser sheets, the higher gradient for these sheets is not surprising. Once in this case there is water inside the cup, the more refined the paper, higher is the humidity equilibrium on the bottom of the stack.

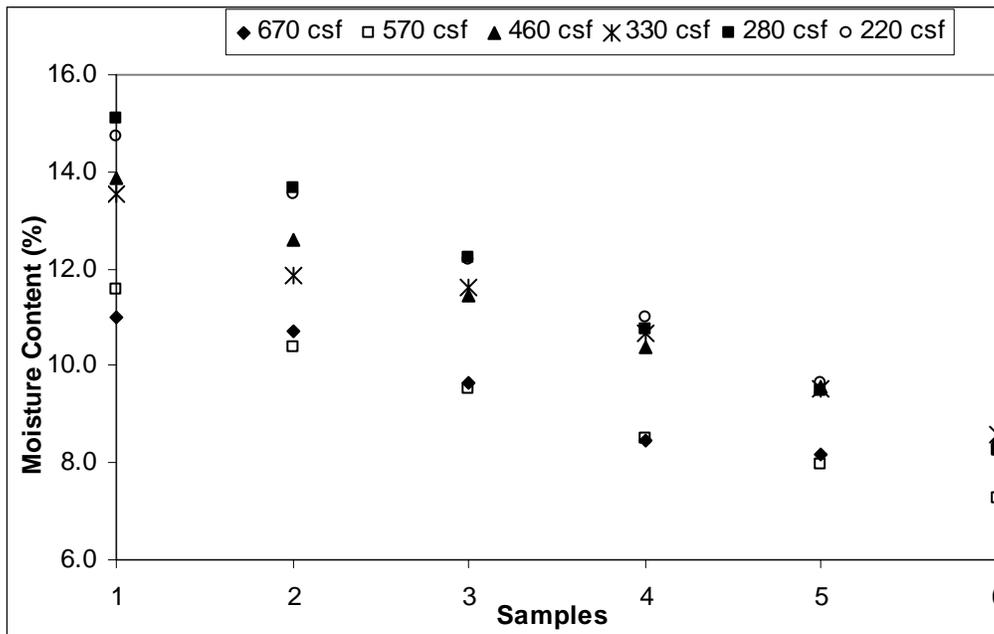


Fig 4.10 - Experimental results show moisture content profile for refined handsheets from 670 CSF to 220 CSF at 30% relative humidity inside chamber.

This chapter also presents some results of weight loss and effective diffusivity of n-propanol as it is allowed to diffuse through the paper sheets in the transverse dimensions, with similar experimental set up used with water and salt solution. The n-propanol was added inside of the cup and the relative humidity was varied in the chamber. Then the effect of pore diffusion was studied as the paper moisture content was changed, and compared with the water diffusion under similar circumstances.

The objective of experiments using n-propanol is to have a better understanding of the moisture diffusion mechanisms, because n-propanol is not adsorbed by cellulose as much as water and a very dominant porous diffusion is expected. Liang et.al [47]

worked with n-propanol and mixtures of it with water in different proportions. They also have mentioned several works in their paper that support the convenience to use n-propanol as option to study moisture diffusion.

We conducted transverse and lateral migration experiments where liquid n-propanol was placed in the diffusion cup assembly and the steady weight loss was measured, but just the transversal transport results are presented in this chapter. After subtracting the resistance due to diffusion within the air gap and assuming the external convective boundary layer negligible, the diffusivity of n-propanol within the paper sheets was estimated. The diffusivity of n-propanol in air was determined from the well known Chapman-Enskog equation shown as follow.

Chapman-Enskog equation:

$$D_{AB} = \frac{1.8583 \times 10^{-7} \cdot T^{\frac{3}{2}}}{P \sigma_{AB}^2 \Omega_{D,AB}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} \quad \text{eq 4.8}$$

where:

(D_{AB}) is diffusivity in m^2/s , (T) is temperature in K, (M_A and M_B) are molecular weight of A and B in $\text{kgmass}/\text{kgmol}$, (P) is absolute pressure in atm, (σ) is an average collision diameter, and ($\Omega_{D,AB}$) is a collision integral based on Lennard-Jones potential.

The ratio of the effective diffusivity of n-propanol in the paper to that of n-propanol in air was determined by the equation:

$$\lambda = \frac{D_{\text{eff,P}}}{D_{\text{air,P}}} \quad \text{eq 4.9}$$

This relation registers the influence of paper tortuosity in diffusivity through the pores, for a medium that have the influence on the fiber minimized. The plotting of this relation, in percentage, against density as shown in the next figure, where the experiments on both directions lateral and transverse are carried out under the same conditions. The density was measured under standard conditions and the diffusivities experiments were carried out in the same humidity chamber, with an internal relative humidity of 30 %.

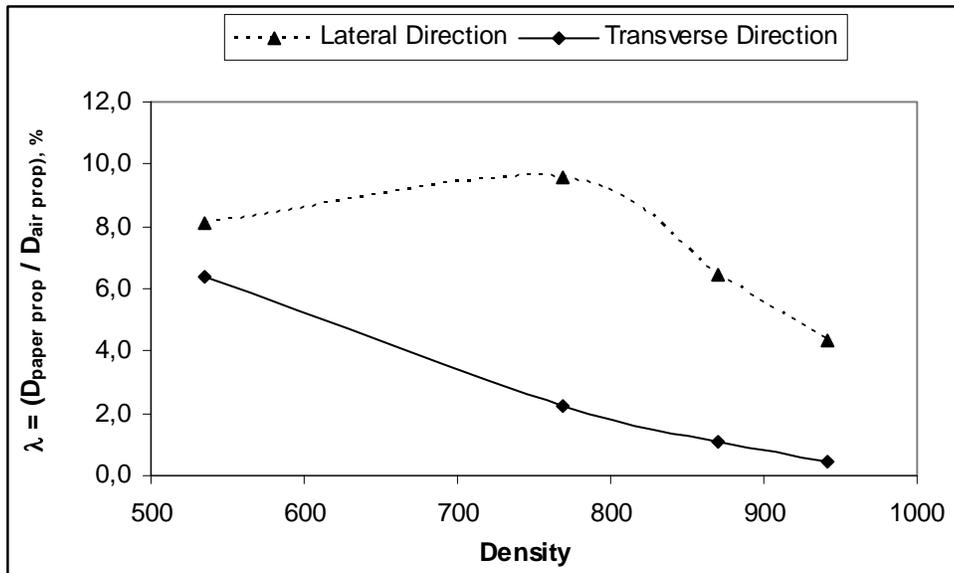


Fig 4.11 – Relation of n-propanol diffusivity in air and in paper with progressive increments of density.

Although the point relative to the smaller density in lateral direction has an odd behavior and deserve to be repeated, it is illustrative on how n-propanol diffusivity in paper decrease with density on both lateral and transverse directions.

Another characteristic shown in this figure is that n-propanol lateral diffusivity in paper always much smaller than diffusion in open air. This is expected due to influence of porosity and tortuosity on this property.

As consequence, the pore diffusion is higher than in transversal direction, which is also expected due to the characteristics of pores in both directions.

These results corroborate other works, although some of them found higher differences using desorption process and different methods.

The relation represented in the equation 4.9 was rearranged to compare now water and n-propanol diffusion in both mediums, air and paper.

The relation, in the figure below, was calculated for diffusion in the transverse dimension at different density levels.

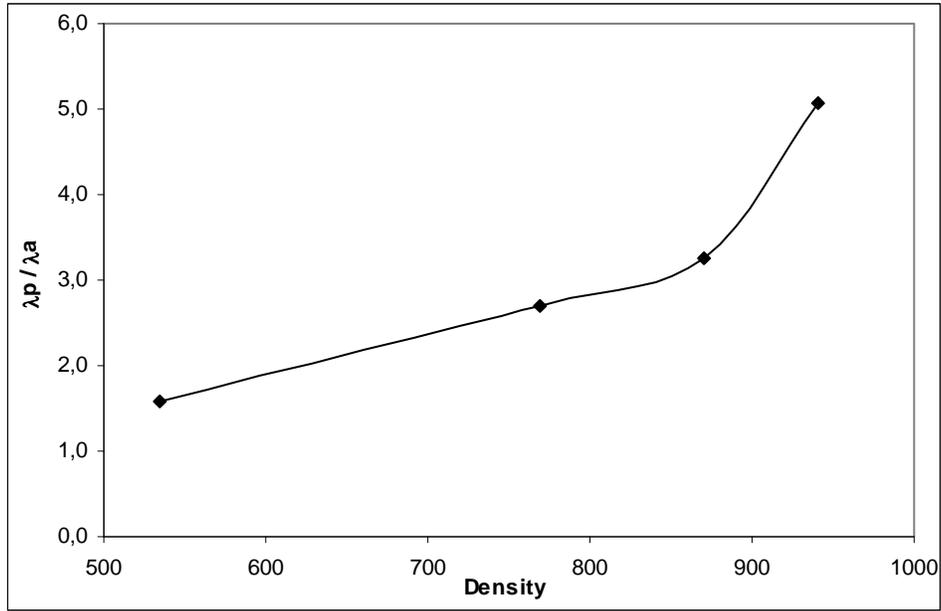


Fig 4.12 – Relation of $\lambda_p = D_{\text{water-paper}}/D_{\text{n-propanol-paper}}$ and $\lambda_a = D_{\text{water-air}}/D_{\text{n-propanol-air}}$ for refined papers at RH 30% inside of humidity chamber.

This graphic shows an interesting characteristic considering that diffusion rate of moisture diffusivity (λ) in paper is higher than the rate of moisture diffusion in air through the entire range of density studied. Moreover, when we compare the two last figures, it is perceptible the effect of density on water diffusivity in paper. The n-propanol diffusion in paper decrease very drastically with density as shown in the figure 4.11. The diffusion of water in paper should then increase in a similar trend and in a reasonably high slope in order to overcome the n-propanol diffusivity in paper tendency as shown on the result in the figure 4.12. Therefore, in spite of the increasing of lambda rate (λ_p/λ_a) in function of decreasing of n-propanol diffusivity in paper, it would be much greater without the effect of water diffusivity in paper. Once the temperatures were kept constant,

the relation of n-propanol and water vapor diffusivity in air are both constant, and the effect of water diffusion in paper in the lateral direction is significant, mainly on high densities.

Further experiments will be carried out in order to confirm these results, or to reinforce the importance of bound water diffusion and the mechanism dominant in such conditions.

4.3.5. Experiments with sensors and profiles

During the search for resources to validate our results, a new miniature humidity sensor was found, which could be applied in our experimental design.

The sensor is a HC-610 with integrated circuit manufactured by Ohmic instruments with high degree of accuracy (± 2 % RH) and repeatability (0.5 %). It use a laser trimmed thermo set polymer capacitive sensing element, with output in a large range of relative humidity.

HC-610 RELATIVE HUMIDITY SENSOR CONNECTION AND EQUATION SHEET

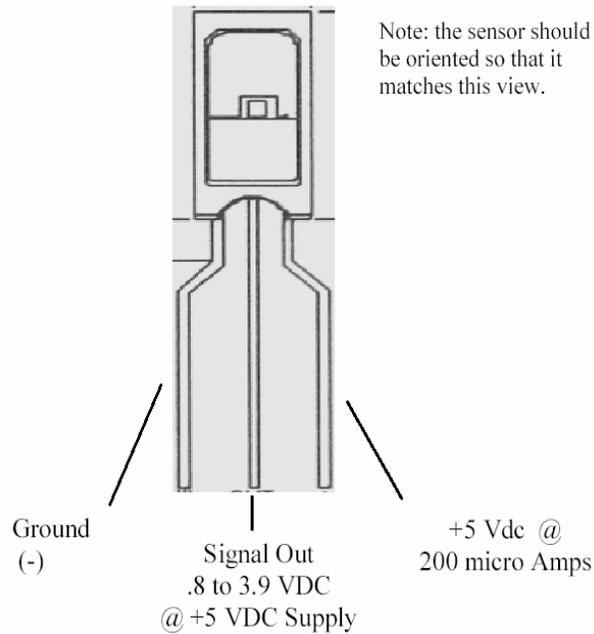


Fig 4.13- Mini Relative Humidity Sensor HC-610 by Ohmic Instruments Company.

The availability of a reliable humidity sensor gave possibility to develop new experiments with direct measurements of relative humidity and relate it with moisture content inside of the paper stack. The results of three experiments carried out for the same paper, a bleached kraft pulp 280 CSF, and put together are showed in the figure below.

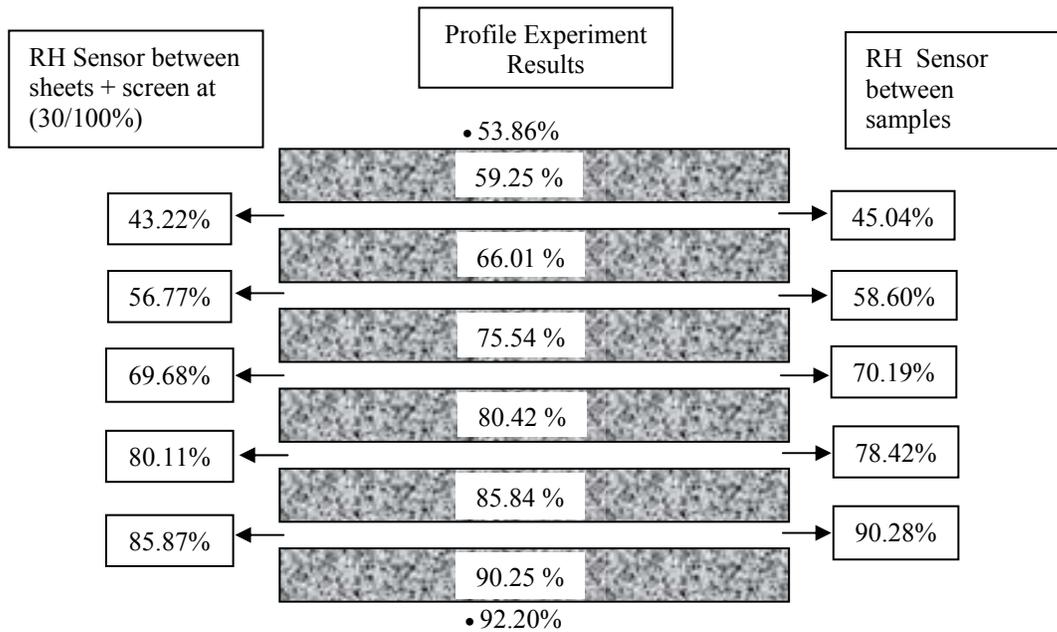


Fig 4.14- Composition of the results of three experiments carried out separately with the mentioned relative humidity sensors and with moisture content profile using the plastic bags. The experiments were performed at temperature 23 °C, relative humidity 30% inside of the chamber, and water inside of the cup.

The results obtained with the sensors, have a good approximation with the measurements related with values of moisture content obtained in the paper samples, in the through paper moisture content experiments. This is more evident as the sample is closer to the bottom of the stack. The possible reason is that water vapor leaks due to preferential ways created by the wires connected to the sensor in the most external measurement points. The results in the left side of the picture show the sensors results when a plastic screen was placed between each paper sheet and the result in the right side

are obtained with the sensors placed between paper sheets. This experiment is still valid to show the consistency of the moisture content experiment measured with the plastic bags and the consistency of the sensors results.

The objective of the shown experiment was to demonstrate the importance of contact among samples at distinct relative humidities in the determination of effective diffusivity or in other words the importance of air gap resistance between sheets on the paper stack experiment.

There were not major conclusions made from these experiments although it gave directions for our main results. Nevertheless, the presentation of this experiment has the objective to show a good tool to measure relative humidity, even at difficult experimental conditions.

The next experiment developed with these sensors show the measurement of paper stack profiles and its progress with time. The experiment is built with four samples and five sensors, one in between each sample and one on top and bottom of the stack. Between these sensors was placed plastic rings in order to give the same space between each sheet, however this procedure did not allow to arrange the 6 samples in the stack as used in the previous experiments, thus the number of sheets must be decreased.

The RH range is 50 to 100% and the experiment is been carried out in lab 107. From the experiment carried out at temperature 25.91°C and average RH in the humidity chamber 50.03 % were calculated the weight lost rate (dw/dt) 0.0405 g/h, and the flux $3.01E-7$ g/cm².s.

