Long-Term Stake Evaluations of Waterborne Copper Systems

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Abstract: Limitations on the use of chromated copper arsenate (CCA) have heightened interest in use of arsenic-free copper-based alternatives. For decades, the USDA Forest Products Laboratory has been evaluating several of these systems in stake plots. Southern Pine 38- by 89- by 457-mm (1.5- by 3.5- by 18-inch) stakes were treated with varying concentrations of acid copper chromate (ACC), ammoniacal copper borate (ACB), or acid copper formate (CF) and buried to one-half their length in plots within the Harrison Experimental Forest in Mississippi. Stakes treated with acidic formulations (ACC and CF) generally performed well at copper oxide retentions above 1.8 kg/m^3 (0.11 lb/ft^3), as did ACB-treated stakes containing 3.5 kg/m^3 (0.22 lb/ft^3) CuO. However, even at retentions where median ratings and the average index of condition remained high for over 20 years, individual stakes occasionally failed in less than 10 years. The results suggest that occasional early failures caused by copper-tolerant fungi may be a concern for use of these treatments in ground contact.

Key Words: stake tests, long term, acid copper chromate, ammoniacal copper borate, copper formate

Introduction

Recent limitations on the use of chromated copper arsenate (CCA) have renewed interest in some of the older, arsenic-free preservative systems. The USDA Forest Service, Forest Products Laboratory has been evaluating a range of preservative systems in stake tests since the 1930s. Although other sites are and have been used, the primary test site is in the Harrison Experimental Forest near Saucier, Mississippi. The long-term nature of this test site, and the large dimensions of stakes used by earlier researchers (nominal 2 by 4 inches, standard 38 by 89 mm), provides valuable insight into the ability of preservatives to protect wood under in-service conditions.

This paper focuses on the evaluation of stakes treated with three types of arsenic-free copper-based systems (acid copper chromate, ammoniacal copper borate, and copper formate) and exposed for a substantial number of years at the Harrison Experimental Forest. Acid copper chromate (ACC) is a preservative that has been standardized for use by the American Wood Preservers' Association at retentions of 4.0 kg/m^3 (0.25 lb/ft^3) for above-ground and 8.0 kg/m^3 (0.50 lb/ft^3) for ground contact applications (AWPA 2002). ACC has been used by a few treaters for several decades, primarily for wood exposed above ground. Ammoniacal copper borate (ACB) has not been standardized as a preservative treatment by the American Wood Preservers' Association. The performance of ACB after 6 years of exposure was discussed in a previous publication (Johnson 1983). Unlike the acid ACC and copper formate systems, ACB uses copper solubilized in an alkaline solvent. Copper formate (CF) also is not a standardized preservative, but it represents perhaps the simplest form of an acidic copper treatment. Wood treated with all three of these formulations could be vulnerable to attack by copper-tolerant fungi. Only ACB contains a co-biocide (boron), and an earlier report noted that 99% of the boron had leached from the groundline portion of the stakes within 11 years of exposure (Johnson and Foster 1991). Three plots contain ACC-treated Southern Pine, with exposure periods of 30, 35, and 55 years. The CF plot has been evaluated for 44 years, and 27-year data is available for the ACB plot. This paper discusses the performance of these systems relative to CCA Type C (CCA-C), which has been evaluated at the Harrison Experimental Forest for 30 years.

Materials and Methods

Site Characteristics: The Harrison Experimental Forest is a pine woodland with sandy loam soil and an average annual rainfall of 1,580 mm (62 inches) per year (Crawford et al. 2002, De Groot and Evans 1998). The relatively high annual rainfall and warm temperatures (average annual temperature of 19.6°C (67°F)) create a severe decay environment. In addition, native subterranean termites are active at the site. Copper-tolerant fungi are also present, but they are not uniformly distributed through all areas of all plots.

