# Biocide Retention Variation and Gradients in Commercially Treated 4 by 4s

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## Abstract

Biocide retentions for copper-based wood preservatives used for residential ground-contact applications are established through field stake tests using small research stakes cut from selected sapwood and then treated in laboratory cylinders. The results from the relatively short-term field tests are then used to specify retentions for commercially treated timbers that have a range of densities and heartwood content. More than 120 4 by 4s that had been commercially treated with four copper-based systems readily available were purchased, with the posts carefully selected for good biocide penetration and a wide outer sapwood band, and analyzed for biocide retentions. Also, biocide gradients from five soluble copper and three particulate copper commercially treated 4 by 4s, all having the same labeled retention, were determined. All four systems gave a range of analyzed retentions, with some fraction of the timbers of each preservative system having a relatively low biocide level. In contrast to previous reports, the biocide gradient for wood treated with a soluble copper formulation was less steep than in wood treated with a particulate copper system.

The widely used waterborne arsenical wood preservatives were replaced in 2004 by copper-based systems for residential applications in North America (Freeman et al. 2006, Schultz et al. 2007). Wood treated with four preservatives that differ in copper formulation and organic cobiocide was readily available in the United States in 2009. The oldest of these is a soluble copper formulation that uses ethanolamine or ammonia to stabilize the soluble copper(II) ion (hereinafter called copper) and an organic water-soluble quaternary ammonium compound (quat) cobiocide to control copper tolerant fungi, called alkaline copper quat (ACQ). Another soluble copper system uses triazole(s) as the organic cobiocide and is called copper azole (CA). Other readily available commercial systems use solid copper compounds, specifically basic copper carbonate that has been milled down to submicron-sized particles with the particulate copper being dispersed in water. One particulate system is called micronized copper quat (MCQ), and the other is called micronized CA (labeled as MCA or μCA-C depending on the supplier; generally known as MCA), with one MCA formulation having both particulate and soluble copper present.

Acceptance agencies set specified retentions for treated wood, which may include a level for ground-contact Use Class 4A (UC4A) applications. These specified ground-contact retentions are based on research stakes treated in a laboratory cylinder and then placed in the field for a relatively short time (Schultz and Nicholas 2009). Such specified UC4A retentions are used for treating 4 by 4 or larger timbers cut from material with varying growth rates and, thus, variable densities, with low-density wood having more porosity and the potential for greater biocide retentions compared with denser timbers (Schultz et al. 2004). Because timbers are often cut from the center of a log they can have some heartwood, with southern pine (*Pinus* spp.) heartwood being essentially impermeable to waterborne preservatives. These and other factors result in commercially treated timbers having variable biocide retentions, even those treated together in the same charge (Schultz et al. 2004).

One characteristic of ground-contact timbers is that deep checks can form with moisture changes in service because of the anisotropic nature of wood. If a steep biocide gradient is present in the treated timber, deterioration organisms can invade through such checks and degrade any inadequately protected interior sapwood (Cooper and Ung 2009). It has been reported that MCQ gives a better/less steep biocide

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gradient than ACQ, suggesting that posts treated with particulate copper systems may involve less concern of the above occurring (Universal Forest Products, Inc. 2006, Cooper and Ung 2009, McIntyre et al. 2009).

The objectives of this preliminary study were (1) to determine the biocide retention variation for 4 by 4 nominal posts (actual dimensions were 3.5 by 3.5 in. or 89 by 89 mm) commercially treated with four waterborne copper systems commonly available in the United States in 2009, using timbers carefully selected for a wide sapwood band, good biocide penetration, and no surface heartwood; and (2) to measure the biocide gradient of samples cut from ACQ or MCQ commercially treated 4 by 4s, with both systems treated to the same labeled retention.

## Experimental Methods

### Biocide retention in 4 by 4 posts

Commercially treated southern pine 4 by 4 posts were obtained from lumber yards treated to the current UC4A ground-contact specified retentions with (1) MCQ at 5.44 kg/m$^3$, (2) ACQ type D (ACQ-D) at 6.4 kg/m$^3$, (3) MCA at 2.24 or 2.40 kg/m$^3$, depending on the supplier, and (4) CA type C (CA-C) at 2.40 kg/m$^3$. The posts were purchased in groups at three or more different times separated by at least 1 month for each treatment so that samples treated in different charges were obtained. Samples from two of the treatments were also purchased from two locations separated by at least 200 miles. A total of 31 or 32 posts treated with each system were obtained over a period of about 5 months. The posts were selected for later installation in a field test and, thus, were chosen based on having no face heartwood, a pith in about the center of the post, a heartwood area (if present) of no more than 30 mm in diameter, and a sapwood zone on the outer edge at least 30 mm deep, with good biocide penetration of 20 mm or deeper based on visually examining the transverse ends. Only a small fraction of the timbers examined were selected as meeting these criteria. No data were kept, but most of the rejections were the result of heartwood on one of the faces, a wide heartwood band, or poor biocide penetration.