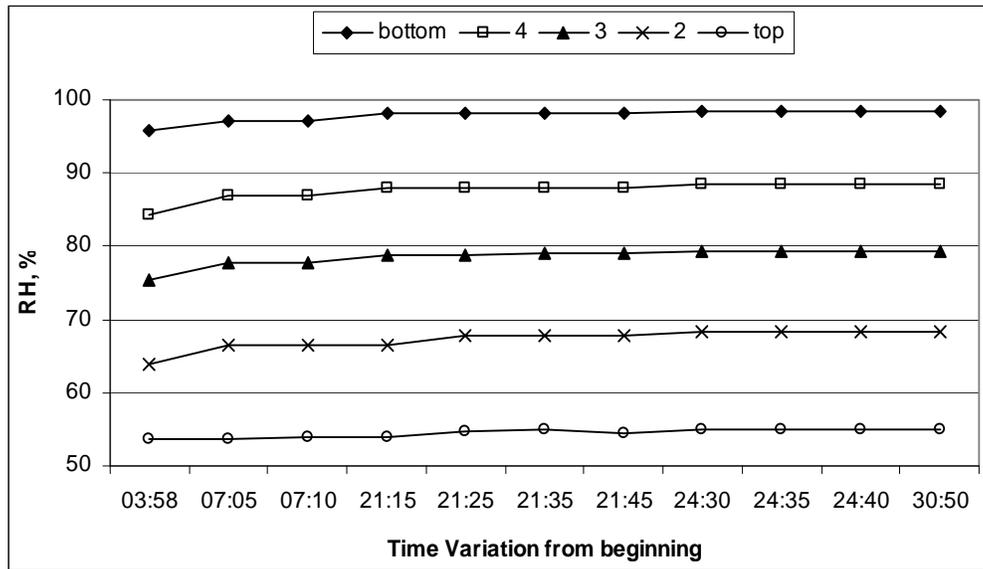


Fig 4.15- Profile of relative humidity measured with RH sensors in a stack of paper and at 50% of humidity at steady state.

The third experiment in which was used sensors is a step of relative humidity where the progress of the profiles can be followed from the initial condition to the equilibrium at the final condition. Initially, the relative humidity in the chamber was set up at 30 % and the equilibrium at this condition was reached. Then the condition in the chamber was changed to 80 % and the equilibrium was reached again. The paper used in this case was a bleached kraft paper refined to 280 CSF which characteristics could be found in this chapter. The cup mentioned before was used in this experiment, thus the bottom of the paper stack is about 2.0 cm from the water inside of the cup. Therefore relative humidity is close to 100 %, depending of the value of paper resistance.

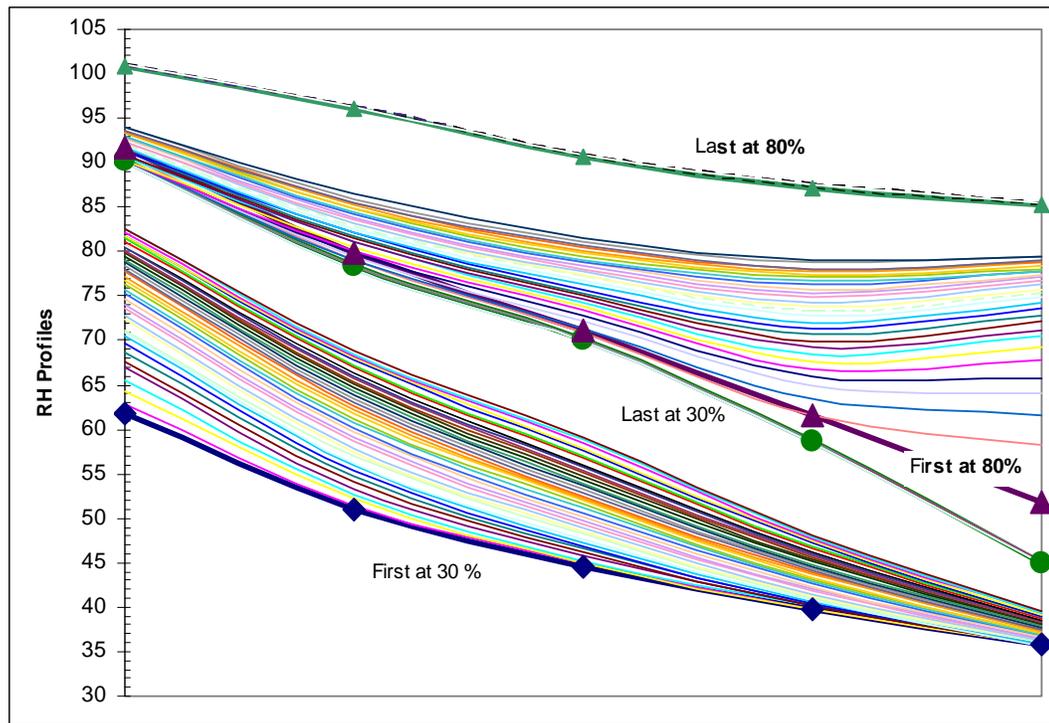


Fig 4.16- Measurement of profiles after a step change of relative humidity inside of the humidity chamber is shown using micro sensors. The equilibrium at the two relative humidities are shown in thicker lines.

As can be seen in the figure above, the steps of relative humidity are bigger as the differences in relative humidity between the paper and the external conditions are higher. Another experiment where the sensors were useful was to verify the mass transfer coefficient (k_f) experiment where the soaked sample was used. The objective of this experiment is to answer the question if the experiment made with the soaked paper is not an over estimation of the variable (k_f). This question rises because the relative humidity is considered 100 % in paper surface. However, the irregularities of paper surface and its hydrophilic character could interfere on this assumption.

These experiments were carried out with a longer tube on top of the cup in order to substitute the metallic ring used regularly. This tube is 81 mm long and is expected to reduce the convection during the weight loss, as well as allow me to install RH sensors to measure the (kf) under more regular conditions.

Due the excess of weight after the addition of the mentioned tube, it was not possible to measure the weight loss in the same chamber were the (RH) were measured, in room 107.

Thus, the weight loss was measured in chamber without control, in room 106. Although the conditions are not the same, once there is no (RH) control in this chamber, only the control of the room itself, could be assumed that the long tube minimize the convection conditions and allow only the (RH) differences to be the driving force for the experiment.

Assuming that the (RH) conditions are close we still have a temperature variation to be considered, and it was of around 2.5 °C between the laboratory 106 and 107, due a problem in laboratory 107 conditioning system.

Nevertheless the results are similar for both (kf), the one with soaked BKP, what suppose that the experiment with (kf) is valid under the conditions preformed.

The parameters estimated with the model were: (D_p), (D_{q0}) and (m) constituting the effective diffusivity as defined by eq. 4.10.

$$D_{eff} = D_p + \frac{\rho_p D_{q0}}{m} \frac{(e^{mq_1} - e^{mq_0})}{(c_1 - c_0)} \quad \text{eq. 4.10}$$

Where: (D_p) represents the diffusivity of water in vapor form through the pore space, (D_{q0}) represents the asymptotic diffusivity of condensed phase moisture through the fiber matrix (incorporating liquid wicking, solid and surface diffusion mechanisms) when the fibers are dry and (m) represents the coefficient of the rate of change of this diffusivity with moisture content. Also presented in Table 4.4 are diffusivity data determined by random walk simulations inside the pore structure for comparison with the (D_p) values.

Table 4.V. Diffusion parameters using experimental data from transversal diffusion						
Paper	ε (IA)	ρ (IA)	D_p (RW)	D_p	D_{q_0}	m
570	0.3586	0.769	0.0135	1.5007E-2	1.4958E-7	136.9
460	0.3103	0.870	0.0082	6.0218E-3	5.1730E-8	262.5
330	0.2859	0.902	0.0035	2.0062E-3	3.2108E-7	107.9
220	0.2457	0.941	0.0033	2.8158E-3	9.5456E-8	174.4

RW – random walk simulations in 3D images of paper samples

IA – image analysis of X-ray micro computed tomography images
of paper samples

Some significant conclusions from this table are that the pore diffusivity in the transverse dimension decreases substantially as the density of the sheets increases. Although the diffusion result with higher density is deviated from this trend. There seems to be no significant trend in the fiber diffusion parameters. This may possibly be due to the fact that as moisture content is the primary determinant for this diffusion. Since the sorption isotherms for the individual sheets do not change substantially with refining, the moisture content does not change and therefore we observe that the moisture diffusivity parameters (D_{q0}) and m also do not change.

The problem of determining the diffusion parameters for a given paper material from experimental data is an exercise in optimal fitting of the diffusion model. Our group developed a method of obtaining these parameters from experimental measurements and compares the efficiency of this method with earlier methods. Thus we implemented a quadratic minimization algorithm based on the Newton method.

The Table 4.6 presents results of optimal parameters estimated by the non-linear minimization technique.

It can be observed that this method also yields parameter sets for the diffusivity although they are subject to higher dispersion than the non-linear least squares.

In Table 4.6, we also present parameter estimates for the sequence of handsheet samples of different refining levels. Also presented in this table are parameters obtained from a sample bleached kraft paperboard which has been investigated quite extensively in the past by us.

Table 4.VI Optimal diffusion parameter sets for synthetic experimental data obtained by two different methods (non-linear minimization and linearized version). Diffusion parameters obtained from experimental measurements on handsheets prepared from refined BKSWP also are shown.

		Method A		Method C	
Type	D_p	D_{q_0}	m	D_{q_0}	m
Synthetic, $f_{err} = 0.0$	3.0E-3	6.0E-09	400.0	5.9723E-9	400.0
Synthetic, $f_{err} = 0.005$	3.1014E-3	3.8873E-9	439.8	4.1594E-9	430.4
Synthetic, $f_{err} = 0.1$	3.2025E-3	2.4416E-9	481.8	1.2843E-8	305.8
Synthetic, $f_{err} = 0.2$	3.4096E-3	8.3284E-10	576.3	2.6568E-8	195.9
Synthetic, $f_{err} = 0.3$	3.6348E-3	1.9699E-10	698.8	5.0858E-8	146.9
Ademilson, H570	1.5007E-2	1.4958E-7	136.9	3.7698E-8	295.5
Ademilson, H460	6.0218E-3	5.1730E-8	262.5	3.5079E-8	302.2
Ademilson, H330	2.0062E-3	3.2108E-7	107.9	3.5361E-7	92.0
Ademilson, H220	2.8158E-3	9.5456E-8	174.4	8.9053E-8	178.6

4.4. Conclusions

In the present chapter, we have showed and discussed the results of our investigations on moisture diffusion in paper materials in the transverse dimension. The experimental design made use of a versatile humidity chamber that follows the model of the Weyerhaeuser company chamber, already described in the chapter II. Besides that,

were built profiles experiments associated, using mini relative humidity sensors, which validate more the results. The several grades of refine and different origin of samples also reinforced the results.

The effect of refining of the pulp was shown to be manifested primarily in the decreased vapor diffusivity through the pore parameter. This was expected due to the decreased of pore volume fraction and increased tortuosity of the pore space. Thus, most moisture diffusion processes will initially be controlled by the pore space of the sheets and how this responds to changes in external variables. When the moisture contents of the sheets are not very high, i.e. far from saturation, pore diffusion dominates and (D_p) controls the moisture transport. This means that sheet density is the primary variable for moisture transport unless the sheets are close to saturation. We can thus expect that bulkier sheets made of mechanical fibers or recycled fibers will tend to have higher diffusivities as compared to sheets made of more swellable fibers. Furthermore, since moisture content is the primary determinant for the fiber matrix transport, processing operations which decrease the fiber moisture content such as higher lignin levels or hornification will tend to decrease fiber diffusivity. Based on general knowledge of pulp science, the fibers with more water retention values (WRV), more hemicelluloses and more surface charges are going to be more susceptible to have water bonded. The hydrophilic sites will be more available in these fibers. Therefore will have more influence of bound water diffusion and at lower relative humidity.

However, there were not found significant effects on the effective moisture equilibrium in the fiber matrix regards to the sorption isotherms due to refining effects. The samples refined at six levels had practically the same isotherm through the all

relative humidity range. These results give us the thought that moisture reaches the very internal parts of the fiber wall. This, independent of how it is opened, at least for the bleached kraft pulp studied.

The effect of swelling is clearly shown on pore diffusion through experiments carried out with n-propanol through large part of the relative humidity range. The experiments with n-propanol diffusivity also help to show the effect of density variation on bound water diffusion in the fiber matrix.

The curve of effective diffusivity shows that up to around 50 % of relative humidity this property is constant. Therefore it increases exponentially after that, and these results repeated for all the refine grades. Thus, the mechanism for this range of relative humidity dominated by water diffusion inside of fiber wall is clearly very different from the pore diffusion mechanism. The refine grade is inversely proportional to effective diffusivity at entire relative humidity range. Although we suspect that at certain density level, when the fibers are close enough, and the bound water diffusion dominates completely the phenomena, the diffusivity would increase.

The expectation is that the variety of experiments and approaches shown in this chapter could bring some important contributions in the moisture diffusion in transversal direction, mainly with respect to changes occurring in the paper structure provoked by refining. The intention also is to improve the understanding on the mechanisms of moisture transport as regards to vapor pore diffusion and bound water fiber diffusion.

4.5. References

1. Koponen S., “Effect of Wood Micro-structure on Mechanical and Moisture Physical Properties”, 348-363, Finland.
2. Crook D.M. and Bennett W.E., “The Effect of Humidity and Temperature on the Physical Properties of Paper”, The British Paper & Board Industry Research Association, United Kingdom, 1962.
3. Benson R.E., “Effects of Relative Humidity and Temperature on Tensile Stress-strain Properties of Kraft Linerboard”, Tappi, vol (54), 5, 1971.
4. Back E., Salmen L., Richardson G., “Transient Effects on Mechanical Properties of Paper During Sorption of Moisture”, Tappi Proceedings, International Paper Physics Conference, 173-179, 1983.
5. Wang J.Z., Dillard D.A., Kamke F.A., “Transient Moisture Effect in Materials. A Review”, Journal of Materials Sci, 26, 5113-5126, 1991.
6. Habeger C.C. and Coffin D. W., “The Role of Stress Concentrations on Accelerated Creep and Sorption-induced Physical Aging”, J. Pulp Paper Sci., 26 (4), 145–157, 2000.
7. Alfthan J., “A Simplified Network Model for Mechano-sorptive Creep of Paper”, Progress in Paper Physics Seminar, 73 – 76, September, Syracuse, NY, 2002.
8. Gurnagul N., Gray D.G., “The Response of Paper Sheet Surfaces Areas to Changes in Relative Humidity”, J. Pulp Paper Sci, 13 (5), 159-164, 1987.
9. Rahman A.A., Urbanik T.J., Muhamid M., “ Moisture Diffusion Through a Corrugated Fiberboard under Compressive Loading: Its Deformation and Stiffness Response”, Progress in Paper Physics Seminar, 85 – 88, September, Syracuse, NY, 2002.

10. Niskanen K.J., Kuskowski S.J., Bronkhorst C.A., "Dynamic Hygroexpansion of Paperboards", *Nordic Pulp and Paper Research*, 12(2), 103-110, 1997.
11. Enomae T., Lepoutre P., "Surface Roughening by Water: Gloss Relaxation Processes", *J. Pulp Paper Sci*, 23 (7), 326-330, 1997.
12. Han S.T., Matters J.F., "Vapor Transport in Fiber Mats During Drying", *Tappi Journal*, vol 49, (1), 1-4, 1966.
13. Ahlen, A.T., "Diffusion of Sorbed Water Vapor Through Paper and Cellulose Film", *Tappi Journal*, vol 53, (7), 1320-1326, 1970.
14. Rounsley R. R., "Vapor Transport Through Paper", *TAPPI Journal*, vol 47, (2), 1964.
15. Lin, S.H., "Moisture Absorption in Cellulosic Materials", *Int. J. Engng Sci.* 28(11):1151-1156 (1990).
16. Lin, S.H., "Moisture Desorption in Cellulosic Materials", *Ind. Eng. Chem. Res.*, 30, 1833-1836, 1991.
17. ten Donkelaar J. R., Jaeger C. R., "Transport and Sorption of Water Vapor in Corrugated Board.", *Proc. 4th Intl. Symp. On Moisture and Creep Effects in Paper, Board and Containers*, Ed. J-M, Serra-Tosio and I. Vullierme, EFPG, Grenoble, France, 245-255, 1999.
18. Ahmad
19. Roisum D. R., "Moisture Effects on Webs and Rolls", *Tappi*, 76, 6, 129-137, 1993.
20. Nilsson L., Wilhelmsson B., Stenstrom S., "The Diffusion of Water Vapor Through Pulp and Paper", *Drying Tech.*, 11, (6), 1205-1225, 1993.
21. Nilsson L., Wilhelmsson B., Stenstrom S., "Effective Vapor Diffusivity in Paper", *Drying* 92, 1115-1123, 1992.

