

# DETERMINATION OF BORON DIFFUSION COEFFICIENTS IN WOOD<sup>1</sup>

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## ABSTRACT

The unsteady-state diffusion of boron through southern pine (*Pinus* spp.) was investigated at various moisture contents, temperatures, and treatment conditions. The fastest rates of diffusion were observed in the longitudinal direction, followed by the radial and the tangential directions. The diffusion rate increased with time in all directions. The longitudinal diffusion rate increased rapidly with moisture content (MC), while a slow increase in the radial diffusion rate was observed at MCs above 90%. Moisture content did not affect the rate of tangential diffusion within the range of MCs in this study (70–110%). The effect of temperature on boron diffusion rates was more pronounced than the effect of MC. The diffusion rate increased with temperature, although slight direction-dependent differences were observed. A repeated dip-treatment increased the rate of diffusion in the tangential direction, but only small differences were found in the longitudinal and the radial directions. No other data were found in the literature for comparison.

Average values of the diffusion coefficients were calculated to predict the concentration profile of boron in wood under various conditions. The longitudinal diffusion coefficients were 10 to 20 times larger than the radial diffusion coefficients, and the radial diffusion coefficients were two to four times larger than the tangential diffusion coefficients. The use of the average boron diffusion coefficients caused some differences between real and predicted values in the early stages of diffusion, but the potential for practical use was demonstrated.

**Keywords:** Boron, boric acid equivalent, dip-diffusion treatment, diffusion coefficients, Egner's solution, Timbor® solution, unsteady-state diffusion.

## INTRODUCTION

Boron, a nonmetallic element, [usually in the form of borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) or boric acid ( $\text{H}_3\text{BO}_3$ )] has been used as an active ingredient in wood preservative systems for

over 50 years (Cockroft and Levy 1973; Barnes et al. 1989; Greaves 1990; McNamara 1990; Murphy 1990). It has several advantages including low cost, low mammalian and environmental toxicity, simplicity of application, effectiveness against insects and basidiomycetes, and high solubility in water (U.S. Borax and Chemical Corp. 1986; Dickinson et al. 1989; Barnes et al. 1989; Murphy 1990; Greaves 1990; Williams 1990).

Wood is treated with boron compounds ei-

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ther through a momentary immersion in a concentrated boric acid/borax solution or a tunnel spray system. Typically, dipped or sprayed wood is stored closely stacked under cover to retard drying. Surface treatments are very effective in treating a variety of refractory species that are difficult to preserve by pressure treatments because boron can diffuse into wood at moisture contents (MC) above the fiber saturation point (FSP) (Fowlie et al. 1988; Lebow and Morrell 1989; Williams 1990; Williams and Amburgey 1987). Attention has focused on accelerating the diffusion processes to improve the cost effectiveness because a long storage time is required to achieve adequate core loadings of 0.2% boric acid equivalent (BAE) or higher based on the oven-dry weight of wood (U.S. Borax and Chemical Corp. 1986; Bianchini 1987). Techniques have been developed to accelerate treatment either by pressure impregnation, steam treatment, or the application of heat to accelerate diffusion (Vinden et al. 1985; Barnes et al. 1990; Greaves 1990), but these processes have not gained general acceptance except in Australia because of the difficulty of devising a treatment as simple and as low cost as dipping and diffusion.

Boron diffusion in wood treated with boron-containing wood preservatives ought to be dependent on wood MC (Smith and Williams 1969; Morrell et al. 1990; Puettmann and Schmidt 1997), since water is the medium for boron movement into wood. Diffusion occurs over a broad range of MC and the diffusion rates should increase with MC, but diffusion is a complex process when the water is not continuous throughout the wood. In unsaturated wood, zones of gas or vapor break up the water phase and act as localized barriers to diffusion (Smith and Williams 1969). This results in a decrease in the number of pathways available for diffusion per unit area. Diffusion is uncomplicated in wood saturated with water where water is present throughout the pore structure of the wood in all directions. Under these conditions, the diffusion rate will be at its maximum. Thus, the diffusion rate

varies depending on the uniformity of the water throughout the wood. Other factors affecting diffusion in wood are temperature, wood thickness, diffusion time, diffusion direction, and wood density. Diffusion will continue as long as there are differences in concentration between the solution at the surface of the wood and the chemical concentration in the free water within the wood.

Fick's first and second laws using the assumption of a constant diffusion coefficient usually express diffusion through wood. This is correct when the diffusion coefficient is independent of concentration and a linear gradient is set up across the diffusion medium; but whenever wood is heated, impregnated with liquids, or dried, there will be a change in the conditions inside the wood over a period of time. Unsteady-state flow will occur and the diffusion coefficient will vary. Fick's first and second laws have been solved for various boundary conditions to determine the varying diffusion coefficients during unsteady-state conditions (Crank and Henry 1949; Crank 1975), but no general solution has been found except for the case where the diffusion coefficients can be expressed as a function of concentration or distance (Skaar 1958; Crank 1975). Fortunately, diffusion coefficients can be determined using Egner's solution at a specified location and time provided the concentration profiles in wood are known (Skaar 1954; Slay 1984).

The determination of boron diffusion coefficients can provide a better understanding of boron diffusion mechanisms. A number of studies have examined boron movement in wood under various MC conditions (Smith and Williams 1969; Morrell et al. 1990; Puettmann and Schmidt 1997), but few trials have mathematically quantified the movement of boron in treated wood. The objective of this research was to investigate the effect of temperature, MC, storage time, flow direction, and dip-diffusion treatment method on the rate of boron diffusion in wood.

## MATHEMATICS OF DIFFUSION

A successful method for determining diffusion equation solutions not only solves the partial differential equation, but also satisfies the boundary conditions. The latter requirement may be the more difficult one. Thus the partial differential equation can be converted into a solvable ordinary differential equation, but it may not be possible to obtain the integration constants with the given boundary conditions. General solutions of the diffusion equations found for a variety of initial and boundary conditions have been well established (Crank and Henry 1949; Skaar 1954; Crank 1975).

Given in Eq. (1) is a solution for Fick's second law for a plane source in an infinite volume when all the diffusing substance is concentrated initially in a plane. This equation is derived assuming a constant diffusion coefficient. The diffusion substance is initially deposited at time  $t = 0$  and left to diffuse throughout the surrounding medium ( $-\infty < x < \infty$ ), from a point  $x = 0$ .

$$C = \frac{M}{2\sqrt{\pi Dt}} e^{-x^2/4Dt} \quad (1)$$

where:  $M$  = the total mass of a diffusing substance (g);  $D$  = diffusion coefficient ( $\text{cm}^2\text{s}^{-1}$ );  $C$  = the concentration of diffusion substance (w/w %); and  $x$  = the thickness of sample in the direction of diffusion (cm).