Preparation of Stakes: The stakes used for each of these treatments were Southern Pine sapwood with dimensions of 38 by 89 by 457 mm (1.5 by 3.5 by 18 inches). The stakes were treated with a full cell process using a pressure period of sufficient duration and intensity to ensure complete penetration. Each stake was weighed immediately before and after treatment to determine preservative uptake; the retention was calculated by multiplying the gross solution uptake by the solution concentration. A range of retentions for each preservative was obtained by adjusting the solution concentration. For the ACC and CF treatments, 20 stakes were treated for each concentration, from which 10 acceptable stakes were selected for installation. In the case of ACB, 20 replicate stakes were installed for each retention. The ACC solutions were prepared as salt formulations (using $CuSO_4$ and Na_2 CrO_4) but will be discussed on the oxide basis (31.8% CuO and 68.2% CrO_3) to simplify comparisons. The ACB solution was composed of 67% CuO and 33% B_2O_3, and CF was presumably prepared by dissolving copper oxide in formic acid. Following treatment, the stakes were allowed to air dry and were then buried, standing upright, to a depth of 225 mm (9 inches) in soil in the respective test plots. Placement of stakes was randomized within the plot.

Rating of Stakes: The stakes were periodically removed and scraped to remove soil and facilitate inspection. The stakes were then rated separately for decay and termite attack using a rating system in accordance with AWPA Standard E07 (AWPA 2002). The ratings express the amount of decay or termite attack as the percentage of the cross-section removed.

Ratings for decay and termite attack[a]	
10	No decay; 1 or 2 termite nibbles allowed
9	Trace to 3% of cross-section
8	3%–10% of cross-section
7	10%-30% of cross-section
6	30%–50% of cross-section
4	50%–75% of cross-section
e	Failed

[a] Separate ratings were given for decay and termite attack.

For the purpose of this paper, older ratings, which were based on a different rating system, were converted to the current scale.

Results and Discussion

The condition of the ACC-treated stakes is shown in Figures 1 to 3. In the oldest plot (Figure 1), the stakes treated to 2.1 kg/m^3 (0.13 lb/ft^3) failed rapidly, with a median life of less than 10 years. The stakes treated to 4.2 or 5.9 kg/m^3 (0.26 or 0.37 lb/ft^3) performed much better, and no failures occurred until more than 20 years of exposure. One-half the stakes treated to 5.9 kg/m^3 (0.37 lb/ft^3) were still intact at the most recent inspection, 55 years after installation. This very encouraging performance was contradicted in a subsequent plot (Figure 2), where stakes treated with ACC to similar retentions all failed within 12 years. Interestingly, the stakes treated to 2.2 kg/m^3 (0.14 lb/ft^3) appeared to fare better than those treated to 4.6 kg/m^3 (0.29 lb/ft^3). It should be noted, however, that the retention in all the stakes evaluated in Figures 1 and 2 was well below 8.0 kg/m^3 (0.50 lb/ft^3), the current AWPA specification for ACC-treated wood to be used in contact with the ground. The performance of ACC treatments at higher retentions is shown in

Figure 3. These data appear to support that in Figure 2 and indicate that an ACC retention of 4.0 kg/m^3 (0.25 lb/ft^3) does not provide long-term protection of wood placed in contact with the ground. Even at the 8.0-kg/m^3 (0.50-lb/ft^3) retention, four stakes failed within 20 years. Interestingly, the remaining six stakes all have very good ratings after 35 years. This pattern is repeated at the highest retention (12.1 kg/m^3, 0.76 lb/ft^3) where two stakes failed within 10 years and the remaining stakes have high ratings after 35 years.

