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Borates in remedial treatments for timber in service

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ABSTRACT

Large preservative-treated timbers and poles can develop internal and external decay as they age in service. Arresting this damage can pose a challenge, especially internal decay. Boron plays an important role in helping arrest fungal attack in a variety of applications. This paper discusses the use of borates as a component in pastes for limiting external decay and the use of boron solutions or rods for arresting internal decay. Long-term field trials show that boron movement is initially slow, but boron was found in Douglas-fir poles almost 30 years after application. The results illustrate the value of boron as a remedial treatment for limiting fungal attack in timber in service.

1. Introduction

Wood is among the most durable cellulosic materials and remains one of the more widely used natural materials for housing and infrastructure. However, a range of organisms has evolved to use wood as either a nutrient source or as habitat [1]. The risk of damage from these organisms can be reduced by using either timbers with naturally durable heartwoods or, where that is not possible, applying supplemental preservatives to minimize the risk of attack. Preservative treatments can prolong the useful life of a timber from as little as 2 to 3 years in soil contact to over 80 years with proper maintenance. Extending the life of wood and wooden structures is a significant issue in terms of economics, life safety and reducing the need to harvest more trees. While proper designs that exclude water are the most common approach to wood protection, water exclusion is not always possible. A variety of alternative approaches have been developed to reduce the susceptibility of wood to biodegradation and these approaches have proven to be highly effective when properly applied [2].

Eventually, even properly treated wood products can begin to experience degradation and must be either replaced or remedially retreated. There are two general degradation patterns observed in timber products, external and internal degradation [3]. As the terms denote, external decay develops on the timber surface and gradually progresses inward. Internal damage can be either fungal or insect related and, as the name implies, degrades the wood away from the surface. As will be discussed in more detail later, delivering chemicals to inhibit the progression of this damage is a major challenge. One attractive treatment option is boron. Nearly all wood-degrading organisms are affected to some extent by boron-based preservatives. These systems are cost effective and low toxicity to non-target organisms. As a result, boron-based products are used for initial protection of timber and composites for interior applications against termites and powder-post beetles as well as for remedial treatments for both internal and external decay in service [4].

2. Wood Degradation and Its Causes

Most wood-degrading organisms have four basic requirements: a nutrient source (usually the wood), oxygen, an adequate temperature (5 to 40 °C) and free water. It is generally difficult to control either temperature or oxygen levels for most timber uses, so most approaches use combinations of design and water excluding barriers to keep wood dry. Decay fungi generally require free water to begin degrading the substrate and that occurs at the fiber saturation point (generally around 30 % moisture content by wt). However, decay tends to be more aggressive as moisture levels rise to 40 to 80 % moisture content. Some organisms, such as powderpost beetles or drywood termites, have evolved to attack much drier wood (12 to 19 % moisture content), while others have evolved mechanisms

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for translocating water to artificially increase the moisture levels [5]. Fortunately, these agents are not as prevalent, allowing moisture exclusion to be the primary wood protection strategy in most applications. The alternative to moisture exclusion is to modify the nutrient source to make it unusable through the use of the heartwood of timbers with natural toxins. Where that is not possible, modifying the moisture behavior of the wood or adding toxins that limit biological attack are used for less durable timbers. Besides the biotic factors mentioned above, abiotic factors are important sources of deterioration in outdoor structures. Energy released as ultraviolet light strikes the wood creates free radicals that induce a series of reactions leading to degradation of lignin on the wood surface. This damage causes light woods to darken and dark woods to lighten and is often accompanied by moisture-associated shrinking and swelling that induces checking and splitting. While the damage is shallow, it markedly alters wood appearance, often leading to premature replacement of structurally sound materials. Weathering is an important cause of premature timber replacement, but we will confine our discussion to biodegradation focusing on fungi while also considering termites as they are often co-located in a deteriorating structure.

