Effect of wood moisture content and rod dosage on boron or fluoride movement through Douglas-fir heartwood

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Abstract

The potential for moisture sorption by boron and fluoride rods following application of rods to wood to affect subsequent chemical diffusion was investigated in small Douglas-fir blocks conditioned to 30, 60, or 90 percent target moisture content (MC). MCs tended to decline over the 180-day test period, but there was no evidence that the rods acted to draw moisture away from the wood. As expected, chemical movement tended to increase with increasing MC. Threshold levels were reached within 180 days for boron, even in blocks at 30 percent target MC. Fluoride levels tended to be much lower, reflecting the much lower dosages applied. There was no evidence that rods sorbed enough water to reduce moisture availability for subsequent diffusion.

Internal decay in large timbers and poles has long been a problem for wood uses such as supporting overhead electric lines and railroad ties. Ideally, decay would be prevented by proper specifications that include pretreatments to enhance initial wood treatment (Graham 1983, Morrell 1996); however, there are vast quantities of materials already in service that are at risk for decay. Arresting the damage once the material is in service poses a major challenge because the heartwood of most wood species is largely resistant to liquid treatment, even under pressure. Globally, two very different approaches have been taken for internal decay control. In North America, fumigants have been the most commonly used treatment for arresting internal decay (Morrell and Corden 1986). These chemicals are applied either as liquids or solids that then volatilize to move as gases through the wood for 1 to 3 m. While these chemicals have been highly effective, an alternative approach has been employed elsewhere. Boron and fluoride are both water-soluble compounds that can move with moisture in wood. Systems based on one or both of these diffusible chemicals have been widely used in Europe and Australasia.

Boron has a long history of use as an initial treatment of freshly sawn lumber to prevent infestations by various species of powder post beetles in both Europe and New Zealand (Cockcroft and Levy 1973, Becker 1976). This chemical has also been used more recently for treatment of lumber in Hawaii to limit attack by the Formosan subterranean termite. Boron is attractive as a preservative because it has exceptionally low toxicity to non-target organisms, especially humans, and because it has the ability to diffuse through wetwood (Smith and Williams 1967). Boron is available for remedial treatments in a number of forms, but the most popular are fused borate rods which are available as pure boron or boron plus copper. These rods are produced by heating boron to its molten state and then pouring the molten boron into a mold. The cooled boron rods are easily handled and applied. In theory, the boron is released as the rods come in contact with water.

Boron has been available for remedial treatments for several decades (Becker 1976), but widespread use of these systems has only occurred in the last two decades (Edlund et al. 1983, Dickinson et al. 1988, Dirol 1988). As a result, there is considerable performance data on boron as a remedial treatment, but relatively little data on the interactions between wood conditions such as moisture content (MC) and chemical migration (Dietz and Schmidt 1988; Morrell et al. 1990, 1992; Ruddick and Kundzewicz 1992; Schneider et al. 1993; Morrell and Schneider 1995; Freitag et al. 2000).

Fluoride has also been used for many years in Europe and has seen some use in the United States for treatment of railway ties (Becker 1973, 1976). Unlike boron, which can be produced in dense, relatively pure rod form, fluoride is usually applied as sodium fluoride in chalk-like rods. Similar to

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boron, however, this compound moves relatively well through wet wood of most species.

Laboratory and field trials with fused boron and fluoride rods suggest that increasing the rod dosage per hole results in lower chemical levels in the wood (Morrell and Schneider 1995). Both the wood and the rods are hygroscopic, thereby creating the potential for competition for moisture in the wood. Sorption of moisture from the wood surrounding a rod could reduce the wood MC to the point that the free water needed for diffusion is limited; however, there are no data demonstrating this effect. In order to assess this potential phenomenon, the following trial was undertaken.

Materials and methods

Douglas-fir heartwood (*Psuedotsuga menziesii* (Mirb) Franco) blocks (50 by 100 by 150 mm long) were oven-dried (105°C / 24 h), weighed, and then pressure treated with water. The blocks were then weighed prior to being air-dried to 30, 60, or 90 percent target MC. Once each block achieved its target MC, it was dipped in molten paraffin to retard further moisture loss. Blocks were then stored at 5°C for 4 to 5 weeks to allow for further equilibration.

