Migration of cesium chloride dissolved in the liquid water of sugi (*Cryptomeria japonica* D. Don) during drying at 65 °C

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Migration of cesium chloride dissolved in the liquid water of sugi (*Cryptomeria japonica*) during drying at 65°C

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Abstract: The objective of this study was the visualization of the migration of a dissolved substance in the liquid water of wood during drying by means of X-ray imaging. The formation of a characteristic deposition pattern has been observed in the course of drying small pieces of sugi soaked in a cesium chloride (CsCl) aqueous solution. Expectedly, CsCl migrated from the inside to the surface and was deposited just below the surface because of the evaporation of water at the evaporation front. At the end of the drying process, the relative concentration of CsCl at the surface of sapwood samples was determined to be 130–400% of the initial amount of dissolved CsCl, while the CsCl concentration deep inside samples was below 50%. Sapwood accumulated more CsCl than heartwood, and the CsCl concentration in latewood was higher than in earlywood.

Keywords: cesium chloride (CsCl), *Cryptomeria japonica*, migration mechanism, redistribution during drying, X-ray imaging

Introduction

A brown discoloration (kiln brown stain) often develops approximately 0.5–1.5 mm under the timber surface after kiln drying (Kreber and Haslett 1997) and causes quality defects, especially for radiata pine (*Pinus radiata*). The browning is caused by Maillard reactions in the presence of dissolved sugars and amino acids in sapwood (sW) (McDonald et al. 2000).

5 King et al. (1974), Terziev et al. (1993), and Theander et al. (1993) reported that kiln drying created a certain gradient of soluble nitrogenous or carbohydrate substances across the inside to the surface of wood. Terziev (1995) suggested that the migration of these substances from the inside to the surface is related to the movement of liquid water in addition to the chemical sugar conversion taking place at high temperatures.

10 Wiberg and Morén (1999) observed by an X-ray approach the rapid formation of a thin dry shell at the surface of sW during drying, while high moisture content (MC) was detected just below this shell. A steep MC gradient was therefore found between them, and a kind of evaporation front was formed 0.5–1.0 mm below the surface, where it remained for a long time. Accordingly, the formation of a kiln brown stain ca. 1.0 mm under the timber surface
15 could be caused by sugars and amino acids dissolved in the sap and that then accumulate at the evaporation front. Salin (2008) calculated the amount of water evaporation at different locations of sW during drying by means of a percolation simulation model with a 30-fiber-thick damaged layer due to the rough sawing process. The most evaporation occurs at ca. 1.0 mm below the lumber surface, which is 35–40 times the amount of water initially

present at that location.

In this context, the migration mechanism of a spilled coffee drop is conclusive (Deegan et al. 1997). Colloids in a drying coffee drop migrate to the edge of the drop and produce ring-like stains at the completion of drying. This so called coffee-ring effect occurs only when the edge of the drop is pinned during drying (Deegan 2000). Droplet size and the shape of colloids also affect the coffee-ring effect (Shen et al. 2010; Yunker et al. 2011). Non-uniform deposition has also been observed in droplets containing nanoparticles (Bigioni et al. 2006) or salts (Kaya et al. 2010).

One environmental concern in Japan is radiocesium (^{137}Cs) contamination of forest and forest products after the Fukushima Daiichi nuclear disaster. Fallout ^{137}Cs is transferred into trees through direct deposition from the air onto the trees and absorption from soil through tree roots (Hasegawa et al. 2009). Kuroda et al. (2013) investigated the contamination levels of ^{137}Cs in wood and bark samples of sugi (*Cryptomeria japonica*), akamatsu (*Pinus densiflora*), and konara (*Quercus serrata*) collected from natural forests in Fukushima Prefecture approximately 6 months after the disaster. The authors detected ^{137}Cs not only in the bark but also in sW and heartwood (hW) and found its concentration of hW less than half of that in sW. Ca. 50–90% of ^{137}Cs in aerosols is soluble in water (Tanaka et al. 2013) and thus it is partly dissolved in the sap of wood. ^{137}Cs dissolved in the sap of green lumber could accumulate at the surface during kiln drying in the same manner as described for organic

compound discussed above but this has not yet been confirmed.

X-ray imaging techniques have several advantages for observing the migration of Cs in wood. The Cs atom has a high X-ray attenuation coefficient because of its large atomic number. The mass attenuation coefficient of Cs with 40 keV photons is ca. 90 times more than that of water (Hubbell and Seltzer 2004; Ida 2008). The non-destructive X-ray imaging enables the continuous observation of Cs distribution in an intact piece of wood. The X-ray densitometry approach is quantitative and permits the determination of certain substances in the same manner as that of MC (Watanabe et al. 2008; Tanaka et al. 2009).