22. Lescanne Y., Moyne C., Perre P., "Diffusion Mechanisms in a Sheet of Paper", *Drying '92*, 1017-1026, 1992.
23. Hellen E. K. O., Ketoja J. A., Niskanen K.J., Alava M. J., "Diffusion Through Fiber Networks", *J. Pulp Paper Science*, vol. 28, (2), 2002.
24. Wadsö L., "A Model for Non-Fickian Sorption of Water Vapour in Wood", *Drying '92*, 1145-1153, 1992.
25. Foss W. R., Bronkhorst C. A., Bennett K. A., Reidemann J. R., "Transient Moisture Transport in Paper in the Hygroscopic Range and its role in the Mechano-sorptive Effect", *Proc. 3rd Intl. Symposium on Moisture and Creep Effects on Paper, Board and Containers*, PAPRO, Rotorua, NZ 221-236, 1997.
26. Foss W. R., Bronkhorst C. A., Bennett K. A., "A Model of Simultaneous Heat and Mass Transport in Paper during Moisture Sorption from Air", *Proc. 4th Int. Symp. on Moisture and Creep Effects on Paper, Board and Containers*, E.F.P.G., Grenoble, France, 267-279, 1999.
27. Foss W. R., Bronkhorst C. A., Bennett K. A., "Simultaneous Heat and Mass Transport in Paper Sheets during Moisture Sorption from Humid Air", *Int. J. Heat and Mass Transf.*, 46, 2875-2886, 2003.
28. Ramarao B.V., Massoquete A., Lavrykov S., Ramaswamy S., "Moisture Diffusion Inside Paper Materials in the Hygroscopic Range and Characteristics of diffusivity Parameters", *Drying Technology* 21(10): 2007-2056, 2003.
29. Ramarao B. V., Chatterjee S. G., Eusufzai A. R. K., Tien C., "Moisture Transport and Sorption by Paper under Cyclic Variations in Humidity", *Mechanics of Cellulosic Materials*, ASME, AMD-Vol.209/MD, vol. 60, 195-214, 1995.

30. Chatterjee S.G., Ramarao B.V., Tien C., "Water-Vapour Sorption Equilibria of a Bleached-Kraft Paperboard – A Study of the Hysteresis Region", *J. Pulp Paper Sci.*, 23(8): J366-J373, 1997.
31. Ramarao B.V., Chatterjee S.G., "Moisture Sorption by Paper Materials under Varying Humidity Conditions", *The Fundamentals of Papermaking Materials*, Transactions of the 11th Fundamental Research Symposium, Cambridge, PIRA International, Leatherhead, England, 703-749, 1997.
32. Bandyopadhyay A., Radhakrishnan H., Ramarao B. V., Chatterjee S. G., "Transient Moisture Sorption of Paper Subjected to Ramp Humidity Changes: Modeling and Experiments", *Ind. and Engng. Chem. Res.*, 39, 1, 219-226, 2000.
33. Radhakrishnan H., Chatterjee S.G., Ramarao B.V., "Steady-State Moisture Transport in a Bleached Kraft Paperboard Stack", *J. Pulp Paper Sci.*, 26 (4): J140–J144, 2000.
34. Ramaswamy S., Huang S., Goel A., Cooper A., Choi D., Bandyopadhyay A., Ramarao B.V., "The 3D Structure of Paper and Its Relationship to Moisture Transport in Liquid and Vapor Forms", 12th Fundamental Research. Symp., Oxford, 1289-1311, 2001.
35. Lavrykov S., Ramarao B. V., "Comparison of Models for Generalized Diffusive Transport in Paper Materials based on Transport through Pores and the Fiber Matrix", *ESPRA Res. Report*, SUNY ESF, Syracuse NY, 117, 39-58, 2002.
36. Gupta H., "Moisture Transport in Paper under Steady and Unsteady Conditions Investigated with a Parallel Diffusion Concept", PhD Thesis Dissertation, Paper Science and Engineering Department, SUNY - ESF, Syracuse, 2003.
37. Gupta H., Chatterjee S.G., "Parallel Diffusion of Moisture in Paper. Part 1: Steady-state Conditions", *Ind. Eng. Chem. Res.*, 42, 6582-6592, 2003.

38. Gupta H., Chatterjee S.G., "Parallel Diffusion of Moisture in Paper. Part 2: Transient Conditions", *Ind. Eng. Chem. Res.*, 42, 6593-6600, 2003.
39. Massoquete A., Lavrykov S., Ramarao B.V., Goel A., Ramaswamy S., "Anisotropic Moisture Diffusion Study on Refined Paper", *International Paper Physics Conference*, Victoria, British Columbia, 2003.
40. Massoquete A., Lavrykov S., Ramarao B.V., "Non-Fickian Behavior of Moisture Diffusion in Paper", *Under Review, J. Pulp Paper Sci*, 2004.
41. Seborg C.O., Stamm A.J., "Sorption of Water Vapor by Papermaking Materials , I Effect of Beating", *Ind. Eng. Chem.*, vol23 (11), 1271-1275, 1931.
42. Seborg C.O., Simmonds F.A., Baird P.K., "Sorption of Water Vapor by Papermaking Materials", *TAPPI*, vol10, 223-228, 1938.
43. Lennholm H., Iversen T., "The Effects of Laboratory Beating on Cellulose Structure", *Nordic Pulp and Paper*, n^o 2, 104-108, 1995.
44. Qiang L.T., Henriksson U., Odeberg L., "Water-Cellulose Interactions Studied by ²H NMR. Effects of Beating", *Paper Conference*, 403-417.
45. Stamm A.J., "Adsorption in Swelling Versus Non-swelling Systems. I Contact Area", *TAPPI*, vol 40 (9), 761-770, 1957.
46. Nilsson L., Stenstrom S., "Gas Diffusion Through Sheets of Fibrous Porous Media", *Chem. Engng. Sci.*, 50, 3, 361-374, 1995.
47. Liang B., Fields R.J., King J.C., "The Mechanisms of Transport of Water and n-Propanol through Pulp and Paper", *Drying Tech.* 8(4):641-665, 1990.

CHAPTER V

MOISTURE DIFFUSION ON PAPER

LATERAL DIRECTION

5.1. Introduction

The moisture diffusion in paper is extensively studied through the thickness direction with a variety of experimental set ups and conditions. However, the study of moisture diffusion in one direction does not answer all the questions on paper material demands. Some use of paper and the increasing requirements of the information support such as increasing of printing velocity, different ink formulations, differentiated the properties desired. In the packaging sector, the progress passes through containers composition, methods of sealing, and conditions of transportation. The great challenge in the container branch is the competition with the plastic material.

The paper anisotropy on the three dimensions is a consequence of its raw material and manufacturing process. As we well know, the machine made paper has around of 80 % of the fibers directed in the machine direction. Therefore, paper material is significantly anisotropic as could be seen in the comparison with others materials, on Table 5.I. Certainly the anisotropy varies according with paper grade and machine design, but it is present and is important for most cases.

Table 5.I – Comparative Anisotropy of Materials				
Material Tested	Material Thickness (mm)	Through-Plane Bubble Point Diameter (microns)	In-Plane Bubble Point Diameter (microns)	Ratio (Through-Plane / In-Plane)
Printer Paper	0.08	12.4	1.1	11.3
Notepad Backing	0.92	6.7	3.53	1.9
Metlblown Sheet	1.8	114.3	68.8	1.66
Poly Felt	2.0	51.8	19.8	2.62

Published by PMI Porous Materials Incorporation, Dr Krishna Gupta.

This characteristic of paper is well known with regard to mechanical properties and dimensional stability. Nevertheless, anisotropy also has significant influence on others applications of paper material, which become more evident with progressive requirements of paper demand. Considering that better understand the relation moisture

and paper is the main interest of this research, one of the objectives of the present work is to study anisotropy related to moisture diffusion in paper, in particular showing results for lateral diffusion, which have not been explored enough.

Although paper is also anisotropic in the thickness direction, this characteristic will be neglected theoretically and experimentally for sake of simplification of the problem. The figure 5.1 shows a cross section of one of the paper that we work with, it is a bleached kraft paperboard refined to 670 CSF. The figure shows the cross section with smaller tortuosity, although this is a handsheet and there is no predominant fiber direction. The effect would be more remarkable in a machine made paper at machine direction. This is one of the probably reason why lateral moisture diffusivity is higher in machine direction. Although this work also consider other contributions for the easier moisture diffusion In-plane.

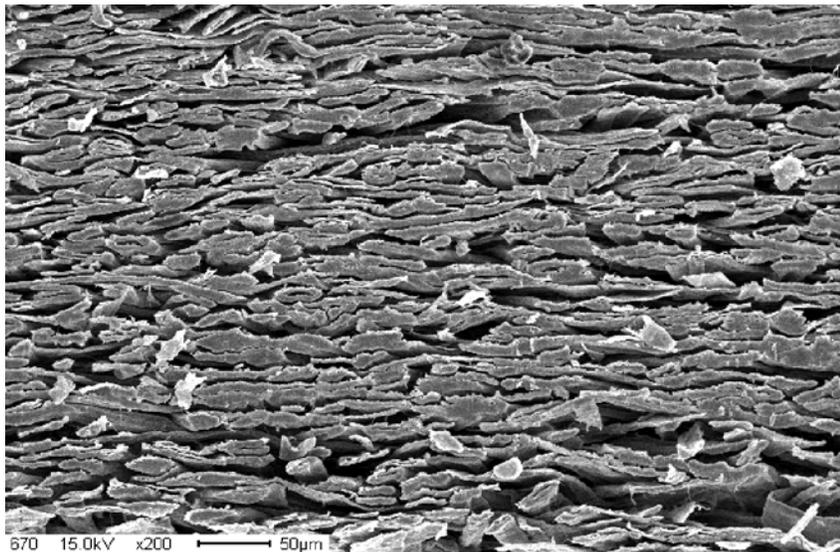


Fig 5.1 – Cross Section of a Paper Sheet (200X) refined to 670 CSF. SEM Photography, a courtesy of Dr Robert Hanna, Director of N. C. Brown Center for Ultrastructure Studies, SUNY-ESF

The pore analysis of these papers also shows that pore distribution in the plane of paper (xy) is quite different from the pores distribution through the thickness (z). The lateral direction (xy) has higher percentage of pores with lower tortuosity than the pores in transverse direction (z), which has higher tortuosity, apart from larger tortuosity distribution. This could be seen in the figure 5.2, obtained from a courtesy of University of Minnesota, with one of the samples used in the present study.

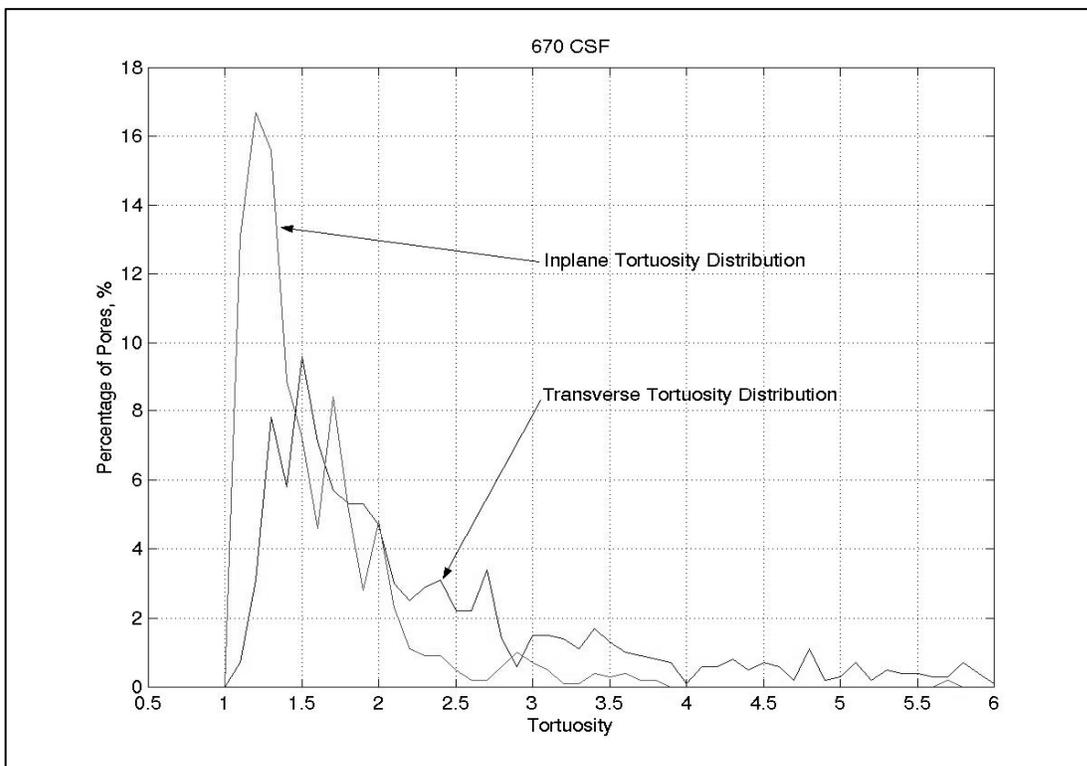


Fig 5.2- Lateral and transverse tortuosity distribution for slightly refined sample 670 CSF, with average of 1000 tracers for each direction. A courtesy of Dr Sri Ramaswamy, Department of Bio-based Products, University of Minnesota.

The moisture diffusion on paper material was always faced as one dimensional process through the paper sheet. Probably it is because paper is seen as a barrier, which is easier crossed on thickness direction. Nevertheless, moisture diffusion on In-plane direction or Lateral direction is particularly interesting for some specific situations. During paper manufacturing could be highlighted a possible effect of In-plane moisture diffusion in drying and calendering. Considering paper applications moisture diffusion In-plane possibly play an important role on liquid containers, where a cross section of the paperboard in the internal part of the container is exposed to liquid, affecting its durability. Another example is on photographic paper where the In-plane diffusion could be responsible by edge sorption affecting the quality of the picture.

Although there are few works specifically on In-plane moisture diffusion, it is consensus that moisture diffusion on this direction is much higher than through paper thickness. Our work also point on this direction, and moreover shows that the dominant mechanism of moisture diffusion is completely different from the dominant mechanism on transversal direction. Experiments with different concepts are carried out in order to proof the dominant mechanism of moisture diffusion in the lateral direction of paper. The samples used also are from different origin, and particularly the experiments with n-propanol corroborate the results of moisture diffusion in paper.

The lateral diffusivity suffer less effect but still decreases slightly with density increasing, in the range initially studied. Nevertheless, with the experiments using further densification of the sample by calendering the effect of lateral diffusivity is changed. The lateral diffusivity then increases significantly due to the intimate contact among fibers. Therefore, in order to make a profounder investigation on moisture diffusion in paper,

experiments and theoretical discussion for In-plane moisture diffusion are presented in this chapter and could be compared with through-plane moisture diffusion presented in the previous chapter.

5.2. Literature Review

The In-plane characteristics of paper studied before were focused on mechanical properties, air permeability, and there were just a couple of introductory papers researches on moisture diffusion. These In-plane characteristics of paper for papermakers were very closely related with the paper formation and fiber flocculation problems. However, around the time our group have started to study the moisture diffusion In-plane, the first specific paper was published by Hashemi et al. [1]. This paper focused on paper moisture desorption measurements, in the boundary conditions of the paper machine dry section. The mass transfer coefficient on the sample surface was corrected in their experiment by adjusting the measured values with ambient drying.

The measurements were with infrared moisture sensor, which measure the superficial local moisture content of paper as function of time. This work has an interesting discussion on water transport in paper, and divides it as “water transport”, when liquid water is present, and “moisture transport”, when liquid water is absent. The authors wrote a review based on diffusivities determined by different approaches on mathematical models.

They show some results, discuss the differences among the values found and the assumptions made on the models. The conclusion shows that the presence of liquid water as boundary condition is not relevant, and assumes that vapor diffusion is isotropic. They also show in two sets of data that adsorption and desorption could be neglected in the comparison of lateral and transversal moisture sorption.

The large difference between the diffusivity in the two directions could be appreciated in the figure below.

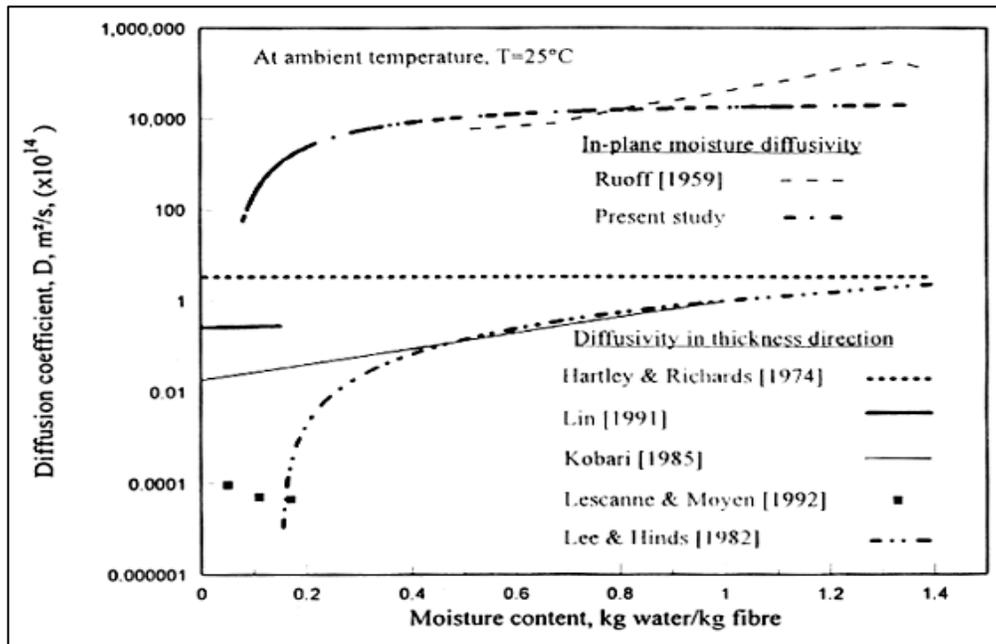


Fig 5.3 – Comparison of moisture diffusivity in paper Through-plane with In-plane, published by several authors. Graphic plotted by Hashemi et al.

