CEM Techniques and X-ray Analytical Microscope Analysis for Evaluating the Combustion Emissions and Char of CCA- and ACQ-Treated Woods after QUV Degradation

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CEM Techniques and X-ray Analytical Microscope Analysis for Evaluating the Combustion Emissions and Char of CCA– and ACQ–Treated Woods after QUV Degradation

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Two types of preservative–treated woods, CCA– (chromated copper arsenate) and ACQ– (ammoniacal copper quats) treated specimens, and *Taiwania cryptomerioides* Hay (Taiwania), as a control specimen, were used in this study. They underwent an accelerated weathering test that consisted of QUV degradation for 0, 104, 200, 400, and 800 h. The emission gas concentrations of O2 and CO2, the emission contents (CO, SO2, and NOX) and the temperature of the emission gases during the combustion of the specimen were measured using Continuous Emission Monitoring (CEM) techniques. X-ray Analytical Microscope (X-ray) Analysis and Elemental Analysis (EA) were used to examine certain residual elements of the char as well as particles from each specimen before combustion. The objectives of this study were to investigate the pollutants from both preservative–treated woods, compare them with those of Taiwania, and assess them as a reference of emission quantity for air pollution. When the specimens that had been subjected to QUV degradation were combusted, the emission gas temperatures of all specimens rose rapidly to about 210–235 °C, then increased slowly up to 260–270 °C and then lowered back down to a steady temperature in the 210–220 °C, shown as a plateau curve. The concentration of O2 decreased linearly from 20.7% to about 16.4–17.5%, and the concentration of CO2 increased from 0.2% to about 2.3–3.4%. Both O2 and CO2 had a close relationship during the combustion. The highest emission quantities of CO and NOX for the CCA–treated specimens were about 264.5–354.0 and 7.7–13.0 ppm, respectively. For the ACQ–treated specimens the ranges were 131.5–281.5 and 23.5–29.5 ppm, respectively, respectively. SO2 was not found in the emission gases during combustion of either of the preserved specimens. The result of the X–rays indicated that for the CCA–treated specimens, the main metal elements Cr, As, and Cu decreased from 0.0676 to 0.0320%, 0.0090 to 0.0079% and 0.0187 to 0.0089% respectively, but Cu for the ACQ–treated specimen decreased from 0.1198 to 0.0010%. The result of the EA indicated that prior to combustion, the amount of N (0.30%) is higher for the ACQ–treated woods than that for the CCA ones; therefore, the NOX gases during combustion were higher for the ACQ–treated woods.

**Keywords:** Preservative–treated woods, Combustion Emissions, Char, QUV degradation

INTRODUCTION

The increased outdoor use of wood products is due to their protection with various preservatives, e. g. chromated copper arsenate (CCA) and ammoniacal copper quats (ACQ). In preservative treated–woods research a great deal of attention is always paid to the influence of amount of leaching that takes place after having been used in various outdoor applications for a longer period of time. This is because the larger the amount of leach-
quantity of CO emission was about 159.3 ppm for the ACQ specimen and 108.0 ppm for the CCA specimen. The quantity of SO₂ emission for both types of samples was zero. The maximum NOₓ for the ACQ specimens was about 23.5 ppm and the basic pollutant was from BK (N-alkyl benzyl dimethyl ammonium chloride) during the combustion. The result of the EDX (Energy Dispersive X-ray Spectrometer) analysis showed that the relative proportion of Cu was 2.67% for the ACQ specimen, and that ACQ–1 (the type 1 of ACQ) was left with a high amount of Cu, 50.14%, but that the char of the CCA specimen had an amount of Cr (7.38%) that was obviously higher than that of As (4.08%) and Cu (5.18%).

The objectives of this research were to investigate the combustion emissions and char of CCA– and ACQ–treated woods after QUV degradation, an accelerated weathering test. Our goals were to obtain a reference for the gas emitted creating air pollution and hopefully to acquire a fundamental knowledge of the residual elements of the char. The examination in this study has been divided into two categories. The first is related to the research in combustion emissions from preservative–treated woods before/after QUV degradation, using a continuous emission monitoring (CEM) technique. The second category of examination applies the X-ray analytical Microscope analysis (X-ray) and Elemental Analysis (EA) to examine certain residual elements of the preservative–treated specimen combustion. The emissions from the discharge gases during the preservative–treated specimen combustion before/after QUV degradation and the residual elements of the char before/after combustion were investigated, respectively.

MATERIALS AND METHODS

Preparations of the control specimen and the preservative–treated woods

Taiwania cryptomerioides Hay (Taiwania), was used as the control specimen (untreated wood), and two types of commercial Chromated Copper Arsenate (CCA)– and Ammoniacal Copper Quats (ACQ)–treated woods (Taiwania), were provided by Kunnyih Co. Ltd., Taiwan.

