J Wood Sci (2003) 49:344–348
DOI 10.1007/s10086-002-0474-x

ORIGINAL ARTICLE

Takeshi Furuno · Liang Lin · Sadanobu Katoh

Leachability, decay, and termite resistance of wood treated with metaborates

Received: May 22, 2002 / Accepted: July 29, 2002

Abstract The formation of insoluble metaborates in wood was investigated by impregnating the wood with borax and metallic salts, after which their properties (e.g., leachability in running water and biological resistance) were evaluated. The solubility of three metaborates in acidic solutions was also evaluated. Double-diffusion treatment was carried out to form the precipitates of metaborates in sapwood specimens of Japanese cedar (*Cryptomeria japonica*) at room temperature. Water-saturated wood specimens were first impregnated by a saturated borax solution and then diffuse-penetrated with Zn^{2+}, Ca^{2+}, or Pb^{2+} solution. The precipitates of the three metaborates in the wood proved to be insoluble or hardly soluble in water by the leaching test. With the decay test using a brown-rot fungus (*Fomitopsis palustris*) and a white-rot fungus (*Trametes versicolor*) and with the termite test using a virulent subterranean termite (*Coptotermes formosanus*), the metaborate-treated woods showed generally good decay and termite resistance with negligible mass loss of the specimens. Particularly, the lead metaborate formed in the wood provided superb biological resistance against decay and termite attacks. In addition, the precipitates of these metaborates were found to be soluble in acidic solution, suggesting a way to remove these chemicals from wood when disposing of waste materials.

Key words Decay resistance · Double diffusion · Leachability · Metaborate · Termite resistance

Introduction

Treatment of wood with a boron compound (inorganic substance) having both fire and biological resistance, dimensional stability, and other features, has been studied by Hashim et al.[1] The high leachability from the treated wood resulted in ineffective treatment for wood that is in ground contact or that is being used in other highly hazardous external applications.[2] For boron compounds to achieve widespread use as preservatives, the chemical treatment must markedly reduce the amount of leaching from the treated wood. Lloyd et al. briefly reviewed research reporting on reducing the leachability of borates.[3]

Wood treated by zinc borate shows good resistance to water leaching. It seems that zinc borate is particularly suitable as a wood preservative. Because of its low solubility in water, it cannot impregnate wood; but zinc borate powder can be sprayed on the surface of the wood or added to the adhesive during board manufacture.[4–6]

A large number of wood–mineral mixtures have been tried during the past 30 years. Because some of them consisted of insoluble inorganic salts, they could not be sufficiently decomposed or burned for disposal. This increasing amount of treated waste wood is becoming a serious environmental problem.[7]

The objectives of the work outlined in this paper were to: (1) investigate a new kind of chemically treated wood by impregnating borax and metal ions into wood specimens and evaluate the leachability of three types of metaborate in running water; (2) evaluate the biological resistance of metaborate-treated woods against attack by wood-decaying fungi and termites; and (3) evaluate the solubility of zinc, calcium, and lead metaborates in solutions with various pH values.

Materials and methods

Wood material and chemicals

Sapwood specimens of Japanese cedar, or sugi (*Cryptomeria japonica* D. Don), were prepared for impregnation treatment at a size of 20 (R) × 20 (T) × 10 (L) mm for leaching, decay, and termite tests. The specimens were initially extracted with an ethanol/benzene solution (1:2, v/v)

T. Furuno (✉) · L. Lin · S. Katoh
Faculty of Science and Engineering, Shimane University, Matsue, Shimane 690-8504, Japan
Tel. +81-852-32-6563; Fax +81-852-32-6123
e-mail: t-furuno@riko.shimane-u.ac.jp

for 48 h using a Soxhlet extractor. Extracted wood specimens were then dried at 105°C for 24 h. The oven-dried weights of the specimens were subsequently measured.

A saturated solution of sodium tetraborate decahydrate (borax) ($Na_2B_4O_7{\cdot}10H_2O$) was prepared for impregnation, and aqueous solutions of zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$), calcium chloride ($CaCl_2$), and lead (II) acetate trihydrate [$(CH_3COO)_2Pb{\cdot}3H_2O$] were prepared at concentrations of 5%, 10%, 20%, and 40% (w/w). These chemical reagents were of chemical grade (Wako Pure Chemical Industries).

