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Determination of Diffusion Coefficients of Boron from Borate Rods in Wood Using Boltzmann's Transformation*[1]

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ABSTRACT

This research was performed to investigate the diffusivity of borate rods in radiata pine (*Pinus radiata* D. Don) conditioned to 40 percent moisture content (MC). The deepest penetration of boron were observed in the longitudinal direction, followed by the radial and the tangential directions. The boron loading on the wood face adjacent to the borate rod tended to increase with diffusion time in all directions. To mathematically quantify boron diffusion, the diffusion coefficient of boron was determined using Boltzmann's transformation by assuming that it was a function of concentration only. The values of the longitudinal diffusion coefficients were between 1.3×10^{-8} cm^2/sec and 9.2×10^{-8} cm^2/sec. The radial diffusion coefficients were between 1.4×10^{-8} cm^2/sec and 9.5×10^{-8} cm^2/sec, and the tangential diffusion coefficients were between 5.2×10^{-9} cm^2/sec and 1.3×10^{-8} cm^2/sec. The differences of diffusion coefficients between the longitudinal direction and the radial direction were slight, although their concentration profiles were markedly different. This indicates that the amount of boron loading on the wood face adjacent the borate rod is one of the most important factor for boron penetration in wood with low MC.

Keywords: borate, borate rod, diffusion, diffusion coefficients, fick's second law, boltzmann's transformation

1. INTRODUCTION

Boron have been proved to be very effective in the control and prevention of termites, wood-boring beetles, and wood decay fungi (Cockroft and Levy, 1973; Barnes *et al.*, 1989; Greaves, 1990; McNamara 1990; Murphy, 1990). Their insecticidal and fungicidal abilities, together with their high diffusivity in water and low mammalian toxicity, make boron attractive for remedial treatment (Barnes *et al.*, 1989; Murphy, 1990; Greaves, 1990; Williams, 1990). Currently, borate rods are used to prevent fungal and insect infestation in window joinery, railroad ties, transmission poles, and archaeological artifacts.

The penetration of boron applied by rods for remedial treatment of wood in use is dependent on wood moisture content (MC) because water is the medium for boron diffusion. The boron diffusion in wood is generally accepted to fall off very greatly below 50 percent MC and extremely slow below fiber saturation point (Smith and Williams, 1969; Lebow and Morrell, 1989; Williams, 1990). The slow diffusion of

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boron under low MC conditions is the major drawback in application of borate rod because most decay fungi can remain viable at MCs of around 25 percent. Morrell and Freitag (1995) reported that the range of MC of the wooden material that need remedial treatment is generally between 20 and 50 percent.

A few researches have been performed to mathematically quantify the diffusivity of boron in wood. Ra *et al.* (2001) investigated the effect of diffusion directions, temperature, and treatment types on diffusion rates of boron in wood under high MC conditions (>70%) by determining boron diffusion coefficients. They reported that 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. However, boron behavior in wood in high MC conditions may be quite different from those in wood in low MC conditions. In the conditions, there is not enough free water in the cell lumen that boron can diffuse easily, resulting in the diffusion through the bound water in cell walls.

The determination of diffusion coefficients of boron is necessary to understand boron diffusion mechanism in wood with low MC. But no trials have been performed to mathematically quantify boron diffusion in the conditions. The objective of this research was to determine diffusion coefficients of boron in wood with low MC, and to investigate the effect of diffusion directions on boron diffusion.

2. MATERIALS and METHODS

2.1. Material Selection and Preparation

Radiata pine (*Pinus radiata* D. Don) board, nominally 50×100 mm in cross section by 120 cm long, was cut into 1.5×3×10-cm defect-free sapwood samples. Samples were ovendried at 103±2°C until the weight of each sample remained constant, and specific gravity (SG) was measured for each sample to minimize sample variation. Only samples with SG (ovendried mass and volume basis) from 0.42 to 0.46 were used for this study. A single hole with 7.5 mm in diameter and 25 mm in depth was drilled in the narrow face of each sample. A hole was aligned along the central axis of the face and located 5 mm from one end to receive a borate rod. The samples were immersed into distilled water until they reached 40% moisture content (MC). Then the samples were wrapped with a plastic bag and stored at 25°C for two months. After two months, the MC profiles of three samples were measured. Since all measurements were within ±2% MC of the target MC, the samples were considered to have uniform moisture profiles.

