# Effectiveness of Copper-Boron Diffusion Treatments for Wood

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## ABSTRACT

Alaskan spruce is one of the major commercial softwood species in Alaska, yet has very little resistance to decay. Hawaiian albezia is a major hardwood species being grown on a large scale in plantations in the Hawaiian Islands. There is interest in developing low-cost chemical treatment of these two species to create new markets for exterior applications. Diffusion treatment of wood is considered as a low-cost, simple means to provide protection against decay and termites. Borates (B) though effective against decay and termites, have one major disadvantage in that they do not chemically fix to the wood structure and so are prone to leaching under exposed conditions. Attempts to overcome this disadvantage have so far been unsuccessful and therefore their use has been restricted to specific end uses such as certain constructional timbers or remedial treatments. Copper (Cu) is a toxic heavy metal with proven preservative quantities, but does not degrade and may become deposited into soil and water causing various environmental concerns. The goal of this research was to determine minimum soak and storage times to achieve suitable levels of preservative penetration and retention through diffusion treatment process and to determine the level of fixation that occurs, since leaching of the chemicals is of concern. Alaskan spruce and Hawaiian albezia wood samples were treated in their green condition. The various preservatives used for this study included a commercial copper-borate formulation, a commercial borate formulation and copper-sulphate. Considerable retention levels of copper and boron were obtained after a 2-day soak as long as the soaked pieces were stored in the wet condition for a period of 2 weeks using 50% copper borate solution for both species. Results from single and double diffusion indicate that the boron was easily leached from the samples, suggesting that minimal fixation occurs with this chemical. Essentially 100% of the boron was lost after only a few days of leaching, regardless of the treatment. The copper did not leach from the samples as much as the boron from wood samples. There was no evidence of formation of a fixed product in wood samples even when the copper and boron were applied in separate solutions in double diffusion. However the leaching rate of copper was reduced in double diffusion when the wood were first treated with copper sulphate and then with borosol compared to the samples treated with borosol and then with copper sulphate.

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# Chapter-1

## 1. Introduction

Wood will give centuries of use under favorable and dry conditions. However, if conditions are conducive to the development of wood-degrading organisms within the wood, protection must be provided during processing, merchandising, and use. The principal organisms that can degrade wood are fungi, insects, bacteria, and marine borers. Most of the damage to wood in the U.S is by fungi. Molds, most sapwood stains, and decay are caused by fungi, which are microscopic, thread-like microorganisms that must have organic material to live. For some of them, wood offers the required food supply. About 10% of the annual timber cut in the United States is used to replace wood that decays in service, much of it primarily from improper use and care. Added to this base raw material cost would be, in many cases, those costs representing processing, fabricating, finishing, mercendising, and assembly or replacement operations (Zabel and Morrel 1992).

The growth of fungi depends on suitably mild temperatures, moisture, and air (oxygen). The water needs of wood-inhabiting fungi can be expressed in terms of water potential (Griffin 1977). Water potential measures the relative availability of the water in the wood to the passive osmotic capabilities of the fungal hyphae in contact with it. Oxygen levels also strongly influence fungal decay rates. Below 0.01 atmospheres of oxygen, only slight decay occurred, and it increased progressively as oxygen pressures rose to 0.1 and 0.2 atmospheres (Zabel and Morrel 1992). Low oxygen levels and carbon dioxide levels substantially reduced decay compared to ambient levels (Highley et al. 1983). Decay is relatively slow at temperatures below 10º C (50º F) and above 35º C (95º F). Decay essentially ceases when the temperature drops as low as 2º C (35º F) or rises as high as 38º C (100º F). Fungi and most bacteria require a food source or substrate that provides three major needs such as energy from the oxidation of carbon compounds, a pool of metabolites for the synthesis of the wide range of compounds needed for growth and development (chitins, glucans, nucleotides, enzymes, proteins, lipids, etc.) and required vitamins, minor elements, carbon dioxide, and nitrogen (Zabel and Morrel 1992). Although some wood such as white oak, chestnut oak, etc, possesses naturally occurring resistance to decay most

wood species are easily affected by fungal decay. Wood can be protected from the attack of decay fungi, harmful insects, or marine borers by applying chemical preservatives. The degree of protection achieved depends on the preservative used and the adequate penetration and retention of the chemicals. Once treated with chemicals, i.e. a wood preservative, the timber represents a totally new habitat. An additional, abiotic factor has been added to the system, i.e. a toxin. The toxins themselves become the all important abiotic factor determining the types of organisms that live in the wood. Some preservatives are more effective than others, and some are more adaptable to certain use requirements. Not only are different methods of treating wood available, but also treatability varies among wood species. To obtain long-term effectiveness, adequate penetration and retention are needed for each wood species, chemical preservative, and treatment method. Penetration is the amount of chemicals that get into wood through radial and longitudinal directions and retention is the amount of chemicals that is retained in the wood after treatment. Wood preservatives that are applied at recommended AWPA (American Wood Preservatives Association) retention levels and achieve satisfactory penetration can greatly increase the life of wood structures. The annual replacement cost of treated wood in service is much less than that of wood without treatment (FPL 1999).

Wood preservatives can be divided into two general classes:(1) oil borne preservatives, such as creosote and petroleum solutions of pentachlorophenol and (2) water borne preservatives, such as chromated copper arsenate, ammoniacal copper zinc arsenate and others that are applied as water solutions. The three exposure categories for preservatives are (1) ground contact (high decay hazard that needs a heavy-duty preservative), (2) above ground contact (low decay hazard that does not usually require pressure treatment), and (3) marine exposure (high decay hazard that needs a heavy-duty preservative).

The conventional method for treating wood uses combinations of vacuum and pressure (Pressure process) to force chemicals into the cell lumens (Zabel and Morrel 1992). Alternative wood treating methods are non-pressure processes that include brushing, spraying, dipping, and variations of soaking (Hunt and Garratt 1967). Each method has its strengths and its weakness, and has different equipment requirements and chemicals.

Treating schedules have been fully developed for some methods and chemical combinations, but some processes have been less thoroughly examined.

Diffusion treatment is a natural process in which molecules of the preservative migrate through a porous medium, wood. These processes employ water borne preservatives that diffuse out of the water of the treating solution or paste into the water of the wood. Diffusion is based on the tendency of certain compounds to equalize differences in concentration of solutes. Examples of diffusible preservatives include: sodium arsenate, borax and boric acid (usually used in combination), disodium octaborate tetrahydrate, copper sulphate, sodium fluoride, and zinc chloride (Thompson 1991). Leaching is the amount of chemical that is dissolved or passed out by a percolating liquid. To percolate means to cause to pass through a permeable substance especially for extracting a soluble constituent. Single diffusion method is the method of using single solution for treating wood. The double diffusion process was developed to overcome leaching issues associated with single diffusion processes. In this method, green wood is sequentially soaked in two aqueous chemical solutions that react within the wood matrix to form a precipitate that is highly resistant to leaching and toxic to fungi and termites (Baechler 1953).

Table 1. Advantages and disadvantages of chemicals used for wood treating (Baechler 1953).

| **Chemical** | **Advantages** | **Disadvantages** |
|---|---|---|
| Copper | Toxic to fungi<br>More economical | Corrosive to tank used for treatment |
| Nickel | Less corrosive to tank | Less toxic to fungi<br>Less economical |
| Zinc | Less corrosive to tank | Less toxic to fungi |
| **Reacting with** | | |
| Arsenic | Restricted use | Restricted use |
| Boron | | Does not form an insoluble precipitate with any metal |

## 1.1 Problem

Alaskan spruce is one of the major commercial softwood species in Alaska. Spruce has very little resistance to decay. The capital investment in treating cylinders of any size is unfeasible for most Alaskans. Treating fresh wood is required in Alaska, because there is very limited drying capacity available. So conventional methods of treating wood like pressure process does not appear advantageous for Alaska. Hawaiian albezia is one of the major hardwood species, which is grown on a large scale in plantations in the Hawaiian Islands. Various industries have been looking for an effective simple, low cost method of treating wood to create new markets for these two species. There is interest in using boron and copper compounds to treat wood through the diffusion process. Boron compounds are well-known, low toxicity preservatives, but are water soluble and prone to leaching. So this chemical performs poorly when in ground contact. Copper is a toxic heavy metal, which does not degrade and may become deposited into soil and water, causing various environmental concerns if leached.

## 1.2 Objectives

The goal of this research was to determine the effectiveness of copper-boron on diffusion treatment for wood. The following questions were addressed:

a) Can acceptable retention levels of copper-borate preservative be achieved in a diffusion treatment process?

b) Can copper and boron become less prone to leaching from wood if they are applied separately and allowed to precipitate in wood?

# Chapter-2

## 2. Literature Review

### 2.1 Wood Preservation

Wood preservation has been around for millenniums. Wooden ships needed protection from marine borers and decay fungi. Initially, shipbuilders used wood that had natural durability against biotic attack. As the availability of these species lessened, shipbuilders looked for treatments that could preserve the wood or at least extend the service life of the ship until it reached its destination. Sheathing with tar, hair and fir boards was an ineffective remedy practiced for centuries. Today, wood preservation plays an important role in our lives. Treated wood is used in foundations and decks of our homes, playgrounds, fences, utility poles, railroad ties, and a host of other applications (Zabel and Morrel 1992). The amount of treatment depends on the level of protection needed. Decay risk, length of service life, cost of treatment, and end-of-life disposal are all considered when determining which treatment method and chemicals to use. There are short-term and long-term levels of protection. Short-term protection, such as dipping in chemical, is used to minimize sapstain fungi on fresh cut lumber. Long-term protection is further divided into aboveground or ground contact levels of protection. Wood in contact with the ground requires more treatment because the decay risk is higher. There are a variety of methods for delivering chemicals into the wood (Zabel and Morrel 1992).

The history of wood preservation dates to 2000 B.C. when natural oils and other materials were used to preserve wood. Modern industrial timber preservation can be traced to John Bethell in England, who developed a process for pressure treating ship timbers with creosote in 1838 (Graham and Nicholas 1973). In 1900 the Director-General of the Silesian Kattowitz mines approached Dr. K H. Wolman to consider improvements to existing methods of preservation and in 1903 the largest creosote pressure cylinder in the world was

established. In 1907 he patented his first fluoride containing preservative. Further development by Dr. Wolman resulted in the first multi-salt preservative of the Triolith type with a composition of sodium fluoride, dinitrophenol and sodium dichromate. In 1933 the first copper, chrome, arsenate formulation (CCA) was invented by an Indian Government research worker, Dr. Sonti Kamesan in the form of copper sulphate, potassium dichromate and arsenic pentoxide. The product was called 'Ascu' and great interest developed during the 1930's culminating in the first full scale commercial installation of CCA-treated PTT poles in 1940-42 by the Bell telephone System. The results were so good that in 1953, The American Wood Preservers Association (AWPA) included the Kamesan formulation as CCA-Type A (Thompson 1991). The early experience with the Bell telephone company of the United States of America was very important in establishing the reputation of the CCA type of formulation. The Type B were developed in Sweden and marketed with the product code K33 by Boliden. The Type B formulations developed were having an increased proportion of arsenic giving the formulation greater effectiveness against wood destroying insects, in particular termites. During 1950's it became apparent that there were optimum ratios of the metallic components, which could give a high degree of efficacy against a wide spectrum of biological wood destroying agencies, together with an improved resistance to leaching of the active ingredients, thereby increasing the service life of the treated community. This led to the development of the development of the last range of CCA formulation, Type C, which have become established worldwide (Findlay 1985).

Table 2. Classification of CCA preservative formulation according to the American Wood Preserving Association (Findlay 1985).

| | **CCA Type A (%m/m)** | **CCA Type B (%m/m)** | **CCA Type C (%m/m)** |
|---|---|---|---|
| Chrome (as $CrO_3$) | 65.5 | 35.3 | 47.5 |
| Copper (as $CuO$) | 18.1 | 19.6 | 18.5 |
| Arsenic (as $As_2O_5$) | 16.4 | 45.1 | 34.0 |

Over the same period in which the use of CCA was developed and expanded, other waterborne preservative products were tried and proposed. The AWPA standards, for

example, include acid copper chromate (ACC), ammoniacal copper arsenate (ACA), chromated zinc chloride (CZC), and fluorochrome arsenate phenol (FCAP). In the Germanic countries copper, chrome, boron (CCB) and copper, chrome fluoride (CFK) products became popular but never succeeded to the same extent as CCA. (Thompson 1991).

The ideal wood preservative should possess characteristics such as high toxicity towards wood destroying organisms, permanency in the treated wood (i.e. low volatility and high resistance to leaching) ability to penetrate deeply into wood, non-corrosion to metals and non-injurious to the wood itself and reasonably safe to handle and without injurious effects on operatives (Cartwright and Findlay 1958).

Today, wood preservation accomplishes two main tasks. First, it allows us to conserve timber. Experts estimate that the failure to control wood-destroying insects and fungi in the United States alone requires the additional cutting of 360,000 acres of forests yearly. Secondly, wood preservation allows us to increase the service life of wood. Treatment of wood affords protection from the principal agents of wood deterioration - fungi, wood-destroying insects (primarily termites), marine borers, fire, and weathering. A better understanding of the causal agents of wood deterioration will help the scientific community design more effective systems for protecting wood while minimizing environmental impact and improving service life. An excellent discussion of causal agents can be found in a recently published treatise (Eaton and Hale 1993).

In recent years, two principal factors have spurred changes in treatment technology and preservative systems worldwide: 1) environmental concerns, including air and water quality standards, and the effect of treated wood on man and nontarget organisms; and 2) the energy crisis, especially in regard to oil and oil-based preservative systems. Of these two, environmental concerns predominate.

## 2.2 Types of preservatives

Wood preservatives can be divided into two general classes 1) oil borne preservatives, such as creosote and petroleum solutions of pentachlorophenol and 2) water borne preservatives that are applied as water solutions.

Coal tar, a product of the distillation of coal was originally used as wood preservative, but the lighter creosote fraction of coal tar was adopted with the introduction of pressure impregnation as its lower viscosity improved penetration (Richardson 1978). It is used in log homes, railroad ties, telephone poles, bridges, fence posts, etc. Advantages of creosote are (a) high toxicity to wood-destroying organisms; (b) relative insolubility in water and low volatility, which impart to it a great degree of permanence under the most varied use conditions; (c) ease of application; (d) ease with which its depth of penetration can be determined; (e) relative low cost (when purchased in wholesale quantities); and (f) lengthy record of satisfactory use. The color of creosote and the fact that creosote-treated wood usually cannot be painted satisfactorily make this preservative unsuitable where appearance and paintability are important. The odor of creosote-treated wood is unpleasant to some people. Also, creosote vapors are harmful to growing plants, and foodstuffs that are sensitive to odors should not be stored where creosote odors are present. Workers sometimes object to creosote-treated wood because it soils their clothes, and creosote vapor photosensitizes exposed skin. In 1986, creosote became a restricted-use pesticide and is available only to certified pesticide applicators. Water-repellent solutions containing chlorinated phenols, principally pentachlorophenol (PCP), in solvents of the mineral spirits type, was first used in commercial dip treatments of wood by the millwork industry about 1931. Because of the toxicity of PCP, care is necessary when handling and using it to avoid excessive personal contact with the solution or vapor. Do not use indoors or where human, plant, or animal contact is likely. PCP became a restricted-use pesticide in November 1986 and is only available to certified applicators. PCP is effective against many organisms, such as decay fungi, molds, stains, and insects. Because PCP is ineffective against marine borers, it is not recommended for the treatment of marine piles or timbers used in coastal waters (FPL 1999).

Water borne preservatives consist of solutions of salts, generally selected because they possess an active ion. The inactive components are important as they assist with solubilization and determine the ability of the preservative to achieve the required distribution of the toxic components in terms of necessary penetration and retention (Richardson 1978).

Advantages of water borne preservatives are (a) they can be transported in solid, or concentrated, form and made up in the place where they are to be used with the cheapest of all solvents-water (b) formulations of water borne chemicals that are equally effective against both fungi and insects can easily be prepared (c) they leave the wood in a clean condition which is not unpleasant to handle (d) the treated wood can be painted over once the water has dried off (e) they are usually odorless (f) they can readily be combined with fire retardant chemicals (Findlay 1985). Standard wood preservatives used in water solution include acid copper chromate (ACC), ammoniacal copper zinc arsenate (ACZA), chromated copper arsenate (CCA- types A and C), alkyl ammonium compound (AAC), inorganic boron, ammonaical copper quat (ACQ), copper bis-dimethyldithiocarbamate (CDDC), ammoniacal copper citrate (CC), and copper azole-Type A (CBA-A).

## 2.3 Preservative treatment methods

Wood-preserving methods are of two general types: pressure processes, in which the wood is impregnated in closed vessels under pressures considerably above atmospheric, and nonpressure processes. Treating methods can use a host of waterborne or oil borne chemical combinations for treating. Many of these chemicals are listed as restricted use pesticides by the EPA, meaning they can only be applied by certified pesticide applicators (Zabel and Morrel 1992). Presently, the waterborne chemicals that are commercially used include: CCA, ACQ, copper azole (CA) and ammoniacal copper zinc arsenate (ACZA). Copper and arsenic are both excellent fungicides, while arsenic also protects wood from insectsand marine borers (Zabel and Morrel 1992). Oilborne chemicals, like creasote, have been around the longest and have proven to be the most reliable preservative. Other major oilborne preservative include PCP, copper naphthenate, and copper-8-quinolinolate.

### 2.3.1 Pressure Processes

Pressure treatment of wood with preservatives is by far the most effective method of protecting wood against attack by decay, insects, fire, and other wood destroying agents. Through pressure treatments, deeper and more uniform penetration of preservative can be obtained, and the retention of preservatives can be more closely controlled. Maximum production of preservative treated forest products can best be achieved through pressure impregnation, since the time required to thoroughly impregnate wood is held to a minimum (Nicholas 1973). Three pressure processes are commonly used: full-cell, modified full-cell, and empty-cell.

#### Full-Cell

The full-cell process generally applies waterborne preservatives and preservative retention is controlled by regulating the concentration of the treating solution. The charge of wood is sealed in the treating cylinder, and a preliminary vacuum is applied for a half-hour or more to remove the air from the cylinder and the wood. The preservative at suitable temperature is admitted to the cylinder without breaking the vacuum. Then pressure is applied until the wood will take no more preservative or until the required retention of preservative is obtained. A short final vacuum may be applied to free the charge from dripping preservative. The modified full-cell process is basically the same as the full-cell process except that the modified full-cell process uses lower levels of initial vacuum

#### Empty-Cell

The Lowry and the Rueping are the two empty-cell processes commonly employed. In Lowry process, after the wood has been closed in the cylinder, preservative is pumped in and no air is allowed to escape. As the cylinder fills the liquid and pressure is applied, the air in the cylinder and in the wood cells is compressed onto a smaller space. When the desired pressure is applied, maximum preservative is filled up in the wood. The process then continues exactly as the full cell process. The final vacuum period can be used to

extract more or less preservative as needed. The Lowry is often called the empty-cell process without initial air pressure. The Rueping process is similar to that of Lowry process. Here an air pressure higher than atmospheric pressure is first applied to the closed cylinder and its charge of wood. A compressor generates the air pressure. Treatment then continues with Lowry or Full cell processes. The Rueping empty-cell process, often called the empty-cell process with initial air, has been widely used for many years in Europe and the United States.

