TECHNICAL NOTE: EFFECT OF SOIL ON THE pH OF TREATED WOOD IN GROUND CONTACT

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Abstract. The pH of treated wood in ground contact will influence the type and activity of decay and nondecay microorganisms present as well as the solubility and leaching of metallic biocides. To determine the soil effect on the pH of treated wood in ground contact, southern pine sapwood samples commercially treated with five copper-based preservatives along with untreated pine were placed in pots filled with five different soils. The pH of the wood samples after a 12-wk exposure to basic soils increased, as anticipated. However, the pH of wood in acidic soils was more complex than expected with the treated wood pH always greater than soil pH. Two possible chemical mechanisms to explain the nonintuitive results for treated wood in acidic soils are given.

INTRODUCTION

Nondurable wood products used in ground-contact applications should be treated to prevent deterioration by the large variety of wood-degrading organisms that can attack wood. The pH of wood in ground contact will influence the type and activity of decay microbes present as well as nonwood-deteriorating fungi and bacteria that might degrade organic biocides. Furthermore, increased acidity will lead to greater copper leaching (Lebow et al 2006). Also, it has been recently theorized that pH will affect the amount of soluble copper in micronized/particulate copper preservative systems and, consequently, wood pH may be a major factor in the fungal efficacy of particulate copper systems (McIntyre et al 2009; McIntyre and Freeman 2009; Zhang and Ziobro 2009).

A reasonable expectation is that wood will attain the pH of the surrounding soil. However, no information is apparently available to verify this assumption. In a preliminary study, we buried small sticks of untreated, alkaline copper quat (ACQ)- and micronized copper quat (MCQ)-treated southern pine sapwood in two fields, one with alkaline and one with acidic soil. After 2 mon of wet summer weather, the samples were dug up and the pH of the outer portion of the untreated and treated wood samples determined. The pH of samples buried in the alkaline soil increased, as expected. However, all wood samples buried in the field with acidic soil unexpectedly had pH values higher than the soil pH (Little et al 2010).

The objective of this study was to conduct a larger study to verify the unintuitive results obtained in acidic soils. Specifically, the pH of southern pine sapwood, commercially treated with five copper-based preservative systems and untreated wood, was determined after burial in pots filled with five wet soils with a range of pH values.

EXPERIMENTAL PROCEDURE

Southern pine 4 × 4 posts were obtained from lumber yards. The posts had been commercially

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treated to UC4A ground-contact specified retentions with: 1) micronized copper quaternary (quat) ammonium compound (MCQ) at 5.44 kg/m^3; 2) alkaline copper quat (ACQ-D) at 6.4 kg/m^3; 3) micronized copper azole (MCA) at 2.24 kg/m^3; and 4) copper azole (CA-C) at 2.40 kg/m^3. Three timbers per treatment were obtained, each post with a center pith and minimal heartwood. In addition, three southern pine 4 × 4 timbers treated before 2004 with chromated copper arsenate (CCA-C) at 6.4 kg/m^3 and three untreated southern pine 2 × 4 boards were obtained.

At least 100 mm was cut from the treated post ends to mitigate any end treatment effect. A 19-mm-thick defect-free slab was then sliced from one edge surface of each of the treated 4 × 4s or the wide face of the untreated 2 × 4s to give three replicate slabs from each of the three 4 × 4 posts treated with each copper-based system or the three untreated 2 × 4 pine boards. The slabs were 600-mm long and 89-mm wide. The 19-mm thickness was used as the biocide penetration zone for 4 × 4 posts is 0-25 mm deep (AWPA 2009); therefore, sapwood from the outer 19-mm zone would be well within the specified 25-mm biocide penetration zone. The 19-mm-thick slabs, which were all sapwood and had good biocide penetration based on visual observation, were then crosscut into strips for 30 × 19 × 89-mm samples. Each sample was then crosscut in half to give two 14 [longitudinal dimension] × 19 × 89-mm matched samples, one of which was exposed to soil and the other unexposed to minimize within-sample biocide retention variation (Schultz et al 2004). The samples to be buried in soil were then individually bagged in a nylon fine-mesh bag. The unexposed samples were stored with the pH of the unexposed and exposed matched samples determined at the same time at the end of the study.

Five soils were obtained in various locations around Mississippi with the soil textures and pHs determined by the Mississippi State University Soil Analysis Laboratory. These were a highly alkaline silt soil from near Granada, MS, with 8.7 pH (alkaline soil), a silt soil from a hardwood forest near Granada, MS, with 7.2 pH (silty soil), silt loam soil from the Dorman Lake wood preservation plot near Mississippi State University with 5.1 pH (Dorman soil), loamy sand soil from the Saucier wood preservation plot near the Mississippi Gulf Coast (Saucier soil) with 4.5 pH, and silt loam soil from a hardwood forested lake lot in Starkville, MS, with 7.8 pH (lake soil).

