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DIFFUSION CONTROLLED KINETICS OF ELECTROLYTE TRANSFER WITHIN THE PULP FIBER WALL: ESTIMATION OF FIBER WALL PORE STRUCTURE

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ABSTRACT

A kinetic model for diffusion of ions within the fiber wall is introduced. A good fit for the model was obtained with data from experiments, where diffusion of electrolyte through the fiber wall was studied by means of simple conductivity measurements. This model together with the respective experimental data makes it possible to study the pore structure of fibers.

For the experiments done, the pore structure of fibers was first controlled by precipitating calcium carbonate within the fiber walls. It was found, that the diffusion coefficient of ions within unfilled and calcium carbonate filled fiber wall was about 1.5 and 0.5 % of that in water, respectively, when experiments were done for fibers without pit apertures. Experiments were made for fibers with different degree of drying as well. The results showed that the diffusion of electrolyte reduced with replicate dryings as expected. After the dryings, the diffusion coefficient was less than half of that within newer dried fiber.

INTRODUCTION

Physical and chemical treatments during papermaking processes have certain effects on fiber wall. In chemical pulping and bleaching the pore structure of fiber wall is altered through dissolution of lignin and other compounds. Fiber hornification which occurs during drying has also an distinctive impact on fiber pore structure through changes in intrafiber bonding. Fiber refining causes internal changes of fibers as well.

Some methods to detect these changes have been introduced and used. A well known method uses the principle of fiber swelling in water, and it is based on the measure of water retention in pulp. Fiber swelling increases the diameter of fiber which can also be measured by microscopic techniques (1). Other methods can be used as a more or less direct measure of fiber pore volume. Exclusion method (2) uses spherical molecules with different size to detect the fiber wall pore size distribution. Furthermore, we can also measure the adsorption of either nitrogen (3) or mercury (4) within the fiber wall.

The new method introduced in this study is based on the fact that mass transfer rate of chemical substances inside the fiber wall changes with fiber pore structure. Many studies concerning diffusion of different substances through wood have been published during the last twenty five years. For example estimation of diffusion of wood preservatives (5), water (6), and pulping chemicals (7) has been investigated. However, diffusion inside the cell wall of pulp fibers has not been studied extensively.

The aim of this study is to present a theoretical model for diffusion of ions within the cell wall of pulp fibers suspended in water. With the aid of this model and with a modest amount of experimental data one can determine the diffusion coefficients of ions inside the cell wall. Furthermore, the measured diffusion coefficients can be linked to the characteristics of the fiber wall pore structure. The experimental data interpreted by this model may also give valuable information about the intrafiber mass transfer taking place during the pulping and bleaching.

THEORY

As the fiber radius is small the diffusion through a fiber wall is rapid and the experimental method for studying this phenomena must be fast enough to give reliable data. However, one can imagine that handling of a single fiber is awkward because of the small dimensions of fibers. We therefore decided to study the diffusion with a known amount of fibers suspended in water and to assume that the diffusion coefficient within the fiber wall of separate fibers remains constant. Furthermore we wanted to establish a method, which overlooks completely the interfiber diffusion between the fibers unlike other known methods (8,9), and which takes into account only intrafiber diffusion.

In order to perform these experiments, the fibers were thoroughly saturated with concentrated electrolyte solution and then pressed until no external solution was present. At the beginning of each experiment the fibers were placed into a small vessel of deionized water provided with efficient stirring. The diffusion was followed by measuring the conductivity of solution outside the fibers as a function of time.

Because the process is rather fast and t = 0 of each measurement is difficult to set accurately, we decided to search a transfer function to describe accurately the dynamic response of our measuring system (stirring, vessel geometry, dynamic response of the conductivity sensor etc.). A detailed description on the application of this transfer function is presented later in this paper.

The mathematical solution of the diffusion problem for an infinite cylinder which in practice describes a fiber of arbitrary length in which diffusion takes place solely through the fiber wall can be found in literature (10). In our model fiber radius R is assumed constant and fiber length L >> R.

When the fiber length is assumed infinite and the concentration of ions zero at the outer surface of fiber (r=R), the time dependent radial diffusion through fiber wall can be described by Fick's second law in cylindrical coordinate system:

$$\frac{\partial C}{\partial t} = D(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r}), \quad 0 \le r \le R$$
(1)

where C is the concentration of electrolyte within fibers, t the time, D the diffusion coefficient of electrolyte within the fiber wall, r the distance from the symmetry axis of fiber, and R is the fiber radius.