Half the diffusing substance moves in the direction of positive  $x$  and the other half in the opposite direction. The solution for diffusion through the semi-infinite medium with an impermeable boundary at  $x = 0$  can be obtained by considering the solution for negative  $x$  to be reflected in the plane  $x = 0$  and superposed on the original distribution in the region  $x > 0$  [Eq. (2)].

$$C = \frac{M}{\sqrt{\pi Dt}} e^{-x^2/4Dt} \quad (2)$$

As the original solution was symmetrical about  $x = 0$ , the procedure of reflection and superposition is mathematically sound. Reflec-

tion at  $x = 0$  simply means the adding of two solutions of the diffusion equation. This equation also shows that the total amount of diffusing substance remains constant and equal to the amount originally deposited in the plane  $x = 0$  at which the condition for an impermeable boundary,  $\partial C/\partial x = 0$ , is satisfied (Crank 1975).

Quantitative measurements of the rate at which a diffusion process occurs are usually expressed in terms of a diffusion coefficient. The diffusion coefficient is defined as the rate of transfer of the diffusing substance across a unit area of a section divided by the spatial gradient of concentration at the section. Most of the earlier methods used to solve the diffusion equations assumed constant diffusion coefficients. When such methods are applied to unsteady-state systems, only a mean value is obtained. When the diffusion coefficients vary, the only correct solution to Fick's second law is by Egner's method (Skaar 1954, 1958) whereby diffusion coefficients are obtained graphically, numerically and analytically. Egner's method solves Fick's 2nd law using plots of concentration vs. distance and total concentration vs. time. The equation is shown in Eq. (3).

$$D = \frac{\partial \left( \int_0^x C dx \right)}{\frac{\partial t}{\frac{\partial C}{\partial x}}} \quad (3)$$

This solution is very sensitive to experimental errors, but Egner's approach requires no cumbersome assumptions. To calculate the diffusion coefficients, however, accurate information is needed about the boron distribution in a wood specimen at various times during the diffusion period.

## MATERIALS AND METHODS

Three different experiments were planned to investigate the effect of MC, temperature, and a repeated immersion of wood on the boron

diffusion coefficient in the radial, tangential, and longitudinal directions. Each experiment had two replications for each combination of variables. The treatment combinations for the three experiments were as follows:

- (1) Experiment I: MC effect  
MC (70, 90, and 110%) × Flow direction (radial, tangential, and longitudinal) × Diffusion periods (0, 1, 4, 9, 16, and 25 days) × Temperature (30°C) × Treatment (single momentary immersion).
- (2) Experiment II: temperature effect  
Temperature (50 and 90°C) × Flow direction (radial, tangential, and longitudinal) × Diffusion periods (0, 1, 4, 9, 16, and 25 days) × MC (110%) × Treatment (single momentary immersion).
- (3) Experiment III: treatment effect  
Treatment (double momentary immersion) × Flow direction (radial, tangential, and longitudinal) × Diffusion periods (0, 1, 4, 9, 16, and 25 days) × Temperature (30°C) × MC (110%)

#### *Material selection and preparation*

A total of 24 pieces of kiln-dried southern pine (*Pinus* spp.) sapwood, nominally 50 × 150 mm in cross section by 120 cm long, was obtained and cut into 5 × 5 × 5-cm defect-free sapwood samples. The samples were oven-dried at 103 ± 2°C until the weight of each sample remained constant, and then weighed to the nearest 0.01 g. To minimize errors from sample variation, specific gravity (SG) was measured for each oven-dry cube. Annual-ring angles and grain angles of both tangential faces (bark-side and pith-side) were measured to the nearest 0.5° using a scribe and protractor. Only samples with specific gravity ranging from 0.53 to 0.58, and ring and grain angles of 0° to 5° were selected for the experiments.

Samples were impregnated with water under a vacuum until they reached the prescribed MC. Overweight samples were carefully air-dried at ambient conditions until they reached the desired moisture levels. Sample surfaces

were then coated with silicone rubber to prevent further MC changes, kept under 100% relative humidity (RH) conditions (over water containing a few drops of formaldehyde) for 48 h until the silicone was cured, and stored for 5 weeks at 30°C and 100% RH to minimize internal moisture gradients. As a check, three samples from each different MC group (70, 90, 110% MC) were cut into 4-mm-thick slices and the MC profiles measured. All measurements were within ±5% MC. No problems with mold or adherence of silicone were noted.

#### *Sample treatment*

Each of the three experiments began by treating the samples with a borate solution. One coated surface was removed from each sample with a radial-arm saw to permit boron flow in the designated direction. A tangential surface was cut for boron diffusion in the radial direction, a radial surface for tangential diffusion, and a transverse surface for the longitudinal diffusion. Immediately after cutting, samples were immersed for 5 min in a 25% BAE Timbor® solution [disodium octaborate tetrahydrate (DOT, Na<sub>2</sub>B<sub>8</sub>O<sub>13</sub>·4H<sub>2</sub>O)] at 50°C. For the double momentary immersion treatment, a second 5-min dip-treatment was performed 24 h after the first immersion treatment using the same solution. The ratio of solution to specimen volumes was large enough that these immersion treatments did not materially affect the solution concentration.

The treated samples were individually wrapped in plastic bags and placed in incubators maintained at the designated temperatures ±0.5°C. Samples were removed from storage after 0, 1, 4, 9, 16, or 25 days of diffusion storage, as specified. Each sample was trimmed with a radial-arm saw to approximately 4.8 × 4.8 × 4.8 cm to remove the remaining silicone coating, and a slicing machine (Slay 1984) was then used to remove slices approximately 0.4 cm thick from the treated samples in serial fashion. Slicing was perpendicular to the flow direction of boron.

The slices were placed into individual capped weighing bottles immediately after being severed from the sample. Each slice and bottle was weighed together to 0.01 g on an analytical balance. The slices were oven-dried in their respective bottles at  $103 \pm 2^\circ\text{C}$  until constant weight was achieved. Moisture contents were calculated on an oven-dry weight basis. The moisture contents of most slices were within  $\pm 5\%$  MC of the target MCs.

#### Boron analysis

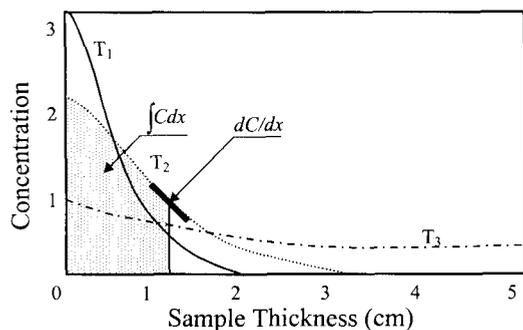
The oven-dried sliced samples were ground to 20 mesh (850  $\mu\text{m}$ ) prior to analysis for boron content. Boron content was determined using the titration method with mannitol according to the AWWA A2-95 procedure (AWWA 1995).

