Remediation and Recycling of WBP-treated Lumber for use as Flakeboard

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ABSTRACT

Laboratory-scale experiments were conducted in which preservative metals (As, Cr, & Cu) were thermochemically extracted from CCA-treated spruce (Picea engelmannii) using oxalic acid and sodium hydroxide. The effects of extraction time, temperature, and pH were examined and laboratory scale optimization was achieved. Two series of experiments were carried out. In the first series, the extractions were done at temperatures ranging from 20 to 80°C and with the pH of 1% oxalic acid solutions adjusted between 1.4 and 3.6 with sodium hydroxide. The second series of experiments were conducted to address practical considerations, such as the effect of mixing, liquid to solid ratio, and the presence of dissolved minerals in tap water (Sabo et al 2008). Based on these preliminary results, additional experiments are now underway to choose the conditions expected to be the most suitable for scaled-up extractions. Two candidate thermochemical extraction conditions were further studied to assess the suitability of the remediated woody materials to make engineered flakeboard. While the engineering and physical properties of the remediated flakeboard composite were similar, they were not equal to that of flakeboard made from matched untreated spruce. Still, these preliminary results were encouraging and the physical and mechanical property results similar enough that it is likely that with further laboratory-scale optimization, a high-quality flakeboard composite can be made from remediated waterborne preservative (WBP)-treated spruce.

Keywords: Preservative, Treatment, remediation, recycling, composite, flakeboard

INTRODUCTION

This report is the second in a series. In this report we describe our preliminary laboratory experiments to manufacture an engineered wood composite product from remediated preservative-treated wood. Our earlier efforts to develop a thermochemical remediation system for treated wood have recently been reported (Sabo et al 2008). In this series of studies, our combined objectives were three-fold. First, we developed a new potentially commercially feasible thermochemical process to remediate WBP-treated wood. This recycling/remediation process is essentially a fully closed system that encompasses the flaking of preservative-treated wood waste and the extraction and recovery of the metals introduced into the wood from chemical preservatives. We then developed methods to produce engineered flakeboard composites using these remediated preservative-treated wood flakes. Both processes developed mimic processes that are practical on an industrial scale. Finally, future work with our Egyptian collaborator(s) will incorporate residual lignocellulosic straw from annual industrial crops such as rice, wheat and flax to develop advanced wood and lignocellulosic biocomposites using mixtures of remediated WBP-treated wood and crop residues from agricultural operations.
BACKGROUND

Preservative-treated Wood

Millions of cubic meters of waterborne preservative (WBP)-treated lumber are removed from service annually in the United States, and most of this spent wood is disposed into landfills or incinerated (Solo-Gabriele et al 2000, Felton & DeGroot 1996). This landfilled wood is potentially lost source of lignocellulosic fiber and to a lesser degree an environmental issue since toxic metals are known to leach from wood treated with waterborne preservatives, such as chromated copper arsenate (CCA). Making use of such discarded WBP-treated lumber could promote the sustainability of our worldwide forest resources.

Remediation of WBP-treated Wood

Although numerous techniques have been shown to effectively remove metals from preservative-treated wood, most of the studies found throughout the literature either used economically infeasible processes or did not evaluate the efficacy of the remediated wood as a raw material for composite materials. Some of the methods reported for removing metals from preservative-treated wood include extraction with hydrogen peroxide (Cooper and Kazi 1999, Kazi and Cooper 2006), various acids (Clausen and co-workers 1998, 2000, 2001a-b, 2004a-c, 2006, Shiu et al 2000, Kazi and Cooper 1998), chelating agents (Kamdem 1999, Kartal & Kose 2003, Kazi and Cooper 1998), bacterial fermentation and/or extraction (Clausen and co-workers 1998, 2000, 2001a-b, 2004a-c), and more recently by electrodialysis (Pedersen et al 2005, Velizarova et al 2002). Many of the reported techniques required days or weeks to effectively remove impregnated metals from treated wood, or they prohibitively expensive. However, some methods have been reported in which virtually all the toxic metals can be extracted from preservative-treated wood in a matter of hours using dilute solutions. For example, extraction of CCA-treated wood in sodium oxalate (oxalic acid and sodium hydroxide) for three hours, following a one hour extraction in oxalic acid, was shown to remove 100% of As and Cr and 96% of Cu (Kakitani et al 2006). Kakitani et al. (2007) reported nearly 100% extraction of arsenic from treated wood after only one hour using oxalic acid at 75°C. Thus, chemical extraction of metals from preservative-treated wood seems promising, but the feasibility of using such remediated wood to make quality composites has yet to be fully demonstrated.