Eq. (1) can be solved for the following initial and boundary conditions (10):

$$C = C_{max}$$
, when $0 \le r \le R$ and $t = 0$ (2a)

$$C = 0, \text{ when } r = R \tag{2b}$$

$$\frac{\partial C}{\partial r} = 0$$
, when $r = 0$ (2c)

The initial condition (2a) provides homogeneous distribution of concentrated electrolyte within the fibers before each experiment is started. The boundary condition (2b) can be stated only if stirring of fiber suspension is effective and/or the diffusion coefficient of the electrolyte is much larger in water than within the fiber wall. Finally, the boundary condition (2c) provides that the fibers are symmetrical and unbroken.

If we assume effective mixing of the fiber suspension and that the radius of fibers is constant, we can write Fick's first law for the molar flow of electrolyte through the fiber wall as follows

$$\dot{n} = AJ = -AD \left(\frac{\partial C}{\partial r}\right)_{r=R}$$
(3)

where n is the molar flow of electrolyte through the fiber wall, J the molar flux of electrolyte through the fiber wall, and A is the total surface area of fibers.

If we make the substitution $C = e^{-D\alpha^2 t} u(r)$, where u(r) is a function of r only, we get from Eq. (1)

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \alpha^2 u = 0$$
⁽⁴⁾

which is Bessel's differential equation of order zero.

As the solution of the second kind of Eq. (4) is infinite at r = 0, the solution is given solely by

$$C = a J_0(\alpha r) e^{-D\alpha^2 t}$$
⁽⁵⁾

where J_0 is the Bessel function of order zero of the first kind.

To satisfy the boundary condition (2b) α must be a root of Eq. (6).

$$J_0\left(\alpha R\right) = 0 \tag{6}$$

This equation has no complex or repeated roots, but has an infinite number of real positive roots. Thus, the solution of Eq. (4) can be given by the series expansion of Eq. (7).

$$C = \sum_{n=1}^{\infty} a_n J_0(\alpha_n r) e^{-D\alpha_n^2 r}$$
(7)

where *n* is the index corresponding to n'th root of Eq. (6) and a_n is the coefficient of n'th term.

The constants a_n in Eq. (7) can be determined from the initial condition of Eq. (2a)

$$C_{\max} = \sum_{n=1}^{\infty} a_n J_0(\alpha_n r)$$
(8)

If we use the theorem of orthogonal functions and substitute integration for summation, we obtain for the constants a_n (11)

$$a_n = \frac{2C_{\max}}{R\alpha_n J_1(\alpha_n R)}$$
(9)

where J_1 is the first order Bessel function of the first kind.

After substitution of the constants a_n into Eq. (7) and by using definition $\beta_n = \alpha_n R$ we obtain

$$C = 2C_{\max} \sum_{n=1}^{\infty} \frac{J_0(\beta_n r / R)}{\beta_n J_1(\beta_n)} - e^{-\beta_n^2 D t / R^2}$$
(10)

where β_n according to Eq. (6) is the n'th root of Equation $J_0(\beta_n) = 0$.

If we differentiate C with respect to r, we get on the fiber surface (r = R)

$$\left(\frac{\partial C}{\partial r}\right)_{r=R} = \frac{-2C_{\max}}{R} \sum_{n=1}^{\infty} e^{-\beta \frac{2}{n}Dt/R^2}$$
(11)

The concentration of electrolyte in the water phase of the fiber suspension C_{s}^{*} can now be calculated from Eq. (12).

$$C_{S}^{\star} = \frac{\int_{0}^{t} dt}{V_{H_{2}O}}$$
(12)

where V_{H2O} is the volume of the suspension.

If we substitute Eq. (11) into Eq. (3) and combine the resulting equation with Eq. (12), we get after integration

$$C_{S}^{*} = \frac{2AC_{\max}R}{V_{H_{2}O}} \sum_{n=1}^{\infty} \frac{1}{\beta_{n}^{2}} (1 - e^{-\beta_{n}^{2}Dt/R^{2}})$$
(13)

Eq. (13) gives the theoretical concentration of electrolyte in the water phase at different times of the diffusion experiment.