### 2.3.2 Nonpressure processes

Wood treating methods include nonpressure-processes such as brushing, soraying, dipping, and many variations of soaking (Hunt and Garret 1967). Many nonpressure-processes require much less equipment than pressure-processes methods and typically limited to small-scale applications by homeowners and farmers (Zabel and Morrel 1992).

#### Brushing and spraying

Typically, oil borne preservatives are used when treating wood by brushing or spraying, but waterborne preservatives can also be used. Penetration via these processes is shallow, and therefore protection is limited. Abrasion or checking can easily break the envelope of protection. Wood has to be dry and warm enough to avoid congealing of the oil borne preservative on the wood surface (Hunt and Garret 1967).

#### Dipping and soaking

Hunt and Garret (1967) differentiated numerous treatment processes that involved dipping or soaking wood. For example, dipping consists of momentarily immersing wood in a bath of preservative, while steeping consists of submerging wood for several days or even weeks in an open container. With steeping, dried wood is treated with waterborne chemicals. Cold soaking is similar to steeping except that wood is soaked in unheated oil borne chemicals for days to one week.

Diffusion

Diffusion methods are similar to steeping in that there is a bulk flow of solution into the wood. Yet, the diffusion method has a second mechanism for moving preservative into the wood using a diffusion period. Wood is wet-stacked for a period of time in order to facilitate diffusion. The theory of diffusion states that the chemicals will move from zones of higher concentration (treating solution) to those with lower concentration (water in wood). Therefore, green wood and waterborne chemicals are used for diffusion treatments. This diffusion method typically involves soaking wood in solutions, but theoretically can extend to the use of pastes and wraps to deliver chemicals into the wood (Hunt and Garret 1967). Chemicals placed in the wood only by diffusion, however, are susceptible to leaching, because chemicals that diffuse into wood matrix can easily leach out during service. Products treated by the diffusion method are used in low hazard building timbers, or out-of-ground contact.

Diffusion treatment processes rely on movement of aqueous solutions of chemicals into unseasoned wood by diffusion. They vary in nature from (a) immersion in a single preservative chemical solution (b) the application of preservative pastes on the surfaces of wood or (c) immersion of wood in two separate solutions, which result in the formation of insoluble compounds within the wood. The first method involves the placing of the unseasoned, frequently posts, in aqueous solutions of preservatives for long periods of time. The second method involves the application of preservatives, dissolved or suspended in thin pastes, to all surfaces of the unseasoned material (Hunt and Garret 1953). Following this, the wood is generally solid piled and covered for several weeks to permit diffusion of the preservatives into the wood. In the third method, the unseasoned wood products are immersed in a solution of a single compound dissolved in water, allowed to remain there for several days, then removed and promptly placed in another aqueous chemical solution (Baechler 1963). The double-diffusion process was developed to overcome leaching issues associated with the single-diffusion processes. In double-diffusion, green wood is sequentially soaked in two aqueous chemical solutions that react within the wood matrix to

form a precipitate that is highly resistant to leaching and toxic to fungi and termites (Baechler 1953).

Single diffusion applications using boron have been commercially accepted in New Zealand, Australia, and New Guinea for decades, and account for 28 percent of all wood treated in the region (Vinden et al.1997). Diffusion is a natural process in which ions or molecules of certain compounds such as borates, penetrate wood through the liquid pathways in wood, such as the free water that is in the cell lumens of unseasoned wood. Diffusion occurs because borate compounds tend to equalize differences in their concentration within wood without external force i.e., without pressure treatment (Williams 1996). Copper is a widely used wood preservative that is broadly effective against fungi and many insects. Water-soluble copper formulations can diffuse into wet wood, although the degree of diffusion is more limited than that found with fluoride. While copper is not strongly reactive with the wood, a certain percentage does react with the wood to become "fixed" (Cooper 1983). Over time, however, this component would be expected to diffuse from the wood under higher moisture regimes. The double-diffusion process was developed to overcome leaching issues associated with the single-diffusion processes. Double diffusion was initially developed in the 1940s for farmers for treatment of posts and timbers (Baechler 1941, 1953). The original process employed copper sulphate immersion followed by sodium dichromate treatment, although other chemicals were also evaluated (Baechler et al. 1959, Baechler and Roth 1964). Fluoride was among the chemicals originally investigated for the double diffusion process (Baechler 1941,Gjovik et al. 1972, Johanson 1975, Gjovik 1985), but it was dropped in favor of the more strongly fixed chromium.

Preserving wood with aqueous preservative salt systems consists of two steps: a) getting a sufficient quantity of the preservative on the surface of wood with a sufficient moisture content to allow diffusion, and b) storing treated wood under proper conditions for sufficient time until the wood is penetrated by the preservative to the desired depth (Thompson 1991). Diffusion treatments with aqueous preservative systems usually results in a concentration gradient of the preservative, with higher concentrations near the wood

surface and lower concentrations deeper within the wood. This “window-frame” pattern of penetration is typical when there is little or no absorption of solution. Depending on the conditions of treatment or final use, it is theoretically possible for a uniform, equilibrium concentration to be reached in wood (Williams and Mitchoff 1990).

The factors affecting the rate of diffusion are the wood structure, temperature during storage, wood moisture content, wood density, and the type of preservative.The rate of diffusion increases as temperature and can be expected to nearly double with each 20º C rise in temperature during diffusion storage, thus halving the length of the storage needed to obtain the same results. For radiata pine (*Pinus radiata* D.Don) stored at 60º C instead of 20º C, there is a four fold increase in the rate of diffusion, reducing the diffusion storage time by three-quarters (Vinden, Fenton and Nasheri 1985). The effect of temperature is one reason diffusion treatment with borates is suitable for tropical woods. Diffusion penetration of low density hardwoods can occur quite rapidly in the constant high temperature and humidity conditions of the tropics. Thirty- eight mm-thick banak (*Virola* spp) wood in the Brazilian Amazon is completely and adequately penetrated after 7 days of storage in a shed following a 1-minute dip in a 25 percent boric acid equivalent (BAE) solution (Williams and Amburgey 1987). The moisture content of the wood being treated is a critical factor because diffusion with aqueous-based preservatives begins at about the fiber saturation point (about 30 percent wood moisture content).The rate of diffusion increases rapidly with increase in wood moisture up to about 100 percent, but increases above this level have little affect ( Smith and Williams 1969). In pratical terms, diffusion is best when the moisture content is much higher. An understanding of the effect of moisture content helps explain why the penetration results are different for sapwood and heartwood and when treating wood already in use. Heartwood and wood wood in service usually have much lower moisture contents. An inverse relationship exists between the density of wood and the rate of diffusion, but few studies of this relationship have been reported (Tamblyn 1985). When comparing treatment of woods with air dry specifice gravities of 0.71 and 0.96, the tranverse diffusion rates are about 4 to 6 times faster in lighter wood and almost 17 times faster in the longitudinal direction (Christensen 1951).

Christensen (1951) found that the rate of diffusion through wood of solutes containing either a bivalent or trivalent anion or cation can be 3 to 10 times slower than that of electrolytes in which both ions are univalent. He showed that the restricted rate appears to be greatest in the heartwood of dense timbers, where pathways often are narrow or partly blocked by chemical deposits. The anion was the restricted ion. This may explain why solutes not dissociated often diffuse rapidly-because they move through wood as electrically neutral molecules (Tamblyn 1985). In 1990, Lloyd and coworkers found that a borate preservative chemically reacts with poly-ols of wood, thus affecting its toxicity to certain organisms (Lloyd, Dickinson and Murphy 1990). This discovery raises the possibility that the rate of diffusion for borates could posibly be aided by formulation enhancement of chemical reactions. This also suggests that the rate of leaching could be reduced in certain wood species by specific borate formulations (Thompson 1991).

Fick's laws of diffusion

Fick's first law is used in steady state diffusion, i.e. , when the concentration within the diffusion volume does not change with respect to time.

$$J = -D\frac{\partial \phi}{\partial x}$$

where $J$ is the diffusion flux in dimensions of ((amount of substance)length$^{-2}$ time$^{-1)}$), (mol m$^{-2}$ s$^{-1}$)

$D$ is the diffusion coefficient or difffusivity in dimensions of (length$^2$ time$^{-1}$), (m$^2$ s$^{-1}$)

$\Phi$ is the concentration in dimensions of ((amount of substance) length$^{-3}$), (mol m$^{-3}$)

$x$ is the position (length), (m)

Fick's Second Law is used in non-steady or continually changing state diffusion, i.e., when the concentration within the diffusion volume changes with respect to time.

$$\frac{\partial \phi}{\partial t} = D\frac{\partial^2 \phi}{\partial x^2}$$

where $\Phi$ is the concentration in dimensions of ((amount of substance) length$^{-3}$), (mol dm$^{-3}$)

$t$ is time (s)

*D* is the diffusion coefficient in dimensions of (length$^2$ time$^{-1}$), (m$^2$ s$^{-1}$)

*x* is the position (length), (m)

Refractory species

Conifer wood must be regarded as a heterogeneous medium with respect to axial permeability. Erickson and Crawford (1959) found that after air-drying; permeability to water was reduced to 1-3% of its value for green wood. Such large changes of permeability are of great importance in wood preservation and in studies of water conduction in the living tree. In this respect, it is generally acknowledged that interfacial forces are partly responsible for many phenomena in timber drying.

In coniferous trees, water in sapwood is known to move longitudinally through the tracheid lumina, passing from one tracheid lumen to the next through the bordered pits. The same pathway is also used by preservative liquids when penetrating wood from a transverse surface. Both longitudinal and tangential flow paths in softwoods are predominantly by way of the bordered pits, while the horizontally aligned ray cells constitute the principal pathway for radial flow (Comstock 1970).

The longitudinal flow of softwoods is much greater than the tangential flow due to the fact that there are fewer pitted cross walls to transverse per unit length in the longitudinal than in the tangential direction (Siau 1984). It is therefore widely believed that in longitudinal flow through wood the greatest bulk fluid transport occurs through the bordered pits of the axial tracheids. Because tracheid lumina provide an unobstructed pathway for flow, it follows that the bordered pits will largely control the movement of fluids in conifer wood (Petty 1970).

The number of pits per tracheid varies from 50 to 300 in earlywood with only 10 to 50 rather small bordered pits in latewood (Stamm 1970), i.e. latewood is more permeable than earlywood in seasoned material whilst earlywood is more permeable than latewood in green wood (Petty and Preston 1969). In green wood, water may pass from one pit aperture to the other through the pit chamber and the pit membrane pores. When wood however is

dried the structure may be modified by the process of aspiration in which the torus moves across the pit chamber to seal off one of the pit apertures, thus preventing fluid flow through the pit.

As mentioned by Eaton and Hale (1993), in green softwood sapwood, longitudinal flow is favoured in the earlywood due to a number of factors, i.e. larger lumen diameters, more and larger bordered pits and larger cross-field pits. However, when dried, earlywood bordered pits aspirate due to surface tension forces and permeability is reduced. As mentioned by Tsoumis (1991), a common modification of bordered pit-pairs is the lateral displacement of the membrane. This phenomenon, called aspiration, usually occurs when sapwood is transformed into heartwood or when wood dries. Apparently, it results from high-tension forces set up by menisci formed in pit apertures and in pit membrane openings through which water (sap) is moving out. In softwoods, the torus seals one of the pit apertures and, therefore, blocks the passage through the pit. Aspiration makes the wood of fir, spruce, and Douglas fir difficult to impregnate with preservatives.

Phillips (1933) made what appears to be the first comprehensive study of pit aspiration. He found that drying sapwood caused a gradual increase in the number of aspirated pits with loss of moisture down to the vicinity of the fibre saturation point. At this point, virtually all the earlywood pits became aspirated, whereas about one-third of the latewood pits remained unaspirated. He described the greater tendency of latewood pits to resist aspiration to the greater rigidity of the latewood pit membrane.

Accordingly, the condition of bordered pits have significant influence on permeability of softwoods. In this case, the amenability of fluid flow is usually greater in green conditions of wood than in its dried conditions. During drying, capillarity and the related surface tension of the withdrawing liquid force the pit membrane and torus against the pit opening, and hence, causing aspiration effectively. So diffusion treatment is much more effective than pressure treatment in refractory species of wood since in diffusion we use the green wood for treating.

Cell types

Softwood cells

The wood substance in softwoods is composed of two different cells: tracheids (90-95%) and ray cells (5-10%). Tracheids give softwoods the mechanical strength required and provide for water transport, which occurs through the thin walled early wood tracheids with their large cavities. The liquid transport from one tracheid to another takes place through bordered pits; their amount in earlywood tracheids is about 200 per tracheid, most of them located in the radial walls in one to four lines. Late wood tracheids have only 10 to 50 rather small-bordered pits. Liquids move from the tracheids to the ray parenchyma cells through half bordered pits. The average length of Scandinavian softwood tracheids (Norway spruce and Scots pine) is 2-4 mm and the width in the tangential directions is 0.02-0.04 mm. The thickness of earlywood and latewood tracheids is 2-4 µm and 4-8 µm, respectively. The width of a ray usually corresponds to one cell. Several parenchyma cell files are placed one top of one another. Ray tracheids are often located at the lower and upper edges of this teir. Parenchyma cells are thin walled, living cells. In Norway spruce and Scots pine their length and width vary between 0.01-0.16 mm and 2-50 µm, respectively. The ray tracheids are of the same size and also provide liquid transport in the radial direction. Resin canals are intercellular spaces building up a uniform channel network in the tree. Horizontal canals are always located inside the rays which appear together in several files (Sjostorm 1993).

Hardwood cells

Hardwoods contain several cell types, specialized for different functions. The supporting tissue consists mainly of libriform cells, the conducting tissue of vessels with large cavities, and the storage tissue of ray parenchyma cells. In addition hardwood contains hybrids of the above-mentioned cells, which are classified as fiber tacheids. Libriform cells are elongated, thick-walled cells with small cavities containing some simple pits. The dimensions of libriform fibers are on an average 1.1-1.2 mm in length, 14-40 µm in width and 3-4 µm in thickness. Vessels are composed of thin walled and rather short (0.3-0.6) and

wide (30-130 μm) elements, which are placed on top of one another to form a long tube. The channels thus formed, which might be several meters in length, are capable of an effective water transport than the softwood tracheids. Hardwood rays consist exclusively of parenchyma cells. The ray account for 5-30% of the stem volume (Sjostorm 1993).

## 2.4 Leaching of preservatives

Waterborne preservative inorganic salts may be classified into three types: those that remain essentially unchanged and are subjected to leaching; those that become partially bound by the wood and are partially resisitant to leaching; and those that are fixed by chemical retention and are essentially leach resisitant. Presevative salts or components of oils that are water soluble will leach from treated wood according to physical laws. Generally, the rate of leaching is concentration-dependent according to the law of mass action. In the case of solutions, the rate of leaching is dependent on the partial coefficient, a constant ratio of the equilibrium concentrations of a chemical species present in small concentrations in two immiscible solvents. Preservatives are generally effective because of their ability to accumulate in the organism through solubility, either in the water or in the organism, by virtue of the distribution coefficient. If the preservative carrier has such a powerful solvency for the preservative that virtually no preservative leaches from the carrier, and if the solution is not absorbed by the organism, then the active ingredient may be ineffective as a wood preservative (Nicholas 1973).

Chemical preservatives bonds with wood to form what is called chemical fixation that prevents chemicals from leaching out. Levi (1969) has presented a discussion on the fixation and distribution of CCA in which he assumes the first stage is the rapid complexing of copper with the cell wall. The hexavalent chromium then reacts with the lignin, causing precipitation of $CrAsO_4$. Finally, residual copper precipitates as chromates and arsenates. Examination of wood treated with CCA by Belford and co-workers (1959), using optical microscopy, X-ray diffraction analysis, and electron microscopy, establishes that the preservative is situated within the cell wall. The orientation and complexing of copper within the cell wall was demonstrated by means of the dichroism associated with

the copper-dithio-oxamide complex. X-ray studies gave diffraction patterns similar to a copper-alkali-cellulose complex. Beford et al. (1960) have demonstrated that a large part of the copper in wood impregnated with a copper-chrome-arsenate solution is located in close assocition with the cellulose, probably bound to the hydroxyl groups. Borates are another class of waterborne chemicals. They do not have any fixation properties. Instead borates seek moisture throughout the wood. Thus, they can be applied with deep penetration without using pressure treatment. They will seek moisture through the wood and distribute themselves. Of course, they can easily come back out as borate treated wood is exposed to precipitation. Water-soluble salts such as zinc chloride, sodium fluoride, borax, and sodium arsenite do not provide long-term protection because they leach from the wood (Blew and Davidson 1969; Waterman and Williams 1934). The leaching of copper, zinc, and arsenic from Douglas-fir wood piles treated with a copper sulphate, zinc sulphate, and arsenic trioxide was studied , and, as is common with such leaching experiments, the rate of loss depended on the concentration, with higher concentrations leaching the most (Seyer 1945). Partial fixation of waterborne inorganic salts may be obtained from the wood itself, but there are differences in leaching between species caused by the differences in anatomical structure and chemical fixation. The amount of copper sulphate leached from blocks of wood after 16 days was 43.6 percent in southern pine sapwood, 51.5 percent in red oak heartwood, 54.3 percent in Sitka spruce heartwood, and 64.9 percent in hard maple sapwood (Baechler and Roth 1956).

Fence posts, utility poles and other wood products used in contact with the ground give extended service life when they have been chemically treated with wood-preserving compounds. Such wood has withstood the destructive attacks of fungi and insects for up to 15 to 25 years or more. Failure due to decay or insects starts because the natural toxicity of the wood or the original preservative concentration has been changed or reduced to a point just below that of retention, defined as the "threshold concentration". Threshold concentration is defined as "The minimum chemical amount impregnated into a block of wood which will completely inhibit the attack of specific fungus organism on that block of wood under the specified test conditions" (Fahlstrom 1964).

Baechler and Roth have reported on the individual threshold concentrations of both sodium borate by the soil-block technique. Similar tests conducted in our laboratory have generally confirmed their results.

