

EFFECTS OF LEACHING MEDIUM ON LEACHABILITY OF WOOD PRESERVING N'N-HYDROXYNAPHTHALIMIDE (NHA)

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Laboratory leaching test procedures usually call for the use of distilled or deionized water; however, treated wood is generally exposed to different types of water, soil, and weather conditions. Thus, factors such as salinity, hardness, pH, temperature etc. might be important in the release of different amounts of biocide compounds. This study evaluates the release of the sodium salt of the calcium precipitating and wood preserving agent N'N-hydroxynaphthalimide (NHA) from treated wood specimens exposed to different types of leaching media. Scots pine wood specimens were treated with NHA at three different solution strengths. Treated specimens were then leached with distilled water, tap water, rain water, synthetic sea water, natural sparkling water, or 1% CaCO₃ solutions for 2 weeks. Leaching with higher ion concentrations reduced NHA losses from the specimens in comparison with that of distilled water and rain water leaching trials. Microscopic evaluations were in good accordance with the results from leaching trials, revealing NHA precipitation onto the tori of pit elements and tracheids. In distilled water and rain water leaching trials, less NHA precipitation on to the tori of pit membranes and tracheid surfaces was observed, whilst the specimens leached with tap water, 1% CaCO₃, sea water, and sparkling water showed higher NHA precipitations on the cell elements. We conclude that the leaching of NHA from treated wood can be decreased by precipitation with ions coming from tap water, sea water, sparkling water, and 1% CaCO₃ solutions as leaching media rather than distilled water or rain water with no or much less ion composition.

Keywords: Leaching; Leaching medium; NHA; N'N-hydroxynaphthalimide; Distilled water; Tap water; Seawater; Rainwater; Sparkling water

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INTRODUCTION

The leaching medium to which preservative-treated wood is exposed is one of the most important factors for evaluation of the leaching of preservative components from wood, since its type and properties determine the amount of the components released from treated wood. Standard test methods to evaluate leaching of wood preservatives generally require use of ion-free de-ionized or distilled water; however, organic and inorganic ions in water may affect the amount of preservative components to be released from treated wood in service (Kartal et al. 2004, 2007). A study by Kartal et al. (2007) indicated that tap water caused less preservative component losses from chromated copper arsenate (CCA)-treated wood blocks when compared to that of distilled water,

seawater, and humic acid at 1% concentration level. Less copper and chromium compared to arsenic was released when the blocks were leached with seawater, and humic acid was the most effective leaching medium, causing considerably higher component releases. Seawater may also affect leaching of copper, chromium, and arsenic elements from CCA-treated wood in service (Lebow 1996). Lebow et al. (1999) found that seawater had a mixed effect on the leaching of copper, chromium, and arsenic elements from CCA-treated wood. Their studies showed that the release rate of copper was much greater in seawater than in de-ionized water; however, arsenic release was greater in de-ionized water and chromium was not affected by seawater. Irvine and Dahlgren (1976) reported that the increased formation of complexes between chloride coming from salt solution and copper might explain the increased leaching of copper at salinities above 24 parts per thousand (ppt). Plackett (1984) stated that inorganic salts, as leaching solutions, caused increased copper leaching when compared to that of distilled water, and copper leaching increased with increased salt solution concentration.

In our previous study (Kartal et al. 2004), we showed that that seawater and tap water containing higher ion concentrations than distilled water resulted in less leaching of a wood preserving and calcium precipitating agent, N,N-hydroxynaphthalimide (NHA), from treated wood specimens. As a selective calcium precipitating agent, NHA-Na has been thought to disrupt normal calcium cycling in the fungal hyphae (Sobota et al. 1988). A number of previous studies have shown that brown-rot fungi, white-rot fungi, and termites are selectively inhibited by NHA-Na in treated wood (Green III et al. 1996, 1997, 2000; Kartal and Imamura 2004). Leaching experiments showed that the release of NHA from NHA-treated wood was reduced by leaching in seawater or by sequential treatment with CaCl_2 (Kartal et al. 2004). Kartal and Imamura (2004) also found that leaching by tap water resulted in more boron leachability from boron- and NHA-treated wood specimens when compared to distilled water; however, tap water caused less NHA release from treated specimens. Reduced NHA leaching is probably explained by the precipitation of NHA by divalent cations, such as calcium, present in the wood as Ca-NHA, and also by the acidic nature of the wood precipitating out the acid form of NHA (H-NHA) (Kartal et al. 2004; Kartal and Imamura 2004) (Fig. 1).

