Diffusion of boron from borate rods in radiata pine

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Abstract

The diffusivity of borate rods was investigated in three anisotropic directions using radiata pine (*Pinus radiata* D. Don) sapwood samples conditioned to 40 and 60 percent moisture content (MC) for 60 days. Varying diffusion coefficients were graphically determined using the measured boron concentration profile of each sample except the longitudinal diffusion at 60 percent MC because the boundary conditions were completely changed during diffusion periods. Wetter samples showed deeper penetration and higher concentration of boron at the wood face adjacent to the borate rod. The deepest penetration of boron was observed in the longitudinal direction, followed by the radial and the tangential directions. But the values of the determined boron diffusion coefficients showed only slight differences. The results indicate that the limiting factor for boron diffusion rates at the given conditions was the diffusion through bound water.

A fused borate rod is the most promising borate formulation for remedial treatment because it has been proven to have many advantages, such as very low mammalian and environmental toxicity, effectiveness against wood decay fungi and insects, and high solubility in water (Cockroft and Levy 1973, Barnes et al. 1989, Greaves 1990, McNamara 1990, Murphy 1990). Although various fumigants currently used have a long history of success in arresting internal decay in wood poles in North America, they have caused handling and safety concerns during field application because of their high volatility and toxicity. Continuing public concerns resulted in encouragement of the use of safer formulations such as borate rods.

Although the use of borate rods has been steadily increasing for remedial treatment of wood, there are still questions regarding their effectiveness in wood with low moisture content (MC) (Dickinson 1990). If there is insufficient moisture in wood for diffusion, boron cannot diffuse well to areas being attacked by wood-destroying fungi or insects. The diffusion rates of boron generally fall off very greatly below 50 percent MC and also extremely decrease below the fiber saturation point (Smith and Williams 1969, Lebow and Morrell 1989, Williams 1990). The ranges of MCs of the wood members that need remedial treatments are generally between 20 and 50 percent (Morrell and Freitag 1995).

The understanding of boron diffusion mechanisms in wood under low MC conditions may provide a practical way to improve effectiveness of the borate rod for remedial treatment. One of the useful ways is to mathematically quantify the movement of boron from borate rods in wood. No research was found that determined diffusion coefficients of boron in wood under low MC conditions. The objective of this research was to determine boron diffusion coefficients in wood with low MC, and to investigate the effect of MC and diffusion directions on boron diffusion from borate rods in wood.

Materials and methods

Radiata pine (*Pinus radiata* D. Don) lumber was cut into 1.5-cm by 3-cm by 10-cm (diffusion direction) defect-free sapwood samples. In order to minimize

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errors due to sample variation, annual-ring angle and grain angle of end-matched samples were measured to the nearest 0.5 degrees using a scribe and protractor. The test samples with annual-ring and grain angles of 0 and 5 degrees were selected for this experiment. A single hole 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.

Samples were ovendried at 103 ± 2°C until the weight of each sample remained constant, and then weighed to the nearest 0.01g. The samples were immersed into distilled water until they reached 40 or 60 percent MC. Overweight samples were carefully air-dried at room temperature until they reached the desired moisture levels. When a sample reached the desired moisture level, it was wrapped with a plastic bag and stored at 25°C for 2 months to allow the wood more complete equilibration. The MC profiles of three samples from 40 and 60 percent MC groups were measured. Since all samples were within ±2 percent MC, the samples were considered to reach moisture equilibrium.

Once samples reached the desired moisture level, a fused borate rod (Impel®) containing 2.5 g of 100 percent anhydrous disodium octaborate was placed in the hole. Samples were then individually wrapped with a plastic bag and stored in an incubator maintained at 25°C. Three replicates were used for each treatment combination of MC (40% and 60%), diffusion direction (longitudinal, radial, and tangential), and diffusion periods (15, 30, 45, and 60 days). After a predetermined period of diffusion storage passed, the samples were removed and were cut into approximately 4-mm-thick slices to measure the boron concentration profiles. The boron content of each slice was determined using Azomethine-H analysis according to the American Wood-Preservers' Association standard A2-94 (AWPA 1997).