Table 3. A comparison of the threshold values of these two chemical preservatives against several common fungi (Fahlstrom 1964).

| **Fungi** | **NaF (lbs/cu ft)** | **$Na_2B_4O_7$ (lbs/cu ft)** |
|---|---|---|
| *Lentiunus lepideus* | 0.12 - 0.15 | 0.05 - 0.07 |
| *Coniofera putena* | 0.15 - 0.17 | 0.05 - 0.07 |
| *Poria monticola* | 0.18 - 0.20 | 0.05 - 0.07 |
| *Polyporus versicolor* | 0.84 - 1.41 | 0.11 - 0.18 |
| *Lentiles frabea* | 0.16 - 0.19 | 0.08 - 0.12 |

Table 4. Threshold concentrations for sodium borate and copper borate (Baechler and Roth 1956; Fahlstrom 1964).

| **Fungi** | **Copper borate (lbs/cu ft)** | **Sodium borate (lbs/cu ft)** |
|---|---|---|
| *N.lepideus* | 0.21 | 0.05-0.07 |
| *C.puteana* | 0.21 | 0.05-0.07 |
| *P.placenta* | 0.41 | 0.05-0.07 |
| *T.versicolor* | 0.53 | 0.11-0.18 |
| *G.trabeum* | 0.62 | 0.08-0.12 |

The highest concentrations against all fungi tested was 0.025 moles, equivalent to 0.632 percent $CuSO_4.5H_2O$ or 0.12 percent copper. At this concentration, which is sufficient to

inhibit the growth of a wide range of fungi, 7 of 8 brown-rotting *Porias* tested grew, but only 3 of the 12 white rot fungi. The two most sensitive white rot fungi, *P. coprosmae* and *P. eupora*, showed no growth at the lowest concentration tested (0.001 moles copper sulphate, equivalent to 0.025 percent $CuSO_4.5H_2O$ or 0.006 percent copper (Costa and Kurruish 1964).

Table 5. Toxicity of copper sulphate in Agar medium to *Poria* species (Costa and Kurruish 1964).

| Species | Percentage of control growth at: | | |
|---|---|---|---|
| | 0.001 M (0.006% Cu) | 0.005 M (0.032% Cu) | 0.025 M (0.16% Cu) |
| A. Brown Rot Fungi | | | |
| *P.cocos* | 124 | 24 | 13 |
| *P.incrassata* | 99 | 88 | 19 |
| *P.otakou* | 101 | 95 | 30 |
| *P.vaillanti* | 93 | 64 | 2 |
| *P.xantha* | 97 | 0 | 30 |
| *Poria sp.* A | 87 | 0 | 0 |
| *Poria sp.* D | 104 | 76 | 8 |
| B. White Rot Fungi | | | |
| *P. coprosmae* | 0 | 0 | 0 |
| *P. eupora* | 0 | 0 | 0 |
| *P. hyposclera* | 95 | 31 | 5 |
| *P. leucoplaca* | 106 | 44 | 0 |
| *P. mutans* | 90 | 54 | 23 |
| *P. nigrescens* | 64 | 12 | 0 |
| *P. pirongia* | 74 | 9 | 0 |
| *P. radula* | 77 | 0 | 0 |
| *P. rata* | 101 | 0 | 0 |
| *P. vulgaris* | 83 | 0 | 0 |
| *P. weirii* | 93 | 33 | 0 |
| *Poria sp. F* | 87 | 73 | 13 |

## 2.5 Borates as preservative

Borate preservatives are readily soluble in water, are highly leachable, and should only be used above ground where the wood is protected from wetting. When used above ground and protected from wetting, this preservative is very effective against decay, termites, beetles, and carpenter ants. Borates are odorless and can be sprayed, brushed, or injected. They will diffuse into wood that is wet; therefore, these preservatives are often used as a remedial treatment. Borates are widely used for log homes, natural wood finishes, and hardwood pallets. The solid or treating solution for borate preservatives (borates) should be greater than 98% pure, on an anhydrous basis (AWPA P5). Acceptable borate compounds are sodium octaborate, sodium tetraborate, sodium pentaborate, and boric acid. These compounds are derived from the mineral sodium borate, which are the same material used in laundry additives (FPL 1999).

Borates are naturally occurring salts that result from the combination of two elements, oxygen and boron. Borates are found as mineral deposits around the world, with a particularly large store in the United States, in the deserts of California. They have long been used in hand soap powders and laundry boosters. Borates are also found in contact lens cleaners, eyewashes, cosmetics, ceramics, medicines and dozens of other common products. Because they are considered benign for human health, borates are perhaps the most suitable wood preservatives for interior construction components. Borates are also inorganic, which means they contain no volatile organic compounds (VOCs). VOCs are air pollutants sometimes associated with various health and odour complaints. Without harming humans, borates are effective at inhibiting pests such as termites, beetles, carpenter ants and wood–rotting fungi. In fact, since the 1940s, borates have been successfully applied to wood products to protect them against insect attack. Two main classes of borate are used in wood preservatives: sodium borate and zinc borate. Disodium octaborate tetrahydrate (DOT) is a sodium borate specifically designed for treating lumber and other solid wood products. Zinc borate, a low solubility borate, is used for the preservative treatment of wood composites such as oriented strandboard, hardboard and wood–fiber/plastic composites. The mode of action is not fully understood, but borates

appear to disrupt the digestive process of the insect, causing it to starve. For fungi, borates are generally thought to work by preventing enzymic activity at the cellular level of the organism. A broad range of insects and fungi are inhibited by relatively low levels of sodium borate (approximately 0.2% by weight) in wood products. Termites require a higher level of preservative, depending on the termite species. For example, the Formosan subterranean termite (one of the world's most economically significant pests for wood products) requires approximately 2% borates by weight in lumber (Forlntek Canada Corp 2002).

Borates are said to be effective, environmentally compatible wood preservative for the 1990s. Relatively few United States producers are providing borate-treated wood products, although borates have been commercially used as wood preservatives for fifty years in other countries. Borate treatments of wood in situ in buildings have been readily accepted by the U.S. commercial pest-control industry within the last six years and are now available nation wide. However, most U.S. building-code and regulatory officials remain reluctant to approve the use of borates or borate-treated wood in structures as a preventive treatment for termites.

Borates have low mammalian toxicity but are toxic to nearly all wood damaging insects and fungi and have low volatility and no odor. Wood treated with borates is not discolored; it may be machined, glued, painted or stained, and is non-corrosive to most fasteners (Williams 1996). A key advantage is that most borates are water-soluble and remain mobile in wood after treatment. This mobility allows to use the available moisture in wood and penetrate difficult-to-treat species by diffusion (Tamblyn 1985, Murphy 1990).

Borates were first tested as wood preservatives in the United States in the early 1900s,but until the last decade most of the research and commercial development has taken place elsewhere. Reports of these early tests may have branded borates as ineffective preservatives because they did not protect wood in ground contact, the major use of treated wood then and now (Williams 1990). Commercial use began in Australia in 1938 and in New Zealand in 1952, where it now accounts for 25 to 30% of all treated wood. Historical

reviews of the use of borates in various world regions are contained in Proceedings 47355 of the First International Conference on Wood Preservation with Diffusible Preservatives (Hamel 1990). Grace and Yamamoto (1994) found that a borate/glycol formulation resulted in much higher borate loadings in extractive-laden, Douglas-fir heartwood than was obtained with a water-based borate solution.

For increased use of borate-treated wood in construction, it is necessary to overcome the perceptions of being too costly and of being leachable and the common U.S. practice of using untreated wood and obtaining remedial treatment after insect problems occur. Several authors (Drysdale 1994, Lloyd 1995, Murphy 1990, Tamblyn 1985) concluded that borate-treated wood should not be used in ground contact but that leaching posed no problem for use in structures where protected by a roof or a well maintained coating such as paint. Others (e.g., Nicholas et al.1990) considered the leachability of borates prohibiting using borate-treated wood.

## 2.6 Environmental Considerations

Copper sulfate is classified as a General Use Pesticide (GUP) by the U.S. Environmental Protection Agency (EPA). Copper sulfate is toxicity class I - highly toxic. Because of its potentially harmful effects on some endangered aquatic species, surface water use may require a permit in some places. Copper sulfate is also called Agritox, Basicap, BSC Copper Fungicide, CP Basic Sulfate and Tri-Basic Copper Sulfate. The pentahydrate form is called bluestone, blue vitriol, Salzburg vitriol, Roman vitriol, and blue copperas. Bordeaux Mixture is a combination of hydrated lime and copper sulfate. Copper sulfate is often found in combination with other pesticides (Extension Toxicology Network 1996).

Copper sulphate is toxic to human beings at high levels. Absorption of copper sulfate into the blood occurs primarily under the acidic conditions of the stomach. The mucous membrane lining of the intestines acts as a barrier to absorption of ingested copper. After ingestion, more than 99% of copper is excreted in the feces. However, residual copper is an essential trace element that is strongly bioaccumulated (U.S. National Library 1995). It is

stored primarily in the liver, brain, heart, kidney, and muscles. Copper sulfate is highly toxic to fish (Pimentel 1971). Even at recommended rates of application, this material may be poisonous to trout and other fish, especially in soft or acid waters. Its toxicity to fish generally decreases as water hardness increases. Fish eggs are more resistant than young fish fry to the toxic effects of copper sulfate (Gangstad 1986). Copper sulfate is toxic to aquatic invertebrates, such as crab, shrimp, and oysters. The 96-hour LC50 of copper sulfate to pond snails is 0.39 mg/L at 20 C. Higher concentrations of the material caused some behavioral changes, such as secretion of mucous, and discharge of eggs and embryos (U.S. National Library 1995).

In 1991, the U.S. Environmental Protection Agency established guidelines for controlling copper levels in public water supplies. Levels of copper found naturally in ground water and surface water are generally very low; about 4 µg/L of copper or less. On the average, drinking water accounts for less than 5% of our daily copper intake. The U.S. Environmental Protection Agency (U.S. EPA) has determined that copper levels in drinking water should not exceed 1300 µg/L. No adverse health effects would be expected if this level is not exceeded. Measures should be taken to reduce exposure to copper if this level is exceeded (Department of Natural Resources, Wisconsin 2003).

Within the last decade, environmental considerations have become a major concern commercial wood treaters and major users of treated wood products. The increased environmental restrictions have stimulated a search for safer, more environmentally acceptable wood preservatives. The major wood preservative used in the U.S. is water-borne CCA. Based on wood volume, about 80% of all treated wood in the U.S. is treated with CCA. However, there are lots of concerns with CCA including a public perception of arsenic exposure, leaching of metal oxides and the question of ultimate disposal of treated wood. The use of CCA has been restricted by 2004 to only non-residential applications. Alternative, second-generation wood preservatives for residential applications are copper-organic mixtures. Although copper is not as toxic as arsenic or chromium accumulation of copper does have some negative environmental effects, especially in aquatic systems and

disposal of any metal-treated wood product may be expensive and difficult in future. Thus copper-organic mixtures may also face future restrictions in the U.S. Indeed, several countries in Europe are already moving towards totally organic preservative systems. A number of organic biocides are already commercially available as agrochemicals and have been examined as potential wood preservative. The relative high cost of these organic biocides, environmental regulations, and public concerns with bioactive compounds will undoubtably result in efforts to minimize the amount of biocide used. In addition to effectively and economically protecting wood against a wide variety of wood decaying organisms, alternative preservative systems must have good weathering and UV protection properties, minimal leaching of the active compound, and be non-corrosive to metal fasteners (Barry, Nicholas and Schultz 2003).

# Chapter-3

## 3. Materials and Methods

### 3.1 Phase I

The first phase of research was to determine minimum soak and storage times to achieve maximum levels of preservative retention and the degree of penetration in wood samples of Alaskan spruce *(Picea glauca)* and Hawaiian albezia (*Albezia falcataria*). The preservative used was commercial copper-borate formulation (Cu-Bor, manufactured by Copper Care Wood Preservatives, Inc., Columbus, NE).

#### 3.1.1 Sample preparation

Twenty 4”x 2”x 2” samples each for Alaskan spruce and Hawaiian albezia were used in each of the treatment schedules. These samples were obtained from ten 48”original samples obtained for the experiment. Two samples were obtained from each of the original sample separately to determine moisture content measurements and specific gravities. One section was cut from the end of the member; the second section was cut from the middle of the member. Moisture content was determined using the oven dry method.

#### 3.1.2 Solution Preparation

The preservative used was commercial copper-borate formulation (Cu-Bor, manufactured by Copper Care Wood Preservatives, Inc., Columbus, NE). 50% of preservative solution was used for the experiment. The active ingredients in the Copper-borate preservative are:
Copper hydroxide ($Cu(OH)_2$) = 3.1%
Sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) = 43.5%
Inert ingredients = 53.4%

3.1.3 Treatment schedule

Treatment Schedule consisted of a 2 days soak, 4 days soak, and 6 days soak in 50% copper-borate solution respectively and each treatment schedule consists of no storage, 2 weeks, 4 weeks, and 6 weeks storage. Five specimens were randomly chosen to obtain penetration samples for each treatment. Chemical solutions were contained in polyethylene tanks to prevent corrosion. Samples were removed to perform visual and chemical analysis to determine the chemical penetration. Twenty 4”x 2”x 2” samples penetration samples were used to determine the degree to which chemicals entered the wood via the longitudinal direction. 15 mm retention samples along the radial direction were taken from each of the treated samples for retention test.

Table 6. Tests that have been carried out in this study.

| Treatment | Penetration | Retention |
|---|---|---|
| Commercial copper-borate formulation | Penetration was measured to determine extent of 1) copper and 2) boron diffusion following AWPA A3-00 | 1) The copper analysis was done via Standard A9-01 "Standard Method for Analysis of Treated Wood and Treating Solutions by X- Ray Spectroscopy"<br><br>2) The boron was analyzed by Standard A2-05 Method 16 "Determination of Boron in Treated Wood using Azomethine-H ". |

### 3.1.4 Chemical analysis for penetration samples

The penetration samples were analyzed according to procedures described in Standard A3-00 (AWPA 2003a) for boron and (AWPA 2003b) for copper by "Standard methods for determining penetration of preservatives and fire retardants." Twenty 4"x 2"x 2" samples penetration samples were used to determine the degree to which chemicals entered the wood via the longitudinal direction. Two different solutions were made for determining penetration of boron. In first solution, 10 g turmeric was dissolved in 90 g of ethyl alcohol and the solution was filtered. The second solution, 20 mL of concentrated hydrochloric acid was diluted in 100 mL of ethyl alcohol and saturated with salicylic acid (about 13 g per 100 mL). The samples for penetration were dried prior to making the final cut to expose the surface for spraying. The first solution was applied by spraying to the surface to be treated. The surface was then allowed a few minutes to dry. Then the second solution was applied in a similar manner to the areas that have been colored yellow by the application of first solution. The color changes were observed carefully after the application of the second solution. In the presence of boron, the yellow turmeric solution was turns red. A solution of 0.5 g Chrome Azurol and 5.0 g of sodium acetate dissolved in 80 ml water and further diluted to 300 ml was used for determining penetration of copper. The solutions were sprayed over the freshly cut surfaces of treated wood. A deep blue color reveals the presence of copper.

### 3.1.5 Chemical analysis for retention samples

The retention test for the treated samples were done in Timber Products Inspection Lab, Conyers, GA. Two retention cores measuring 15 mm in length along the radial direction were taken from each of the 5 specimens for each of the treatment schedule. The cores was dried to 0 % moisture content and was ground to a fine powder and was sent for the retention analysis. The copper analysis was done via A9-01 (AWPA 2003e) Standard Method for Analysis of Treated Wood and Treating Solutions by X- Ray Spectroscopy and the boron was analyzed by Standard A2-05 (AWPA 2003d) Determination of Boron in Treated Wood using Azomethine-H.

Copper analysis

Copper in the treated wood was analyzed according to procedures described in A9-01 (AWPA 2003e) by X- Ray Spectroscopy. The samples were dried to achieve 0% moisture content. The entire samples were milled to sufficient fineness to pass a 30-mesh screen. After milling samples were recovered as much as from the grinding device. Samples were compressed into pellets for analysis. The samples were then irradiated. Sensitive detectors measured the characteristic X-rays of the atom that were emitted. Detector output was related to the concentration of copper with calibration curves. Series of standards were prepared by impregnating sawdust of the same species and approximate density with known amounts of solutions spanning the entire rage of retentions were used in determining calibration curves. Copper detected by the X- Ray Spectroscopy was reported as % wt/wt in the wood dust.

Boron analysis

Boron in the treated wood was analyzed according to procedures described in Standard A2-05 (AWPA 2003d) Method 16 "Determination of Boron in Treated Wood using Azomethine-H or Carminic Acid. The wood was dried to 0% moisture content and was ground to a fine powder, 30 mesh. Wood was weighed to 1 to 2 g of sample, to nearest 0.01 g, into 250 ml Erlenmeyer flask. 75 to 100 ml of distilled water was added to the flask containing wood samples. The contents of the flask were boiled gently and continued heating for 30 minutes. The contents were allowed to cool and filtered through Whatman # 4 filter paper. A stock solution, containing 100 ppm boron, was prepared by dissolving 0.5715 g of reagent grade boric acid in one liter of water. Standards containing 1 to 10 ppm boron were prepared by diluting stock solution with water. 1.0 ml of each of the standard and unknown solutions were pipetted into 1 cm cuvettes. Cuvettes with 1.0 ml of ditilled water were also prepared as a reagent blank. 1.0 ml of the buffer solution was added to each cuvette and the solutions were mixed. 1.0 ml of azomethine-H was added and the solutions were mixed again. The absorbance at 420 nm was measured 30 to 40 minutes after addition of the azomethine-H. The reagent blank was used to zero the instrument. A standard curve was made by plotting the absorbance on the y-axis and ppm boron on the x-axis. The ppm of boron of the unknown was determined from the graph by reading the concentration on the x-axis. Boron in the

solution was reported in as µg/mL. Using suitable conversion factor the results were reported in % wt/wt in the wood dust.

3.2 Phase II

Our Second objective was to determine level of fixation that occurred with both single and double diffusion treatments of copper and borate solutions since leaching of the chemicals is of concern. American Wood-Preservers' Association (AWPA) Standards were used to determine penetration and leaching of the copper and borate components of the individual treatments. The preservatives used were commercial copper-borate formulation (Cu-Bor, manufactured by Copper Care Wood Preservatives, Inc., Columbus, NE), borosol preservative and copper sulphate.

Table 7. Tests that have been carried out in this study.

| Treatment | Leaching |
|---|---|
| Commercial copper-borate formulation | Samples treated with this solution were leached following AWPA E11-97 |
| Commercial borate solution | Samples treated with this solution were leached following AWPA E11-97 |
| Double-diffusion of copper sulphate, then borate solutions | Samples treated with this process were leached following AWPA E11-97 |
| Double diffusion of borate, then copper sulphate solutions | Samples treated with this process were leached following AWPA E11-97 |

The leaching analysis provided insights into how well the chemicals, which easily diffuse into green wood, remain in wood during prolonged soaking. The leaching test Standard E11-97 (AWPA 2003c) evaluates the amount of chemical lost during prolonged soaking of small sample blocks measuring 19 mm (3/4") on each side.