2.1. External Decay

External decay often occurs as the timber ages and loses preservatives to the surrounding soil. Nearly all preservatives have some degree of water solubility which allows them to dissolve in the free water in the wood cells where they can inhibit the wood-degrading organisms. The ideal preservative has just enough solubility to produce an inhibitory level in the water within the wood. Over time, however, this dissolved preservative moves out of the wood and into the surrounding soil and is replaced by a newly dissolved preservative. This process eventually depletes the original preservative concentration to the point that fungi can begin to invade the wood. The initial invaders tend to be either extremely tolerant to chemicals or capable of degrading the preservatives to allow other fungi to invade.

The most common invaders are a group of organisms called soft rot fungi. Soft rot fungi tend to be tolerant of preservatives and are able to grow in more extreme environments that restrict the growth of other decay fungi. Soft rot tends to be confined to the outer zones of the wood where the fungus rapidly reduces the residual wood strength. Although originally isolated from timber cooling towers, soft rot fungi are found in a range of environments. One of the more common habitats is in wood utility poles, especially hardwood species but also pine poles with lower preservative retentions. These fungi either erode the wood cell wall from the lumen outward or tunnel longitudinally along the cell wall to create diamond-shaped cavities that severely weaken the affected area. Continued damage caused by soft rot fungi decreases the effective circumference of the pole to the point where it can no longer support the design load and must be replaced (Figure 1).

Figure 1. Example of soft rot damage on the surface of an untreated Douglas-fir pole.

2.2. Internal Decay

Internal degradation can be caused by either fungi or insects (primarily termites). Internal decay is common in the heartwood of less durable species [3]. Preservative treatments primarily penetrate into the sapwood with only a shallow band of treatment in the less permeable heartwood. This envelope of treatment protects the untreated wood inside as long as the barrier remains intact. However, most large timbers are treated while the moisture content remains higher than it will be while in service. Once installed, the wood continues to dry to reflect the ambient conditions. Wood shrinks as it dries and this shrinkage leads to the development of stresses that can exceed the strength of the bonds between cells, especially along the radial planes. These stresses result in the development of radial checks or cracks that can penetrate beyond the depth of the original preservative treatment. Checks provide access to the exposed, non-durable heartwood for moisture, fungal spores and insects (especially termites). Unlike soft rot fungi, internal decay fungi do not need to be preservative tolerant since they can enter the interior through checks that expose untreated wood. Over time, fungi and insects can degrade the interior of the timber to the point where it is hollow and can no longer support a load. Internal decay is an important cause of premature failures in species with thin sapwood bands surrounding a non-durable heartwood.

3. Remedial Treatments

Arresting decay in service poses a challenge. Initial treatments often use combinations of vacuum and pressure to drive large amounts of chemicals onto the wood. This is not possible for most wood in service and any treatments must depend on some form of diffusion for the chemicals to move from the point of application to affect actively growing organisms within the wood. Both internal and external application methods are available for remedial treatment using pastes, oil- and water-borne solutions/emulsions, preservative rods/pads, and fumigants to arrest active degradation and extend service life of wood and wooden structures (previously untreated or even initially treated) [6, 7]. The preservative formulations for remedial treatments can be applied by spraying, immersing, brushing, injection, or insertion into drilled holes depending on the type of chemical, the dosage required, the size of the wood member and the type of decay.

3.1. Preservative Systems Used for Remedial Treatments

Diffusible preservatives are among the mostly used remedial treatments since they move through the wood structure that was initially resistant to fluid movement. There are two types of diffusible systems, gaseous and water diffusible. Gaseous systems, or fumigants, are applied as liquids or solids and then decompose/sublime to produce volatiles that diffuse as gases through the wood structure to arrest fungal attack. Fumigants are widely used in North America to arrest internal decay in utility poles. Water-diffusible systems are capable of diffusing with free water in the wood cell lumens to control fungal attack. This review will focus on water-diffusible treatments. Water-diffusible systems tend to be less reactive with the wood, allowing them to continue to distribute in the wood and eventually diffuse outward as long as free water is present (>30 % moisture content). Fluorides (sodium fluoride), boron compounds (disodium octaborate tetrahydrate-DOT; boric acid, sodium tetraborate decahydrate-borax), glycol borates, borate gels, boron rods, and paste formulations are the most important water-diffusible preservative systems for remedial treatments [7]. Non-diffusible systems are also often incorporated into external treatments to limit renewed fungal attack from the outside of the timber; however, these components do not move in the wood structure as deeply as diffusible preservatives.