The soils were put into flower pots 150 mm high with a top diameter of 160 mm and a drainage hole in the bottom. Three pots were used per soil with the pots first partially filled with soil. Then six individually bagged sapwood samples, one sample of each the five copper treatments and untreated pine, were placed horizontally in the pot and the pot was then filled with additional soil. The three replicate pots per soil type were then placed in a plastic box and the soil saturated with deionized water with 30 mm of standing water in the bottom of the plastic box. The plastic boxes were covered with aluminum foil to minimize water evaporation and left for 12 wk at room temperature.

After 12 wk of burial in wet soil, the samples were removed and air-dried, the nylon bags cut away, any soil on the wood surface brushed off, the samples were further air-dried, and the samples were divided into two 45-mm-wide half sections. One half-sample was retained and the other was chopped into small slivers. The slivers were placed into clean glass jars with distilled water added at 10 parts water to 1 part air-dried wood (Stamm 1964). The matched unexposed wood samples that had been stored were treated similarly at the same time. Also, a small portion of air-dry soil from each pot was put into a glass jar with distilled water added in a 1:1 ratio. The pH of the wood and soil samples was taken using a glass electrode at 24 and 72 h after placing the samples in the distilled water with the pH meter calibrated using buffer solutions. The 24- and 72-h pH measurements for each the three replicate wood and soil samples were averaged per wood treatment and soil type. No large differences or consistent pattern were observed between the pH measured at the two water-immersion times, which suggests that chopping rather than grinding the wood samples to a smaller particle size such as was done by Zhang and Ziobro (2009) is sufficient for pH measurements. Because of the large number of samples, the pH measurements were taken over a period of 5 da with matched exposed and unexposed samples of one soil run together to minimize among-day pH measurement variation.

RESULTS AND DISCUSSION

The average pH of the three replicate matched unexposed and exposed wood samples per treatment/soil, grouped by soil type with the most alkaline soil first, are given in Table 1 along with the soil pH. Because the sapwood samples had a short longitudinal dimension of only 14 mm, in water-saturated soil, moisture should quickly migrate through the samples in the fiber direction to give a uniform pH throughout. The soil pH values, determined at the end of the experiment, were apparently influenced by the wood samples in which the alkaline soils decreased in pH and the acidic Dorman and Saucier soils increased in pH. Consequently, the ending pHs are different from the initial values of the soils.

The average untreated and unexposed southern pine sapwood pH values were all 4.9, within the range typically reported (McIntyre et al 2009; Zhang and Ziobro 2009). Unexposed CCA-treated sapwood, cut from the three 4 × 4 timbers that had been stored for 5 yr, had pH values slightly less than the untreated sapwood. Unexposed wood treated with the two soluble copper systems, ACQ and CA-C, had 6.0 and 6.1 pH, respectively. Unexposed wood treated with the two particulate copper-based systems, MCQ and MCA, had 5.9 and 5.8 pH, respectively. The pH values of the latter four systems are all higher than untreated and CCA-treated southern pine sapwood, likely from formula tion with ethanolamine for the soluble copper systems and basic copper carbonate for the particulate copper systems. This pH increase in southern pine treated with the two micronized/particulate copper systems is different from that theorized by McIntyre et al (2009) and Zhang and Ziobro (2009), who suggested that the pH of wood treated with particulate copper systems should remain at about the pH of untreated southern pine.

Table 1. Average ending pH of the soils and average pHs of the unexposed and exposed southern pine sapwood samples.[a]

	Average pH		
Wood treatment	Soil	Unexposed wood	Exposed wood
Alkaline soil (8.7)			
Untreated	8.4	4.9	7.2
CCA-C	8.4	4.8	7.5
ACQ-D	8.4	6.0	7.8
MCQ	8.4	5.9	7.7
MCA	8.4	5.8	7.8
CA-C	8.4	6.1	7.8
Lake soil (7.8)			
Untreated	7.2	4.9	6.8
CCA-C	7.2	4.8	7.2
ACQ-D	7.2	6.0	7.2
MCQ	7.2	5.9	7.4
MCA	7.2	5.8	7.3
CA-C	7.2	6.1	7.4
Silty soil (7.2)			
Untreated	6.6	4.9	6.5
CCA-C	6.6	4.8	6.7
ACQ-D	6.6	6.0	6.9
MCQ	6.6	5.9	7.0
MCA	6.6	5.8	6.9
CA-C	6.6	6.1	7.0
Dorman soil (5.1)			
Untreated	6.1	4.9	6.3
CCA-C	6.1	4.8	6.5
ACQ-D	6.1	6.0	6.6
MCQ	6.1	5.9	6.6
MCA	6.1	5.8	6.7
CA-C	6.1	6.1	6.8
Saucier soil (4.5)			
Untreated	5.1	4.9	5.7
CCA-C	5.1	4.8	5.7
ACQ-D	5.1	6.0	5.8
MCQ	5.1	5.9	6.1
MCA	5.1	5.8	6.2
CA-C	5.1	6.1	6.0

