THE RECYCLING POTENTIAL OF PRESERVATIVE-TREATED WOOD

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RODNEY C. DE GROOT

Abstract
This paper is an assessment of the potential for recycling spent, preservative-treated wood products. Approximately $6 \times 10^6$ m$^3$ of wood treated with chromated copper arsenate (CCA), pentachlorophenol, and creosote are disposed of annually and about $19 \times 10^6$ m$^3$/year will be available for recycling by 2020. Currently, about $1.3 \times 10^6$ m$^3$/year of creosote-treated railroad ties and $2 \times 10^6$ m$^3$ of utility poles treated with pentachlorophenol and creosote are available for recycling. The balance is primarily from CCA-treated dimension lumber and the amount is forecasted to increase significantly due to its use in housing and decking. The recent expansion of the wood recycling industry has not included preservative-treated wood because of technical problems and regulatory uncertainties. The most viable recycling option for wood treated with arsenic is probably composite manufacturing, but problems such as characterization of comminution emissions and adhesive compatibility remain. Composting is also a potentially viable option, particularly for pentachlorophenol- and creosote-treated wood, although comminution emissions need to be characterized and questions need to be answered about the effects of microbial growth inhibition from the potentially large preservative concentrations.

Spent preservative-treated wood products are a potentially significant resource for recycling. Popular waste disposal options for spent preserved wood, such as combustion and landfilling, are becoming more and more costly because of increasingly strict regulatory requirements. Recycling options are economically attractive; however, many technical problems and regulatory questions remain that are inhibiting the development of a recycling industry analogous to the expanding non-treated wood recycling industry (19). The most economically attractive unpreserved wood recycling options appear to be composite manufacturing and compost production.

Figure 1 shows the historical trends in consumption of wood pressure treated with creosote, pentachlorophenol (penta), and chromated copper arsenate (CCA). Assuming a 30-year lifetime for all treated wood, approximately $6 \times 10^6$ m$^3$/year is being disposed of now and about $19 \times 10^6$ m$^3$/year will be available for recycling by 2020. The notable recent increase in consumption of wood treated with CCA is due to the treatment of dimension lumber used for decking and housing. More than 50 percent of all southern pine lumber produced in the United States is pressure treated with preservatives. Currently, about $1.3 \times 10^6$ m$^3$ of creosote-treated railroad ties (13) and $2 \times 10^6$ m$^3$ of penta- and creosote-preserved utility poles (48) are removed from service and are available for recycling each year. Some military bases dispose of 4000 m$^3$ of treated pallets, shokk (wire-bound boxes), and boxes annually (5), of which about 80 percent have been penta treated with non-pressure processes (dip or spray) and about 15 percent have been pressure treated with CCA.

Preservatives
CCA, penta, and creosote are the predominant preservatives in spent treated wood today. However, treated wood may also contain preservatives such as acid copper chromate (ACC), ammoniacal copper arsenate (ACA), ammoniacal copper quaternary ammonium compound (ACQ), ammoniacal copper zinc arsenate (ACZA), bis-(Tri-n-butyl tin) oxide (TBTO), borate, chromated zinc chloride (CZC), copper naphthenate, copper-8-quinolinolate (CU-8-Q), fluorochrom arsenate phenol (FCAP), sodium fluoride, and zinc naphthenate.

Creosote is a general term for the products of coal-cracking (catalytic or...
pyrolytic) reactions that distill between 210°C and 355°C. The oils are a mixture of aromatic hydrocarbons usually including naphthalene, phenanthrene, pyrene, biphenyl, and acenaphthene. CCA is a waterborne preservative that is widely used to treat exterior lumber and usually contains CuO, CrO$_3$, and As$_2$O$_5$. Penta, which has been a widely used wood preservative, usually contains 85 to 90 percent penta, 4 to 8 percent tetrachlorophenol, and 2 to 6 percent higher molecular weight phenols and neutrals and is usually dissolved in an application oil.

Table 1 shows typical preservative concentrations in preservative-treated wood products. Many other preservatives that have had limited use are not discussed here. The biological, physical, and chemical properties differ significantly between the common preservatives and dictate their recycling options.

Pressure treatment with preservatives results in deep penetration of the sapwood; however, the heartwood of many species is relatively untreated. Southern pine lumber is mostly sapwood and is, therefore, deeply penetrated by preservatives. Dip and spray treatments usually only coat the wood surface with preservative.

### REGULATIONS AND ENVIRONMENTAL CONCERNS

Current environmental regulations restrict the use of wood preserved with penta and creosote from use in residential, industrial, and commercial interiors (24), except as laminated beams or building components that are in ground contact and subject to decay or insect infestation and where two coats of an appropriate sealer are applied. Dip and spray treatments usually only coat the wood surface with preservative.