As mentioned earlier, we want to describe the dynamics of the measuring system with a transfer function in order to enhance accuracy. For this we use linear concept of transfer functions, i.e., describe the transfer function G in Laplaceplane by Eq. (14).

$$f_{out}(s) = G(s) f_{in}(s)$$
(14)

where $f_{in}(s)$ is the Laplace transform of the theoretical concentration of electrolyte in water phase, i.e., $f_{in}(s) = C_s(s) = L\{C_s(t)\}$, where L is the Laplace operator. $f_{out}(s)$ is the Laplace transform of the measured concentration of electrolyte in water phase, $f_{out}(s) = C_s(s) = L\{C_s(t)\}$. G (s) is the transfer function which describes the system's dynamic behaviour satisfactorily.

The transfer function can be obtained from an experiment where no pulp is used in the system but concentrated electrolyte is added to the measurement vessel at t = 0. For this case the shapes of the functions $f_{in}(t)$ and $f_{out}(t)$ are given schematically in Fig. 1.



Fig. 1. The shapes of functions $f_{in}(t)$ and $f_{out}(t)$ in an experiment where no pulp is used in the system and instead concentrated electrolyte is added at t = 0.

$$f_{in}(t) = 1$$
, when t > 0 (15 a)

$$f_{out}(t) = 1 - e^{-(t-T)/k}$$
, when t > T (15 b)

where k is the time constant and T length of time delay.

By finding Laplace transforms for Eq. (15a) and (15b) and placing the results into Eq. (14), and moreover by solving G(s), we obtain

$$G(s) = \left(\frac{\frac{1}{k}}{s + \frac{1}{k}}\right)e^{-Ts}$$
(16)

Next we consider experiments made by adding pulp in the measuring vessel at t = 0.

When we substitute $B = \frac{2AC_{\max}R}{V_{H_2O}}$ and $\gamma_n = \frac{D\beta_n^2}{R^2}$, we can find the Laplace-transform for C^{*}_S given in Eq. (13) as follows

$$f_m(s) = B \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \left(\frac{1}{s} - \frac{1}{s + \gamma_n} \right)$$
(17)

Substituting Eqs. (16) and (17) into Eq. (14) gives

$$f_{out}(s) = Be^{-Ts} \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \left(\frac{\frac{1}{k}}{s+\frac{1}{k}} \right) \left(\frac{\gamma_n}{s(s+\gamma_n)} \right)$$
(18)

Finally, if we put u = t - T, take the inverse Laplace transform of Eq. (18), and divide the left side of the resulting equation by the term $C_{S(max)}(u)$, we get

$$\frac{C_{S}(u)}{C_{S(\max)}(u)} = B \sum_{n=1}^{\infty} \frac{1}{\beta_{n}^{2}} \left[1 + \left(\frac{\gamma_{n}}{\frac{1}{k} - \gamma_{n}} \right) e^{\left(\frac{-u}{k} \right)} - \left(\frac{\frac{1}{k}}{\frac{1}{k} - \gamma_{n}} \right) e^{-\gamma_{n} u} \right]$$
(19)

where $C_S(u) = f_{out}(u)$ and $C_{S(max)}(u)$ describes the concentration in the plateau region at the end of each experiment. The left hand side of Eq. (19) can now conveniently be considered as relative concentration.

In this study seven first terms of Eq. (19) were found to adequately describe our experimental data. First ten roots of Equation $J_{\theta}(\beta_n) = 0$ are as follows (13):

 $\beta_1 = 2.40483, \beta_2 = 5.52009, \beta_3 = 8.65373, \beta_4 = 11.79153, \beta_5 = 14.93092, \beta_6 = 18.07106, \beta_7 = 21.21164, \beta_8 = 24.35247, \beta_9 = 27.49348, \beta_{10} = 30.63461.$

EXPERIMENTAL

Materials

Unbeaten never dried Birch TCF pulp was first selected for diffusion measurements. This pulp was selected because of special interest in it. Moreover, it does not have pit apertures like softwood pulp does and thus better fulfills the requirements of the mathematical model.

Diffusion experiments were also made with the fiber wall loaded pulp containing 10 % calcium carbonate. The fiber wall loading was achieved by a precipitation process which utilizes the reaction between calcium hydroxide and carbon dioxide.

According to SEM images and confocal laser microscopy the average diameter of fibers used in this study was approximately 30 μ m and 35 μ m, when fibers were dryed and suspended in water, respectively.

Potassium chloride (Merck, p.a.) was used in these experiments as model electrolyte.