All specimens were clear wood, measuring 110 mm long × 75 mm wide × 6 mm thick. They were prepared and air-dried at ambient temperatures until they had a moisture content of less than 15.0%. The manufacturing standard of the preservative–treated woods was in accordance with CNS 3000 01018 (2001). Two types of wood preservatives were used: type 3 of CCA (CCA–3) and type 1 of ACQ (ACQ–1). The basic contents and the basic properties of both wood preservatives were the same as in previous reports (Lin et al., 2006; Lin et al., 2007). The “Breant–Bethell” procedure, a full–cell treatment was applied using a laboratory type of pressure impregnation facility. The condition of the full–cell treatment and the average amount of impregnation of both wood preservatives were the same as in previous reports (Lin et al., 2006; Lin et al., 2007). Both treated woods are considered grade k 3 in the CNS 3000 (2001) in Taiwan. All specimens underwent the accelerated weathering test prior to the emissions test of the discharge gases during combustion.

Basic properties of the preservative–treated specimens

Density and moisture content

All specimens were conditioned to equilibrium at 20 °C with 65% relative humidity (RH) for about four weeks. The average density and moisture content of Taiwania and either the CCA– or the ACQ–treated specimen before QUV degradation were measured in accordance with CNS 451 O2002 (1996) and CNS 452 O2003 (1996), respectively.

Surface texture

The surface texture of each specimen was measured using a surface texture–measuring instrument (Semitsu, Tokyo). The average degree of surface texture on the centerline of the specimen (Ra), the degree of texture at the highest point on the surface of the specimen (Rmax), and the average degree of texture for ten points on the surface of the specimen (Rz) were measured.

Color value

The specimens for Taiwan and both CCA– and ACQ–treated specimens were measured using a colorimeter (Nippon Denshoku NR–3000) at 3 randomly selected spots. In the CIE 1976 L* a* b* color system employed in this study, color is considered to consist of three major dimensions: hue, chroma, and lightness. L* is the lightness or brightness variable and is generally the most important aspect of wood color changes to a viewer’s eye, while a* and b* represent the chromaticity (hue and chroma) coordinates.

Accelerated weathering tests

The accelerated weathering tests (QUV degradation) were carried out by a Q–U–V accelerated weathermeter (Q–Panel Co.). The conditions for an experimental cycle were temperature 60 °C with 4 h UV (ultraviolet) irradiations and temperature 40 °C with condensation of mist exposure for 4 h according to ASTM G53–83. Seventy–two specimens impregnated with CCA–3 or ACQ–1 and 18 control specimens were processed, that is, six replicates of each sample were prepared and treated with 0, 13, 25, 50, and 100 cycles. In other words, the course of QUV degradation was 0, 104, 200, 400, and 800 h. Afterwards, all specimens were investigated for emission from the discharge gases during combustion, and the chars were analyzed using an Elemental Analyzer and the X–ray analytical Microscope.

Experimental combustion methods

Continuous Emission Monitoring (CEM) techniques are widely utilized for detecting gaseous emissions such as CO, SO₂, NOₓ, and O₂ and CO₂ concentrations at the chimney exit of furnaces to determine the concentrations of various pollutants (Jang, 2000; Ladomersky,
of various specimens were statistically analyzed based on Duncan’s multiple range tests at 5% significant level analysis, using the Statistical Package for Social Science (SPSS) software.

RESULTS AND DISCUSSION

Basic properties

The basic properties, including density, moisture content, surface texture and color value, of Taiwania and both preservatives–treated specimens are shown in Table 1. Based on the type of specimen, the density and moisture content varied insignificantly (5%) by Duncan’s multiple range tests, expressed by the same letters, even for different types of specimens. The average moisture content of all specimens was about 12%, and the density at this moisture content was about 0.39 g/cm³. When comparing the surface texture between the control specimens and both preservative–treated woods, Duncan’s multiple range tests varied significantly. In general, a porous material can contribute to swelling/absorption of the constituents and change the direction of the microfibers after soaking with a water type of solution (Takeuchi, 2000). For the color value, the results showed that the changes for L* a* b* in both CCA– and ACQ–treated specimens were significant compared with the control. This is due to the types of experimental preservatives used: CCA–3 and ACQ–1 were deeply colored solutions; the color of CCA–3 is a yellow–green and ACQ–1 is a deep blue.

Emission gases from the control wood and the preservative–treated woods before/after QUV degradation

Figure 1 shows the relationships between emission gas temperatures, the concentration of O₂ and CO₂ and the combustion time for these specimens before/after QUV degradation. The gases emitted by 90 specimens during combustion were examined. The specimens were divided into 3 groups, including the control, CCA– and ACQ–treated woods, with 30 specimens in each group. In other words, the specimens were processed under accelerated weathering conditions for 104, 200, 400 and 800 h. The results were then compared with the control specimens of 0 h (unprocessed with QUV degradation).

