

PREDICTING BORON DIFFUSION IN WOOD FROM SURFACE SORPTION

J.B. RA*
H.M. BARNES*
T.E. CONNERS

ABSTRACT

Constant radial diffusion coefficients of boron through southern pine (*Pinus* spp.) were determined from the total amount of boron diffusing through wood and the amount of boron remaining on the wood surface after different diffusion periods. The concentration profiles of the treated samples were measured using a slicing technique. Another coefficient representing the effect unexplained by the diffusion coefficients at the given conditions was calculated by comparing the real values of boron concentration through the wood with the predicted values calculated using the diffusion coefficients. This method shows a potential way to easily predict the boron diffusion coefficients for dip-diffusion treatment. If the coefficients represent the difference among species characteristics, they might be useful as species indices. Future research is needed to determine additional coefficients of different species at various conditions.

Boron diffusion in wood is dependent on factors such as wood moisture content (MC), temperature, diffusion period, solution strength and temperature, diffusion direction, and treatment method (Puettmann and Schmidt 1997, Morrell et al. 1990, U.S. Borax 1986, Smith and Williams 1969). Research has been performed to predict boron behavior in wood, but only a few trials have been performed to mathematically quantify the boron diffusion.

One approach to predict the boron behavior in wood is to determine the boron diffusion coefficients. Ra and others (Ra et al. 2001, Ra and Barnes 1999) determined the radial boron diffusion coefficients of southern pine (*Pinus* spp.) using Egner's solution, a modified form of Fick's second law for diffusion. Egner's solution can be used for any diffusible system because it has no cumbersome assumptions (Skaar 1954). Although various diffusion coefficients can be

obtained from Egner's solution, the method has some disadvantages for practical application. If the calculated diffusion coefficients are not expressed as a function of MC, temperature, or thickness, it is very difficult to apply Egner's solution for predictive purposes. Constant diffusion coefficients should be calculated from the various diffusion coefficients to predict the boron movement in wood using Egner's solution.

In this research, constant radial boron diffusion coefficients were determined

from the total amount of boron diffusing through wood and the amount of boron remaining on the wood surface at various diffusion periods. Applications for predicting boron diffusion in wood are also discussed.

MATERIALS AND METHODS

SAMPLE PREPARATION AND TREATMENT

A kiln-dried southern pine (*Pinus* spp.) sapwood board, nominally 50 by 150 mm in cross section by 120 cm long, was cut into 5- by 5- by 5-cm defect-free sapwood samples. The samples were oven-dried at $103 \pm 2^\circ\text{C}$ to a constant weight, and then weighed to the nearest 0.01 g. To minimize sample variation, specific gravity (SG) was measured for each cube. Only samples with SGs (oven-dry mass and volume basis) between 0.53 and 0.58 were used for this study.

Samples were treated with water under a vacuum until they reached 110 percent MC. Overweight samples were carefully air-dried at ambient conditions until they reached the desired moisture levels. Once samples reached the desired moisture level, all surfaces of sam-

The authors are, respectively, Former Graduate Student, currently Lecturer, Dept. of Forest Products Engineering College of Science and Engineering, Chonju National Univ., Republic of Korea; Professor, Forest Products Lab., Mississippi State Univ., Box 9820, Mississippi State, MS 39762-9820.; and Extension Specialist, Dept. of Forestry, Univ. of Kentucky, Lexington, KY 40546. Approved as J. Article FP 222 of the Forest & Wildlife Res. Center, Mississippi State Univ. This paper was received for publication in June 2001. Reprint No. 9330.

*Forest Products Society Member.

©Forest Products Society 2002.

Forest Prod. J. 52(10):67-70.

TABLE 1. — Assay values for boron in samples taken in the radial direction.^a

Thickness (cm)	Diffusion period (days)				
	1	4	9	16	25
	----- (% BAE) -----				
0.0 to 0.4	0.746	0.585	0.396	0.248	0.143
0.4 to 0.8	0.235	0.332	0.252	0.209	0.130
0.8 to 1.2	0.047	0.127	0.172	0.172	0.109
1.2 to 1.6	ND	0.042	0.120	0.132	0.093
1.6 to 2.0	ND	ND	0.053	0.077	0.074
2.0 to 2.4	ND	ND	0.047	0.050	0.054
2.4 to 2.8	ND	ND	0.031	0.036	0.030
2.8 to 3.2	ND	ND	ND	0.020	0.022
3.2 to 3.6	ND	ND	ND	ND	0.018
3.6 to 4.0	ND	ND	ND	ND	0.015

^a The value is the total amount of boron in the thickness and represents the average of two replicates; ND = not detected

ples were coated with silicone rubber to prevent further MC changes. Samples were kept under 100 percent relative humidity (RH) conditions for 48 hours until the silicone was cured and then they were stored for 5 weeks at 30°C and 100 percent RH to minimize internal moisture gradients.

