ABSTRACT: Equilibrium moisture content (EMC) was measured over a range of relative humidities at 22.5°C to determine whether certain wood preservatives increase the hygroscopicity of southern pine (Pinus sp.). The treatments studied were alkaline copper quaternary (ACQ) at a retention of 6.6 kg·m⁻³, chromated copper arsenate (CCA) at 6.9 kg·m⁻³, and disodium octaborate tetrahydrate (DOT) at 3.8 kg·m⁻³ (equivalent to 2.6 kg·m⁻³ as B₂O₃). All treatments examined increased the EMC at relative humidities above 60%. Wood treated with DOT was the most hygroscopic. At high relative humidities, the ratio of the EMC of ACQ-treated wood to CCA-treated wood was 1.08. It is unlikely that the higher corrosiveness of ACQ compared with CCA is due to this slight increase in hygroscopicity.

KEYWORDS: equilibrium moisture content (EMC), water vapor sorption, preservative treatments, chromated copper arsenate (CCA), alkaline copper quaternary (ACQ), borates, disodium octaborate tetrahydrate, corrosion

Introduction

Wood is treated with waterborne preservatives to increase service life in environments where biodeterioration hazards such as decay or termites are present. One of the most common waterborne wood preservatives, chromated copper arsenate (CCA), was voluntarily withdrawn for use in residential applications as of December 31, 2003 [1]. Research has found that replacements to CCA, such as alkaline copper quaternary (ACQ) and copper azole, are more corrosive toward metallic fasteners in contact with the treated wood than CCA is [2,3].

Choi and Ruddick hypothesized that ACQ-treated wood is more corrosive than CCA-treated wood because ACQ-treated wood is more hygroscopic [4]. However, the hygroscopic properties of ACQ-treated wood have not previously been studied, and in general, sorption data on treated wood are sparse [5–7]. Assuming that ACQ-treated wood is more hygroscopic than CCA-treated wood, the hypothesis of Choi and Ruddick seems plausible, as the metal corrosion rate is strongly dependent on the wood moisture content and embedded metals do not corrode below a threshold wood moisture content of between 15% and 18% [8–11].

Below fiber saturation, the equilibrium moisture content (EMC) of wood depends on temperature, relative humidity (RH), and previous history. A sorption isotherm is the locus of points relating EMC to RH at a given temperature (Fig. 1). Sorption isotherms for wood cannot be derived from first principles. The experimentally determined isotherms are used to predict in-service moisture contents for a given temperature and RH. The sorption isotherm is defined as the adsorption isotherm when measured from an initially dry condition, and the desorption isotherm is denoted when measured from an initially water-saturated condition. The EMC for a given RH is subject to hysteresis: The moisture content is generally higher on the desorption isotherm than on the adsorption isotherm.

Several studies have examined the sorption characteristics of wood treated with waterborne preservatives: Dulat studied borates [5], Shupe and co-workers studied CCA [6], and Cao and Kamdem studied copper ethanalamine [7]. Dulat collected sorption isotherms of pine (Pinus sylvestris L.) treated with disodium octaborate tetrahydrate (DOT) (Na₂B₄O₇·10H₂O), boric acid (H₃BO₃), and borax (Na₂B₄O₇·10H₂O) and compared the isotherms to isotherms of untreated pine. Dulat pointed out that these boron compounds lose their waters of hydration when oven-dried and claimed that wood treated with borates was not more hygroscopic than untreated wood when the waters of hydration were subtracted. However, this analysis assumes that the structure of the hydrated boron compounds remains unaltered within the wood cell wall. From a practical standpoint, though, this extra water is still present in the wood, and it is not clear if it is complexed with the boron compounds or bound to the cell wall.

Shupe and co-workers [6] examined whether CCA-treated wood was more likely to warp, cup, or twist in service because it was more hygroscopic than untreated wood. Instead of displaying the sorption data as isotherms, they presented their data in terms of the ratio of the adsorption to desorption moisture content. They found that this A:D ratio was the same for treated and untreated wood at all RH levels and concluded that the CCA-treated wood was not more hygroscopic. However, the absolute hygroscopicity of CCA- or untreated wood cannot be determined from the data presented in the paper of Shupe. While the CCA-treated wood and untreated wood had the same A:D ratio, the absolute EMCs could have been greater for CCA-treated than for untreated wood.