Therefore, one of the primary aims of this series of studies is to identify conditions favorable for producing composites from preservative-treated wood. The optimal conditions, including chemical concentrations, temperature, and time, for extracting metals from treated lumber are examined with the aim of producing durable composite products from the remediated wood. Furthermore, suitable adhesive resin systems will have to be chosen for making composites from wood that has undergone chemical extractions. Finally, long-term goals call for evaluating methods for removing and/or recovering extracted metals from liquid streams and for evaluating the commercial feasibility of an integrated remediation scheme.

Composites

There are two types of standards that apply for wood-based panels: Product Standards and Performance Standards. Standards for frequently used panel products are given in Table 1. Product standards may be further classified as manufacturing method standards and laboratory test standards. The American National Standards Institute (ANSI) has promulgated a performance-based evaluation standard for flake strandboard and for particleboard, fiberboard, and hardboard. These tests standards are known as ANSI PS 2-04 (ANSI 2004) and A208.1-1999, A208.2-2002, and A135.4-2004 (CPA1999, 2002, 2004). However, the test methods for evaluation of properties of composite panel materials are standardized by ASTM (American Society for Testing and Materials). We used ASTM D1037-06a test method to evaluate the properties of our wood-based flakeboard materials (ASTM 2007).

Composites made from preservative-treated wood, with and without remediation, have shown mixed performance results. Huang and Cooper (2000) showed that cement-bonded composites made from CCA-treated wood had better mechanical and physical properties than those made with untreated wood. However, without the remediation step, flakeboards made from recycled CCA-treated wood had significantly inferior physical and mechanical properties (Vick 1996). Regardless of the performance of composite materials made from spent lumber, products containing significant quantities of metals are unlikely to be well received.

Good performance of composites made from remediated preservative-treated wood is necessary for the viability of a commercial remediation process. Only a limited number of studies are available in which the remediated materials were constructed into composites and tested for performance. In one recent important
study, Clausen et al (2006) found that the performance of flakeboard made from remediated CCA-treated materials and 5% phenol-formaldehyde resin was shown to be comparable to that made from untreated materials, however the same study found the properties of particleboard (containing 10% urea-formaldehyde resin) were considerably diminished when using recycled CCA-treated wood.

Table 1. Commercial product or performance standards for wood-based composites

<table>
<thead>
<tr>
<th>Product Category</th>
<th>Applicable standard</th>
<th>Name of Standard</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardboard</td>
<td>ANSI A135.4-2004</td>
<td>Basic Hardboard</td>
<td>CPA 2004</td>
</tr>
<tr>
<td></td>
<td>ANSI A135.5-2004</td>
<td>Prefinished hardboard paneling</td>
<td>CPA 2004</td>
</tr>
<tr>
<td></td>
<td>ANSI A135.6-2006</td>
<td>Hardboard siding</td>
<td>CPA 2006</td>
</tr>
<tr>
<td>Medium-density fiberboard</td>
<td>ANSI A208.2-2002</td>
<td>MDF standard</td>
<td>CPA 2002</td>
</tr>
<tr>
<td>Particleboard</td>
<td>ANSI A208.1-1999</td>
<td>Particleboard standard</td>
<td>CPA 1999</td>
</tr>
<tr>
<td>Oriented strandboard</td>
<td>PS 2-04</td>
<td>Voluntary product standard PS 2-04 performance standard for wood-based structural-use panels</td>
<td>NIST 2004</td>
</tr>
<tr>
<td>Plywood</td>
<td>PS 1-07</td>
<td>Voluntary product standard PS 1-07 construction and industrial plywood</td>
<td>NIST 2007</td>
</tr>
<tr>
<td>Structural composite lumber (including laminated veneer lumber (LVL), laminated strand lumber (LSL), parallel strand lumber (PSL))</td>
<td>ASTM D5456-07</td>
<td>Standard specification for evaluation of structural composite lumbers products</td>
<td>ASTM 2007</td>
</tr>
<tr>
<td>Glued laminated timber (Glulam)</td>
<td>ANSI/AITC 190.1</td>
<td>American National Standard for Wood Products - Structural Glued-laminated Timber</td>
<td>AITC 2007</td>
</tr>
</tbody>
</table>