2.2. Sample Treatment and Borate Analysis

Borate rods containing 2.5 g of 100% anhydrous disodium octaborate were placed in the hole of each sample. Samples were then individually wrapped with plastic bags and stored in an incubator maintained at 25°C. Three replicates were used for each treatment combination of diffusion direction (radial, tangential, and longitudinal direction), and diffusion periods (15, 30, 45, and 60 days). After predetermined period of diffusion storage passed, the samples were removed and were cut into approximately 4 mm- thickness slices to measure the boron concentration profiles. The boron content of each slices were determined using Azomethine-H analysis according to the AWPA A2-94 procedure (AWPA 1997).

2.3. Determination of Borate Diffusion Coefficient

Constant diffusion coefficients of boron were determined using Boltzmann's transformation (Crank, 1975). The unsteady-state diffusion is governed by Fick's second law. But when diffusion coefficient varies, the Fick's law must be replaced by the differential equations shown in equation (1).

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}(D\frac{\partial C}{\partial x}) = D\frac{\partial^2 C}{\partial x^2} + \frac{\partial D}{\partial C}(\frac{\partial C}{\partial x})^2 \quad (1)$$

where: C = the concentration of diffusing substance (w/w %); x = the thickness of sample in the direction of diffusion (cm); t = diffusion time (sec); and D = diffusion coefficients ($cm^2 \cdot sec^{-1}$)

When D is variable, the substitution $z = x/\sqrt{t}$ enabled Boltzmann's transformation by substitution into the partial differential equation.

$$\frac{d}{dz}(D\frac{dC}{dz}) = -\frac{z}{2}\frac{dC}{dz} \quad (2)$$

The equation (2) is easier to be numerically solved by integral of equation (2) than is the equation (1). The integral of equation (2) is shown in equation (3).

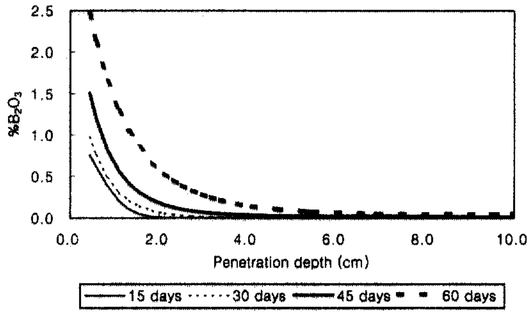
$$(D\frac{dC}{dz})_2 - (D\frac{dC}{dz})_1 = -\frac{1}{2}\int_{C_1}^{C_2} z\,dC \quad (3)$$

When measurement of concentration in terms of $z = x/\sqrt{t}$ are known, this equation can be used to find an average value of diffusion coefficients over some small or large range of concentrations.

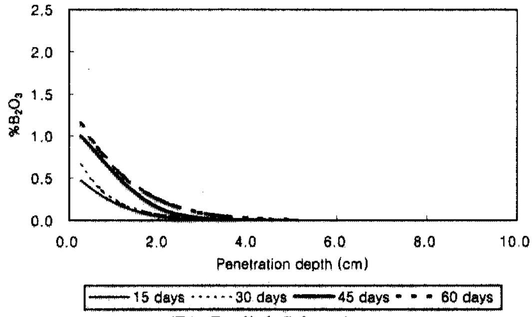
3. RESULTS and DISCUSSION

3.1. Boron Penetration

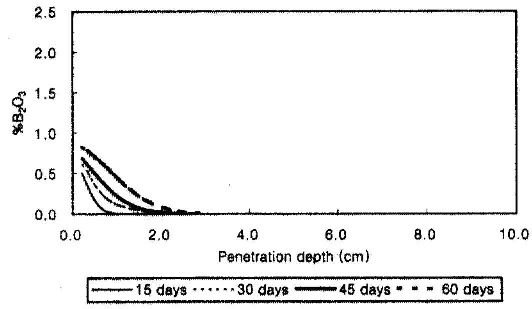
The boron concentration profiles in three anisotropic directions of samples conditioned to 40 percent MC are shown in Fig. 1. The deepest



(A) Longitudinal Direction



(B) Radial Direction



(C) Tangential Direction

Fig. 1. Concentration profiles of boron diffused from borate rods in radiata pine at 40% MC.

penetration was observed in the longitudinal direction, followed by the radial and the tangential directions. The depth of boron penetration increased with diffusion time but boron penetration was not complete at 40 percent MC in all directions. After 60 days of diffusion, boron penetration was limited to the depth about 5 cm from the treatment hole for the longitudinal direction, about 4 cm for the radial

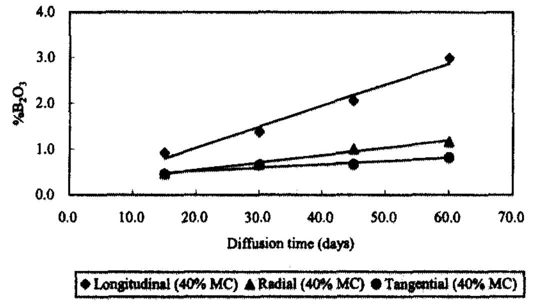


Fig. 2. Change of boron loadings on the wood face adjacent to borate rod under various time conditions

diffusion, and about 3 cm for the tangential direction. The boron diffusion from borate rod will be continued until there is no concentration difference through wood; however, few centimeters after 60 days diffusion at 40 percent MC is too shallow to prevent the attack of wood decay fungi. The results indicated that borate rod should be located near the entry of water source.