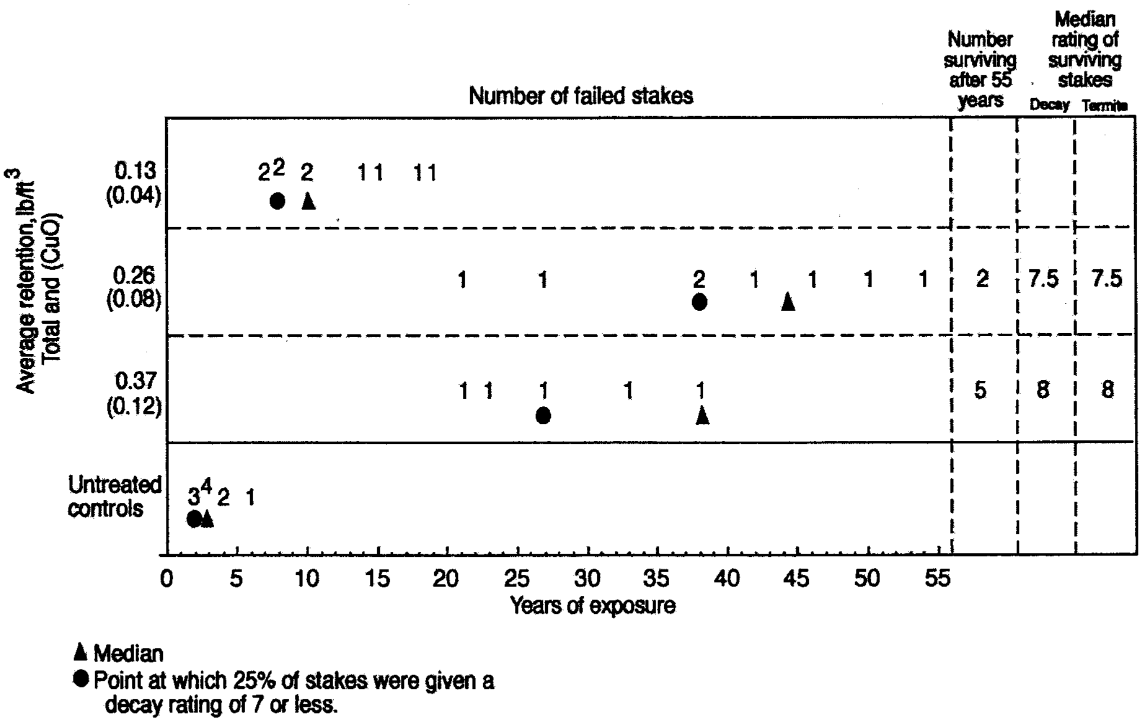

Figure 1. Performance of ACC-treated stakes in plot evaluated for 55 years.

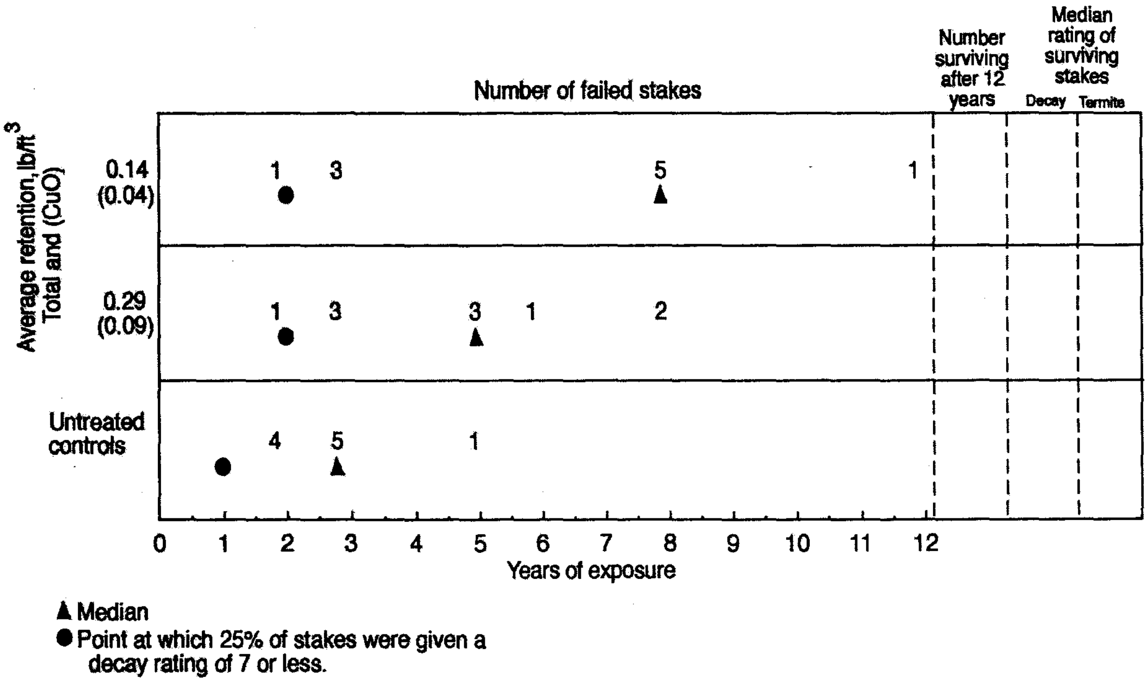

Figure 2. Performance of ACC-treated stakes in plot evaluated for 30 years. All stakes failed within 12 years.