The increase in emission gas temperature corre-
responded to the increase in combustion time for each type of specimen, increasing linearly to about 210–235 °C from the start of the combustion treatment. Subsequently, this increasing tendency resulted in a continuous but slow increase of the emission gas temperature to about 260 to 270 °C, and then lowered back down to a steady temperature in the 210–220 °C, shown as a plateau curve. The results of the change in O₂ and CO₂ concentrations showed that an increase of CO₂ and a decrease of O₂ corresponded to the increase in combustion time for the specimens shown in the middle and bottom of Fig. 1. The increase in CO₂ and the decrease in O₂ had a linear tendency from the start of combustion. The control and two types of preservative–treated specimens showed a range of O₂ concentration linearly decreasing from 20.7% to about 16.4–17.5%. On the contrary, the concentration of CO₂ increased from 0.2% to about 2.3–3.4%. The results also showed that the increase...
in CO₂ and the decrease in O₂ before QUV degradation were lower at either maximum or minimum point (about 115 to 117 sec) than after QUV degradation. This seems to indicate that the ignition point and/or the heat decomposition of the different preservatives may influence the combustion time and change the concentration of O₂ and CO₂ during gaseous emissions. After the peak point of CO₂ and the lowest point of O₂ were reached, the concentration of O₂ and CO₂ slowed down until complete combustion was reached at about 18.2–18.9% and 1.4–1.8% respectively. The concentration of O₂ showed to be negatively related and CO₂ showed to be positively related to the emission gas temperature. The concentration of O₂ and CO₂ are closely related to each other. This result agrees with those of previous works (Lin et al., 2001; Lin and Huang, 2004; Lin, 2005; Lin et al., 2007).

To show that the preservative–treated specimens produced serious pollution gases, CO₂, SO₂ and NOX, before/after QUV degradation, the combined results of the emission contents are shown in Fig. 2. The results showed that the peak for the CO gas of Taiwania were at 40 sec with 116.0 ppm; for the CCA specimens a maximum value of CO was obtained at about 115 sec with 108.0 ppm, and for the ACQ specimens the peak of the CO gas increased linearly to about 80 sec with 159.3 ppm. After that, all specimens before QUV degradation became a plateau curve and remained so until the end of the combustion time. However, the amount of CO gas for the specimens after processing with the accelerated weathering tests increased even though the emitted CO gas was the same as that of the specimens before QUV degradation. This indicates that the emission of CO gas is not only related to the ignition time (Ladomersky, 2000; Lin et al., 2001) of the specimens with different types of preservatives (Lin et al., 2007), but also to either CCA– or ACQ–treated wood resulting in incomplete combustion due to the influence of time degradation, inferring that the preservatives were leached from the surface of the specimens. The highest point of CO gas for Taiwania after QUV degradation was about 146.0–324.0 ppm, 264.5–354.0 ppm for CCA–treated wood, and 131.5–281.5 ppm for ACQ–treated wood. When comparing the CO emitted quantity to that emitted by Taiwania and both preservative–treated specimens after QUV degradation, it shows that the specimens treated with CCA–3 produced the highest quantity and were also higher than the specimens before QUV degradation by about 250 ppm.

As expected, in this experiment there was no emission of SO₃ in the emission gases during the combustion of Taiwania and both preservative–treated specimens before/after QUV degradation because the sulphur content was not included in 2 types of preserved woods from their typical chemical compounds (Nicholas and Schultz, 1994). It is suggested that the specimens treated with either CCA–3 or ACQ–1 before/after time degradation in this study are not the origin of the SO₂ in environment when it comes to final disposal (combustion).

The results in Fig. 2 also show that the Taiwania and both preservative–treated specimens before/after QUV degradation all produced the emission gas, NOX. However, during the combustion of Taiwania and the specimen treated with CCA–3 they produced less NOX than the specimens treated with ACQ–1, even though all specimens were processed with different time degradation. Lin et al. (2007) reported that ACQ–1 and BKC were more significant for the emission of NOX during combustion. This is because the main combinations of ACQ–1 are BKC, and in addition nitrogen (N) is also included in the BKC (Nicholas and Schultz, 1994). This indicates that NOX is a main source of pollution in wood with ACQ–1, even if the specimens treated with ACQ–1 were processed by different time degradation. The maximum NOX for the specimens treated with ACQ–1 before/after time degradation was about 23.5–29.5 ppm. The NOX gas was higher than that of the Taiwania (12.5–18.0 ppm) and the specimens treated with CCA–3 (7.7–13.0 ppm).