The figure 5.3 shows that diffusivities In-plane in both cases available are several orders of magnitude higher than through-plane, characterizing the anisotropy of paper.

However, have to be considered that these data are relative to different papers. In spite of that, these results indicate that In-plane moisture diffusion could be an important factor on relation paper-moisture. The transverse direction is explained to have more tortuosity for moisture diffusion due to fiber alignment. This effect become more important, second the authors, when fiber shrink and contact area decreases creating a neck to the moisture passage.

Hojjatie et al. [2] developed an interesting work using infrared thermography to measure surface temperature and determine In-plane moisture distribution in paper. The method related the surface temperature of paper with moisture content measured gravimetrically. They found that the temperatures were linearly related with moisture content measured gravimetrically. The authors express the opinion that there are limited qualitative results on In-plane moisture diffusion, what we agree. Although the samples are apparently exposed to air convection several times, seems that the gravimetric and infrared methods are compatible.

Considering the effect of In-plane diffusion on paper process and applications presented before, some studies could be related to the effects of moisture diffusion In-plane. Myat Htun [3] studied the changes on In-plane mechanical properties of paper during drying. He found that elastic modulus of paper increases drastically during drying, and fibers were also treated with isopropanol with the conclusion that interaction forces among fibers affect the elastic modulus.

Some researchers [4, 5] studying effect of moisture on superficial calandered paper properties have come to the conclusion that moisture content affects substantially these properties due structural fiber relaxation. This effect causes fiber expanding with

change in porosity, resulting on paper structural modification In-plane and through plane. Ernest Back [6] studying pore anisotropy of fiberboards with use of vary fibers verified that swelling fibers decrease porosity of paper, and that density has primary influence on pore anisotropy. Lif et al. [7] measured the In-plane hygroexpansion of paper using an electronic speckle photographic system. Two applications were proposed for the technique, first the determination of the displacement field after expose the sample to moisture variation, and second is the determination of hygroexpansion orientation. A linear relation between tensile stiffness orientation and hygroexpansion orientation was obtained for machine made papers. This measurement is considered easy to do, but a better accuracy is estimated with the technique development.

Adams and Rebenfeld [8] study of In-plane fabrics shows that in heterogeneous multilayer the flow is governed by the high permeability layer and a transverse flow feed another layers, in a process in series. As driving pressure is high enough, the most important property was the fabric structure. Horstmann et al. [9] studied the anisotropic permeability of photographic paper In-plane and found that it is approximately 20 % faster in machine direction than cross direction. They claim that the degree of anisotropy does not change significantly with fiber swelling, although In-plane permeability changes with time. Jeffrey Lindsay [10] work focused on anisotropic permeability of paper, with variation of compression on sample. He found that permeability for the machine made paper analyzed is higher on machine direction than on cross direction, and that the ratio permeability of lateral to transverse direction is 2 to 3 in most cases. His conclusion also state that the mentioned ratio does not change significantly with compression. In two other articles Lindsay and Brady [11, 12] worked on In-plane and transverse permeability

of the paper. The anisotropy is studied considering several factors of influence, and show that In-plane permeability is much greater than transverse permeability either for hardwood and softwood, the difference can reach from 2 to 40 times. They found also that anisotropy persists for various type of pulp and small changes on freeness may cause large changes on permeability. The second article focus on anisotropic permeability applied to water removal from paper. They show the effect of hornification and other factors such as recycling, pores and aeration on permeability.

Vomhoff [13] worked in an equipment to measure permeability In-plane of water saturated fibers. This permeability was analyzed in function of porosity, and was found to decrease exponential and directly proportional to porosity. The permeability was higher as lower was the basis weight, and the flow path also has a significant influence on permeability in the method used.

Hagglund et al. [14] worked on diffusion of water vapor in paper through transient moisture sorption experiments. They build a moisture sorption tester to carry out the experiments and compare the results with a model, with good agreement. The model considered diffusion on fiber surface and in pore through the thickness direction.

Pierron et al. [15] presented a novel method for composite materials that can identify parameters of Fickian moisture diffusion in three dimensions. This method can use gravimetric obtained data, and in his work was applied on glass/epoxi composites. The equilibrium conditions are determined by experimental data, and the Fickian and Non-Fickian regions are identified. The authors claim that their approach has fewer limitations.

Adams et al. [16] studied the flow of a epoxy resin in the In-plane direction of a fibrous network. They forced the resin through an apparatus and measured the woven and nonwoven fabrics permeability. They found the medium anisotropic if the distribution of fiber orientation is not random, and suggest the technique to characterize composite reinforcement materials on their flow properties.

Berger and Habeger [17] measured mass specific elastic stiffness of papers with ultrasonic and resonant methods In-plane during moisture sorption and equilibrium. They found that loss tangent and ultrasonic stiffness obtained under moisture equilibrium were equal those obtained under equilibrium. Although, others studies have shown increasing in loss tangent and decrease in stiffness. The authors discard the ultrasonic test frequency for this difference, and presume that it could be due the low strain amplitude applied in the method. The authors claim as practical contribution of this work the evidence that is not necessary to correct the transient moisture effects for online ultrasonic measurements.

As the paper was calendered to confirm our hypotheses in the In-plane diffusion, some calendered effects on three-dimensional paper structure are included in this bibliographic review.

Forseth and Helle [18] studied the effect of moisture variation on cross section of paper, once this material increase its roughness with moisture. The cross section is analyzed with Scanning Electron Microscope. The mechanical pulp containing in the material seems to have great effect on roughness, and these calendered fibers recovery its cross section shape before calendaring when moisturized. The authors detected an increasing on interfiber pores too, which could be due to pushing up fiber recovery or wetting stress releasing of fibers.

Gratton [19] measured the web deformation of calendered paper in the cross and machine directions, and he found a relation between cross section elongation and thickness reduction. This work concerned about the degree and rate of change of such deformations, as well as describes a method to measure the deformations. The author shows that the method is repeatable and the cross direction variations are one order of magnitude higher than machine direction. The recovery of deformations vary according with the furnishes, being high for mechanical pulp and significantly smaller for chemical pulps.

Goel et al [20] used the X-ray microtomography to study the three dimensional structure, most specifically to describe the porosity and pore size distribution of paper. They compared the method with well known mercury intrusion with good agreement. They found that the transverse pore structure is more opened, with larger pore size distribution than the in-plane distribution. The pores distributions are compared between wet pressed and vacuum dewatered sheets, and a difference is detected. This work measured specific surface area and pore size distribution for the same refined samples used in the present thesis. They found a narrower pore size distribution moving towards the smaller pore size with refine.

Ramaswami et al. [21] presented a relation between the three dimensional structure of paper and moisture transport through the pores and fiber wall. They used x-ray microtomography and image analysis to construct the paper structure and determined the characteristics of pore distribution on lateral and transverse directions. The samples in this work are refined at several levels of CSF and were determined properties such as porosity, specific surface area, and pore size distribution.

Massoquete et al. [22] investigated experimentally the moisture transport on water and vapor form and in the lateral and transverse direction of diffusion in paper structure. The gravimetric experiments were carried out at steady and unsteady state conditions under a large relative humidity range. The effective diffusivity for several levels of refine was calculated and its dependence on relative humidity conditions was determined. Air permeability and diffusivity are related. The mathematical model was compared with experimental data, moisture fluxes and profiles showing good agreement.

Ramarao et al. [23] published a review on paper moisture diffusion analyzing some models and compared their approach. They comment the necessity of consider an internal relaxation parameter that show the complexity of moisture diffusion in paper. The effect of paper properties such as density and the effect of wet pressing, calendering and refining is also theme of this work. Their conclusion suggested that moisture diffusion in paper is anisotropic.

Massoquete et al. [24] investigated the anisotropic moisture diffusion on refined paper using bleached kraft paperboard. Diffusivities on lateral and transverse directions were determined experimentally, and were calculated in the pore and fiber wall. They concluded that diffusivity is higher in lateral than transverse direction. Both diffusivity behave different at high density, and refine show some effect on pore diffusivity probably due to increasing of tortuosity. This mechanism is very important on most part of relative humidity scale, when the moisture content of the sheet is not very high, as shown in several investigations.

As could be concluded in this bibliographic review, although there are few papers about anisotropic behavior of moisture diffusion in paper material, its importance is well demonstrated.

Therefore, the research on In-plane moisture diffusion in paper could bring contributions for several important clients of paper industry, as well as improve its manufacturing process. This work present experimental results as well as theoretical approach for moisture diffusion In-plane. The theory is based on a model with one-directional moisture flux, where moisture diffusivity has two components. Pore diffusion in the form of vapor through the paper pores, and bound diffusion in the form of condensed water through the fibers wall. This model account with fiber mass transfer coefficient either, and was proposed by Ramarao and Chatterjee [25].

In the experiments In-plane the wire and felt side of the paper sheet are isolated by a hydrophobic polymer, and allow moisture diffusion only through the thickness direction of the paper sample.

Experimental results of In-plane diffusion involve gravimetric experiments where relative humidity gradients are responsible for diffusion across paper samples, experiments with n-propanol diffusion across paper where exclusively pore diffusion is measured, and investigation on significant paper modifications related with moisture transport such as refining and calendering. The experimental procedures will be detailed in the subsequent sections of the present work.

5.3. EXPERIMENTAL METHODS AND CALCULATIONS

5.3.1. Experimental Set Up for Lateral Moisture Transport

These experiments are more challenging than transverse moisture diffusion because the moisture flux has to be directed through the parallel plane of the paper. Any leaking between the paper samples has to be avoided or accounted in order to secure a reliable result. Another challenge is the time of diffusion that is very long due to the experimental design. The paper sample is composed of a stack of paperboard samples, but every sample is insulated from each other. A figure 5.4 shows a schematic of a modified diffusion cup used to determine planar diffusivities (i.e. lateral or in the x-y plane).

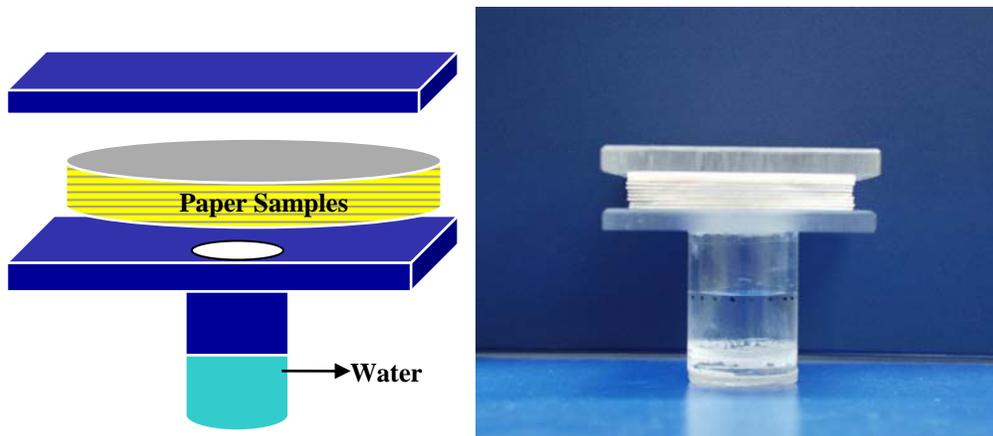


Fig 5.4- Representation and picture of cup used to support the paper samples in the lateral diffusion experiments.

The diffusion cup is build with plexiglass due to its easy feasibility and low cost. When compared with transverse diffusion, the cup is much narrower, now with dimensions (6.0 cm diameter x 4.0 cm height), it can hold a volume of approximately 5.0 ml of water in each experiment once the distance between the sample and the paper is fixed on 1.5 cm.

A set of paper sheets is cut into circles of 2.54 cm of radius with a concentric hole of diameter equal to the inner diameter of the cup, which is 1.0 cm. Therefore, the diffusion path in lateral direction is approximately 1.54 cm, through the logarithm area formed by the perimeter of the inner circle and the out circle multiplied by the paper thickness. The paper sheets were assembled in a group with several samples separated by layers of PIB 1.5 mil thick. We applied different number of layers as a test, just to find out that one layer is enough to build the paper stack.

The paperboard used is bleached kraft softwood refined on several grades of freeness. The first set of samples was made by University of Minnesota as consequence of a work developed together with our group and resulted in several publications. These handsheets were formed in a standard Tappi handsheet former.

The second set of handsheets was formed in a MK former, which has a press and dry cylinder in the same equipment. These sheets were refined in a Valley beater at four refine grades. The preparation of these samples have the objective to extend the experiments and investigate further some aspects of bound water diffusion in lateral direction.

Some of these samples were calendered to improve the fibers contact and investigate further this effect on bound water diffusion.

The following table shows some important properties of the mentioned samples:

Sample	Grammage	Thickness	Density	Permeability -1
H670	390	0.729	0.535	5.2
H570	347	0.451	0.769	31.7
H460	389	0.447	0.870	121.4
H330	333	0.369	0.902	221.0
H280	354	0.391	0.905	360.8
H220	399	0.424	0.941	973.4
MK1	230	0.344	0.669	120.1
MK2	217	0.342	0.633	206.1
MK3	228	0.313	0.728	500.8
MK4	232	0.303	0.767	1093.1

Table 5.II- Properties of the refined paper most considered to relate with moisture diffusion in this chapter.

These samples are built in stacks of several samples in order to have a larger area of diffusion with measurable diffusivities. Between each paper sample is placed a layer of

poly-isobutylene (PIB) that does not allow moisture to migrate through another direction in paper than lateral.

5.3.2. Polyisobutylene (PIB)

This hydrophobic plastic resin [26] used in lateral diffusion experiments is manufactured by Adhesives Research Corporation and given as a courtesy for our research. The PIB is a tackified based pressure sensitive adhesive that fills most of the surface irregularities but does not get inside of the paper. The pressure sensitive adhesive is defined as materials that adhere to a substrate with light pressure and leave no residual adhesive upon their removal. The PIB resin layer in our experiment is 1.5 mil thick and occupies the intervening space between the paper sheets, and blocks any moisture migrating through gaps created by the roughness of the sheets.

The polyisobutylene are elastomeric polymers commonly used as primary base polymer and tackifier depending of its degree of polymerization. The low molecular weight polymers are very viscous, soft and tacky, therefore used as tackifier. The high molecular weight polymers are tough and elastic rubbery like, and used as adhesive polymers. The PIB are homopolymers of isobutylene with a regular structure of carbon and hydrogen with a terminal unsaturation. This characteristic give a product that is chemically inert with good resistance to weathering, ageing, heat and chemicals. The stability of polyisobutylene come from the highly paraffinic and nonpolar nature, which

makes the resin insoluble in common alcohols, esters ketones, and others oxygenated solvents. Their highly close structure and unstrained molecular packing leads to an extremely low air, moisture and gas permeability. The Polyisobutylenes are preferred for use as drugs carriers with low solubility parameters and low polarity. The use of this polymers as drugs deliverers has become very common mainly lately with nicotine and contraceptives. In our case the adhesive is a middle part of a sandwich with two sheets of polyester release liner with 2 mil of thickness. These outside layers are removed, one each time, according with the application on paper surface. Then the stack is lightly pressed and the PIB excess removed. The top and bottom of the stack is covered with aluminum foil, which is an excellent barrier against moisture diffusion. The bottom aluminum sheet has a donut format and the top is a full circle.

The blocking action of the adhesive layer to migration can be visualized by the transverse and lateral cross sections of a sample paper sheet shown in Figure 5.5 and figure 5.6. The figure 5.5 shows a cross section of the samples stack, where the darker section is the polymer. The figure 5.6 shows a view of paper samples that was covered with PIB, as we can see the layer of polymer is homogeneous and blocks very well the paper sample.

The PIB layer is not hygroscopic and also provided an effective moisture barrier. These characteristics were checked by coating a sample of paper completely with the adhesive and monitoring its weight loss. No measurable weight loss was observed over a long time period indicating the effectiveness of the PIB layer as an effective moisture barrier.