3.2. Boron-Based Remedial Treatments

Boron-based formulations are widely used for both initial and remedial treatments due to their low toxicity to non-target organisms and minimal environmental footprint. Boron compounds can diffuse through moist wood and easily penetrate into areas that initially resisted preservative treatment such as heartwood [8, 9]. Boron-based remedial preservatives are available as powders, gels, glycol solutions, solid rods, and pastes. Inorganic and organic boron compounds available for wood preservation include boric acid, borax, DOT, zinc and calcium borates, trimethyl borates, and triethyl borates (Table 1) [5, 7]. Raw boron minerals such as ulexite ($NaCaB_5O_9 \cdot 8H_2O$-sodium-calcium pentaborate octahydrate), colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$-di-calcium hexaborate pentahydrate) with different water solubilities have also been explored and could help decrease the overall costs of boron-based systems when such minerals are employed without purification processes [9-12].

3.3. Remedial Treatments for External Decay

External decay is usually arrested by application of external preservative pastes that supplement the original treatment and there are a number of tests evaluating different systems [13-27]. The paste is applied to the exposed surface (usually below the ground) and covered with a kraft wrap to help contain the chemicals before the soil is replaced. Pastes can also be applied on prepared bandages (Figure 2).

Figure 2. Example of a self-contained copper/boron preservative bandage

Most external preservatives contain a water-soluble component that can diffuse into the wood to arrest fungal growth and an oil-soluble component that stays near the surface to limit renewed fungal attack. The most common water-soluble component is boron as either disodium octaborate tetrahydrate (DOT) or

Table1. Characteristics of boron compounds evaluated as potential groundline paste components.

Trade Name	Source	Chemical Name	Elemental Boron Content (%)	Water Solubility at 25°C (%)
TIMBOR	Rio Tinto Minerals (Boron, CA)	Sodium octaborate tetrahydrate (DOT)	67	~20
Borax Decahydrate	Etimine USA INC (Pittsburgh, PA)	Sodium tetraborate decahydrate (NaTBD)	36.47	5.8
Etibor48	Etimine USA INC	Sodium tetraborate pentahydrate (NaTBP)	47.80-49	4.4
Ulexite	Etimine USA INC	Sodium-calcium pentaborate octahydrate (CaPDO)	37	0.76
Colemanite	Etimine USA INC	Di-calcium hexaborate pentahydrate (CaHBP)	40	0.81
Borogard ZB	Rio Tinto Minerals	Zinc borate (ZnB)	48.05	<0.28

sodium tetraborate decahydrate. Boron is especially attractive as an external paste component because it is effective against both insects and most fungi, it has a low toxicity profile against non-target organisms and, most importantly, it has the ability to diffuse into wood with moisture [28-35]. While there have been some concerns about the potential effects of higher levels of boron on human health [36], the levels used in poles represent a relatively low risk because of the low dosages and high probability of dispersion to background levels in the soil surrounding a structure

Most older studies did not include boron in the paste; however, more recent studies show that boron readily diffuses into wet wood. Untreated Douglas-fir pole sections treated with pastes or prepared bandages containing copper naphthenate/boron systems showed that boron was present at threshold levels up to 75 mm inward from the surface after one year (Figure 3).

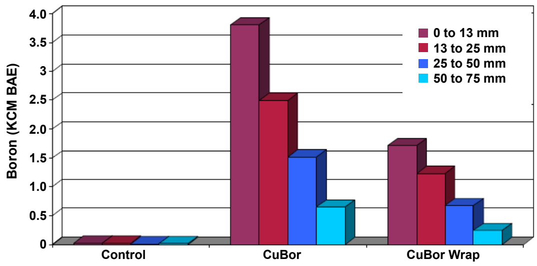

Figure 3. Boron levels at selected distances from the surface of Douglas-fir pole sections one year after application of a copper/boron paste or a self-contained bandage containing the same material showing boron concentrations above the lower toxic threshold (~0.6 kg/m^3) 75 mm inward from the pole surface [37].

