Evaluating ACQ as an Alternative Wood Preservative System

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This evaluation addresses the waste reduction/pollution prevention and economic issues involved in replacing chromated copper arsenate (CCA) with ammoniacal copper/quateryrnary ammonium (ACQ\textsuperscript{a}) as a way to preserve wood. The evaluation was conducted at McArthur Lumber & Post Co., Inc., in McArthur, OH. The most obvious pollution prevention benefit gained by using ACQ is eliminating the use of arsenic and chromium, both of which generate hazardous wastes and a risk of contaminating the environment via chemical spills. Because most treatment plants are self-contained in that they reuse all wastewater produced within the plant and on the drip pads, no liquid waste problems were addressed for either the CCA or the ACQ treating process.

The ACQ system generates more air pollution than does the CCA system, mainly as ammonia (NH\textsubscript{3}). For a plant with an annual production of 1 million ft\textsuperscript{3} (or about 20 million board feet), 90,000 lb of NH\textsubscript{3} would be released per year from the ACQ treatment operations and the ACQ-treated wood. In contrast, a CCA plant in Virginia annually producing four times as much treated wood released \(< 0.021\) lb of arsenic (as As\textsubscript{2}O\textsubscript{3}) and only trace amounts of chromium (as CrO\textsubscript{3}) and copper (as CuO). During air monitoring of CCA treatment, airborne concentrations of inorganic arsenic were above the Ocupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) of 0.01 mg/m\textsuperscript{3}. Full-shift personnel exposures to ammonia during ACQ treatment were below applicable exposure limits, but exposures to ammonia during unloading of the ACQ treating cylinder were above the short-term personnel exposure limit of 35 ppm.

The treated wood, after being transferred from the drip pads to the outside storage yard, could become a major source of contamination. For a plant with an annual production of 1 million ft\textsuperscript{3} (or about 20 million board feet) of CCA-treated wood at 0.4 lb/ft\textsuperscript{3} retention, 157 lb of As\textsubscript{2}O\textsubscript{3}, 1,506 lb of CrO\textsubscript{3}, and 39 lb of CuO could be washed away by stormwater every year. For the same amount of ACQ-treated wood, at the same retention, 1,299 lb of CuO, 3,148 lb of total organic carbon (TOC) (exclusive of extractable wood organics and qua [as didecylmethylammonium ion, or DDA]), and 3,172 lb of NH\textsubscript{3} could be released into the stormwater runoff every year. It must be noted that these releases were estimated based on exposure of all treated wood to about 18 in. of rainfall 4 days after treatment.

Converting from CCA to ACQ would require a capital investment of about $181,000. The operating costs for ACQ wood treatment would be higher — a net expense of up to $1,100,000. More than 71% of that net expense would be used to purchase ACQ chemicals. Therefore, switching from CCA to ACQ
would not produce any immediate quantifiable benefits. Because the economic analysis did not take into account factors such as long-term liability, safety, and the company’s public relations, the real benefit of using ACQ could be more than what it would appear.

This Project Summary was developed by the EPA’s Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The objective of the U.S. Environmental Protection Agency’s (U.S. EPA’s) Resource Conservation and Recovery Act (RCRA) Problem Wastes Technology Evaluation Program is to evaluate, in a typical workplace environment, examples of innovative technologies that demonstrate a potential (1) to reduce or, preferably, eliminate the use of RCRA-banned metals, including arsenic, in various industrial and agricultural applications, or (2) to minimize the RCRA problem wastes through recycling and recovery. The goal of this study was to evaluate the use of ACQ as an alternative to CCA for preserving wood. Specifically, this study evaluated (1) ACQ’s waste reduction/pollution prevention potential and (2) the economics. The long-term effectiveness of ACQ or CCA as a preservative was not examined, because such evaluations require a lengthy test time (e.g., 1 to 5 years) and many resources. However, ACQ’s ability to protect wood and the chemical and physical properties of ACQ-treated wood have been studied recently by many researchers.

The wood-preserving industry uses primarily waterborne arsenical preservatives for wood treatment. Because of the solubility of arsenic compounds in water, wood treatments have been using mixed-salt preservatives for wood treatment since the early 1910s. The mixed-salt preservatives usually contain various arsenic compounds and metal salts from the metals chromium (Cr), copper (Cu), or zinc (Zn). Currently, the most predominant arsenical preservative used in the United States is CCA-Type C (per the American Wood-Preservers’ Association [AWPA] Standard P5-92).

Because of its toxicity and carcinogenicity, arsenic poses a serious threat to the environment and human health. Increasingly stringent federal and local regulations concerning arsenic have been proposed and enacted. Because about 70% of the total arsenic demand is used to produce industrial chemicals such as arsenical wood preservatives, the arsenic consumption would be greatly reduced if the use of CCA and other arsenical wood preservatives could be eliminated or reduced.