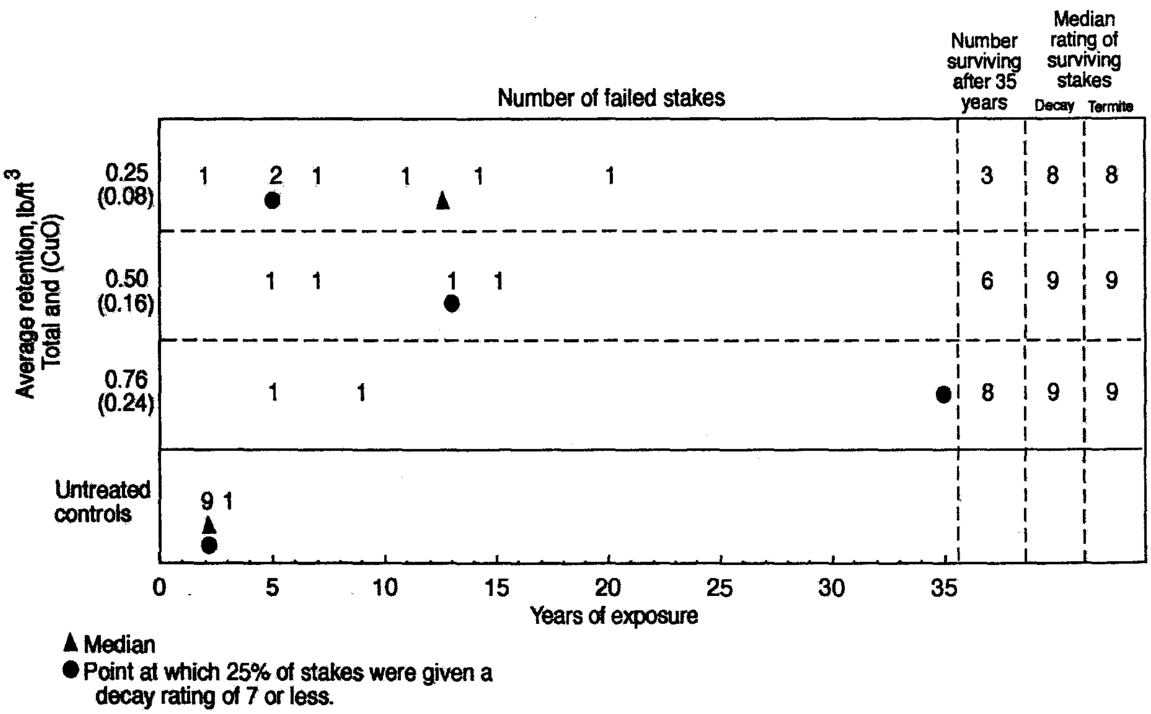

Figure 3. Performance of ACC-treated stakes in plot evaluated for 35 years.