Similarly, samples removed 1 to 5 years after the application of a copper/boron system showed that boron was still detectable but at very low levels (Figure 4).

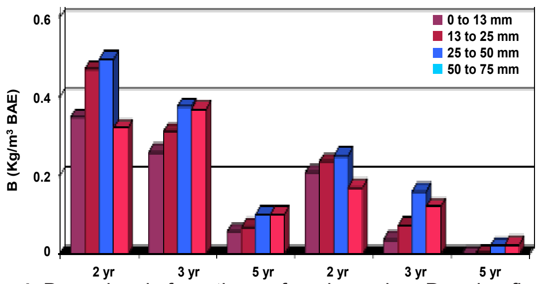

Figure 4. Boron levels from the surface inward on Douglas-fir pole sections 1 to 5 years after application of self-contained copper/boron and copper/fluoride boron bandages showing uniform boron concentrations up to 75 mm inward 2 years after treatment, then a sharp decline between three and five years after treatment [37].

The structure of the system evaluated in the latter case contained an insufficient amount of boron at the start of the test and was never commercialized.

While most external pastes use boron with some copper compound, there is at least one boron-based paste that uses mixtures of boron compounds with differing degrees of water solubility (Table 1). The premise is that the highly soluble components will rapidly diffuse from the paste into the wood but will also be more rapidly lost from the wood into the surrounding soil. The less water-soluble components will move more slowly from the paste into the wood and also be less likely to leach into the surrounding soil (Figure 5). Thus, it may be possible to design a boron-based paste that provides longer-term protection and laboratory studies suggest that this is possible [12].

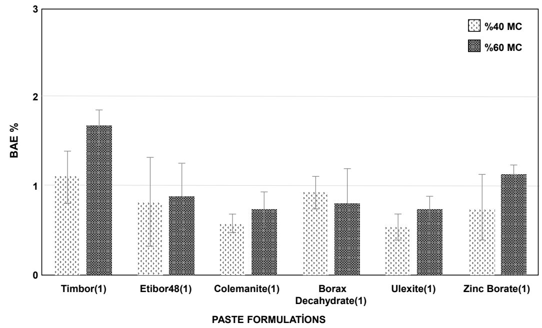

Figure 5. Boron levels 0-6 mm from the surface in Douglas-fir sapwood blocks conditioned to 40% or 60% MC, treated with one of six different paste formulations, and incubated for three weeks (BAE: boric acid equivalent) [12].

Kartal et al. (2022) evaluated preservative paste formulations containing ulexite alone or with either copper or fluoride and found that boron levels from paste formulations with ulexite exceeded the 0.1% boric acid equivalent (BAE) threshold level in most assay zones and incubation times [38]. The results suggest that ulexite paste formulations might be particularly useful when wood material is in service at high moisture conditions for prolonged durations. Ulexite is not highly refined, potentially decreasing formulation costs.

3.4. Remedial Treatments for Internal Decay

The challenge in using chemicals to arrest internal degradation is that these chemicals need to be able to move through the heartwood. This is a major problem since it was not possible to deliver preservatives to these zones, even using elevated pressure and, sometimes, temperature. The problem of controlling internal degradation needs to be addressed in terms of termite and fungal control. Termites produce discrete, interconnected tunnels that create the potential for injecting conventional liquid biocides into the termite galleries, often under slight pressure. The main problem is locating the termite galleries for treatment. Borates have been used for termite treatments with some success, although there are generally more effective treatments that have the potential to affect an entire colony, thereby limiting the risk of reinfestation. Borate solutions have also been injected into large voids to coat the internal surfaces and presumably restrict future insect attack. The advantages of using borates for void treatments are their relatively low cost and minimal toxicity.

Arresting internal fungal attack poses a much greater challenge and this damage is far more prevalent in most systems. As with termite control, the goal is to identify chemicals capable of moving through the liquid-impermeable heartwood at levels capable of inhibiting or killing fungi established in the wood. There are two general approaches to this problem; gases that can diffuse through the wood or water-soluble chemicals that can diffuse with liquid water. Gaseous reagents are termed fumigants and are widely used in North America for controlling internal decay in large timbers [39]. These chemicals are applied in solid or liquid form to steep-angled holes drilled into the timbers. Metham sodium, methyl isothiocyanate (MITC), dazomet, and chloropicrin are all used to arrest fungal attack of timber in service. These chemicals diffuse up and down from the point of application and are less affected by wood moisture content. They also have some physical and chemical interactions with the wood that result in them remaining detectable for 3 to 20 years after treatment, depending on the fumigant. All of these chemicals are effective for at least 7 to 10 years but require special handling procedures.