These concerns have prompted a search for more environmentally friendly wood preservative systems for wood treatment. The alternatives must be safe to handle during treatment, the treated products must be safe to use, and the alternatives must effectively protect wood against decay, marine borers, and insects. Further, the alternatives must not leach from the treated wood to the environment. Economics also should be considered, although there may exist harder-to-quantify justifications such as reduced liability, greater safety, better morale, and improved company public relations.

This study evaluated ACQ, a relatively new, commercially available wood preservative system that was developed and patented in Canada. It is a two-chemical-component preservative system comprised of ammoniacal copper and quat. The combined biocidal effect of copper and quat protects wood from biodeterioration and exhibits relatively low mammalian toxicity and environmental impact. ACQ was approved and commercially used first in Scandinavian countries in 1988 and, more recently, in Japan. In the United States, two ACQ formulations have been accepted by the AWPA Preservatives Committee as preservative standards.

Waste Reduction and Pollution Potential Evaluation

Pollution prevention is achieved primarily by reduction of waste at the source. Pollution prevention considers all waste types, such as hazardous waste, solid waste, wastewater, and air emissions. Reductions must be true reductions in volume and/or toxicity of waste and not simply a transfer of waste from one medium to another.

The waste reduction potential was measured in terms of volume reduction and toxicity reduction. The reductions were quantified by comparing waste volumes and types from the CCA treatment process with those produced by the ACQ treatment process. Volume reduction addressed the gross wastewater, such as chemical spills, air emissions, and stormwater runoff. Toxicity reduction considered concentrations and types of contaminants, such as As, Cr(VI), and Cu in the CCA gross wastewater versus NH₃, total organic carbon (TOC), and total Kjeldahl nitrogen (TKN) in the ACQ gross wastewater. The pollution prevention potential also considered hazards that any toxic emissions might pose to workers. Air quality was measured in terms of airborne metal concentrations and NH₃ concentrations. The results of these measurements would determine the proper safety attire to be worn by the plant operators.

During wood treatment, it is necessary for a treatment plant to maintain good housekeeping practices and to avoid any major chemical spills in and around the plant. Dirt, dust, and debris on the drip pads must be collected and disposed of according to applicable regulations. However, the characteristics of solid wastes were not evaluated because little was accumulated on the drip pad after either treatment.

Air Emissions and Worker Exposures

During CCA and ACQ wood treatment, As, Cr(VI), Cu, and NH₃ could be emitted to the air as toxic contaminants. Therefore, air samples were collected and analyzed to ascertain the total (8-hr) and short-term (15-min) occupational exposures to these contaminants, National Institute for Occupational Safety and Health (NIOSH) sampling devices were positioned in the employee’s breathing zone or in stationary locations. Exposures were calculated as the time-weighted average (TWA) of the full-shift and 15-min samples. The Dräger tube, a semi-quantitative detecting device, was also used to obtain a rough estimate of ammonia concentrations which, in turn, were used to obtain estimates of NH₃ emission quantities from the stack (vent).

During CCA wood treatment, airborne concentrations of inorganic arsenic were above the OSHA PEL of 0.01 mg/m³ among all workers and in all monitoring locations. The highest concentration of 0.12 mg/m³ was measured at the door to the CCA mixing cylinder. The full-shift and short-term exposures to Cr(VI) and Cu, however, were less than OSHA PELs. NIOSH Recommended Exposure Limits (RELs), and American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs). No stack test or isokinetic test was performed; however, a CCA treatment plant in Virginia that in 1992 treated four times as much wood as McArthur Lumber & Post emitted only 0.021 lb As₂O₃ that year.

During ACQ wood treatment, the 8-hr, TWA concentrations of NH₃ ranged from 0.45 ppm to 8.4 ppm, less than 35% of the NIOSH REL and ACGIH TLV-TWA of 25 ppm. The short-term exposure of 38
ppm, measured in the breathing zone of the drip pad ground man during unloading and stacking of ACQ-treated lumber, exceeded the short-term exposure limits of 35 ppm recommended by OSHA, NIOSH, and ACGIH. Using the ammonia concentrations measured at the vent and at the treated wood, an annual ammonia emission of up to 90,000 lb would result if the treatment plant were to treat 1 million ft³ (or about 20 million board feet) of commodities per year.