3.2.1 Sample preparation

Test blocks of Alaskan spruce and Hawaiian albezia were milled to 19.0 mm ± 0.2mm (3/4") cubes. The volume of each block was 6.9 ± 0.2 mL as determined by caliper measurement. The test blocks were conditioned to moisture content of 9-10%. Blocks were weighed and sorted them into weight range groups with differences of less than 0.5 g.

3.2.2 Solution Preparation

The chemical used for the first leaching test was 33.3% (1X) of the Copper- borate solution. The second leaching test was carried out using 8% Borosol solution. The third leaching test were carried out using 8% Copper sulphate and 8% Borosol solutions (i.e. treating the wood samples in 8% Copper sulphate solution (impregnated) and then one day dip in 8% Borosol solution). The fourth leaching test was carried out using 8% Copper sulphate and 8% Borosol solutions (i.e. impregnating the wood samples with 8% Borosol solution followed by a one day dip in 8% Copper sulphate solution).

The active ingredients in these preservatives are

Copper-borate (Cu-Bor)

Copper hydroxide ($Cu(OH)_2$) = 3.1%

Sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) = 43.5%

Inert ingredients = 53.4%

Borosol (Commercial borate solution)

Disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) = 98%

Inert ingredients = 2%

Copper-sulphate

Cupric sulphate ($CuSO_4.5H_2O$) = 100%

3.2.3 Impregnation procedure

Twelve blocks from a single weight range group for each retention group were selected. Blocks to be treated were placed in a suitable beaker and weighed down to prevent floating during treatment. The beaker was placed in a dessicator of the impregnation apparatus. The apparatus was attached to a vacuum and the pressure in the treating chamber was reduced to 13.3 kPa for 20 minutes. After 20 minutes the vacuum was released and covered with a plastic film for 30 minutes. The retention was calculated for each block:

Calculation of retention- Retention, $kg/m^3 = GC/V * 10$

Retention, $lbs/ft^3 = (GC * 62.4)/100V$

Where:

G = The weight in grams of the treating solution absorbed by wood.

C = Grams of the preservative in 100 grams of treating solution.

V = Volume of wood in mL.

Blocks for double diffusion were followed by a one day dip in the next chemical solution, thus, blocks impregnated with copper sulphate were dipped in borosol (commercial borate solution) solution for 24 hours and blocks impregnated with borosol (commercial borate solution) were dipped in copper sulphate solution for 24 hours.

3.2.4 Leaching procedure

For each retention level 6 blocks were selected with the most uniform retention levels. Six blocks were impregnated using a maximum of 300 ml deionized water. For each retention group, six water-impregnated blocks were placed in the leaching flask. The residual impregnating water was quantitatively washed into the leaching flask to a total volume of 300 mL. The leaching flask was covered with a lid to prevent the evaporation of the leachate. It was stirred slowly with a tip speed of 250-500 mm/sec with the same size and type of magnetic stir bar. The temperature was maintained at 23 ± 0.5º C.

Leachate samples were collected after 6, 24, and 48 and thereafter at 48-hour intervals for a total of 14 days. All the leached blocks and leachate samples are saved for analysis. Each leachate sample was analyzed for each preservative component (Cu and B). The amount of chemicals from wood that was leached was expressed in terms of milligrams per liter (mg/l).

Percent of chemical leached = A/B*100

Where:

A = Total weight of component(s) in leachate

B = Total weight of components(s) in unleached blocks.

One of the unleached blocks with average retention and six leached blocks of each of the treatment were selected and was sent for analysis for each of the preservative components (Cu and B). The analysis was performed by Timber Products Inspection Lab, Conyers, GA. The copper analysis was done via Standard A9-01 (AWPA 2003e) "Standard Method for Analysis of Treated Wood and Treating Solutions by X- Ray Spectroscopy" and the boron was analyzed by Standard A2-05 (AWPA 2003d) Method #16 "Determination of Boron in Treated Wood using Azomethine-H ". Copper and boron were determined on the dry weight basis and the results were obtained in % wt/wt basis of the dry wood.

3.2.5 Leachate analysis

Copper analysis

Leachate samples were collected after 6, 24, and 48 and thereafter at 48-hour intervals for a total of 14 days. All the leached blocks and leachate samples are saved for analysis. Each leachate sample was analyzed for each preservative component (Cu and B). The copper analysis in the leachate was done using "Neocuproine method" (Standard methods 2005b). 100 mL of each sample was transferred to a 250 mL beaker and 1 mL of conc. $H_2SO_4$ and 5 mL of conc. $HNO_3$ was added to it. A few boiling chips were added and cautiously evaporated to dense white fumes on a hot plate to make solution colorless. The solution was cooled and filtered into a 100 mL volumetric flask. 50 mL of the solution containing copper from the preliminary treatment was pipetted into a 125 mL separatory funnel. 5 mL of $NH_2OH.HCl$ solution and 10 mL sodium citrate solution was added and mixed thoroughly.

10 mL of neocuproine reagent and 10 mL $CHCl_3$ are added to it and shaken vigorously. The mixture was separated into two layers and the lower $CHCl_3$ layer was separated into a 25 mL volumetric flask. The extraction was repeated with an additional 10 mL $CHCl_3$ and the combine extracts. The combined extract was diluted to 25 mL with $CH_3OH$. An appropriate portion of the extract was transferred to a suitable absorbance cell of UV- spectrometer and absorbance was measured at 4571 nm. A standard curve was made by pipetting 1.00 to 10.00 ml (20.0 to 200 µg copper) standard copper solutions into a series of 125 mL separatory funnels and was diluted to 50 mL with water. The copper in final solution was determined by reference to the appropriate standard curve.

$$\text{Mg Cu/L} = \frac{\mu\text{g Cu (in 25 mL final volume)}}{\text{mL portion taken for extraction}}$$

Boron analysis

The boron analysis of leachate was done using "Curcumin method" (Standard methods 2005a). One mL from each of the samples was pippetted into an evaporating dish. Four mL of curcumin reagent was added to each of the evaporating dishes and was swirled gently to mix the contents thoroughly. The dishes were floated on a water bath set at 55º C for 80 mins to allow complete drying and complete removal of HCl. After the dishes are cooled at room temperature, 10 mL 95 % ethyl alcohol was added to each dish and stirred with a polythene rod to ensure complete dissolution of the red-colored product. All the dish contents were washed into a 25 mL volumetric flask using 25 % ethyl alcohol and were made up to the mark. An appropriate portion of the extract was transferred to a suitable absorbance cell of UV- spectrometer and absorbance was measured at 540 nm. Pipetting 0, 0.25, 0.50, 0.75, and 1.00 µg boron made a standard curve. The boron in final solution was determined by reference to appropriate standard curve.

$$\text{mg B/L} = \frac{\text{Absorbance of the sample}}{\text{Absorbance of the standard * mL sample}}$$

# Chapter-4

## 4. Results and Discussion

### 4.1 Phase. I

#### 4.1.1 Moisture content and Specific gravity

The moisture content of Alaskan spruce ranged from 35.7 to 51.4% and the moisture content of Hawaiian albezia showed a wide distribution from 63.5 to 146.5%. The Specific gravity of Alaskan spruce ranged from 0.33 to 0.35 g/cm$^3$ and that of Hawaiian albezia ranged from 0.28 to 0.35 g/cm$^3$. Percentage moisture content of Alaskan spruce was considerably lower than that of Hawaiian albezia. The lumber was transported in green state. One of the possible reasons for wide range of moisture content may be the stacking pattern after processing. Processed lumber towards the interior of the stack can retain higher moisture content than lumber located towards the edges. A possible explanation for low moisture content in the Alaskan spruce samples may be attributed to high percentage of heartwood in the lumber.

Table 8. Moisture content and specific gravity (green volume, oven dry weight) of Alaskan spruce specimens used in this study.

| | Moisture content (%) | Specific gravity (g/cm$^3$) |
|---|---|---|
| **Alaskan spruce** | 36.4 | 0.35 |
| | 48.9 | 0.35 |
| | 45.5 | 0.35 |
| | 35.7 | 0.35 |
| | 51.4 | 0.33 |
| | 40.8 | 0.35 |
| Mean | 43.1 | 0.35 |
| Std dev | 6.56 | 0.008 |

Table 9. Moisture content and Specific gravity (green volume, oven dry weight) of Hawaiian albezia specimens used in this study.

| | Moisture content (%) | Specific gravity ($g/cm^3$) |
|---|---|---|
| **Hawaiian albezia** | 65.5 | 0.32 |
| | 95.5 | 0.28 |
| | 63.7 | 0.29 |
| | 133.3 | 0.31 |
| | 63.5 | 0.28 |
| | 146.5 | 0.33 |
| | 140.7 | 0.34 |
| | 119.6 | 0.33 |
| | 140.4 | 0.35 |
| | 98.4 | 0.32 |
| Mean | 106.7 | 0.32 |
| Std dev | 33.91 | 0.025 |

4.1.2 Penetration and Retention results

Our first objective was to determine minimum soak and storage times to achieve suitable levels of preservative retention and the degree of penetration in a single diffusion process. The extent of longitudinal penetration was measured for each of the soak and storage times. Readings were taken from each of samples and were averaged after calculating the outliers and are presented in tables below. Graphical representations are also shown with the degree of penetration along the Y-axis and the storage time along the X-axis. The penetration analysis indicates that a maximum longitudinal penetration of copper for Alaskan spruce was 9.23 mm and can be achieved with a 2-day soak, as long as the soaked pieces are stored in the wet condition for a period of 6 weeks. Maximum longitudinal penetration of boron for Alaskan spruce was 10.2 mm and can be achieved with a 6-day soak, as long as the soaked pieces are stored in the wet condition for a period of 6 weeks. The penetration analysis indicates that a maximum longitudinal penetration for Alaskan spruce of approximately 8-10 mm for both copper and boron can be achieved with a 2-, 4-, or 6-day soak period, as long as the soaked pieces are stored in the wet condition for a period of 2-6 weeks. The longer storage period of 6 weeks was necessary to achieve maximum penetration in the samples soaked for the minimum 2-days. The greatest diffusion occurred during the first two weeks

of storage after that the diffusion occurred fairly lower rate. So maximum quantity of the preservative is obtained in Alaskan spruce by a soak period of 2- days and the storage period of 6 weeks under proper conditions is necessary for obtaining the penetration to the maximum depth.

Table 10. Longitudinal penetration results for 2-day soak in 50% Cu-Bor solution for Alaskan spruce.

| Storage (Weeks) | Copper penetration (mm) | Boron penetration (mm) |
|---|---|---|
| 0 | 5.56 | 3.69 |
| 2 | 6.81 | 6.28 |
| 4 | 7.67 | 7.30 |
| 6 | 9.23 | 9.45 |

Figure 1. Longitudinal penetration of 50% Cu-Bor solution after a 2-day soak and storage for up to 6 weeks for Alaskan spruce.

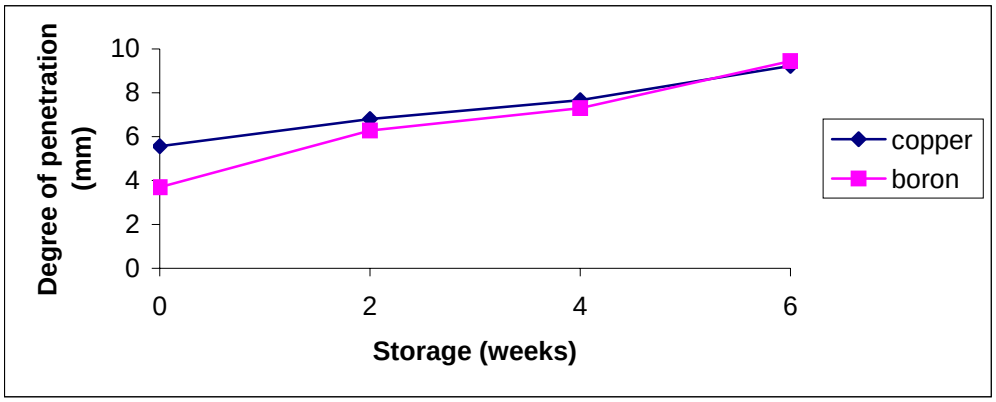



Table 11. Longitudinal penetration results for 4-day soak in 50% Cu-Bor solution for Alaskan spruce.

| Storage (Weeks) | Copper penetration (mm) | Boron penetration (mm) |
|---|---|---|
| 0 | 6.40 | 6.31 |
| 2 | 8.53 | 8.15 |
| 4 | 8.80 | 8.51 |
| 6 | 8.77 | 8.51 |

Figure 2. Longitudinal penetration of 50% Cu-Bor solution after a 4-day soak and storage for up to 6 weeks for Alaskan Spruce *(Picea glauca)*.

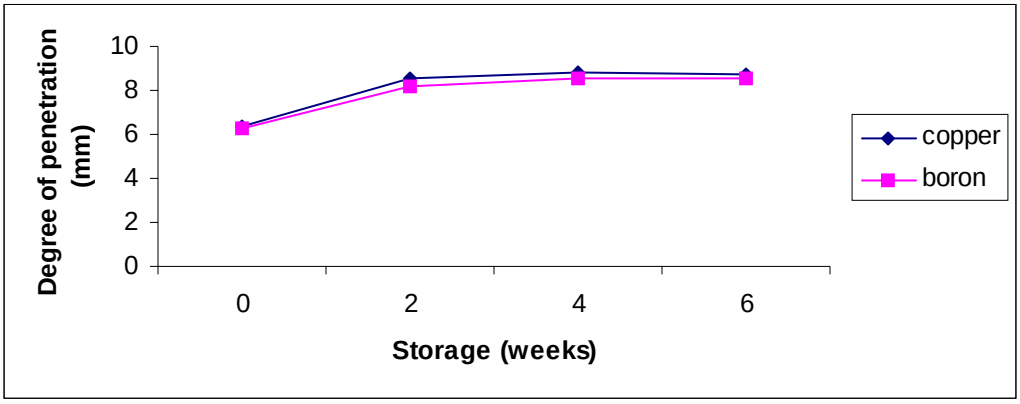
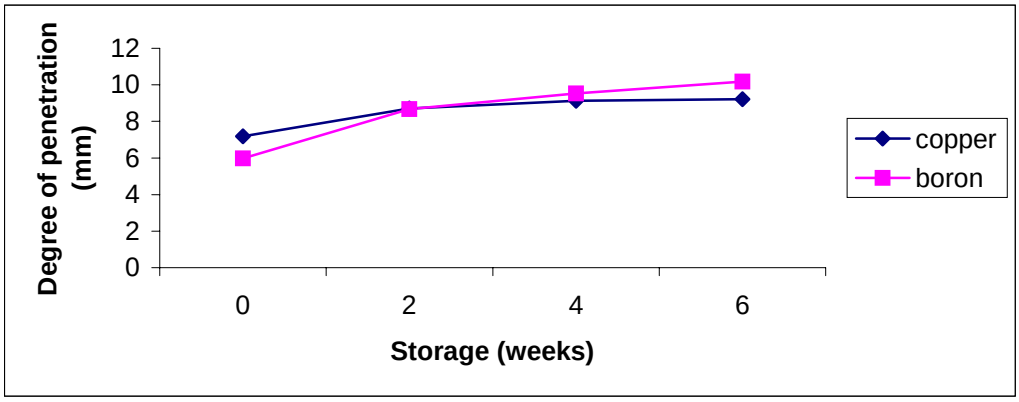



Table 12. Longitudinal penetration results for 6-day soak in 50% Cu-Bor solution for Alaskan spruce.

| Storage (Weeks) | Copper penetration (mm) | Boron penetration (mm) |
|---|---|---|
| 0 | 7.19 | 5.97 |
| 2 | 8.70 | 8.68 |
| 4 | 9.12 | 9.53 |
| 6 | 9.22 | 10.17 |

Figure 3. Longitudinal penetration of 50% Cu-Bor solution after a 6-day soak and storage for up to 6 weeks for Alaskan spruce.




The penetration analysis indicates that a maximum longitudinal penetration of copper for Hawaiian albezia was 13.45 mm and can be achieved with a 4-day soak, as long as the

soaked pieces are stored in the wet condition for a period of 4 weeks. Penetration analysis indicates that for Hawaiian albezia the penetration of copper was in a declining stage after 4 weeks of storage for 4 days and 6 days soak wood samples. The penetration analysis indicates that a maximum longitudinal penetration for Hawaiian albezia of approximately 10-13 mm can be achieved with a 2-, 4-, or 6-day soak period, as long as the soaked pieces are stored in the wet condition for a period of 2-4 weeks. The boron penetration was found to be very high for Hawaiian albezia. After the storage period in each of treatment schedules, the boron penetration was found to be almost complete in all samples (50 mm from both directions). A soak period of 4- days and a storage period of 2 weeks was necessary for obtaining chemical penetration to its maximum depth for Hawaiian albezia. One of the reasons for high penetration in Hawaiian albezia may be attributed to the high moisture content of the specimens. The average moisture content of Hawaiian albezia was 106.7% compared to 43.1% in Alaskan spruce. The wood structure of Hawaiian albezia may also be attributed to high penetration. The vessels in Hawaiian albezia form several channels capable of a more effective water transport than the softwood tracheids. In coniferous trees, water in sapwood is known to move longitudinally through the tracheid lumina, passing from one tracheid lumen to the next through the bordered pits. The condition of bordered pits has significant influence on permeability of softwoods. Pit aspiration makes the wood of fir, spruce, and Douglas fir difficult to impregnate with preservatives. This can be one of the reasons for less penetration in Alaskan spruce.

Table 13. Longitudinal penetration results for 2-day soak in 50% Cu-Bor solution for Hawaiian albezia.

| Storage (Weeks) | Copper penetration (mm) | Boron penetration (mm) |
|---|---|---|
| 0 | 5.41 | 4.09 |
| 2 | 7.67 | 50+ |
| 4 | 10.15 | 50+ |
| 6 | 10.98 | 50+ |

Figure 4. Longitudinal penetration of 50% Cu-Bor solution after a 2-day soak and storage for up to 6 weeks for Hawaiian albezia.