An outer tangential surface was removed using a radial-arm saw to permit boron flow only in the radial direction. Immediately after cutting, duplicate samples were dip-treated for 5 minutes in 25 percent boric acid equivalent (BAE) TIM-BOR[®] solution (disodium octaborate tetrahydrate [DOT] [Na₂B₈O₁₃·4H₂O]) at 50°C (U.S. Borax 1986). The ratio of solution to specimen volumes was large enough so 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 30°C. Samples were sliced radially into nominal 0.4-cm wafers after either 0, 1, 4, 9, 16, or 25 days of diffusion storage. After diffusion storage, samples were removed, and trimmed with a radial-arm saw to approximately 4.8 by 4.8 by 4.8 cm to remove the remaining coating, and sliced into 0.4-cm wafers in the radial direction (Ra et al. 2001, Ra and Barnes 1999). The wafers were placed into individual capped weighing bottles immediately after being severed from the sample, then oven-dried in their respective bottles until constant weight was achieved.

The oven-dried wafers were ground to pass a 20 mesh screen prior to analysis for boron content. Boron content was

determined using the titration method with mannitol according to the AWP A2-95 procedure (AWPA 1995). Duplicate wafers for each combination of radial distance and diffusion period were analyzed.

DETERMINATION OF DIFFUSION COEFFICIENTS

General solutions of diffusion equations for a variety of initial and boundary conditions have been previously published (Crank 1975, Skaar 1954, Crank and Henry 1949). Equation [1] shows the solution of Fick's second law for an infinite volume when all the diffusing substance is concentrated initially in a plane. This equation is derived assuming a constant diffusion coefficient. The diffusing substance is initially deposited at time $t = 0$ and left to diffuse throughout the surrounding medium ($-\infty < x < \infty$).

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

where M = total amount of a diffusing substance (g); D = diffusion coefficient (cm² sec⁻¹); C = concentration of diffusion substance (%); and x = thickness of sample in the direction of diffusion (cm).

Equation [1] describes the spreading by diffusion of an amount of substance M deposited at time $t = 0$ in the plane $x = 0$. Half the diffusing substance moves in the positive x direction and the other half along negative x coordinates. 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]).

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

This equation 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).

Constant diffusion coefficients were determined using Equation [2]. At $x = 0$ the variation of boron concentration with time is shown in Equation [3]. This supplies a simple means of measuring the constant diffusion coefficient.

$$\frac{C}{M} = \frac{1}{\sqrt{\pi Dt}} \quad [3]$$

The diffusion coefficient, D , did not fully explain the observed results. For this reason, another coefficient, E , was added to Equation [2] to more precisely enable the prediction of actual boron concentration as shown in Equation [4].

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

where E = a coefficient representing the effect unexplained by the diffusion coefficients as discussed in the following section.

RESULTS AND DISCUSSION

The total amount of boron at each thickness interval was calculated by multiplying the boron concentration of the sliced samples by the sample thickness, 0.4 cm (Table 1). Except for the 25-day diffusion samples, similar amounts of boron were absorbed on wood surfaces when they were treated. This means that the wood surface conditions were one of the factors affecting the initial amount of boron absorbed on the wood surface. The depth of borate penetration increased with time, and the penetration was limited to the depth of about 4 cm after 25 days of diffusion (Table 1).

Constant diffusion coefficients were determined using Equation [3] at various diffusion periods, and the average amounts of boron in the first sliced samples were used as the boron amount at $x = 0$. They increased proportionally with time (Fig. 1). The constant diffusion coefficients could not entirely explain the distribution of boron in wood. As seen

in **Figure 2**, the predicted values calculated using the diffusion coefficients were slightly higher than the actual values. The differences may be explained by two reasons: 1) assumptions included in Fick's second law; and 2) the characteristic of wood related to the medium of boron diffusion. Fick's first and second laws assume constant diffusion coefficients, which is not true for most cases. The diffusion coefficients can be taken as constants in the case of diffusion through a dilute solution, but in most cases they are very dependent on the chemical nature of both the diffusing substance and the diffusion medium (Hart 1964). They also depend on temperature and concentration (particularly in liquids) and vary with direction in anisotropic bodies such as crystals, fibers, and wood. Studies of moisture diffusion in wood have shown that the diffusion coefficients change with temperature, SG, MC, and other variables (Wengert and Skaar 1978, Choong and Fogg 1968, Choong 1965, Comstock 1963, Stamm 1960). Accordingly, only the boron diffusion through an ideal medium at ideal conditions is assumed to satisfy Equation [2].