Our objective in the present study was to evaluate the effects of rainwater, natural sparkling water, seawater, and 1% CaCO_3 , along with distilled water and tap water, on NHA release from treated wood specimens.

EXPERIMENTAL

Materials

Scots pine (*Pinus sylvestris* L.) specimens, 19 by 19 by 19 mm, were cut from the sapwood portions of lumber. Before treatment, all specimens were conditioned at $20\pm 2^\circ\text{C}$ and $65\pm 5\%$ relative humidity (RH) for 2 weeks. The specimens were vacuum-treated with 1.0, 0.50, or 0.10% N,N-hydroxynaphthalimide, sodium salt (Na-NHA) (Fig.1). The vacuum cycle consisted of a 30-min vacuum (-88 kPa gauge pressure) period. All treated specimens were conditioned at $20\pm 2^\circ\text{C}$ and $65\pm 5\%$ RH for 2 weeks before leaching.

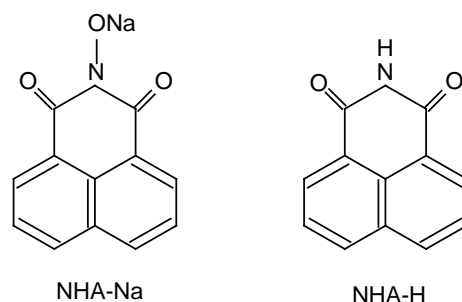


Fig. 1. Molecular formulas of NHA-Na and NHA-H

Methods

Leaching media

Different types of leaching media were selected containing different amounts and types of ions, since ions can affect biocide leaching. Properties of all leaching media used in the study are given in Tables 1 through 3. A bulk rainwater sample was collected manually on a daily event basis to reduce the amount of dust entering the sampler to a minimum. The rain sampler consisted of high-density polyethylene (HDPE) funnel and bucket. The rain water was collected in Istanbul, Turkey in August 2010. The 34-ppt dilution for seawater was chosen to represent typical seawater found in the open ocean, and was prepared from Instant Ocean (Aquarium Systems, Mentor, OH), a commercial synthetic sea salt that contains the major ions typically found in seawater, including Na^+ , Mg^{2+} , Ca^{2+} , and K^+ (Lebow et al. 1999). Natural sparkling water was provided by Turkish Red Crescent Mineral Water Enterprises, Turkey.

Table 1. Major Ion Composition of Instant Ocean Synthetic Sea Salt (Lebow et al. 1999)

Ions		Ionic concentration at 34 ppt salinity (mg/L)
Chloride	Cl^-	18,740
Sodium	Na^+	10,454
Sulfate	SO_4^{2-}	2,631
Magnesium	Mg^{2+}	1,256
Calcium	Ca^{2+}	400
Potassium	K^+	401
Bicarbonate	HCO_3^-	194
Boron	B	6.0
Strontium	Sr^{2+}	7.5
Solids total		34,089.50

Table 2. Ion Composition of Natural Sparkling Water *

Ions		(mg/L)
Fluorine	F	0.81
Phosphate	PO ₄	0.0033
Bicarbonate	HCO ³⁻	2123
Carbonate	CO ₃	0
Chloride	Cl ⁻	97.4
Nitrate	NO ₃	0
Nitrite	NO ₂	0
Silicium dioxide	SiO ₂	55.4
Sulfate	SO ₄ ²⁻	5.35
Sulfur	S	0.006
Aluminum	Al	0.07
Ammonia	NH ₄	0
Calcium	Ca ²⁺	40.8
Magnesium	Mg ²⁺	13.3
Potassium	K ⁺	5.4
Sodium	Na ⁺	770.4
Iron	Fe ²⁺	0.01
Antimony	Sb	0
Arsenic	As	0.01
Copper	Cu	0.01
Barium	Ba	0.005
Borate	B ₂ O ₃	25.76
Mercury	Hg	0
Cadmium	Cd	0
Chromium	Cr	0.005
Lead	Pb	0
Manganese	Mn	0.041
Nickel	Ni	0.001
Selenium	Se	0