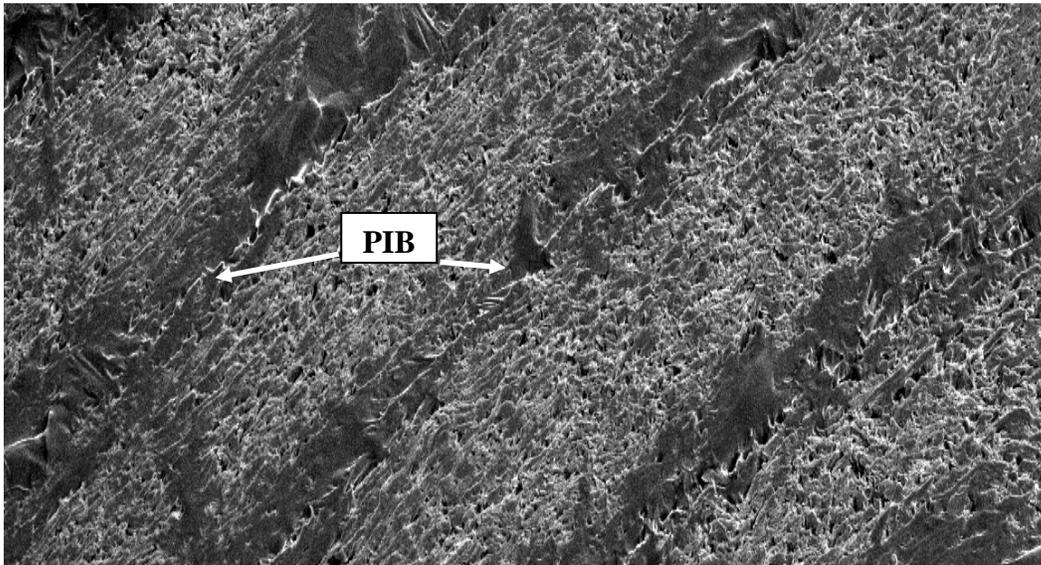


Fig 5.5- SEM Picture (50X) Cross Section of a paper stack showing the layers of PIB between paper sheets. A courtesy of Dr Robert Hanna, Director of N. C. Brown Center for Ultrastructure Studies, SUNY-ESF

The cross section show the PIB spread a little on the paper surface due to the cut technique used to prepare the sample for microscope, but it still show the magnitude of the components forming the sandwich.

The figure 5.6 complements the necessary information and show the surface of a paper sample uniformly covered by the PIB resin. The PIB film is thick enough to fill the paper irregularities on the surface on both paper samples that face it. Sometimes were placed two layers of PIB to build the paper stack, but we realize later that it was not necessary.

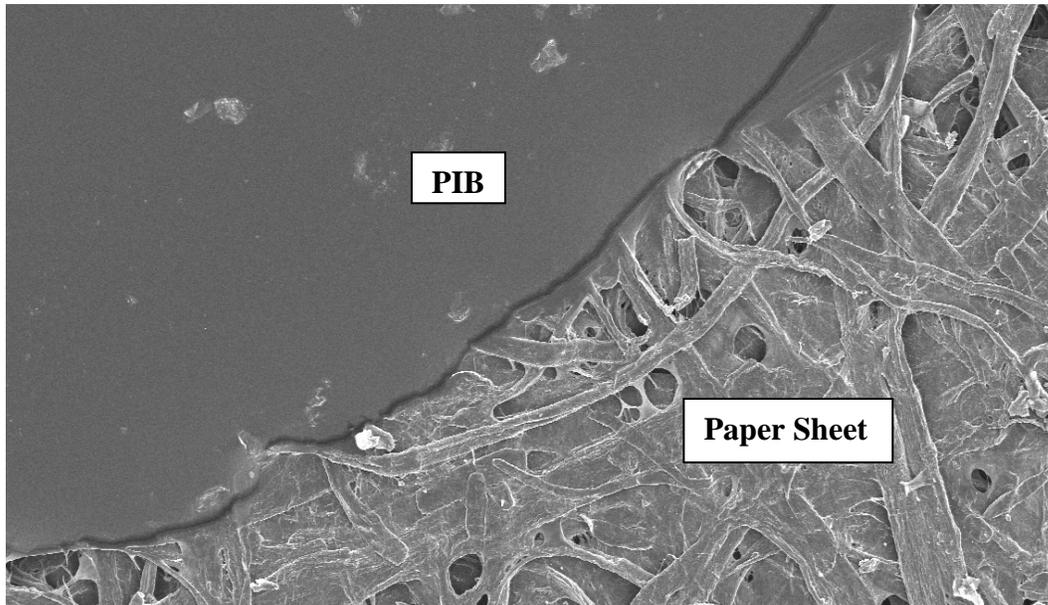


Figure 5.6– SEM Picture (110X) shows distribution of PIB on paper surface. A courtesy of Dr Robert Hanna, Director of N. C. Brown Center for Ultrastructure Studies, SUNY-ESF

These sheets could be also cut into 4 rings after the diffusivity experiment in steady state in order to provide the sample moisture content profile measurements at the conclusion of the experiments.

Although the profile was not calculated in all cases because it was considered difficult to do, and to be subject of several possible experimental errors. Some results of profiles are going to be shown anyway.

5.3.3. The Experimental Method

The experiment to obtain the mass flux of vapor is similar to the one used in transverse diffusion, although the time necessary to reach steady state is considerably higher and the sample preparation demand more care to insulate moisture flux.

After experiments carried out at different times with bleached kraft paper, it was concluded that 120 hours was enough time for the experiment in question. The stack samples was placed on the cup shown in the figure 5.4 and vaseline was applied between the cup surface and the sample, with the help of a plastic ring, to seal the passage of moisture. Inside of the cup is added an amount of water or salt solution up to the mark that fix the liquid volume constant. The entire assemble is then placed in the humidity chamber until reach the steady state.

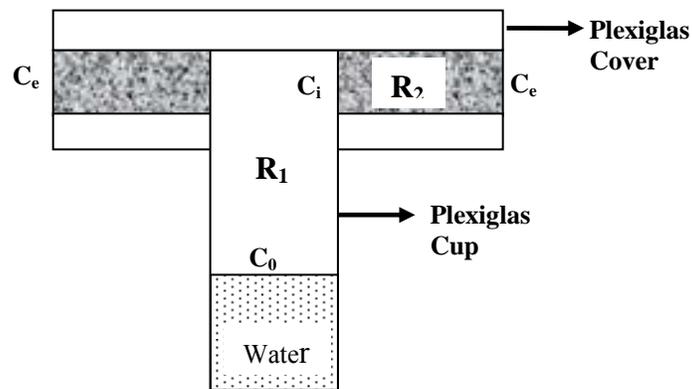


Fig 5.7- Schematic of the diffusion cup that is used for measuring diffusivity in the Lateral (xy) dimension of paper sheets. When suspended in a chamber which RH is controlled, gravimetric measurements provide transient and steady state moisture fluxes.

The figure 5.7 shows the concentrations and resistances that play important role in moisture diffusivity calculation. These concentrations form the two most important resistances for this specific case of In-plane or lateral diffusion, which are nominated R_1 and R_2 . These mass transfer resistances are: the resistance of moisture through the stagnant air gap between the water and the paper surface and the resistance through the stack of paper itself. Notice that when compared with the moisture diffusion through the paper thickness, discussed in the chapter IV, the third resistance due to the air boundary layer at the end of the paper stack external surface is neglected. The resistance from the air boundary layer external to the paper stack was neglected since the paper resistance in this case is much higher than the transverse case, and when such resistance was considered in the calculation, the value of moisture diffusivity did not change significantly. This is understandable once the thermodynamic effect of water sorption is in a smaller area.

The diffusion area through the round sample of paper increases from the inner to the outer surface, although is considered here one-dimensional in the radius direction. The area modification towards the end of paper sample is calculated by considering a logarithmic area calculation with the internal and external radius of the paper sample.

The next experimental set up used in the present work is to calculate diffusivity using the profiles as in the case of transverse diffusion. Although the difficulties to measure the moisture profile are considerable due to the thick paper stack and the short diffusion path that have to be analyzed. The fiber stack was cut with a scissor in four

parts and placed in a plastic bag to be weighted. Then the rings were dried in an oven and weighted again to calculate the moisture content in each ring.

The samples are bleached Kraft paper refined at several levels of Canadian Standard Freeness in order to measure this effect on lateral diffusion. The samples were also pressed and calendered then the fiber contact could be evaluated as a factor of influence in the mechanism of moisture transport inside of the paper sheet. Then the importance of this mechanism and the conditions that it could occur can be definitely established.

5.4. Results and discussion

Following the before mentioned intentions to work with the structural modifications of paper to demonstrate the mechanisms do moisture diffusion, the refined samples were first used. As shown in table 5.2 the variation on density is relatively large on the refine range worked in this case.

The following figure 5.8 shows the lateral diffusivities as a function of sheet density obtained from four levels of refining of the sample obtained from Minnesota University.

The figure indicates that there is a general decreasing trend with increment of sheet density. Therefore, the lateral diffusivity decreases just when the pores close to a certain size that make water vapor diffusion slower.

However, the trend in this diffusion is not as marked as the transverse diffusion. This difference could be explained by the pore size distribution showed in the beginning of this chapter where the transverse direction show higher range of pores with bigger radius which are apparently most affected by the refined consequences.

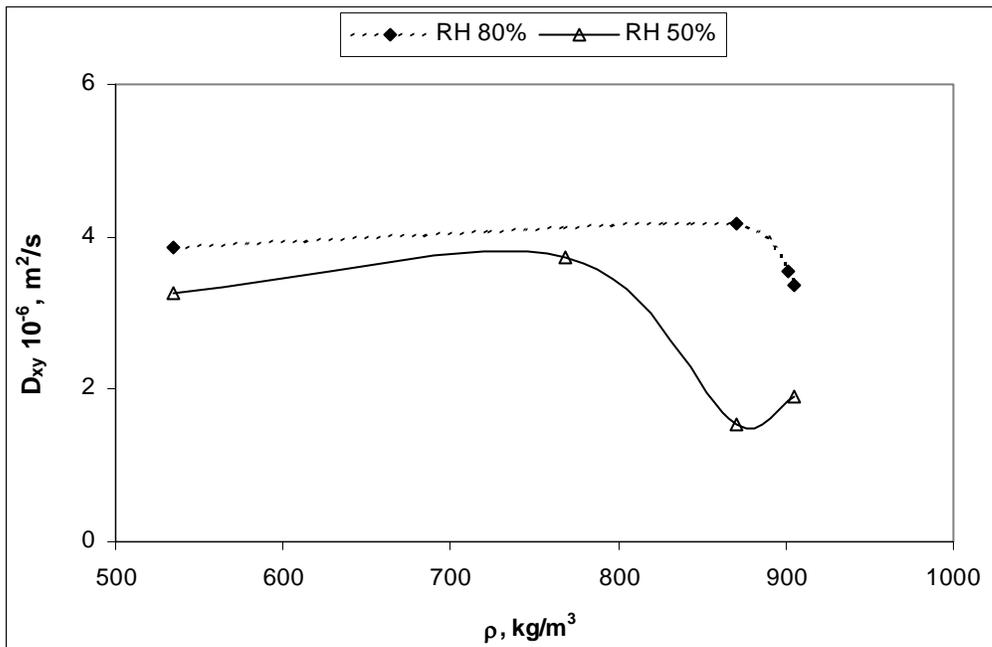


Fig 5.8- Lateral diffusivity (D_{xy}) as a function of sheet density. Two different values of RH conditions are shown.

The lateral diffusivity decreases first at 50 % of relative humidity inside of the chamber probably because at this condition the pore diffusion is more important on moisture migration inside of paper sample than at 80 % of relative humidity.

Goel et al. [27] have measured the tortuosity of the pore structure in these sheets using reconstructions of the three dimensional structure from X-Ray Micro-Tomographed sections. Their results indicate that lateral tortuosities are smaller by a factor of 2 to 10 than transverse tortuosities for these same pulp sheets.

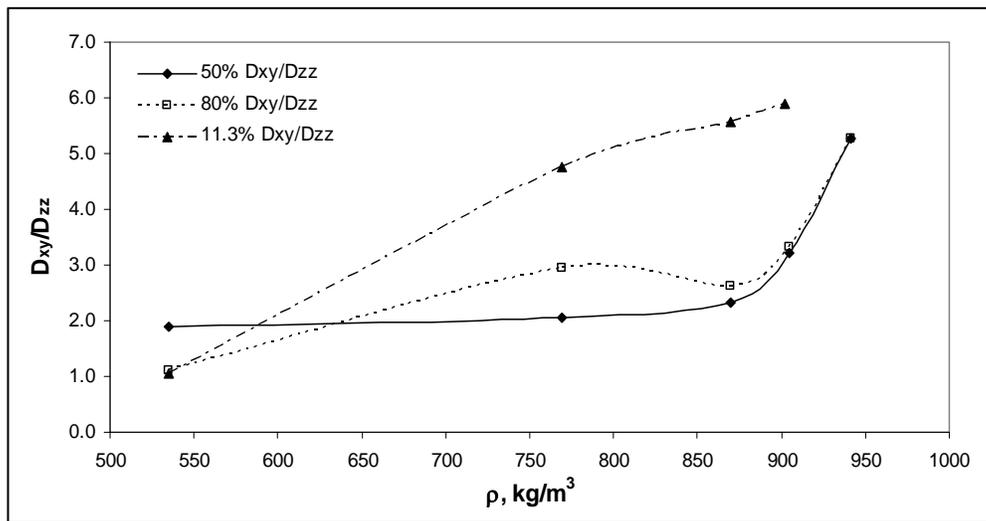


Fig 5.9- The relation between lateral and transverse moisture diffusivity for some of the samples in study, at three conditions of relative humidity gradient.

The Figure 5.9 shows a plot of the ratio of the lateral to transverse diffusivity as a function of sheet density under different moisture conditions. The behavior suggest that for the lowest relative humidity the ratio increase faster due to decreasing of D_{zz} in consequence of pore decreasing and increasing of tortuosity, once vapor diffusion is the main moisture transport under this condition. At highest relative humidity, the increasing

of the ratio could be attributed to the decreasing of pore diffusion with refine and most important the increasing of bound water diffusion once fibers contact is increased, and fiber diffusion is highly dependent on moisture content of fiber. Then, the transverse diffusivity that is more pore diffusion oriented decrease, and the lateral diffusivity that is more fiber diffusion oriented increase.

Apparently at 50 % relative humidity the decreasing of the diffusivity ratio just happens at higher density, when it interferes more significantly on bound water diffusion in fiber wall and increase lateral diffusivity. Either at high and low relative humidity the ratio transversal and lateral diffusivity are more or less equivalent at lower density.

This is because at low relative humidity the pores are very much opened that both directions have similar path, and at high relative humidity the smaller amount of fiber bound would make these two diffusivities equivalent. Thus, the higher differences between transversal and lateral diffusivities would be in the intermediate ranges of relative humidity.

As the figure shows the lateral diffusivity is higher through entire range of density and relative humidity in this work, mainly in the higher relative humidities.

In order to confirm this trend, new samples were prepared in our laboratories using softwood bleached pulp from Northeast pine, which was refined at four grades of Freeness in a Valley beater according with TAPPI standard methods.

The sheets were made in a MK dynamic sheet former, with a format 12x12 inches, pressed to 30 psia and dried to temperature of 110 °C. The change of diffusivity in lateral diffusivity with refine for these samples, considering the higher and lower refine grades, is shown in figure 5.10 below.

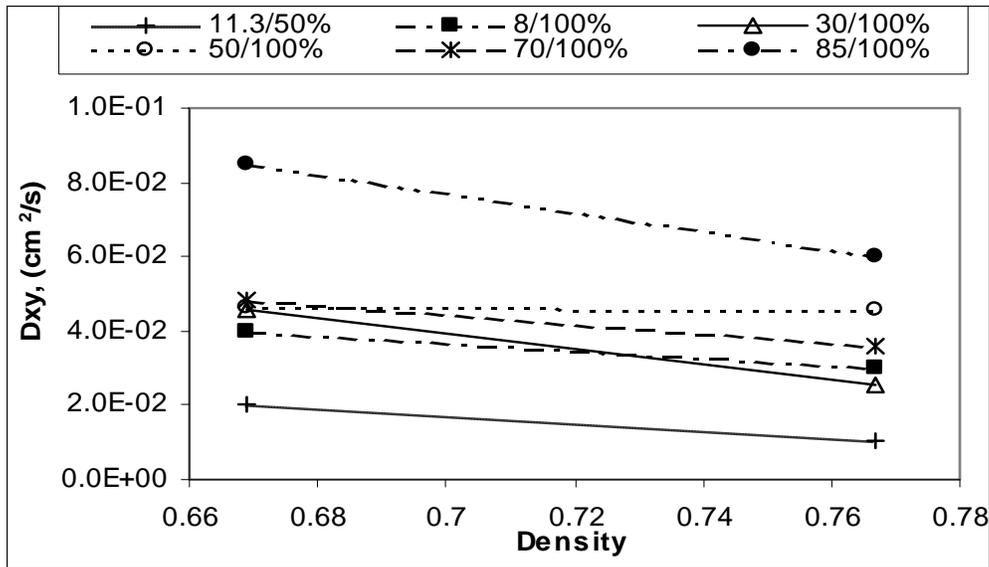


Fig 5.10-. Lateral diffusivity of paper (MK1, MK4) made with bleached kraft pulp refine from 559 to 199 CSF. Experiments carried out at several relative humidities.

These samples show that effectively lateral diffusivity decreases with density, and that it increases with relative humidity. Therefore, the lateral diffusivity behavior is expected to have an important contribution from fiber diffusion. Thus we decided to investigate how lateral diffusivity change when density increases further by confirming how important would be this mechanism when fibers are intimately in contact. In another words, when the pores are closing, and tortuosity as well as the fiber contact is increasing, how important would be the moisture diffusion in fiber. Hence, we calendered the samples made in MK equipment in a laboratory supercalender. This supercalender has an upper steel nip and a down fiber roll, and the pressure applied was 1500 PLI with two passes between the nip for each sample.

