

# Effects of inorganic ions on leachability of wood preserving N'N-hydroxynaphthalimide (NHA)

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## Abstract

Southern yellow pine sapwood stakes and blocks were treated with the sodium salt of the calcium-precipitating compound N'N-hydroxynaphthalimide (NHA) and leach tested for 2 weeks using the American Wood-Preservers' Association (AWPA) standard. Leachates were measured for NHA using a microplate optical density ultraviolet reader, and leach rates were estimated for tap water, distilled water, and seawater. The percentage of NHA lost from blocks ranged from a low of 5.0 percent for seawater to 26.4 percent for distilled water. Clearly, higher inorganic ion concentrations in the leaching solutions resulted in less chemical leaching of NHA. To further reduce NHA leachability, additional groups of NHA-treated blocks were post-fixed with 2 percent CaCl<sub>2</sub>. With CaCl<sub>2</sub> post-fixation prior to leaching, the percentage of leached NHA was reduced to 4.3 percent for seawater and 12.7 percent for distilled water. Additional stakes were pressure-treated with aqueous NHA concentrations ranging from 0.1 to 2.0 percent and then leached in distilled water. The percentage of release of NHA in 2 percent treated stakes was 9.1 percent in distilled water; in 0.1 percent treated stakes, 31.5 percent NHA was released. We conclude that NHA leach rates can be decreased by precipitation with inorganic ions (such as calcium) and increased concentration levels of NHA during pressure treatment.

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The use of broad-spectrum biocides for wood preservation is being limited because they include chemical components that are potentially toxic to nontarget organisms. Because of these environmental concerns with broad-spectrum biocides, there is increasing incentive to look for new wood preservatives. Ideally, new preservative systems would incorporate an inexpensive water-soluble organic chemical moiety, which binds to or precipitates into wood and protects it against a wide variety of decay fungi and termite attack (Highley 1989, Kersten 1994).

One approach to developing new, environmentally friendly wood preservatives for the control of wood decay fungi

is targeted inhibition, which interferes with a specific wood decay mechanism (Brent 1995). Hydrolysis of wood pectin from ray parenchyma cells and tori of pit membranes has been hypothesized as an early step in the colonization of wood by brown- and white-rot fungi (Green and Clausen 1999). One key to pectin hydrolysis by plant pathogens has been shown

to be fungal production of oxalic acid, which lowers the pH of the substrate and chelates calcium ions. Production of oxalic acid may serve a similar role during incipient wood decay since calcium oxalate has been found by scanning electron microscopy during both brown- and white-rot decay (Graustein et al. 1977, Bech-Anderson 1987, Green et al.

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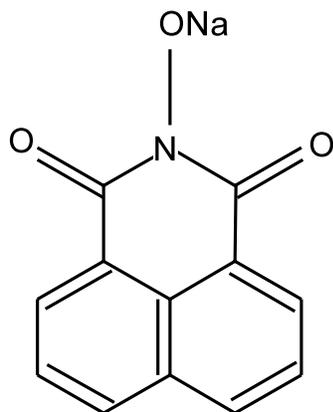


Figure 1. — *N'*-*N*-hydroxynaphthalimide (NHA) ( $C_{12}H_6NO_3Na$ ).

Table 1. — NHA treatment groups.

Treatment group	Process	Treatment solution
A	Single	1% Na-NHA
B	Single	1% Na-NHA + 0.25% boric acid
C	Sequential	1% Na-NHA / 2% $CaCl_2$
D	Sequential	1% Na-NHA + 0.17% NaOH/2% $CaCl_2$

1991, Dutton et al. 1993, Connolly and Jellison 1995). Therefore, *in situ* precipitation of existing calcium ions in wood may prevent the cascade of biochemical events involved in colonization of wood by decay fungi, especially hydrolysis of pit membranes (Green et al. 1995).