*Based on chemical analyses run by the Ministry of Health by Turkish Red Crescent Mineral Water Enterprises, Turkey (www.kizilaymadensuyu.com.tr)

Table 3. pH and Hardness of the Leaching Media Used *

Leaching medium	pH	Total hardness (mg/L)	Ca-hardness (mg/L)	Ca (mg/L)	Mg (mg/L)
Distilled water	6.88	57.13	21.51	4.62	18.71
Tap water	7.56	387.11	129.04	51.72	62.97
Rain water	6.45	258.07	0.00	0.00	68.22
Natural sparkling water	8.54	559.16	150.54	40.80	13.30
Synthetic sea water	7.20	6021.68	1677.47	400.00	1256.00
1% CaCO ₃	8.10	N.D.	N.D.	N.D.	N.D.

* Analyses were run at the laboratory of Department of Watershed Management, Forestry Faculty, Istanbul University.

Leaching

The leaching procedures for the specimens were similar to the AWWPA Standard Method E11-06 (AWPA 2010). After the conditioning period, two replicate sets of five specimens for each treatment group were removed from the conditioning room and reweighed. Leaching sets of five specimens were chosen based on uptake of NHA retention in the specimens.

Each set of five specimens was placed into a 500-mL bottle, submerged in 250 mL of either distilled water, tap water, sea water, 1% CaCO₃, or natural sparkling water, and subjected to a vacuum to impregnate the specimens with the relevant leaching solutions.

The sample bottles were subjected to mild agitation, and the leaching solutions were replaced after 6 hours, 1 day, 2 days, and every 2 days thereafter, for a total of 14 days (6, 24, 48, 96, 144, 192, 240, 288, and 336 h). Leachates were collected after each leaching solution replacement and analyzed for NHA content.

NHA Content in Leachates and Wood

The leachates were analyzed for the amounts of NHA with a UV-VIS spectrophotometer at 340 nm according to Green III et al. (1989), Kartal and Green III (2002), and Kartal et al. (2004). Standard curves were prepared by plotting the absorbance values and concentrations of NHA standard solutions.

An unleached subset of treated specimens were ground to pass through a 40-mesh (0.420-mm openings) screen in the Wiley mill (Thomas Scientific, Swedesboro, NJ), and 1.5 g of ground wood was weighed to the nearest 0.01 g into a 250-mL flask. Then, 100 mL of distilled water was added to the flask containing the ground wood. The flask was placed in a water bath at 90 to 95°C for 60 min. The flask in the bath was shaken for 2 to 3 min every 15 min. After being cooled, the contents in the flask were filtered through Whatman #4 filter paper (Maidstone, England), rinsed three times with 20 mL of hot distilled water, and diluted to 200 mL in a volumetric flask. After being cooled, the solution was then analyzed according to the described UV VIS spectrophotometric method. More detailed discussion of this method can be found in Kartal and Green III (2002).

Microscopic Evaluations

Microscopic evaluations were performed on both leached and unleached wood specimens, treated with 1% NHA solution only and with untreated wood specimens. Only treated wood specimens were dry-cut into thin sections (about 30 µm) by using a Leica SM2010 R sliding microtome, whereas slides for untreated wood specimens were prepared by using standard techniques. The sections were mounted on Entellan-coated slides.

Evaluations were performed by using an Olympus BX51 Light Microscope, and images were taken by using analysis FIVE Software; a DP71 Digital Camera was installed and adapted on the microscope. All microscopic evaluations were realized only on radial sections.

RESULTS AND DISCUSSION

Table 4 shows retention levels of NHA in treated wood specimens. NHA retentions by uptake were slightly higher when determined by chemical analyses.

Table 4. NHA Retention in Wood Specimens

NHA concentration (%)	NHA retention ¹		NHA retention ²	
	(kg/m ³)	(g)	(kg/m ³)	(g)
1.0	5.21 (0.11)	0.0350 (0.0002)	5.24 (0.13)	0.0360 (0.0002)
0.5	1.75 (0.05)	0.0110 (0.0002)	1.81 (0.07)	0.0120 (0.0001)
0.1	0.67 (0.02)	0.0044 (0.0001)	0.69 (0.05)	0.0046 (0.0001)

¹Analysis by UV-VIS spectrophotometer ²Uptake retention

Values are the mean values of 120 and 3 treated wood specimens for each treatment group for uptake and analysis, respectively. Values in parentheses are standard deviations

The total NHA releases from the specimens leached with the leaching media employed in the study during the 14-day leaching course are shown in Table 5.