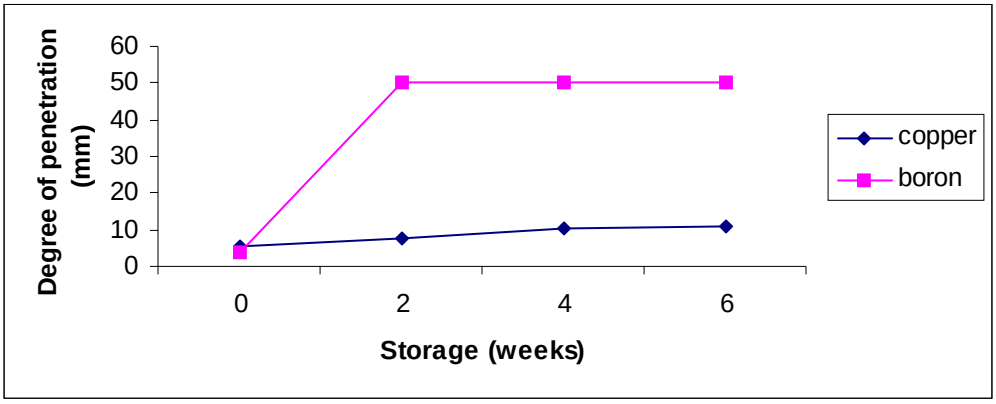



Table 14. Longitudinal penetration results for 4-day soak in 50% Cu-Bor solution for Hawaiian albezia.

| Storage (Weeks) | Copper penetration (mm) | Boron penetration (mm) |
|---|---|---|
| 0 | 6.32 | 5.9 |
| 2 | 11.41 | 50+ |
| 4 | 13.45 | 50+ |
| 6 | 9.45 | 50+ |

Figure 5. Longitudinal penetration of 50% Cu-Bor solution after a 4-day soak and storage for up to 6 weeks for Hawaiian albezia.

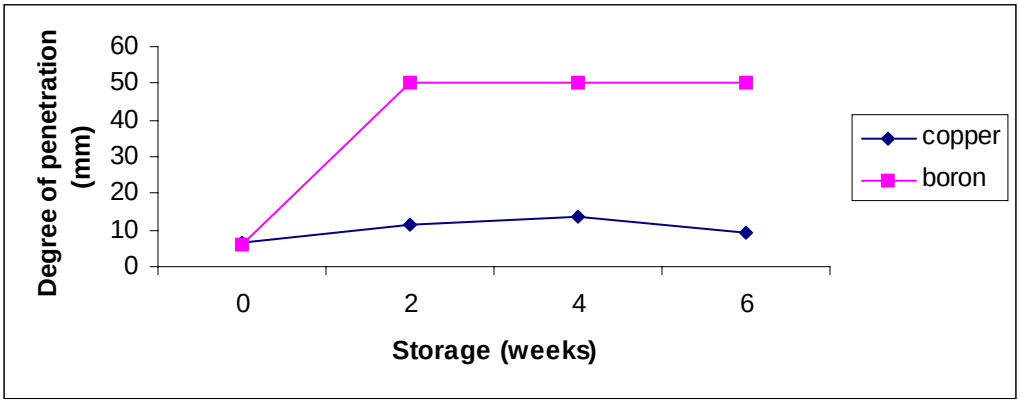
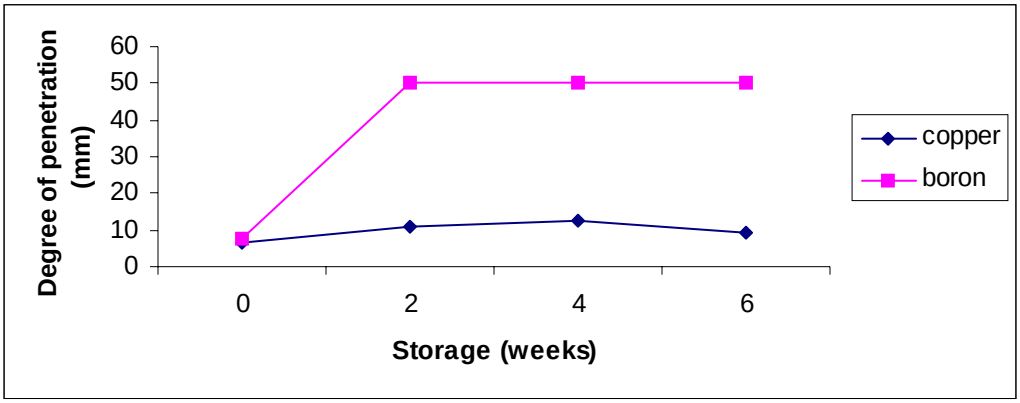


Table 15. Longitudinal penetration results for 6-day soak in 50% Cu-Bor solution for Hawaiian albezia.

| Storage (Weeks) | Copper penetration (mm) | Boron penetration (mm) |
|---|---|---|
| 0 | 6.63 | 7.69 |
| 2 | 10.83 | 50+ |
| 4 | 12.31 | 50+ |
| 6 | 9.43 | 50+ |

Figure 6. – Longitudinal penetration of 50% Cu-Bor solution after a 6-day soak and storage for up to 6 weeks for Hawaiian albezia.




The retention test indicates that a maximum retention of 0.04 lbs/cuft (0.2 (% wt/wt)) for copper along the radial surface of Alaskan spruce can be achieved with a 6-day soak period and as long as the soaked pieces are stored in the wet condition for a period of 6 weeks using 50% Cu-Bor solution. A maximum retention of 0.03 lbs/cuft (0.16 (% wt/wt)) for boron along the radial surface for Alaskan spruce can be achieved with a 2-day soak period and as long as the soaked pieces are stored in the wet condition for a period of 6 weeks using 50% Cu-Bor solution. The retention test indicates that a maximum retention of 0.08 lbs/cuft (0.42 (% wt/wt)) for copper along the radial surface of Hawaiian albezia can be achieved with a 6-day soak period and as long as the soaked pieces are stored in the wet condition for a period of 6 weeks using 50% Cu-Bor solution. A maximum retention of 0.07 lbs/cuft (0.34 (% wt/wt)) for boron along the radial surface of Hawaiian albezia can be achieved with a 2-day soak period and as long as the soaked pieces are stored in the wet condition for a period of 4 weeks using 50% Cu-Bor solution. In Alaskan spruce a penetration of 9.22 mm along the

longitudinal direction and retention of 0.04 lbs/cuft along the radial surface (15mm) can be achieved with a 6-day soak period as long as the soaked pieces are stored in the wet condition for a period of 6 weeks using 50% Cu-Bor solution. However in Hawaiian albezia a high copper penetration of 13.45 mm along the longitudinal direction was achieved with a 4-day soak and as long as the soaked pieces are stored in the wet condition for a period of 4 weeks. Further storage of soaked pieces did not increase the longitudinal penetration. Maximum retention of 0.07 lbs/cuft for boron along radial surface (15 mm) and maximum longitudinal penetration (>50 mm) was achieved with a 2 day soak and as long as the soaked pieces are stored in the wet condition for a period of 4 weeks using 50% Cu-Bor solution for Hawaiian albezia. These results indicate that substantial retention levels of Cu and B are obtained after 2-day soak and as long as the soaked pieces are stored in the wet condition for a period of 2 weeks using 50% Cu-Bor solution for Alaskan spruce and Hawaiian albezia. These levels are adequate for protecting the wood from attack by most fungi, except copper-tolerant brown-rot species (DaCosta and Kerruish 1964; Fahlstrom 1964).

Table 16. Retention results of 15 mm samples along the radial direction for Alaskan spruce and Hawaiian albezia treated with 50% Cu-Bor solution.

| Time period of treatment (Alaskan spruce) | 0-15 mm Cu retention (% wt/wt) | 0-15 mm Cu retention (lbs/cuft) | 0-15 mm B retention (% wt/wt) | 0-15 mm B retention (lbs/cuft) |
|---|---|---|---|---|
| 2-day dip and no storage | 0.06 | 0.01 | 0.03 | 0.01 |
| 2-day dip and 2-weeks storage | 0.16 | 0.03 | 0.15 | 0.03 |
| 2-day dip and 4-weeks storage | 0.09 | 0.02 | 0.13 | 0.03 |
| 2-day dip and 6-weeks storage | 0.14 | 0.03 | 0.16 | 0.03 |
| 6 day dip and 6 weeks storage | 0.20 | 0.04 | 0.13 | 0.03 |

| Time period of treatment (Hawaiian albezia) | 0-15 mm Cu retention (% wt/wt) | 0-15 mm Cu retention (lbs/cuft) | 0-15 mm B retention (% wt/wt) | 0-15 mm B retention (lbs/cuft) |
|---|---|---|---|---|
| 2-day dip and no storage | 0.11 | 0.02 | 0.13 | 0.03 |
| 2-day dip and 2-weeks storage | 0.27 | 0.05 | 0.30 | 0.06 |
| 2-day dip and 4-weeks storage | 0.17 | 0.03 | 0.34 | 0.07 |
| 2-day dip and 6-weeks storage | 0.26 | 0.05 | 0.29 | 0.06 |
| 6 day dip and 6 weeks storage | 0.42 | 0.08 | 0.33 | 0.06 |

4.2 Phase II

Our Second objective was to determine level of fixation that occurs, since leaching of the chemicals is of concern. American Wood-Preservers' Association (AWPA) Standards were used to determine retention and leaching of the copper and borate components of the individual treatments. The results of the leaching study of single diffusion using 16.65% copper-borate solution indicate that the boron were easily leached from the samples, suggesting that minimal fixation occurs with this chemical. Essentially 100% of the sodium tetraborate decahydrate from copper borate formulation was lost after only a few days of

leaching, regardless of the treatment. Approximately 97.74% from Alaskan spruce and 95.10% from Hawaiian albezia of sodium tetraborate decahydrate leached from the blocks. The copper did not leach from the samples as much as the boron from samples treated with 16.65% copper-borate formulation. About 20.08% of copper hydroxide ($Cu(OH)_2$) was lost from Alaskan spruce samples and about 28.26% of copper hydroxide ($Cu(OH)_2$) was lost from Hawaiian albezia samples. The average retention of copper hydroxide ($Cu(OH)_2$) in Alaskan spruce was 0.06 lbs/cuft before leaching and 0.05 lbs/cuft after leaching. The average retention of copper hydroxide ($Cu(OH)_2$) in Hawaiian albezia was 0.06 lbs/cuft before leaching and 0.04 lbs/cuft after leaching. The average retention of sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) in Alaskan spruce was 0.91 lbs/cuft before leaching and the average retention of sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) in Hawaiian albezia was 0.87 lbs/cuft before leaching. The final retention of sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) in Alaskan spruce after leaching was 0.02 lbs/cuft and 0.04 lbs/cuft for Hawaiian albezia. The average retention of copper and boron in unleached blocks of Alaskan spruce samples was 0.23% wt/wt and 0.336% wt/wt respectively. The average retention of copper and boron in leached blocks of Alaskan spruce samples was 0.186% wt/wt and 0.002% wt/wt respectively. The average retention of copper and boron in unleached blocks of Hawaiian albezia samples was 0.21% wt/wt and 0.343% wt/wt respectively. The average retention of copper and boron in leached blocks of Hawaiian albezia samples was 0.152% wt/wt and 0.013% wt/wt respectively.

The results indicate that copper became partially bound by the wood and was partially resistant to leaching. But boron remains unchanged and almost fully subject to leaching. The average % wt/wt retention of copper and boron in leached blocks was sufficient to inhibit the growth of wide range of fungi (DaCosta and Kurruish 1964). The initial retention of copper-borate before leaching was more than sufficient to inhibit the growth of wide range of fungi but due to high leaching of boron, the retention of copper-borate was too low to inhibit growth of most fungi (Baechler and Roth 1956; Fahlstrom 1964). The initial retention levels of sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) was more than enough inhibiting the growth of wide range of fungi, but after the high leaching of boron after the leaching period the retention levels are too low to inhibit the various growth of different fungi (Fahlstrom 1964).

Table 17.Various test blocks of Alaskan spruce treated with 16.65% copper-borate solution and retention of active ingredients.

| Test blocks | RT (lbs/cuft) of copper as copper hydroxide ($Cu(OH)_2$) | RT (lbs/cuft) of boron as sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) |
|---|---|---|
| B1 | 0.07 | 1.04 |
| B2 | 0.07 | 0.96 |
| B3 | 0.06 | 0.85 |
| B4 | 0.06 | 0.85 |
| B5 | 0.07 | 0.99 |
| B6 | 0.06 | 0.87 |

Table 18. Amount of Cu and B leached during the various hours of leaching from test blocks of Alaskan spruce treated with 16.65% copper borate solution.

| Hours of leaching | 6 | 24 | 48 | 96 | 144 | 192 | 240 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|---|
| Cu leached (mg/l) | 2.27 | 11.99 | 2.77 | 3.23 | 1.71 | 1.42 | 0.79 | 0.40 | 0.66 |
| % Cu leached | 1.8 | 9.5 | 2.2 | 2.6 | 1.4 | 1.1 | 0.6 | 0.3 | 0.5 |
| B leached (mg/l) | 152.66 | 78.66 | 34.56 | 16.22 | 7.40 | 5.08 | 4.87 | 5.25 | 1.94 |
| % B leached | 48.7 | 25.1 | 11.0 | 5.2 | 2.4 | 1.6 | 1.6 | 1.7 | 0.6 |

Figure 7. Graphical representation of leaching of copper and boron from Alaskan spruce treated with copper borate (16.65% wt/wt) solution.

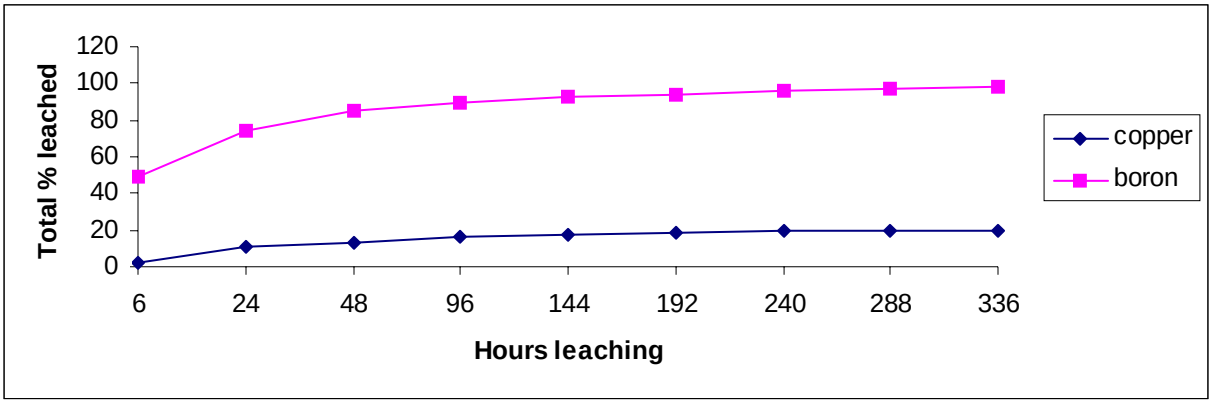


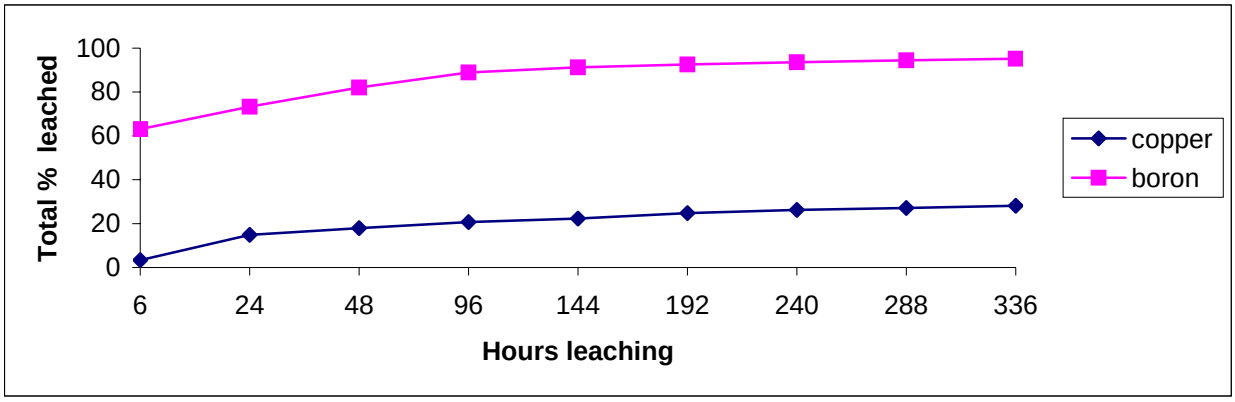
Table 19. Various test blocks of Hawaiian albezia treated with 16.65% copper borate solution and retention of active ingredients.

| Test blocks | RT (lbs/cuft) of copper hydroxide (Cu (OH) $_2$) | RT (lbs/cuft) of boron as sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) |
|---|---|---|
| B1 | 0.07 | 0.92 |
| B2 | 0.06 | 0.84 |
| B3 | 0.06 | 0.89 |
| B4 | 0.05 | 0.76 |
| B5 | 0.06 | 0.88 |
| B6 | 0.06 | 0.85 |

Table 20. Amount of Cu and B leached during the various hours of leaching from test blocks of Hawaiian albezia treated with 16.65% copper borate solution.

| Hours of leaching | 6 | 24 | 48 | 96 | 144 | 192 | 240 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|---|
| Cu leached (mg/l) | 3.29 | 11.56 | 3.11 | 2.80 | 1.54 | 2.46 | 1.52 | 0.93 | 0.98 |
| % Cu leached | 3.3 | 11.6 | 3.1 | 2.8 | 1.5 | 2.5 | 1.5 | 0.9 | 1.0 |
| B leached (mg/l) | 156.88 | 25.60 | 21.99 | 16.90 | 5.86 | 3.15 | 2.39 | 2.17 | 1.67 |
| % B leached | 63.0 | 10.3 | 8.8 | 6.8 | 2.4 | 1.3 | 1.0 | 0.9 | 0.7 |

Figure 8. Leaching of copper and boron from Hawaiian albezia treated with copper borate (16.65% wt/wt) solution.




The results of the leaching study of single diffusion using 8% borosol solution indicate that the boron was easily leached from the samples, suggesting that minimal fixation occured with this chemical. 91.91% of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) was lost from Alaskan spruce by leaching and 88.22% of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) was lost from Hawaiian albezia by leaching. The average retention of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) in Alaskan spruce was 1.08 lbs/cuft before leaching and 0.09 lbs/cuft after leaching. The average retention of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) in Hawaiian albezia was 0.88 lbs/cuft before leaching and 0.1 lbs/cuft after leaching. The average retention of boron in unleached blocks of Alaskan spruce samples was 0.8% wt/wt and average retention of boron in unleached blocks of Hawaiian albezia samples was 0.909% wt/wt. The average retention of boron in leached blocks of Alaskan spruce samples was 0.004% wt/wt and the average retention of boron in leached blocks of Hawaiian albezia samples .010% wt/wt.

Boron remains unchanged and was almost fully subject to leaching. One of the interesting results we can see is that the retention of copper in both of the single diffusion was high in Alaskan spruce. This can be attributed to affinity of copper towards cellulose and lignin. Alaskan spruce being denser than Hawaiian albezia has more cellulose and lignin.

