FINAL REPORT

Double-Diffusion Treatment of Colorado Species

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ABSTRACT

This project evaluated the effect of treatment time on chemical penetration and retention of copper sulfate and sodium fluoride in wood treated using the double diffusion process. Two treatment trials were conducted. Trial 1 utilized eight-foot ponderosa pine 4x4s, and was conducted in Sigurd, Utah. Trial 2 utilized two-foot sections of end sealed lodgepole pine posts, and was conducted in Fort Collins, Colorado. Three Treatment Schedules comprised of 2,4, and 6-day soak times in four percent by mass solutions of sodium fluoride, and ten percent by mass solutions of copper sulfate, were investigated. Significant sapwood penetration of the fluoride was noted in all Treatment Schedules, in both Trials. Copper penetration was limited to the first 25 mm (1 inch) of sapwood, in both Trials. Penetration of copper and fluoride into heartwood occurring on the surface of the sawn 4x4s was topical, and did not exceed 3-4 mm (.12-.6 inches). Copper retentions in all Treatment Schedules in Trial 2 were higher than required by AWPA for CCA treated wood rated for ground contact. Fluoride retentions did not meet published threshold levels for number of fungi.

INTRODUCTION

The double diffusion wood preservative treatment process has been identified as a simple, low cost method for small forest products companies to produce value-added treated wood products. The process doe not require the large capital investment common to pressure-treating system, and consists of only soaking green wood in one chemical solution for a period of time, removing the wood, and placing it in a second chemical solution. The chemicals in solution diffuse into the wood, moving from an area of high concentration, to an area of lower concentration. Once inside the wood, the two chemicals combine to form an insoluble compound that resists leaching.

The double diffusion method was described in USDA Forest Service publications dating back to 1963, and was initially described as a low cost method for farmers and private landowners to treat fence posts before installation. In addition, copper sulfate and sodium fluoride, the chemicals used in this series of tests, are low in cost, typically less than one dollar a pound when purchased in bulk. The process has only two requirements that should be considered. The first is that the wood to be treated is wet (i.e. typically above 30 percent moisture content); the second is that the tanks containing the treatment solution be either non-metallic, or separated from the solution with a non-metallic material (such as polyethylene sheeting), as both treatment solutions have been found to be corrosive to steel. Finally, the double diffusion treatment process is not meant to replace current pressure treating systems. The double-diffusion treatment method is intended to allow small forest products operations the ability to manufacture a value-added treated product.

This study was undertaken to investigate the effect of various treatment schedules on the penetration and diffusion of treatment chemicals into the wood. Results are intended for use by manufacturers who choose to adopt the double-diffusion treatment system, in choosing the treatment schedule that will minimize the time the wood spends in the treatment solutions, while maximizing the penetration of the chemicals into the wood. Results regarding the retention of treatment chemicals in the wood will be added as an addendum later, as they become available from the USDS Forest Service Forest Products Lab, who is currently analyzing material treated in this study.

TRIAL 1, SIGURD, UTAH

Methods and Materials

Treatment Schedules

Three Treatment Schedules were investigated in Trial 1. Treatment Schedule 1 consisted of a two day soak in a four percent by mass solution of sodium fluoride, followed by a two day soak in a ten percent by mass solution of copper sulfate. Treatment Schedules 2, and 3, consisted of 4, and 6 days soaks in each of the chemical solutions, respectively. Chemical solutions were contained in steel tanks measuring 12x5x2 foot. The interior of the tanks were covered with 6 mil polyethylene to prevent corrosion

Treatment Samples

Twenty-six ponderosa pine 4x4 members, eight-feet in length were used in each of the three Treatment Schedules. The 4x4s were sawn at Stoltze Sawmill, a local pine/aspen mill in Sigard, UT. The members used in each Treatment Schedule were typically sawn within the same day, and were sawn no more than 4 days prior to treating. Twenty-four of the members were tested, two of the members were used to determine moisture content Moisture content measurements were obtained from two 1 inch thick sections cut from each of the moisture content members. One section was cut two feet from the end of the member; the second section was cut from the middle of the member. Moisture content was determined using the oven dry method (ASTM 4442,1997).

Sampling Procedures

Samples were taken immediately after treatment, and at specified points during storage. Samples were removed to perform visual and chemical analysis to determine treatment chemical penetration, diffusion, retention, and fixation. Plans for chemical analysis to determine retention and fixation were abandoned due to the lack of an available laboratory, and affordable and reliable procedure to analyze fluoride. However, all samples were utilized in this study.