A 9-mm-diameter hole (20 mm deep) was drilled on the narrow face of each block and a single fused borate (6.45 g of rod measuring 8 mm in diameter by 40 mm long) rod or fluoride (4.6 g of rod measuring 5 by 8 by 38 mm long) rod was added. The treatment hole was sealed with duct tape, and the blocks were incubated at room temperature for 7, 30, 90, and 180 days. At each time point, six blocks conditioned to a given MC were removed and sections were sawn immediately adjacent (0 to 5 mm) to the original treatment hole as well as at 5 to 10 mm and 10 to 20 mm away from the treatment hole (**Fig. 1**). These sections were immediately weighed, ovendried, and reweighed to determine wood MC. The wood was then ground to pass a 20-mesh screen. For wood treated with boron, the sawdust was extracted with hot water. The extract was analyzed for boron using the azomethine/H carminic acid method (American Wood-Preservers' Association Standard A2 Method 16 [AWPA 2004]). Fluoride in fluoride rod treated blocks was analyzed by hot water extraction according to procedures described by Chen et al. (2003). The resulting extract was analyzed using a specific

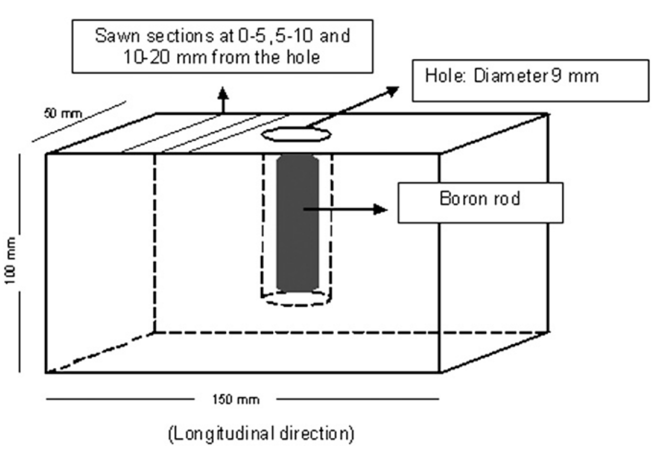

Figure 1. — Representation of a Douglas-fir heartwood block treated with a boron or fluoride rod showing the hole dimensions, pattern of cutting, and grain direction.

ion electrode according to AWPA Standard A2 Method 7 (AWPA 2006). The MCs of the residual boron or fluoride rods in the treatment hole were also determined by weighing each rod, oven-drying the rod, and then reweighing.

For the purposes of assessing chemical distribution, the threshold values presumed to be effective against internal decay were 0.050 percent for fluoride and 0.10 percent boric acid equivalent (BAE) (Freitag and Morrell 2005).

Results and discussion

MCs of the blocks were generally lower than the target levels for all three target MCs. The differences were slight at 30 percent target MC, but became increasingly larger with target moisture level (**Table 1**). MCs immediately adjacent to the treatment hole at the time of cutting (0 days) for the 30, 60, and 90 percent target MC blocks were 24.7, 49.6, and 79.6 percent, respectively. Moisture levels tended to be slightly higher 5 to 10 mm from the treatment site, but the differences were slight for the 60 and 90 percent target MC blocks. Moisture levels immediately adjacent to the treatment hole in the 30 percent target MC blocks at the time of treatment were almost one-fourth lower than those 5 to 10 or 10 to 20 mm from the surface, which suggests that drilling altered the moisture gradient in these blocks. Moisture gradients, however, tended to become uniform over time, and there was little difference in the moisture level 7 days after treatment.

Overall moisture levels declined over the 180-day period for blocks at all three target MCs, reflecting the increased potential for moisture loss through the sealed treatment hole as well as some loss through the wax coating. At the end of the 180-day period, MCs for the 30 and 60 percent target MC blocks were below the fiber saturation point, which suggests that free water was no longer available to allow boron to diffuse through wood. MCs dropped substantially in blocks originally conditioned to 90 percent target MC, but moisture was still available for boron diffusion. The original hypothesis was that the rods sorbed moisture from the wood surrounding the hole, thereby reducing moisture and the ability of the boron to diffuse into the wood. If that were true, moisture levels around the hole would be expected to drop relatively sharply, creating a steep moisture gradient away from the treatment hole. While there were slight negative moisture gradients away from the treatment hole in the 30 percent target MC blocks immediately after treatment, the difference had disappeared 7 days later. There was no evidence that the rod acted to reduce moisture availability around the hole.

Boron contents tended to increase with increasing initial MC as well as with incubation time (**Table 2**). Boron levels immediately adjacent to the treatment hole tended to be well above the threshold for protection against internal attack even at 30 percent target MC (Fahlstrom 1964, Williams and Amburgey 1987, Freitag and Morrell 2005). Boron levels were above the threshold at all distances sampled in blocks conditioned to 60 or 90 percent target MC within 7 days after treatment, but remained below threshold 5 to 20 mm away from the treatment site in the 30 percent MC blocks until the 90 day sampling point. Boron levels tended to follow consistent concentration gradients with distance away from the treatment hole. Chemical levels tended to be consistently higher in 60 and 90 percent target MC blocks. Since free water is necessary for boron diffusion, this would suggest that sufficient moisture was present in the blocks to

Table 1. — Moisture and boron contents at selected locations away from the treatment zone in Douglas-fir blocks conditioned to 30%, 60%, or 90% MC and incubated for 0, 7, 30, 90, or 180 days at room temperature.