Wood impregnation

Oven-dried wood specimens were water-saturated by vacuum treatment. Water-saturated wood specimens were impregnated with a saturated solution of borax at atmospheric pressure and room temperature; they were maintained in the solution at atmospheric pressure for 24 h. Two types of impregnation treatment were carried out: with the first, specimens were diffuse-penetrated only with the borax solution and oven-dried at 105°C for 24 h ("single treatment"). With the second, the borax-treated specimens were diffuse-penetrated with an aqueous $ZnSO_4{\cdot}7H_2O$, $CaCl_2$, or $(CH_3COO)_2Pb{\cdot}3H_2O$ solution at atmospheric pressure for 24 h and then oven-dried at 105°C for 24 h. The latter process was designated "double treatment" for convenience in this study.[8] Ten specimens were used for each treatment to determine mass percent gains of metaborate-treated wood.

Leaching procedure

The leaching procedure in water was conducted according to the Japanese Industrial Standard (JIS) JIS K 1571-1998. Ten specimens per treatment were immersed in a 1000-ml beaker containing 400 ml distilled water (10-fold volume of specimens) under a vacuum for 20 min. After the vacuum was released, the specimens were kept in the distilled water and stirred with a magnetic stirrer (400–500 rpm) at room temperature for 8 h, followed by drying at 60°C for 16 h. After each leaching period the water was exchanged with fresh water, added in a ratio of 10 volumes of water to 1 volume of wood. These procedures were repeated 10 times.

Fungal decay resistance tests

Fungal decay resistance tests were conducted according to JIS K 1571-1998 using a brown-rot fungus [*Fomitopsis palustris* (Berk. et Curt.) Gilbn. & Ryv., FFPRI 0507] and a white-rot fungus [*Trametes versicolor* (L.: Fr.) Pilát, FFPRI 1030]. Untreated, control (solvent-extracted), and treated specimens were sterilized in gaseous propylene oxide after measuring the initial dry mass. These test specimens were set on a mat of test fungus in a glass jar containing quartz sands and nutrient solution (0.002% $MgSO_4$, 0.003% KH_2PO_4, 0.025% glucose, 0.01% malt extract, 0.005% peptone); nine specimens were used for each level of treatment and test fungus. They were incubated at 26°C for 2 months. The extent of fungal attack was determined from the percentage mass loss of the specimens tested.

Termite resistance tests

Untreated, control, and treated specimens were exposed to subterranean termites (*Coptotermes formosanus* Shiraki) in accordance with the Japan Wood Preserving Association (JWPA) Standard No.12-1981. Each test specimen with a half-size of 20 (R) × 10 (T) × 10 (L) mm cut from the original size was placed at the bottom of a cylindrical test container (8 cm diameter, 6 cm height). A total of 150 termite workers and 15 soldiers were introduced into each test container. The assembled containers were placed on damp cotton pads and kept at 28°C under high humidity in the dark for 3 weeks. Five test specimens were used for each level of treatment. Mass losses of specimens by termite attack were calculated after the test.

Solubility tests of metaborate salts

Excessive $ZnSO_4{\cdot}7H_2O$, $CaCl_2$, and $(CH_3COO)_2\,Pb{\cdot}3H_2O$, respectively, were poured into a saturated solution of borax to form precipitates. After the precipitates were water-washed and oven-dried, 50 g of precipitate was poured into 100 g of aqueous solutions (pH 2.5, 2.9, 3.3, 4.2, 5.1, 6.0, 7.2, and 8.5 adjusted with acetic acid and sodium hydrogen carbonate) and fully stirred at 25°C. The solubilities of the three metaborates were calculated from the weights before and after dissolution.

