

Manufacture and Properties of Inorganic Chemical Treated Wood by Introducing of Fluorides^{*1}

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ABSTRACT

Inorganic chemical treated wood was prepared by impregnation of calcium or magnesium chloride (CaCl_2 or MgCl_2) solution and immersion in saturated solution of ammonium fluoride (NH_4F) as a reactant in order to make an introduction of a refractory fluorides with fungicidal and insecticidal effects in wood.

The weight percent gains (WPGs) were increased with increase in concentration of calcium chloride or magnesium chloride solution, and were higher in treatment with calcium chloride than with magnesium chloride. Inorganic substances were produced mainly in the lumina of tracheides. These substances were proved to be the calcium fluoride or magnesium fluoride by the energy dispersive X-ray analyzer in conjunction with a scanning electron microscope (SEM-EDX).

The treated wood showed good decay resistance because the weight losses were hardly occurred by the test fungi such as *Tyromyces palustris* and *Trametes versicolor*. The fire resistance effect was superior to the treated wood compared with that of the untreated wood.

Keywords : Wood-inorganic composites, fluoride, fire resistance, decay resistance.

1. INTRODUCTION

Wood is a good natural material because of an organic substance, formed during the growth of a tree by photosynthesis. However, it has some unfavorable properties, such as degradation, combustion and dimensional instability. In order to improve these disadvantage of wood, various inorganic chemical treatments including combination of wood and silicate have been attempted. The wood-inorganic composite is one of the improved wood materials. Many re-

searches showed that inorganic substances introduced in the wood contribute to the enhancement of decay and fire resistance of wood (Furuno *et al.*, 1991; Saka *et al.*, 1992; Yoon & Lee 2001).

Attempts to produce wood-inorganic composites by using calcium chloride and sodium sulfate have been conducted (Lee & Kim 2008). Calcium sulfate, namely, gypsum, which is known to be effective as fire retardants of construction materials (Moon 1995), was produced in wood by double diffusion process using cal-

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cium chloride and sodium sulfate solution. The gypsum-wood showed a good fire resistance and poor decay resistance throughout the decay and fire resistance tests.

Fluoride is used as ingredient of water borne preservatives because of fungicidal and insecticidal effects (Japan wood preserver's association 1982). Fluoride is highly mobile in wet wood and is an effective toxicant, but its mobility makes it prone to leaching. The incorporation of higher levels of dichromate was developed to prevent fluoride leaching from treated wood (Eaton & Hale 1993).

The purpose of this study was to produce of a new composite material with good fire and decay resistance by introducing refractory fluorides such as calcium or magnesium fluoride into the wood.

2. MATERIALS and METHODS

2.1. Wood Materials

Rotary cut veneers of radiata pine (*Pinus radiata*) sapwood were used for the introduction of fluorides. Specimen size for the determination of weight percent gains (WPGs) and decay resistance was 20 (T) \times 2 (R) \times 50 (L). The specimen, 150 (T) \times 2 (R) \times 150 (L) mm, was used for the fire resistance test.

2.2. Chemicals

The solutions of 10, 20, 30%, saturated calcium chloride (CaCl_2) and magnesium chloride (MgCl_2) were used as the first treatment solution. Saturated solution of ammonium fluoride (NH_4F) was secondly treated as a reactant to produce fluoride.

2.3. Wood Impregnation

After evacuating for about 1 h (4 mmHg) in

vacuum desiccator, the specimens were impregnated with calcium chloride or magnesium chloride solutions. Then, they were soaked in the saturated solution of ammonium fluoride at atmospheric pressure for 48 h. In order to remove unreacted solutions and by-products such as ammonium chloride (NH_4Cl), the treated specimens were leached in flowing tap water for 24 h. The treated specimens were dried at room temperature for 24 h and then completely dried at 60°C to constant weight. Weight percent gains of specimens were determined for each concentration of calcium chloride or magnesium chloride solutions.

2.4. SEM-EDX

The small samples of the radial section were prepared from the central portion of each treated specimens. They were coated with carbon *in vacuo* by carbon thread evaporation device (BALTEC, CED 030). The formation of fluorides within the treated specimens was observed by environmental scanning electron microscope (ESEM, PHILIPS XL 30). Furthermore, the detection and distribution of constituent elements of fluorides contained as calcium and magnesium and fluoride were examined using energy dispersive X-ray microanalysis (EDX, EDAX).