**Table 1.** — Concentration levels of preservatives in treated wood products.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Condition</th>
<th>Use</th>
<th>Preservative (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Penta</td>
</tr>
<tr>
<td>Pressure</td>
<td>Soil</td>
<td>Utility poles</td>
<td>0.8 to 1.3</td>
</tr>
<tr>
<td></td>
<td>Above ground</td>
<td>Lumber, timber, ties</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Soil, fresh water</td>
<td>Lumber, timber, ties</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Marine</td>
<td>Lumber, timber</td>
<td>44</td>
</tr>
<tr>
<td>Pressure-dual*</td>
<td>Tropical marine</td>
<td>Lumber, timber</td>
<td>38</td>
</tr>
<tr>
<td>Dipbrush</td>
<td>Normal</td>
<td>Wood packaging</td>
<td>0.5 to 2.5</td>
</tr>
</tbody>
</table>

*Sources: (4,21,47,82). Retentions are for freshly treated wood, levels in wood removed from service can be significantly less.

**Preservative concentrations are for the assay zone (0 to 5 cm from surface of wood) and are calculated based on southern yellow pine with a density of 510 kg/m³.

**Treatment involves application of both CCA and creosote for severe conditions in marine exposure.**

Used treated-wood products that are reused in somewhat the same form as the original products and in a manner compatible with their original intended purpose are usually not considered waste. Treated wood removed from service that has no other useful application as a product is considered solid waste and is generally not classified as hazardous waste at the federal level. This is because penta- and creosote-treated wood usually pass the Toxic Characteristic Leaching Procedure (TCLP) limits in U.S. Code of Federal Regulations 40 part 260 (22,30), and the chromium and arsenic from wood preservatives such as CCA are excluded from the limits. Although most states have hazardous waste classification regulations that mirror federal regulations, some states have regulations that are significantly more stringent and restrictive. California exempts treated wood that is managed for reuse from hazardous waste management requirements except when it is burned for energy recovery, speculatively accumulated, or reused or recycled in a manner that constitutes disposal or is inconsistent with the use of the preservative. The Environmental Protection
Agency’s (EPA) recent Universal Waste Rule (25) simplified regulations regarding recycling of certain hazardous wastes with the intention of increasing recycling. Preservative-treated wood was not included in the list of target wastes; however, a petition process allows for its addition to the list.

In addition to hazardous- and solid-waste handling regulations, there are health concerns with processing spent preservative-treated wood. Of particular concern is worker exposure to air emissions associated with recycling processes such as comminution, sawing, and composite manufacturing. The primary concern with the comminution of preserved wood is worker exposure to airborne particles and fumes.

Comminution of the spent preserved wood to flakes, fibers, or particles will prepare the treated wood for composite manufacturing processes and allow the effective use of biodegradation processes and preservative extraction processes. Except for flake production, which requires large uniform timbers for uniform flake production, most techniques currently used to reduce woodwaste (19,76) should be suitable for spent preserved wood. All wood comminution processes produce some airborne particles, and although there is some debate among the National Institute for Occupational Safety and Health (NIOSH), the American Conference of Governmental Industrial Hygienists (ACGIH), and the Occupational Safety and Health Administration (OSHA) about the health standards for untreated wood dust, exposure to the compounds in preservative-treated wood dust particles is regulated according to the standards indicated in Table 2. The size of wood dust particles generated from arsenically treated wood during comminution needs to be determined. The fine dust from western red cedar has low concentration limits. Composite manufacturers often do not use cedar because of this.

In addition to particle emissions, the blades and knives in comminution equipment can heat up and may cause vaporization of the organic preservatives that are also regulated by OSHA (Table 2). The often extreme temperatures during composite manufacturing (Table 3) can also cause vaporization of organic preservatives. Significant creosote fume emissions were reported at >96°C during a composite railroad tie manufacturing process (29). Similar industrial processes would probably require the installation of ducting and incinerators or carbon-bed absorbers to reduce worker exposure and prevent atmospheric emissions.

In addition to air emissions, composite manufacturing processes and storage of preservative-treated woodwaste may result in the production of water that contains wood preservatives. Some facilities that separate and store preservative-treated woodwaste are being required to either cover the stockpile to prevent exposure to rain, or install a leachate recovery system. Wood-based composites such as medium density fiberboard often use water-based size reduction equipment such as steam refiners, which may require wastewater treatment before discharge. Manufacturing of inorganic cement-based composites can use significant amounts of water and may need processing of wastewater as well as control of leachates and runoff during the curing period. Leaching of wood preservatives may also occur after the matrix has cured.