Results and discussion

Mass percent gains

Mass percent gains (MPGs) of wood specimens made using the borax solution and the metallic salt solutions are shown in Fig. 1. Wood specimens treated only with the saturated borax solution showed MPGs of 14.0% ± 0.13% (SD). For the double treatments, the MPG values had hardly changed by treatment with low concentrations of the metallic salt solutions (5% and 10%); but at a high concentration (40%), three metallic salt solutions of Pb^{2+}, Zn^{2+}, and Ca^{2+} produced high MPG values of 39.5% ± 1.43%, 29.2% ± 0.53%, and 26.7% ± 0.62%, respectively, suggesting the formation of inorganic substances in wood specimens.

Leachability of metaborates

To determine the leachability of metaborates, borate (B_4O_7) anion was reacted with Zn^{2+}, Ca^{2+}, or Pb^{2+} to form metaborate (MB) precipitates as illustrated in Fig. 2, which shows fixation of boron in wood specimens. The results of the leaching tests of metaborate-treated woods are shown in

Fig. 3. It was found that zinc and calcium metaborates have slight solubility in water. These results were in agreement with previous data for zinc and calcium metaborates.[9] The abrupt reduction of two chemicals at the first cycle of leaching means removal of unreacted chemicals; afterward, retention of chemicals decreased slightly. After 10 cycles of leaching, for wood-zinc metaborate (W-ZMB) and wood-calcium metaborate (W-CMB) specimens the chemical retention was reduced by 65%–70%. These results indicated that the W-ZMB and W-CMB specimens must be fully washed to remove unreacted chemicals after treatment. On the other hand, during the leaching test, the weights of wood-lead metaborate (W-LMB) specimens decreased slightly at first and then remained almost unchanged, showing little or no mass reduction after leaching. The reason for high leaching resistance for W-LMB is that the $Pb(BO_2)_2$ formed in the wood seems to have lower solubility and less unreacted chemical than the others[9]; moreover it easily absorbs water to form crosslinked compounds,[10] which can prevent leaching from running water.

Biological resistance tests

Fungal decay resistance tests

The results of decay tests in specimens before and after leaching are shown in Table 1. When the samples were exposed to decay fungi without any leaching procedure, the woods treated with the borax solution only or the double treatments (borax and metallic salt solutions) showed small mass losses during exposure to both *T. versicolor* and *F. palustris* compared with 42%–47% loss in untreated wood. A small loss in the mass of the metaborate-treated woods was thought to be due to the strong resistance of borax or metaborate compounds to fungal attack by *T. versicolor* and *F. palustris*.

When the borax-treated wood after leaching was exposed to the test fungi, the mass loss increased greatly, up to 31%–34%, revealing no decay resistance because of the thorough leaching of borax from the wood. On the other hand, mass losses after double treatments were still small. In particular, the double treatments with lead acetate trihydrate, even with a low-concentration (10%) solution, showed excellent decay resistance against the attack by both fungi (*T. versicolor* and *F. palustris*), similar to the results with the 40% solution. For zinc sulfate heptahydrate and calcium chloride, double treatments with the 40% solution also produced good decay resistance after leaching because of the extremely small mass losses (<3%).

The decay tests revealed that formation of metaborate compounds in the wood provided good protection against fungal attack and greatly enhanced decay resistance even after leaching.

Termite resistance tests

Mass losses of wood specimens treated with borax and metaborate compounds after exposure to termites of *Coptotermes formosanus* are shown in Table 2. The mass losses of untreated and control woods were about 18%–20%, and feeding holes due to termite attacks were clearly observed on these specimens. It suggested that

$$\begin{matrix} ZnSO_4\cdot 7H_2O, \\ CaCl_2 \text{ or} \\ Pb(COOCH_3)_2\cdot 3H_2O \end{matrix} + Na_2B_4O_7\cdot 10H_2O \longrightarrow M(BO_2)_2\downarrow + NaX$$