2.5. Decay-Resistance Test

The test specimens were exposed to test fungi, *Tyromyces palustris* and *Trametes versicolor*, at 26°C for 3 months according to the method of attached standard No. 2 of KS M 1701. The decay resistance was evaluated from the average weight losses of the specimens.

2.6. Fire-Resistance Test

The fire resistance test was examined with microburner according to the flame test method

for wood meal-gypsum composite board. The specimens were fixed with clamps at 9 cm from the microburner, and the surfaces of the specimens were touched by the flame. The temperature on the back side of specimens was measured by a thermocouple thermometer every 5 seconds for 1min.

3. RESULTS and DISCUSSION

3.1. Weight Percent Gains (WPGs)

WPGs of wood treated with saturated solution of ammonium fluoride as a reactant at the each concentrations of the calcium chloride or magnesium chloride solution were shown in Fig. 1. In the all specimens, the WPGs increased with increase in the concentration of the calcium chloride or magnesium chloride solution. Particularly, remarkable increase of WPGs was found by the impregnation of calcium chloride solution. The reaction of ammonium fluoride with calcium chloride was more effective than that of magnesium chloride. On the other hand, there were no distinctive differences in WPGs between calcium chloride and magnesium chloride for impregnation in saturated solutions.

3.2. SEM-EDX

SEM-EDX micrographs of a radial section of a specimen treated with 10% calcium chloride solution and saturated solution of ammonium chloride were shown in Fig. 2. From the secondary electron image (Fig. 2A), inorganic substances were found to be existed in a granules within tracheids of treated woods. Because the spectra (Fig. 6B) and distribution maps (Fig. 2C and D) of the Ca-K α and F-K α characteristic X-rays were detected from the same region of secondary electron image (Fig. 2A), it can be assumed that the substances in the tracheids are

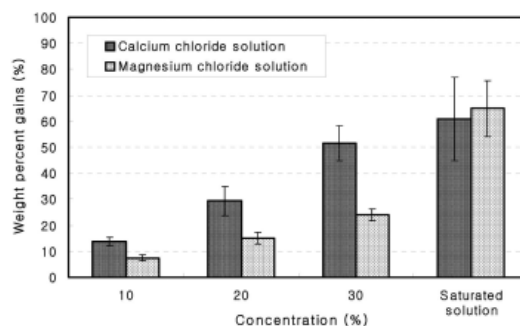


Fig. 1. Relationships between weight percent gains and concentrations of calcium chloride and magnesium chloride solution in the woods treated with saturated solution of ammonium fluoride as reactant.

calcium fluoride. The almost same results as that of wood treated with calcium chloride were obtained from the SEM-EDX on the woods treated with magnesium chloride (Fig. 3). Therefore, it can be supposed that the substances in treated wood are magnesium fluoride.

From the results shown in Figs. 2 and 3, it was proved that the refractory fluorides to water can be introduced in wood by impregnation of calcium or magnesium chloride solutions followed soaking in ammonium fluoride solution as reactants.

3.3. Decay Resistance

The decay test results on the treated woods are shown in Figs. 4 and 5. The weight losses of the treated woods were reduced considerably after 3 month exposed to *Tyromyces palustris* and *Trametes versicolor*. Thus calcium or magnesium fluorides produced in treated wood can be said to have decay resisting effects against wood-decaying fungi.

In order to verify decay resistant effects of treated woods, SEM-EDX was conducted to observe the characteristics of wood decayed by *T. palustris* for 3 months. The hypae of *T. pal-*