A variety of posts cut from slow-, medium-, and fast-growth material were obtained so that a range of biocide retentions would likely be obtained, because fast-grown wood often has greater porosity and, thus, more void volume for treating solutions to give higher retentions than denser wood (Schultz et al. 2004). Once purchased, the posts were cut and the biocide penetration visually examined based on the color of the freshly cut transverse surface; posts with poor penetration were rejected and replaced. Several 5-mm-thick cross sections were then cut at least 600 mm from one end of the 4 by 4 posts in an area where no knots were present, and then the sapwood was obtained from the 0- to 25-mm-deep specified biocide retention zone from all four faces (American Wood Protection Association [AWPA] 2009). The samples were analyzed by an ISO 17025 laboratory certified to run preservative retention analyses. The copper or copper oxide retentions were analyzed based on AWPA Standard A9, the quat retentions by A18-05, and the azole retentions by AWPA Standard A28-08. At the same location, a 50-mm-thick cross section was cut and retained for reference.

### Gradient study

For the second study, to determine biocide gradients in ACQ and MCQ timbers, five southern pine ACQ posts treated to a specified retention of 6.4 kg/m$^3$ were obtained. Earlier, the MCQ retention had been lowered from 6.4 to 5.4 kg/m$^3$, but three dusty southern pine MCQ posts labeled as treated to 6.4 kg/m$^3$ were located in a corner of a hardware building.

A section at least 100 mm long was cut from the post ends to mitigate any end treatment effect, with 19-mm-thick, defect-free slabs then sliced from the surface of the 4 by 4s to give lengths of 500 mm or more. The 19-mm-thick slabs were then cut into strips to give 19 by 19-mm cross-sectional samples. The 19 by 19-mm size sample was used because the biocide penetration zone for 4 by 4 posts is 0 to 25 mm deep (AWPA 2009), so samples from the outer 19-mm zone would be well within the specified 25-mm biocide penetration zone. Twenty samples from each treatment were then selected that had no heartwood and good visual biocide penetration based on color. At least three samples were cut from each timber to minimize the effect of the different densities of the earlywood and latewood bands affecting the biocide retentions (Schultz et al. 2004). Each sample was then cut into two parts, an outer 0- to 8-mm section and an inner 11- to 19-mm section. These samples were analyzed by an ISO 17025–certified laboratory for copper oxide and quat retentions as described earlier.

## Results and Discussion

### Biocide retention in 4 by 4 posts

Table 1 gives the retention average and variation for each preservative system for the carefully selected posts. Timbers from all four systems had average retentions that met or

*Table 1.—Biocide retention variations for southern pine 4 by 4 posts commercially treated to ground-contact UC4A-specified retentions with four copper-based systems commonly available in the United States in 2009.*[a]

| Treatment | No. of samples | Specified UC4A retention (kg/m$^3$) | Avg (SD) retention (kg/m$^3$) | Percent treated to <75% of specified retention | Percent treated to >150% of specified retention |
|---|---|---|---|---|---|
| MCQ | 31 | 5.45 | 6.7 (1.9) | 3 | 19 |
| ACQ | 31 | 6.4 | 7.1 (1.9) | 13 | 13 |
| MCA | 31 | 2.40/2.24[b] | 2.4 (0.8) | 19 | 6 |
| CA-C | 32 | 2.4 | 2.9 (0.8) | 3 | 22 |

[a] The posts were carefully chosen to have no surface heartwood, a wide sapwood band with good biocide penetration, and inner heartwood (if present) no more than 30 mm in diameter. If the timbers had instead been randomly chosen, the average retentions would likely have been lower.

[b] Both MCA and μCA-C posts, which are treated with micronized copper azole systems supplied by different suppliers with slightly different specified UC4A biocide retentions, were obtained. The higher specified retention was used to determine the percent treated to greater than 150 percent, and the lower retention was used to determine the percent treated to less than 75 percent.

exceeded the specified level (Table 1). However, a few posts in each set had relatively high or low biocide levels, resulting in timbers with retentions sometimes greatly above or below the mean. The percentage of posts treated to more than 150 percent of the specified retention ranged from a low of 6 percent to a high of 22 percent. Conversely, the percentage of timbers treated to less than 75 percent of the specified retention ranged from a low of 3 percent to a high of 19 percent of the four groups.