**Stormwater Runoff**

After the treated wood units had remained on the drip pad for 4 days, two 36 in. x 42 in. x 8 ft wood units (each consisting of 42 pieces of rough-cut timber, 6 in. x 6 in. x 8 ft) from each treatment were subjected to artificial rainfall on the drip pad. One untreated unit served as a control. The wood units tested were stacked crosswise on top of three or four similar units spaced approximately 4 ft apart (see Figure 1), with a sheet of heavy-duty polyethylene liner placed underneath each of the top units. The separating liners then were arranged as illustrated in Figure 1 to allow collection of runoff directly under each of the top units. A garden sprinkler placed about 6 ft above the floor and about 9 ft away from the units tested was used to produce artificial rainfall. The amount of rainfall, as measured by five rain gauges, ranged from 0.6 to 0.9 in./hr during a 20- to 21-hr period. The runoff collected within the liner boundary flowed to a 32-gal plastic container. At different time intervals, the volume of the runoff was measured and runoff samples were taken for testing for heavy metals (including As, Cr, and Cu), total suspended solids, total dissolved solids, pH, TKN, and TOC. After sampling, the water in the plastic containers was disposed of to the cylinder door pits.

Significant amounts of As and Cr were leached from the CCA-treated wood units. Arsenic concentrations up to 8.84 mg/L were found in the runoff samples collected during the first 2 hr; the As concentrations slowly decreased to between 2.36 and 3.67 mg/L after 17 hr. Chromium concentrations ranging from 58.8 to 78.5 mg/L were detected during the first 2 hr and remained at 16.1 to 20.5 mg/L after 17 hr. The amount of Cu leached was less; only 3.05 to 3.84 mg/L was detected during the first 2 hr.

The mass of each CCA active ingredient leached in 24 hr was calculated by adding together the products of the concentration of each sampling interval and the corresponding runoff volume. Some concentrations were estimated based on best-fit curves. The percentage loss of each active ingredient, therefore, could be estimated by dividing the mass lost by the amount of that active ingredient absorbed by a wood unit. The active ingredient absorbed by wood could be calculated by multiplying the specific retention of that ingredient by the wood volume having CCA penetration. As a result, the percentage loss would range from 0.16 to 0.27% for As, from 1.08 to 1.67% for Cr, and from 0.08 to 0.13% for Cu.

Copper concentrations up to 288 mg/L were found in the ACQ runoff samples collected during the first 5 hr; the concentrations tapered down to 28.7 to 72.2 mg/L after 20 hr. TKN up to 620 mg/L was measured initially; its concentrations decreased to 154 to 265 mg/L after 15 hr. TOC as high as 890 mg/L was analyzed during the first 2 hr; its concentrations were reduced to 170 to 382 mg/L after 15 hr. The TKN analyzed was attributed primarily to dicyclohexylammonium (DAA) ion and ammonium (NH4⁺) ion and, to a lesser extent, to nitrogen-containing wood organics. The TOC analyzed comprised mainly the organic carbon of water-soluble wood organics and DAA ion.

The percentage loss of each ACQ active ingredient in 24 hr was estimated using the method discussed earlier. The percentage loss was 0.99 to 1.02% for Cu, 3.84 to 5.62% for TOC (inclusive of extractable wood organics and quat [as DAA]), and 3.23 to 3.82% for NH4. It must be noted, however, that up to 41% of NH3 had been assumed to have been lost during air drying. This assumption was made according to a laboratory test done by an ACQ vendor.

The yearly losses of the CCA and ACQ active ingredients through stormwater runoff were estimated and are presented in Table 1. For small-sized plants with an annual production of 1 million ft³ (or about 20 million board feet), the plants could release 157 lb of As₂O₃, 1,506 lb of Cr₂O₃, and 39 lb of CuO every year. For medium-sized, large-sized, and very large-sized plants, the annual release would increase proportionally. Converting from CCA to ACQ would significantly reduce the release of toxic metals, but the release of other less toxic contaminants would greatly increase. For example, a small-sized plant could release 1,290 lb of CuO, 3,148 lb of TOC (inclusive of extractable wood organics and quat [as DAA]), and 3,172 lb of NH₄⁺, and the release from medium-sized to very large-sized plants also would increase proportionally.

**Economic Evaluation**

Cost comparisons were made for CCA versus ACQ. Converting from CCA to ACQ would require a capital investment of $191,000. The operating costs for ACQ were higher; a net expense of up to $1,100,000 was required, 71% of which would be used to purchase ACQ chemicals. Based on an ACQ vendor, the selling price for every 1,000 board feet of ACQ-treated wood would be $55 more expensive than that for CCA-treated wood (including $37 for chemicals, $4 for production, $9 for lumber stacking and capping, and $2 for longer shed turnaround).

**Conclusions and Recommendations**

The waste reduction and pollution prevention potential for ACQ is summarized in Table 2. The data presented are based on a treatment plant with an annual production of 1 million ft³ (or about 20 million board feet). Of course, the most obvious benefit gained by using the ACQ system is the complete elimination of As and Cr use, which eliminates the generation of hazardous wastes and the risk of contaminating the environment via chemical spills. Because most treatment plants are self-contained in that they reuse all wastewater produced within the plant and on the drip pads, no liquid waste problems need to be addressed for either CCA or ACQ.

