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In investigating wood treatment as a possible processing option for Alaska forest products manufacturers, the double-diffusion method using sodium fluoride followed by a copper sulfate appeared to be the most advantageous approach. Yet, little information was available as to the chemical retention after treating and its resistance to leaching.

Green Sitka spruce (*Picea sitchensis*) heartwood samples were treated using the double-diffusion method with a 2.2% sodium fluoride solution followed by a 6.2% copper sulfate solution. Samples were analyzed for chemical retention after treating, after a 30-day diffusion period, and after leaching in water for two weeks.

There was a slight trend for solution uptake to increase with initial wood moisture content and decrease with wood density. There was selective fluoride absorption from the solution into the wood, but there was no evidence of selective copper absorption.

Some of the sodium fluoride was lost from the wood during treatment in the copper sulfate solution. Therefore, fluoride retention should not be assessed without sequential copper sulfate treatment. Copper sulfate solution uptake was confounded by the loss of sodium fluoride and therefore, should not be used to assess chemical retention. While not statistically significant, copper retention increased between two and three days of treatment. Copper retention was greater in samples initially treated in sodium fluoride solution.

Fluoride was more mobile than copper during the 30-day diffusion period and during leaching. Most of the copper stayed in the outer six-mm of the wood matrix during the 30-day diffusion period. While not statistically different, 15% to 62% of the fluoride and copper initially deposited in the samples was lost during leaching. The potential impacts of these losses on the surrounding environment merit further study.

Wood Treatment by Double-Diffusion

Using Copper Sulfate and Sodium Fluoride

by

K. Josephine Pavia-Jones

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ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF APPENDIX TABLES

Wood Treatment by Double-Diffusion Using Copper Sulfate and Sodium Fluoride

1. INTRODUCTION

For decades, the wood industry in Alaska focused on producing cants and chips for export to Asia (FPL 1999). Because exporting rules and the Asian market have changed drastically, producers in Alaska are looking into other uses for their wood. At the present time, all treated lumber used in Alaska is imported from the forty-eight contiguous states and Canada because there are no wood-treating facilities in Alaska. Over ten million board feet of treated lumber are imported every year (McDowell Group 1998).

There are many methods for treating wood. The conventional method for treating wood uses combinations of vacuum and pressure to force chemical into the cell lumens (Zabel and Morrell 1992). Alternative wood treating methods are non-pressure processes that include brushing, spraying, dipping, and many variations of soaking (Hunt and Garratt 1967). Each method has its strengths and its weaknesses, 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.

The double-diffusion method of treating wood was identified because it can be used to treat freshly cut or green wood. This is was an important factor to consider, due to the limited drying capacity in Alaska. The double-diffusion method is based on sequentially treating green wood 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. Sodium fluoride and copper sulfate are potential components for this process because each chemical could be shipped in crystalline form to producers and neither is labeled as a restricted-use pesticide. The literature advocates the use of sodium fluoride (Baechler 1963) in the double-diffusion process; however, this use is not included on the sodium fluoride label currently registered with the Environmental Protection Agency (EPA). The copper sulfate

label allows it to be used in wood treatment, and requires a first solution of sodium salt or sodium chromate (Griffin 1997). The label indicates that the wood is to be sequentially soaked in each solution for up to three days, without regard to wood species or retention.

The lack of information on double-diffusion treatment using sodium fluoride and copper sulfate led to investigate the effect of treatment times up to three days in each solution on chemical retention. Because chemicals that diffuse into the wood matrix could leach out during service, the extent of such leaching was also investigated. During this work, the potential for selective chemical absorption from the solution to the wood, the migration of chemicals after a 30-day diffusion period, and location of chemicals after leaching were also examined.

Results of this investigation are part of a collective effort to bring useable technical information to Alaska forest product manufacturers about a wood treating method that will successfully treat locally grown species. This project was done in cooperation with the Wood Utilization Research and Development Center in Sitka, Alaska.