Preliminary studies have shown that brown-rot fungi, white-rot fungi, and termites are inhibited by the water-soluble calcium-precipitating agent *N'*-*N*-hydroxynaphthalimide-sodium salt (Na-NHA) (Fig. 1) (Green et al. 1996a, 1996b). Na-NHA forms a very stable and selective complex with calcium (Ca-NHA), which is insoluble in 100 mM ethylene glycol tetraacetic acid (EGTA) (Sobota et al. 1988) and is 130 times less toxic than copper for *Daphnia* spp. (Crawford and Green 1999). Na-NHA is a heterocyclic compound that is readily water-soluble. It is used as a precipitating agent for the histochemical detection of calcium.

Studies of decay inhibition by the selective precipitation of calcium with Na-NHA have shown that Na-NHA at sufficient concentrations protects southern yellow pine (SYP) from fungal decay and termites in laboratory tests (Green et al. 1996b, 1997a, 1997b, 2000; Green and Highley 1997; Green and Kuster 1999). Field tests have also shown that pressure treatment with 1 percent Na-NHA can protect SYP to the same degree as chromated copper arse-

nate (CCA-C) in high degradation environments for Ø48 months (Green and Highley 1997, Crawford and Green 1999).

Although NHA has been shown to provide protection against wood-degrading fungi and termites via precipitation on wood structures, some leaching does occur from NHA-treated wood (Crawford and Green 1999, Kartal and Green 2002). Leaching of NHA from treated wood reduces the efficacy because of the decrease in retention. The objectives of this study were to 1) determine if NHA leaching differs in tap water, distilled water, and seawater and to compare the amount of leaching with prior results with other waterborne preservatives; and 2) adapt a colorimetric microassay technique for estimating NHA retention in leachates and SYP.

## Materials and methods

### Treatment of wood specimens

SYP blocks, 19 by 19 by 19 mm, were cut from the sapwood portions of lumber. Before treatment, all blocks were conditioned at  $20 \pm 2^\circ C$  and 65 ± 5 percent relative humidity (RH) for 2 weeks. The blocks were vacuum-treated with 1.0 percent Na-NHA (treatment group A) or 1.0 percent Na-NHA + 0.25 percent boric acid equivalent (BAE) boric acid ( $H_3BO_3$ ) (treatment group B) in single processes (Table 1). Boric acid

was included in the trial because previous research indicated that borate:NHA interactions could reduce leaching of boron from treated wood (Kartal and Green 2002). Boric acid also lowers the pH of the treating solution closer to the transition to the acid form of NHA (H-NHA) (pH Ω6.0). Some blocks were vacuum-treated with 1.0 percent Na-NHA and 2.0 percent  $CaCl_2$  solutions (treatment group C) or 1.0 percent Na-NHA + 0.17 percent NaOH and 2.0 percent  $CaCl_2$  solutions (treatment group D) in sequential processes (Table 1). In the sequential processes, blocks treated with first treatment solutions were dried at  $60^\circ C$  for 1 day and then conditioned at  $20 \pm 2^\circ C$  and 65 ± 5 percent RH for 2 weeks before the second treatment step. The vacuum cycle consisted of a 30-minute vacuum (-88 kPa gauge pressure) period in the first step of treatment and a 10-minute vacuum period in the second step. All treated blocks were conditioned at  $20 \pm 2^\circ C$  and 65 ± 5 percent RH for 2 weeks before leaching.

In addition, to determine the effect of NHA concentration on NHA leaching, 19- by 19- by 457-mm SYP stakes were cut from sapwood sections of lumber. Before treatment, all stakes were conditioned at  $20 \pm 2^\circ C$  and 65 ± 5 percent RH. The stakes were then pressure-treated with aqueous Na-NHA (2.0, 1.4, 1.0, 0.5, and 0.1% weight) according to a pressure cycle consisting of a 30-minute vacuum (-88 kPa) followed by a 2-hour pressure period (880 kPa). After treatment, all stakes were blotted dry and reweighed to determine gross Na-NHA retention. Treated stakes were conditioned at  $20 \pm 2^\circ C$  and 65 ± 5 percent RH for 2 weeks before leaching tests.