#### Determination of boron diffusion coefficients

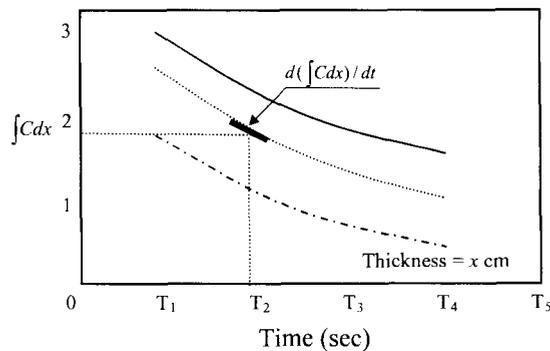
Diffusion coefficients were calculated for each of the three experiments using Egner's solution. A graphical illustration of the derivative and integration terms in Egner's solution is shown in Fig. 1. A linear combination of arbitrary functions is generally used to model data when lines or polynomials can not, but there are times when the flexibility of this method is insufficient and the data should be modeled not by a linear combination of data, but by some function whose parameters must be chosen. In this research, an exponential function was chosen to fit the concentration vs. distance curves. To find the exponent that best fit a dataset, boron concentration,  $C$ , was expressed as a function of distance  $x$  and parameters  $u_0$ ,  $u_1$ ,  $u_2$  (Eq. 4). The fitted equations showed coefficients of determination ( $r^2$ ) above 0.91.

$$C(x) = \exp(u_0 + u_1x + u_2x^2) \quad (4)$$

The derivative terms ( $\partial C/\partial x$ ) and integration terms ( $\int Cdx$ ) were calculated at various sample thicknesses from the fitted equations, and the calculated integration terms at various distances were graphed against time (Fig. 1). The data were assumed to be exponentially related



(A) Denominator in Egner's solution



(B) Numerator in Egner's solution

FIG. 1. Graphical description of the terms in Egner's solution.

to time and were fitted using a least squares approximation (Eq. 5).

$$y = a \cdot e^{bx} \quad (5)$$

The diffusion coefficients of boron that were calculated from the derivatives of the fitted equations are equivalent to the ratio of the numerator and denominator from Egner's solution.

#### Prediction of boron penetration

The diffusion coefficients varied with the sample thickness. To predict the boron penetration regardless of sample thickness, average diffusion coefficients were calculated from the values measured using Egner's solution. The predicted values were found using Eq. (2). The total amount of boron ( $M$ ) was calculated from the integration of each of the fitted concentra-

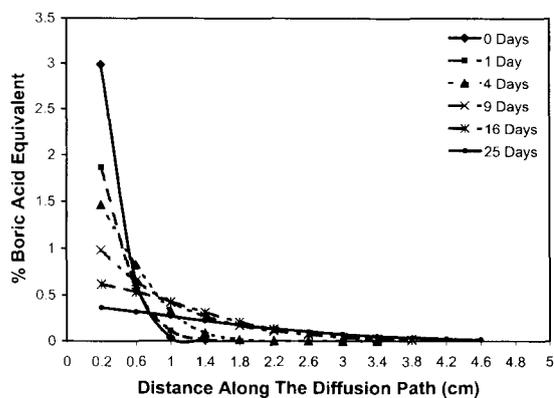


FIG. 2. Diffusion of boron in the radial direction of southern yellow pine sapwood treated with a 25% BAE solution using a single-dip diffusion treatment and stored at 110% MC and 30°C.

tion vs. distance curves to minimize the error caused by sample variance.

## RESULTS AND DISCUSSION

### *Borate penetration*

There was little effect of 5 min of immersion treatment on MC; only the slices from the surface of the samples cut right after treatment showed small increases in MC. Most sliced samples were in the range of target MC  $\pm$  5%. The samples were regarded as having reached equilibrium.

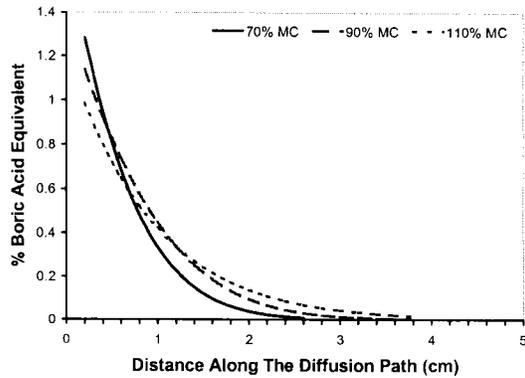
The depth of borate penetration increased with storage time as shown in Fig. 2. The boron diffusion rate decreased during the course of diffusion as concentration differences decreased throughout the medium; the processes theoretically will continue until there is no difference in concentration. The decrease in diffusion rate also depends on the hygroscopicity of the borates (Becker 1976). As expected, for a given temperature and time, borates penetrated deeper in the wetter samples, illustrating the benefits of free water in the wood. The diffusion rates of boron were the fastest for the longitudinal direction, followed by the radial direction and then the tangential direction.

Borate penetration was virtually complete for the longitudinal diffusion in 9 days regardless of MC. Penetration in the radial and tan-

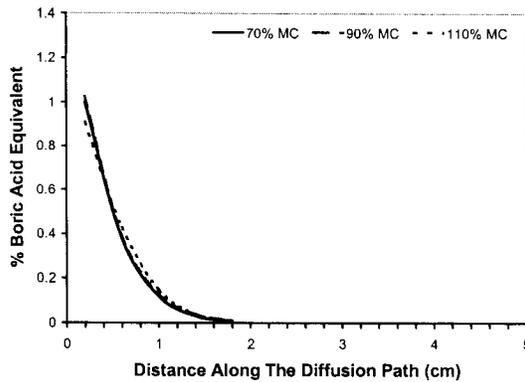
gential directions was not complete in 25 days, even in 110% MC samples where the penetration was limited to the depth of about 3 cm from the surface for tangential diffusion and about 4 cm for radial diffusion.

*Effect of moisture content.*—The moisture effect on the rates of boron diffusion was much more significant in the longitudinal direction than in the radial direction. For tangential diffusion, little effect of MC on the boron diffusion was observed (Fig. 3). The differences in the rates of boron diffusion result from the feasibility of boron movement in each direction. In high MC conditions (70% or greater), cell walls are saturated with water and there is enough free water in the cell lumens that boron molecules can diffuse more easily through them than through the bound water in cell walls. Thus boron diffusion is faster in the direction where more free water is in the continuous phase, longitudinally along cell lumens and pits. In the tangential direction, the cell-wall thickness remains constant, whereas in the radial direction both the thin cell walls in the earlywood cells and the thick parts in the latewood cells inhibit migration. The high permeability of the rays provides for easier pathways in the radial direction, resulting in the higher penetration compared to the tangential cell walls. Similar trends have been noted previously with salt; Becker (1976) reported that the depth of penetration of salt in the tangential direction was about half, and in the radial direction about two thirds, of the depth of penetration in the longitudinal direction. In high MC conditions, the limiting factor for boron diffusion is the rate of boron diffusion in bound water, not in free water. This explains why the increase of MC may have little effect on accelerating boron diffusion in the radial and tangential directions above a certain MC.