**Char from preservative–treated woods before/after QUV degradation**

An X-ray analytical microscope analyzer including a fluorescence X-ray can be applied directly to the material to check for harmful elements. It is a powerful tool for studying the minerals, expressing by relative percentage (%), in a material, especially for heavy metal trace elements, such as Cr, As, Cu etc. In this portion of the experiment, all specimens before/after being burned in a 45° flammability test cabinet were analyzed with a fluorescence X–ray analyzer (X–ray). The results are shown in Table 2.

The main elements of Taiwania and both preservative–treated woods before QUV degradation were CH₄, 99.9999% for the Taiwania, 99.9047% for the specimens treated with CCA–3, and 99.8802% for the specimens treated with ACQ–1. After combustion, the relative percentage of CH₄ was the same as the control specimen before the combustion, 99.9999%, but CH₄ gradually increased through the time degradation for both preservative–treated specimens. The results for the CCA–treated specimens showed that CH₄ decreased to 99.9300% for 200 h of QUV degradation, 99.9376% for 400 h and 99.9512 for 800 h. For the ACQ–treated specimens, CH₄ decreased to 99.9072% for 200 h, 99.9989% for 400 h and 99.9990 for 800 h. It is suggested that wood treated with either CCA–3 or ACQ–1 is basically considered to be a type of cellulose material (Humphrey, 2002), even if it has been through time degradation and combustion.

The results also showed that for CCA–treated specimens, the main metal elements (Cr, As, Cu) decreased through the time degradation; Cr went from 0.0676 to 0.0320% during 0 to 800 h, As went from 0.0090 to 0.0079% and Cu from 0.0187 to 0.0089%. As to the results of the ACQ–treated specimens, Cu decreased from 0.1198 to 0.0010% during 0 to 800 h of QUV degradation. These findings indicate that three types of compounds, CrO₃, AS₂O₅ and CuO, of CCA–treated woods and the main inorganic compound, CuO, of ACQ–treated wood had been leached out in the course of the time.
degradation. From the above results, it is evident that the amount of leaching of the main element from the CCA–treated wood was less than that of the ACQ ones. This is because the fixation of CCA preservatives in the wood is better than that of ACQ one (Lebow, 1996; Temiz et al., 2006). Moreover, based on time degradation, the variation in Cr content was insignificant (5%) by Duncan’s multiple range tests, expressed by the same letters, indicating that Cr from the char of the CCA preservatives is a stable element. This result agrees with those of previous works (Hirata et al., 1993; Kercher and Nagle, 2001; Cooper, 2003; Helsen and Bulck, 2005; Lee et al., 2005; Lin et al., 2007).

Furthermore, the specimens before/after having been examined in a 45° flammability test cabinet were analyzed with the Elemental Analyzer (EA). The results are shown in Table 3. The high level of carbon (C) for all specimens was about 75–80% after combustion was obtained, compared with the specimens (about 49.24–49.49%) before combustion. The results also show that before combustion, the amount of N (0.30%) was higher for ACQ–treated specimens than that for the Taiwania and the CCA samples, and that after combustion the N element decreased significantly (5%) by Duncan’s multiple range tests, expressed by different letters. This infers that the ACQ–treated specimen can produce substantial amounts of NOX gases (Fig. 2) during combustion, even if the specimen has been time degraded. The above results suggest that by using X–ray and EA to analyze the residual elements in char, the results can provide experimental data for referencing the char of preservative–treated woods.

CONCLUSIONS

This paper examined the emission gas concentration of the preservative–treated specimens before/after QUV degradation under combustion. The concentration of O2 was negatively and that of CO2 was positively related to the emission gas temperature. The main pollutants dur-
ing combustion were from the incomplete combustion and the chemical compounds of the preservatives. They are the main variables relating to the majority of emission contents (CO, NOX), and the change of O2 and CO2 concentration in the air, even if the specimens were processed by QUV degradation. SO2 was not produced during combustion because the two types of water-based preservatives used did not have a sulfur-base.

The emission contents of preservative-treated woods after QUV degradation were higher than before QUV degradation, especially for CO gas. This is because the incomplete combustion occurring due to the influence of time degradation. The NO2 content in the emission from the combustion of ACQ-treated woods were found to produce more pollution gas than the others, even if the specimen was processed by time degradation. The result of the X-ray analysis indicated that the main element of this pollution gas was more than 95–99% CH2 for the char after combustion. The results of the Cr, As and Cu analysis showed that the char of both preservative-treated specimens indicated the amount of leaching (%) that had taken place. The results of the EA analysis inferred that the ACQ-treated specimen produced NOX gases during combustion, because prior to combustion, the amount of N (0.30%) was higher for ACQ-treated woods than for the other specimens.

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