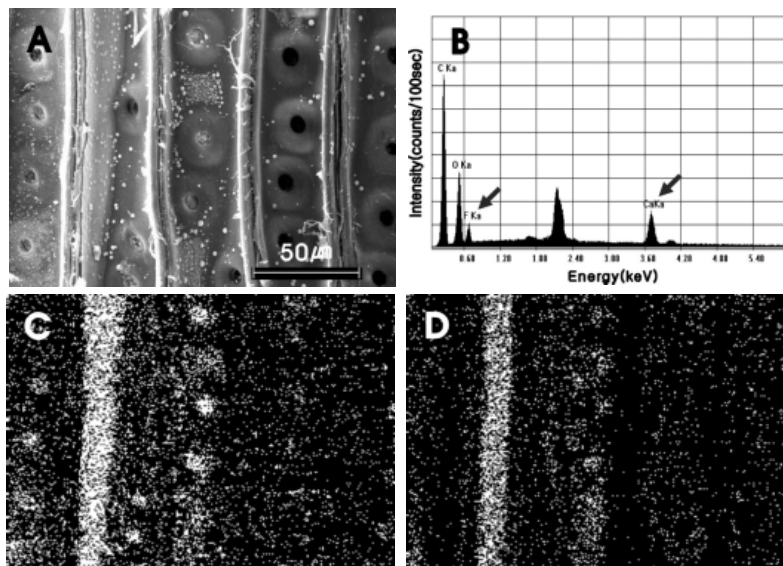


Fig. 2. SEM-EDX micrographs of a radial section of a specimen treated with 10% calcium chloride solution and saturated solution of ammonium chloride (WPGs 13.1%) ; A : Secondary electron image, B : Characteristic X-ray spectra, C : Distribution map of Ca-K α X-rays and D : Distribution map of F-K α (D) X-rays.

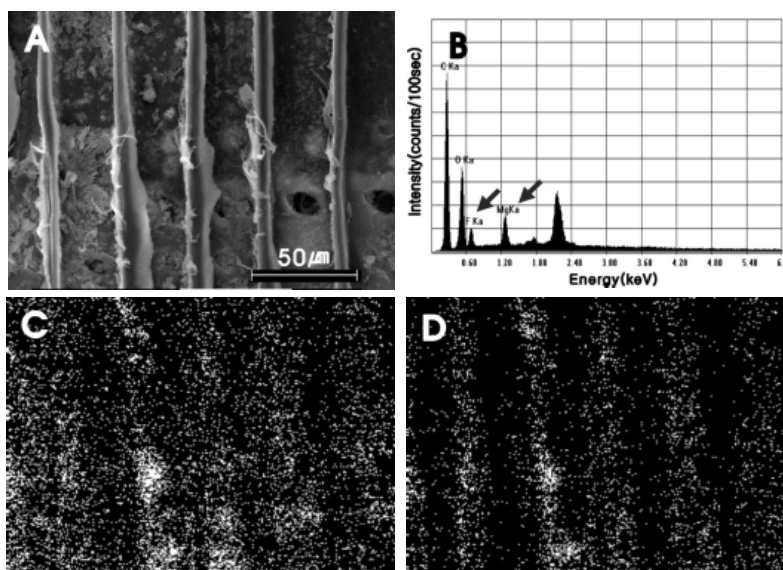


Fig. 3. SEM-EDX micrographs of a radial section of a specimen treated with 10% magnesium chloride solution and saturated solution of ammonium chloride (WPGs 6.1%) ; A : Secondary electron image, B : Characteristic X-ray spectra, C : Distribution map of Mg-K α X-rays and D : Distribution map of F-K α (D) X-rays.

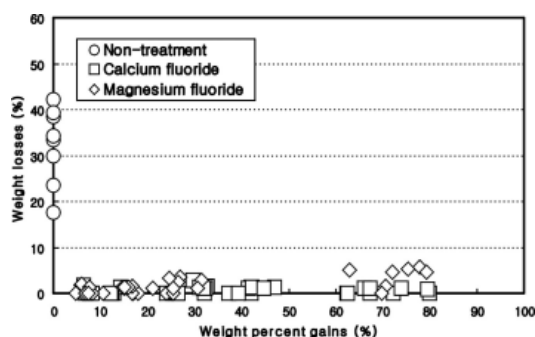


Fig. 4. Relationships between weight losses and weight percent gains of specimens after 3 months exposure to *Tyromyces palustris*.

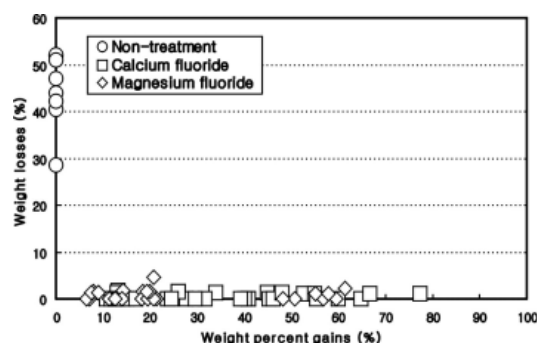


Fig. 5. Relationships between weight losses and weight percent gains of specimens after 3 months exposure to *Trametes versicolor*.