The measurements of lateral diffusivity with calendered samples show that after certain density the lateral diffusivity increases significantly when submitted to high relative humidity. This behavior is due to more effective contact among fibers and consequent facility to transfer liquid water from one fiber to another.

The pore diffusivity in calendered samples drop significantly, this could be noticed by the values of porosity Sheffield measured with the equipment TMI model 58-24. The porosity was measured air permeability, with air pressure 1.43 psi and orifice diameter 9.5mm, in sccm standard cubic centimeter units.

The figure 5.11 showed next illustrate the variation of lateral diffusivity of the sample MK1, which was refined to freeness 559, and Sheffield porosity change from 212 sccm to 72 sccm after calendering.

As expected, the lateral diffusivity of moisture increases significantly for higher ranges of relative humidity where liquid water diffusion become a more important mechanism of diffusion.

On the other hand the pore diffusivity inside of paper obviously is reducing significantly. Measurements of the air permeability in these samples showed significant decreases with calendering, corroborating the reduction in the pore space.

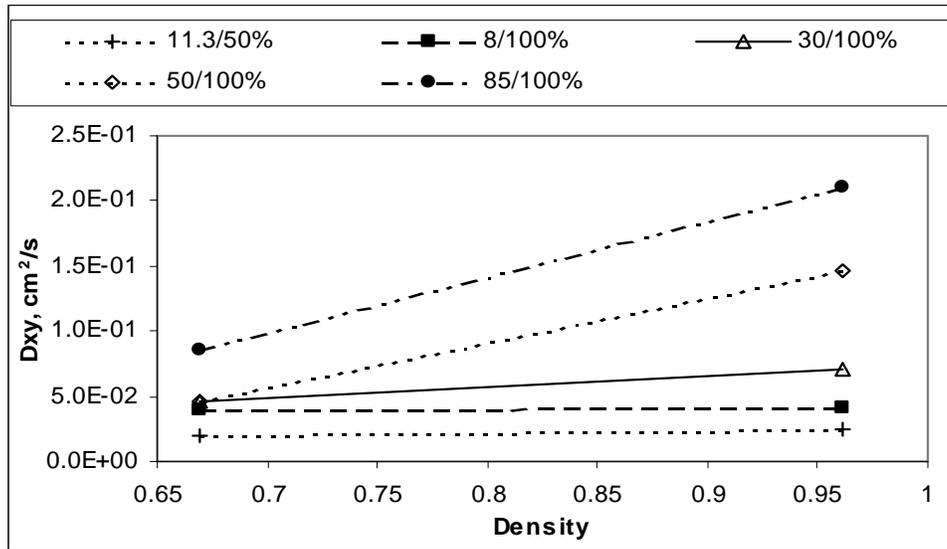


Fig 5.11- Lateral moisture diffusivity measured in MK1 paper with density values before and after calendering. Experiments carried out at several relative humidity.

These results validate the hypothesis that besides pore diffusion the fiber bound diffusion is important, mainly at high relative humidity and even the fibrils angles could be important factors of moisture diffusion. As mentioned in others work the tortuosity of pore formed in the transverse direction of paper is higher than that formed in the lateral direction. This is more evident the most anisotropic is the paper. Besides, the lower tortuosity of the moisture path inside of the fiber in the lateral dimension of the paper compared to the transverse could have great influence on these higher diffusivities.

Lindsay and Brady [28] found that the lateral saturated water permeability is higher than transverse permeability by the same magnitudes, although this difference increases drastically beyond fiber saturation point.

Hamlen [29] explained this by considering a model paper sheet formed by the deposition of fibers in a regular array. The results of Hamlen showed that lateral permeabilities of pores in paper tend to be higher by up to an order of magnitude than transverse values for typical paper structure densities. Only at very high sheet densities do fibers between adjacent layers interfere with each other and affect the lateral tortuosities. Our inference is that lateral diffusivities tend to be higher than transverse ones due to smaller tortuosities in the former compared to the latter dimension. Both these independent experimental and theoretical observations are supportive of our inference that lateral diffusivities tend to be higher than transverse ones due to smaller tortuosities in the former against the latter dimension.

In another experimental set up, the figure 5.12 shows the profile of moisture content through the diffusion path in lateral direction, for all grades of refined paper. The set of sheets are under steady moisture transport in the transverse dimension. We observe that the slopes of the moisture content profiles are steeper for the denser sheets at relative humidity gradient from 50 % to approximately 100 %. This is because denser sheets offer more resistance to diffusion in pores, which is the dominant mechanism in this case. The behavior is similar with the one that occur in transversal direction. Although one would expect steeper moisture content slope, what we believe is diminished due to bound fiber diffusion.

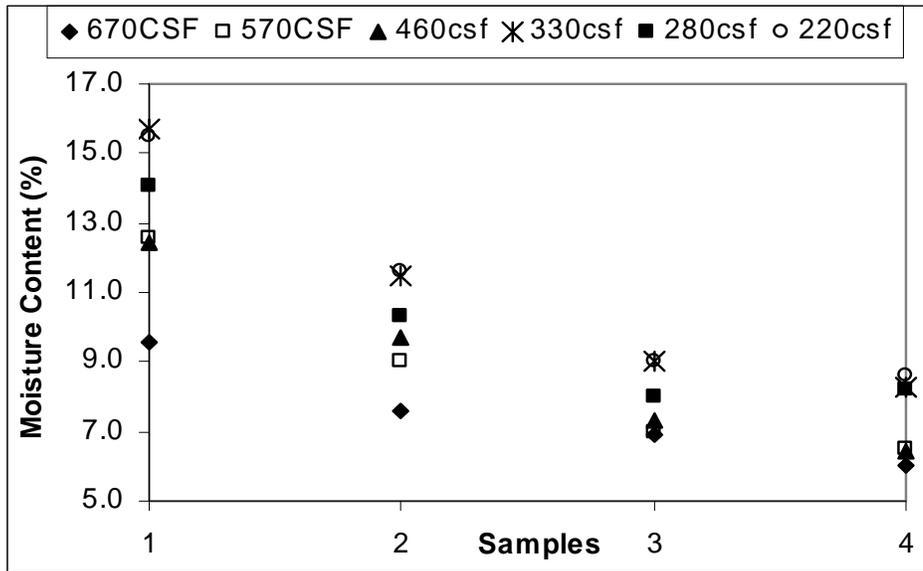


Fig 5.12- Lateral moisture content profile for refined handsheets from Freeness 220 to 670 CSF, at RH 50% inside of humidity chamber

Another experiment carried out was one using n-propanol as penetrant agent, which give us a different approach to understand moisture diffusion in paper. This is because the n-propanol is not adsorbed by cellulose as much as water and a very dominant porous diffusion is expected. Liang et al. [30] used similar experiments for transverse diffusion and have mentioned several works in his paper that support this claim. We conducted both transverse and lateral transport experiments where liquid n-propanol was placed in the diffusion cup assembly and the steady weight loss was measured.

After subtracting the resistances due to diffusion within the air gap and assuming the external convective boundary layer negligible for n-propanol, the diffusivity of n-propanol within the paper sheets was estimated. The diffusivity of n-propanol in air was determined from the Chapman-Enskog equation and the ratio of the effective diffusivity

of n-propanol in the sheets to that of n-propanol in air was determined ($D_{\text{eff,p}}/D_{\text{air,p}}$). The tortuosity of the diffusion path was calculated from the following equation 5.2.

$$\tau_p = \frac{\varepsilon D_{p,a}}{D_{p,\text{eff}}} \quad \text{eq. 5.2}$$

where: (τ_p) is the tortuosity of the sheets for n-propanol diffusion, ($D_{p,a}$) is the diffusivity of n-propanol in air and ($D_{p,\text{eff}}$) is the diffusivity through the sheet.

The corresponding tortuosity for water vapor is given by

$$\tau_w = \frac{\varepsilon D_{w,a}}{D_{w,\text{eff}}} \quad \text{eq. 5.3}$$

where: (τ_w) is the tortuosity of the sheets for water vapor diffusion, ($D_{w,a}$) is the diffusivity of water vapor in air and ($D_{w,\text{eff}}$) is the diffusivity of water vapor through the sheet.

Since the tortuosity is a geometric property of the pore space, it is expected to be independent of the diffusing species but dependent on the direction through the paper sheets for n-propanol. However, since moisture diffuses through both the fiber space and

the pore space, the tortuosity for moisture shows the combined effect and is likely to be different from tortuosity for n-propanol (τ_p).

The tortuosity for n-propanol in the transverse dimension increases with density as indicated in figure 5.11.

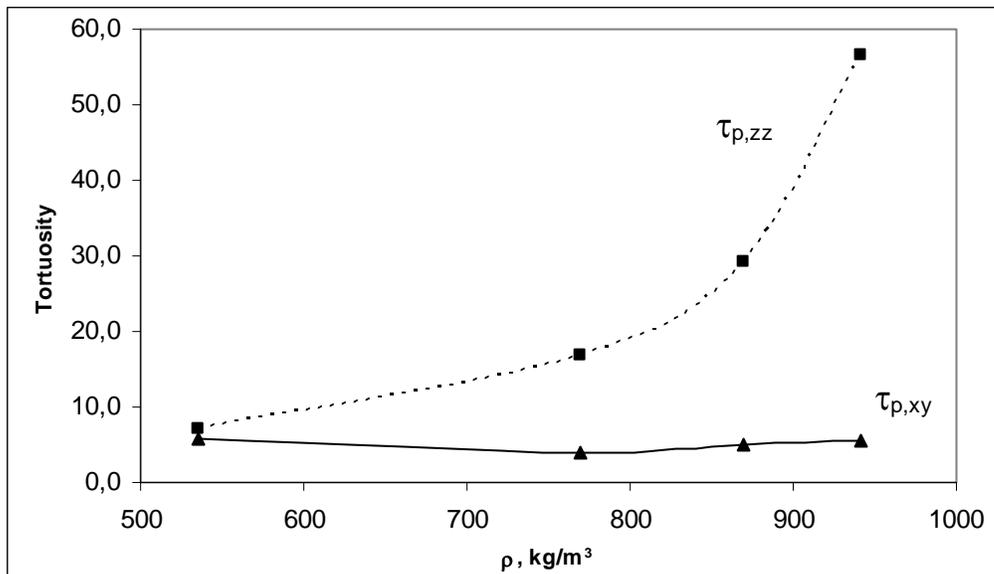


Fig 5.13- Tortuosity calculated through experimental n-propanol diffusivity in Lateral and Transversal directions with bleached kraft paperboard at several densities obtained by refine.

This effect is primarily due to the constriction of the void space and increased path length for diffusion at higher refining levels, therefore due to the lower porosities of these sheets or the decreasing of pore size as effect of refining.

These effects show again the importance of pore diffusion in this direction. The tortuosity in the lateral dimension also increases slightly with density, whereas the dependence is smaller indicating smaller changes in the lateral path lengths for diffusion. Although the first point on lateral diffusivity is certainly displaced. The figure 5.14 shows

the ratio of the tortuosity calculated for water and n-propanol as penetrant in paper. The diffusivities experiments using papers with different densities show also that in transverse direction there is more influence of density on tortuosity rate than at lateral direction. Besides, while in lateral direction this influence is just noticed at densities above 800 kg/m^3 , in transverse direction the ratio increases over the all range of density studied. This is basically due to the diffusivity of n-propanol in paper that is very influenced by the pore distribution and increasing of the path length.

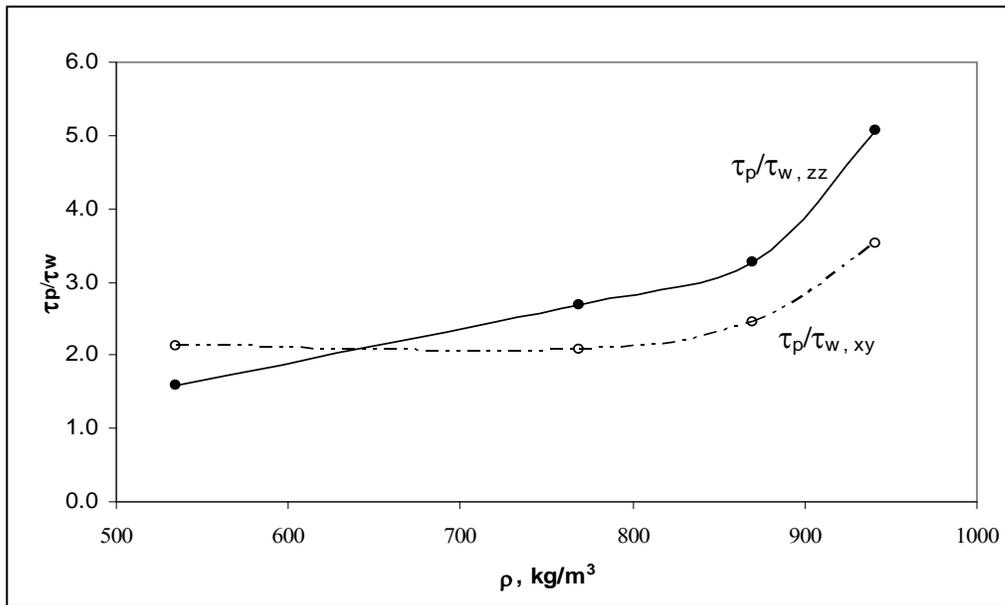


Fig 5.14- Relation between tortuosity calculated using n-propanol and water vapor experimental diffusivities in both directions, lateral and transversal

However, the mechanism of moisture diffusion inside of the fiber wall is also considered important for many authors at high relative humidity. The anisotropy of paper and the characteristics of paper formation suggest that for lateral direction the bound water diffusion in fiber wall is the most important mechanism. Nevertheless, there are two requirements to activate this mechanism: first the close contact among fibers and second the necessary relative humidity that will increase this diffusion exponentially.

In order to confirm this hypothesis that fiber diffusion is a more significant mechanism in the lateral dimension as compared to the transverse dimension, we increased the contacts between fibers by calendering the sheets to different levels.

New samples of Northeast pine bleached kraft pulp were refined to different freeness levels in a Valley beater, in the Department of Paper Science and Engineering, in Syracuse. Handsheets were made in a MK dynamic sheet former, in a 12x12 inches format (0.3048 x 0.3048 m).

A portion of these samples were calendered in a laboratory supercalender equipped with an upper steel nip and a lower fiber roll, at an applied pressure of 1500 PLI with two passes between the nip for each sample.

The effect of calendering in lateral diffusivity with different levels of relative humidity for one of the samples is shown in figure 5.15, which corroborate the increasing of diffusivity with moisture content in paper showed in the figure 5.11. These indicate that the lateral diffusivity increases significantly when subjected to high relative humidity.

More effective contacts among fibers occur in this case and facilitate moisture transfer from one fiber to another. Measurements of the air permeability of these samples showed significant decreases with calendering, indicating reductions in the pore space.

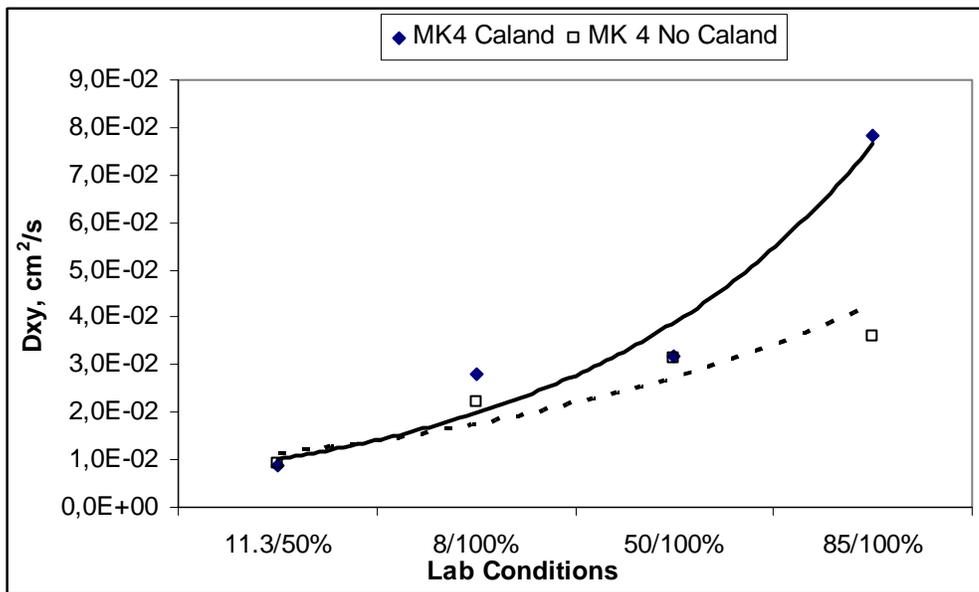


Fig 5.15- Relation between lateral moisture diffusivity in paper and relative humidity gradient conditions through the diffusion path for uncalendered and calendered paper.