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 those 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. Today, wood preservation plays an important role in our lives. Treated wood is used in foundations and decks for our homes, playgrounds, fences, utility poles, railroad ties, and a host of other applications (Zabel and Morrell 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 damage on fresh cut lumber. Long-term protection is used to extend the service life of wood used as an end product. Long-term protection is further divided into above-ground 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 Morrell 1992).

2.2. Treated Wood in Alaska

2.2.1. Market

The McDowell Group (1998) estimated that the market for treated lumber in Alaska was 10 to 15 million board feet per year. Demand for treated dimensional lumber was heaviest in Southeast Alaska, which represented 25 to 30 percent of that estimate. The Alaska Railroad (2003) also uses an additional two to three

million board feet of treated railroad ties every year. Since 1996, 520,000 ties have been replaced, and there are plans to add track to the system.

All the treated lumber used in Alaska is imported from the forty-eight contiguous states and Canada because there are no wood-treating facilities in Alaska. For decades, the wood industry had focused on producing cants and chips for export to Asia (FPL 1999). Because exporting rules and the Asian market have changed drastically, producers in Alaska are looking into other uses for their wood (Alaska Wood Utilization Research and Development Center 1999). One of those other uses could be treated wood products.

2.2.2. Raw Material

Much of Alaska is publicly owned. Therefore, mills are dependent upon public lands, mainly the Tongass National Forest, for their timber supply. In fiscal year 2003, 115 MMBF were offered for sale (Brink 2003). The amount available each year is subject to change due to legislative and political issues. The uncertainty of the supply from year to year limits the amount of credit banks are willing to extend to mills. Thus, mills trying to adapt to changing markets are hindered by the lack capital available for investing in manufacturing equipment.

Alaska has four commercial softwood species: Sitka spruce (*Picea sitchensis*), white spruce (*Picea glauca*), western hemlock (*Tsuga heterophylla*), and yellow-cedar (*Chamaecyparis nootkatensis*). Spruces and hemlocks are used to make dimension lumber. They have very little natural resistance to decay, and therefore, would have to be treated to withstand the moderate decay risk typical of Southeast Alaska and the low decay risk for use in the interior region (Scheffer 1971, Hunt and Garratt 1967). Yellow-cedar is primarily used for decking and other exterior uses because it is naturally resistant to decay.

Sitka spruce and western hemlock are most abundant in southeast Alaska, while white spruce is abundant in interior Alaska. Western hemlock is considered moderately difficult to treat, while Sitka and white spruce are considered difficult

to treat (FPL 1999). Therefore, it is likely that a preservation process successfully used to treat Alaska-grown Sitka spruce would also be able to treat white spruce.

2.3. Conventional Wood Treating

The conventional method for treating wood uses combinations of vacuum and pressure to force chemical into the cell lumens. This process produces a deep, uniform penetration of chemicals in wood for applications requiring a long, reliable service life in regions with high decay hazards (Zabel and Morrell 1992).

2.3.1. Equipment

Conventional treating requires treatment cylinders that are typically two to three meters in diameter, and built to handle pressures around 1034 kPa (150 psi). The length of the cylinder is based on production, but can extend up to 55 m (180 ft) long. These cylinders are supported by pumps, chemical tanks, thermometers, gauges, controllers, piping, valves, a boiler, and wood transporting systems (Hunt and Garratt 1967). There can be tracks on both the infeed and outfeed of the treating cylinder that allows lumber on trams to be rolled in and out of the cylinder. The outfeed area must capture any liquid coming off the treated wood to avoid environmental contamination. In addition, this area is usually covered to avoid rainwater contamination, since all water runoff must be captured and cleaned. The capital investment for this equipment can easily exceed $1,000,000 (Reader 2000).

2.3.2. Chemical Combinations

Conventional treating methods can use a host of waterborne or oilborne 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 Morrell 1992).