### Leaching of wood blocks

The leaching procedures for the blocks were similar to AWP Standard Method E11-97 (AWPA 1999). After the conditioning period, four replicate sets of six blocks for each treatment group were removed from the conditioning room and reweighed. Leaching sets of six blocks were chosen based on uptake of Na-NHA retention in the blocks. Each set of six blocks was placed into a 500-mL bottle, submerged in 300 mL of tap water, distilled water, or seawater adjusted to salinity of 34 parts per thousand (ppt) and subjected to a vacuum to impregnate the blocks with the relevant

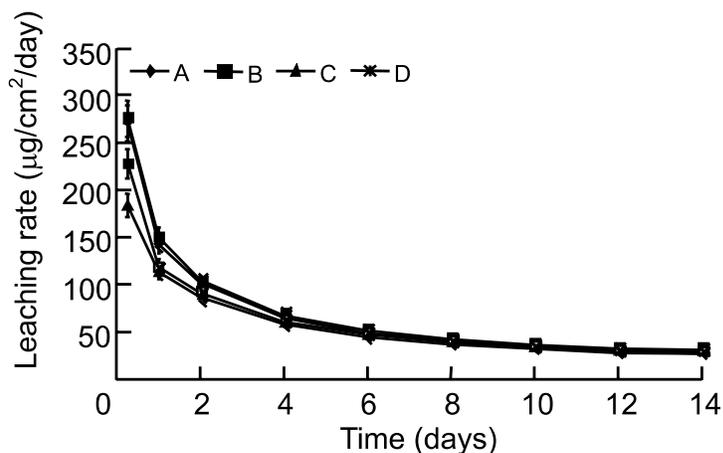


Figure 2. — NHA leaching rates from tap-water-leached wood blocks for treatment groups A, B, C, and D. Bars show standard deviations.

Table 2. — Total NHA loss from wood blocks leached with tap water, distilled water, and seawater.

Treatment group	NHA retention (g)	Total NHA loss <sup>a</sup>		
		Tap water	Distilled water	Seawater
A	0.103 (0.00)	6.31 (1.50)	26.40 (1.86)	5.04 (0.98)
B	0.114 (0.00)	6.28 (0.79)	22.94 (3.16)	4.44 (0.34)
C	0.111 (0.00)	5.58 (0.74)	12.73 (0.52)	4.27 (0.13)
D	0.125 (0.00)	4.98 (1.05)	15.10 (2.04)	4.26 (0.99)

<sup>a</sup> Each value represents average of four replicates of six specimens. Numbers in parentheses are standard deviations.

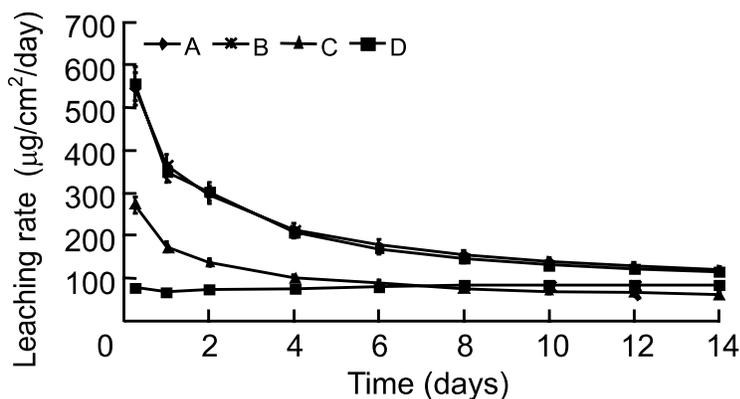


Figure 3. — NHA leaching rates from distilled-water-leached wood blocks for treatment groups A, B, C, and D. Bars show standard deviations.

leaching solutions. The 34-ppt dilution was chosen to represent typical seawater found in the open ocean. The seawater solution was prepared from Instant Ocean (Aquarium Systems, Mentor, Ohio), a commercial synthetic sea salt that contains the major ions typically found in seawater, including Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and K<sup>+</sup> (Lebow et al. 1999). 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. Leachates were collected after each leaching solution replacement and analyzed for NHA content.