Table 21. Various test blocks of Alaskan spruce treated with 8% borosol solution (commercial borate solution) and retention of active ingredient.

| Test blocks | RT (lbs/cuft) of Disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$ |
|---|---|
| B1 | 1.04 |
| B2 | 1.09 |
| B3 | 1.06 |
| B4 | 1.14 |
| B5 | 1.06 |
| B6 | 1.21 |

Table 22. Amount of B leached during the various hours of leaching from test blocks of Alaskan spruce treated with 8% borosol solution (commercial borate solution).

| Hours of leaching | 6 | 24 | 48 | 96 | 144 | 192 | 240 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|---|
| B leached (mg/l) | 224.63 | 95.40 | 55.04 | 22.75 | 12.78 | 5.00 | 1.95 | 1.53 | 1.51 |
| % B leached | 49.1 | 20.8 | 12.0 | 5.0 | 2.8 | 1.1 | 0.4 | 0.3 | 0.3 |

Figure 9. Leaching of boron from Alaskan spruce treated with borosol (commercial borate solution) (8% wt/wt) solution.

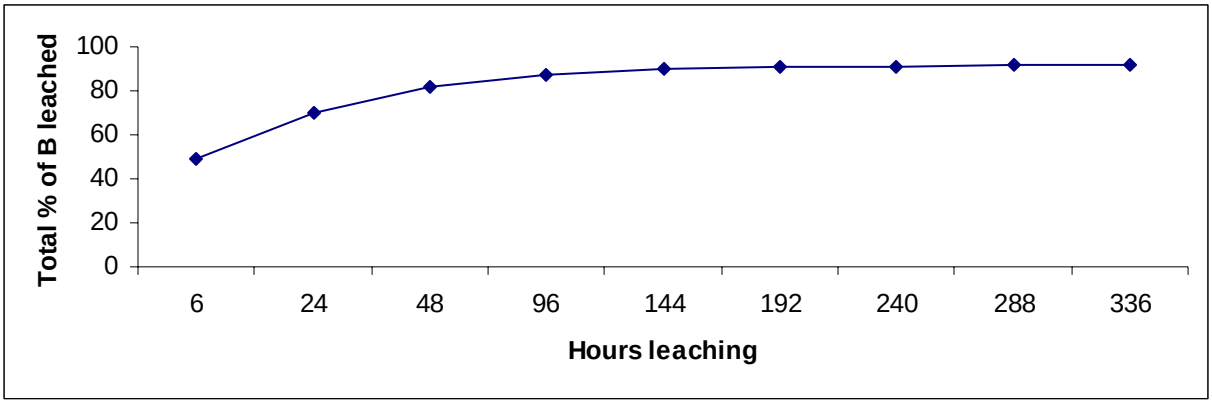


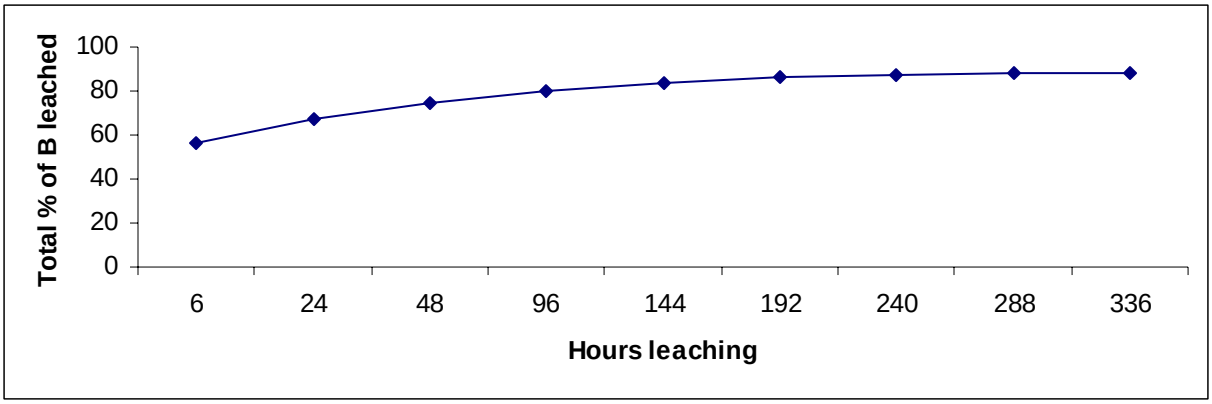
Table 23. Various test blocks of Hawaiian albezia treated with 8% borosol solution (commercial borate solution) and retention of active ingredient.

| Test blocks | RT (lbs/cuft) of Disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$ |
|---|---|
| B1 | 0.82 |
| B2 | 0.89 |
| B3 | 0.84 |
| B4 | 0.91 |
| B5 | 0.82 |
| B6 | 0.93 |

Table 24. Amount of B leached during the various hours of leaching from test blocks of Hawaiian albezia treated with 8% borosol solution (commercial borate solution).

| Hours of leaching | 6 | 24 | 48 | 96 | 144 | 192 | 240 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|---|
| B leached (mg/l) | 223.24 | 41.42 | 29.69 | 22.90 | 14.81 | 10.98 | 2.23 | 1.75 | 1.53 |
| % B leached | 56.5 | 10.5 | 7.5 | 5.8 | 3.7 | 2.8 | 0.6 | 0.4 | 0.4 |

Figure 10. Leaching of boron from Hawaiian albezia treated with borosol (commercial borate solution) (8% wt/wt) solution.



The results of the double-diffusion leaching study in which the samples were first impregnated with indicate that the borate solutions were easily leached from the samples, suggesting that minimal fixation occurs with this chemical. Essentially 100% of the (disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$)) was lost after only a few days of leaching, regardless of the treatment. 98.44% of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$)) was lost from Alaskan spruce by leaching and 97.50% of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$)) was lost from Hawaiian albezia by leaching. The copper sulphate solution (cupric sulphate ($CuSO_4.5H_2O$)) did not leach from the samples as much as the borosol (disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$)) especially treated with a double-diffusion process in which samples were first treated with copper sulphate and then soaked in a borosol solution. The percentage of leaching of copper-sulphate was only 8.01% for Alaskan spruce and 11.53% for Hawaiian albezia. During this process the average retention of cupric sulphate ($CuSO_4.5H_2O$) after the impregnation stage was 1.12 lbs/cuft for Alaskan spruce and 0.93 lbs/cuft for Hawaiian albezia. The retention of copper was 0.09 lbs/cuft in Hawaiian albezia and 0.13 lbs/cuft in Alaskan spruce after leaching but the retention of boron after leaching was very low. The retention of boron in Alaskan spruce was 0.004 lbs/cuft and retention of B in Hawaiian albezia was 0.005 lbs/cuft after leaching. The average retention of copper and boron in leached blocks of Alaskan spruce samples was 0.606% wt/wt and 0.018% wt/wt respectively. The average retention of copper and boron in leached blocks of Hawaiian albezia samples was 0.484% wt/wt and 0.024% wt/wt respectively.

The results indicate that the retention of copper in leached wood of Alaskan spruce and Hawaiian albezia are more than sufficient to tolerate most of the white rot fungi except for copper tolerant brown rot fungi (DaCosta and Kurruish 1964). Even though we got sufficient retention levels of boron in unleached wood for Alaskan spruce (1.089%wt/wt) and Hawaiian albezia (0.921% wt/wt), almost 80% of the boron leached away within first 2-days of leaching from both wood. From the results we can see that boron appear to have an effect on copper retention under leaching conditions, as evidenced by higher levels of residual copper in leached blocks. So sequential treatments with copper sulphate followed by commercial borate solution had some benefits over simple copper sulphate treatment. The leaching rate

copper has been substantially reduced, since the potential loss of element copper is a major concern in environmentally sensitive exposures.

Table 25. Amount of Cu and B leached during the various hours of leaching from test blocks of Alaskan spruce first treated with 8% copper sulphate and then with 8% borosol solution (commercial borate solution).

| Hours of leaching | 6 | 24 | 48 | 96 | 144 | 192 | 240 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|---|
| Cu leached (mg/l) | 1.60 | 6.15 | 1.49 | 4.13 | 3.64 | 1.95 | 1.61 | 1.91 | 1.80 |
| % Cu leached | 0.5 | 2.0 | 0.5 | 1.4 | 1.2 | 0.6 | 0.5 | 0.6 | 0.6 |
| B leached (mg/l) | 269.77 | 97.40 | 87.54 | 60.24 | 15.40 | 17.82 | 2.08 | 2.17 | 2.14 |
| % B leached | 47.9 | 17.3 | 15.5 | 10.7 | 2.7 | 3.2 | 0.4 | 0.4 | 0.4 |

Figure 11. Leaching of copper and boron from Alaskan spruce treated with copper sulphate (8% wt/wt) solution and then with borosol (commercial borate solution) (8% wt/wt) solution.

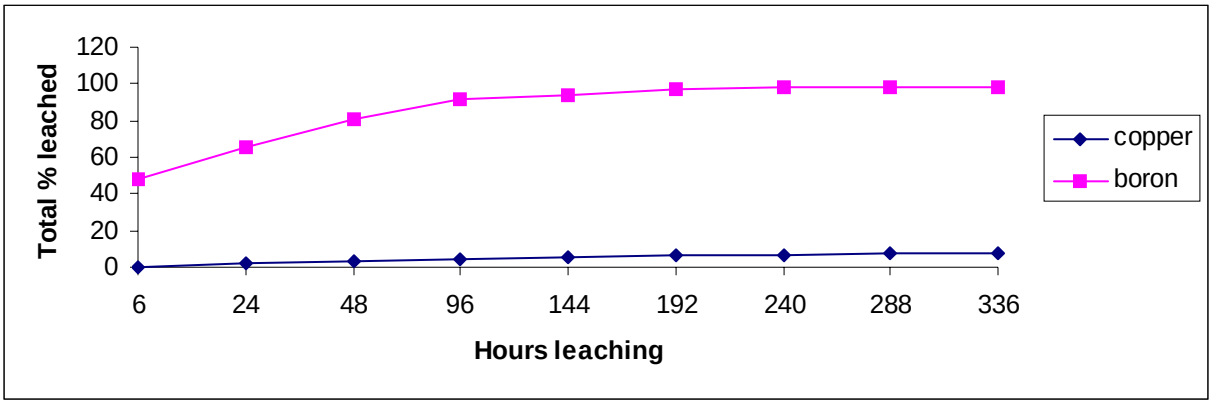


Table 26. Amount of Cu and B leached during the various hours of leaching from test blocks of Hawaiian albezia first treated with 8% copper sulphate and then with 8% borosol solution (commercial borate solution).

| Hours of leaching | 6 | 24 | 48 | 96 | 144 | 192 | 240 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|---|
| Cu leached (mg/l) | 2.38 | 8.37 | 5.04 | 11.68 | 4.95 | 2.22 | 0.88 | 1.32 | 0.44 |
| % Cu leached | 0.7 | 2.6 | 1.6 | 3.6 | 1.5 | 0.7 | 0.3 | 0.4 | 0.1 |
| B leached (mg/l) | 208.02 | 126.44 | 67.61 | 28.35 | 2.91 | 2.31 | 2.72 | 2.31 | 1.34 |
| % B leached | 45.9 | 27.9 | 14.9 | 6.3 | 0.6 | 0.5 | 0.6 | 0.5 | 0.3 |

Figure 12. Leaching of copper and boron from Hawaiian albezia treated with copper sulphate (8% wt/wt) solution and then with borosol (commercial borate solution) (8% wt/wt) solution.

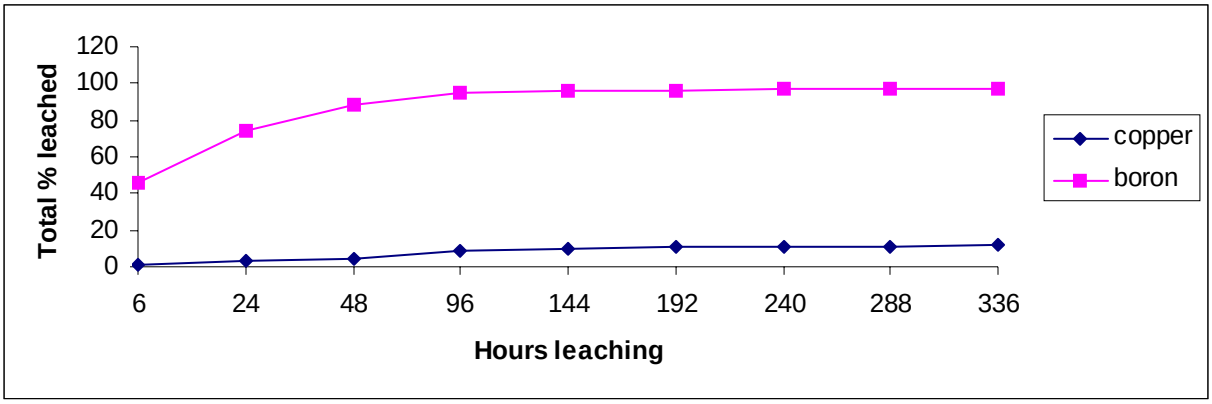


Table 27. Retention levels of cupric sulphate ($CuSO_4.5H_2O$) in Alaskan spruce and Hawaiian albezia after first treatment with 8% copper sulphate solution in double diffusion.

| Alaskan spruce<br><br>Test blocks | RT (lbs/cuft) of cupric sulphate ($CuSO_4.5H_2O$) | Hawaiian albezia<br><br>Test blocks | RT (lbs/cuft) of cupric sulphate ($CuSO_4.5H_2O$) |
|---|---|---|---|
| B1 | 1.12 | B1 | 1.01 |
| B2 | 1.12 | B2 | 0.94 |
| B3 | 1.19 | B3 | 1.05 |
| B4 | 1.06 | B4 | 0.84 |
| B5 | 1.11 | B5 | 0.92 |
| B6 | 1.13 | B6 | 0.78 |

About 71.75% of copper sulphate leached from Hawaiian albezia and 78.94% of copper sulphate leached from Alaskan spruce for samples treated with double-diffusion process in which they were first impregnated with borate (disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$)) and then soaked in a copper sulphate solution (cupric sulphate ($CuSO_4.5H_2O$)). Essentially 100% of the borate was lost after only a few days of leaching. Almost 93.29% of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) and almost 93.70% of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) from Alaskan spruce and Hawaiian albezia respectively. Even though high percentage of copper leached, the final retention of copper in samples after leaching was high due to high uptake of copper during the double diffusion. The retention of copper was 0.15 lbs/cuft in Hawaiian albezia and 0.17 lbs/cuft in Alaskan spruce after leaching. The retention of boron in Alaskan spruce was 0.001 lbs/cuft and retention of boron in Hawaiian albezia was 0.003 lbs/cuft after leaching. The average retention of copper and boron in leached blocks of Alaskan spruce samples was 0.814% wt/wt and 0.004% wt/wt respectively. The average retention of copper and boron in leached blocks of Hawaiian albezia samples was 0.779% wt/wt and 0.014% wt/wt respectively.

The results indicate that the retention of copper in leached wood of Alaskan spruce and Hawaiian albezia are more than sufficient to tolerate most of the white rot fungi except for copper tolerant brown rot fungi (DaCosta and Kurruish 1964). We can see the retentions of

copper in leached wood (0.814% wt/wt for Alaskan spruce and 0.779% wt/wt for Hawaiian albezia) are much more than the double diffusion when wood blocks were treated with copper sulphate first and with borosol second. But the leaching rates for copper was fairly very high for double diffusion when blocks are treated with borosol first and then with copper sulphate (78.94% for Alaskan spruce and 71.75% for Hawaiian albezia) compared to 8.01% for Alaskan spruce and 11.53% for Hawaiian albezia for double diffusion in which the blocks were treated with copper sulphate first and borosol second. So wood treated with borosol first and then with copper sulphate can cause potential threats, since the potential loss of element copper is a major concern in environmentally sensitive exposures.

Table 28. Amount of Cu and B leached during the various hours of leaching from test blocks of Alaskan spruce first treated with 8% borosol (commercial borate solution) and then with 8% copper sulphate.

| Hours of leaching | 6 | 24 | 48 | 96 | 144 | 192 | 240 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|---|
| Cu leached (mg/l) | 442.86 | 242.27 | 77.87 | 33.72 | 17.51 | 5.75 | 7.63 | 4.41 | 2.68 |
| % Cu leached | 38.1 | 20.8 | 6.7 | 2.9 | 1.5 | 0.5 | 0.7 | 0.4 | 0.2 |
| B leached (mg/l) | 36.55 | 33.98 | 9.17 | 2.95 | 1.25 | 1.65 | 3.00 | 0.91 | 0.70 |
| % B leached | 37.8 | 35.2 | 9.5 | 3.1 | 1.3 | 1.7 | 3.1 | 0.9 | 0.7 |

Figure 13. Leaching of copper and boron from Alaskan spruce treated with borosol (commercial borate solution)(8% wt/wt) solution and then with copper sulphate (8% wt/wt) solution.

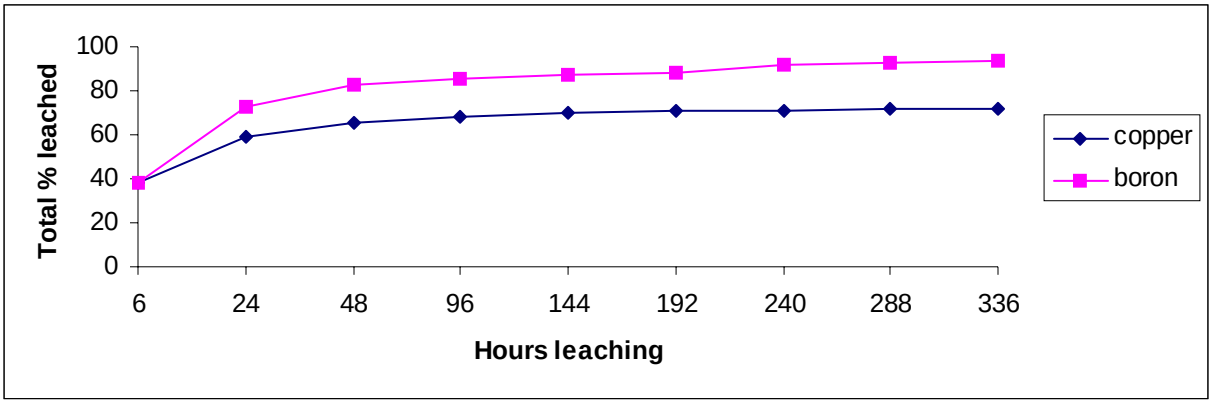



Table 29. Amount of Cu and B leached during the various hours of leaching from test blocks of Hawaiian albezia first treated with 8% borosol solution (commercial borate solution) and 8% copper sulphate.

| Hours of leaching | 6 | 24 | 48 | 96 | 144 | 192 | 240 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|---|
| Cu leached (mg/l) | 330.00 | 277.41 | 53.67 | 29.14 | 20.00 | 14.08 | 6.22 | 3.27 | 3.03 |
| % Cu leached | 35.4 | 29.7 | 5.8 | 3.1 | 2.1 | 1.5 | 0.7 | 0.4 | 0.3 |
| B leached (mg/l) | 36.55 | 20.26 | 20.91 | 5.23 | 4.78 | 3.77 | 1.79 | 2.72 | 0.81 |
| % B leached | 35.4 | 19.6 | 20.2 | 5.1 | 4.6 | 3.6 | 1.7 | 2.6 | 0.8 |

Figure 14. Leaching of copper and boron from Hawaiian albezia treated with borosol (commercial borate solution)(8% wt/wt) solution and then with copper sulphate (8% wt/wt) solution.