Apparatus and Measurements

All measurements were done in a thermostated vessel at 5 $^{\circ}$ C with a liquid volume of 500 ml provided with effective stirring. A schematic of the apparatus is shown in Fig. 2.



Fig. 2. Schematic setup of the apparatus used for the diffusion measurements. T₁ = thermostat filled with ice water for controlling temperature of the cooling circulation of thermostat T₂, T₂ = thermostat for controlling temparature of measurement vessel to 5 °C, T = temperature gauge, K = conductivity gauge.

The stirring rate was 750 1/min and the hydrodynamic conditions in each experiment were kept as constant as possible.

In order to determine the time delay T and time constant k which originate from small errors in starting data collecting at t = 0 and dynamic effects of mixing and conductivity monitoring, conductivity of water where 3M KCl solution was added at t = 0 was first measured. The total amount of KCl added was set to the same level as in experiments using fibers.

To obtain the electrolyte diffusion coefficients the fibers were first thoroughly saturated with 3 M KCl solution and pressed until the fibers did not contain any external solution. At t = 0 a sample of fibers were placed into the measurement vessel and suspended instantly with stirring. The increase of KCl concentration outside the fibers was followed by measuring the conductivity of solution with

respect to time. It is generally known, that concentration and conductivity are almost directly proportional in dilute solutions. The diffusion coefficients of KCl inside the cell wall were calculated from the concentration curve as described in the Theory section.

Preliminary experiments showed that fiber consistency had no effect on the diffusion coefficients. In the actual measurements the amount of fibers in each measurements was 0.25 g O.D. Experiments were done both for fibers with and without precipitated calcium carbonate inside the cell wall.

RESULTS

According to the preliminary experiments the amount of fibers did not affect the dynamics of the conductivity measurements at concentrations less than 2 g dry fibers per 1000 ml of suspension. The amount of fibers used in actual experiments was small enough to let us assume zero concentration of electrolyte at the fiber surface. The final concentration of electrolyte in water phase at the end of each experiment of course was not zero but remained so small compared with that inside the fibers at the beginning of each experiment that we could make this assumption with reasonable accuracy.

The value of time constant k was first determined to be as 0.79 s from the results of conductivity measurements with only electrolyte by fitting Eq. (15 b) to the experimental data.

In order to calculate the diffusion coefficients within the fiber wall we fitted Eq. (19) to the experimental data obtained from measurements with pulp suspensions by means of the "Curve Fit" option of Sigma Plot program from Jandel Scientific Co. As a result we could solve the best fit values for parameters B, D/R^2 , T, and the initial level of relative concentration. We did not want to fix the initial level of relative concentration because of possible slight deviations from zero. Furthermore the value of time delay T was impossible to control exactly. Therefore it was not fixed but changed as a fitting parameter in each individual experiment. From the values of parameter D/R^2 we could evaluate the diffusion coefficient D within the fiber wall when the average radius R of fibers was

known. The theoretical Equation (solid curve) fitted quite accurately to the experimental data (dots) as can be seen from the data fit example presented in Fig. 3.



Fig. 3. Results from a typical experiment, where diffusion of KCl through fiber wall was followed by measuring the concentration (conductivity) of electrolyte outside the fibers at 5 °C.

In order to test the model and experimental setup the pore structure of fibers was first controlled by precipitating calcium carbonate within the fiber walls. Calcium carbonate which is located in the pores of fiber wall decreases the free pore volume where diffusion can take place. Measurements were replicate for filled and unfilled fibers as well as with electrolyte alone in order to minimize the effect of the variation. Average relative concentration curves for each case were obtained (Fig. 4).



Fig. 4. Results (average curves) from diffusion experiments, where diffusion of KCl through both unfilled and calcium carbonate filled fiber wall was followed by measuring the concentration (conductivity) of electrolyte outside the fibers at 5 °C compared with the case of KCl alone at 5 °C.

Diffusion coefficients were calculated as presented in the Theory section and are tabulated in Table I together with the values of parameters from curve fit of Eq. (19). Confidence intervals were calculated from the variation of repetitive measuments.

	unfilled fiber	calcium carbonate filled fiber
D _{KCl.} m ² /s	$14.6 \pm 4.5 \cdot 10^{-12}$	$5.7 \pm 1.0 \cdot 10^{-12}$
B, mol/m ³	4.3 ± 0.04	4.3 ± 0.10
D/R^2 , s ⁻¹	$47.8 \pm 14.9 \cdot 10^{-3}$	$18.6 \pm 3.2 \cdot 10^{-3}$

Table 1. Values of diffusion coefficients of KCl within both unfilled and calcium carbonate filled fiber wall when the average radius of dry fibers is taken to be 15 μm, and parameters from the curve fit of Eq. (19) with confidence intervals at 95 % confidence level.