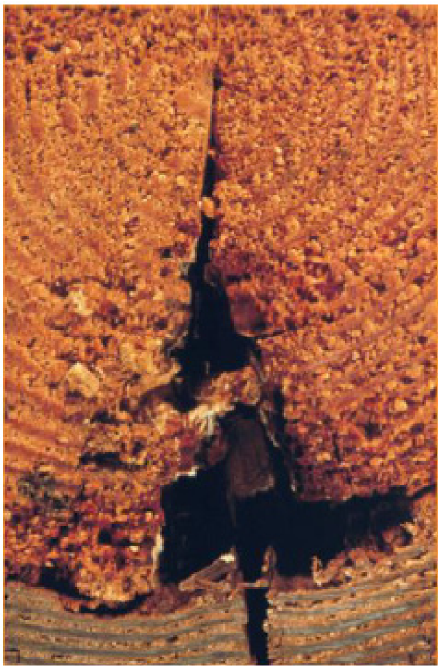

Figure 6. Example of a check through the preservative-treated shell (lower part of the photograph) and the decay pocket developing in the untreated heartwood of a Douglas-fir pole.

Alternatively, boron has been used in several forms as an internal treatment [40-58]. Boron-based treatments for large timbers and poles are applied to holes drilled into the timber in the same fashion as the fumigants. In all cases, the boron is presumed to be released and migrate through the wood as boric acid. Boron finds use in internal decay control in the form of water-based solutions, boron solutions amended with glycol or as solid rods that contain boron alone, boron with a small amount of copper and boron with sodium fluoride. In all cases, the boron is applied through holes drilled into the timber. In some cases, these application points are the original inspection holes, although additional holes may be required to deliver effective dosages to larger timbers.

Boron solutions are typically produced using disodium octaborate tetrahydrate (DOT) since it has the highest water solubility of the commercially available systems (Table 1). DOT can be used at solution strengths up to ~20 % boric acid equivalent with some heating. The major limitation with the use of DOT alone is that the amount of boron that can be applied is limited by the volume of the treatment holes and every hole drilled into a timber has the potential to reduce strength. Too little boron and the concentrations never reach inhibitory levels. Thus, water-based DOT solutions are limited to smaller timbers, and this is a major limitation for boron in water.

Glycol and other compounds can be added to water to increase the potential boron concentration upwards to 40 or 50 % BAE. The glycols also help boron diffuse through drier wood. These treatments have been used in a variety of timber types, especially railway sleepers or bridge timbers. Previous studies show that the boron in glycol can readily diffuse from the point of application and into the surrounding wood of many difficult to treat species, although the differential penetration in drier timbers can be slight [47].

While liquid boron solutions can be effective, the primary limit is the inability to deliver a sufficient amount of solution in larger timbers without drilling too many holes. The alternative to liquids is to use solid rods that can be inserted into treatment holes that are plugged to help retain chemicals (Table 2; Figure 7).

Table 2. Examples of water diffusible boron and fluoride rods.

Trade Name	Content	Manufacturer
Impel Rods	Anhydrous disodium octaborate	Osmose Utilities Services WoodCare Systems
Cobra-Rods	Anhydrous disodium octaborate/boric acid/Copper oxide	Genics, Inc
FluRods	Sodium fluoride	Osmose Utilities Services
PoleSaver Rods	Anhydrous disodium octaborate/sodium fluoride	Preschem, LTD

The boron rods then sorb water from the surrounding wood and the solubilized boron diffuses into the wood. Numerous previous studies have shown that the wood moisture content must be above 30% (wt/wt oven dry basis) for substantial diffusion to occur [33]. This is generally not an issue with wood in direct soil contact but can become a problem with wood in desert areas or in wood exposed above ground. There is evidence that addition of small amounts of glycol or a boron/glycol compound will enhance short-term movement in drier wood.