Table 5. Percentage Total NHA Loss from Treated Wood Specimens*

Leaching medium	NHA		
	1.0%	0.50%	0.10%
Distilled water	32.38 (2.14)A	57.08 (3.56)A	97.69 (4.12)A
Tap water	1.73 (0.34)D	4.75 (0.32)E	14.95 (1.24)E
Rain water	24.72 (1.18)B	24.32 (2.18)B	66.41 (2.98)B
Natural sparkling water	6.01 (0.45)C	15.94 (2.12)C	40.57 (3.12)C
Synthetic sea water	1.93 (0.11)D	7.55 (0.98)D	26.25 (1.87)D
1% CaCO ₃	1.50 (0.10)DE	4.24 (1.01)E	13.46 (2.09)E

* Values are the mean values of two leaching sets (two replicate sets of five specimens for each treatment group). Values in parentheses are standard deviations. The same letters on each column indicate that there is no statistical difference between the specimens according to Duncan's multiply range test ($p < 0.05$).

The NHA leaching rates during the leaching course are given in Fig. 2. The percentage of NHA leached decreased with increased NHA retention in the specimens. This phenomenon, which also was observed in our previous study, might be explained by both more precipitation of NHA on the ray parenchyma cells and tori of the pits with higher NHA retention and shell treatment of NHA at low treating concentrations of NHA (Kartal et al. 2004). Green III et al. (1997) stated that higher NHA precipitation and retention of NHA in wood may cause decreasing wood pit permeability (Kartal et al. 2004). The specimens with higher NHA retention levels may also tend to leach at a lesser rate because of less rapid movement of the leaching media. A similar phenomenon was reported by Kartal and Lebow (2002) that the appearance of greater leaching of CCA from wood that had lower retention is an effect of their lower original retention.

However, Lebow et al. (1999) found that the CCA retention level had a slight effect on the rate of copper, chromium, and arsenic release from treated lumber and piles. Kartal et al. (2007) found that the percentage of the CCA components leached was always higher in wood treated at high retention. A review study by Lebow (1996) pointed out that a number of previous studies have suggested that leaching does not increase in direct proportion to retention. Taylor and Cooper (2003) suggest that wood treated to lower initial preservative loading does not always leach less than higher retention samples.