Description of samples

Penetration samples were used to determine the degree to which chemicals entered the wood via the longitudinal and radial directions. Eight members were randomly chosen to obtain penetration samples in each Treatment Schedule. Two members were selected immediately after treating, and at 2,4, and 6 weeks during storage. Penetration samples were ¾ inch thick, and were cut in six-inch increments from the end to the middle of the member.

Chemical penetration measurements were made on the transverse face of each sample. Fluoride penetration measurements required the use of a chemical indicator (ASTM 3507,1997), as the fluoride is colorless inside of the wood. The dark green coloration of copper allowed for direct measurement of penetration.

Diffusion samples were used to determine the degree to which the treatment chemicals diffused into the thickness of the wood during storage. Two members were randomly chosen to obtain diffusion samples in each Treatment Schedule. The diffusion samples were obtained by cutting a two foot section from the end of the 4x4 member after treating, and removing two ¾ inch thick samples from the remaining longer section. The cut end was then covered with plastic wrap and the member was placed back into the storage pile. Two additional ¾ inch sections were removed at weeks 2,4 and 6, during storage. Diffusion measurements were made on transverse face of each sample, using the same method as was used for chemical penetration measurements.

Retention samples were to be used to determine the quantitative amount of treatment chemicals that were deposited into the wood during treatment. Six members were chosen to obtain retention samples in each Treatment Schedule. Two members were selected immediately after treatment, and at 3, and 6 weeks during storage.

Chemical analysis to determine treatment chemical retention was not performed due to difficulties in identifying a suitable method for analyzing fluoride, and in locating a lab that could undertake such analysis. Retention samples were used to verify penetration and diffusion measurements, however.

Fixation samples were to be used to determine the treatment chemicals resistance to leaching. Eight members were randomly chosen as fixation samples. Two members were chosen immediately after treating, and at 2,4, and 6 weeks, during storage. The members were not cut, but were just marked for identification and set aside. Chemical analysis was not performed on these samples due to the same difficulties discussed above. However, the fixation samples were later used to construct a retaining wall in Durango, CO.

Results

Fluoride penetration into the sapwood of the samples was significant. In all Treatment Schedules, the fluoride penetrated the majority of the sapwood, and portions of the heartwood, when the heartwood was located into the center of sample. However, when the heartwood was located on the exposed face of one or more of the sides of the sample, penetration was essentially topical in this location, and did not reach a depth of more than 3-4 mm (0.12-0.16 inches).

There was not a significant difference between the degree of fluoride penetration in samples that were taken immediately after treatment, and samples that were kept in storage for six weeks. The majority of fluoride penetration appears to have occurred during the initial treatment process. However, only the presence of fluoride, and not the quantity can be determined with the indicator spray. The fluoride may continue to diffuse during storage from higher concentrations in the outer portion of the wood, to the lower concentrations found deeper in the wood.

Copper penetration into heartwood located on the exposed face of the samples was limited to 3-4 mm (0.12-0.16 inches). Measurements of copper penetration into sapwood immediately following treatment reveal penetration depths of 6.9, 7.4, and 11 mm (0.27, 0.29, and 0.43 in) for Treatment Schedules 1,2, and 3, respectively. Measurements taken after six weeks of storage revealed copper penetration had increased to 12.7, 14.2, and 20.6 mm (0.50, 0.56, and 0.81 in), for Treatment Schedules 1,2, and 3, respectively (Table 1).

	Initial Copper Penetration (mm/*in*)	Copper Penetration after 28 days storage (mm/*in*)	Copper penetration after 42 days storage (mm/*in*)
Treatment Schedule 1	6.9 / *0.27*	13.5 / *0.53*	12.7 / *0.50*
Treatment Schedule 2	7.4 / *0.29*	11.4 / *0.45*	14.2 / *0.56*
Treatment Schedule 3	11 / *0.43*	20.5 / *0.81*	20.6 / *0.81*

Table 1. Copper penetration measurements for Trial 1, conducted in Sigard, UT.

The diffusion of the copper occurred throughout the storage period. However, the greatest rate of diffusion occurred during the first 14 days of storage. Diffusion rates during this time were, 0.25, 0.29, and 0.50 mm/day (.009, .011, and .012 in/day), for Treatment Schedules 1,2, and 3, respectively. After the initial 14 days, diffusion rates dropped slightly for Treatment Schedule 1, but more significantly for Treatment Schedules 2, and 3, as shown in Figure 1.