Varying diffusion coefficients of boron were determined using Egner's solution, a modified Fick's second law Equation [**1**]. Since Egner's solution graphically solves the diffusion coefficients, the accuracy of the determined diffusion coefficients is highly dependent on the exactness of the fitted equations of boron concentration profiles. Ra and Barnes (1999) reported that Egner's solution is the only way to determine varying diffusion coefficients without any cumbersome assumptions such as constant diffusion coefficients, and it can be applicable for any diffusible system. More detailed explanation about Egner's solution can be found in the literature (Skaar 1954, Ra and Barnes 1999, Ra et al. 2001).

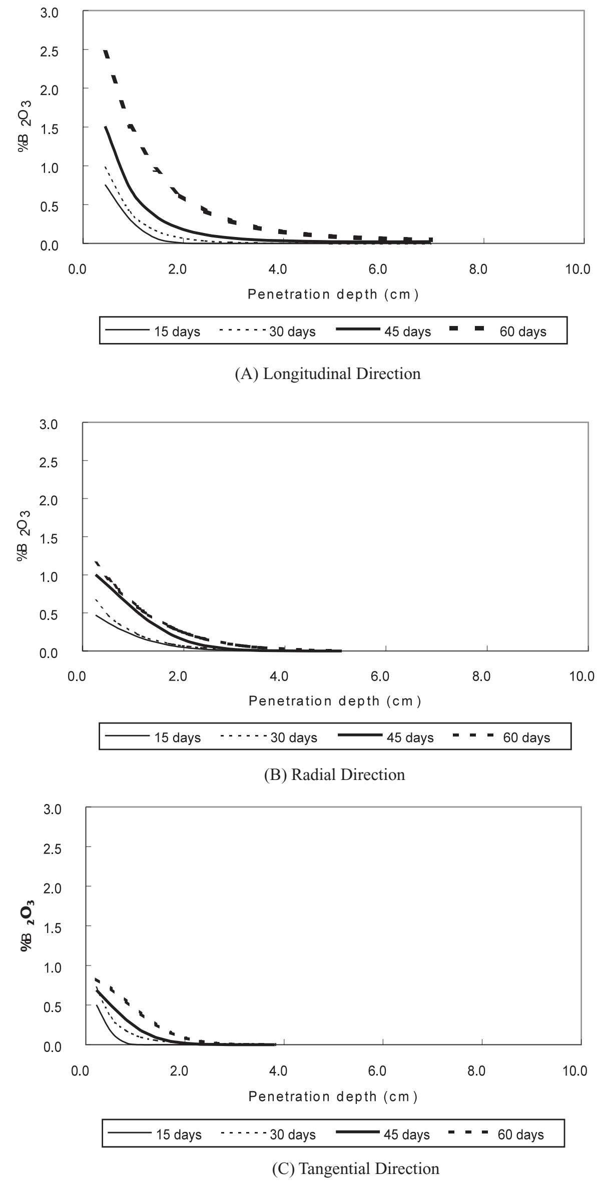

Figure 1 — Concentration profiles of boron diffused from borate rods at 40 percent MC in longitudinal (A), radial (B), and tangential (C) directions.

$$D = \frac{\partial\left(\int_0^x C\,dx\right) \big/ \partial t}{\partial C \big/ \partial t} \qquad [\mathbf{1}]$$

where:

D = diffusion coefficient (cm^2/sec.)