#### Leaching of wood stakes

After each conditioning period, three replicates of stakes at each concentration were placed into 2250-mL glass

containers and submerged in 2000 mL of distilled water. The water was replaced after 6 hours, 1 day, 2 days, and every 2 days thereafter for a total of 14 days. Leachates were collected after each water replacement and analyzed for NHA content.

#### Colorimetric microassay for estimation of Na-NHA in leachates and wood specimens

The leachates were analyzed for the amounts of Na-NHA with an MRX microplate reader (Dynex Technologies Inc., Chantilly, Virginia), modified according to Green et al. (1989). In a 96-well microplate, 50 µL of the leachate was placed in each well and optical density (OD) was read at 340 nm. Standard curves were prepared by plotting the OD and concentrations of NHA standard solutions.

An unleached subset of treated blocks were ground to pass through a 40-mesh (0.420-mm openings) screen in the Wiley mill (Thomas Scientific, Swedesboro, New Jersey), 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°C to 95°C for 60 minutes. The flask in the bath was shaken for 2 to 3 minutes every 15 minutes. 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 colorimetric microassay method. Further discussion of this method can be found in Kartal and Green (2002).

#### Results and discussion

The total NHA losses from the blocks leached with tap water, distilled water, and seawater during the 14-day leaching exposure are shown in Table 2. The NHA leaching rates during the 14-day leaching from the blocks are given in Figures 2, 3, and 4. The greatest leaching in all treatment groups was observed in the distilled-water-leached blocks. In treatment group A and B, NHA losses in tap and seawater were four to five times less than those in distilled water. The rating of amount of NHA leaching for the four treatment groups is generally A>B>C>D. The results show that treat-

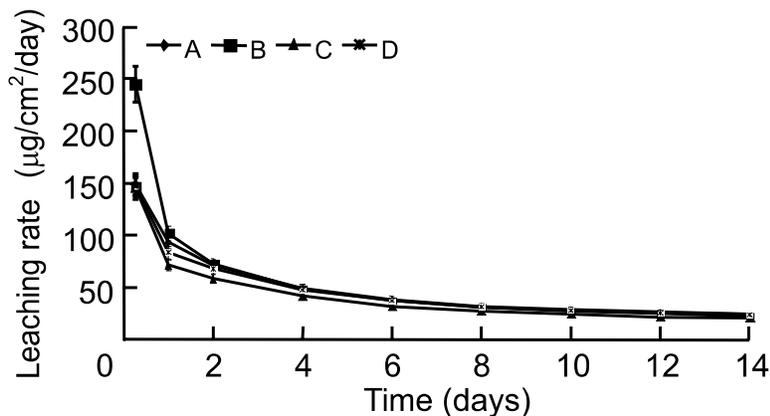


Figure 4. — NHA leaching rates from seawater-leached wood blocks for treatment groups A, B, C, and D. Bars show standard deviations.

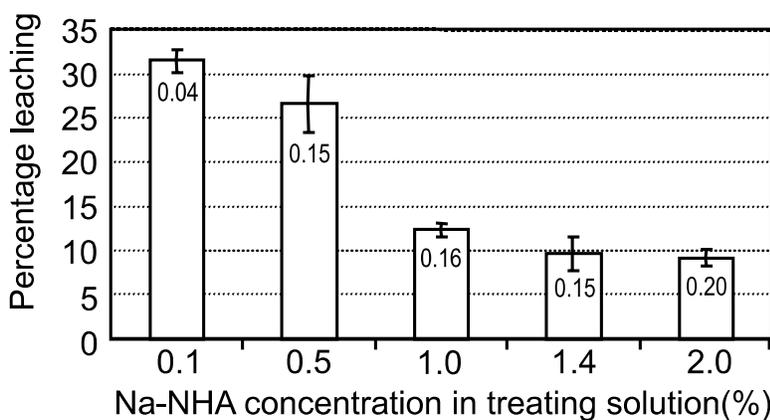


Figure 5. — Effect of Na-NHA concentration on NHA leaching from stakes. Values within bars are amount of NHA leached (grams). Bars show standard deviations.

ment of the blocks with  $\text{CaCl}_2$  solutions in sequential processes causes a significant decrease in NHA leaching in distilled water compared with the losses induced by tap and seawater.