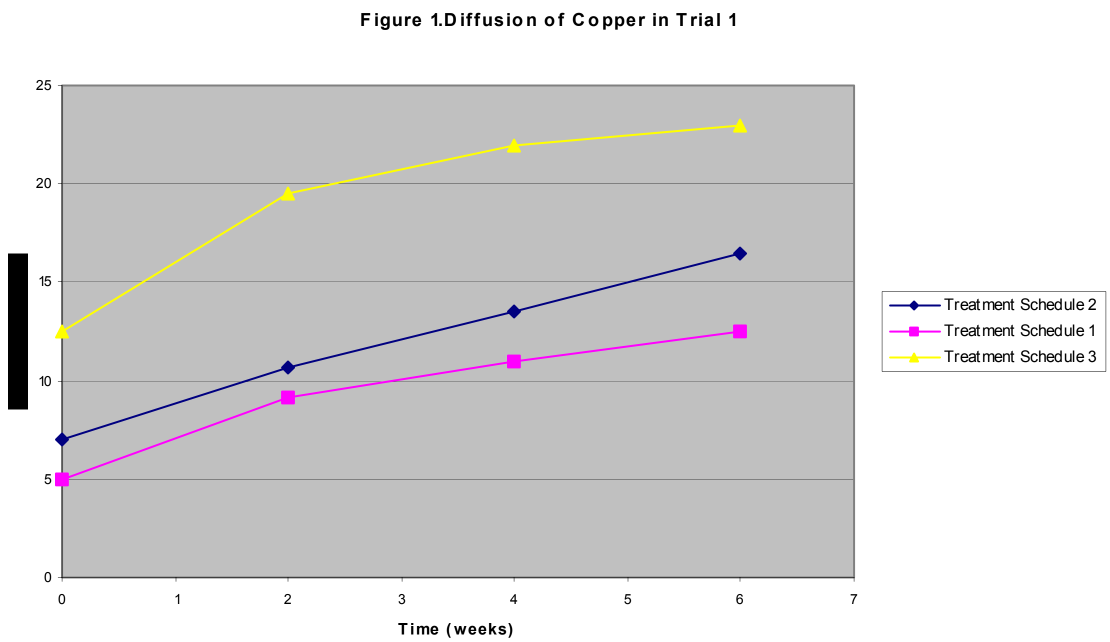


Figure 1. Diffusion of copper in each Treatment Schedule in Trial 1.

TRIAL 2, FORT COLLINS, COLORADO

Materials and Methods

Treatment Schedules

Three Treatment Schedules were investigated in this trial. Treatment Schedule 1 consisted of a two-day soak in a four percent by mass solution of sodium fluoride, followed by a two day soak in a ten percent by mass solution of copper sulfate. Treatment Schedules 2, and 3, consisted of 4, and 6–day soaks in each of the chemical solutions, respectively. Chemical solutions were contained in fifty-gallon plastic barrels. Solution concentrations were measured with a hydrometer between trials, and solutions were fortified as needed.

Treatment Samples

A total of nine 8-foot lodgepole pine posts, ranging in diameter from four to five inches (small end diameter), were used in this trial. One-foot sections were removed from each end of the posts, and discarded. A ¾ inch thick section was removed from each end of the remaining six-foot post. The ¾ inch thick sections were used to determine moisture content using the oven-dry method (ASTM 4442, 1997). The remaining six-foot section of post was cut into 3 two-foot sections. The ends of these sections were covered with silicone sealant to prevent the longitudinal movement of treatment chemicals into the wood. Each section was then labeled, and randomly assigned to one of the Treatment Schedules.

Sampling Procedures

Following treatment, a six-inch sample was cut from the end of the treated section. The six-inch sample was allowed to dry, and was later used for determining chemical penetration. The cut end of the original treated sections was then covered with silicone sealant and placed into a plastic bag that was placed on a pallet, and covered with 6 mil polyethylene. Additional six-inch samples were cut from the treated sections at seven, and fourteen days during storage. The remaining six-inch section was removed from storage 28 days after treatment.