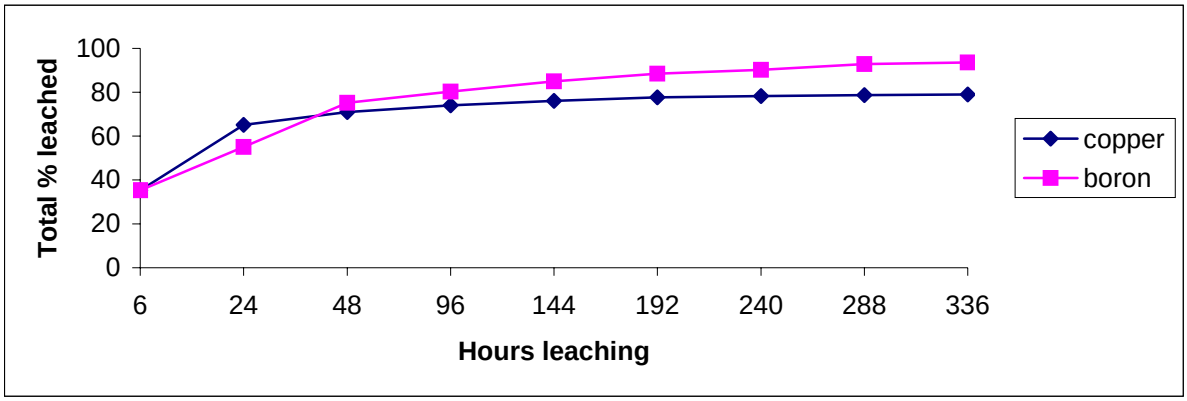



Table 30. Retention levels of disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) in Alaskan spruce and Hawaiian albezia after first treatment with 8% borosol solution (commercial borate solution) in double diffusion.

| Alaskan spruce<br><br>Test blocks | RT (lbs/cuft) of Disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) | Hawaiian albezia<br><br>Test blocks | RT (lbs/cuft) of Disodium octaborate tetrahydrate ($Na_2B_8O_{13}.4H_2O$) |
|---|---|---|---|
| B1 | 1.15 | B1 | 0.86 |
| B2 | 1.05 | B2 | 0.87 |
| B3 | 1.11 | B3 | 0.96 |
| B4 | 1.09 | B4 | 0.98 |
| B5 | 1.02 | B5 | 0.98 |
| B6 | 1.04 | B6 | 0.78 |

# Chapter-5

## 5.Conclusions

The penetration analysis of a 50% commercial copper-borate solution indicates that a maximum longitudinal penetration for Alaskan spruce of approximately 8-10 mm for both copper and boron can be achieved with a 2-, 4-, or 6-day soak period, as long as the soaked pieces are stored in the wet condition for a period of 2-6 weeks. The longer storage period of 6 weeks was necessary to achieve maximum penetration in the samples soaked for the minimum 2-days. A maximum longitudinal penetration for Hawaiian albezia of approximately 10-13 mm can be achieved with a 2-, 4-, or 6-day soak period, as long as the soaked pieces are stored in the wet condition for a period of 2-4 weeks. The boron penetration was found to be very high for Hawaiian albezia. The greatest diffusion occurred during the first two weeks of storage and after that the diffusion occurred fairly lower rate. Considerable retention levels of copper and boron were obtained after the 2-day soak and as long as the soaked pieces were stored in the wet condition for a period of 2 weeks using 50% Cu-Bor solution. One of the reasons for high penetration in Hawaiian albezia may be attributed to high moisture content in the specimens. The average moisture content of Hawaiian albezia was 107% compared to 43% in Alaskan spruce specimens. Wood structure of Hawaiian albezia may also be attributed to high penetration. The vessels in Hawaiian albezia form several channels are capable of a more effective water transport than the softwood tracheids. In Alaskan spruce, water in sapwood is known to move longitudinally through the tracheid lumina, passing from one tracheid lumen to the next through the bordered pits. The condition of bordered pits has significant influence on permeability of softwoods. Pit aspiration makes the wood of spruce difficult to impregnate with preservatives. This can be one of the reasons for less penetration in Alaskan spruce, in addition to the lower moisture content of the samples.

Results from single and double diffusion indicate that the boron was easily leached from the samples, suggesting that minimal fixation occurs with this chemical. Essentially 100% of the boron was lost after only a few days of leaching, regardless of the treatment. The copper did

not leach from the samples as much as the boron from wood samples. The leaching rates for copper was fairly very high for double diffusion when blocks are treated with borosol first and then with copper sulphate (79% for Alaskan spruce and 72% for Hawaiian albezia) compared to 8% for Alaskan spruce and 11.5% for Hawaiian albezia for double diffusion in which the blocks were treated with copper sulphate first and borosol second. So wood treated with borosol first and then with copper sulphate can cause potential threats, since the potential loss of element copper is a major concern in environmentally sensitive exposures.

The results indicate this study show that essentially 100% of the boron was lost after only a few days of leaching, regardless of the treatment. There was no evidence of formation of a fixed product in wood samples even when the copper and boron were applied in separate solutions in double diffusion. However, the leaching rate of copper was substantially reduced in double diffusion when the wood were first treated with copper sulphate and then with borosol compared to the samples treated with borosol and then with copper sulphate.

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American Wood-Preservers' Association (AWPA). 2003a. Standard A3-00: Standard Methods for Determining Penetration of Preservatives and Fire Retardants. Method 1 Determining penetration of Boron- containing preservatives and Fire Retardants. *In*: AWPA Book of Standards. AWPA, Granbury, TX. pp.245.

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**Appendix 1. Results of the moisture content and specific gravity of Alaskan spruce.**

| | Dimensions (mm) | | | Wet wt (g) | Dry wt (g) | Moisture content % | Specific Gravity ($g/cm^3$) | Wood density (lbs/cuft) |
|---|---|---|---|---|---|---|---|---|
| 1A | 27.51 | 56.79 | 56.40 | 40.38 | 29.66 | 36.14 | 0.337 | 20.97 |
| 1B | 25.15 | 56.74 | 56.70 | 38.38 | 28.10 | 36.58 | 0.347 | 21.63 |
| 2A | 26.98 | 57.27 | 57.02 | 47.64 | 30.99 | 53.73 | 0.352 | 21.91 |
| 2B | 27.07 | 57.22 | 57.00 | 43.48 | 30.18 | 44.07 | 0.342 | 21.29 |
| 3A | 23.96 | 56.98 | 56.90 | 40.87 | 27.20 | 50.26 | 0.350 | 21.81 |
| 3B | 23.95 | 56.81 | 56.79 | 37.44 | 26.59 | 40.80 | 0.344 | 21.43 |
| 4A | 21.65 | 57.32 | 57.05 | 31.74 | 23.84 | 33.14 | 0.337 | 20.97 |
| 4B | 21.17 | 57.27 | 57.15 | 34.11 | 24.69 | 38.15 | 0.356 | 22.20 |
| 5A | 27.27 | 57.77 | 57.32 | 46.73 | 29.43 | 58.78 | 0.326 | 20.30 |
| 5B | 27.41 | 57.72 | 57.14 | 42.65 | 29.61 | 44.04 | 0.328 | 20.40 |
| 6A | 23.99 | 57.68 | 57.13 | 38.25 | 28.61 | 33.69 | 0.362 | 22.54 |
| 6B | 23.48 | 57.46 | 57.38 | 39.14 | 26.47 | 47.87 | 0.342 | 21.30 |

**Appendix 2. Results of the moisture content and specific gravity of Hawaiian albezia.**

| | Dimensions (mm) | | | Wet wt (g) | Dry wt (g) | Moisture content % | Specific Gravity ($g/cm^3$) | Wood density (lbs/cuft) |
|---|---|---|---|---|---|---|---|---|
| 1A | 23.81 | 60.58 | 55.90 | 31.17 | 18.24 | 70.89 | 0.226 | 14.09 |
| 1B | 21.93 | 47.37 | 51.8 | 37.01 | 22.87 | 61.83 | 0.425 | 26.47 |
| 1M | 24.65 | 57.54 | 62.82 | 42.04 | 25.68 | 63.71 | 0.288 | 17.95 |
| 2A | 25.53 | 56.88 | 57.11 | 40.84 | 22.73 | 79.67 | 0.274 | 17.07 |
| 2B | 24.43 | 56.45 | 57.26 | 52.05 | 22.22 | 134.25 | 0.281 | 17.53 |
| 2M | 25.77 | 54.48 | 56.85 | 39.53 | 22.91 | 72.54 | 0.287 | 17.88 |
| 3A | 24.10 | 58.91 | 51.73 | 35.38 | 21.98 | 60.96 | 0.299 | 18.64 |
| 3B | 24.24 | 57.66 | 52.54 | 33.55 | 19.81 | 69.36 | 0.270 | 16.80 |
| 3M | 25.38 | 52.15 | 57.23 | 36.75 | 22.87 | 60.69 | 0.302 | 18.81 |
| 4A | 24.35 | 56.01 | 57.77 | 54.83 | 23.73 | 131.06 | 0.301 | 18.76 |
| 4B | 24.36 | 56.16 | 55.65 | 58.38 | 24.65 | 136.84 | 0.324 | 20.17 |
| 4M | 25.09 | 54.64 | 57.01 | 54.26 | 23.40 | 131.88 | 0.299 | 18.65 |
| 5A | 25.37 | 52.31 | 60.98 | 36.09 | 21.40 | 68.64 | 0.264 | 16.47 |
| 5B | 23.93 | 51.44 | 62.28 | 34.39 | 21.34 | 61.15 | 0.278 | 17.34 |
| 5M | 24.40 | 52.75 | 62.64 | 37.16 | 23.13 | 60.66 | 0.287 | 17.87 |
| 6A | 23.09 | 56.53 | 56.92 | 60.25 | 24.15 | 149.48 | 0.325 | 20.25 |
| 6B | 23.03 | 56.05 | 56.67 | 58.25 | 24.13 | 141.40 | 0.330 | 20.55 |
| 6M | 23.80 | 57.10 | 56.39 | 64.90 | 26.12 | 148.47 | 0.341 | 21.23 |
| 7A | 23.27 | 56.25 | 57.62 | 55.04 | 24.60 | 123.74 | 0.326 | 20.32 |
| 7B | 24.10 | 56.20 | 58.35 | 69.37 | 27.37 | 153.45 | 0.346 | 21.57 |
| 7M | 24.78 | 56.60 | 58.17 | 70.30 | 28.72 | 144.78 | 0.352 | 21.93 |
| 8A | 24.07 | 55.75 | 53.49 | 55.58 | 24.87 | 123.48 | 0.346 | 21.58 |
| 8B | 26.35 | 54.66 | 55.67 | 47.91 | 23.83 | 101.05 | 0.297 | 18.51 |
| 8M | 24.47 | 56.82 | 54.17 | 61.06 | 26.08 | 134.13 | 0.346 | 21.57 |
| 9A | 26.09 | 65.16 | 58.37 | 85.55 | 35.27 | 142.56 | 0.355 | 22.14 |
| 9B | 25.00 | 57.91 | 65.13 | 70.85 | 31.04 | 128.25 | 0.329 | 20.50 |
| 9M | 24.15 | 58.30 | 65.68 | 80.27 | 32.07 | 150.30 | 0.347 | 21.60 |
| 10A | 26.01 | 57.22 | 57.01 | 53.14 | 29.02 | 83.12 | 0.342 | 21.30 |
| 10B | 22.93 | 58.96 | 57.96 | 44.82 | 23.12 | 93.86 | 0.295 | 18.38 |
| 10M | 24.54 | 56.93 | 58.04 | 54.15 | 24.80 | 118.35 | 0.306 | 19.05 |

**Appendix 3. Results of penetration tests for Alaskan spruce (2 day soak).**

| 2 days no storage | | 2 days 2 weeks storage | | 2 days 4 weeks storage | | 2 days 6 weeks storage | |
|---|---|---|---|---|---|---|---|
| B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) |
| 3.82 | 5.56 | 6.60 | 6.42 | 7.04 | 8.21 | 10.49 | 9.79 |
| 4.54 | 5.23 | 7.65 | 6.28 | 7.36 | 9.34 | 7.58 | 8.21 |
| 4.60 | 9.40 | 6.56 | 6.60 | 7.05 | 7.79 | 7.11 | 9.37 |
| 3.20 | 5.73 | 5.57 | 8.14 | 8.53 | 7.78 | 10.29 | 9.31 |
| 3.21 | 5.70 | 5.89 | 7.94 | 7.76 | 6.91 | 12.30 | 9.01 |

**Appendix 4. Results of penetration tests for Alaskan spruce (4 day soak).**

| 4 days no storage | | 4 days 2 weeks storage | | 4 days 4 weeks storage | | 4 days 6 weeks storage | |
|---|---|---|---|---|---|---|---|
| B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) |
| 7.13 | 6.57 | 7.21 | 8.45 | 8.19 | 9.69 | 7.84 | 8.96 |
| 6.84 | 6.54 | 7.04 | 9.29 | 8.47 | 9.62 | 9.52 | 7.89 |
| 5.20 | 6.28 | 7.93 | 7.02 | 9.73 | 7.61 | 8.40 | 9.77 |
| 5.70 | 6.21 | 9.30 | 9.61 | 8.42 | 8.53 | 9.28 | 8.85 |
| 6.39 | 7.99 | 9.51 | 7.84 | 7.79 | 8.26 | 7.11 | 8.50 |

**Appendix 5. Results of penetration tests for Alaskan spruce (6 day soak).**

| 6 days no storage | | 6 days 2 weeks storage | | 6 days 4 weeks storage | | 6 days 6 weeks storage | |
|---|---|---|---|---|---|---|---|
| B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) |
| 6.02 | 7.39 | 9.08 | 8.10 | 8.77 | 9.18 | 9.36 | 8.91 |
| 6.01 | 6.74 | 8.52 | 9.35 | 9.43 | 8.66 | 10.72 | 8.68 |
| 5.65 | 8.10 | 6.21 | 8.93 | 9.04 | 9.05 | 9.10 | 9.81 |
| 4.77 | 5.92 | 7.85 | 7.56 | 10.11 | 10.22 | 10.45 | 9.47 |
| 6.18 | 6.54 | 8.43 | 9.06 | 10.13 | 9.13 | 11.33 | 11.16 |

**Appendix 6. Results of penetration tests for Hawaiian albezia (2 day soak).**

| 2 days no storage | | 2 days 2 weeks storage | | 2 days 4 weeks storage | | 2 days 6 weeks storage | |
|---|---|---|---|---|---|---|---|
| B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) |
| 3.92 | 6.63 | 50+ | 7.76 | 50+ | 8.49 | 50+ | 10.98 |
| 4.56 | 5.53 | 50+ | 11.41 | 50+ | 10.75 | 50+ | 9.75 |
| 3.80 | 5.54 | 50+ | 7.12 | 50+ | 10.63 | 50+ | 8.41 |
| 3.04 | 5.44 | 50+ | 6.02 | 50+ | 9.08 | 50+ | 13.31 |
| 5.02 | 5.13 | 50+ | 9.33 | 50+ | 12.21 | 50+ | 12.20 |

**Appendix 7. Results of penetration tests for Hawaiian albezia (4 day soak).**

| 4 days no storage | | 4 days 2 weeks storage | | 4 days 4 weeks storage | | 4 days 6 weeks storage | |
|---|---|---|---|---|---|---|---|
| B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) |
| 4.90 | 6.91 | 50+ | 7.70 | 50+ | 9.02 | 50+ | 8.32 |
| 5.65 | 6.62 | 50+ | 15.36 | 50+ | 13.56 | 50+ | 16.30 |
| 7.51 | 6.62 | 50+ | 11.75 | 50+ | 4.08 | 50+ | 14.87 |
| 7.15 | 3.54 | 50+ | 9.44 | 50+ | 14.61 | 50+ | 7.76 |
| 3.68 | 5.14 | 50+ | 13.04 | 50+ | 16.60 | 50+ | 6.83 |

**Appendix 8. Results of penetration tests for Hawaiian albezia (6 day soak).**

| 6 days no storage | | 6 days 2 weeks storage | | 6 days 4 weeks storage | | 6 days 6 weeks storage | |
|---|---|---|---|---|---|---|---|
| B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) | B (mm) | Cu (mm) |
| 7.56 | 6.08 | 50+ | 9.30 | 50+ | 14.44 | 50+ | 21.23 |
| 10.06 | 8.08 | 50+ | 10.54 | 50+ | 10.95 | 50+ | 11.04 |
| 7.37 | 6.34 | 50+ | 10.17 | 50+ | 16.53 | 50+ | 8.13 |
| 8.15 | 6.22 | 50+ | 13.75 | 50+ | 7.05 | 50+ | 7.59 |
| 5.52 | 9.92 | 50+ | 11.78 | 50+ | 11.55 | 50+ | 10.98 |

**Appendix 9. Results of the retention levels of blocks (Alaskan spruce) treated with copper borate (16.65 %) solution.**

| Initial wt (g) | Dimensions (mm) | | | Final wt (g) | Volume ($mm^3$) | Difference in wt (g) | Retention (lbs/cuft) |
|---|---|---|---|---|---|---|---|
| 3.73 | 21.63 | 21.06 | 21.52 | 5.76 | 9802.96 | 2.03 | 13.30 |
| 3.47 | 21.52 | 20.73 | 21.14 | 5.24 | 9430.76 | 1.77 | 12.05 |
| 3.64 | 20.89 | 21.75 | 20.81 | 5.37 | 9455.18 | 1.73 | 11.75 |
| 3.73 | 21.06 | 20.82 | 20.67 | 5.38 | 9063.16 | 1.65 | 11.69 |
| 3.77 | 21.65 | 21.31 | 20.89 | 5.34 | 9637.84 | 1.57 | 10.46 |
| 3.64 | 22.07 | 20.36 | 20.07 | 5.54 | 9018.36 | 1.9 | 13.53 |
| 3.40 | 21.15 | 20.64 | 21.09 | 5.46 | 9206.54 | 2.06 | 14.37 |
| 3.67 | 21.68 | 21.17 | 20.42 | 5.67 | 9372.08 | 2.00 | 13.70 |
| 3.74 | 22.05 | 21.00 | 21.70 | 6.27 | 100048.19 | 2.53 | 16.17 |
| 3.56 | 22.08 | 20.40 | 20.80 | 5.66 | 9368.99 | 2.10 | 14.39 |
| 3.74 | 22.13 | 21.14 | 20.46 | 5.46 | 9571.77 | 1.72 | 11.54 |
| 3.77 | 21.00 | 21.33 | 21.51 | 5.44 | 9634.97 | 1.67 | 11.13 |