C = the concentration of diffusion substance (w/w%)

x = the thickness of sample in the direction of diffusion (cm)

Results and discussion

The boron concentration profiles in three anisotropic directions of samples conditioned to 40 or 60 percent MC are shown in **Figs. 1** and **2**. The depth of boron penetration increased with diffusion time, and boron penetrated deeper in wetter samples. The fastest penetration was observed in the longitudinal direction, followed by the radial and the tangential directions. Boron penetration was virtually complete for the longitudinal diffusion at 60 percent MC after 60 days, while it was not complete at 40

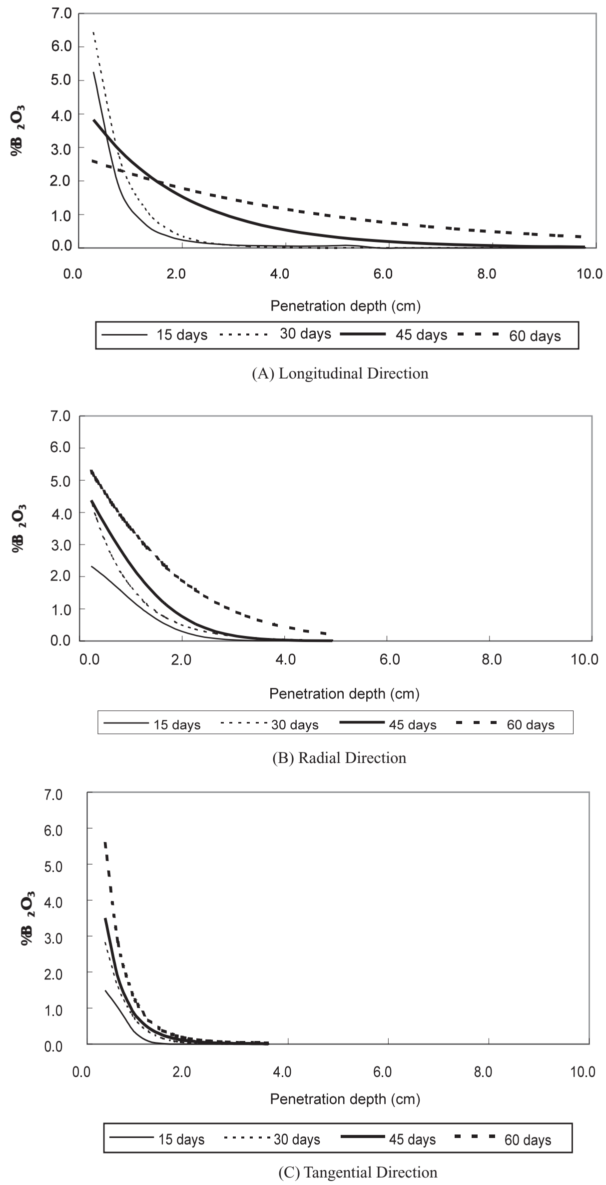

Figure 2. — Concentration profiles of boron diffused from borate rods at 60 percent MC in longitudinal (A), radial (B), and tangential (C) directions.

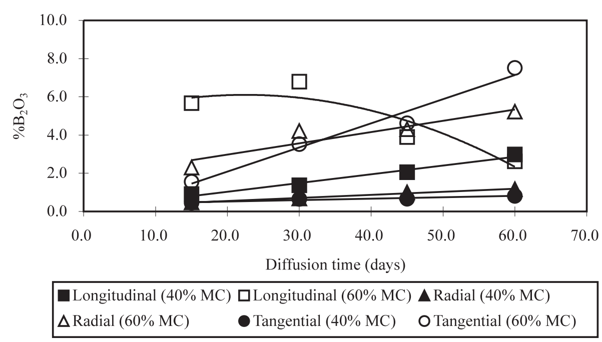

Figure 3. — Change of boron concentration on the wood face adjacent to the borate rod during diffusion periods.

percent MC. Boron penetrated relatively poorly in the radial and the tangential directions in all MC conditions tested, where the penetration was limited to the depth about 4 cm from the treatment hole for the radial direction and about 3 cm for the tangential direction. The highest boron concentration at the wood face adjacent to the borate rod was observed in the longitudinal direction. The boron concentration at the face in the radial direction was slightly larger than that in the tangential direction in all MC conditions tested, although the differences were sometimes slight. The rate of boron diffusion from the borate rod into wood appeared to proportionally increase with time in all directions except the longitudinal direction at 60 percent MC (**Fig. 3**). The boron concentration declined rapidly after approximately 30 days diffusion, although most of the borate rod remained in the treatment hole. The loosened contact of the borate rod with the wood face as diffusion time passed might explain this phenomena.