It can be seen from the Fig. 4 that the concentration of electrolyte increases much faster in experiments with unfilled fiber than with cell wall filled fiber. This indicates that the diffusion through the unfilled fiber wall is distinctly faster than the diffusion through the calcium carbonate loaded fiber wall with smaller pore volume. This is also indicated as a decrease of diffusion coefficient of KCl within the loaded fiber wall.

In order to gain more information on relation between diffusion coefficients and porosity, experiments were made for fibers with different degree of drying. Dryings were done by making sheets and repulping the same sheets again etc. Diffusion coefficients from these experiments are presented in Fig. 5 as a function of the number of drying cycles.



Fig. 5. Results from diffusion experiments, where diffusion of KCl through fiber wall with different degree of drying was followed by measuring the concentration (conductivity) of electrolyte outside the fibers at 5 °C.

It can be seen from Fig. 5 that diffusion of electrolyte reduces with replicate dryings. After the dryings, the diffusion coefficient was only less than half of that within never dried fiber. The decrease in diffusion coefficient can be explained by the decrease in fiber wall porosity caused by fiber hornification.

DISCUSSION

A good fit for the theoretical model was obtained with data from experiments. Very little information is available in literature on diffusion coefficients within the pulp fiber wall. Still, in order to validate our results, we briefly refer literature available concerning both methods and results obtained in other diffusion studies with other kind of materials.

Conductometry was found to be promising method to measure consistency of pulp suspensions since the conductance of a pulp suspension is known to be linear function of pulp consistency (14). However, conductometry is sensitive to the natures of both the fibers and the aqueous medium, which restricts its use for this purpose. Since the ionic diffusivities are directly proportional to the ionic mobilities, analysis of pulp suspension conductivity data may however give some insight of the rate of diffusion inside the fiber wall. Been and Oloman (8) (9) estimated from the conductivity data of a fiber suspensions, that the ionic diffusivity in the TMP fiber wall was about 50 % of the corresponding value in the bulk solution. However, the brokennes of TMP fibers complicated calculation of real diffusivities just inside the fiber wall.

Ostrowska et al. (15) calculated concentration-dependent diffusion coefficients of a dispersed dye in anionically modified polyester fiber by using the grid method and data from experimental concentration profiles. Regarding cylindrical symmetry of the fiber the value of diffusion coefficient varied between $0.6 \cdot 10^{-15}$ m²/s and $2.0 \cdot 10^{-15}$ m²/s depending on the concentration.

Briggs et al. (16) measured diffusivities of counter ions inside beet disks which were 11 to 13 times smaller than that at infinite dilution. According to Stamm (17) and Cady et al. (18) diffusion rates in the cross direction of wood are usually 10-35 % of the values in water and the decrease is linked to physical properties of wood, such as redused effective cross-sectional area and mechanical blocking. Diffusion within the fibers and wood is however difficult to compare, because diffusion in wood takes place also through cracks and other defects, i.e., interfiber diffusion is possible. Also both chemical and physical characteristics of wood and pulp are different. Diffusion coefficients even within different types of fibers may differ appreciably depending on the origin of fiber and the method of cooking and bleaching.

In this study we wanted to establish a method, which omits completely the diffusion between the fibers unlike many other methods, and takes into account only intrafiber diffusion. With the aid of this method and theory presented in this

study one can measure diffusion just within the fiber wall. Moreover, experimental data in this study was collected as a function of time which is an obvious method to study kinetic phenomena like diffusion.