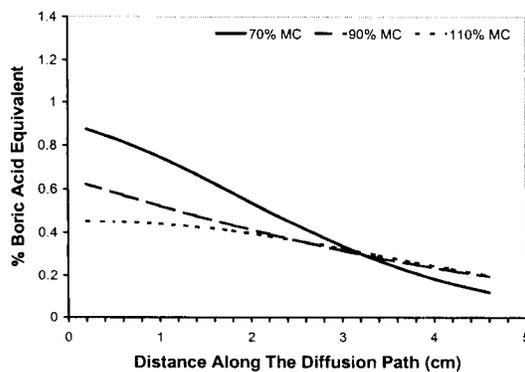
The rate of boron diffusion generally increased with MC, but in the early phase of boron diffusion, faster rates were occasionally observed in the lower MC conditions. This trend may reflect the differences in the continuity of water phase and MC gradient



(A) Radial Direction



(B) Tangential Direction



(C) Longitudinal Direction

FIG. 3. Comparison of boron after 9 days' diffusion in radial (A), tangential (B), and longitudinal (C) directions under various MC conditions.

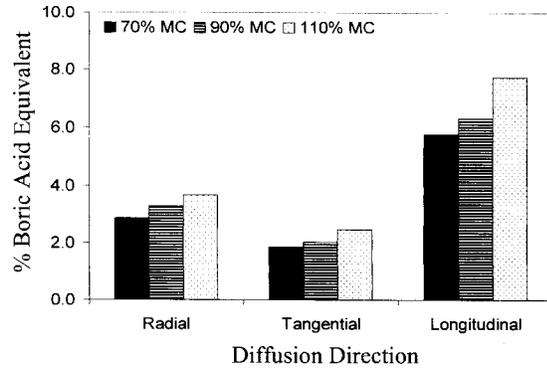
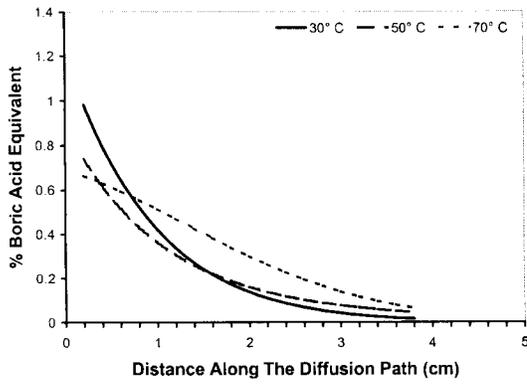


FIG. 4. Absorption of boron under various MC conditions immediately after a single momentary immersion treatment.

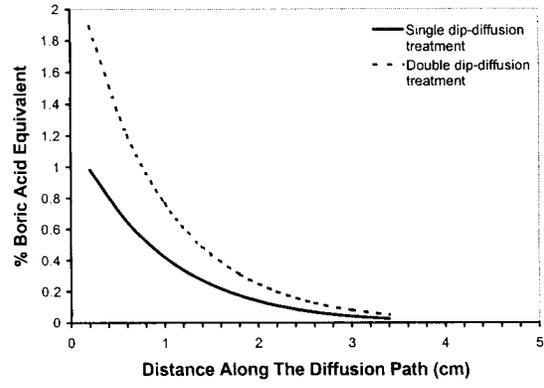
throughout the samples. The rate of boron diffusion is greatest in wood fully saturated with water because water is the medium for boron movement, and there are no air bubbles to act as barriers against diffusion (Smith and Williams 1969). The rate of steady-state flow may depend on the uniformity of the medium.

The MC of the sample surface affected the initial uptake of borates (Fig. 4), which tended to be higher with higher MC. This suggests that surface MC is one of the factors controlling the total amount of borates available for subsequent diffusion into wood. It was observed that the transverse surface took up the greatest amount of borate followed by the tangential and the radial surfaces. The blocks for tangential and radial diffusion showed that most of the borate remained within 0.4 cm of the wood surface immediately after the treatment, while boron penetrated about 0.8 cm into the wood in the longitudinal direction immediately after treatment.

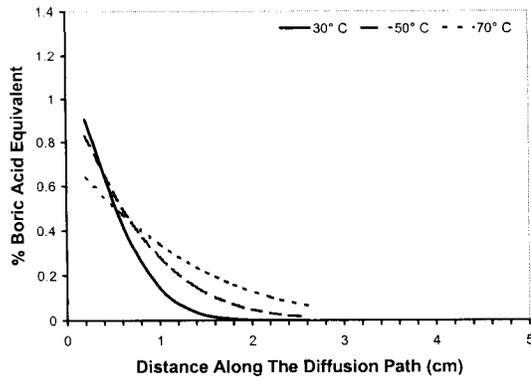
*Effect of temperature.*—The effect of temperature on the rate of boron diffusion in the 110% MC samples treated with a single immersion treatment is shown in Fig. 5. It took about 4 days to achieve complete penetration in the longitudinal direction. Complete penetration in radial diffusion was observed at 70°C after 9 days, but the 30°C and 50°C treatments lagged behind. No complete penetration of boron was observed in the tangential direc-



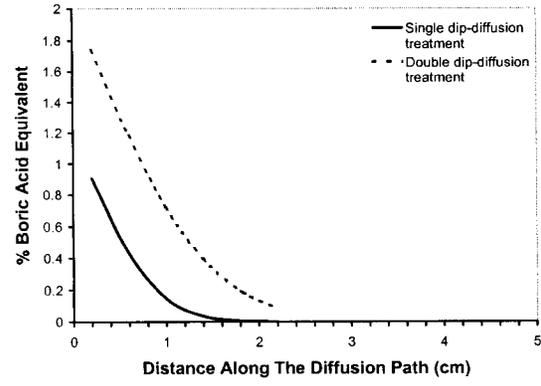
(A) Radial Direction



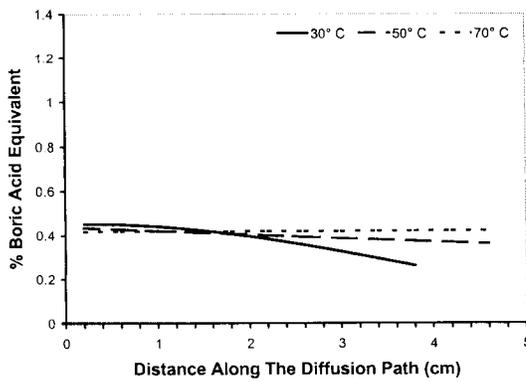
(A) Radial Direction



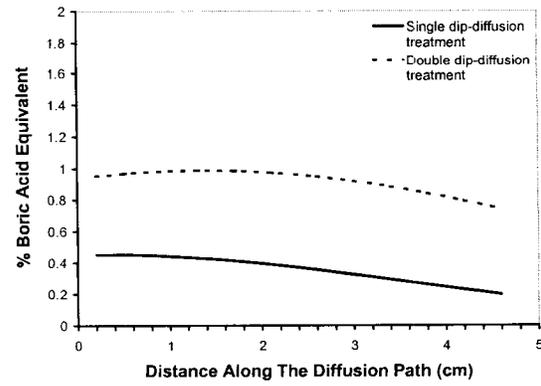
(B) Tangential Direction



(B) Tangential Direction



(C) Longitudinal Direction



(C) Longitudinal Direction

FIG. 5. Comparison of boron after 9 days' diffusion in the radial (A), tangential (B), and longitudinal (C) directions under various temperature conditions.