Compared with distilled water leaching, NHA losses in tap- and seawater-leached blocks were significantly reduced in all treatment groups. The tap water and seawater used in this study contained many more ions, such as calcium, magnesium, potassium, copper, and sodium, whereas distilled water has essentially no ions. It is probable that during leaching, NHA in wood may have captured ions from the tap water and seawater solutions, since NHA can chelate with cations other than calcium. Thus, ions from tap water and seawater may have precipitated with NHA in the wood. It is also possible that sources of hardness in tap water and seawater may have actually inhibited loss of NHA by forming a precipitate on or near the wood surface. This phenomenon may be

of even greater significance in the natural environment, where NHA-treated wood in service would be exposed to water with a wide range of inorganic ions.

The NHA losses in the treatment groups ranged from 4 to 6 percent in tap- and seawater-leached blocks and 13 to 26 percent in distilled-water-leached blocks. Cooper and Stokes (1993) showed that the total percentage of CCA losses in distilled water during 14-day leaching in 19-mm SYP blocks were 0.6, 4.6, and 6.1 percent for chromium, copper, and arsenic, respectively. Lebow et al. (1999) found that release rate of copper was much greater in seawater than in distilled water. In contrast, arsenic losses were somewhat greater in distilled water than in seawater. Lebow and Kartal (1999) showed that copper, chromium, and arsenic losses from CCA-treated piles were 0.5, 0.4, and 0.4  $\sigma\text{g}/\text{cm}^2/\text{day}$ , respectively, after a 14-day leaching with seawater with a salinity of

23 ppt at  $2^\circ\text{C}$ . Irvine and Dahlgren (1976) suggested that at low salinities, NaCl had a coagulating effect on the crystallite copper fixation complexes increasing surface area and decreasing solubility, while at salinities greater than 24 ppt, the increased formation of complexes between chloride and copper might explain the increased leaching. Plackett (1984) indicated that leaching solutions that contain salts ( $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{Mg}(\text{NO}_3)_2$ ) caused enhanced copper leaching relative to distilled water, and copper leaching increased with salt solution concentration.

Compared with the copper losses ( $1 \sigma\text{g}/\text{cm}^2/\text{day}$ ) from CCA-C treated wood in fresh water (Crawford and Green 1999), NHA losses in all treatments in this study were higher (Figs. 2, 3, 4). In a study by Green et al. (1996b), there was no difference in weight losses between 14-day distilled-water-leached and unleached blocks caused by wood-degrading fungi. These results suggest that NHA in treated wood may inhibit wood decay even in severe leaching conditions.

The percentage of NHA leached from stakes treated with 2, 1.4, 1, 0.5, and 0.1 percent NHA solutions after a 14-day leaching course is shown in Figure 5. The percentage of NHA leached decreased with increased NHA concentration. The NHA retention levels in the stakes were 13.4, 9.6, 7.6, 3.4, 0.7  $\text{kg}/\text{m}^3$  for 2, 1.4, 1, 0.5, and 0.1 percent NHA solutions, respectively. The percentage release rate of NHA in the 2 percent NHA treated stakes is 9.1 percent, while it is 31.5 percent in the 0.1 percent NHA treated stakes. This may be explained by high precipitation on the ray parenchyma cells and tori of the pits in the wood treated with higher NHA concentrations, or NHA may be acting as a shell treatment at low treating concentrations.

Higher NHA precipitation and retention of NHA in wood may cause decreasing wood pit permeability (Green et al. 1997b), and stakes treated with higher NHA concentrations may tend to leach at a lesser rate because of less rapid movement of leachate. Lebow et al. (1999) reported that CCA retention had a slight effect on the rate of copper, chromium, and arsenic release from CCA-C treated lumber and piles. Kartal and Lebow (2002) stated that appear-