Cao and Kamdem [7] found that wood treated with copper ethanalamine, the form of copper used in ACQ, decreased hygroscop-
icity of treated wood compared with untreated wood. They attributed this to copper occupying water adsorption sites.

The present study looks to build on these previous works by comparing the effects of ACQ, CCA, and DOT on the hygroscopicity of southern pine (*Pinus* sp.). Although there is a standard method for examining the hygroscopicity of wood treated with fire retardants (ASTM D3201-08ae1) [12], it prescribes only a single non-equilibrium measurement at 92 % RH; the specimen is weighed after 7 days regardless of whether it has come to equilibrium. This method may be valuable for rapidly evaluating the hygroscopic nature of new wood treatments. However, the objective of this study is to measure EMC over the full RH range. The method used was similar to ASTM C1498-04a [13] for measuring sorption isotherms with modifications as described below.

**Materials and Methods**

Southern pine (*Pinus* sp.) lumber was used in the present study. Prior to treatment and sorption testing, the lumber had been in a room maintained at 23 °C and 65 % RH for several years. The samples were most likely sapwood. All specimens came from one parent board (original dimensions were 25 by 127 by 370 mm), which was cut into thin sections along the transverse section, resulting in final specimens with approximate dimensions of 62 by 9.5 mm with a depth in the longitudinal direction of 3.5 mm. No effort was made to cut the 62 by 9.5 mm specimens along the true radial and tangential directions. The average oven-dry specific gravity of the specimens was 0.52 ± 0.02 (standard deviation).

Specimens were pressure-treated with ACQ type D, CCA type C, and DOT; additional specimens were left untreated as controls. Retention was verified with inductively coupled plasma atomic emission spectroscopy. Average retention was 6.6 kg·m⁻³ for ACQ, 6.9 kg·m⁻³ for CCA, and 3.8 kg·m⁻³ for DOT (equivalent to 2.6 kg·m⁻³ on a B₂O₃ basis). Sixteen replicates were used for each treatment: Eight replicates for adsorption measurements and eight for desorption measurements. Adsorption and desorption measurements were run concurrently on different replicates rather than running all specimens through both cycles. After treatment, the adsorption specimens were placed in a fume hood to dry to ambient conditions and then in a sealed container above calcium chloride desiccant. The purpose of the calcium chloride was to dry the specimens to near 0 % EMC while avoiding potential loss of hygroscopicity from oven drying [14]. After reaching equilibrium, the specimens were weighed and placed in containers at sequentially higher RHs. Immediately after treatment, the desorption specimens were placed in a sealed container and equilibrated at 97 % RH and then at sequentially lower RHs. The untreated desorption speci-

![FIG. 1—Sorption isotherms for (a) untreated, (b) ACQ-treated, (c) CCA-treated, and (d) DOT-treated southern pine. The solid line represents the overlay of the parabolic model.](image-url)
mens were equilibrated at 97 % RH from an initial condition of 65 % RH.

RH was controlled by use of saturated-salt solutions. The samples were placed on a platform above a saturated-salt solution in a jar with a screw-top lid, with four specimens per container. The jar had a diameter of 80 mm and a height of 80 mm. The containers were placed in a room maintained at 22.5 °C ± 0.2 °C (standard deviation) and 50 % RH. The specific salts used and the corresponding RHs they produced are given in Table 1 [15].

The specimens were weighed with a SA 210D analytical balance (Scientech, Inc., Boulder, Colorado), which gave readings to the nearest 0.1 mg. Balance calibration was checked prior to any measurements with a series of standard weights. Functional uncertainty in balance readings was 0.2 mg (compared to a specimen weight between 1–2 g). Specimens were weighed immediately after removal from the sealed containers. Equilibrium was defined as a mass change of no more than 0.2 mg within 48 h. Measurements were taken no less than 48 h apart and typically at 1 week intervals.