The value of diffusion coefficient of KCl in very dilute aqueous solution at 5 °C extrapolated by using the data of Lobo et al. (19) at different temperatures is $1.0155 \cdot 10^{-9}$ m²/s. Thus, the value of diffusion coefficient of KCl in the tranverse direction of fibers within the unbeaten never dried birch fiber wall found in this study was 70 times smaller than that in dilute aqueous solution. Luner (20) reviewed, that swelling of fibers affects considerably diffusion in the transverse direction of fibers. As we know, the tendency of unbeaten fiber to swell is quite small. Furthermore birch fibers do not have pit apertures facilitating diffusion. By taking into account these information and the facts discussed above, the diffusion coefficients obtained in this study seem to be of right order of magnitude and in harmony with the results from studies with other kinds of cellulosic materials. Moreover, the difference between the diffusion coefficients of KCl in water and within the fiber wall justifies as to assume the boundary condition (2b), i.e., diffusion in concentration polarization layer located on the surface of the fiber is much faster compared with diffusion within the fiber wall.

It can be assumed that the diffusion model and experimental setup presented in this paper can be used and also further developed to estimate the pore structure of pulp fiber wall as the diffusion coefficient decreases with decreasing pore volume where diffusion can take place within the fiber wall. The analysis is very rapid to perform compared to the methods known earlier.

CONCLUSIONS

Experimental data obtained is well described by the model established in this study. Diffusion coefficients of ions within unfilled and calcium carbonate filled fiber wall were estimated to be about 1.5 and 0.5 % of that in dilute aqueous solution, respectively, when experiments were done for fibers without pit apertures. The diffusion of electrolyte within the fiber wall reduced with replicate dryings of fibers. After the dryings, the diffusion coefficient was less than half of

that within newer dried fiber wall. The decrease in diffusion coefficient is explained by the decrease in pore volume of fiber walls.

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REFERENCES

- SHALLHORN, P.M., KARNIS, A., Zwei neue Masskriterien von aufgeschwennten Fasen zur Beurteilung der Blattfestigkeit, Svensk Papperstid. 66 (2):37-41, 1963.
- STONE, J.E., SCALLAN, A.M., ABRAHAMSON, B., Influence of Beating on Cell Wall Swelling and Internal Fibrillation, *Svensk Papperstid.* 71 (19): 687-694, 1968.
- STONE, J.E., SCALLAN, A.M., A Study of Cell Wall Structure by Nitrogen Adsorption, *Pulp Paper Mag. Can.* 66(8) T407-414, 1965.
- MCKNIGHT, T.S., MARCHESSAULT, R.H., MASON, S.G., The Distribution of Pore Sizes in Wood Pulp Fibres and Paper, *Pulp Paper* Mag. Can. 59 (2):81-88, 1958.

- KREITUS, A., DRUZ, N., CHIRKOVA, E. and LUSE, I., Estimation of Diffusion and Distribution of Chemical Compounds in Wood, TAPPI Int. Symp. Wood & Pulping Chem., Raleigh, Proc.: 13-19, 1989.
- SKAAR, C. and SIAU, J., Thermal Diffusion of Bound Water in Wood, Wood Sci. Technol. 15 (2):105-112, 1981.
- HEAZEL, T. and MCDONOUGH, T., Cell-Wall Sulfur Distribution in Sulfonated Southern Pine Latewood. Effects of Process Variables and Mathematical Modeling of Intrafiber Diffusion with Reaction, TAPPI Int. Paper Physics Conf., Konala, HI, Proc. (Book 1): 225-246, 1991.
- BEEN, J. and OLOMAN, C.W., Electrical Conductivity of Pulp Suspensions Using the Donnan Equilibrium Theory, J. Pulp and Paper Sci. 21 (3):J80-J85, 1995.
- BEEN, J., A Novel Approach to Kinetic Modeling of the Hydrogen Peroxide Brightening of Mechanical Pulp, *Tappi J.* 78 (8):144-152, 1995.
- CARSLAW, H.S. and JAEGER, J.C., Conduction of Heat in Solids, 2nd ed., Oxford University Press, Oxford, 214-229, 1959.
- 11. TLUCHOR, D. and GOSMAN, A., Kinetics of Diffusion in Dialysis Cells, *Acta Polytechnica Scandinavica*, Ch 178:43-55, 1987.
- 12. CHURCHILL, R.V., Operational Mathematics, 3rd ed., McGraw-Hill Kogakusha Ltd., Tokyo, 1972.