The ACQ system produces a greater amount of air emissions, mainly as NH₃. For an annual production of 1 million ft³ (or about 20 million board feet), 90,000 lb of NH₃ would be released per year. In contrast, a CCA plant that produced four times as much commodities released only < 0.021 lb of As₂O₃ and trace amounts of Cr₂O₃ and CuO every year. During the air monitoring of the CCA treatment, however, airborne concentrations of inorganic arsenic were above the OSHA PEL of 0.01 mg/m³ among all workers and in all monitoring locations. Therefore, appropriate respiratory protection should be used until engineering controls are in place to reduce exposures to acceptable levels. During ACQ treatment, full-shift personnel exposures to ammonia were below applicable exposure limits. Ceiling exposures to ammonia during unloading and stacking of ACQ-treated lumber on the drip pads exceeded the short-term exposure limit of 35 ppm. Those working in the immediate areas must use appropriate respiratory protection. Engineering controls also should be considered to reduce exposures.
Figure 1. ACQ-treated and control wood units with plastic liners (A) and sprinkler setup (B).
### Table 1. Yearly CCA and ACQ Losses Due to Leaching

<table>
<thead>
<tr>
<th>Plants with Annual Production (million ft³)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td><strong>CCA Ingredients</strong></td>
<td></td>
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<tr>
<td>As (as As₂O₃)</td>
<td>0.20</td>
<td>0.40</td>
<td>0.60</td>
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<td>Cr (as CrO₃)</td>
<td>1.92</td>
<td>3.84</td>
<td>5.76</td>
<td>7.68</td>
<td>9.60</td>
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<tr>
<td>Cu (as CuO)</td>
<td>0.05</td>
<td>0.10</td>
<td>0.15</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td><strong>ACQ Ingredients</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu (as CuO)</td>
<td>2.76</td>
<td>5.52</td>
<td>8.28</td>
<td>11.04</td>
<td>13.80</td>
</tr>
<tr>
<td>quat (as DDA (a))</td>
<td>6.69</td>
<td>13.38</td>
<td>20.07</td>
<td>26.76</td>
<td>33.45</td>
</tr>
<tr>
<td>NH₄⁺ (as NH₄Cl)</td>
<td>6.74</td>
<td>13.48</td>
<td>20.22</td>
<td>26.96</td>
<td>33.70</td>
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(a) DDA = didecyldimethylammonium ion.

### Table 2. Summary of Yearly Pollution Prevention Potential for ACQ Wood Preservative Systems (a)

<table>
<thead>
<tr>
<th>Environmental Media/Concern</th>
<th>CCA</th>
<th>ACQ</th>
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<tbody>
<tr>
<td>Liquid waste</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Solid waste</td>
<td>75 to 100 lb hazardous waste/yr</td>
<td>75 to 100 lb hazardous waste/yr</td>
</tr>
<tr>
<td>Air emissions</td>
<td>&lt;0.021 lb As₂O₃/yr(b)</td>
<td>90,000 lb NH₄⁺/yr</td>
</tr>
<tr>
<td></td>
<td>Trace CrO₃</td>
<td>Trace CuO</td>
</tr>
<tr>
<td>Stormwater runoff</td>
<td>200 lb As₂O₃</td>
<td>2,760 lb CuO</td>
</tr>
<tr>
<td></td>
<td>1,920 lb CrO₃</td>
<td>6,690 lb quat (as DDA)</td>
</tr>
<tr>
<td></td>
<td>50 lb CuO</td>
<td>6,740 lb NH₄⁺ (as NH₄Cl)</td>
</tr>
</tbody>
</table>

(a) Assuming 1 million ft³ annual production.
(b) Arsenic emission of a CCA treatment plant that treated four times as much wood as McArthur Lumber & Post in 1992.

The treated wood, after being transferred to the uncovered storage yard, could become a major source of contamination to the environment. For a CCA treating plant with 1 million ft³ (or about 20 million board feet) of annual production, 157 lb of As₂O₃, 1,506 lb of CrO₃, and 39 lb of CuO could be washed away annually by stormwater. For an ACQ treating plant with the same amount of annual production, 1,299 lb of CuO, 3,148 lb of TOC (inclusive of extractable wood organics and quat [as DDA]), and 3,172 lb of NH₄⁺ could be released annually. Converting from CCA to ACQ totally eliminates the release of As and Cr to the environment.

Although converting to ACQ requires a capital investment and higher operating costs, the benefits of reduced long-term liability, greater safety, increased morale, and improved public relations for the company as a result of using ACQ can be significant.

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The complete report, entitled "Evaluating ACQ as an Alternative Wood Preservative System," (Order No. PB94-159928; Cost: $27.00, subject to change) will be available only from:

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