Chemical penetration and diffusion measurements

Each six-inch sample that was removed from a treated section was allowed to dry. A ¾ inch thick section was then removed from the sample for chemical penetration and diffusion measurements. Chemical penetration and diffusion measurements were made on the transverse face of each sample. Copper penetration and diffusion measurements were made at eight locations even spaced around the circumference of the sample. The dark green coloration of copper allowed for direct measurement of penetration. Determining fluoride penetration and diffusion required the use of a chemical indicator (ASTM 3507, 1997), as the fluoride is colorless inside of the wood.

Chemical retention analysis

Retention analysis was conducted by scientists at the USDA USFS FPL, in Madison, Wisconsin. Analysis was conducted on composite samples from each Treatment Schedule. Composite samples were prepared from discs removed from samples that had been stored for 28 days after treatment. The outer 19.5 mm (0.75 in) of discs approximately 12.7 mm (0.5 in) thick were removed and ground in a Wiley mill, until the material passed through a 2 mm screen. The resulting ground material was mixed with ground material from the other samples within the same Treatment Schedule. The composite samples were then sent to FPL for analysis. Scientists at FPL conducted retention analysis according to AWPA A2, Standard Methods for Analysis of Waterborne Preservatives and Fire-Retardant Formulations.

Results

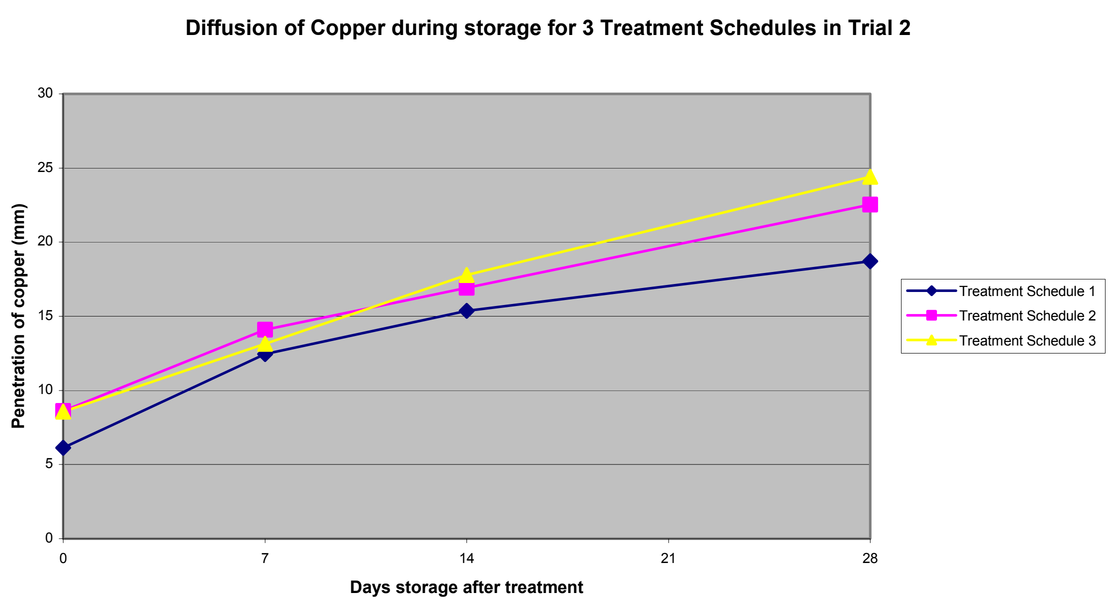
<u>Chemical penetration and diffusion</u>
Fluoride penetration into the sapwood of the treated posts was significant. In all Treatment Schedules, fluoride had penetrated the majority of the sapwood, and in some cases, limited penetration of the heartwood was noted. Diffusion of the fluoride into the wood did not appear to be significant between the time the samples were initially removed from treatment, and after 28 days of storage.

Copper penetration was limited to within the first inch of sapwood depth, in all Treatment Schedules. Copper depth initially after treating was 6.1, 8.6, and 8.6 mm (0.24, 0.34, and 0.34 inches) for Treatment Schedules 1,2, and 3, respectively. Copper penetration after 28 days of storage increased to 18.7, 22.5, and 24.4 mm (0.76, 0.89, and 0.96 inches) for Treatment Schedules 1,2, and 3, respectively (Table 2).

