Fixation and Leaching Characteristics of CCA- and CCFZ- Treated Domestic Softwood Species*1

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ABSTRACT

The fixation and leaching characteristics of chromated copper arsenate (CCA Type C) and chromium-copper-fluoride-zinc (CCFZ) in domestic softwood (Japanese red pine, Korean pine, and Japanese larch) sapwood were investigated using the expressate method to follow chromium fixation and the American Wood-Preservers' Association (AWPA) leaching procedure to determine leaching properties after fixation. The rates of fixation were affected by preservative types; CCA was fixed much faster than CCFZ for all species evaluated. There were definite differences in the fixation rates of different species, with Korean pine requiring shorter to fix than the other species evaluated. Chromium fixation was greatly enhanced by elevated temperatures, and fixation time can be estimated according to fixation temperatures applied. The percentage of arsenic and zinc leached from domestic softwoods was relatively high compared to chromium and copper, indicating that there is still a relatively high unfixed arsenic and zinc components after complete chromium fixation in CCA-and CCFZ-treated samples, respectively.

Keywords: Fixation, leaching, CCA, CCFZ, Japanese red pine, Korean pine, Japanese larch

1. INTRODUCTION

It is well known that complete fixation of the waterborne preservative components in wood is crucial to the environmental safety of the treated products before placing them in service. The fixation reaction is generally monitored by the reduction of hexavalent chromium (Cr^{VI}).

This fixation reaction is highly temperature dependent, and differences in the rates of fixation have been observed for different wood species. It is therefore important to understand the fixation characteristics of species such as Japanese larch that are being contemplated for treated products in Korea. However, little work has been done to investigate the fixation characteristics

^{*1} Received on May 13, 2003; accepted on June 20, 2003.

This research was supported by Agricultural R&D Promotion Center

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and leaching characteristics, the ultimate measure of the quality of the fixation reaction, of chromiumcontaining preservatives for domestic softwood species.

The purpose of this study, which was performed to elucidate the environmental safety of CCA- and CCFZ-treated wood, was to investigate the chromium fixation in CCA- and CCFZ-treated domestic softwood species, and to relate it to the leaching of preservative components in treated wood.

2. MATERIALS and METHODS

2.1. Fixation Study

Thirty sapwood specimens measuring 15 by 15 by 200 mm were cut from boards of Japanese red pine (*Pinus densiflora*), Korean pine (*Pinus koraiensis*), and Japanese larch (*Larix kaempferi*), and then conditioned at room temperature to approximately 15 percent moisture content before treatment. The specimens were vacuum-pressure impregnated with a two percent (w/v) solution of CCA Type C or CCFZ. The treatment schedule was a full-cell process consisting of a 30-minute vacuum (760 mmHg), then the cylinder was filled under vacuum, followed by a pressure of 14 kg/cm² until refusal.

Immediately after treatment, specimens were wrapped in aluminum foil individually and stored in the dark at 15°C, which is the mean temperature of central part of Korean peninsular. Extra sapwood specimens of Japanese red pine were pressure treated and stored at 40, 60, and 80°C to determine the effect of temperature on preservative fixation. At selected time intervals after treatment, five 15 mm cubes were crosscut and compressed in a laboratory hydraulic press to express or squeeze out excess preservative solution in the wood. The expressed solution was analyzed for the Cr^{VI} using the diphenyl-

carbazide method (ASTM, 1996). The time required after treatment for the preservative components to become immobilized or fixed in the wood was determined using the method suggested by Cooper and Ung (1992).

2.2. Leaching Study

Six 15 mm cubes were machined by cross-cutting from fully fixed specimens (15 by 15 by 200 mm) of Japanese red pine, Korean pine, and Japanese larch, and air dried to approximately 15 percent moisture content. The blocks were leached according to the AWPA Standard E11-87 (AWPA, 2001). The leachate was analyzed for copper, chromium, and arsenic contents (zinc for CCFZ) using an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The accumulated leaching losses of the preservative components were computed at each leaching time from the mass of chemical in the leachate and the original content of components in the treated block.

3. RESULTS and DISCUSSION

3.1. Fixation Study

The rates of Cr^{VI} fixation with time in the CCA- and CCFZ-treated wood samples are shown in Fig. 1. The CCA-treated samples fixed faster than the CCFZ-treated sample for all species. This finding conflicts with that of Kim and Ra (1996), who reported that the rates of CCFZ fixation in radiata pine (*Pinus radiata*) sapwood samples at 25°C were similar to those found for CCA. The reason for this difference is as yet unknown. Little information is available on the fixation mechanisms on the components of CCFZ, although it is probable that the process of chromium reduction is very similar to that of CCA.