**Appendix 10. Results of the retention levels of blocks (Hawaiian albezia) treated with copper borate (16.65 %) solution.**

| Initial wt (g) | Dimensions (mm) | | | Final wt (g) | Volume ($mm^3$) | Difference in wt (g) | Retention (lbs/cuft) |
|---|---|---|---|---|---|---|---|
| 2.85 | 20.73 | 20.22 | 19.27 | 4.40 | 8077.23 | 1.55 | 12.32 |
| 3.08 | 20.32 | 19.26 | 21.05 | 4.56 | 8238.20 | 1.48 | 11.54 |
| 3.02 | 20.33 | 19.13 | 20.19 | 4.49 | 7852.15 | 1.47 | 12.02 |
| 3.06 | 19.33 | 19.36 | 20.88 | 4.46 | 7813.90 | 1.40 | 11.51 |
| 2.82 | 20.27 | 19.09 | 20.38 | 4.23 | 7886.13 | 1.41 | 11.48 |
| 2.73 | 20.26 | 20.81 | 19.25 | 4.10 | 8116.00 | 1.37 | 10.84 |
| 2.77 | 20.45 | 19.91 | 19.24 | 4.21 | 7833.75 | 1.44 | 11.81 |
| 2.72 | 20.70 | 19.03 | 21.23 | 4.09 | 8362.94 | 1.37 | 10.52 |
| 3.07 | 20.73 | 19.30 | 20.56 | 4.69 | 8225.83 | 1.62 | 12.65 |
| 2.70 | 20.47 | 19.05 | 19.57 | 4.10 | 7631.39 | 1.40 | 11.78 |
| 2.90 | 21.02 | 19.26 | 19.60 | 4.87 | 7934.97 | 1.97 | 15.94 |
| 2.98 | 19.79 | 20.76 | 19.25 | 4.48 | 7908.68 | 1.50 | 12.18 |

**Appendix 11. Results of the retention levels of blocks (Alaskan spruce) treated with borosol 8 % (commercial borate solution) solution.**

| Initial wt (g) | Dimensions (mm) | | | Final wt (g) | Volume ($mm^3$) | Difference in wt (g) | Retention (lbs/cuft) |
|---|---|---|---|---|---|---|---|
| 2.45 | 17.93 | 18.61 | 18.36 | 3.72 | 6126.32 | 1.27 | 13.31 |
| 2.61 | 18.32 | 18.87 | 17.93 | 3.86 | 6198.37 | 1.25 | 12.95 |
| 2.83 | 17.81 | 18.77 | 18.18 | 4.08 | 6077.46 | 1.25 | 13.21 |
| 2.68 | 18.02 | 18.50 | 18.92 | 3.98 | 6307.36 | 1.3 | 13.24 |
| 2.53 | 17.75 | 18.65 | 18.34 | 4.71 | 6071.23 | 2.18 | 23.06 |
| 2.56 | 18.20 | 18.86 | 17.93 | 3.80 | 6154.51 | 1.24 | 12.94 |
| 2.64 | 18.12 | 18.95 | 18.35 | 4.01 | 6300.91 | 1.37 | 13.96 |
| 2.58 | 18.19 | 18.41 | 18.61 | 3.89 | 6232.08 | 1.31 | 13.50 |
| 2.55 | 18.41 | 18.91 | 17.86 | 4.09 | 6217.66 | 1.54 | 15.91 |
| 2.50 | 18.21 | 19.00 | 17.72 | 3.75 | 6130.94 | 1.25 | 13.09 |
| 2.62 | 17.87 | 18.25 | 18.83 | 4.01 | 6140.98 | 1.39 | 14.54 |
| 2.58 | 17.93 | 18.92 | 18.32 | 3.90 | 6214.80 | 1.32 | 13.64 |
| 2.49 | 17.91 | 18.33 | 19.03 | 3.80 | 6247.36 | 1.31 | 13.47 |
| 2.53 | 17.75 | 18.37 | 18.80 | 4.51 | 6130.07 | 1.98 | 20.74 |
| 2.56 | 17.90 | 18.41 | 18.83 | 4.05 | 6205.22 | 1.49 | 15.42 |

**Appendix 12. Results of the retention levels of blocks (Hawaiian albezia) treated with borosol 8 % (commercial borate solution) solution.**

| Initial wt (g) | Dimensions (mm) | | | Final wt (g) | Volume ($mm^3$) | Difference in wt (g) | Retention (lbs/cuft) |
|---|---|---|---|---|---|---|---|
| 2.72 | 19.47 | 18.41 | 19.10 | 3.84 | 6846.26 | 1.12 | 10.51 |
| 2.22 | 18.46 | 18.49 | 19.47 | 3.40 | 6645.61 | 1.18 | 11.40 |
| 2.81 | 18.46 | 19.25 | 18.81 | 3.93 | 6684.23 | 1.12 | 10.76 |
| 2.21 | 19.04 | 19.25 | 18.65 | 3.37 | 6835.60 | 1.16 | 10.90 |
| 2.74 | 18.61 | 18.20 | 18.61 | 4.13 | 6303.24 | 1.39 | 14.16 |
| 2.17 | 19.05 | 18.97 | 18.67 | 3.25 | 6746.94 | 1.08 | 10.28 |
| 2.36 | 18.56 | 19.39 | 18.69 | 3.57 | 6726.13 | 1.21 | 11.55 |
| 2.65 | 18.52 | 19.38 | 19.39 | 3.79 | 6959.41 | 1.14 | 10.52 |
| 2.36 | 18.48 | 18.63 | 19.04 | 3.57 | 6555.14 | 1.21 | 11.85 |
| 2.23 | 18.62 | 19.24 | 19.17 | 3.24 | 6867.63 | 1.01 | 9.44 |
| 2.34 | 18.57 | 19.43 | 18.58 | 3.62 | 6703.95 | 1.28 | 12.26 |
| 2.59 | 18.58 | 18.67 | 18.56 | 3.96 | 6438.25 | 1.37 | 13.67 |
| 2.83 | 18.32 | 18.78 | 19.28 | 3.88 | 6633.28 | 1.05 | 10.17 |
| 2.59 | 18.55 | 19.05 | 19.22 | 3.84 | 6791.92 | 1.25 | 11.82 |
| 3.07 | 19.25 | 21.01 | 18.6 | 4.3 | 7522.63 | 1.23 | 10.50 |

**Appendix 13. Results of the retention (RT) levels of blocks (Alaskan spruce) treated with 8 % copper sulphate impregnated and the dip in 8 %borosol (commercial borate solution) solution.**

| Initial wt (g) | Dimensions (mm) | | | Final wt (g) | Volume ($mm^3$) | Diff in wt (g) | RT after impreg (lbs/cuft) | Final diff in wt (impreg and dip) (g) | Final RT (lbs/cuft) |
|---|---|---|---|---|---|---|---|---|---|
| 2.47 | 17.79 | 18.76 | 18.19 | 3.75 | 6070.74 | 1.28 | 13.54 | 2.15 | 22.74 |
| 2.56 | 18.33 | 18.12 | 18.97 | 3.76 | 6300.69 | 1.2 | 12.23 | 2.10 | 21.40 |
| 2.55 | 17.86 | 18.23 | 18.96 | 3.89 | 6173.15 | 1.34 | 13.94 | 2.09 | 21.74 |
| 2.68 | 17.79 | 18.44 | 18.96 | 4.04 | 6454.75 | 1.36 | 13.96 | 2.13 | 21.87 |
| 2.62 | 18.27 | 18.96 | 17.77 | 4.05 | 6155.51 | 1.43 | 14.92 | 2.10 | 21.91 |
| 2.54 | 18.32 | 17.92 | 18.89 | 3.82 | 6201.48 | 1.28 | 13.26 | 2.00 | 20.71 |
| 2.51 | 17.93 | 18.71 | 18.32 | 3.60 | 6145.82 | 1.09 | 11.39 | 1.83 | 19.12 |
| 2.57 | 18.37 | 19.02 | 17.88 | 4.09 | 6247.23 | 1.52 | 15.63 | 2.32 | 23.85 |
| 2.57 | 18.23 | 18.31 | 18.97 | 3.98 | 6332.02 | 1.41 | 14.30 | 2.21 | 22.41 |
| 2.54 | 18.02 | 18.67 | 18.39 | 3.88 | 6187.01 | 1.34 | 13.91 | 2.02 | 20.97 |
| 2.55 | 18.06 | 18.59 | 18.37 | 3.91 | 6167.46 | 1.36 | 14.16 | 1.93 | 20.10 |
| 2.57 | 18.49 | 18.31 | 18.78 | 4.08 | 6358.01 | 1.51 | 15.25 | 2.23 | 22.52 |

**Appendix 14. Results of the retention (RT) levels of blocks (Hawaiian albezia) treated with 8 % copper sulphate impregnated and the dip in 8 %borosol (commercial borate solution) solution.**

| Initial wt (g) | Dimensions (mm) | | | Final wt (g) | Volume ($mm^3$) | Diff in wt (g) | RT after impreg (lbs/cuft) | Final diff in wt (impreg and dip) (g) | Final RT (lbs/cuft) |
|---|---|---|---|---|---|---|---|---|---|
| 2.67 | 18.57 | 19.08 | 18.57 | 3.96 | 6579.64 | 1.29 | 12.59 | 2.12 | 20.69 |
| 2.40 | 18.84 | 19.27 | 18.38 | 3.92 | 6672.80 | 1.52 | 14.63 | 2.72 | 26.18 |
| 2.72 | 19.30 | 19.26 | 18.58 | 3.98 | 6906.52 | 1.26 | 11.72 | 2.1 | 19.53 |
| 2.39 | 18.58 | 19.16 | 18.46 | 3.73 | 6571.63 | 1.34 | 13.10 | 2.34 | 22.87 |
| 2.13 | 18.57 | 19.15 | 18.57 | 3.21 | 6603.78 | 1.08 | 10.50 | 1.81 | 17.60 |
| 2.09 | 19.21 | 18.56 | 19.13 | 3.12 | 6820.56 | 1.03 | 9.70 | 1.64 | 15.44 |
| 2.73 | 19.23 | 19.21 | 18.60 | 3.96 | 6870.99 | 1.23 | 11.50 | 1.95 | 18.23 |
| 2.13 | 18.41 | 19.23 | 18.60 | 3.23 | 6584.85 | 1.10 | 10.73 | 1.76 | 17.16 |
| 2.76 | 19.42 | 18.96 | 18.62 | 4.03 | 6855.94 | 1.27 | 11.90 | 2.06 | 19.30 |
| 2.37 | 18.54 | 19.20 | 18.86 | 3.48 | 6713.56 | 1.11 | 10.62 | 1.74 | 16.64 |
| 2.79 | 18.58 | 18.95 | 18.95 | 4.20 | 6672.12 | 1.41 | 13.57 | 2.55 | 24.54 |
| 2.18 | 19.25 | 18.99 | 18.71 | 3.22 | 6839.58 | 1.04 | 9.77 | 1.83 | 17.18 |

**Appendix 15.Results of the retention (RT) levels of blocks (Alaskan spruce) treated with 8 % borosol (commercial borate solution) solution impregnated and then dip in 8 % copper sulphate.**

| Initial wt (g) | Dimensions (mm) | | | Final wt (g) | Volume ($mm^3$) | Diff in wt (g) | RT after impreg (lbs/cuft) | Final diff in wt (impreg and dip) (g) | Final RT (lbs/cuft) |
|---|---|---|---|---|---|---|---|---|---|
| 2.47 | 17.99 | 18.43 | 18.69 | 3.88 | 6196.78 | 1.41 | 14.61 | 2.63 | 27.26 |
| 2.69 | 18.44 | 18.90 | 17.93 | 4.02 | 6248.89 | 1.33 | 13.69 | 2.49 | 25.59 |
| 2.77 | 18.35 | 18.42 | 18.73 | 3.93 | 6330.87 | 1.16 | 11.77 | 2.22 | 22.52 |
| 2.56 | 17.81 | 18.69 | 18.29 | 3.92 | 6088.17 | 1.36 | 14.35 | 2.39 | 25.21 |
| 2.77 | 18.27 | 17.98 | 18.95 | 4.03 | 6224.97 | 1.26 | 13.00 | 2.18 | 22.49 |
| 2.78 | 18.00 | 18.16 | 21.19 | 4.22 | 6926.59 | 1.44 | 13.35 | 2.89 | 26.80 |
| 2.54 | 18.17 | 18.79 | 18.28 | 3.91 | 6241.05 | 1.37 | 14.10 | 2.49 | 25.62 |
| 2.81 | 17.98 | 18.29 | 19.07 | 4.05 | 6271.25 | 1.24 | 12.70 | 2.22 | 22.73 |
| 2.69 | 17.90 | 18.26 | 18.83 | 4.02 | 6154.66 | 1.33 | 13.88 | 2.23 | 23.27 |
| 2.56 | 17.76 | 18.84 | 18.36 | 3.80 | 6143.23 | 1.24 | 12.96 | 2.29 | 23.94 |
| 2.71 | 18.08 | 18.40 | 18.95 | 4.01 | 6304.13 | 1.30 | 13.24 | 2.34 | 23.84 |
| 2.65 | 17.93 | 18.47 | 18.87 | 4.16 | 6249.12 | 1.51 | 15.52 | 2.95 | 30.32 |

**Appendix 16.Results of the retention (RT) levels of blocks (Hawaiian albezia) treated with 8 % borosol (commercial borate solution) solution impregnated and then dip in 8 % copper sulphate.**

| Initial wt (g) | Dimensions (mm) | | | Final wt (g) | Volume ($mm^3$) | Diff in wt (g) | RT after impreg (lbs/cuft) | Final diff in wt (impreg and dip) (g) | Final RT (lbs/cuft) |
|---|---|---|---|---|---|---|---|---|---|
| 2.15 | 18.6 | 18.81 | 19.27 | 3.3 | 6741.92 | 1.15 | 10.95 | 2.20 | 20.96 |
| 2.64 | 18.57 | 18.62 | 18.99 | 3.77 | 6566.24 | 1.13 | 11.05 | 2.26 | 22.10 |
| 2.77 | 18.63 | 19.30 | 19.01 | 3.98 | 6835.22 | 1.21 | 11.37 | 2.54 | 23.86 |
| 2.26 | 18.45 | 18.57 | 19.13 | 3.51 | 6554.25 | 1.25 | 12.25 | 2.50 | 24.50 |
| 2.33 | 18.52 | 18.52 | 19.23 | 3.62 | 6595.71 | 1.29 | 12.56 | 2.57 | 25.02 |
| 2.84 | 18.49 | 19.18 | 18.60 | 4.07 | 6596.27 | 1.23 | 11.98 | 2.92 | 28.43 |
| 2.33 | 18.65 | 18.43 | 19.14 | 3.61 | 6578.79 | 1.28 | 12.50 | 2.70 | 26.36 |
| 2.47 | 18.5 | 19.2 | 19.23 | 3.76 | 6830.50 | 1.29 | 12.13 | 2.89 | 27.17 |
| 2.57 | 18.62 | 18.49 | 19.01 | 3.62 | 6544.84 | 1.05 | 10.30 | 1.79 | 17.56 |
| 3.06 | 18.5 | 19.16 | 21.11 | 4.18 | 7482.65 | 1.12 | 9.61 | 2.30 | 19.74 |
| 2.18 | 18.59 | 18.88 | 19.19 | 3.23 | 6735.29 | 1.05 | 10.01 | 2.08 | 19.83 |
| 2.09 | 19.2 | 19.12 | 18.58 | 3.09 | 6820.79 | 1.00 | 9.42 | 1.68 | 15.82 |

**Appendix 17. Results of copper and boron analysis.**

| Sample | Cu (% wt/wt) | B (% wt/wt) |
|---|---|---|
| Hawaiian albezia- 2 days soak no storage | 0.110 | 0.133 |
| Hawaiian albezia- 2 days soak 2 weeks storage | 0.270 | 0.299 |
| Hawaiian albezia- 2 days soak 4 weeks storage | 0.170 | 0.344 |
| Hawaiian albezia- 2 days soak 6 weeks storage | 0.260 | 0.289 |
| Hawaiian albezia- 6 days soak 6 weeks storage | 0.420 | 0.332 |
| Alaskan spruce-2 days soak no storage | 0.060 | 0.034 |
| Alaskan spruce-2 days soak 2 weeks storage | 0.160 | 0.152 |
| Alaskan spruce-2 days soak 4 weeks storage | 0.090 | 0.126 |
| Alaskan spruce-2 days soak 6 weeks storage | 0.140 | 0.156 |
| Unleached block of Hawaiian slbezia- (16.65 % copper borate solution) | 0.210 | 0.343 |
| Unleached block of Alaskan spruce- (16.65 % copper borate solution) | 0.230 | 0.336 |
| Leached block of Hawaiian albezia- (16.65 % copper borate solution) | 0.152 | 0.013 |
| Leached block of Alaskan spruce- (16.65 % copper borate solution) | 0.186 | 0.002 |
| Unleached block of Hawaiian albezia- (8 % borosol (commercial borate solution) | | 0.909 |
| Unleached block of Alaskan spruce- (8 % borosol (commercial borate solution) | | 0.800 |
| Leached block of Hawaiian albezia- (8 % borosol (commercial borate solution | | 0.010 |
| Leached block of Alaskan spruce- (8 % borosol (commercial borate solution) | | 0.004 |

| | | |
|---|---|---|
| Unleached block of Hawaiian albezia- (copper sulphate 8 % impregnated and 8 % borosol (commercial borate solution) dip) | 0.657 | 0.921 |
| Unleached block of Alaskan spruce- (copper sulphate 8 % impregnated and 8 % borosol (commercial borate solution) dip | 0.590 | 1.089 |
| Leached block of Hawaiian albezia- (copper sulphate 8 % impregnated and 8 % borosol (commercial borate solution) dip | 0.484 | 0.024 |
| Leached block of Alaskan spruce- (copper sulphate 8 % impregnated and 8 % borosol (commercial borate solution) dip | 0.606 | 0.018 |
| Unleached block of Hawaiian albezia- (8 % borosol (commercial borate solution) impregnated and copper sulphate 8 % dip) | 2.018 | 0.222 |
| Unleached block of Alaskan spruce- (8 % borosol (commercial borate solution) impregnated and copper sulphate 8 % dip) | 2.214 | 0.184 |
| Leached block of Hawaiian albezia- (8 % borosol (commercial borate solution) impregnated and copper sulphate 8 % dip) | 0.779 | 0.014 |
| Leached block of Alaskan spruce- (8 % borosol (commercial borate solution) impregnated and copper sulphate 8 % dip) | 0.814 | 0.004 |