Special care was taken with the samples above the K2SO4 solutions (~97 % RH). Following the procedure of Carll and Ten-Wolde [16], sealed jars with the wood specimens, platforms, and saturated K2SO4 solution were placed in an oven at 85 °C for 2 h to inhibit mold growth. The lids were retightened and the containers remained sealed for at least 6 months before weighing. It was assumed that the specimens were at equilibrium after this time.

At the end of the adsorption and desorption cycles, specimens were oven-dried at 103 °C for 24 h. Specimens were then removed from the oven, placed in a container over desiccant while being transferred from the oven location to the balance location, weighed, and returned to the oven. The specimens were deemed dry when their weight changed by less than 0.1 % between successive weighings over a 4-h period.

The EMC (expressed as a fraction m) was calculated by

\[ m = \frac{w - w_0}{w_0} \]  

where:

\[ w \] = mass of the specimen at equilibrium and

\[ w_0 \] = mass of the oven-dry specimen.

The mass of the preservatives retained by the oven-dried wood was not subtracted, that is, it is included in \( w_0 \).

**Results**

Average adsorption and desorption isotherms for each treatment are given in Fig. 1. The overlay in the figures is a generic three-parameter sorption model that will be described further in the Discussion section. Overall, the replicates showed little variability; error bars are excluded in Fig. 1 because they are smaller than the data symbols. The highest coefficient of variation (COV, the ratio of the standard deviation to the arithmetic mean) was 6 %, although for most conditions the COV was much lower. Average COVs over all RH conditions ranged from 1–2 % depending on the treatment.

For the untreated specimens, the K2SO4 (~97 % RH) condition was reached by adsorption for both the “adsorption” and “desorption” data sets. The treated desorption specimens were placed in the K2SO4 jars immediately after treatment and approached equilibrium from a fully saturated condition. In contrast, the untreated desorption specimens were placed in the K2SO4 jar after spending several years in a room at 23 °C and 65 % RH and reached equilibrium by adsorbing water vapor. This explains why the K2SO4 data are coincident for untreated specimens, but treated specimens have a higher moisture content on the desorption curves for this condition.

**Discussion**

It is customary to fit a statistical mechanical adsorption model to sorption isotherms in wood, such as the BET (Brunauer-Emmett-Teller) isotherm [17], the Dent isotherm [18], or the GAB (Guggenheim-Anderson-de Boer) isotherm [19]. Simpson showed that these models [20] are useful for fitting the sorption data and accurately describing the relationship between RH and moisture content. However, Simpson cautioned that the physical parameters predicted by the sorption theories, such as heat of sorption, drastically differ from experimental values. Furthermore, three popular sorption models—Dent, GAB, and Hailwood and Horrobin [21]—are mathematically equivalent but have different molecular level interpretations and give different values for the amount of monolayer moisture. To avoid misleading physical pictures associated with the above isotherms, we instead fit our data to a parabolic model

\[ h/m = Ah^2 + Bh + C \]  

TABLE 1—Saturated salt solutions used and the corresponding RHs (from Greenspan [15]).

<table>
<thead>
<tr>
<th>Solution</th>
<th>RH at 22.5 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>11.3 ± 0.3</td>
</tr>
<tr>
<td>MgCl2</td>
<td>32.9 ± 0.2</td>
</tr>
<tr>
<td>K2CO3</td>
<td>43.2 ± 0.4</td>
</tr>
<tr>
<td>NaBr</td>
<td>58.4 ± 0.4</td>
</tr>
<tr>
<td>NaCl</td>
<td>75.4 ± 0.1</td>
</tr>
<tr>
<td>KCl</td>
<td>84.7 ± 0.3</td>
</tr>
<tr>
<td>K2SO4</td>
<td>97.4 ± 0.5</td>
</tr>
</tbody>
</table>

\[ w = \text{mass of the specimen at equilibrium and} \]

\[ w_0 = \text{mass of the oven-dry specimen.} \]

TABLE 2—Parameters from the parabolic model fit of the average adsorption and desorption isotherms.