		Boron content (BAE %)[a]			Wood MC		
Incubation time	Assay zone	30% MC	60% MC	90% MC	30%	60%	90%
(days)	(mm)	(%)					
7	0 to 5	**0.94** (0.90)	**8.10** (3.73)	**12.28** (2.83)	25.3 (5.5)	45.2 (2.7)	68.9 (9.7)
	5 to 10	**0.47** (0.52)	**2.49** (2.55)	**5.25** (3.83)	23.7 (1.6)	38.3 (6.1)	60.8 (9.2)
	10 to 20	**0.15** (0.26)	**0.78** (0.22)	**2.45** (1.28)	24.2 (2.3)	42.2 (4.2)	62.0 (6.5)
30	0 to 5	**0.45** (0.27)	**4.70** (2.80)	**6.22** (4.55)	20.7 (1.0)	32.2 (4.3)	69.1 (7.2)
	5 to 10	**0.13** (0.08)	**2.38** (1.55)	**5.42** (3.20)	20.9 (1.5)	29.9 (3.3)	68.4 (8.9)
	10 to 20	0.04 (0.02)	**0.91** (0.86)	**3.47** (2.31)	21.8 (1.3)	31.1 (4.2)	70.3 (7.2)
90	0 to 5	**2.68** (4.42)	**9.19** (6.04)	**10.97** (3.13)	18.2 (10.3)	17.0 (3.2)	46.8 (4.7)
	5 to 10	**1.92** (4.08)	**4.33** (1.83)	**9.19** (2.61)	18.4 (10.5)	16.0 (2.3)	44.3 (4.1)
	10 to 20	**1.15** (2.63)	**1.46** (0.52)	**5.07** (1.72)	21.1 (11.4)	18.9 (4.3)	50.9 (5.5)
180	0 to 5	**0.90** (0.70)	**7.72** (4.07)	**8.39** (2.81)	16.3 (1.4)	14.6 (0.5)	56.1 (5.1)
	5 to 10	**0.51** (0.63)	**4.98** (2.67)	**6.94** (1.13)	14.9 (1.9)	14.1 (0.3)	55.1 (6.6)
	10 to 20	0.09 (0.06)	**2.13** (1.59)	**4.44** (2.18)	16.9 (2.3)	14.5 (0.7)	53.3 (7.9)

[a] BAE = boron acid equivalent. Values represent means of six blocks per time per MC. Values in parentheses represent 1 standard deviation. Boron values in **bold** exceeded the minimum threshold for protection against internal decay (0.10% BAE).

Table 2. — MC of fused boron rods inserted into holes in Douglas-fir blocks conditioned to 30%, 60%, or 90% MC and incubated for 7 to 90 days.

		Rod MC[a]			
Wood MC	Chemical	7 days	30 days	60 days	90 days
(%)		(%)			
30	Boron	3.5	4.2	5.9	10.6
60		6.1	22.5	N/A	N/A
90		3.6	N/A	N/A	N/A
30	Fluoride	3.8	3.2	1.3	0.6
60		5.3	5.8	0.2	< 0.03
90		5.8	6.3	8.8	11.4

[a] Values represent means of six rods per MC per time point. N/A = rods too badly degraded to be removed from holes for weighing.

Table 3. — MC of fused boron rods inserted into holes in Douglas-fir blocks conditioned to 30%, 60%, or 90% MC and incubated for 7 to 90 days.

		Rod weight loss[a]			
Wood MC	Chemical	7 days	30 days	60 days	90 days
(%)		(%)			
30	Boron	1.1 (1.4)	0.1 (3.0)	0.4 (1.5)	−1.4 (2.9)
60		38.7 (14.2)	41.5 (24.2)	100 (0)	100 (0)
90		54.9 (4.5)	80.4 (30.9)	100 (0)	100 (0)
30	Fluoride	2.1 (1.4)	3.2 (0.8)	2.5 (0.8)	2.7 (0.7)
60		5.1 (0.8)	9.2 (1.8)	6.1 (0.9)	6.6 (1.3)
90		5.3 (2.8)	9.5 (3.4)	13.1 (2.0)	22.4 (2.8)

[a] Values represent means of six rods per MC per time point. Values in parentheses represent 1 standard deviation. N/A = rods too badly degraded to be removed from holes for weighing.

allow diffusion to occur at some point in the exposure period, even at the lowest moisture level tested. It is also clear that the rods do not sorb excessive moisture to the point where further movement of boron from the rods is inhibited. This finding, however, does not explain the lack of a dose response when increasing amounts of boron are used.