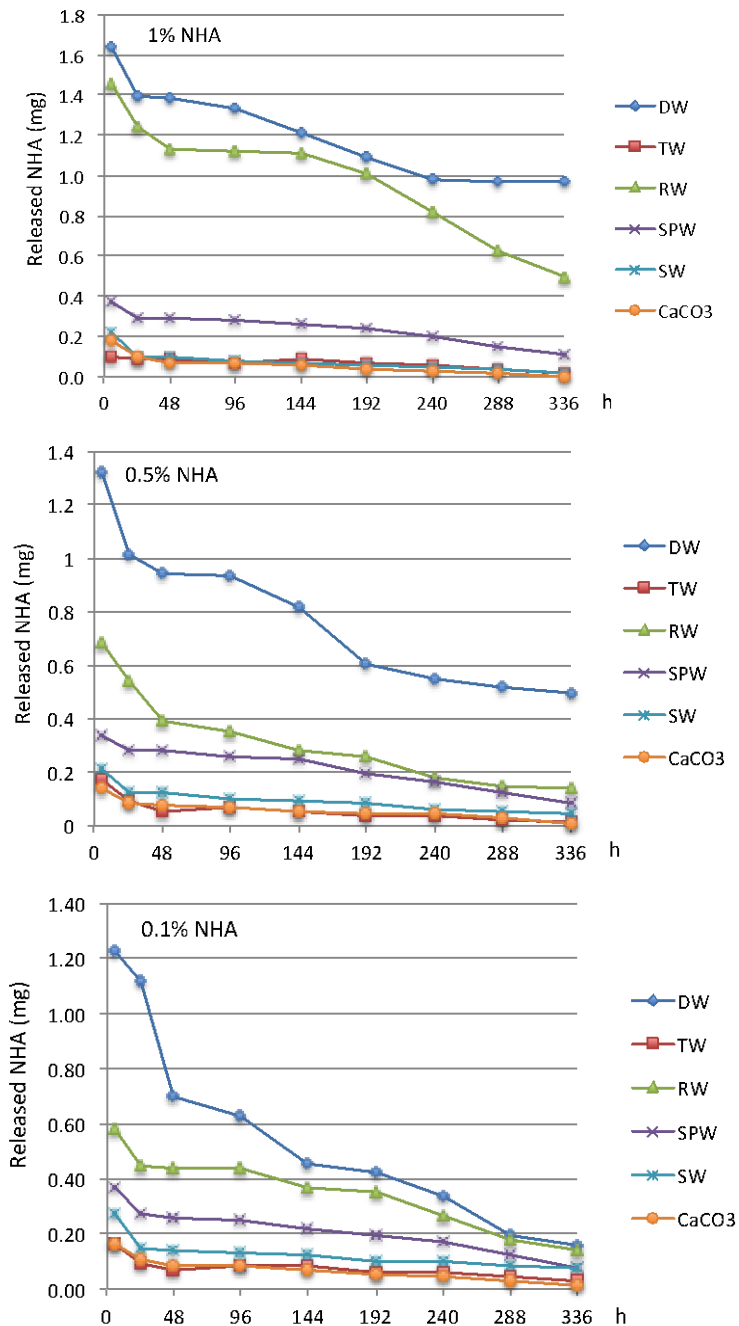


Fig. 2. NHA released from one wood specimen during leaching (hours). DW: Distilled water; TW: Tap water; RW: Rain water; SPW: Natural sparkling water; SW: Synthetic sea water

The highest NHA release in all treatment groups was seen in the distilled water-leached specimens (Table 5). NHA losses in 1% CaCO₃, tap water, sea water, and natural sparkling water were considerably lower than those in distilled water and rain water. The rating of amount of NHA release for the three retention levels was generally 1% CaCO₃ < tap water < sea water < natural sparkling water < rain water < distilled water.

The tap water, sea water, natural sparkling water, and 1% CaCO₃ employed in this study contained various ions such as calcium, magnesium, potassium, copper, sodium, chloride, bicarbonate, borate, etc.; however, distilled water and rain water had basically no, or much less, ions. One reason for less NHA release when ion-rich leaching media is used might be precipitation of ions with NHA in the wood. Such precipitation might have occurred on the wood surface or near the wood surface, as our previous study has discussed (Kartal et al. 2004). It is also possible to observe less NHA losses from wood placed outdoor where a wide range of natural ions are present. Microscopic evaluations in the study confirmed that the precipitation of NHA on to the torus of pit membranes is a result of NHA's precipitation mechanism on to pectin-rich wood elements (Green III et al. 1997).

Microscopic evaluations showed that the distribution of NHA was not uniform in wood specimens. It was observed that NHA localized in the lumen side of the longitudinal tracheid walls, which are not rich in pectin, and in pectin rich areas such as bordered pits of the both longitudinal tracheids and ray tracheids, and cross-field pits in the all specimens (Figs. 3a - 3c, Figs. 4a - 4b, Figs. 5a - 5b, and Figs. 6a - 6b).