Wood Samples
Nominal 2-by 4-inch (38 by 89-mm) Spruce-Pine-Fir lumber was treated with chromated copper arsenate (CCA) Type C using a -82 kPa vacuum followed by 0.8MPa pressure for a total cycle time of about three hours, resulting in about 8.3 kg/m³ of preservative retention (Anderson et al 1997). The lumber was naturally weathered for numerous years in an open-air loft at the Forest Products Laboratory (FPL) in Madison, WI. The spruce lumber was of MSR grade 2250f/1.9E and had 660, 7mm-deep incisions per
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square foot. The lumber was first cut into 6 inch sections and pressure-soaked with water for approximately one hour at approximately (120 psi) to facilitate flaking. The wood was milled into flakes approximately 0.7-mm thick by 75-mm long using a disc flaker. The wood flakes were dried overnight at 105°C in a tray drier. Additionally, wood particles were prepared for a limited number of supplemental extraction experiments by grinding flakes to #20 mesh in a Wiley Mill.

Remediation of WBP-treated Wood

A complete discussion of the thermochemical process developed to extract Cu, As, and Cr from WBP-treated spruce lumber has recently been presented by Sabo et al (2008). These methods are briefly reviewed below and limited results are then presented (in Results section).

Solutions of oxalic acid were prepared in deionized water unless otherwise explicitly stated as containing tap water. The ACS-grade oxalic acid weight concentrations were prepared on the basis of anhydrous oxalic acid. The pH of the oxalic acid solutions were adjusted by adding 10% (wt) sodium hydroxide (reagent grade) solution.

The concentration of arsenic, chromium, and copper in wood samples was measured by inductively coupled plasma (ICP) atomic emission spectrometry in accordance with American Wood Preservers' Association (AWPA) standard A-21-00 (AWPA 2001).

In most cases, laboratory-scale extractions were performed in a 3L glass reaction vessel using 50g (oven dry basis) of wood flakes and a 20:1 liquid to solid ratio. Extraction solutions (1.4, 1.8, 2.4, 3.0, 3.6 or deionized water) were preheated to the appropriate temperature (20, 50 or 80°C) before the wood was added. The vessel was removed from the heat source after the designated extraction duration (1, 2, or 6 hours), and the wood flakes were separated from the liquid by straining. Flakes were thoroughly rinsed with deionized water, and the wood was dried overnight.

Composite Processing and Evaluation

Four groups of spruce flakes were evaluated in our flakeboard experiments. The first two were obtained from untreated controls and from CCA-treated but not extracted flakes. The other two groups used different thermochemical remediation processes selected based on previously reported work (Sabo et al 2008). One group was extracted using an oxalic acid solution a pH of 2.4 for 6 hrs at 80°C while the other was extracted for 1-hour using a solution at pH 1.4 followed by another 1-hour extraction at pH 3.0. For this latter group, both 1-hour segments of the extraction were performed at 80°C. After extractions, the flakes of the treated and untreated control groups were equilibrated to a moisture content of 5 percent. The two sets of wet extracted flakes were dried to a moisture content of 2-3 percent for 12-hours in a tray drier held at 105°C. After drying, the two sets of extracted flakes were re-wetted to 5 percent MC to match that of the two control groups.

A 100% solids solution of diphenylmethane diisocyanate (MDI) resin was separately applied at 3.5% to the four groups of spruce flakes in a rotating-drum blender. To make the flakeboard panels, a randomly oriented 457- by 457-mm by 200-220-mm high mat was formed. Hot-pressing followed the general instructions of the resin manufacturer using a 180°C platen temperature with a 30-s uniform-rate initial press closing time to the target thickness, held for 270 s at target thickness of 12.6-mm, and followed by a 30-s degassing/press opening time (300 s total). Final panel specific gravities were 0.74 at a 12.7-mm final panel thickness after hot-pressing and 24-hr storage in a thermally insulated hot-box.