Leaching of ash from the combustion of treated wood is also a concern. A recent ruling by the U.S. Supreme Court requires the ash from most municipal incinerators to be regularly tested for hazardous waste classification by the TCLP (72). Because the combustion of CCA results in ash that greatly exceeds TCLP limits for arsenic (26), the presence of even small amounts of arsenically treated wood in municipal waste can result in ash classified as hazardous waste.

**REUSE**

GIVEAWAY programs have been an important outlet for used railroad ties and utility poles, but this practice is becoming restricted. Many utility companies are requiring recipients of such products to sign liability release forms that outline proper procedures for handling treated wood.

Sawing and milling operations that are in concert with the growing construction and demolition debris recycling industry are currently limited to beams and large structural members consisting of untreated wood (19). A significant portion of the spent treated-wood resource

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**Table 3.** Typical wood composite manufacturing specifications.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Formulation</th>
<th>Wood component</th>
<th>Process temperature</th>
<th>U.S. market m³/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particleboard</td>
<td>5% to 15% UF</td>
<td>Softwoods 10 to 40 mesh (no cedar)</td>
<td>140 to 200</td>
<td>6.9 x 10⁶ (1992)</td>
</tr>
<tr>
<td>Flakeboard</td>
<td>7% to 4% PF</td>
<td>Softwoods 0.2 to 0.5 mm x 20 to 200 mm (no cedar)</td>
<td>140 to 200</td>
<td>1.5 x 10⁶ (1997)</td>
</tr>
<tr>
<td>Fiberboard</td>
<td>0 to 8% UF</td>
<td>Cellulose or wood fibers, fiber bundles wet or dry</td>
<td>140 to 200</td>
<td>1.7 x 10⁶ (1992)</td>
</tr>
<tr>
<td>Portland cement</td>
<td>5% to 30% wood</td>
<td>Fibers, flakes, particles, chips, excelsior</td>
<td>20 to 150</td>
<td>1.1 x 10⁶ worldwide (1998) 0 in USA</td>
</tr>
<tr>
<td>Gypsum</td>
<td>5% to 30% wood</td>
<td>Particles, flakes, wood fibers, fiber bundles</td>
<td>20 to 100</td>
<td></td>
</tr>
</tbody>
</table>

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Sources: (23,55).

UF = urea-formaldehyde; PF = phenol-formaldehyde.

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consists of large poles and timbers that are suitable for resawing and remilling into other products.

The heartwood of most wood species including southern pine and western red cedar is not usually penetrated by preservatives during treatment. The untreated wood cores from these species could probably be remilled into high-value decking or specialty products with an existing technology such as thin kerf sawing. Such a process would be especially applicable to western redcedar utility poles, which typically have sapwood less than 2 cm thick.

Examples of treated-wood reuse operations include a utility company in Alberta (2) that has tried shaving sapwood off penta-treated western redcedar poles using commercially available equipment. The poles are then regraded, treated, and put back into service. A utility pole remanufacturing process is also being developed at Michigan State University (39) where the deteriorated portions of spent southern yellow pine poles are cut off and the good portions are spliced together using cold-press adhesives.

**Biodegradation**

Before some disposal or recycling operations can be performed, the preservative content of the wood must be reduced. For example, creosote may have to be removed from the wood fibers before they can effectively bond with adhesives in the manufacture of wood composites. Although biodegradation is generally slower than physicochemical processing, fungi or bacteria can be used to decompose a wide variety of compounds to levels approaching the detection limits of modern analytical techniques. Many microbes have been identified that are capable of decomposing penta and the constituents of creosote and oxidizing or reducing metals in wood preservatives such as Cr, Cu, and As to water-soluble forms, which can then be removed from the wood. The major disadvantage of biological degradation is the inability of many organisms to tolerate or metabolize wood that contains high preservative concentrations. Therefore, biodegradation may need to be used in conjunction with a preliminary preservative extraction process, such as the extraction of creosote-treated utility poles with ethanol before comporting (65).

The kinetics of biological substrate utilization can often be described with Michaelis-Menten kinetics; however, the difficulty with applying models to biodegradation of toxic compounds in treated wood is the inhomogeneity of the preservative level in the treated wood. With pressure-treated wood, the preservatives are distributed throughout the sapwood but are often absent from the heartwood. Preservative concentrations also vary widely in dip or brush-treated wood; the surface and end-grain portions have high preservative concentrations and center portions have little or no preservative. Thus, when treated wood is chipped, the preservative concentration in the chips can be distributed bimodally. And because microbes are generally inhibited by high concentrations of wood preservatives, biodegradation may result in a mixture of both totally biodegraded and undegraded chips.