The present paper is aiming at the quantitative observation of dissolved Cs in wood during drying. To this purpose, wood impregnated with CsCl will be dried and the migration of Cs should be observed by X-ray densitometry. The differences of Cs migration between sW and hW as well as earlywood and latewood will also be in focus. The expectation is that new insights will be gained concerning the movements of water soluble extractives during drying in general and in terms of the handling of radiocesium contaminated wood in Japan.

Materials and methods

Twenty sugi (*Cryptomeria japonica*) samples with dimensions of $15 \times 15 \times 15 \text{ mm}^3$ (RxTxL) were cut from two lumber and four trees (Table 1) with a circular table saw. Half of them were soaked in an aqueous solution of 3% (wt) cesium chloride (CsCl) and the rest were

soaked in distilled water. A lower pressure of 10 kPa was intermittently exerted on samples to saturate them with the solutions. Then, the saturated samples were softly wiped with cleaning tissues.

X-ray apparatus: SR-1010, Softex Co., Ltd., Ebina, Japan equipped with a digital X-ray sensor (NX-04H, Softex Co., Ltd., Ebina, Japan). Samples were scanned from three different directions (40-kVp tube voltage, 14-mA tube current, 1.0-mm-thick aluminum filter). Samples were exposed to X-ray for 1 s, and the scanned image was saved in a “.dcm” format at a resolution of 5340×5000 pixels (20 pixel mm^{-1}) in 12-bit (0–4095) grayscale. Samples were then placed in a conditioning chamber at 65°C and 32% RH for drying. The samples were removed from the chamber after 20, 50, 71, 91, 126, and 220 min of drying, scanned, and then immediately placed back into the chamber. Experiments were stopped after 220 min of drying because the weights of samples soaked with distilled water were lower than their air-dry weights.

Fourteen poly(methyl methacrylate) (PMMA) plates of various thicknesses (1.0–30 mm) were also X-ray scanned with the parameters indicated above. Based on this image, the thickness of PMMA y to the brightness value, x were derived by the Eq. 1:

$$y = -26.65 \ln x + 209.12 \quad (\text{Eq. 1})$$

All X-ray images were converted to PMMA-equivalent-thickness distributions (PMMA-EThD) according to Eq. 1. Changes in PMMA-EThD before soaking and after

drying were evaluated by subtracting the PMMA-ETHD before soaking from that after 220 min drying. To avoid sample deformation during drying, images were registered by ImageJ 1.45s (Wayne Rasband, National Institute of Health, USA) and its extension bUnwarpJ 2.6 (Ignacio Arganda-Carreras, Massachusetts Institute of Technology) before subtracting.

- 5 Changes in the PMMA-ETHD predominantly indicate the concentration distribution of deposited CsCl at the end of drying because of the 90 times higher X-ray attenuation of Cs compared to water (see Introduction). The concentration distribution of deposited CsCl compared to initially dissolved CsCl was determined by dividing the changes in PMMA-ETHD at each pixel by the average value of the change in PMMA-ETHD.

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Results and discussion

- Figure 1 shows X-ray images of the tangential sections of samples during drying. An almost uniform brightness was observed in samples soaked in CsCl solution before drying. However, a sharp contrast between the surface and subsurface of wood was formed gradually during drying. Figure 2 shows the changes in the brightness profiles between the lines T and L in Figure 1. As drying progressed, a lower brightness was observed approx. 0–2 mm below the surface of each section, indicating the accumulation of Cs on the surface during drying. The contrast between the surface and subsurface was absent in samples soaked with distilled water (Figure 1), which is an additional proof that the accumulated substance was CsCl. The
- 15

micrographs in Figures 3 and 4 show the cross and radial sections of samples obtained before and after drying, respectively. The accumulation of CsCl was also observed on the surface of the tangential sections of samples. It is obvious that Cs initially dissolved in sW migrates from the inside to the surface during drying and accumulates just below the surface once drying is completed.

Figure 5 shows the brightness profiles during drying over lines T' and L' shown in Figure 1. After 20 min of drying, a steep brightness gradient was observed at the surface, indicating the formation of an evaporation front. The sharp front gradually receded in deeper layers and then nearly disappeared at approx. 1.5 mm below the surface after 91 min drying.

The MC of the resulting sample was 66%, which is only 36% higher than the average fiber saturation point (FSP) of wood (Glass and Zelinka 2013). Because the initial MC was greater than 200%, at least 8 to 10th of liquid water evaporated mainly from the evaporation front.

The trace of the evaporation front shows that it is within close proximity to the line where the most accumulation of CsCl took place (Figure 2). Thus the deposition of dissolved substances

occurs at the evaporation front. The trace of the evaporation front makes also visible the ca. 1 mm thick damaged surface layer caused by the circular saw during sample preparation.