M = Zn, Ca or Pb
X = SO_4, Cl or $COOCH_3$

Fig. 2. Reactions between borax and metallic salts

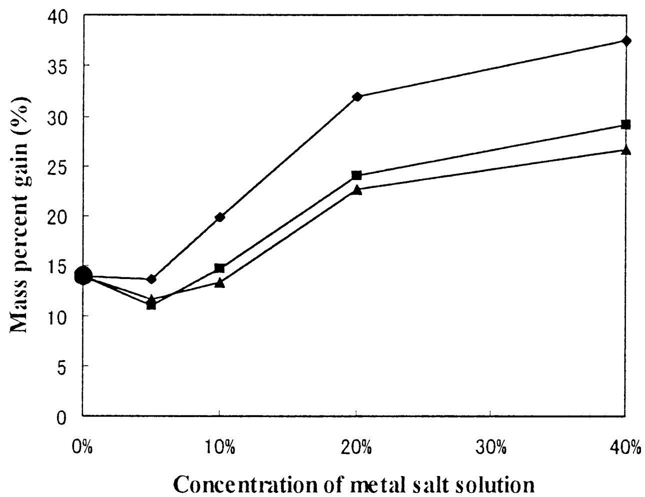

Fig. 1. Relation between mass percent gains and concentrations of metal salt solutions. *Diamonds*, W-LMB, or wood treated with lead metaborate; *squares*, W-ZMB, or wood treated with zinc metaborate; *triangles*, W-CMB, or wood treated with calcium metaborate; *circles*, wood treated with borax solution

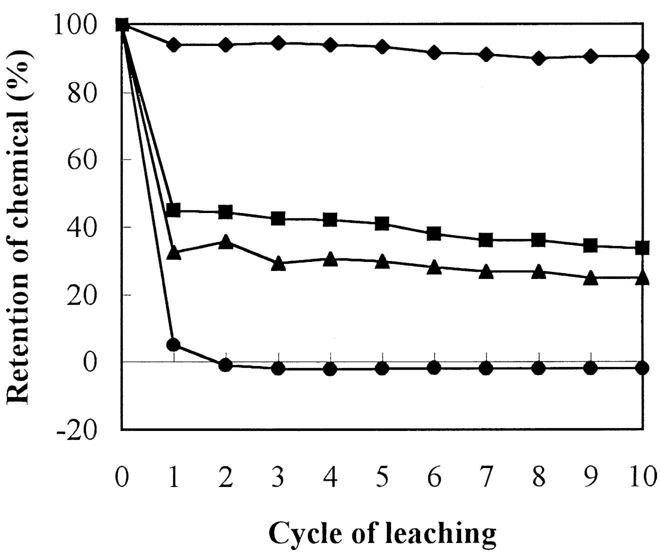

Fig. 3. Leachability of metaborates from treated wood specimens. See Fig. 1 for explanation of symbols

Table 1. Mass losses of treated and untreated wood specimens, by the decay test

Treatment	MPG (%)	Mass losses (%)			
		Without leaching		With leaching	
		TRV	FOP	TRV	FOP
None	–	42.3 (7.03)	47.2 (6.01)	–	–
Control[a]	–	28.4 (4.45)	31.1 (6.66)	–	–
Borax-treated					
No leaching	7.2 (0.52)	−1.7 (0.09)	−2.3 (0.09)	30.9 (0.93)	33.8 (1.49)
Leaching	−0.8 (0.45)				
Calcium metaborate 10%					
No leaching	13.6 (0.18)	−1.4 (0.07)	−2.5 (0.05)	5.3 (0.87)	6.5 (0.72)
Leaching	3.3 (0.27)				
Calcium metaborate 40%					
No leaching	24.4 (0.93)	−1.2 (0.12)	−1.6 (0.12)	1.4 (0.08)	2.5 (0.04)
Leaching	7.9 (0.22)				
Zinc metaborate 10%					
No leaching	15.2 (1.23)	−2.7 (0.07)	−0.6 (0.04)	5.8 (0.81)	6.5 (0.59)
Leaching	5.6 (0.68)				
Zinc metaborate 40%					
No leaching	27.1 (0.77)	0.5 (0.10)	0.7 (0.01)	2.1 (0.06)	2.8 (0.09)
Leaching	11.1 (0.20)				
Lead metaborate 10%					
No leaching	21.1 (0.50)	0.8 (0.09)	0.9 (0.14)	0.7 (0.05)	0.7 (0.06)
Leaching	18.3 (0.34)				
Lead metaborate 40%					
No leaching	37.6 (0.32)	0.7 (0.08)	0.2 (0.06)	0.4 (0.06)	0.6 (0.07)
Leaching	33.6 (0.22)				