Ideal conditions for boron diffusion cannot be achieved in wood since free and bound water are not uniformly distributed through wood. Even in wood saturated with water, small bubbles exist and act as barriers against boron diffusion. Also, there exist many uncontrollable factors affecting boron diffusion. Factors like MC, temperature, solution concentration, and diffusion period are controllable, but factors like a continuous water phase through wood are not. The uncontrollable factors are closely related to anatomical, physical, and chemical characteristics of wood, which vary with wood species. Accordingly, wood characteristics may account for the differences in boron movement among wood species because they affect the distribution of the media, free and bound water.

To account for the differences between actual and predicted observations, a coefficient, E , was selected to produce closer approximations for boron concentration. According to **Figure 2**, the best value for predicting the boron diffusion in southern pine at 30°C and 110 percent MC conditions appeared to be near 2. When E is 1, Equation [4] be-

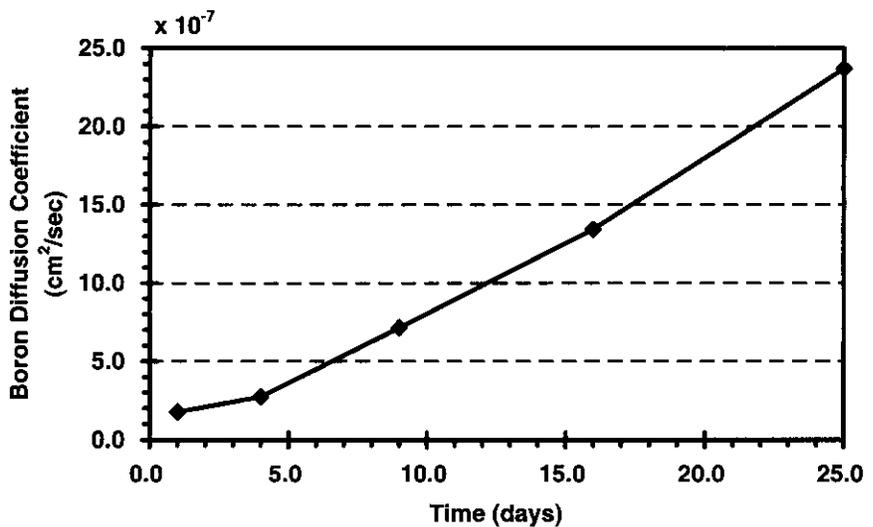


Figure 1.— Change of constant radial diffusion coefficients of boron with time at 110 percent MC and 30°C.

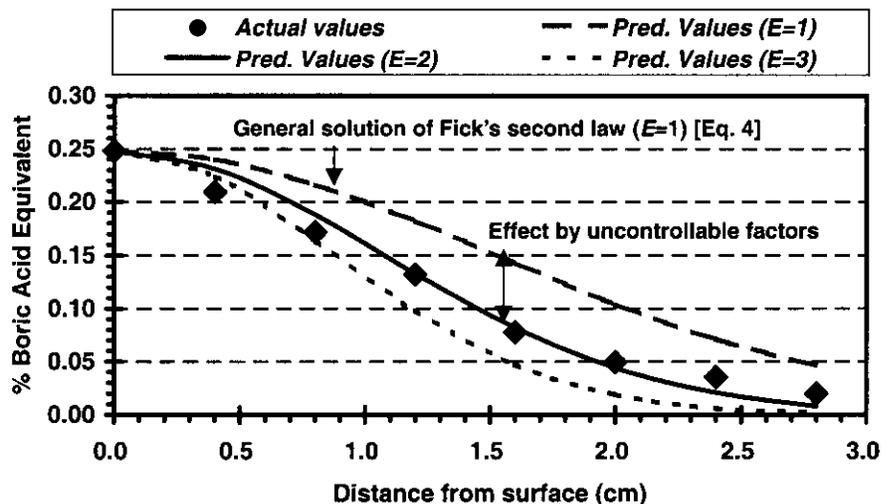


Figure 2.— Comparison of the actual values with the predicted values at various E values.