Figure 6 shows the distribution of the relative concentration of CsCl in sW samples at the end of the drying process compared to that of initially dissolved CsCl. The concentration of CsCl just below the transverse surface was 200–350%, whereas its concentrations below

the radial and tangential surfaces were 150–300% and 130–200%, respectively. Surface accumulation occurred on all sample surfaces, but the concentration of CsCl depended on the grain direction. In contrast, the concentration of CsCl at the center of each image shown in Figure 6 was ca. 50%. Considering that the values in the images shown in Figure 6 account for accumulated CsCl at surfaces perpendicular to the X-ray transmission direction, its concentration deep inside the samples probably dropped below 50%.

The observed surface accumulation effect in the present study is not as strong as that in the simulation results reported by Salin (2008). This author estimated the amount of precipitated compounds 1.0 mm below the timber surface to be 35–40 times more than the initial amount dissolved in the sap when the effect of diffusion was ignored. Taking into account the effect of diffusion, deposited Cs at the evaporation front will start to move toward the inside in accordance with a gradient of Cs concentration. In case of the small samples in the present study, the lower effects of surface accumulation are imperative compared to the larger samples observed in the quoted study. Furthermore, sample species and drying temperature might also have affected the strength of the surface accumulation.

Figure 7 shows the relative concentration of CsCl at the end of the drying process in the hW samples. The concentration just below the transverse surface in the hW samples was 150–200%, which is significantly lower than that in sW samples. These data agree with the low permeability of hW due to pit aspiration and encrustation with extractives (Siau 1995).

The accumulation of CsCl in latewood (LW) was greater than that in earlywood (EW) (Figures 6 and 7). This indicates liquid water in EW tracheids was less energetically stable due to wider pit pairs in EW tracheids (Siau 1995), and thus migrated to the evaporation front earlier. In contrast, liquid water in LW migrated later or was partly trapped in LW due to the energetic stability of liquid water in LW tracheids, resulting in local accumulation of CsCl in LW.

Conclusions

The results of this study indicate that CsCl initially dissolved in wood migrates from the inside to the surface during drying. A large amount of liquid water forms an evaporation front just below the wood surface during the drying process. At the end of the drying process, the relative concentration of CsCl at the surface of sW samples was determined to be 130–400% compared to the initial concentration of dissolved CsCl. The concentration of CsCl inside samples was probably below 50%. Sapwood accumulates more CsCl at the surface than hW, and the concentration of CsCl in latewood is higher than that in earlywood. Concerning the radiocesium (^{137}Cs) from contaminated forests in the Fukushima region, it is recommendable to plane the surface of dried wood before commercialization.

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Table 1. Testing samples of heartwood (hW) and sapwood (sW) of lumbers and trees of different origin.

Lumber and tree and their origin	Sample no.	sW or hW	Density at (20°C, 65% RH)	Solution for soaking
Lumber 1*	1s_Cs	sW	0.31	CsCl aq. sol.
	1s_w	sW	0.32	Distilled water
Lumber 2*	1h_Cs	hW	0.32	CsCl aq. sol.
	1h_w	hW	0.32	Distilled water
Tree 1**	2s_Cs	sW	0.42	CsCl aq. sol.
	2s_w	sW	0.43	Distilled water
	2h_Cs	hW	0.41	CsCl aq. sol.
	2h_w	hW	0.42	Distilled water
Tree 2**	3s_Cs	sW	0.39	CsCl aq. sol.
	3s_w	sW	0.38	Distilled water
	3h_Cs	hW	0.41	CsCl aq. sol.
	3h_w	hW	0.39	Distilled water
Tree 3**	4s_Cs	sW	0.34	CsCl aq. sol.
	4s_w	sW	0.36	Distilled water
	4h_Cs	hW	0.33	CsCl aq. sol.
	4h_w	hW	0.33	Distilled water
Tree 4***	5s_Cs	sW	0.26	CsCl aq. sol.
	5s_w	sW	0.26	Distilled water
	5h_Cs	hW	0.31	CsCl aq. sol.
	5h_w	hW	0.31	Distilled water

* Akita prefecture (plantation forest), ** Semboku, Akita prefecture (plantation forest), *** Kita-akita, Akita prefecture (natural forest)

Figure 1. X-ray images of tangential sections of sapwood samples before and after treatment with CsCl solution or distilled water and drying for 20 min, 50 min, 71 min, 91 min, 126 min, and 220 min. The vertical and horizontal directions of each image represent the longitudinal and tangential directions of each sample, respectively.

Figure 2. Brightness profiles of tangential and longitudinal directions (indicated by the lines T and L in Figure 1, sample 1s_Cs) during drying.

Figure 3. Cross sections of sapwood samples before and after drying.

Figure 4. Radial sections of sapwood samples before and after drying.

Figure 5. Brightness profiles along the lines T' and L' shown in Figure 1 (sample 1s_w) during drying.

Figure 6. Relative concentrations of cesium chloride in sapwood at the end of drying compared to initial cesium chloride concentrations.

Figure 7. Relative concentrations of cesium chloride in heartwood at the end of drying compared to initial cesium chloride concentrations.