This quantity was calculated for diffusion in the lateral direction at different relative humidity conditions. The trend curve for uncalendered sample show increasing of diffusivity In-plane. However, the calendered paper shows a trend line that suggest a higher increment of moisture diffusion that is assumed to be due to increasing of fiber contact.

5.5. Conclusion

In the present chapter were discussed results of experimental investigations exploring particularities of moisture diffusion in paper materials towards the lateral dimensions. Initial results confirmed some published works that moisture diffusivity increase with relative humidity after approximately 50 %. The effect of refining on the pulp was shown primarily in the decreased vapor diffusivity parameter due to the decreased volume fraction and increased tortuosity of the pore space. Thus, most moisture diffusion processes will initially be controlled by the pore space of the sheets and how this responds to changes in external variables.

When the moisture contents of the sheets are not high enough, pore diffusion dominates and pore diffusivity (D_p) controls the moisture transport. This is more evident in transversal direction, probably due to the alignment of fiber during paper formation. At higher moisture content the water diffusivity in fiber dominates the transport phenomena and increases with density, as consequence of connections improvement that facilitates water percolation. However, the refining effect from 559 CSF to 199 CSF shows decreasing of lateral diffusivity, probably because the ratio pore to fiber diffusivity decreased at this density gradient. The calandered paper as well as the experiments with n-propanol corroborates that diffusion in fiber wall have an important role in effective diffusion. This relevance is more evident under higher relative humidity due to more interaction among water clusters, and when the paper has high density due to increasing fibers contact. We can thus extend our thoughts and expect bulkier sheets made of mechanical fibers or recycled fibers will tend to have higher diffusivities as compared to sheets made of more swellable fibers. Furthermore since moisture content is determinant

for the fiber matrix transport, processing operations that decrease the fiber moisture content such as higher lignin levels or hornification will tend to decrease fiber diffusivity.

5.6. References

1. Rashemi S.J., Gomes V.G., Crotofino R.H., Douglas W.J.M., "In-plane Diffusivity of Moisture in Paper", *Drying Technology*, 15(2), 265-294, 1997.
2. Hojjatie B., Abedi J., Coffin D.W., "Quantitative Determination of In-plane Moisture Distribution in Paper by Infrared Thermography", *Tappi J.*, vol 48 (5), 71, 2001.
3. Htun M., "Changes in In-plane Mechanical Properties During Drying of Handsheets", *Tappi J.*, vol. 67 (9), 124-127, 1984.
4. Enomae T. and Lepoutre P., "Surface Roughening by Water: Gloss Relaxation Processes", *J. Pulp Paper Sci.*, vol 22(7), J326-J330, 1997.
5. Forseth T. and Helle T., "Effect of Moistening on Cross-sectional Details of Calandered Paper Containing Mechanical Pulp", *J. Pulp Paper Sci.*, vol 23 (3), J95-J100, 1997.
6. Back E., "The Pore Anisotropy of Paper Products and Fiber Building Boards", *Svensk Papperstidning*, vol 7(15), 219-224, 1966.
7. Lif J.O., Fellers C., Söremark C., Sjö Dahl M., "Characterization of In-plane Hygroexpansivity of Paper by electronic Speckle Photography", *J. Pulp Paper Sci.*, vol 21 (9), J302-J309, 1995.
8. Adams K.L. and Rebenfeld L., "In-plane Flow of Fluids in Fabrics: Structure/Flow Characterization", *Textile Research Journal*, 647-654, November 1987.

9. Horstmann D.H., Lindsay J.D., Stratton R.A., "Using Edge-Flow Tests to Examine the In-plane Anisotropic Permeability of Paper", Tappi J., vol. 74 (4), 241:247, 1991.
10. Lindsay J.D., "The Anisotropic Permeability of Paper", Tappi J., vol. 73 (5), 223-229, 1990.
11. Lindsay J.D. and Brady P.H., "Studies of Anisotropic Permeability with Applications to Water Removal in Fibrous Webs. Part 1: Experimental Methods, Sheet Anisotropy, and Relationships with Freeness", TAPPI Journal vol 76 (9), 119-127, 1993.
12. Lindsay J.D. and Brady P.H., "Studies of Anisotropic Permeability with Applications to Water Removal in Fibrous Webs. Part 2: Water Removal and other Factors affecting Permeability", TAPPI Journal vol 76 (9), 128-127, 1993.
13. Vomhoff H., "On the In-plane Permeability of Water-saturated Fibre Webs", Nordic Pulp and Paper Research Journal, vol 15 (3), 200-204, 2000.
14. Hagglund R., Westerlind B., Gulliksson M., Nordstrand T., "Diffusion of Water Vapour in Paper", AIChE Annual Meeting, Florida, 1998.
15. Pierron F., Poirette Y., Vautrin A., "A Novel Procedure for Identification of 3D Moisture Diffusion Parameters on Thick Composites: Theory, Validation and Experimental Results", Journal of Composite Materials, vol. 36 (19), 2219-2243, 2002.
16. Adams K.L., Miller B., Rebenfeld L., "Forced In-plane of an Epoxy Resin in Fibrous Networks", Polymer Engineering and Science, vol 26 (20), 1434-1441, 1986.
17. Berger B.J., Habeger C.C., "Influences of Non-equilibrium Moisture Conditions on the In-plane, Ultrasonic Stiffness of Cellulose", Journal of Pulp and Paper, vol 15 (5), 160-165, 1989.

18. Forseth T., Helle T., ““Effect of Moistening on Cross-sectional Details of Calandered Paper Containing Mechanical Pulp”, J. Pulp Paper Sci., vol 23 (3), J95-J100, 1997.
19. Gratton M.F., “Three-dimensional Web Deformations from Calendering in a Hard Nip”, TAPPI Journal, vol 80 (4), 210-218, 1997.
20. Goel A., Huang S., Ramaswamy S., Choi D., Ramarao B.V., “ Transverse and In-plane characterization of the pore structure of paper.” APPITA Journal, 2002.
21. Ramaswamy S., Goel A., Choi D., Bandyopadhyay A., Ramarao B. V. “The 3 Dimensional Structure of Paper and its Relationship to Liquid and Vapor Transport.”, Trans. 13th Fundamental Research Symposium on Papermaking and Paper Materials, England PIRA International, Oxford, England, 2001.
22. Massoquete A., Lavrykov S., Ramarao B.V., Goel A., Ramaswamy S., “Behavior of Lateral and Transversal Moisture Diffusion in Paper”, Ind. Eng. Chem.Res., under review, 2004.
23. Ramarao B. V., Massoquete A., Lavrykov S., Ramaswamy S., “Moisture Diffusion Inside Paper Materials in the Hygroscopic Range and Characteristics of Diffusivity Parameters”, Drying Technology, vol 21, (10), 2007-2056, 2003.
24. Massoquete A., Lavrykov S., Ramarao B.V., Goel A., Ramaswamy S., “Anisotropic Moisture Diffusion Study on Refined Paper”, International Paper Physics Conference, Victoria, British Columbia, 2003.
25. Ramarao B.V. and Chatterjee S.G., “Moisture Sorption by Paper Materials under Varying Humidity Conditions”, Trans. 11th Fund. Res. Symp., vol.2, 703-749, Cambridge, UK, 1997.

26. Tan H.S., Pfister W.R., "Pressure –sensitive Adhesives for Transdermal Drug Delivery Systems", PSTT, vol (2), 2, 1999.
27. Goel A., Tzanakakis M., Huang S., Ramaswamy S., Choi D., Ramarao B.V., "Characterization of the 3 Dimensional Structure of Paper using X Ray Microtomography", TAPPI , vol 84 (5), 72, 2001.
28. Lindsay J.D., Brady P.H., "Studies of Anisotropic Premeability with Applications to Water Removal in Fibrous Webs. Part 1 and Part 2", TAPPI Journal, Vol 76 (9), 119-174, 1993.
29. Hamlen R.C., "Paper Structure, Mechanics and Permeability: Computer – Aided Modeling", PhD Thesis University of Minnesota, 1991.
30. Liang B.S., King C.J., "The Mechanisms of Transport of Water and N-propanol Through Pulp and Paper", Drying technology, vol. 8 (4), 641-665, 1990.

CHAPTER VI

THEORETICAL ANALYSIS FOR MOISTURE DIFFUSION ON PAPER MATERIAL

6.1. Introduction

The moisture diffusion in paper in the hygroscopic range has been studied by our group for a while, and the anisotropic aspect of this phenomenon is accounted with the adaptation of the model from transverse to lateral direction. In general, two main types of diffusion models can be recognized. Models of the first type are called Fickian because follow his law, or in other words treat paper as a homogeneous medium with moisture flux that is proportional to the gradient in moisture content. Although useful in some instances this approach fails frequently because it homogenizes the internal dynamics and relaxation processes occurring within the paper material. Previous studies made with

others materials like polymers for example, show that hygroscopic materials, such as paper present the exothermic phenomena of surface absorption. This characteristic and the process of fiber swelling and stress release digress from the moisture diffusion in paper material of the classic Fickian diffusion, as shown in the chapter III.

Our studies have shown that a consistent approach which treats paper as a composite of fibers and void spaces, and consider the diffusion as two paths, is more successful at describing moisture transport dynamics. The parameters appearing in such models can be identified with the physical processes of diffusion through the void space and through the fiber matrix. Diffusivities in these individual phases are supplemented by a local kinetic coefficient representing moisture flux interchange between the void and fiber phases.

In this chapter, it is our intention to analyze steady state diffusion through the paper sheets considering them as homogeneous but anisotropic media. The diffusivity coefficients in the transverse (z) and lateral (xy) dimensions are not equal to each other due to the anisotropic structure of paper. They are denoted by $D_{\text{eff},zz}$ and $D_{\text{eff},xy}$ respectively. The transverse and lateral dimensions are also often referred to as through plane and In-plane dimensions. The experimental set up for studying diffusion described in chapter III will be analyzed to determine how the rate of moisture transport through the paper sheets can be used to determine the individual diffusivities. We identify the important external resistances to moisture transport and quantify their effect on the measured diffusivities.

6.2. Mathematical Model of Steady State Moisture Diffusion in Transverse Direction

Moisture diffusion in paper materials under both steady and unsteady conditions has been the subject of intensive investigations through the years with a relatively slow progress of concepts. Probably the difficulty in define the real interaction between water and paper contribute with this slowness. The early works assumed a homogeneous model of paper and determined overall diffusion coefficients for moisture in many samples. Later works focused on identifying the important mechanisms of transport within the paper sheets and clarifying their interactions during steady and unsteady transport.

Consider the stack of paper sheets shown in Fig 6.1.

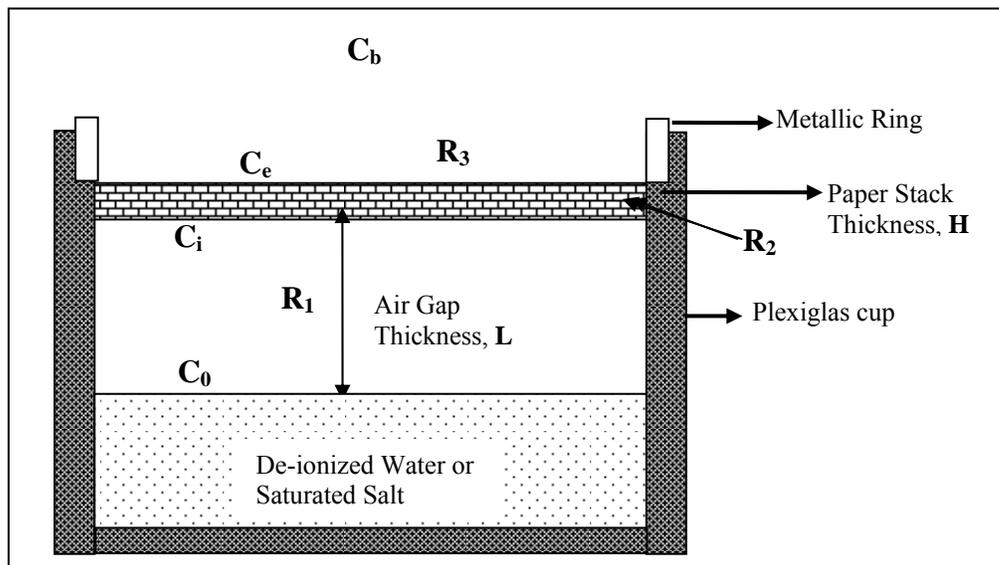


Fig 6.1- Schematic of the diffusion cup that is used for measuring diffusivity in the transverse (z) dimension of paper sheets.

The bottom of the paper stack is exposed to the air space between the surface of the liquid and the paper samples. If the liquid surface is denoted by ($z = 0$), the concentration of water vapor in the air at this position is given by (C_0).

The following equation can be used to determine the concentration of water vapor in air from the relative humidity, (h).

$$c = \frac{h}{RT} p_{sat}(T) \quad \text{eq. 6.1}$$

Where: (c) is the concentration (kgmol/m^3), (h) is the relative humidity given as a fraction, ($0 \leq h \leq 1$), ($p_{sat}(T)$) is the saturation vapor pressure of water (Pa) and temperature is (T (K)).

When the liquid in the diffusion cup is pure water, the relative humidity is 100% ($h = 1$). Saturated salt solutions could be used to obtain different humidity conditions within the air space in the diffusion cup. In the present work the only saturated salt solution used was with Lithium Chloride (LiCl), which gives a relative humidity of 11.3 % under saturated conditions.

We assume that stagnant moisture diffusion is dominant within the air space and ignore the contribution of natural convection due to concentration differences between the top and bottom of this air space. The one dimensional steady state diffusion equation for transport within the paper sheets is written as:

$$\frac{dj_w}{dz} = \frac{d}{dz} \left(D_{eff,zz} \frac{dc}{dz} \right) = 0 \quad \text{eq. 6.2}$$

The concentration of water assumed to be in vapor form is (c) and the water flux is (j_w) at position (z). This equation shows that the water flux (j_w) is independent of position (z) under steady state conditions. The solution of this differential equation is given by

$$c = K_1 z + K_2 \quad \text{eq. 6.3}$$

The constants (K_1) and (K_2) can be determined by applying the conditions that at the bottom of the stack the water vapor concentration is given by (C_i) and that at the top is (C_e).

The final result is

$$c = C_i + (C_e - C_i) \left[\frac{1}{H} z - \frac{L}{H} \right] \quad \text{eq. 6.4}$$

The solution given in eq. 6.4 shows that the concentration profile is linear within the sheets. The water flux is given by $(-D_{eff,zz}dc/dz)$ as follows.

$$j_w = D_{eff,zz} \frac{(C_i - C_e)}{H} \quad \text{eq. 6.5}$$

We can represent moisture transport as a moisture current, given by dw/dt , and identify an equivalent resistance diagram relating the resistances shown in Fig 6.1 and named (R_1) , (R_2) and (R_3) .

The mass transfer resistances are defined as the ratio of the driving forces (i.e. concentration differences) to the flux. Thus,

$$R_2 = \frac{(C_i - C_e)}{j_w} = \frac{H}{D_{eff,zz}} \quad \text{eq. 6.6}$$

We observe that there are three resistances to moisture transport, all acting in series. The first is the diffusion resistance of water vapor in the air phase, denoted by

(R_1). The second is the diffusion resistance within the stack of paper sheets (R_2) and the third is the mass transfer resistance within the air adjacent to the stack's top surface (R_3).

The mass transfer resistance occurs within a concentration boundary layer set up in the air flow environment. This resistance decreases with increasing air velocity and can be minimized by providing strong air circulation within the chamber.

The resistances to transport (R_1) and (R_2) can be written as below from conventional theory of diffusion and convective mass transfer in air.

$$R_1 = \frac{L}{D_{w,a}} \quad \text{eq. 6.7}$$

$$R_3 = \frac{1}{k_f} \quad \text{eq. 6.8}$$

Therefore, the total resistance is the sum of the three individual transport resistances since they occur in series. This is given by

$$R_t = R_1 + R_2 + R_3 = \frac{L}{D_{w,a}} + \frac{H}{D_{eff,zz}} + \frac{1}{k_f} \quad \text{eq. 6.9}$$

Since the moisture flux is the ratio of the overall driving force, $(c_0 - c_b)$ is to the total resistance of the transfer path, and then the following equation can be written.

$$j_w = \frac{c_0 - c_b}{R_t} = \frac{c_0 - c_b}{\frac{L}{D_{w,a}} + \frac{H}{D_{eff,zz}} + \frac{1}{k_f}} \quad \text{eq. 6.10}$$

From this equation, the relation between the diffusivity $D_{eff,zz}$ and the measured water flux can be written as

$$D_{eff,zz} = \frac{H}{\frac{(c_0 - c_b)}{j_w} - \frac{1}{k_f} - \frac{L}{D_w}} \quad \text{eq. 6.11}$$

This equation incorporates the effects of the diffusion resistance within the air gap (R_1) and the convective resistance in the concentration boundary layer adjacent to the top surface of the samples, (R_3). The exact values of these resistances cannot be measured accurately. Both (R_1) and (R_3) will be subject to uncertainties. (R_1) will be affected by natural convection within the air gap and (R_3) will be affected by the interaction between the surface of the paper sheets, the air flow within the chamber, and the thermodynamics of sorption. In a later section we provide an analysis of the effect of errors in these resistances on the diffusivity calculations.