<table>
<thead>
<tr>
<th></th>
<th>Desorption</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Untreated</td>
<td>–9.60</td>
<td>8.69</td>
<td>1.96</td>
</tr>
<tr>
<td>ACQ( ^a )</td>
<td>–8.63</td>
<td>10.36</td>
<td>1.55</td>
</tr>
<tr>
<td>CCA( ^b )</td>
<td>–7.11</td>
<td>8.85</td>
<td>1.77</td>
</tr>
<tr>
<td>DOT( ^c )</td>
<td>–8.12</td>
<td>9.71</td>
<td>1.47</td>
</tr>
</tbody>
</table>

\( ^a \)Alkaline copper quaternary.

\( ^b \)Chromated copper arsenate.

\( ^c \)Disodium octaborate tetrahydrate.
This model is mathematically equivalent to the Dent, GAB, and Hailwood–Horrobin isotherms, but we do not ascribe any further meaning to the parameters $A$, $B$, and $C$.

Average fit of the parabolic model is overlaid in Fig. 1. Two approaches were taken to arrive at the average fit. The first approach was to average moisture content over all eight specimens at each RH and then fit the model to these average EMCs. The second approach was to fit the model to each experimental isotherm and then average the model parameters $A$, $B$, and $C$. The resulting parameters from the model fit are listed in Table 2. Parameters from both methods of averaging are the same to the second decimal place, which is further evidence of low variability in the data.

Several trends can be observed in the data. To compare effects of the preservative treatment, we have presented the data as the difference in moisture content between treated and untreated wood (Fig. 2). At all RHs, the borate-treated wood has the highest moisture content of all treatments regardless of whether the measurements were taken in adsorption or desorption. At the highest RH (97%), borate-treated wood had the highest moisture content, followed by ACQ-, CCA-, and finally untreated woods. At lower RHs, it is harder to distinguish between ACQ-, CCA-, and untreated woods, and the relative hygroscopicity depends on whether the measurements were taken in adsorption or desorption. For the adsorption isotherms, the ACQ treatment was always higher in EMC than CCA and untreated wood. For desorption isotherms, the ACQ curve intersects the CCA curve at roughly 80% RH. Below 60% RH, the differences between CCA, ACQ, and untreated is less than 1% MC.

In contrast to Cao and Kamdem [7], who found that copper ethanolamine-treated wood was less hygroscopic than untreated wood, we found that ACQ-treated wood was more hygroscopic than untreated wood. The difference between ACQ-treated wood and copper ethanolamine-treated wood is that ACQ-treated wood also contains didecyldimethylammonium chloride/carbonate (DDAC). Therefore, this increase in hygroscopicity is likely caused by the DDAC. Likewise, Dulat’s analysis [5] could be applied to the DOT-treated wood, which would yield a lower EMC for this treatment. However, the EMC for all preservatives was calculated from Eq 1, which does not subtract the weight of the preservative. This gives a fair comparison across all treatments.

One of the motivations of this research was to see if increased corrosiveness of ACQ-treated wood compared with CCA-treated wood was due to ACQ-treated wood being more hygroscopic. These data do not seem to suggest that the difference in corrosiveness is due to differences in hygroscopicities. There is little difference between the moisture content of ACQ- and CCA-treated woods except at high RHs. Even in the most extreme case, the ratio of the EMC of ACQ-treated wood to CCA-treated wood was 1.08. Conversely, borates, which have been shown to have a lower corrosion rate than CCA [2], are the most hygroscopic of these preservatives. Although it is known that wood moisture content influences corrosion, the difference in corrosiveness in CCA- and ACQ-treated woods is more likely caused by a difference in preservative chemistries rather than a difference in moisture contents.

### Summary and Conclusions

Water vapor sorption measurements were collected on treated and untreated southern pines to see if large differences could be detected between the moisture contents that could explain the difference in corrosiveness between the preservatives. This study found that woods treated with borates were the most hygroscopic, followed by ACQ and CCA. Untreated wood was the least hygroscopic. Differences between ACQ-, CCA-, and untreated wood were most noticeable at high RH. Previous studies on corrosion of metals in contact with wood have shown that ACQ is the most corrosive, followed by CCA, then borates. This suggests that differences in corrosiveness between preservatives are not attributable to differences in hygroscopicity.

### References