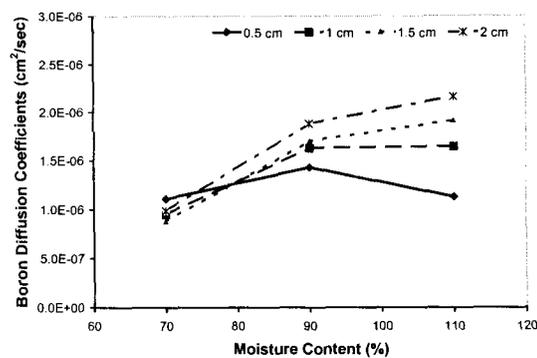
FIG. 6. Comparison of boron after 9 days' diffusion in the radial (A), tangential (B), and longitudinal (C) directions between single- and double-dip treatments.

TABLE 1. The diffusion coefficients of boron in the samples treated using single-dip diffusion treatment and stored at 30°C under various MC conditions.

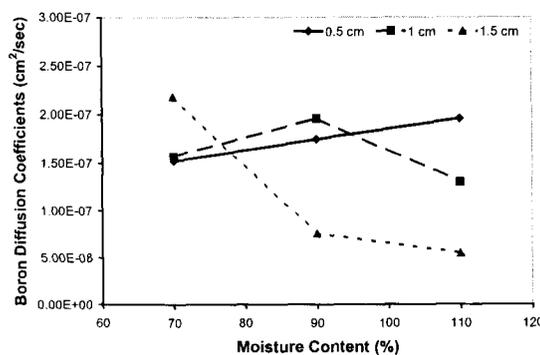
| Direction                             | MC (%) | Time (days) | Thickness (cm) |       |       |       |
|---------------------------------------|--------|-------------|----------------|-------|-------|-------|
|                                       |        |             | 0.5            | 1.0   | 1.5   | 2.0   |
| (10 <sup>-7</sup> cm <sup>2</sup> /s) |        |             |                |       |       |       |
| Radial                                | 70     | 4           | 1.9            | 7.8   | —     | —     |
|                                       |        | 9           | 3.0            | 6.3   | 11.5  | —     |
|                                       |        | 16          | 4.2            | 7.6   | 10.6  | 15.3  |
|                                       |        | 25          | 11.1           | 9.5   | 8.8   | 9.9   |
|                                       | 90     | 4           | 3.0            | 7.7   | —     | —     |
|                                       |        | 9           | 4.5            | 8.6   | 13.9  | —     |
|                                       |        | 16          | 7.8            | 10.8  | 13.1  | 17.1  |
|                                       |        | 25          | 14.3           | 16.3  | 17.0  | 18.8  |
|                                       | 110    | 4           | 3.0            | 6.6   | —     | —     |
|                                       |        | 9           | 4.7            | 10.1  | 16.0  | —     |
|                                       |        | 16          | 10.0           | 11.3  | 12.3  | 15.1  |
|                                       |        | 25          | 11.3           | 16.4  | 19.1  | 21.6  |
| Tangential                            | 70     | 4           | 0.8            | 3.1   | —     | —     |
|                                       |        | 9           | 1.2            | 2.5   | 6.7   | —     |
|                                       |        | 16          | 1.0            | 2.0   | 6.9   | —     |
|                                       |        | 25          | 1.5            | 1.6   | 2.2   | —     |
|                                       | 90     | 4           | 0.8            | 3.3   | —     | —     |
|                                       |        | 9           | 1.3            | 2.8   | 2.1   | —     |
|                                       |        | 16          | 1.1            | 2.0   | 2.6   | —     |
|                                       |        | 25          | 1.8            | 2.0   | 7.6   | —     |
|                                       | 110    | 4           | 0.7            | 1.6   | —     | —     |
|                                       |        | 9           | 1.0            | 1.5   | 1.6   | —     |
|                                       |        | 16          | 0.9            | 1.2   | 1.4   | —     |
|                                       |        | 25          | 2.0            | 1.3   | 0.6   | —     |
| Longitudinal                          | 70     | 1           | 8.0            | 15.9  | 32.1  | 76.6  |
|                                       |        | 4           | 27.9           | 30.9  | 31.1  | 32.1  |
|                                       |        | 9           | 44.2           | 56.6  | 57.4  | 53.6  |
|                                       |        | 9           | 9.5            | 17.2  | 29.1  | 54.3  |
|                                       | 90     | 1           | 9.5            | 17.2  | 29.1  | 54.3  |
|                                       |        | 4           | 37.1           | 68.5  | 93.7  | 115.1 |
|                                       |        | 9           | 39.2           | 70.3  | 92.7  | 107.6 |
|                                       |        | 9           | 20.1           | 21.8  | 30.2  | 52.2  |
|                                       | 110    | 1           | 20.1           | 21.8  | 30.2  | 52.2  |
|                                       |        | 4           | 59.9           | 99.9  | 123.3 | 133.4 |
|                                       |        | 9           | 372.0          | 253.4 | 214.7 | 188.1 |

tion over the same time period. The rate of boron diffusion increased with the increase of temperature and the fastest increasing rates were observed in the longitudinal direction, followed by the radial and the tangential directions.