- TUMA, J.J., Handbook of Numerical Calculations in Engineering, McGraw-Hill, New York, 1989.
- 14. SCALLAN, A.M., The Electrical Conductance of Pulp Suspensions, *Tappi J.* 72 (11):157-162, 1989.
- 15. OSTROWSKA, B. and NAREBSKA, A., Diffusion of Dyes in Polyester Fibers. II. Diffusion Coefficients from the Radial Distribution Curves, J. Applied Polymer Sci. 25:2845-2855, 1980.
- BRIGGS, G.E., HOPE, A.B. and ROBERTSON, R.N., Electrolytes and Plant Cells, Blackwell Scientific Publications, Oxford, 1961.
- STAMM, A.J., An Electrical Conductivity Method for Determining the Effective Capillary Dimensions of Wood, *J. Phys. Chem.* 36:312-325, 1932.
- CADY, L.C. and WILLIAMS, J.W., Molecular Diffusion into Wood, J. Phys. Chem. 39:87-102, 1935.
- LOBO, V.M. and QUANESMA, J.L., Electrolyte Solutions: Literature data on thermodynamic and transport properties, Vol 2, Faculdade de Ciências da Universidade de Coimbra, Coimbra, 1981.
- 20. LUNER, P., The Effect of Pre-Treatments on Diffusion Through Wood, Pulp and Paper Mag. Canada 57 (3):216-220, 1956.

Transcription of Discussion

Diffusion controlled kinetics of electrolyte transfer within the pulp fiber wall: estimation of fiber wall pore structure

Petri Silenius, Project Co-ordinator, Metsa Serla Group, Finland

Professor Murray Douglas, McGill University, Canada

I am sure you realise the approximations you had to make in taking the structure of your cell wall as two concentric cylinders. The electrolyte that actually diffuses through the wall stumbles and falls endlessly through the black forest of polymer molecules. But these holes in the fibre wall have been referred to repeatedly today, particularly for wet fibres. Isn't it likely that most of the electrolyte transfer, which you noted was remarkably fast, takes place not through the black forest but through the autobahns of the big holes in the fibre walls?

Petri Silenius

Actually that might be true in certain cases. Because of this I should maybe use the term apparent diffusion coefficient.

Murray Douglas

The medium through which the transfer process is taking place is a highly non-uniform medium. It has areas of solid polymer molecules which offer enormous resistance to diffusion, and it is chock full of holes. The electrolyte transfer will take the path of least resistance and not much of it may actually diffuse through the polymer wall.

Petri Silenius

That may be true depending on fibre type. In this study, we used birch fibres because of special interest on it, and birch fibres do not contain pit apertures. Moreover the pulp was unbeaten and thus contained only a small amount of cracks and holes. So, in this study I think we measured pretty well the diffusion through the fibre wall. Let's us however that it is apparent diffusion coefficient. If fibre would be pine pulp for example with pit apertures, you are absolutely right with your comment and in that case diffusion takes place also through holes.

Bengt Svens, R & D Manager, Ahlstrom Kauttus Limited, Finland

Could you please define the fibre - Birch TCF pulp - and the bleaching sequence which has been used. Also the other experimental conditions, pH and other things used during your experiment?

Petri Silenius

The fibre is the first we got from our new TCF plant and I am not really sure what the real sequence was. It was about 3 years ago.

The bleaching sequency was OZPP.

Experiments were done under the pH conditions of the pulp.

Siddharth G Chatterjee, Assistant Professor, Syracuse University, USA

Did you account for the mass transfer resistance in the liquid phase outside the fibres in your mathematical model or did you assume it to be well mixed.

Petri Silenius

It was assumed to be well mixed.

Siddharth Chatterjee

You said the diffusion coefficient was 70 times lower than that for KCL in the bulk solution. So that means the fibre is very tortuous? The tortuosity factor is very high?

Petri Silenius

Yes.

Siddharth Chatterjee

In our experiments we find that the diffusion coefficient of water vapour inside the pulp sheet is about 10-30 times smaller than the diffusion coefficient in the bulk phase.

Petri Silenius

Actually that makes sense, because diffusion that you measured is from paper sheet. So inter-fibre diffusion is possible in your measurements and that could explain the difference. Our measurement overlooks inter-fibre diffusion completely.

Professor Bandaru Ramarao, ESPRI, USA

How did you measure the thickness of the fibres walls to determine the diffusion path length?

Petri Silenius

In this study we measured the radius from cross-section of fibres by microscopic techniques. Anyway, I have to say there is still work to do on how we determine the radius of the fibres because collapse of fibres is also happening. If the fibres are very badly collapsed, the plate geometry would perhaps be better than this and in that case there is no radius. Collapse can be taken care of by slight modification with mathematics. We have a good method to gain a relative scale of diffusion coefficients but there is still work to do in this area.