There are three different types of boron-based rods used for remedial treatment (Table 2). Boron can be heated to its molten state and then poured into molds to produce glass-like rods that contain almost 100%

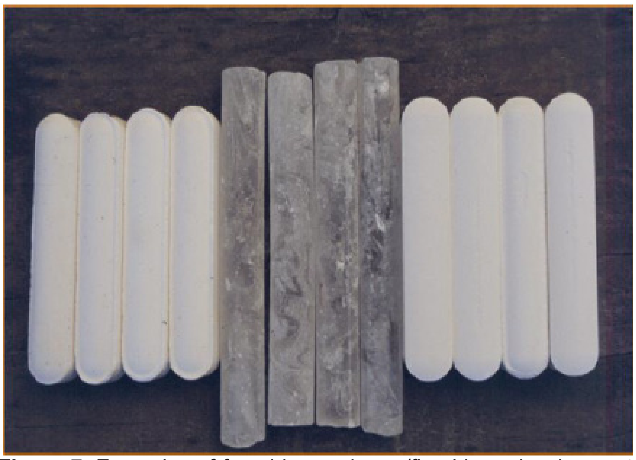

Figure 7. Examples of fused boron, boron/fluoride and a dazomet rod (left to right).

anhydrous DOT. These rods then react with water to release boric acid, which diffuses into the surrounding wood. Rods are available in two forms: a completely boron-based system and a second rod containing boron plus a small amount of copper. Field trials indicate that both systems move at similar rates through the wood and provide 7 to 10 years of protection to wood beneath the treatment site as there is very little upward diffusion. The third type of boron-based system contains a mixture of boron (~10%) and fluoride (11%) in a chalk-like rod. Fluoride also diffuses with water in the wood and the premise is that the two chemicals diffuse together and act synergistically. Field trials in softwoods have shown that the boron remains detectable for up to a decade after treatment, but the fluoride distribution is much more variable [24, 59-61]. These rods are also less concentrated than the fused boron/boron-copper systems, resulting in a lower overall dose. Field trials of fused boron rods and the boron/fluoride rods indicate that both deliver effective levels of boron into softwoods and provide protective periods consistent with the return cycle for inspection and retreatment (5 to 10 years, depending on location).

There are relatively few long-term field trials of boron rods in large timbers or poles, but one nearly 30-year study is helpful for understanding how these treatments perform. Douglas-fir poles received either 180 or 360 g of boron rod evenly distributed among three holes drilled around groundline. Boron movement was sampled periodically by removing increment cores from around the treatment zone, extracting the wood

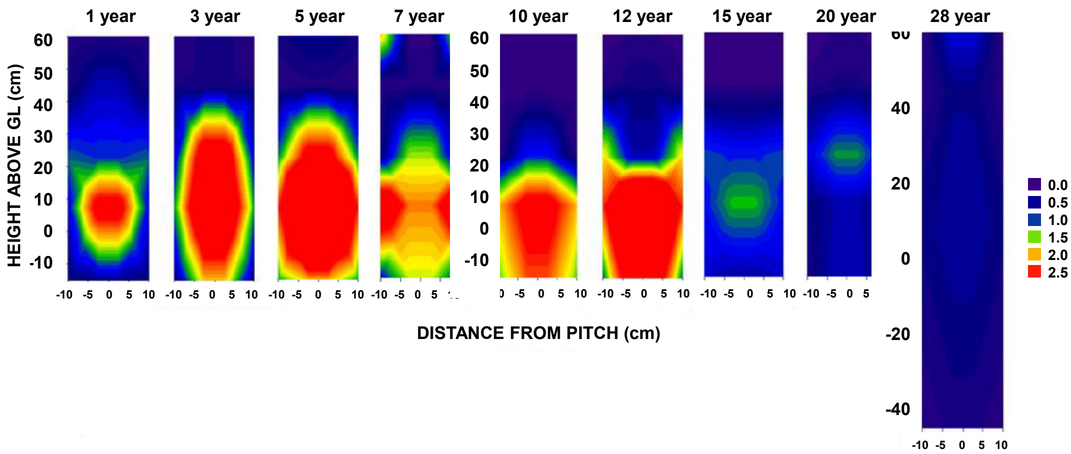

Figure 8. Heatmaps showing boron levels over 28 years in Douglas-fir pole stubs treated with 180 (a) and 360 (b) g of fused borate rods. Boron levels are represented as kg/m³ BAE. Dark blue signifies boron levels below the threshold for fungal protection. Green to red colors signify protective boron levels [33, 62, 63].