Boron loading on the wood face adjacent to the borate rod tended to be increased with diffusion time (Fig. 2). It was 1.5 to 2 times higher in the longitudinal direction than in the radial directions. That of the wood face in the radial direction was slightly larger than that in the tangential direction, although the differences were sometimes slight. The results indicated that one of the most important factor related to the diffusion is the amount of free water contacting directly with borate rod. More free water is exposed on the transverse surface compared to the radial and tangential surfaces, which resulting in more loading and deepest penetration in the longitudinal direction because the driving force of boron diffusion is concentration difference.

3.2. Boron Diffusion Coefficient

To determine the diffusion coefficients using

Table 1. Average diffusion coefficients determined using Boltzmann's transformation.

Diffusion direction	Thickness (cm)			
	0.5	1.0	1.5	2.0
	(10^{-8} cm^2/sec)			
Longitudinal	1.3	7.1	9.2	0.75
Radial	1.4	7.4	9.5	-
Tangential	1.4	0.9	0.5	-

Boltzmann's transformation, boron concentrations were expressed in terms of a single variable $z=x/\sqrt{t}$. By introduction of a new variable z, and the assumption of diffusion coefficients expressed as a function of concentration only, equation (1) is reduced to an ordinary differential equation [equation (2)]. The transformation can be used when diffusion take place in infinite or semi-infinite media provided the concentration is initially constant in the regions $x > 0$ or $x < 0$; the transformation can be used for diffusion and semi-infinite media when the initial concentrations are uniform and may be zero. When measurement of concentration in terms of $z=x/\sqrt{t}$ are known, this equation can be used to find an average value of diffusion coefficient over some small or large range of concentrations.

Shown in Table 1 are the boron diffusion coefficients calculated using Boltzmann's transformation. The required derivatives and integrals were obtained numerically. The determined diffusion coefficients represents the average diffusion coefficients at various thickness of samples for 60 days. The values of the longitudinal diffusion coefficients were between 1.3×10^{-8} cm^2/sec and 9.2×10^{-8} cm^2/sec. The radial diffusion coefficients were between 1.4×10^{-8} cm^2/sec and 9.5×10^{-8} cm^2/sec, and the tangential diffusion coefficients were between 5.2×10^{-9} cm^2/sec and 1.4×10^{-8} cm^2/sec. The values of longitudinal and the radial diffusion coefficients appeared to be larger than those of the tangential diffusion coefficients; This results can be explained by anisotropic characteristics of wood related to water because boron diffusion is faster in the direction where more free water is in the continuous water phase. Compared to tangential direction, there are easier pathways for boron diffusion in the longitudinal and the radial directions: cell lumens and pits in the longitudinal and cell lumens of the rays in the radial.

The values of determined diffusion coefficients between the longitudinal and the radial directions did not differ noticeably although the concentration profiles was markedly different. This indicates that the diffusion rates of boron between the longitudinal and the radial directions were not significantly different in 40 percent MC conditions (Table 1). Therefore, the markedly different penetration depths of boron in the longitudinal and the radial directions can be explained only by the different boron loadings on the wood face.

4. CONCLUSIONS

The radial, tangential, and longitudinal diffusion coefficients for boron were calculated using Boltzmann's transformation under 40 percent MC conditions by assuming that diffusion coefficient was a function of concentration only. The values of the longitudinal diffusion coefficients were between 1.3×10^{-8} cm^2/sec and 9.2×10^{-8} cm^2/sec. The radial diffusion coefficients were between 1.4×10^{-8} cm^2/sec and 9.5×10^{-8} cm^2/sec. The tangential diffusion coefficients were between 5.2×10^{-9} cm^2/sec and 1.4×10^{-8} cm^2/sec. Compared to the concentration profiles, the values of determined diffusion coefficients did not differ noticeably according to diffusion directions. This indicates that at 40 percent MC, most of boron diffuse through the bound water, not in free water, and the boron loading on the wood face adjacent to borate rod was one of the most important factors for boron penetration.

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