Values represent the means of nine replicates per treatment. Values in parentheses represent standard deviations
MPG, mass percent gain; TRV, *Trametes versicolor*; FOP, *Fomitopsis palustris*
[a] Extracted with an ethanol and benzene solution

Table 2. Mass losses of treated and untreated wood specimens, by the termite test

Treatment	MPG (%)	Mass losses (%)	
		Without leaching	With leaching
None	–	18.27 (2.51)	–
Control[a]	–	19.75 (1.50)	–
Borax			
No leaching	7.5 (0.13)	0.72 (0.22)	6.51 (1.82)
Leaching	−0.5 (0.86)		
Calcium metaborate 10%			
No leaching	13.2 (0.26)	1.30 (0.79)	3.78 (2.11)
Leaching	4.0 (0.88)		
Calcium metaborate 40%			
No leaching	24.3 (0.62)	3.83 (2.39)	5.05 (2.93)
Leaching	9.5 (1.52)		
Zinc metaborate 10%			
No leaching	14.6 (0.42)	1.66 (1.31)	1.28 (1.60)
Leaching	5.1 (0.76)		
Zinc metaborate 40%			
No leaching	29.1 (0.53)	0.91 (0.37)	0.25 (0.21)
Leaching	11.6 (0.83)		
Lead metaborate 10%			
No leaching	19.5 (0.37)	0.94 (0.39)	0.96 (0.89)
Leaching	17.6 (1.11)		
Lead metaborate 40%			
No leaching	39.1 (1.43)	1.44 (0.75)	1.14 (0.67)
Leaching	34.1 (2.65)		

Values represent the means of five replicates per treatment. Values in parentheses represent standard deviations
MPG, mass percent gain
[a] Extracted with an ethanol and benzene solution

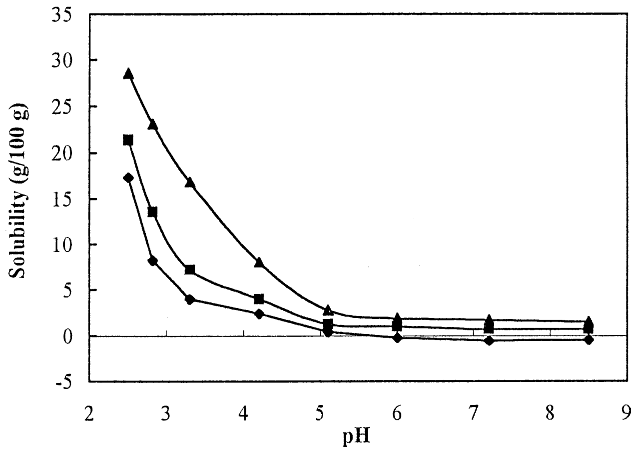

Fig. 4. Relation between solubilities of metaborates and pH values. *Diamonds*, lead metaborate (LMB); *squares*, zinc metaborate (ZMB); *triangles*, calcium metaborate (CMB)

$$M(BO_2)_2 + 2H_2O \xrightarrow{2H^+} 2H_3BO_3 + M^{2+}$$

Fig. 5. Decomposition of metaborates in acidic solution

C. formosanus could easily attack the wood specimens that had not been treated with chemicals.

When the samples not exposed to leaching were subjected to a force-feeding test of the subterranean termite *C. formosanus*, the wood treated with borax solution showed little or no mass loss. However, after leaching they had mass losses of more than 6% and only slight termite resistance. Feeding holes were also present because almost all of the borax was leached from the sample wood.