Varying diffusion coefficients were determined using Egner's solution except the longitudinal diffusion coefficients at 60 percent MC because the boundary conditions were completely changed during the diffusion periods (**Table 1**). The diffusion coefficients steadily increased with diffusion depth but the rapidly increasing values were observed in the areas where the slope of boron concentration profiles was small. A small amount of boron at the thickness explained the phenomena because it rapidly decreased the values of the slope of concentration profiles and quickly increased the values of diffusion coefficients. This indicates that Egner's solution is not valid in areas where the slope of the concentration-distance curves approaches zero.

The values of diffusion coefficients determined in 40 percent MC samples did not change noticeably regardless of diffusion direction although the boron concentration profiles differed markedly. The results suggest that most of the boron diffused through the bound water. The amount of free water in wood at 40 percent MC was not enough to rapidly move boron from cell to cell, so that boron should diffuse through bound water in cell walls regardless of the diffusion direction. If there is enough free water for boron diffusion, the differences among the values of the determined diffusion coefficients should be much larger. Previous studies of boron diffusion have shown that under high MC conditions (above 70% MC) the longitudinal diffusion coefficients of boron in wood were 20 to 40 times larger than the tangential diffusion coefficients, and the radial diffusion coefficients were 2 to 4

Table 1. — The diffusion coefficients of boron diffused from the borate rod in wood at 25°C under 40 and 60 percent MC conditions.

MC	Diffusion direction	Penetration depth	Diffusion time 15 days	30 days	45 days	60 days
(%)		(cm)	(10^{-7} cm^2/sec.)			
40	Longitudinal	0.4	0.3	0.2	0.2	0.4
		0.8	0.5	0.7	0.8	0.9
		1.2	1.2	1.8	1.9	1.8
		1.6	3.9	4.3	4.1	3.3
		2.0	18.7	9.2	8.1	5.7
	Radial	0.4	0.3	0.2	0.3	0.3
		0.8	0.6	0.6	0.6	0.8
		1.2	1.1	1.4	0.9	1.4
		1.6	2.1	2.8	1.5	2.4
	Tangential	0.4	0.05	0.05	0.1	0.2
		0.8	0.7	0.4	0.4	0.5
		1.2	33.5	1.3	0.7	0.6
		1.6	--	3.7	2.0	1.2
60	Radial	0.4	0.4	0.1	0.3	0.4
		0.8	0.6	0.4	0.6	0.8
		1.2	0.9	0.9	1.0	1.4
		1.6	1.5	1.9	1.7	2.2
	Tangential	0.4	0.5	0.2	0.3	0.3
		0.8	0.5	0.7	0.9	1.0
		1.2	2.0	1.8	2.8	3.1
		1.6	24.8	5.2	7.3	8.4

times larger than the tangential diffusion coefficients (Ra et al. 2001).

The radial and tangential diffusion coefficients of boron showed only slight differences in all MC conditions tested. The result indicates that even in 60 percent MC, the limiting factor for boron diffusion across the grain should be the rate of boron diffusion in bound water, not in free water. The different penetration depths of boron may be explained by the different boron concentrations on the wood face adjacent to the borate rod, which resulted from the differences of the amount of free water available for contacting with the borate rod.

Conclusion

Diffusivity of borate rod in wood could be mathematically quantified by determining boron diffusion coefficients. Results of this research showed that the concentration profiles of boron were markedly different according to diffusion direction, but the effect of MC and diffusion direction on diffusion coefficients was very slight. This result indicates that although free water plays a role in increasing boron concentration differences, the limiting factor for boron diffusion rates at the given conditions was the diffusion through bound water.

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