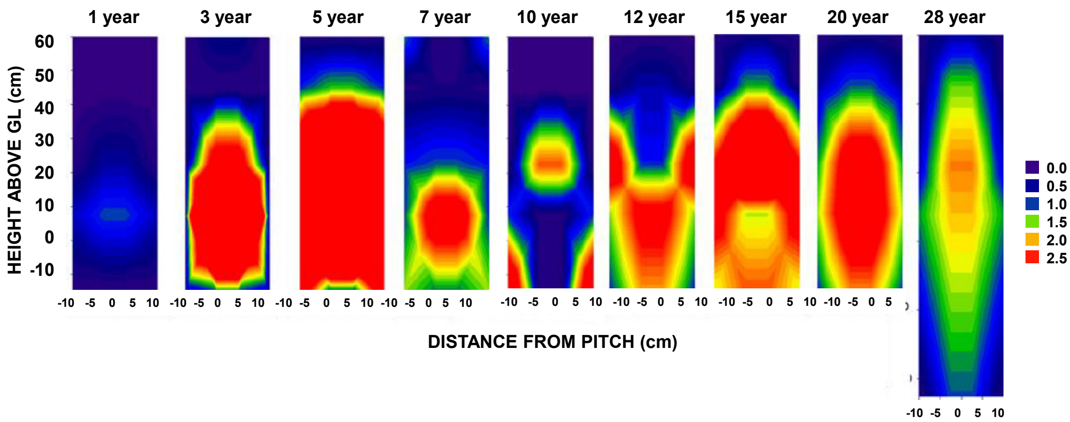

Figure 9. Heatmaps showing boron levels over 28 years in Douglas-fir pole stubs treated with 360 g of fused borate rods. Boron levels are represented as kg/m³ BAE. Dark blue signifies boron levels below the threshold for fungal protection. Green to red colors signify protective boron levels [48, 53].

and analyzing the extract for boron. Boron levels were above the protective threshold around groundline one year after treatment in poles receiving 180 g of rod, while levels were much lower in poles receiving the higher dosage (Figure 8, 9). The lower boron levels in the poles receiving the higher dosages may reflect water sorption from the wood surrounding the treatment holes by the rods that slowed subsequent diffusion. Boron levels were well above the threshold 2 years after treatment with either rod dosage and remained so for over 12 years. Boron levels were still over the threshold 28 years after treatment with the higher dosage. The results illustrate the potential for using water-diffusible boron rods for arresting internal decay where moisture levels are sufficient for diffusion. Similar studies in poles in a desert environment showed little or no boron movement over a 10-year period. The results highlight the limitations of moisture-dependent internal treatments [33, 62, 63].

More recent results indicate that boron levels also reached threshold levels (0.1% BAE) in poles treated with ulexite or colemanite in ethylene glycol [6]. However, solid boron rods made from ulexite and colemanite were associated with much lower boron levels, illustrating the value of the glycol [9]. Ulexite rods were associated with higher boron levels than the less soluble colemanite rods. The results suggest the potential for combining components in rods to produce differential boron release that could extend the protective periods afforded by these treatments.

4. Conclusions

While the use of boron as a stand-alone initial preservative treatment in exterior exposures is limited by the risk of leaching, boron-based systems are extremely useful as remedial treatments because of their ability to diffuse into the wood and inhibit further fungal attack. As a result, boron is a common component in external preservative pastes and is increasingly used as an internal treatment in rod form. Boron has an array of applications for arresting both external and internal fungal attack in large timbers. Field trials show that these materials can move well through wet wood and remain at protective levels for long periods that correlate well with typical inspection cycles.

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