For each group, three replicate panels were made. Each of the 12 panels was then trimmed to remove a 25-mm wide section from all four edges and individual test specimens were then cut from each panel. From each 406- by 406- by 12.7-mm thick trimmed panel, two 76- by 356-mm flexural bending specimens, two 152 by 152-mm thickness swell/water absorption specimens and four 51- by 51-mm internal bond specimens were cut. All mechanical and physical property specimens were conditioned at 23°C, 65% relative humidity (RH) prior to testing. Mechanical and physical properties were tested in accordance with ASTM D 1037-06a (ASTM 2007) for thickness swell and water absorption after a 24-hour soak, for internal bond strength, and for flexural modulus of elasticity (MOE) and bending strength (modulus of rupture (MOR)).
RESULTS

Remediation of WBP-treated Wood

The amount of metals extracted from preservative-treated wood was significantly impacted by pH and extraction time (Figures 1). Also, as expected higher temperatures facilitated the removal of As, Cr, and Cu, although Cu removal appears to be less impacted by time or temperature (Figure 2). Typically, the removal levels of As & Cr were similarly affected by extraction conditions, while the amount of copper extracted was affected differently. For example, as pH increased from 1.4 to 3.0, the amount of As & Cr remaining in the wood increased, whereas the amount of copper decreased (Figure 1). In other words, the extraction of As & Cr was more effective at pH 1.4 than at pH 3.0, whereas the extraction of Cu was more effective at pH 3.

Also, it is noteworthy that extractions at either room temperature or with deionized water were not effective at removing metals from flakes of treated wood. Sabo et al (2008) reported that most of these types of experiments resulted in less than 20% of the metals being removed after six hours, and none resulted in more than 52% removal.

After the extractions were complete, the wood flakes had a significant amount of remaining metals that could be readily rinsed with water. Sabo et al (2008) compared the amount of metals remaining on wood flakes before and after thoroughly rinsing with water following extraction with 1% oxalic acid at 80°C for one hour. At a pH 1.8, 22% of the initial As remained on the wood immediately following the extraction, but only 2% remained after rinsing. They concluded that, a supplemental water-extraction step was necessary to further remove the residual water-soluble metal complexes following initial acid extraction.

The liquid to solids mass ratio and the water source (tap versus deionized) was also studied by Sabo et al (2008). A large amount of precipitated minerals were visible after adding oxalic acid to municipal tap water, so the source of water was expected to impact the amount of metals extracted from the treated wood. However, the amount of As, Cr, & Cu extracted was similar using 1% (wt) oxalic acid solutions in either deionized or tap water. In addition, extractions performed using a smaller liquid to solid mass ratio of 10:1 without mixing resulted in less As and Cr being removed from the wood than when using a 20:1 ratio.

Composite Processing and Evaluation

The results of the thickness swell and 24-hr water absorption tests are shown in Figure 3. For the internal bond tests, two observations that exhibited internal voids that affected the internal bond results for those two specimens were discarded. The results of the internal bond strength tests and the flexural tests are shown in Figure 4 and 5, respectively.
Figure 1. Extraction of wood flakes with 1% oxalic acid and 80°C after rinsing.
Figure 2. Extraction at pH 2.4 for 6 hours, without rinsing

Figure 3. Thickness swell and 24-hr water absorption of flakeboard made using remediated and unextracted control materials.
Figure 4. Internal bond strength of flakeboard made using remediated and unextracted control materials.

Figure 5. Modulus of Elasticity (MOE) and modulus of rupture (MOR) derived from flexural tests of flakeboard made using remediated and unextracted control materials.

DISCUSSION

Nearly all the metals impregnated into wood samples by treatment with chromated copper arsenate (CCA) were readily extracted using one-percent oxalic acid solutions that were pH adjusted with sodium hydroxide. Increased temperatures facilitated the removal of arsenic, chromium and copper, although the effect of temperature on copper removal appeared less pronounced than on arsenic and chromium (Figure
2. Oxalic acid alone was rather ineffective at extracting copper but was quite effective at extracting arsenic and chromium. The addition of sodium hydroxide to oxalic acid resulted in increased copper removals but decreased the amount of arsenic and chromium removed. Furthermore, the extracted wood flakes contained a significant amount of residual water-soluble metal compounds that could be rinsed with water. Although a significant amount of dissolved minerals in local tap water were precipitated by oxalic acid, solutions prepared from tap water were equally effective as those prepared from deionized water. While the effects of continuous mixing and liquid to solid ratio were not deemed statistically significant, extractions carried out at the lower liquid to solid ratio of 10 with no mixing resulted in lower metals removals than other extractions.