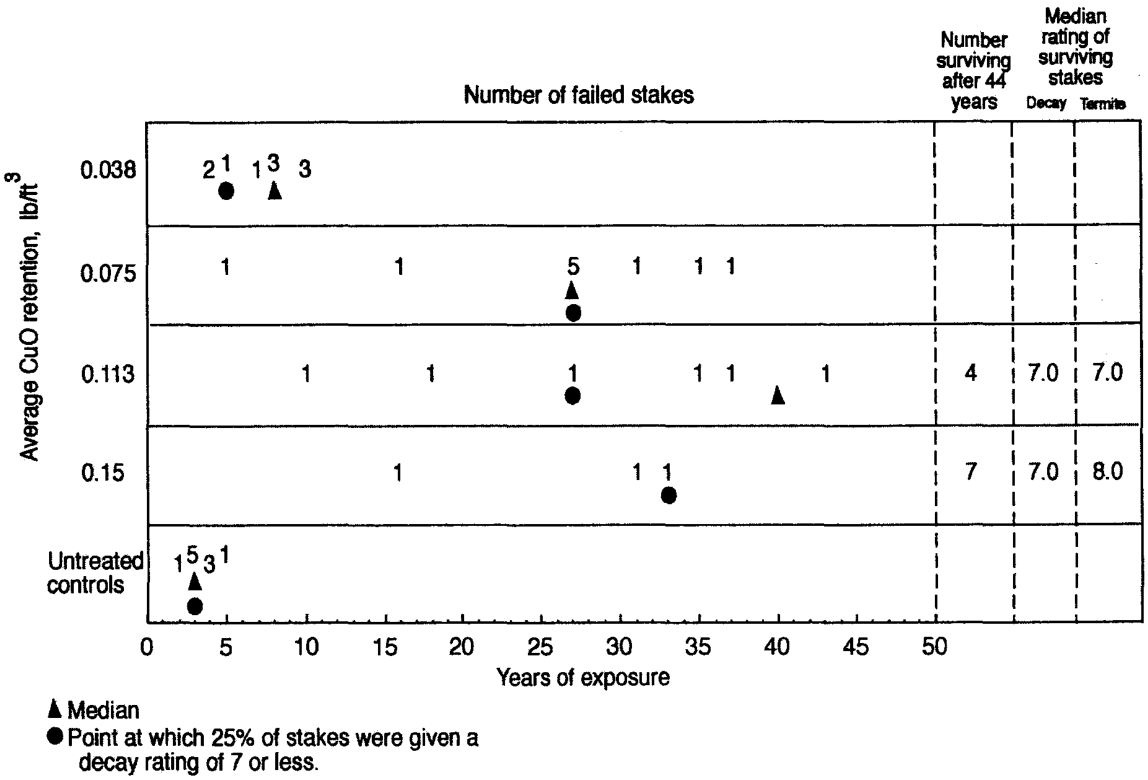

Figure 4. Performance of CF-treated stakes in plot evaluated for 44 years.

The performance of the CF-treated stakes is shown in Figure 4. At retentions of 1.2 kg/m^3 (0.075 lb/ft^3) or higher, the copper formate treatment provided substantial protection. At the highest retention (2.4 kg/m^3, 0.15 lb/ft^3), 7 of the 10 stakes remain after 44 years of exposure and still maintain a median rating of 7. Note that on a copper oxide basis, this retention roughly corresponds to an ACC retention of 8.0 kg/m^3 (0.50 lb/ft^3). However, as was noted for ACC, a few stakes failed completely much earlier in the exposure. Interestingly, in a soil block test initiated at about the same time that this plot was established, copper formate was found to be ineffective against the copper-tolerant fungus *Poria moniticola*, even at CuO retentions as high as 4.8 kg/m^3 (0.31 lb/ft^3) (McKnight and Merrall 1958).

The retentions of ACB evaluated were generally higher than those used in the ACC or CF treatments (Figure 5). The ACB-treated stakes generally performed well at retentions of 5.3 kg/m^3 (0.33 lb/ft^3) and higher, with no failures after 27 years at retentions of 7.2 kg/m^3 (0.45 lb/ft^3) and 21.3 kg/m^3 (1.33 lb/ft^3). However, in a trend similar to that of stakes treated with ACC and CF, one ACB-treated stake failed within 10 years at retentions of 5.3 kg/m^3 (0.33 lb/ft^3) and 10.6 kg/m^3 (0.66 lb/ft^3). Although not directly evaluated in these plots, a comparison of the ACB data to the ACC and CF data indicates that with the ammoniacal copper system, a higher retention of CuO is needed to prevent fungal and termite attack. The majority of ACC- and CF- treated stakes were durable at CuO retentions above 1.8 kg/m^3 (0.11 lb/ft^3), while this CuO threshold appeared to be about 3.5 kg/m^3 (0.22 lb/ft^3) for ACB.

Stakes treated with chromated copper arsenate Type C (CCA-C) are also being evaluated in plots at the Harrison Experimental Forest. The oldest of these plots has been under evaluation for 30 years and includes stakes treated to retentions of 3.2, 6.4, and 9.6 kg/m^3 (0.2, 0.4, and 0.6 lb/ft^3). Although the condition of the stakes treated to the lowest retention of 3.2 kg/m^3 (0.2 lb/ft^3) is gradually declining, none of the stakes has failed and the lowest rating of any individual stake is 6 for decay. The stakes treated to higher CCA retentions have suffered little attack and also have had no early failures. The data indicate that the CCA-C treated stakes will fail very gradually over a much longer period of time.