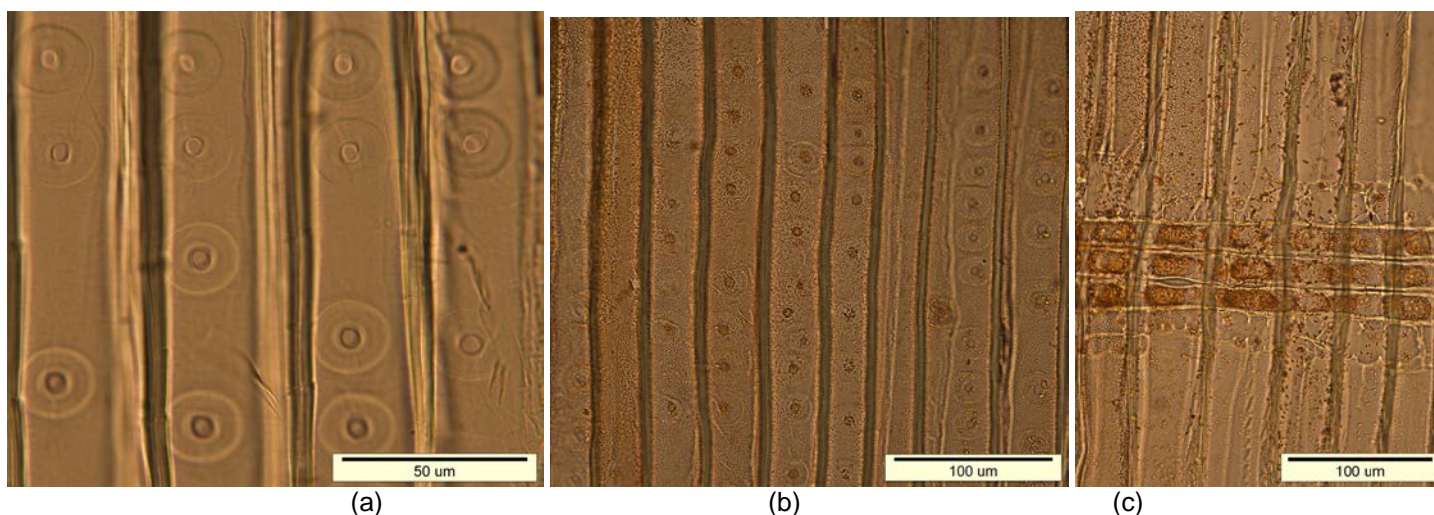


Fig. 3. Tracheids and pits in untreated wood (a), 1% NHA treated wood (unleached) (b) and (c)

NHA penetration in the longitudinal tracheids of earlywood regions was higher than that in latewood regions. While NHA showed a sandy-like distribution in the lumen side of longitudinal tracheids in earlywood regions close to the cross-section surfaces in all specimens, it was only seen in slightly bigger particle size in deeper parts of unleached wood specimens. Also, NHA was precipitated in cross-field pits and tori of pits in all specimens.

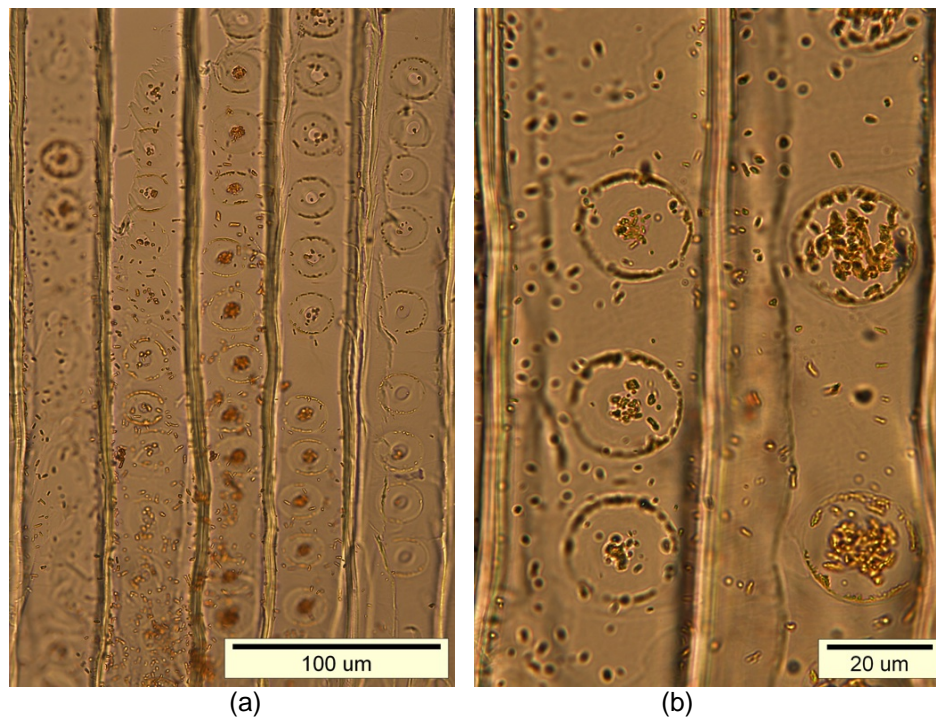


Fig. 4. Bordered pits in wood specimens leached with distilled water (a) and rain water (b)

However, the specimens leached with tap water, 1% CaCO_3 , sea water, and sparkling water showed a higher degree of NHA precipitation on to the all cell elements in some regions (particularly in earlywood), than the specimen leached with distilled water and rain water.