In addition, extrapolating rate data in other systems to wood or other media is difficult because of the lack of standard methods of experimentation and reporting of results. The primary deficiency is in the reporting of the initial mass of bacteria used to achieve the reported conversion. Therefore, only generalizations can be made regarding the biodegradation of preservative-treated wood. Comparison of penta biodegradation in relatively dry wood particles and liquid suspensions of wood particles showed significant differences, and indicated that rate data cannot be extrapolated between systems because of the general inaccessibility of microbes to the preservatives in wood (49). Certain generalizations about biodegradation can be made, however. In general, effective bioremediation methods require: a reasonably low initial toxic substrate concentration; inoculation with a consortium of acclimatized microbes; using a high energy, easily metabolized co-substrate; and temperature, pH, and oxygen control.

**Organic preservative biodegradation**

**Fungi.** — Substantial literature is available on the use of fungi to degrade penta in soil (20,49,60). In contrast to bacterial decay, fungi are able to decompose wood by penetrating the hyphae into cell walls and excreting enzymes, which are used to decompose toxic compounds (49). Degradation of penta-treated ammunition boxes and pallets by white-rot fungi (basidiomycetes) has been performed in field and 8-L bioreactor tests (45). The <4-cm chipped wood contained an average of about 400 ppm penta. Although penta was not evenly distributed throughout the wood, the important results were: the best degradation rate was 84 percent in 4 weeks by *Trametes hirsuta*; fungi were more effective in hardwoods than softwoods; the addition of co-substrates increased wood degradation but not penta degradation; and significant amounts of penta were converted to pentachloroanisole and concentrated in the fungal hyphae. Similar results were also observed with fungal degradation of penta-treated poles (49).

**Marine environment.** — The marine environment has proved to be the most hostile to preserved wood. Docks and pilings are rapidly attacked by marine borers and a wide variety of organisms. Most decay is caused by cellulolytic bacteria. This decay is inhibited by aromatic compounds such as those found in creosote, which prevent attachment of microorganisms to the wood (73). Because marine organisms have a high tolerance for wood preservatives, these microbes could be used to remove preservatives and/or degrade treated-wood products. Inoculation with marine-based microbes and maintenance of a highly aerobic saline environment would be necessary.

**Bacteria.** — Many bacteria, anaerobic and aerobic, have the ability to metabolize organic compounds. Aliphatics are generally successively oxidized to alcohols, aldehydes, acids, and carbon dioxide and water. Resistance to degradation is usually caused by multiple branching of the carbon chain. Cyclic aliphatics are usually converted to aromatics, which are then oxidized to aliphatics by hydroxylation and ring cleavage. Polyhalogenated compounds are usually metabolized by anaerobic bacteria through reductive dehalogenation reactions. In general, mixed cultures are necessary for full dechlorination and subsequent oxidation, although a few species have been isolated or engineered to do both (81,86).

**Inhibition.** — In soils, polyhalogenated compounds have been successfully degraded to low levels at total initial concentrations up to 8,000 ppm (11,29,36,60). However, substrate inhibition from penta has been observed at concentrations between 0.35 ppm (54) and 60 ppm (88) in water. Penta applied to farm soil at 100
ppm was converted to carbon dioxide at a first order rate of 0.2/d; however, at 1,000 ppm, the rate was significantly reduced (78). Solvents were used to reduce aromatic hydrocarbon concentrations in creosote-treated wood to <400 ppm, before composting, presumably to avoid inhibition (65).

In addition to substrate and media inhibition, the copper, chromium, and arsenic in CCA, which may be contaminants because of poor sorting of material or dual treatment processes, can inhibit the degradation of organic preservatives. Cu⁺ exceeding 8 g/L significantly inhibited the growth and penta degradation rate of a Flavobacterium species (87), and an uncured aqueous CCA formulation with Cu²⁺, Cr⁶⁺, and As³⁻ at 0.5, 0.3, and 0.5 g/L, respectively, caused a significant reduction in the rate of penta degradation (12). Electron acceptors such as sulfur, SO₄⁻, NO₃⁻, and Fe³⁺ have also been shown to inhibit anaerobic dehalogenation of 2, 3, 6 TCP and may interfere with the overall penta dehalogenation process (36,53).

**Degradation rate.** — The polyaromatic hydrocarbons in creosote-contaminated soil can be degraded at a rate of about 0.3/d except for fluoranthene, pyrene, chrysene, and 1,2 benzanthrene, which do not degrade significantly (11). Penta in soil can be degraded at a rate of about 0.1/d at an initial concentration of 30 ppm (52). In water, maximum observed penta degradation rates include 1.2 mg/g/h (64); and 2 mg/L/d at a concentration of 10 mg/L at 50°C (46) and 15 mg/g/d in a UASB with cometabolites (88).