Moisture can diffuse through paper by a variety of mechanisms, which have been hypothesized for several authors. Nissan [1] made an interesting analysis and identified the following mechanisms: water vapor diffusion through the void spaces, moisture transport in condensed phase through the cell wall, Knudsen diffusion through intra-fiber and inter-fiber pore spaces, surface diffusion along the fiber-void interfaces and liquid water transport caused by capillary action along intra-fiber and inter-fiber pores. Another well focused review on this relation of moisture transport mechanisms is provided by Hashemi et al. [2].

Radhakrishnan et al. [3, 4] analyzed steady state moisture transport in stacks of bleached kraft paperboard using a diffusion cup apparatus. An effective diffusivity was defined by the ratio of the moisture flux to the total water vapor concentration gradient and was found to be an increasing function of average relative humidity of the stack. The moisture transport was considered to occur in two pathways, one through the void space in the form of water vapor and the other through the fiber matrix in the form of

condensed water can explain this variation as shown by them. The resulting total moisture flux can be represented as that due to diffusion in along the two paths as:

$$\dot{j}_{\text{tot}} = \dot{j}_p + \dot{j}_q = -D_p \frac{dc}{dz} - \rho_p D_q(q) \frac{dq}{dz} \quad \text{eq. 6.12}$$

Where: (c) is concentration of moisture in vapor, (q) is moisture concentration in paper and (ρ_p) is paper density.

The authors used the following equation for the diffusivity of moisture through the fiber space based on similar forms used for transient diffusion used in earlier work.

$$D_q(q) = D_{q0} e^{mq} \quad \text{eq. 6.13}$$

Where: (D_{q0}) is reference bound water diffusivity within the fiber matrix and (m) is the coefficient of the rate of change of this diffusivity with moisture content.

The effective diffusivity was defined by the following equation.

$$D_{\text{eff}} = \frac{\dot{j}_{\text{tot}}}{(c_1 - c_0)} \quad \text{eq. 6.14}$$

The effective diffusivity can also be related to the diffusivities in the individual pathways (D_p) and (D_q). Note that at steady state, the net moisture flux (\dot{j}_{tot}) is invariant with position along the thickness of the sheet. Thus,

$$\frac{d\dot{j}_{\text{tot}}}{dz} = 0 \quad \text{eq. 6.15}$$

By integrating this equation with respect to (z) over the sheet thickness (L) and assuming that the fiber moisture contents on either side are given by (q_1) and (q_0), we obtain for the effective diffusivity,

$$D_{\text{eff}} = D_p + \frac{\rho_p D_{q0}}{m} \frac{(e^{mq1} - e^{mq0})}{(c_1 - c_0)} \quad \text{eq. 6.16}$$

For more details of this derivation, please see Radhakrishnan et al. [3, 4] and Bandyopadhyay et al. [5,6], which are precursors of the present work. The majority of the research seems to indicate an increase in diffusivity as moisture content increases in the higher hygroscopic range. At very high humidities or sufficiently high moisture contents, data from various sources indicate a saturation trend and the diffusivities approaching constant values. A rationalization of these contradictory trends can be made by viewing moisture transport as a composite of diffusion phenomena through the two phases, void pores and fiber matrix. Diffusion through the void space would be restricted at high moisture contents due to the crowding of the pore space by the swelling fibers. This would increase the tortuosity for vapor phase diffusion while reducing the pore space, both effects tending to reduce the vapor phase diffusivity and the effective diffusivity as consequence. Diffusion through the fiber matrix, including surface and capillary phenomena, would increase with moisture content due to increased moisture solvation or mobility. This increment of moisture increases the clusters of moisture which eventually become connected and facilitate the moisture diffusion up to the saturation point. Increased contact between fibers and increased fiber space would be other contributing factors.

6.3. Steady State Diffusion in the Lateral Dimension

Let us consider the case of diffusion in the lateral or In-plane dimensions of paper. For this purpose, we measured the steady state moisture loss from paper sheets in the configuration shown in Fig 6.2.

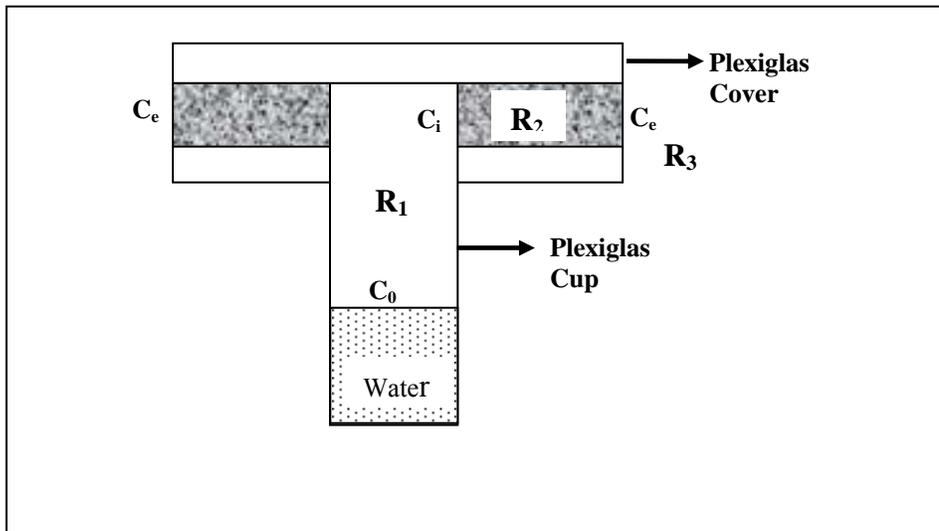


Fig 6.2- Schematic of the diffusion cup that is used for measuring diffusivity in the Lateral (xy) dimension of paper sheets measurements provide transient and steady state moisture fluxes.

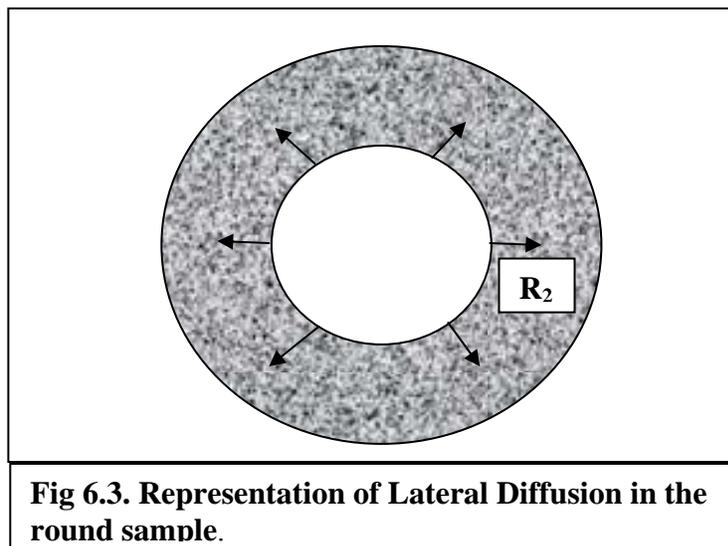
Radial diffusion pertains in this situation and the transport path for moisture can be idealized by a set of three resistances in series as represented in Fig 6.2 as (R_1) , (R_2) and (R_3) .

As water vapor diffuses through the air gap, a two dimensional concentration field is set up. However, the effect of two-dimensionality may be neglected if the ratio of the sample height (H) to the air gap length is (L) is small ($H/L \ll 1$). Thus, the diffusion resistance within the air gap is approximated by the formula given in eq. (6.7). Similarly, the convective resistance within the air boundary layer is represented by eq. (6.8) and the mass transfer coefficient, (k_f).

For practical purposes, we assumed the same value of the transfer coefficient (k_f) as in the transverse case. The actual (k_f) value is likely to be somewhat and thus increase the resistance (R_3). However, this increase is not significant and it is likely that errors in the other measurements will contribute to the uncertainty in the overall diffusivity measurements than this transport coefficient.

In-plane diffusion through the paper sheets occurs along the radial dimension as long as the sheets are isotropic in the (xy) plane. The handsheet samples we chose for our analysis were isotropic and therefore axisymmetry in diffusion is expected.

Fig 6.3 shows a schematic of the diffusion within the plane.



The steady state diffusion equation in polar coordinates is given by

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c}{\partial \theta^2} = 0 \quad \text{eq. 6.17}$$

Since the concentration (c) is not expected to depend on the angular coordinate (θ), the third term in the above equation vanishes and (c) is a function of only the radial coordinate, (r). The partial derivatives with respect to (r) can be replaced by the total derivatives and eq. 6.17 can be rewritten as

$$\frac{d^2 c}{dr^2} + \frac{1}{r} \frac{dc}{dr} = 0 \quad \text{eq. 6.18}$$

Upon solving this differential equation for (c), by applying the conditions that the concentration on the inner surface of the sheets is (C_1), and that on the outer surface is (C_2), we obtain the following profile for (c).

$$\frac{c - C_1}{C_2 - C_1} = \frac{\ln(r / r_1)}{\ln(r_2 / r_1)} \quad \text{eq. 6.19}$$

The rate of moisture transport is given by

$$\frac{dW}{dt} = 2\pi D_{eff,xy} H \frac{(C_1 - C_2)}{\ln(r_2 / r_1)} \quad \text{eq. 6.20}$$

The diffusion resistance in the planar dimension (xy) is therefore

$$R_2 = \frac{\ln(r_2 / r_1)}{2\pi H D_{eff,xy}} \quad \text{eq. 6.21}$$

We can obtain the following equation relating the diffusivity $D_{eff,xy}$ with the moisture transport rate and other resistance parameters in an analogous manner to eq. 6.11 in the previous section.

$$D_{eff,xy} = \frac{\ln(r_2 / r_1)}{2\pi h} \frac{1}{\left(\frac{c_0 - c_b}{\frac{dW}{dt}} - \frac{L}{D_w \cdot \pi r_1^2} - \frac{1}{k_f \cdot 2\pi r_2 \cdot h} \right)} \quad \text{eq. 6.22}$$

The equation 6.22 defines the calculations of effective diffusivity in lateral direction, considering the three resistances mentioned before.

6.4. Effect of papermaking parameters on moisture transport in paper

The effect of typical papermaking variables on moisture migration is necessary to understand how the moisture response may be estimated and more importantly controlled in the final product. Knowledge of how moisture transport is affected will also be of help in tuning the papermaking process to achieve optimal production.

Moisture transport in paper can be considered by using the effective diffusivity (D_{eff}) as a suitable composite parameter. Understanding how the components of (D_{eff}) change as papermaking variables are altered will enable us to estimate moisture migration and its effects in paper.

6.5. Effect of Sheet Density – Refining, Calendering

The first critical parameter effecting moisture diffusivity is sheet structure that may change according with density, refining and calendering. However, since paper sheets could be substantially heterogeneous due to flocculation and such effects, sheet density is to be considered only in an averaged sense. It is established that the effective diffusivity decreases as a function of sheet density Nilsson and Stenstrom [7] and Massoquete et al. [8]. The major cause seems to be the sharp decrease in porosity and increase in tortuosity of paper sheets resulting in small values of the pore diffusivity component, (D_p). Higher sheet density can be caused by higher levels of wet pressing or vacuum application and calendering of the sheets. An important effect seems to be that of refining of fibers, although others factors are involved in this process of densification.

6.6. Effect of Chemical and Structural Characteristics of Fibers

There is sufficient data in the literature for us to draw some broad conclusions and estimate how the nature of the fiber changes moisture transmission response of paper sheets. First we note that fiber morphology and chemical nature in its native state is a critical factor in determining its behavior in the papermaking process. Therefore, factors such as its conformability, swelling, fines and surface structure tend to dictate the nature of the formed sheet. Thus the critical parameter (D_p) representing diffusion of water vapor in the void space is effected by the nature of the fibers indirectly but significantly.

For instance, paper containing thermo mechanical pulp (TMP) or other mechanical pulps is generally more porous and bulky leading to higher (D_p) values. However, the lignin is a hydrophobic component and therefore a barrier for moisture diffusion. Similar remarks would be true for recycled paper sheets made of kraft fibers. Thus, the nature of the fibers needs to be accounted in considering the diffusivity of moisture inside paper sheets even in the vapor form. In brief, we can expect that any parameter which tends to make the sheets more porous, bulky or pore space less tortuous tends to increase pore diffusivity. Therefore pore diffusivity is expected to increase with recycling and with higher lignin content fibers or high yield pulps.

Condensed phase diffusivity is a different issue altogether though. In order to project the effect of the nature and composition of fibers on (D_q), one has to refer to a theoretical model. For example, a typical high yield fiber is rigid and nonporous. The cell wall may not contain a substantial nanoporous network as can be expected for a bleached kraft pulp. In such a case internal migration of moisture may be hindered because the wicking mechanism may be inoperative or substantially slowed. Note here that for the wicking mechanism to convey moisture, both the wetting characteristic and the permeability of the nanoporous structure must be favorable. Since high yield fibers contain significant lignin, both of these factors would be affected adversely. On the other hand, it is possible that the surface adsorption and surface diffusion of moisture is higher for lignin containing pulps. Therefore, one would expect some type of a cross-over of mechanisms of diffusion between fibers pulped by different processes. Another significant feature of diffusion in the internal of fibers is the orientation of the microfibrils along the lamellae in the cell wall. One would expect that for acute

microfibrillar angles, moisture diffusion inside the cell wall is enhanced along the axial direction of the fibers. Diffusion in other orthogonal directions may not be affected or adversely effected by this angle. Furthermore, the water absorbing capability of the fibers themselves can be expected to be critical. Whether one views this from an increased free volume point of view or due to increased cluster mobility, the conclusion would be the same. Therefore, bleached softwood kraft pulps refined well would tend to have high moisture diffusivities.

6.7. Conclusion

Moisture transport in paper materials tends to be quite complex and occurs by a number of mechanisms. These include diffusion as vapor in the void space and diffusion/migration through the bulk of the fiber cell wall. It is possible to group all the diffusion mechanisms into two groups, identifying each one as occurring through the void spaces or the fiber matrix. Thus, the internal void/fiber structure of these materials becomes a critical factor in determining transport. This same approach could be considered for both direction of diffusion, lateral and transverse. Therefore, considering the lateral diffusion uni-dimensional through the radius dimension, the association of lateral and transverse moisture diffusion is quite simple.

The parameter referred to moisture diffusion in fiber wall incorporated in the models used to solve our diffusion problem is the fiber mass transfer coefficient (k_i). This parameter takes in consideration the moisture diffusion in direction of the fiber thickness. However, it does not incorporate possible variability through the fiber wall. Nevertheless,

the fiber mass transfer coefficient determines a Non-fickian model for mass transfer diffusion, which is proofed to be correct as shown in chapter III. Diffusivity through the cell wall can be expected to be anisotropic and intimately influenced by the ultra-structure of the cell wall, its porosity, the connectivity of the nanopores inside it and the availability of water reactive sites. MRI techniques have provided some fascinating glimpses into how this transport can be studied. More work on characterizing the dependence of intra-fiber moisture transport on the cell wall chemical nature and physical structure needs to be done.

6.8. References

1. Nissan, 1975.
2. Hashemi S. J., Gomes V. G., Crotogino R. H., Douglas W. J. M., “In-Plane diffusivity of moisture in paper”, *Drying Technology*, vol 15, 2, 265-294, 1997.
3. Radhakrishnan H., Chatterjee S. G., Ramarao B. V., “Moisture Transport Through a Bleached Kraft Paperboard Stack in a Diffusion cup Apparatus”, *ESPRA Research Report No. 109*, 63-74, 1998.
4. Radhakrishnan H., Chatterjee S. G., Ramarao, B. V., “Steady-State Moisture Transport in a Bleached Kraft Paperboard Stack”, *Journal Pulp Paper Science*, vol 26, 4, 140-144, 2000.
5. Bandyopadhyay A., Radhakrishnan H., Ramarao B.V., Chatterjee S.G., “Transient Moisture Sorption of Paper Subjected to Ramp Humidity Changes: Modeling and Experiments”, *Ind. and Engng. Chem. Res.*, vol 39, 1, 219-226, 2000.
6. Bandyopadhyay A., Ramarao B.V., Ramaswamy S., “Transient Moisture Diffusion through Paperboard Materials”, *Colloids and Surfaces, A: Physicochem. Engng. Aspects*, 206, 455-467, 2002.

7. Nilsson L., Stenstrom S., "Gas Diffusion Through Sheets of Fibrous Porous Media", Chem. Engng. Sci., 50, 3, 361-374, 1995.
8. Massoquete A., Lavrykov S., Ramarao B.V., Goel A., Ramaswamy S., "Anisotropic Moisture Diffusion Study on Refined Paper", International Paper Physics Conference, Victoria, British Columbia, 2003.

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