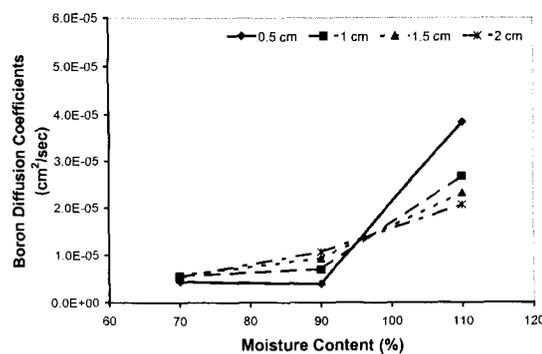
*Effect of treatment type.*—The effect of a second immersion treatment is shown in Fig. 6. The initial absorption was more than double that of the samples treated using a single immersion treatment, and also yielded greater penetration. Much greater penetration of boron



(A) Radial Direction



(B) Tangential Direction



(C) Longitudinal Direction

FIG. 7. Effect of moisture content on boron diffusion coefficients in the radial (A), tangential (B), and longitudinal (C) directions.

was observed in the samples treated using a double-dip treatment. This resulted from the fact that more boron was deposited on the surface during the second treatment, creating the

TABLE 2. The diffusion coefficients of boron in the 110% MC samples treated using single-dip diffusion treatment and stored under various temperature conditions.

| Direction                             | Temp (°C)  | Time (days) | Thickness (cm) |       |       |       |       |
|---------------------------------------|------------|-------------|----------------|-------|-------|-------|-------|
|                                       |            |             | 0.5            | 1.0   | 1.5   | 2.0   |       |
| (10 <sup>-7</sup> cm <sup>2</sup> /s) |            |             |                |       |       |       |       |
| Radial                                | 50         | 4           | 3.2            | 7.8   | 15.5  | 29.5  |       |
|                                       |            | 9           | 5.3            | 11.1  | 17.3  | 24.2  |       |
|                                       |            | 16          | 7.9            | 13.1  | 16.6  | 19.5  |       |
|                                       |            | 25          | 17.3           | 22.4  | 23.7  | 24.0  |       |
|                                       | 70         | 4           | 7.8            | 12.0  | 15.6  | 19.7  |       |
|                                       |            | 9           | 8.0            | 12.0  | 14.6  | 17.2  |       |
|                                       |            | 16          | 9.3            | 16.9  | 22.7  | 26.9  |       |
|                                       |            | 25          | 24.8           | 44.1  | 57.6  | 65.7  |       |
|                                       | Tangential | 50          | 4              | 1.7   | 3.7   | 7.2   | —     |
|                                       |            |             | 9              | 2.0   | 4.0   | 6.4   | —     |
|                                       |            |             | 16             | 3.9   | 4.8   | 5.4   | —     |
|                                       |            |             | 25             | 3.3   | 5.2   | 6.2   | —     |
| 70                                    |            | 4           | 2.2            | 4.3   | 10.1  | —     |       |
|                                       |            | 9           | 4.0            | 7.7   | 11.7  | —     |       |
|                                       |            | 16          | 4.5            | 7.8   | 10.3  | —     |       |
|                                       |            | 25          | 9.8            | 11.0  | 10.8  | —     |       |
| Longitudinal                          |            | 50          | 1              | 10.9  | 22.1  | 33.6  | 45.9  |
|                                       |            |             | 4              | 38.3  | 71.3  | 98.1  | 117.0 |
|                                       |            |             | 9              | 160.2 | 311.1 | 448.4 | 568.1 |
|                                       |            | 70          | 1              | 13.5  | 30.8  | 34.5  | 34.4  |
|                                       | 4          |             | 130.7          | 278.0 | 247.7 | 193.2 |       |

larger concentration differences which moved the boron molecules through the wood more quickly.

#### Boron diffusion coefficients

Shown in Table 1 are the boron diffusion coefficients calculated using Egner's solution under various MC conditions. For the samples treated using a single-dip treatment and stored at 30°C, the values of the radial diffusion coefficients calculated by Egner's solution were between  $1.89 \times 10^{-7}$  cm<sup>2</sup>/s and  $1.91 \times 10^{-6}$  cm<sup>2</sup>/s. The tangential diffusion coefficients were between  $0.77 \times 10^{-7}$  cm<sup>2</sup>/s and  $7.57 \times 10^{-7}$  cm<sup>2</sup>/s, and the longitudinal diffusion coefficients were between  $7.91 \times 10^{-7}$  cm<sup>2</sup>/s and  $9.27 \times 10^{-6}$  cm<sup>2</sup>/s. The higher diffusion coefficients were observed from the area where the concentration gradient approached zero.

*Effect of moisture content.*—Figure 7 shows the change of the diffusion coefficients of boron with MC. The diffusion coefficients generally increased with MC, although there are

only slight differences between 90 and 110% MC. Above 90% MC, the rates of boron diffusion in radial direction changed little with change in MC. A clearer effect of MC on the boron diffusion was found for diffusion in the longitudinal direction. The longitudinal diffusion coefficients of boron increased as MC increased, and the effect was more pronounced at higher MCs. No clear relationship between the tangential boron diffusion coefficients and MC was observed in this experiment.

*Effect of temperature.*—Elevating temperature can be used to shorten the time of boron diffusion in wood. Table 2 shows the boron diffusion coefficients under various temperature conditions. In the radial direction, the boron diffusion coefficients did not increase in the early stage of diffusion, but the values did increase for longer diffusion periods. After 25 days, the diffusion coefficients at 70°C were significantly higher than the values at 50°C, but the difference was slight between 30°C and 50°C. The trend is very similar to that of

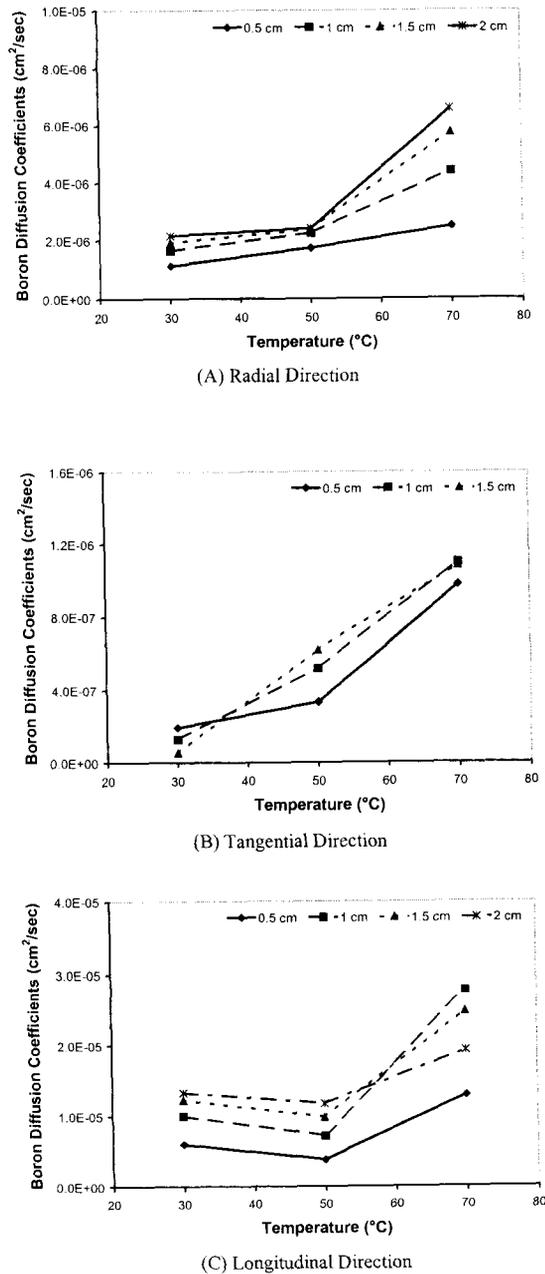


FIG. 8. Effect of temperature on boron diffusion coefficients in the radial (A), tangential (B), and longitudinal (C) directions.