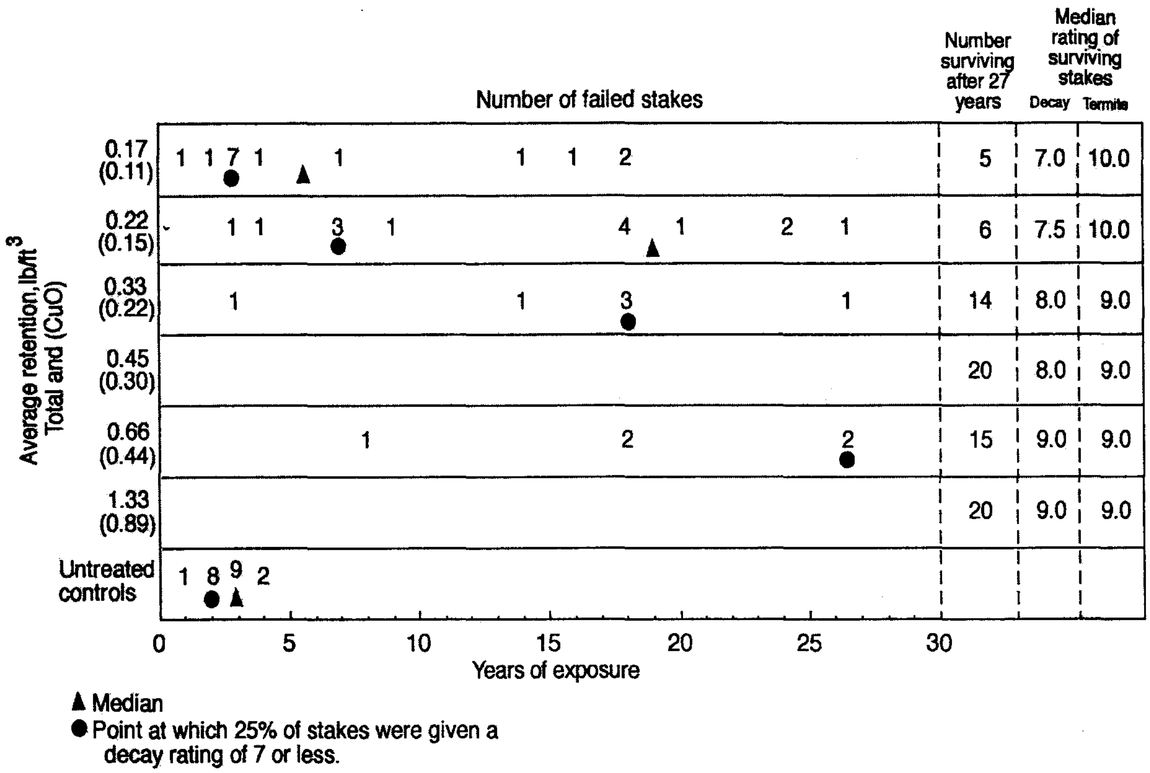

Figure 5. Performance of ACB-treated stakes in plot evaluated for 27 years

Generally, the performance of ACC-, ACB-, and CF-treated stakes shows similar trends. The majority of stakes are durable at sufficient copper loadings, and the median ratings of the stakes remain high. However, even at these effective copper retentions a few stakes have failed completely in a much shorter time. This pattern suggests that copper-tolerant fungi are attacking some stakes, while others remain unaffected. The reason for this is uncertain. It may be a result of the patchy distribution of copper-tolerant fungi within the plots or of some characteristic of these stakes that makes them more vulnerable than others treated to a similar retention. It also appears that increasing the copper retention provides little benefit in preventing these early failures. Again, this may reflect attack by copper-tolerant fungi. De Groot and Woodward (1999) evaluated the ability of several copper-tolerant fungi to degrade treated wood and found that several could degrade wood treated to CuO retentions as great as 16 kg/m^3 (1.0 lb/ft^3).