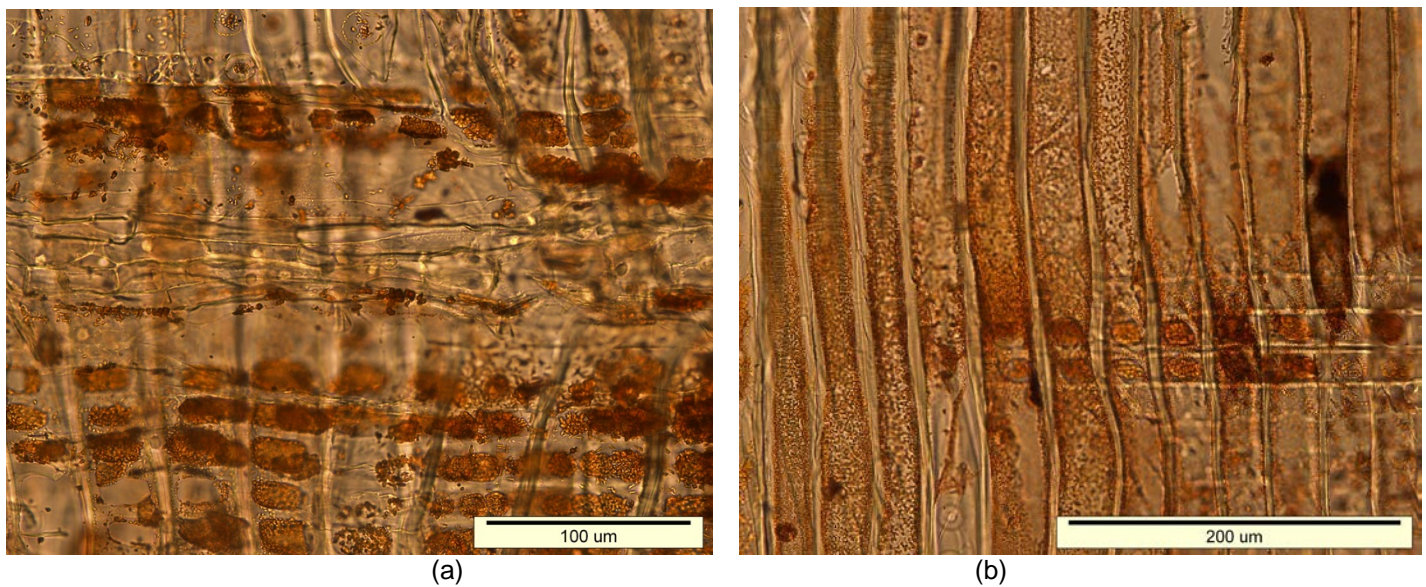


Fig. 5. Rays in wood specimens leached with tap water (a) and 1% CaCO_3 (b)