The thickness swell of remediated flakeboard specimens varied from about 30–50 percent less than for untreated flakeboard (Figure 3). These differences were significant at *pr*<0.05. Thickness swell and water absorption were similar for flakeboard made from unextracted CCA-treated material and flakeboard made using flakes that had been extracted at 80°C for 6 hours at pH 2.4. Thickness swell and water absorption results for flakeboard made from flakes that had been extracted at 80°C for 1 hour at pH 1.4 followed by another hour at pH 4.0 was intermediate between the untreated controls and those to the two similar groups (unextracted CCA-treated material and flakeboard made using flakes that had been extracted at 80°C for 6 hours at pH 2.7).

The internal bond strength results were virtually identical for untreated control flakeboard and flakeboard made using flakes that had been extracted at 80°C for 6 hours at pH 2.7. The internal bond strength of unextracted CCA-treated flakeboard and flakeboard using flakes that had been extracted at 80°C for 6 hours at pH 2.7 was about 3% less, but not significantly different than the other two groups. This infers that adequate resin bonding is achieved when using 3.5 percent MDI resin regardless of treatment or extraction process. There were however large differences in face failures with internal bond specimens. Face failure results when the hot-melt adhesive used to bond the flakeboard specimen to the metal test blocks fails to achieve adequate penetration and adhesion. From the results in Figure 4, it is obvious that CCA-treated flakeboard was more difficult to properly adhere to the metal blocks than were specimens of the other three groups.

The flexural modulus and bending strength results were encouraging for a preliminary experiment (Figure 5). The flexural MOE of flakeboard made from unextracted CCA-treated flakes was 13% less than the untreated controls. The MOE of the two extracted groups was 8 percent less for the group extracted at 80°C for 6 hours at pH 2.7 and 24 percent less for the group extracted at 80°C for 1 hour at pH 1.4 followed by another hour at pH 4.0. The bending strength results when compared to untreated controls were not as encouraging with MOR being 25 percent less for flakeboard made from unextracted CCA-treated flakes, 17 percent less for the group extracted at 80°C for 6 hours at pH 2.7 and 33 percent less for the group extracted at 80°C for 1 hour at pH 1.4 followed by another hour at pH 4.0. For a first preliminary experiment, the flexural MOE and MOR results were encouraging. Past experience leads us to believe that with additional experience and refined composite processing techniques, we expect to meet or exceed all performance requirements.

Based on these results from our preliminary laboratory experiments, engineered wood composite products made from remediated preservative-treated wood were successfully manufactured to meet some but not all commercial performance requirements for flakeboard (ANSI 2004). With additional experience we hope to further control and optimize the composite manufacturing processes so to meet all commercial performance requirements for flakeboard and other similar composite products using remediated WBP-treated wood (ANSI 2004, CPA 1999, 2002, 2004).

**CONCLUSIONS**

The main findings from our previous experiments on development of a thermochemical remediation process for WBP-treated wood (Sabo et al 2008) are as follows:

1. Metal removals were enhanced with increasing temperature, but the effect of temperature on copper removal was less dramatic than for arsenic and chromium.
2. As pH of 1% oxalic acid solution is increased by the addition of sodium hydroxide, the removal of As & Cr decreases, whereas the removal of Cu increases.
3. Most of the As and Cr can be removed at low pH in only one hour.
4. After six hours, essentially all As and Cr is removed over the pH range of 1.4-3.0.

The main findings on the performance and utility of flakeboard composites made from remediated flakes from the above thermochemical remediation processes have been discussed in this report, and our conclusions are as follows:
1. Thickness swelling and water absorption of all flakeboards made from remediated flakes was significantly less than that of flakeboard made with matched untreated spruce.
2. Internal bond strength of flakeboard made from remediated flakes was not significantly different than that made with matched untreated spruce.
3. Flexural MaE was 8-24 percent less while MaR (i.e. bending strength) was 17-33 percent less for flakeboards made from remediated flakes than those made with matched untreated spruce.
4. With additional work to optimize both the thermochemical remediation and composite manufacturing processes, it appears that a high-quality flakeboard composite product can be made for remediated WBP-treated wood.

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