**Cometabolism.** — Successful cometabolites include sewage sludge and manure for composting and soil biodegradation operations (11, 52, 60). Organic acids, alcohols, and glucose are typically used with water treatment. Cometabolites may not always increase the specific rate of dechlorination or degradation of halogenated compounds; however, they can usually increase the overall rate by increasing the amount of biomass in the reactor as well as reduce the level of inhibition and the time lag before degradation starts (31,34,35,58,88). Sodium glutamate has been used as a cometabolite in the successful degradation of penta in a two-phase (water and wood chips) bioreactor (49).

**Biodegradation.** — Data are not available on the biometabolism of inorganic wood preservatives in wood matrices. Because arsenic, chromium, and copper cannot be transformed into nontoxic forms, the objective with biodegradation is to reduce or oxidize these elements to water-soluble forms. Valence change and alkylation are the main routes of transformation of inorganic compounds. Many strains of common, naturally occurring aerobic and anaerobic bacteria are able to reduce metals. However, because reduction of metals does not directly provide energy to the bacteria and only low levels of metals are necessary for cell function, detoxification is the motive for metal metabolism.

**Arsenic.** — The primary form of arsenic in treated wood is in water-insoluble Cr₂AsO₄. Arsenate is also the predominant form of arsenic found in both marine and fresh aqueous environments (61). Both anaerobic and aerobic heterotrophs in fresh and marine aqueous environments have demonstrated the ability to transform As(V) by reduction to methyl arsines (37,61). Anaerobic bacteria methyleate As(V), and sulfate-reducing anaerobes form methylated thiocarboxenals (37). Yeasts and fungi also metabolize As(V) and As(III) by forming Me₃As, and marine and freshwater organisms, including plants (algae), metabolize arsenic almost as easily as phosphorus (27,61) and have been found to contain high concentrations of arsenic.

**Chromium and copper.** — Most chromium in fixed, CCA-treated wood is in the form of Cr₂O₃, with possibly small amounts of Cr (VI) -lignin complexes. The copper is primarily in the form of Cu²⁺-lignin and Cu⁺-cellulose complexes, with some CuCrO₂-lignin complexes (57,64). Removal of arsenic from CCA-treated wood with bacteria results in a complex relationship between bacteria that oxidize and reduce copper and chromium, the complexes formed by their metabolizes (citrate, oxalate, and formate) and chromium precipitates (primaarily Cr(OH)₃). Bidentate metal-citrate complexes are easily degraded (28); however, tridentate citrate-Cu⁺ complexes, formed with equimolar concentrations of citrate and Cu⁺, are difficult to degrade.

**Composite manufacturing.** — Composite manufacturing appears to be one of the most economically attractive recycling options for utilizing waste-wood (19). Table 3 shows the specifications for manufacturing some of the common composites that utilize wood particles.

**Wood-based composites.** — Conventional wood-based composites are usually available in panel form and are widely used for housing and furniture. The lignocellulosic components of such composites are typically pressed together in the presence of a heat-curing adhesive, such as urea-formaldehyde (UF) or phenol-formaldehyde (PF). Worldwide, about 90 percent of all wood composite products are bonded with water-resistant UF. The more expensive PF-based products are waterproof and generally used in external applications.

Conventional wood-based composites fall into three main categories based on the physical configuration of the com- mitted wood: fiberboard, flakeboard, and particleboard (Table 3). All three composites can generally use softwoods and hardwoods; however, fiberboard is stronger with softwoods because hardwood fibers tend to be shorter than soft-wood tracheids.

There are several processes where the composite is preservative treated after bonding, such as creosote-treated resorcinol adhesive-based laminated timbers for exterior construction (74), laminated veneer lumber (43), and laminated hardwood timbers (6). Utilizing preservative-treated wood in existing conventional wood manufacturing processes presents two significant problems: preservative interference with fiber/adhesive bonding and the volatile properties of the organic preservatives may cause processing and industrial hygiene problems.

The hydrophobic nature of creosote and penta (with its application oil) would preclude their use in conventional wood-based composites that rely on the ability of the adhesive to wet the surface of the normally hydrophilic wood fibers. At the USDA Forest Service, Forest Products Laboratory (FPL), reconstituted railroad ties containing 6 percent creosote were manufactured by hot-pressing flakes with 5 percent PF. The resulting ties had difficulty withstanding vacuum-pressure-soak-drying cycle tests and indicated weak adhesive-fiber bonds (29). In
addition, organic preservatives could melt or vaporize during the high-temperature pressing operations (Table 3), possibly causing voids in the composites as well as a significant health hazard.

With one exception (67), many studies have shown that treatment of wood with chromium-containing preservatives impairs the performance of phenolic adhesives (1,10,33,56,62,68,80,83). Presence of CCA following completion of the fixation reaction does not interfere with the normal curing reaction of PF adhesives; however, CCA physically blocks most opportunities for bonding on the fiber surface (85). The FPL has recently developed a deep penetrating phenolic adhesive that produces excellent bonds to CCA-treated southern pine (84).