Bandaru Ramarao

When you do this kind of fitting to experimental data frequently you have multiple solutions. That means various values of the diffusion coefficient and other parameters will be able to describe the same experimental data. Did you have that problem or were you able to pick out a unique set of parameters that will fit the experimental data?

Petri Silenius

We have defined the areas where each parameter can vary and that is why we did not have very many problems.

Lars Ödberg, Vice President Basic Research, STFI, Sweden

A graduate student of mine has measured the diffusion constant of water in fibres. You can do it with a pulsed gradient NMR method. The diffusion measured for water inside

fibres is almost like free water during a short time. So this water is not bound. It diffuses as quickly as free water. All we see is the tortuosity effect. With the NMR method you can determine in which direction you are measuring the diffusion constant. The diffusion constant along the fibres is much larger than the diffusion constant perpendicular to the fibres.

Dr Kari Ebeling, Director, UPM Kymmene Group, Finland

The stirring speed was 750rpm. Is it possible that that creates enough flexing and compression forces in the fibres adding to the observed phenomenon; ie why the diffusion should be so fast?

Petri Silenius

Actually - I do not believe that. The stirring has to be pretty active in order to make sure that the concentration of tracer is really near zero on the surface of fibres. If we compare the values of these diffusion coefficients they are pretty much the same as with other kinds of cellulose materials.

Prepared contribution from

Professor Douglas Wahren, The Paper Professor AB, Sweden

We all know what fibres are supposed to look like. We have already seen the classical picture twice this morning: fibres neatly aligned and separated by the middle lamellae, the p-imary wall, the S1, the 52, and the 53 layers. We have heard learned discourses on how various chemicals may interact with or diffuse into pores of various sizes; from maybe 100 nm up to micrometers. Yesterday I showed, very briefly, a picture of what I have recently learned about the ultrastructure of fibre walls. Here it is.



The left part is a 240% enlargement of a part of the right hand diagram. The distance between the tips of the two 45° arrows is 200 nm.

It was produced by Dr. Geoffrey Daniel at the new Wood Ultrastructure Research Center (WURC) located at the Swedish University of Agricultural Sciences. This is what a wall of a never dried softwood kraft pulp fibre surface may look like at very high magnification. It was prepared by a new technique where the sample is rapidly frozen in liquid nitrogen slush.

This may be the S1 layer, rather than the primary wall, but you can see that it is composed of fibrils, 20 to 40 nm wide and very long. Difflision of small molecules into this structure should be no problem at all. I would like to hear your reactions.

Comment by Dr. Derek Page

It is an artifact.

Dr. Wahren

Unfortunately, I am not able to go into a detailed discussion on how this image was prepared but I will try to find out.

Following the symposium Dr. Daniel kindly provided the following comments.

In order to reveal greater details of the surface structure and structural organization of wood fibres, high resolution Cryo -Field Emission scanning electron microscopy (HR-Cryo-FE-SEM) was used. This technique eliminates specimen dehydration and drying. Rapid freezing, etching and coating of samples is followed by SEM observations of samples in the frozen hydrated state.

In the present work samples of sulphate bleached (undried, unfreezed) softwood pulp fibres were mounted on brass stubs using minimal amounts of Tissue-Tek. The stubs plus fibres were rapidly plunged into LN2 slush (ca -210 C) using an Oxford Cryo-station and later transferred under vacuum into an Oxford CT1 50011F Cryo Transfer Chamber where they were maintained at -160 C on a specimen cold stage. The temperature of the cold stage was then raised to about -95 C and maintained there for 2-3 minutes in order to sublimate surface ice and "deep etch" the fibres revealing details of their outer surface. The temperature of the cold stage was then lowered to -140 C and the samples coated with a thin layer of Au/Pd (ca 2-4 nm).

Samples were then transferred into the specimen chamber of an Hitachi 5-4500 FE-SEM onto a cold stage maintained at temperatures of -130 to -140 C. Observations were made using an accelerating voltage of 5.0 kV. Studies indicated that the surface structure of the softwood fibres was comprised of an intricate meshwork of "macrofibrils" of the order 20-40 nm although considerable variation existed.

While the present observations are preliminary, it demonstrates the great possibilities that HRCryo-FE-SEM may have for pulp fibre research. Current studies involve the use of cryogens with more rapid freezing rates.

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