Presently, the waterborne chemicals that are commercially used include: chromated copper arsenate (CCA), ammoniacal copper quaternary (ACQ), copper azole (CA), and ammoniacal copper zinc arsenate (ACZA). Copper and arsenic are both excellent fungicides, while arsenic also protects wood from insects and

marine-borers (Zabel and Morrell 1992). Chromium bonds with the lignin inside the wood matrix as well as forming a complex with the copper and arsenic, thereby limiting the leaching of chemicals while the wood is in service (Hartford 1986). Some waterborne chemicals can be shipped dry and mixed on site using a local water supply, reducing transportation costs, while others are shipped as concentrates and diluted on site. Treating wood with waterborne chemicals leaves the wood surfaces clean and paintable.

Oilborne chemicals, like creosote, have been around the longest and have proven to be the most reliable preservatives. Creosote is a by-product made during the manufacturing of coke that is used for steel production. Other major oilborne wood preservatives include pentachlorophenol (PCP), copper naphthenate, and copper-8-quinolinolate. Most oilborne chemicals are transported to treating facilities as concentrates or, in the case of penta, in solid blocks.

2.3.3. Treatment Processes

Conventional pressure treating is divided into two processes, the full-cell process and the empty-cell processes. The full-cell or Bethell process is used when maximum retention is paramount. A vacuum is first used to remove some air from the wood, and then preservative is added while increasing pressure. The empty-cell process is used when limited preservative retentions are needed. This process does not use a vacuum but pressure is introduced before the preservative. Variations in the pressure applied have been further named as either the Rueping or Lowry empty-cell processes. Both full and empty-cell processes require dried wood, unless some form of conditioning can be performed in the cylinder prior to treating (Hunt and Garratt 1967).

Lumber or poles can be treated within hours depending on specifications. Since the wood is secured in the cylinder, the environment is controllable. This allows treaters the option to adjust retention and penetration in order to meet end user specifications.

2.3.4. Pretreatments

Over the years there have been many mechanical innovations used to aid preservative penetration including incising, radial drilling, through-boring, and kerfing. While they have been proven effective in many groundline applications for posts and timber, they are destructive and care must be taken to maintain required mechanical strength properties. Incising also reduces the aesthetic quality of lumber if a smooth surface is desired.

2.3.5. Refractory Issues

Some commercially-important refractory species such as Douglas-fir and spruces have been excluded from certain end uses because of the inability to attain the required preservative penetration despite attaining the recommended chemical retention (Baines and Saur 1985). Lebow and Morrell (1993) had mixed results pressure treating Sitka spruce. None of the charges using CCA achieved the American Wood Preservers' Association (AWPA) specifications for penetration despite incising, while 12 of 14 charges using ACZA met both penetration and retention specifications. Blew et al. (1967) found that pressure treating wood grown in Alaska offered less protection than treating the same species grown in Oregon. These results were based on retention differences in round and sawn wood in Sitka spruce and other species.

2.3.6. Other Factors to Consider in Alaska

Even if enough chemical can be impregnated in Sitka spruce grown in Alaska using conventional wood treating processes, there are still other factors to consider. The capital investment in treating cylinders of any size is unfeasible for most Alaskans. The climate in Alaska forces mills to close during the winter months, thus reducing the production time available to help repay any capital investment. The low annual production for any one mill, often less than 1 MMBF per year, results in a high capital cost per unit treated (Kilborn 2002). Transporting chemicals, especially oilborne chemicals, over the marine highway system in Southeast Alaska can be very costly, again cutting into an already limited profit

8

margin. Since many Alaskan wood manufacturers use portable processing equipment, the treating system should also be capable of moving seasonally or as the harvest location changes. Treating fresh cut wood is required, because there is a very limited amount of drying capacity available. Taking into account all of these factors, conventional treating does not appear advantageous for Alaska. Therefore, alternative methods of treating wood must be investigated.

2.4. Alternative Wood Treating

Alternative wood treating methods include non-pressure processes such as brushing, spraying, dipping, and many variations of soaking (Hunt and Garratt 1967). Many alternative treating methods require much less equipment than conventional methods and are typically limited to small-scale applications by homeowners and farmers (Zabel and Morrell 1992).