The distribution, sporadic nature, and implications of attack by copper-tolerant fungi have been discussed by Morrell (l989) and Williams and Fox (1994). Both papers note the importance of these fungi in causing sudden failures of isolated stakes. Williams and Fox (1994) stress the importance of conducting laboratory tests to evaluate the performance of preservatives against known copper-tolerant fungi. The practical implications of copper tolerant fungal attack of treated wood in service are less clear, as it is difficult to predict the percentage of structures that might be affected. In addition, as noted by Morrell (1989), preservative treated products of all types do occasionally fail for a variety of reasons. However, if the number of sudden early failures were as great as 1 in 10 or 1 in 20, as indicated by the experimental plots discussed in this paper, the use of these types of treatments could have negative consequences for the treated wood industry. The early failure of one or two stakes, combined with high ratings for the remaining stakes, is also a concern for the manner in which stake data is reported. Typically, stake data are reported as the "average index of condition" over time as described in AWPA Standard E07 (AWPA 2002). This method of reporting could mask early failures. For example, if 10 replicates are used and 1 stake fails completely, the average index of condition could still be as high as 90 if all other stakes are rated as "10." This effect is shown for one retention of ACC and one retention of ACB in Figure 6. The average index of condition for the stakes shows a generally downward trend, with only small drops to indicate early failures. These small drops could easily be misinterpreted as a small reduction in the ratings of several stakes. This possibility needs to be considered when reviewing data on new preservatives that utilize copper as the primary fungicide.

CCA alternatives for residential structures will be used primarily above ground, and the stake data in this paper suggest that ACC-, ACB-, and CF-treated wood should all be very durable in above-ground applications. ACC has been used above ground for decades with few reports of premature failures. Little is known about the ability of copper-tolerant fungi to attack treated wood exposed in above-ground applications, but it is likely to be less of a concern than for wood used in ground contact. As the use of arsenic-free treated wood evolves, it will become more important to understand factors affecting the above-ground durability of copper systems.

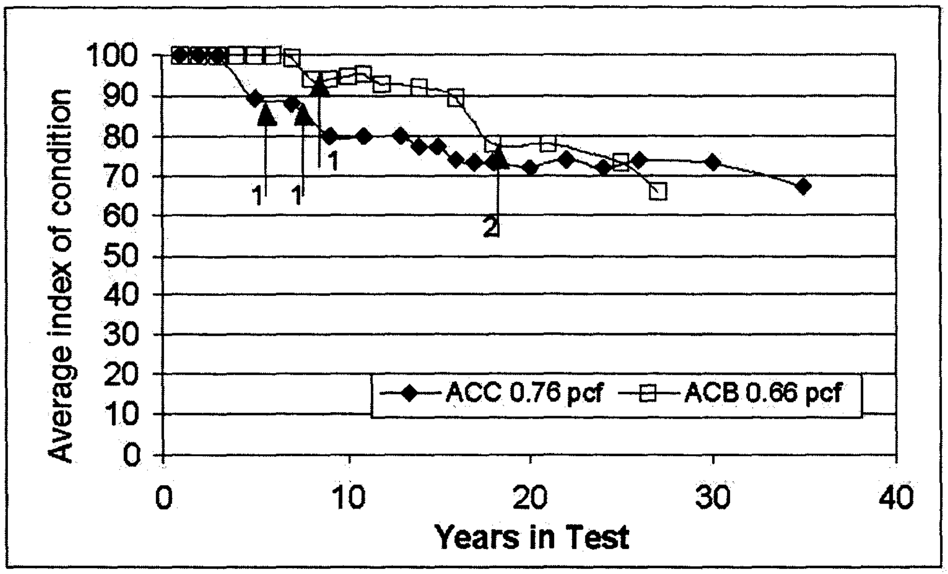

Figure 6. Plot of average index of condition for one retention of ACC stakes (from Fig. 3) and ACB stakes (from Fig. 5). Arrows indicate early stake failures; numerals indicate number of failed stakes.

Conclusions

The three arsenic-free copper-based systems evaluated in this paper all provided good long-term protection of the majority of stakes at higher copper retentions. For ACC and CF, this retention appeared to be approximately 1.8 kg/m^3 (0.11 lb/ft^3) of CuO, while for ACB the threshold CuO retention was approximately 3.5 kg/m^3 (0.22 lb/ft^3). However, even at effective CuO retentions, stakes occasionally failed early in the study. This pattern of occasional early failures suggests that wood treated with these preservatives may be vulnerable to attack by isolated patches of copper-tolerant fungi. The practical implications of these occasional early failures for treated wood in service are unclear, but should be a consideration if these preservatives were to be used in ground-contact applications. The data indicate that wood treated with these preservatives would be durable in above-ground applications.

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Discussion

Dr. Morrell: Thank you, Stan. Once again, we'll avoid questions till the end. Our next speaker, breaking the other FPL mold, I suppose, is Dr. Danel Nicholas, who will give us a little presentation about the evaluation of reactive silanes as water repellants for wood. Darrel?

PROCEEDINGS

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