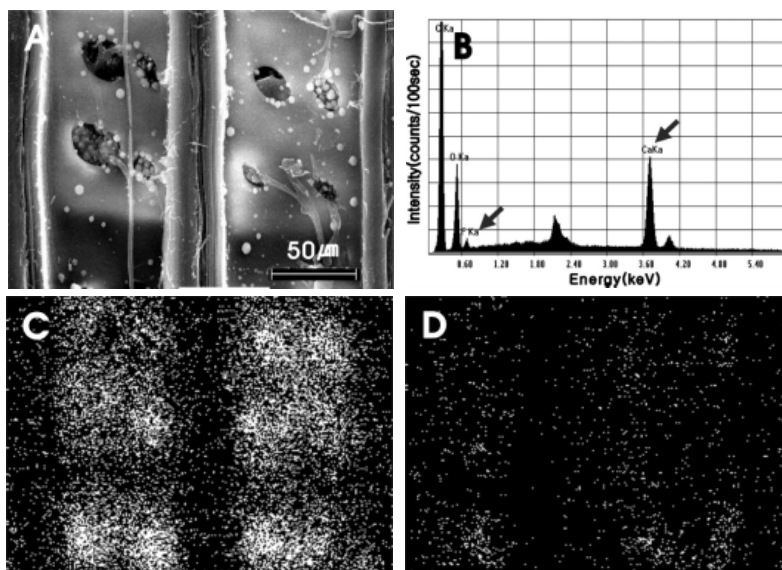


Fig. 6. SEM-EDX micrographs of a radial section of a specimen after 3 months exposure to *Trametes versicolor* ; A : Secondary electron image, B : Characteristic X-ray spectra, C : Distribution map of Ca-K α X-rays and D : Distribution map of F-K α (D) X-rays. This specimen was impregnated with 20% calcium chloride solution, and then soaked in saturated solution of ammonium chloride (WPGs 23.6%).

ustris were found in the lumina of tracheids and cross-field pitting of pinoid type (Fig. 6A). Though the hyphae penetrated into cells of treated wood, the cell walls were not decomposed by hyphae. Furthermore, the substances in granule were remained in the lumina of tracheids and cross-field pitting in spite of decay testing

for 3 months (Fig. 6A), and these were identified as calcium fluorides by spectra (Fig. 6B) and distribution maps of Ca-K α and F-K α X-rays (Fig. 6C and D). Therefore, it can be estimated that the calcium or magnesium fluoride formed in treated wood was significantly effective on decay resistance.

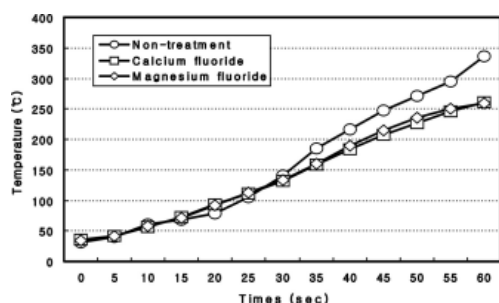


Fig. 7. Relationships between temperatures on the back sides of specimens treated with saturated solution of calcium chloride (WPG 60.9%) or magnesium chloride (WPG 65%) and ammonium fluoride and the burning times in the fire-resistance test.

3.4. Fire Resistance

Fig. 7 shows a relationship between the temperature and burning time for the specimens treated with saturated solution of calcium chloride, magnesium chloride and ammonium chloride. The temperature on the back side of the specimens began to rise as soon as burning by microburner flame because of thin thickness (2 mm) of specimens. The temperature on the back side of all specimens increased with increase in the burning time. However, with the lapse of burning, there showed a difference in the rising of temperature between untreated and treated specimens. From 35 sec after burning, the temperature of treated specimens was lower than that of untreated specimen, and the difference of temperature was enlarged with increase in the burning time. From these results, it can be estimated that fluorides produced in the wood contribute to the improvement of the fire resistant effect of wood. However, it requires further research to prove that these substances are effective in fire resistance.

4. CONCLUSION

We found that there were inorganic sub-

stances in the lumina of tracheids and cross-field pitting of the woods for both treatments of calcium and magnesium. These substances were proved to be the calcium fluoride or magnesium fluoride by analysis of SEM-EDX. WPGs were distinctively higher in calcium chloride treatment. From these results, we could assume that the woods treated calcium chloride were effective in resistances of decay and fire compared with treatment of magnesium chloride under intrinsic treatment of ammonium fluoride.

Conclusively, the calcium fluoride would be desirable as the substance of fire and decay prevention.

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