TABLE 3. The diffusion coefficients of boron in the 110% MC samples treated using double-dip diffusion treatment and stored at 30°C.

| Direction                             | Time (days) | Thickness (cm) |       |       |       |
|---------------------------------------|-------------|----------------|-------|-------|-------|
|                                       |             | 0.5            | 1.0   | 1.5   | 2.0   |
| (10 <sup>-7</sup> cm <sup>2</sup> /s) |             |                |       |       |       |
| Radial                                | 4           | 3.1            | 9.2   | 19.7  | 36.4  |
|                                       | 9           | 4.4            | 9.2   | 15.0  | 22.6  |
|                                       | 16          | 23.1           | 12.5  | 11.2  | 13.0  |
|                                       | 25          | 17.3           | 22.5  | 23.3  | 22.8  |
| Tangential                            | 4           | 2.2            | 4.3   | 10.1  | —     |
|                                       | 9           | 4.0            | 7.7   | 11.7  | —     |
|                                       | 16          | 4.5            | 7.8   | 10.3  | —     |
|                                       | 25          | 9.8            | 11.1  | 10.8  | —     |
| Longitudinal                          | 1           | 11.3           | 19.8  | 27.8  | 36.3  |
|                                       | 4           | 102.4          | 139.2 | 145.2 | 134.2 |

the longitudinal diffusion of boron where the coefficients greatly increased at 70°C. The tangential diffusion of boron tended to proportionally increase with temperature, perhaps because the cell-wall thickness remains more constant in the tangential direction than in the longitudinal and radial directions (Becker 1976). The change in the boron diffusion coefficients with temperature is shown in Fig. 8.

*Effect of treatment.*—Table 3 lists the boron diffusion coefficients for single- and double-dip diffusion treatments. Double-dip diffusion treatments resulted in higher boron diffusion coefficients, and the largest differences of boron diffusion coefficients were observed near sample surfaces (Fig. 9). This indicated that the boron absorbed by a second immersion caused higher concentration differences of boron, especially near the surface, which resulted in faster rates of boron diffusion.

A much more significant effect of the second dip-diffusion treatment was observed in the tangential direction (Fig. 9). This result may be explained by the larger concentration differences found in the tangential direction compared to the other two directions. In the tangential direction, there are no feasible pathways for a continuous water phase such as the lumens of ray cells in the radial direction or the lumens of longitudinal tracheids in the longitudinal direction.

### The prediction of boron diffusion

The boron diffusion coefficients calculated using Egner's solution varied with sample thickness. For practical use, an average of the boron diffusion coefficients at various thicknesses is needed. Shown in Table 4 are the average boron diffusion coefficients under various conditions. The differences among the diffusion coefficients in the radial, tangential, and longitudinal directions tended to be larger as MC and temperature increased. The longitudinal diffusion coefficients are 20 to 40 times larger than tangential diffusion coefficients, and the radial diffusion coefficients are two to four times larger than the tangential diffusion coefficients. The average values were used to predict boron diffusion under various conditions.

Figure 10 shows the difference between the predicted values and the real values of the sample treated using a single-dip diffusion treatment and stored at 30°C. The larger differences observed near sample surfaces resulted from the assumptions used for the equation such as constant diffusion coefficients. The predicted values were most similar to the observed values in the tangential direction. The reason is unclear. One explanation may be that there is a constant cell-wall thickness in the tangential direction and more uniform pathways for diffusion compared to the radial and longitudinal directions.

### CONCLUSIONS

The data presented here are the first reported results of experiments on boron diffusion in wood. The radial, tangential, and longitudinal diffusion coefficients for boron were calculated using Egner's method and measured under various MC, temperature, and treatment conditions. The diffusion coefficients increased with increasing MC in the longitudinal and radial directions. The increase of the radial diffusion coefficient was very slight above 90% MC, although the longitudinal diffusion coefficients were significantly higher. The differences among the diffusion coefficients in

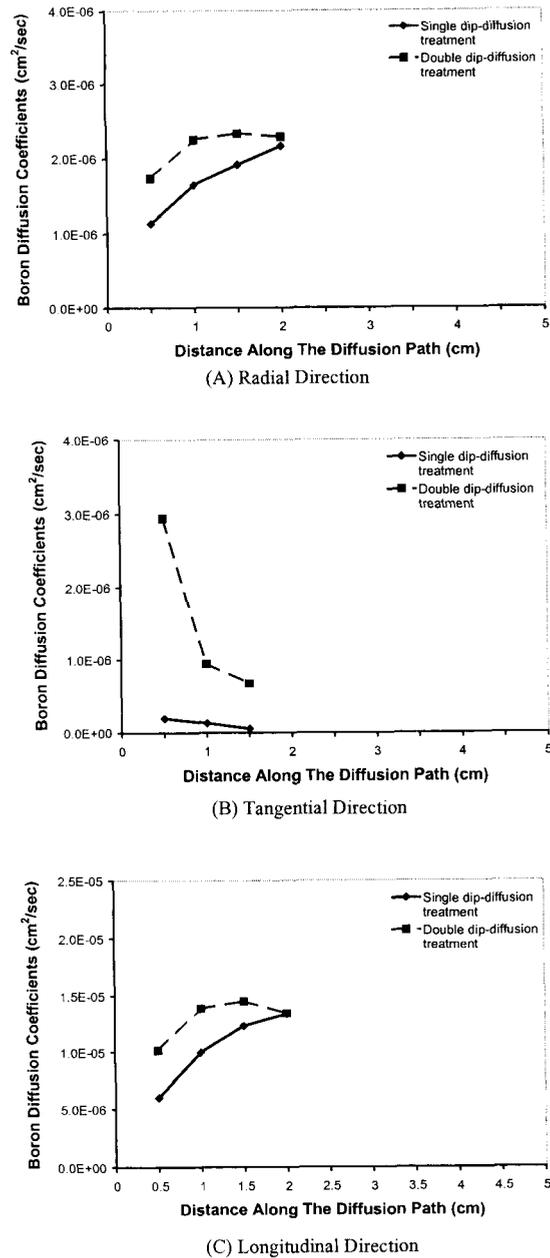


FIG. 9. Effect of treatment on boron diffusion coefficients in the radial (A), tangential (B), and longitudinal (C) directions.

each direction tended to be larger as MC and temperature increased. The longitudinal diffusion coefficients were 20 to 40 times larger than tangential diffusion coefficients, and the

TABLE 4. The average diffusion coefficients under various conditions.