[a] Each value is the average of two analyses on three replicate matched unexposed and exposed sets. The initial pH of each soil prior to exposure to the wood samples is shown in parentheses.

CCA-C, chromated copper arsenate; ACQ-D, alkaline copper quat; MCQ, micronized copper quat; MCA, micronized copper azole; CA-C, copper azole.

After exposure to alkaline soil that had a final pH of 8.4, the pH of all wood samples increased as would be anticipated. The untreated southern pine had the lowest average pH of 7.2 and all treated samples had pH of 7.5-7.8. Samples exposed to the lake soil, which had the second highest ending soil pH of 7.2, also had increased pH but with values that were slightly less than for alkaline soil.

However, a different trend was apparent with the relatively neutral silty soil having a final 6.6 pH. The untreated southern pine had a pH similar to the soil pH, but all the treated samples had pH values slightly above the soil pH by 0.1-0.4 units. Wood pHs that were greater than the soil pH were even more apparent with the two relatively acidic soils, Dorman with an ending 6.0 pH and Saucier with 5.1 pH. For wood samples exposed to Dorman soil, the wood pH values were all higher than the soil pH by 0.2-0.7 units. For the wood samples buried in the Saucier soil, the wood pH values were higher than the soil pH by 0.6-1.0 units. Consequently, the results of this study that used wood samples buried in different soils in small pots confirms the unanticipated results in an earlier preliminary study in which small stakes had been buried in two fields with alkaline (where the lake soil was obtained) or acidic (from which the Dorman soil was obtained) soils (Little et al 2010).

The unexpectedly higher wood alkalinity of 0.1-1.0 pH units than the soil pH for treated wood buried in the three soils, which had pH below 7.0 at the end of the experiment, is different than what was theorized by Zhang and Ziobro (2009). They instead suggested that the initial acidity of untreated southern pine, and acidic rainwater and the acidic water of wet soil, will result in ground-contact-treated wood being acidic. Our results also agree with a just-released study by Vidrine et al (2010), who found that untreated southern pine sapwood buried in acidic soil in large tubs had a 5.09 pH after 8 wk of exposure in soil with an ending pH of 4.15.

One possible explanation for the unexpected results from acidic soils is that wood pH decreases during and after treatment with copper-based systems as the copper complexes with acidic groups to release H^+. More copper will leach from treated wood as soil acidity decreases (Lebow et al 2006). Thus, as copper is leached from treated wood in acidic soils it would be expected that the wood pH may increase, and increase more as the soil pH decreases from additional copper leaching. However, because an increase in pH was also observed for untreated wood buried in the acidic Dorman and Saucier soils, the unexpectedly relatively high pH for untreated pine sapwood exposed to acidic soils cannot be explained solely by copper leaching. Alternatively, wood contains acidic groups and, thus, can be considered a cation exchange resin. We propose that when wood is exposed to wet acidic soil, some soil salts will diffuse into the wood. On exposure to the carboxylic acid groups, the cation of the salt can exchange with the acidic proton. This results in the wood acidic group undergoing an ion exchange reaction to form a wood carboxylate salt of the cation and a water-soluble acid with the anion, and the wood pH consequently increases. The proposed reaction would occur only in acidic soils, because in basic soils, the wood carboxylic groups would be ionized. For wood treated with copper-based systems, it is possible that both the latter ion-exchange and former copper-leaching mechanisms may increase the wood pH in acidic soils. This dual mechanism for copper-treated wood would explain the consistently lower pH of untreated wood in the three acidic soils relative to the pH of all five copper-treated samples. Further research is necessary to determine a mechanism for the nonintuitive pH results obtained for untreated and copper-treated wood exposed to acidic soils.

CONCLUSIONS

The pH of copper-treated and untreated southern pine sapwood in basic soils increased to near that of the soil pH. However, in the three soils that had pH below 7 at the end of the experiment, the treated wood pH was always greater than the soil pH. This nonintuitive finding might be caused by an ion-exchange reaction between soil salts and acidic groups in the wood and/or by copper leaching.

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