Inorganic composites. — Worldwide, a variety of building materials are manufactured using inorganic binders, such as Portland cement or gypsum and wood (Table 3). Inorganic-bonded composites are stable, highly pest and fire resistant, and generally are manufactured by curing (via hydration) the woodfiber/binder mix in a form. Several companies in the United States and Europe are placing recycled paper fiber in dry wall (gypsum) to increase its strength and stiffness. Gypsum-bonded composites are normally limited to interior applications, and Portland cement composites are generally used in exterior applications.

In the United States, the most successful tests have been conducted with southern pine, which generally produces the best cement composites. The least desirable species for use in wood-cement composites include Douglas-fir, hemlock, and larch as well as most hardwoods, due to interference with the curing process from water soluble (at pH ≈ 12) and hydrolyzable compounds in the wood. Water is often successfully used to extract soluble compounds from the wood before combining it with cement (55). Compared with Portland cement, gypsum composites appear to be less sensitive to wood species because of their relatively fast cure times.

CCA- and CrO₄⁻, treated red pine and lodgepole pine used in stick pull-out, compressive strength, and flexural strength tests in Portland cement composites showed significantly improved performance relative to untreated wood (71). The improvement in properties resulting from the addition of chromium was shown to be independent of, and added to, the improvement resulting from water extraction. The hydroxyl groups of aqueous calcium, silicon, aluminum, and iron oxides probably hydrogen bond with the hydroxyl and carboxyl groups of cellulose, lignin, and oxidized end groups (18).

The use of inorganically treated wood with moieties that can complex with the hydrolyzed wood or prevent the hydrolysis of the chromium-complexed lignin and cellulose in Portland cement composites seems promising. Not only will the use of inorganically treated wood in cement composites provide an outlet for treated wood, it will also improve the resistance of these products to infestation by pests. Wood treated with creosote or penta is probably not compatible with Portland cement or gypsum, because the preservatives might interfere with the cement curing processes as well as inhibit wetting and ultimate bonding with the wood surface.

P RESERVATIVE E XTRACTION

Solvent extraction of preservatives from spent treated wood will allow the use of biodegradation processes that are sensitive to high concentrations of preservatives. It will also permit the use of composite manufacturing processes that are sensitive to the presence of certain preservatives. The objective of extracting preservatives from wood is to solvate the preservative that is either bound to the lignin or cellulose in the wood or has been precipitated within the cell walls and pores and remove it to a level compatible with the intended composite manufacturing or biodegradation process.

The design of a process for extracting preservatives from wood chips or particles must consider diffusion, reaction rates, and equilibrium thermodynamics. Important steps in the overall extraction process are as follows: 1) diffusion of solvent or completing agent to the wood particle surface; 2) diffusion of solvent or completing agent through the pores into the wood particle; 3) reaction or solvation of the preservative with the completing agent or solvent; 4) diffusion of the solvated or complexed preservative through the pores to the particle surface; and 5) diffusion of the solvated or complexed preservative from the particle surface to the bulk fluid.

A mathematical model of the process will allow a process design with minimal errors in scale-up. Mathematical models of steps 1 and 5, which are affected by fluid flow in the process and properties of the solvants and preservatives, have been solved for many generic situations (75) and are not discussed here. The significance of step 3 can only be determined experimentally, however. Likely candidates for solvents and completing agents are discussed later. Steps 2 and 4 are significantly influenced by physical properties of the wood and solvents and directly affect the time necessary for the desired level of extraction.

D IFFUSION

With wood particles <1 mm in length and reactions slower than kraft pulping delignification, diffusion within the particle is not considered to be a limiting step (38) and so it is ignored. Solvation and complexation reactions are generally fast, and useful wood particle sizes are significantly >1 mm in many cases. Therefore, diffusion may be an important consideration and the equations describing diffusion and reaction in porous media, similar to those described for catalytic reactions (75), should be solved. These equations have been solved for the pulping of wood and hydrolysis of wood for ethanol production (38,42). Extraction processes in wood have not been analyzed, however.