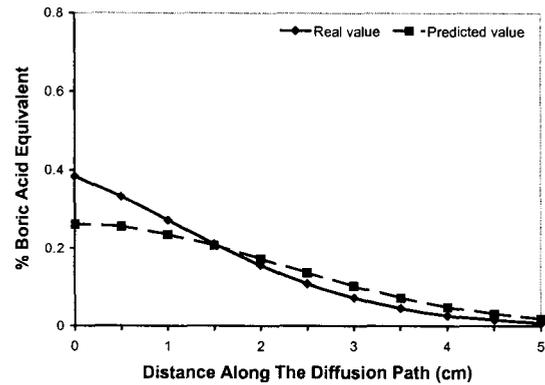
| Direction    | Temp (°C) | MC (%) | Treatment  | Diffusion coefficient ( $10^{-7}$ cm <sup>2</sup> /s) |
|--------------|-----------|--------|------------|---|
| Radial       | 30        | 70     | Single dip | 7.8   |
|              | 30        | 90     | Single dip | 11.0  |
|              | 30        | 110    | Single dip | 11.1  |
|              | 50        | 110    | Single dip | 16.2  |
|              | 70        | 110    | Single dip | 23.5  |
| Tangential   | 30        | 110    | Double dip | 16.6  |
|              | 30        | 70     | Single dip | 2.6   |
|              | 30        | 90     | Single dip | 2.5   |
|              | 30        | 110    | Single dip | 1.3   |
|              | 50        | 110    | Single dip | 4.1   |
| Longitudinal | 70        | 110    | Single dip | 7.3   |
|              | 30        | 110    | Double dip | 8.5   |
|              | 30        | 70     | Single dip | 73.1  |
|              | 30        | 90     | Single dip | 68.5  |
|              | 30        | 110    | Single dip | 121.0   |
|              | 50        | 110    | Single dip | 188.6   |
|              | 70        | 110    | Single dip | 239.3   |
|              | 30        | 110    | Double dip | 139.2   |

radial diffusion coefficients were two to four times larger than the tangential diffusion coefficients. No consistent trend with MC was shown for the tangential diffusion coefficients. Moisture content also affected the initial absorption of boron. More boron was absorbed on the surface of wetter wood and the cross section showed the highest absorption, followed by the tangential and radial surfaces.

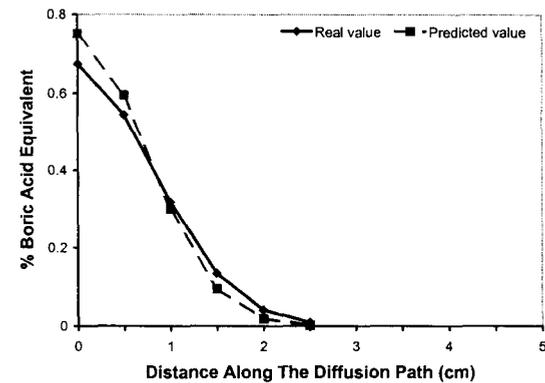
Higher temperatures raised the boron diffusion coefficients in the radial, tangential, and longitudinal directions. In the radial and longitudinal directions, the diffusion tended to be accelerated with the increase of MC, while in the tangential direction the diffusion coefficients increased proportionally with temperature.

The double immersion treatment increased the penetration of boron. The amount of boron was more than double that from a single immersion treatment. The diffusion coefficients were slightly larger than those for the single-dip diffusion treatment, but this is due to the effect of larger concentration differences.

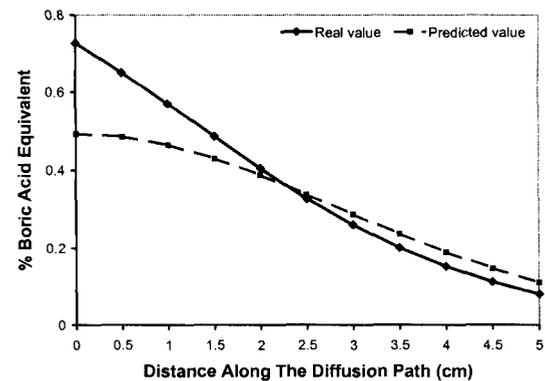
Average values of the diffusion coefficient at various distances along the diffusion path



(A) Radial Direction



(B) Tangential Direction



(C) Longitudinal Direction

FIG. 10. Comparison of predicted and real values of boron concentration in the radial (A), tangential (B), and longitudinal (C) directions. Samples were treated using a single-dip diffusion treatment and stored at 30°C for 25 days.

were calculated and used for the prediction of the concentration profile of boron in wood. The largest differences between the real values and the predicted values were found nearest the exposed surface in the diffusion direction. This method offers a potential way for predicting boron diffusion.

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# EQUILIBRIUM MOISTURE CONTENT OF WOOD IN HIGH-TEMPERATURE PRESSURIZED ENVIRONMENTS

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## ABSTRACT

Experiments were conducted on the water sorption characteristics of three wood species, for both juvenile wood and mature wood, at conditions above and below 100°C. A pressurized chamber was constructed for this purpose. At 50°C, equilibrium moisture content (EMC) behavior deviated only slightly from predictions based on the published data for Sitka spruce. At 160°C, the sorption behavior was distinctly different from the 50°C data, or any extrapolation from published low-temperature data. The data suggested that a change in the sorptive properties of the wood occurred as temperature and moisture conditions exceeded the glass transition temperature for lignin. At 50°C, juvenile wood tended to equilibrate at a higher moisture content than mature wood. At 160°C, however, juvenile wood exhibited a markedly lower EMC than mature wood. Thermal degradation of wood was detected during the experiments. Reduction in the sorptive behavior as a result of thermal degradation is proposed as a possible explanation for differences in EMC behavior for juvenile and mature wood at 160°C.

*Keywords:* EMC (equilibrium moisture content), wood, thermal degradation, high-temperature, sorption.

## INTRODUCTION

This research effort focused on investigations of the wood-water relationship at conditions relevant to the hot pressing of wood-based composites. Very little information has been documented on the equilibrium moisture content (EMC) behavior of wood in environments of elevated temperature and pressure. Such data are essential in understanding the influence of moisture on the viscoelastic behavior of wood. The specific objectives of this study were: to develop apparatus and techniques suitable for collecting sorption isotherm data at high temperatures and pressures,

and to characterize the EMC vs. relative humidity behavior of selected wood species in environments relevant to hot pressing.

## BACKGROUND

During the hot pressing of wood-based composites, internal mat temperature has been measured in excess of 150°C and relative humidity calculated to reach or exceed 75% (Humphrey and Bolton 1989; Kamke and Casey 1989; Kamke and Wolcott 1991). In some cases, saturation occurs (Kamke and Johnson 1994). Such severe processing conditions are adequate to transcend the glass transition of the viscoelastic wood polymers (Kelly et al. 1987) and have been reported to change the properties of the wood component (Geimer et

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