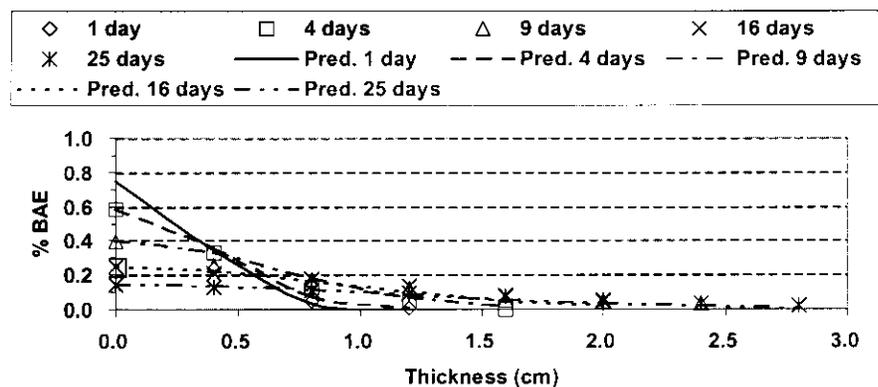


Figure 3.— Comparison of the actual values (symbols) and the predicted values (lines) for five time periods when E is 2.

comes Equation [2] - Fick's second law. Shown in **Figure 3** are the differences between the real and the predicted values when E is 2 as diffusion time passed.

If the addition of E into Fick's second law minimizes the differences between the real and the predicted, E represents the effect unexplained by the diffusion coefficients that may be caused by wood characteristics. Although wood characteristics vary considerably, even in the same species, it may be possible to obtain the range of E at given conditions. Since the coefficient mathematically quantifies the effect of the uncontrollable factors, E might be used as a species index. Future research is required to determine the coefficients of different species at various conditions and to express E as a function of wood characteristics.

CONCLUSIONS

Constant radial boron diffusion coefficients in southern yellow pine sapwood at 30°C and 110 percent MC could be determined from the total amount of boron diffusing into wood and the amount of boron remaining on the wood outer surface over time. The diffusion coefficients proportionally increased with time. To obtain more precise ap-

proximation for prediction, another coefficient was determined by comparing the real values with the predicted values. We speculate that the coefficient represents the effect of the uncontrollable factors such as wood characteristics, so it may be used as a species index to account for differences in boron diffusion among wood species.

LITERATURE CITED

- American Wood-Preserver's Association (AWPA). 1995. Book of Standards, Standard A2. Standard methods for analysis of water borne preservatives and fire-retardant formulations. AWPA, Woodstock, MD.
- Choong, E.T. 1965. Drying coefficients of softwoods by steady-state and theoretical methods. *Forest Prod. J.* 15(1):21-27.
- _____, and P.J. Fogg. 1968. Moisture movement in six wood species. *Forest Prod. J.* 18(5):66-70.
- Comstock, G.L. 1963. Moisture diffusion coefficients in wood as calculated from adsorption, desorption, and steady-state data. *Forest Prod. J.* 13(3):97-103.
- Crank, J. 1975. *The Mathematics of Diffusion*. Oxford Univ. Press, New York. 414 pp.
- _____, and M.E. Henry. 1949. Diffusion in media with variable properties. Part I. The effect of a variable diffusion coefficient on the rates of absorption and desorption. *Trans. Faraday Soc.* 45:636-650.
- Hart, C.A. 1964. Principles of moisture movement in wood. *Forest Prod. J.* 14(5):207-214.
- Morrell, J.J., C.M. Sexton, and A.F. Preston. 1990. Effect of moisture content of Douglas-fir heartwood on longitudinal diffusion of boron from fused borate rods. *Forest Prod. J.* 40(4):37-40.
- Puettmann, M.E. and E.L. Schmidt. 1997. Boron diffusion treatment of aspen lumber stored under various relative humidities. *Forest Prod. J.* 47(10):47-50.
- Ra, J.B. and H.M. Barnes. 1999. A method for determining boron diffusion coefficients in wood. Doc. No. IRG/WP/99-30200. The Inter. Res. Group on Wood Preservation, Stockholm, Sweden. 10 pp.
- _____, _____, and T.E. Conners. 2001. Determination of boron diffusion coefficients in wood. *Wood & Fiber Sci.* 33(1): 90-103.
- Skaar, C. 1954. Analysis of methods for determining the coefficients of moisture diffusion in wood. *Forest Prod. J.* 4(12):403-410.
- Smith, D.N. and A.I. Williams. 1969. Wood preservation by the boron diffusion process: The effect of moisture content on diffusion time. *J. of the Inst. of Wood Sci.* 22(4):3-10.
- Stamm, A.J. 1960. Combined bound-water and water-vapor diffusion into Sitka spruce. *Forest Prod. J.* 10(12):644-648.
- U.S. Borax and Chemical Corp. 1986. TIM-BOR® Preservative Plant Operators' Manual. Valencia, CA.
- Wengert, E.M. and C. Skaar. 1978. Additional considerations in measuring transverse moisture conductivity in wood. *Wood Sci.* 11(2): 102-104.