Apart from the reaction or solvation rate, the effective diffusivity is the most significant and variable factor in the extraction process. The effective diffusivity is:

$$D_e = D \varepsilon \xi^{-1}$$

where:

- $D$ = molecular diffusivity
- $\varepsilon$ = porosity of wood
- $\xi$ = tortuosity

**Table 4.** Penetration factors for some common wood species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Penetration factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Douglas-fir</td>
<td>70</td>
</tr>
<tr>
<td>White pine</td>
<td>100</td>
</tr>
<tr>
<td>Shortleaf pine</td>
<td>120</td>
</tr>
<tr>
<td>Red oak</td>
<td>4,000</td>
</tr>
<tr>
<td>White oak</td>
<td>0.7</td>
</tr>
<tr>
<td>American aspen</td>
<td>2,500</td>
</tr>
<tr>
<td>American ash</td>
<td>80</td>
</tr>
<tr>
<td>Sweet gum</td>
<td>1,200</td>
</tr>
<tr>
<td>Lodgepole pine</td>
<td>300</td>
</tr>
</tbody>
</table>

<sup>a</sup> Source: (70).
The effective diffusity should be constant for a particular system of wood, solvent, and solute. Porosity data on various types of wood are available from mercury porosimetry data; however, data on the overall tortuosity of the pores are not generally available and must be determined experimentally (32).

Table 4 lists penetration factors for various species of wood, which indicate the variability of permeability between heartwood and sapwood and between species. The penetration factor is defined as the fourth power of the radius of a glass capillary that will permit the same rate of airflow as 1 cm$^2$ of dry wood in question. It may be possible to determine effective diffusivities by “back calculating” from penetration factor data. For comparison, the effective diffusivity of glucose through water in chips of American aspen was found to be $2.1 \times 10^{-6}$ cm$^2$/s and the tortuosity was 3.3 (38). The molecular diffusivity of glucose in water is significantly greater at $6.9 \times 10^{-6}$ cm$^2$/s and indicates the importance of particle diffusion and knowledge of the type of wood that is involved in process design.

The difficulty with directly applying a model to the extraction process is the lack of homogeneity in the levels of preservative in both pressure- and dip- or brush-treated wood. Except for treated southern pine lumber, which is mostly sapwood, the preservative concentration of chipped treated wood is distributed bimodally with significant numbers of high concentration chips and untreated chips. Incorporation of a distribution function into a process model may be necessary.

During wood preservation, swelling agents such as NH$_3$, water, and heat are used to reduce diffusion limitations and allow the penetration of the microporous cell walls. Effective extraction processes may require the use of swelling agents.

### Thermodynamics

Selection of a suitable solvent or complexing agent requires evaluation of the equilibrium relationship between all components. Significant data are available on the solubilities of penta and individual components in creosote in various common solvents. However, limited data are available on the equilibria involving the aqueous mixtures of inorganic preservatives and complexing agents. Knowledge of the equilibrium concentrations of the various system components does not indicate the amount of time required to achieve equilibrium, however. Many reactions have large activation energies, which necessitate catalysts (which lower the activation energy) or heat. Reaction rate data can only be obtained experimentally.

**Chromated copper arsenate.** — With CCA, the objective is to form water-soluble compounds from the water-insoluble compounds precipitated in and bound to cured wood. This should be done without oxidizing Cr(III) to Cr(VI) because of the increased toxicity of Cr(VI) and the increased difficulty with removing it from wastewater. Inorganic preservatives form complexes with the wood lignin and cellulose as well as water-insoluble precipitates during curing processes that can take several weeks. The major components of cured CCA wood include: CuCrO$_4$-lignin complexes, CrAsO$_4$-lignin complexes, Cu$_2$-lignin complexes, Cu-cellulose complexes, and Cr$_2$(OH)$_4$Cr$_2$O$_7$ precipitates (56). Chromium also forms complexes with cellulose and lignin during the Cr(VI) reduction and curing process (63,69). Most stable complexes are thought to be with the guaiacyl (2-methoxy phenol) groups common in softwood lignin and the syringyl (1,2-dimethoxy benzene) groups common in hardwood lignin (57,63).

Arsenic, chromium, and copper form soluble complexes with a number of water-soluble compounds (17,44,80). Copper and arsenic form complexes with carboxylic acids, and it is well documented that both arsenic and copper are leached from CCA-treated wood by dilute carboxylic acids (14,17). These carboxylic acids are products of the degradation of wood by fungi. Simple inorganic acid extraction has been shown to be relatively unsuccessful (14,17); however, the leaching of copper-chromate-treated wood pulp to less than 100 ppm total of copper and chromium has been demonstrated (77). In that study, acetic acid was twice as effective in leaching chromium as H$_2$SO$_4$ at pH = 2.

There was little difference between malic, acetic, formic, and oxalic acids as complexing agents. Copper, however, was more effectively complexed with formic acid and generally more difficult to remove from the wood than chromium.