This study analyzed samples that were obtained at three different times for each preservative system to ensure that samples from different treating charges were incorporated. This study was restricted in the number of samples, but it did show that some timbers had biocide retention of 75 percent or less of the specified UC4A retention. Furthermore, the timbers for this study had been carefully selected for a wide sapwood band and no heartwood on the surface and the pith in the timber center. In addition, timbers were selected that had a relatively small-diameter inner heartwood (if present) and a biocide penetration of at least 19 mm. The AWPA-specified biocide retention zone between 0 and 25.4 mm in the permeable sapwood was analyzed.

In the present study, the carefully selected timbers with wide sapwood bands and good biocide penetration would give optimally high biocide retentions, as opposed to an earlier study in which all timbers treated together in one charge with chromated copper arsenate were analyzed (Schultz et al. 2004). Consequently, it is not possible to directly compare the results from these two studies. Many of the timbers examined for the present study were rejected because of heartwood on one or more faces, a wide heartwood zone so that the sapwood zone was less than 1 inch deep in areas, or poor penetration of the biocide. If all timbers from a particular charge had been analyzed—as opposed to selecting only a few chosen timbers—the average biocide retentions would likely have been lower than those found in this study. Because of proposed retentions, which have been lowered in recent years to the minimum necessary for protection of the research stakes during the relatively short field exposure period (Freeman et al. 2006, Schultz and Nicholas 2009), there is less of a safety factor; thus, achieving the minimum specified retention has become more important.

### Gradient study

The average copper gradient for the 20 MCQ samples cut from the three 4 by 4 timbers was 1.15 (retention in the outer 0- to 8-mm zone divided by the 11- to 19-mm zone), with samples from each of the three timbers having an average copper gradient of 1.40, 1.15, and 0.98. The overall total biocide gradient was 1.28, with averages from each of the three timbers being 1.41, 1.34, and 1.13. The average copper gradient for the 20 ACQ samples cut from the five 4 by 4 timbers was 1.04, with the sample averages from each of the five timbers being 1.11, 0.97, 1.00, 1.02, and 1.08. The average total biocide gradient was 1.13 for all ACQ samples, with averages from each timber of 1.32, 1.02, 1.18, 1.14, and 1.08.

Based on the results of this study, in which three or more samples were cut from each of five ACQ and three MCQ 4 by 4s to minimize the variation due to density differences in an annual ring, with all timbers having a labeled retention of 6.4 $kg/m^3$, the soluble copper formulation had a better/more level copper and total biocide gradient in the outer 19-mm zone than the particulate copper system. By contrast, earlier reports (Universal Forest Products, Inc. 2006, Cooper and Ung 2009, McIntyre et al. 2009) found that MCQ gave more level gradients than ACQ. One explanation for the higher gradients with MCQ- versus ACQ-treated timbers reported here using commercially treated lumber might be that the treating solution had aged and picked up water-soluble compounds, perturbing the dispersion formulation and leading to the particulate copper flocculating to form larger-sized aggregates, as sometimes happens with particles dispersed in water (see, e.g., Hu et al. 2000, Bolto and Gregory 2007, Tavacoli et al. 2007). Furthermore, the dispersant used in particulate copper systems may have solubilized some woody hydrophobic compounds, such as resin acids and fatty acids, which might also lead to some particles aggregating. Aggregated particles in an aged formulation might give a steeper biocide gradient than a fresh particulate copper formulation. The small number of posts from which the gradient samples were cut may also have influenced the results. Further research will be needed to study this possibility.

## Conclusions

Analysis of commercially treated 4 by 4 posts showed a range of biocide retentions for wood treated with four waterborne copper-based preservative systems commonly available in the United States in 2009, with significant numbers of the timbers for some systems being well below the specified retention. In a separate study, the copper and total biocide gradient for 4 by 4 timbers commercially treated with ACQ was less steep than that for timbers treated with MCQ.

This preliminary study suggests that a comprehensive biocide retention variation study at multiple treating sites may be worthwhile. Such a study would entail analyzing samples from many charges at each participating treating facility, taking samples from numerous randomly selected timbers from each charge at specified points, with surface heartwood, density, width of sapwood band, and other timber properties as cofactors.

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