For the double-treated specimens (borax and metallic salt solutions), small mass losses of 0.9%–3.8% without leaching were shown in the termite test. The mass losses after double treatments with $ZnSO_4$ and $Pb(CH_3COO)_2$ were particularly low (<1.7%) both with and without leaching, demonstrating an excellent termite-resistant effect against attack by *C. formosanus*. The results of these termite tests agreed well with those of the decay tests. Moreover, it was suggested that wood specimens treated with even a low-concentration solution of metallic salts (10%) could protect wood adequately against termite attack.

Solubility of metaborates in solutions with various pH values

The relation between the solubilities of three metaborate compounds and pH values are shown in Fig. 4. The solubilities of ZMB, CMB, and LMB increased as the pH values of the solutions decreased. In particular, when the pH is <5, the solubility increased markedly. The metaborates reacted easily with the acid, forming boric acid and soluble salts (Fig. 5). Therefore, it was found that the acidic solution could remove metaborates from wood. This provides a possible method to extract preservative chemicals from wood materials prior to disposal, thereby reducing a serious environmental problem and conserving resources. There is a need to investigate further the removal of metaborates from treated wood specimens.

Conclusions

It was possible to produce wood treated with metaborates by the diffusion-penetrating process in a wood, inorganic borax, and metallic salts system. The precipitates of three metaborates in the wood were insoluble or hardly soluble in water, as shown by the leaching test. This formation of metaborates in treated wood proved to contribute much to the enhancement of decay and termite resistance, with negligible mass losses of specimens. The lead metaborate formed in the wood was particularly nonleachable, and it provided high levels of biological resistance against decay and termite attacks.

In addition, the metaborates were soluble in the acidic solution, providing a method of removing the chemicals from the wood prior to burning or decomposing the waste wood materials.

Acknowledgments The authors thank Dr. Tomonori Kobayashi, Chief of Central Research Department, Nippon Eisei Center Co., Osaka, Japan, and his staff for their assistance in termite testing.

References

1. Hashim R, Murphy RJ, Dickson DJ, Dinwoodie JM (1994) Vapor boron treatment of wood based panels: mechanisms for effect upon impact resistance. Document no. IRG/WP 94-40036. International Research Group on Wood Preservation, Nusa Dua, Bali, Indonesia, pp 1–26
2. Nicholas DD, Jin L, Preston AF (1990) Immediate research needs for diffusible boron preservatives. Presented at the First International Conference on Wood Protection with Diffusible Preservatives. Proceedings no. 47355. Forest Products Research Society, Madison, WI, USA, pp 121–123
3. Lloyd JD, Fogel JL, Vizel A (2001) The use of zirconium as an inert fixative in preservation. Document no. IRG/WP 01-30256. International Research Group on Wood Preservation, Nara, Japan, pp 1–26
4. Manning MJ, Laks PE (1996) Field performance of borate-containing wood composites. In: Proceedings of 3rd Pacific Rim Bio-Based Composites Symposium, Kyoto, Japan, pp 535–543
5. Manning MJ (2000) Inorganic borates as preservatives for wood composites. In: Proceedings of 5th Pacific Rim Bio-Based Composites Symposium, Canberra, Australia, p 717; appendix pp 1–7
6. Laks PE, Verhey SA (2000) Decay and termite resistance of thermoplastic/wood fiber composites. In: Proceedings of 5th Pacific Rim Bio-Based Composites Symposium, Canberra, Australia, pp 727–734
7. Kajimoto T, Takagaki M, Hata T, Imamura Y (2000) Separation of components of CCA-treated wood by rapid thermolysis method (in Japanese). In: Abstracts of the 50th Annual Meeting of the Japan Wood Research Society, Kyoto, Japan, p 706
8. Furuno T, Imamura Y (1998) Combinations of wood and silicate. Part 6. Biological resistances of wood-mineral composites using water glass-boron compound system. Wood Sci Technol 32:161–170
9. Weast CR, Astle MJ (1981–1982) Physical constants of inorganic compounds. In: Weast CR (ed) CRC handbook of chemistry and physics, 62th edn, vol B. CRC, Boca Raton, FL, pp 86–110
10. Editorial Committee (1997) Lead borate. In: Encyclopedia chimica (in Japanese), 36th edn, vol 9. Kyoritsu, Tokyo, p 112