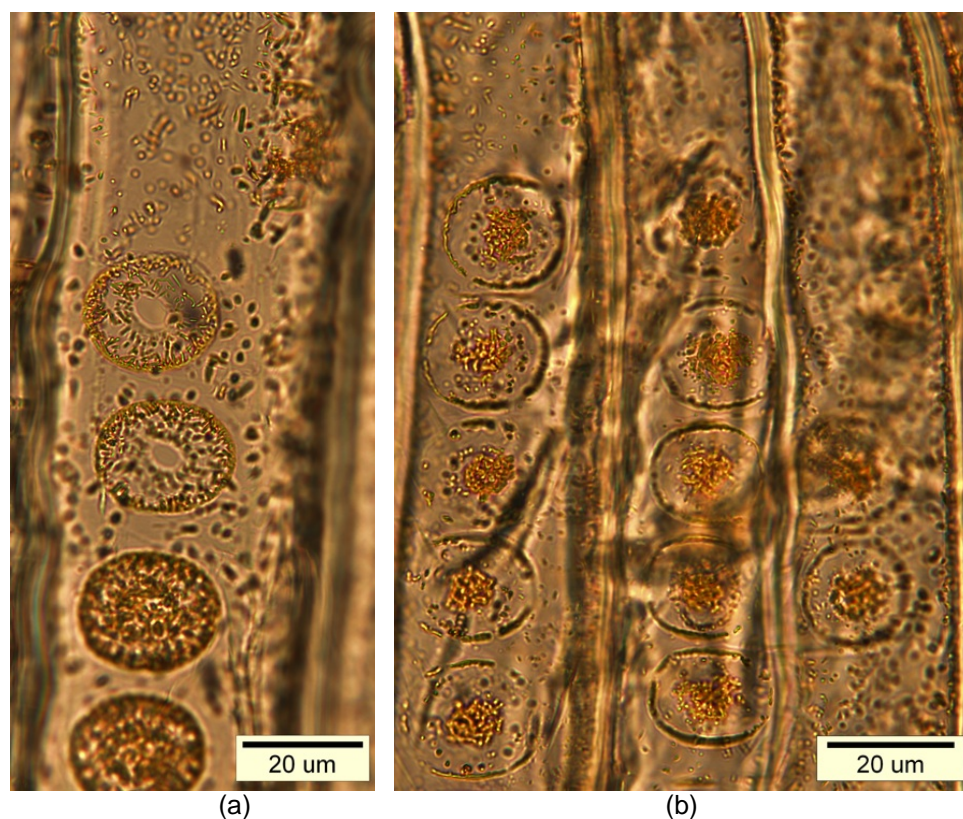


Fig. 6. Bordered pits in wood specimens leached with sea water (a) and sparkling water (b)

The results of microscopic investigations in all specimens, which were interpreted as the depth of penetration and amount of precipitation, are not only associated with the presence of pectin in the cell walls, but also the sizes of cells and pits.

Our previous studies showed that NHA losses from treated wood specimens in tap water and sea water at 34 ppt salinity were four times less than those in distilled water (Kartal et al. 2004), suggesting that ions such as Ca^{2+} from tap water and sea water may have precipitated with NHA in the wood. Another study by Kartal and Imamura (2004) indicated that NHA losses from wood specimens were always lower in tap water leaching when compared to that of de-ionized water; however, more boron was released from the wood specimens with tap water leaching.

Lebow (1996) noted in a review of the literature that the composition of wood preservatives could affect fixation reactions and amount of leached components from treated wood. Preservative retention levels in treated wood are also an important factor affecting fixation reactions (Kartal and Lebow 2001). In a study by Lebow et al. (1999), sea water always caused more copper losses from CCA-treated wood than de-ionized water. In that study, the rate of chromium leaching was consistently much lower than that of copper and arsenic, and not affected by the salinity of sea water. A study by Brown and Eaton (2000) showed that release of copper was always higher than release of chromium and arsenic in sea water from CCA-treated wood panels.

CONCLUSIONS

The type and composition of leaching medium, including various factors such as treatment and conditioning parameters, preservative formulation and retention, time exposed, wood species, size, and chemical composition, could affect the amount of wood preservatives released from treated wood. Leaching trials in this study confirm that the release of NHA leached by 1% CaCO₃, tap water, sea water, and natural sparkling water with high ion content can be reduced relative to leaching by ion-free water. The precipitation of NHA by such ions in the wood pits and other elements might explain this phenomenon. In distilled water and rain water leaching trials, where considerably higher NHA losses occurred, remarkably less NHA precipitation onto the tori of pit membranes and tracheid surfaces was seen. However, the specimens with the lowest NHA releases with tap water, 1% CaCO₃, sea water, and sparkling water leaching showed, again, higher NHA precipitations on the cell elements when compared to distilled water and rain water-leached specimens.

Results from leaching tests might play an important role in developing more realistic standard methods for evaluating component losses from treated wood in order to avoid unnecessary high preservative loadings, which might cause, in turn, higher preservative release to the environment. It is clear that the composition of rain water and tap water will highly depend on the geographic characteristics of a given country and change from location to location. Therefore, such leaching media cannot be standardized for leaching methods.

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