	Initial Copper Penetration (mm/*in*)	Copper Penetration after 28 days storage (mm/*in*)
Treatment Schedule 1	6.1 /*0.24*	18.7 /*0 .74*
Treatment Schedule 2	8.6 / *0.34*	22.5 / *0.86*
Treatment Schedule 3	8.6 / *0.34*	24.4 / *0.96*

Table 2. Copper penetration depths for Trial 2.

Diffusion rate of copper during the 28-day storage period was 0.45, 0.50, and 0.57 mm/day (0.018, 0.019, and 0.022 inches/day), for Treatment Schedules 1,2, and 3, respectively. The greatest rate of diffusion occurred during the first seven days of storage for Treatment Schedules 1,and 2. Diffusion rates for Treatment Schedule 3 remained fairly consistent throughout the storage period (Figure 2.).
After 28 days of storage, the average percentage of sapwood penetrated by copper was 70, 76, and 85 percent, for Treatment Schedules 1,2, and 3, respectively.



Chemical Retention

Retention values for copper and fluoride measured in composite samples from each Treatment Schedule are shown in Table 3., below.

Treatment Schedule	F Retention (mg/g)	F Retention (lbs/cubic foot)	Cu Retention (mg/g)	Cu Retention (lbs/cubic foot)
1	0.37	0.009	5.28	0.127
2	0.42	0.010	7.23	0.174
3	0.48	0.012	7.17	0.172

Table 3. Retention values for copper and fluoride composite samples from each Treatment Schedule.

DISCUSSION – TRIAL 1 AND TRIAL 2

Fluoride penetration

In both trials, the penetration of the fluoride into sapwood was significant for all Treatment Schedules. There did not appear to be significant differences in the depth of fluoride penetration between the various Treatment Schedules. Additionally, no significant difference in fluoride penetration could be noted between samples taken immediately after treatment, and samples that had been kept in storage for either 28 or 42 days. Although the location of fluoride could be determined, the quantity of the fluoride at different depths within the wood could not be determined. It could be that retention levels of fluoride deeper in the wood increased over time, as the chemical diffused from areas of greater concentration at the surface to the lower concentration at the greater depths of the sample. However, based on the depth of the fluoride penetration into the sapwood, it appears that the minimum treatment time (Treatment Schedule 1, 2 day soak) should be sufficient to treat either ponderosa or lodgepole pine.

Effect of heartwood on preservative treatment

When utilizing small diameter trees in sawn products, there is a greater chance for the occurrence of heartwood along one or more of the sawn surfaces, as opposed to the heartwood being "boxed" within the sapwood as is found in roundwood products. Although the heartwoods of some species are resistant to fungi and insect attack, the heartwoods of pines are not considered resistant to such degradation. Sawn pine products that contain heartwood on the surface of the product would require preservative treatment, if they were to be used in exterior applications. However, the limited chemical penetration into heartwood located on the surface of samples in Trial 1 may indicate that the double diffusion process may not be suitable for sawn products containing surface heartwood, without some modification. Incising the surface of the product may increase chemical penetration, as was shown in work done by Gjovik (1972).

Differences in copper penetration between Trials

Although the copper penetration initially measured after samples were removed from treatment were similar between Trials 1 and 2, the copper penetration after 28 days of storage was greater in Trial 2, than in Trial 1. The difference between the species utilized in the Trials does not seem to explain the difference. For example, the ponderosa pine utilized in Trial 1 is a species that is considered to be relatively easy to treat, while the lodgepole pine in Trial 2 is considered a difficult species to treat (Anon., 1999).

The difference between the copper penetration in the two Trials may be due to the temperature differences during the post-treatment storage period. Thompson (1991) found that the diffusion of borate essentially doubled with each 20 F rise in post-treatment temperature. If a correlation between temperature and diffusion of copper also exists, it may be responsible for the differences between the depth of copper penetration in the two Trials. Trial 1 was conducted in Sigurd, UT, starting in mid-February, while Trial 2 was conducted in Fort Collins, CO during the summer months. Temperature differences between the two Trials would have been significant.

Another possible reason could have been due to the lack of control of treatment chemical solution concentration in Trial 1. If the concentration gradient between the wood and solution falls, the diffusion of the chemical into the wood should slow. As packets of wood are treated, the uptake of chemical into the wood should lower the concentration of the remaining solution, unless it is offset by evaporation of the water in solution. It is necessary to measure the concentration of the solutions between treatments to determine whether the concentration has changed appreciably. Complications arose on site during Trial 1 that prevented the measurement of solution concentration between Treatment Schedules. It is possible that the solution concentration decreased between Treatment Schedules in Trial 1, resulting in lesser quantities of copper entering the wood, and subsequently lessening the ultimate depth of copper penetration.