The MCs of the boron rods tended to increase over time after application to the wood (**Table 2**). Rods in 60 and 90 percent target MC blocks could not be removed after 90 and 30 days, respectively, because they had sorbed moisture to the point where they crumbled when touched. Clearly, the rods had sorbed moisture from the surrounding wood, but the overall effect on wood MC was negligible, even immediately adjacent to the hole. The overall rates of boron loss varied with block MC. Rods in blocks conditioned to 30 percent target MC lost negligible amounts of weight, while rods in wetter blocks lost 50 to 60 percent weight within 7 days at the higher target MCs. These results indicate that the conditions were conducive to boron solubilization and diffusion from the rods (**Table 3**).

Fluoride levels in blocks at the various MCs were consistently lower than those found with boron (**Table 4**). These lower levels reflect, in part, the lower initial dosage applied to the blocks. Fluoride levels in blocks at 30 percent target MC remained extremely low over the entire 180-day incubation period, even immediately adjacent to the treatment hole. Fluoride levels increased slightly in blocks at 60 percent target MC, but there appeared to be little difference in fluoride level with distance from the treatment site 90 or 120 days after treatment. Fluoride levels appeared to be much higher in blocks at 90 percent target MC, and the levels rose steadily with incubation time. Fluoride levels, however, tended to show little evidence of a concentration gradient from highest near the treatment site to lowest further away. The reasons for this are unclear, although rod MCs might have influenced movement.

MCs of rods in blocks at 30 percent target MC were highest 7 days after treatment and then declined with incubation period (**Table 2**). Rods in blocks at 60 percent target MC followed similar trends, but they reached higher initial moisture loadings and contained much less moisture at the end of the test. Moisture levels were generally low in rods in blocks conditioned to 30 or 60 percent target MC, suggesting that

Table 4. — *Fluoride levels and final wood MCs in Douglas-fir heartwood blocks conditioned to 30%, 60%, or 90% MC, then treated with fluoride rod, and incubated for 7 to 180 days.*

Incubation time	Assay zone	Fluoride content[a]			Wood MC		
		30% MC	60% MC	90% MC	30%	60%	90%
(days)	(mm)	(%)					
7	0 to 5	0.03	**0.05**	**0.05**	25.7	43.7	68.7
	5 to 10	0.01	0.04	0.04	26.4	47.0	74.7
	10 to 20	0.01	0.03	0.04	27.7	48.6	80.0
30	0 to 5	0.02	**0.11**	**0.15**	23.2	31.9	69.9
	5 to 10	0.01	**0.08**	**0.13**	22.9	31.9	73.5
	10 to 20	0.01	**0.06**	**0.11**	23.9	34.7	77.9
60	0 to 5	0.01	**0.06**	**0.11**	17.6	16.4	61.3
	5 to 10	0.01	**0.05**	**0.15**	17.5	16.4	63.4
	10 to 20	ND	0.04	**0.17**	19.7	19.2	70.7
120	0 to 5	0.02	**0.05**	**0.24**	15.5	13.5	47.5
	5 to 10	0.01	**0.06**	**0.32**	15.3	13.2	49.7
	10 to 20	0.01	**0.05**	**0.31**	15.6	14.0	51.6

[a] Values in **bold** are at or above the 0.05% wt/wt threshold level for protection against internal fungal attack.

moisture was not selectively sorbed by the rods in these materials. MCs of rods in blocks at 90 percent target MC experienced steady increases over time, suggesting that moisture levels in the wood were not limiting in these blocks at the end of the test. The moisture behavior in fluoride rods differed markedly from that found with boron at the two lower moisture regimes although there was no apparent reason for any difference. Fluoride losses from rods in blocks conditioned to the 30 percent MC were slightly higher than those for boron rods, but still small, even 90 days after treatment. Fluoride losses were higher in blocks conditioned to 60 or 90 percent MC, but even these levels were far lower than those found with boron rods at similar moisture levels (**Table 3**). The combination of an initially lower overall fluoride content and a lower rate of movement from the rods in comparison with those found with the boron rods may help explain the resulting lower levels of fluoride found in the wood.

Conclusion

The negative dose-responses observed in field tests with boron and fluoride rods do not appear to be caused by increased sorption of moisture by the higher rod dosages. Further studies are planned to understand the cause of the dosage effect.

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