Copper forms bidentate (15,16) and tridentate (28) complexes with citrate and binuclear complexes with citrate and tartrate at higher concentrations (9). The effectiveness of the complexing agent in solubilizing a metal can be given by its stability constant (ratio of the concentration of the complexed metal and the uncomplexed metal oxynitrate). Stability constants at pH = 7 for copper and chromium and some common complexing agents in simple binary systems are shown in Table 5 (44). Chromium(III) also forms weak complexes with Cl- and SO$_4^2-$ (9). Minerals (66) as well as metal hydroxides (40) are also effective absorbents of aqueous arsenic anions and chromate ions. This is accomplished via ligand exchange reactions whereby the anion displaces OH- from the surface. The stabilities of the desired soluble chromium, copper, and arsenic complexes relative to their respective precipitates and lignin complexes are unknown.

When the preservatives are solubilized and removed from the wood, separation of the ligands from the water must be considered. Many commercial technologies, which are most effective with As(V) and Cr(III), are available for these separations, such as ion exchange, reverse osmosis, and precipitation (41).

**Penta and creosote.** — One pilot process involves the extraction of pentaland shavings produced during the recycling of western redcedar utility poles (2). The treated wood on the outside of the pole is shaved and heated to 410°C in the presence of nitrogen at atmospheric pressure in a continuous process. The gaseous penta and its associated application oil (4) are then separated from the nitrogen in a solvent scrubber. The mix-

### Table 5. — Stability constantsa for metal complexing agents (0.1 M, pH = 7).

<table>
<thead>
<tr>
<th>Element</th>
<th>Acetate</th>
<th>Fluoride</th>
<th>Salicylate</th>
<th>Citrate</th>
<th>Cymate</th>
<th>EDTA</th>
<th>Oxalate</th>
<th>Tartrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>7.2</td>
<td>11.2</td>
<td>14</td>
<td>7.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>3.6</td>
<td>7.3</td>
<td>-</td>
<td>9</td>
<td>-</td>
<td>20</td>
<td>13.8</td>
<td>-</td>
</tr>
</tbody>
</table>

a $\log_{10}$ (complexed metal concentration/uncomplexed metal oxygen concentration).
ture is then flash-distilled to produce pure solvent, which is internally recycled, and a penta-oil mixture, which can be reused. The resulting wood product consists of hydrophobic fibers marketed as an oil absorbent. In a similar process that decomposes the wood (8, 79), heat and concentrated alkali solutions are used to remove and decompose penta from treated wood to less than 10 ppb (parts per billion) at 350°C. In another process, used utility poles are recycled using hot alcohol in a continuous process to extract creosote-laden wood chips to about 1,000 ppm before comporting (65).

Penta is commonly found adsorbed and deposited within the cell walls of wood (45). Removal of penta requires its dissolution in an appropriate solvent. Evaluation of potential solvents may be complicated by the existence of its application solvent, which is approximately #2 diesel oil (4). Although penta-wood adsorption isotherms have not been determined, penta has been shown to be adsorbed by biomass such as bacteria. The Freundlich adsorption isotherm was used to describe the adsorption of penta to wastewater treatment sludge (7). Its absorption capacity was determined to be less than half that of activated carbon. A strong adsorption isotherm would have the effect of reducing penta's volatility.

Although the composition of the originally applied creosote varies and many compounds have been partially oxidized over time, probably no compounds bind significantly to the cell walls or lignin within the wood. Therefore, extraction is a matter of choosing an inexpensive and effective solvent. Creosote volatility calculations may be difficult because of the many compounds that constitute creosote. With most creosote solutions, both naphthalene and anthracene are compounds that each constitute at least 10 percent by weight. Anthracene and naphthalene (and most other compounds in creosote) as well as penta are soluble in alcohols at near ambient temperatures.

**Conclusions**

Overall, the possibilities for recycling preservative-treated wood are great. Large consistent sources of wood with consistent treatment histories, such as army ammunition boxes, utility poles, and railroad ties, show the greatest opportunity. Large amounts of arsenically treated wood are also becoming available for recycling and these amounts will only increase, such as with ACA- and ACZA-treated wood in Hawaii.

As a result of the restrictions on use and concerns about toxicity, creosote- and penta-protected wood recycling presents a challenge. Some spent, creosote-treated wood is combusted with energy recovery; however, recent rulings regarding ash disposal present further limitations. Biodegradation seems to be the preferable option for penta- and creosote-treated wood, but this option requires answers regarding emissions from comminution and the development of extraction processes to lower preservative concentrations so that degradation by comminuting microbes will not be inhibited.

Wood treated with CCA and other similar inorganic preservatives such as ACA and ACZA show a potential for recycling into composite products. Arsenically treated wood seems to be compatible with cement-based composites, which are starting to appear in the United States. Adhesives are also being developed that are compatible with CCA for use in wood-based composites. With simple extraction processes, CCA-treated wood could probably be used in a wide variety of conventional wood-based composites. However, health concerns during processing and environmental durability need to be addressed.

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