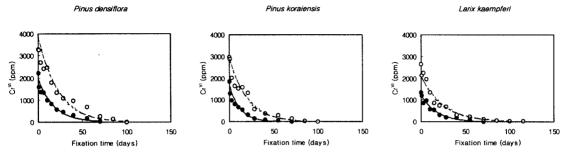


Fig. 1. Comparison of fixation rates of hexavalent chromium between CCA and CCFZ-treated wood samples during nondrying fixation at 15°C. (solid circle: CCA, open circle: CCFZ)

Table 1. Estimated fixation times at 15°C as affected by species and preservatives

Preservative		Wood species	
	Japanese red pine	Korean pine	Japanese larch
CCA	87 days	72 days	76 days
CCFZ	125 days	107 days	125 days

Table 2. Effect of fixation temperature on fixation time in CCA-treated Japanese red pine samples

Temperature	15°C	40°C	60°C	80°C
Fixation time	87 days	9 days	1.2 days	7 hours

The rate of fixation is highly species dependent (Table 1). CCA-treated Japanese red pine took significantly longer to fix than the other species evaluated. The other species were not significantly different in fixation rates although CCA fixed somewhat faster in Korean pine than in Japanese larch. CCFZ fixed faster in Korean pine than in Japanese red pine and Japanese larch. The different fixation rates among species might be attributed to the differences in chemical properties, such as pH, lignin content, and extractive content, and density properties of species.

Increasing the fixation temperatures can accelerate the rates of fixation. The estimated fixation times are shown in Table 2 for Japanese red pine samples treated with CCA at a range of fixation temperatures. Since the correlation between fixation temperature and ln[estimated]

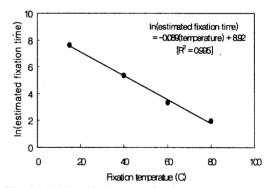


Fig. 2. Relationship between fixation temperature and ln[estimated fixation time] in CCA-treated Japanese red pine samples.

fixation time] was excellent (Fig. 2), proper fixation time according to fixation temperatures applied can be estimated by using the regression equation as shown in Fig. 2.

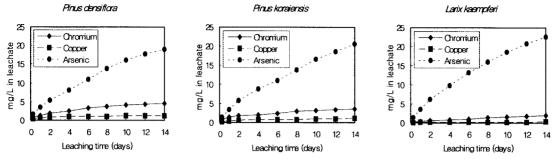


Fig. 3. Cumulative leaching losses of preservative elements from the CCA-treated samples.

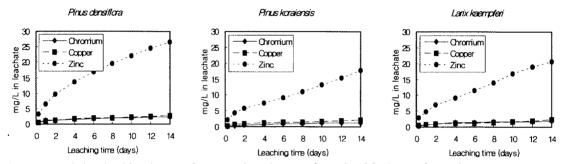


Fig. 4. Cumulative leaching losses of preservative elements from the CCFZ-treated samples.

3.2. Leaching Study

Figs. 3 and 4 show the cumulative leaching losses of preservative components from CCAand CCFZ-treated samples, respectively. The sequence of elemental leaching amount was arsenic, chromium, and copper in CCA-treated samples, and was zinc, copper, and chromium in CCFZ-treated samples. Cumulative leaching losses of preservative components were somewhat different among wood species. The total CCA losses were $0.047 \sim 0.108$ percent total chromium, $0.023 \sim 0.091$ percent copper, and $0.688 \sim 0.817$ percent arsenic depending on wood species. Leaching losses of total chromium, copper, and zinc from CCFZ-treated samples were 0.022~ 0.038, $0.205 \sim 0.267$, and $1.659 \sim 2.487$ percent, respectively.

Over the 14-day leaching period, leaching losses of arsenic and zinc from CCA- and

CCFZ-treated sample were considerably higher compared to those of chromium and copper, and arsenic and zinc leaching is thought to be continued beyond 14 days. Although the losses of CCA elements are within the normal range observed for CCA-treated other softwood, this high arsenic leaching observed in this study wherein the chromium has been fully fixed may be cause for public concern for treated wood used in environmentally sensitive locations.

4. CONCLUSIONS

The rates of CCA fixation were faster than those of CCFZ fixation for all species evaluated. CCA-treated Japanese red pine took significantly longer to fix than the other species evaluated. The other species were not significantly different in fixation rates although CCA fixed somewhat

faster in Korean pine than in Japanese larch. CCFZ fixed faster in Korean pine than in Japanese red pine and Japanese larch. Fixation time can be greatly reduced by exposing treated samples to elevated temperatures, and it can be estimated according to fixation temperatures applied. After complete chromium fixation, there is still a relatively high amount of unfixed arsenic and zinc components in CCA-and CCFZ-treated samples, respectively. This may result in unusually high arsenic and zinc leaching losses from treated wood in service.

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