Study results compared to published standards for chemical penetration

The American Wood Preservers Association has established a Use Category System (UCS) for defining exposure and expected product performance for treated wood products. The UCS ranges from dry interior exposure applications (UC1), to exposure to saltwater (UCS5C). Products in ground contact, or exposed to fresh water, such as treated fence posts, are classified as UCS4A. Each UCS specifies recommended chemical penetration and retention levels for various species of wood. Penetration levels are expressed as either actual depths, or as percentages of sapwood that is treated.

Although AWPA does not currently recognize the double-diffusion process in their standards, penetration results from this study can be compared against requirements outlined in the AWPA standards for other chemical and treatment methods. For example, AWPA recommends that chemical penetration in lodgepole pine fence posts reach depths of 1.25 inches, or penetrates 85 percent of the sapwood (whichever is less). For ponderosa pine, the depth of penetration increases to 2 inches, however, the sapwood penetration percentage remains the same. In Trial 2, the average depth of copper penetration is less than 1.25 inches, however, the average percentage of sapwood that was penetrated was equal to 85 percent. It should be noted, however, only four of the nine samples achieved the sapwood penetration percentage requirement.

Chemical Retentions

AWPA Standard C1 lists minimum retentions of copper in pressure-treated wood rated for ground contact applications. Retention values for the three recognized formulations of CCA, the most commonly used pressure treating chemical formulation, range from .065 to .071 lbs/cubic foot. The copper retention values measured in this study are almost two and one-half times greater than the values required by AWPA. However, copper retention values do no appear to vary significantly between Treatment Schedules 1 and 2.

AWPA does not list minimum retentions for fluoride, as it is not used in pressure treating applications. However, fluoride threshold concentration levels for various fungi have been published. A summary of fluoride threshold levels is shown in Table 4.

Fungi	Threshold concentration range (lbs/cubic foot)
Coniophora cerebella	0.025-0.050
Polyporus vaporarious	0.006-0.019
Lentinus sqamosus	0.006-0.019
Lentiunus lepideus	0.12 - 0.15
Coniofera putena	0.15 - 0.17
Poria monticola	0.18 - 0.20
Polyporus versicolor	0.84 - 1.41
Lentiles frabea	0.16 - 0.19

(Source: Fahlstrom, 2002, and VanGroenou, et al. 1951)

Table 4. Fluoride threshold concentration levels for various fungi.

As shown in Table 4., the fluoride retention values measured in this study are below the threshold concentration range for all but one of the fungi listed. Scientists at the FPL who conducted the retention analysis believe that fluoride retentions would have been higher if it were measured on samples that had not been treated with copper. They believe that some of the fluoride may have been leached from the samples during treatment in the copper solution.

A review of the literature showed that Douglas fir posts butt-treated with the double diffusion process showed much higher values of fluoride retention than was encountered in this study (Table 5). The low fluoride retention values may indicate that the insoluble copper-fluoride bond is not being formed, and that the chemicals may leach from the wood upon prolonged contact with water.

Location of sample	Rentention values (lbs/cubic foot) *NaF*	*CuSO4*
6" from top	0.05	0.025
midlength	0.097	0.087
ground level	0.14	0.53

(Source: Miller, et al. 1970)

Table 5. Copper and fluoride retentions for Douglas fir posts soaked for 3 days in 3.2% NaF followed by 3 days in 5.3% $CuSO_4$, with the top of posts brushed.

Conclusions

Fluoride will adequate penetrate sapwood with only a 2-day soak.

Copper penetration is not as great as fluoride penetration, and may not meet AWPA penetration depth requirements in all samples.

Chemicals will not adequately penetrate heartwood occurring on the surface of sawn products.

Longitudinal penetration of chemicals into products completely submerged, as opposed to butt-soaked, will be limited.

Copper retention values should be more than adequate for ground contact exposure, as they exceed AWPA requirements for copper retention in CCA treated wood.

The lower than expected fluoride retention values need to be investigated, as they do not meet the published threshold levels for a number of fungi, and may indicate a loss of fluoride during the copper soak.

Leaching of treatment chemicals from the wood needs to be investigated to determine whether adequate amounts of fluoride are reacting with the copper in the wood.

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