2.4.1. Brushing and Spraying

Typically, oilborne 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 oilborne preservative on the wood surface (Hunt and Garratt 1967).

2.4.2. Dipping and Soaking

Hunt and Garratt (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 oilborne chemicals for two days to one week.

The *thermal process* involves the immersion of dried wood in successive baths of hot and cool preservative. The purpose of the hot and cool baths is to form a partial vacuum, whereby atmospheric pressure would force the preservative into the wood. Either oilborne or waterborne solutions can be used with this method if the temperature used does not cause excessive chemical loss through evaporation. Depending on the standard, the hot bath is around 102° C and the cool bath around 38° C. Several variations of this method were patented. In one variation, the wood was heated in a kiln instead of a hot bath and then submerged in the cool bath. The theory of creating a partial vacuum using hot and cool baths was improved by actually creating a *vacuum* in an air tight container by exhausting the air with a pump (Hunt and Garratt 1967).

Diffusion methods are similar to steeping in that there is 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 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 Garratt 1967).

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). Chemicals placed in the wood only by diffusion, however, are susceptible to leaching, because chemicals that diffuse into the 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 (Vinden 1990).

The double-diffusion process was developed to overcome leaching issues associated with the 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).

2.4.3. Other Factors to Consider in Alaska

There many factors to consider when comparing alternative treatment methods for use in Alaska. Dipping is only recommended as a method to deliver long-term wood protection for wood that has been dried and impractical to treat by more effective methods. Limited drying capacity in Alaska makes dipping impractical. The schedule for the steeping method recommends steeping one day for each 25 mm of material thickness plus one more day for good measure, but penetration rarely exceeds 6 mm. The poor penetration and the requirement for dried wood eliminate steeping as a choice for Alaska. The thermal process can attain suitable penetration, but the hot bath temperature may be unattainable or not maintainable in Alaska. In addition, the hot and cool solutions need to be pumped into and out of the treatment tank, or the wood must be moved between two separate tanks. This requires either pumps or equipments to move the wood back and forth between tanks, and equipment to heat the solution. The vacuum method requires a sealed container and only works well with easily treated wood, again precluding refractory species. Diffusion methods utilize green wood, open tanks, and are the suggested alternative for treating refractory species (Hunt and Garratt 1967). Taking into account all of these factors, the alternative wood treating method of diffusion, particularly double-diffusion, appears most suitable for Alaskan woods.

2.5. Double-Diffusion Wood Treating

As previously stated, treating wood by diffusion typically refers to soaking wood, but theoretically can also extend to the use of pastes and wraps to deliver chemicals into the wood. Two mechanisms help move preservative into the wood, bulk flow and diffusion (Greaves 1990, Hunt and Garratt 1967). Bulk flow is considered the initial mechanism of treatment by the diffusion method, and consists

of liquid flowing into the wood due to a pressure difference. The second mechanism is diffusion whereby the chemical absorbed in the bulk flow phase becomes more evenly distributed as it moves from areas of high to lower concentration. This allows the chemicals to penetrate deeper and more uniformly into the wood (Vinden 1990). Baechler (1953) noticed a possible third mechanism, capillary pull. If the water column inside the wood matrix was still continuous, evaporation from the top of the post would draw solution upward. Capillary pull is a form of bulk flow that mimics a tree's natural water transport system; it is limited to extremely green posts, treated upright in a barrel with post tops exposed.

2.5.1. Theory of Diffusion

If the wood is at its highest possible moisture content and there is no interaction with the wood substance, the rate of diffusion of such chemicals should follow Fick's law. This law states that the rate of transfer per unit area of a section equals the negative of the diffusion coefficient times the derivative of the concentration with respect to the space co-ordinate measured normal to the section. The rate of diffusion is greatest in the longitudinal direction and lowest in the transverse directions (Vinden 1983).

Mathematical models can help predict real world results, establishing relationships between variables, and optimizing of treatment schedules. Models must take into account the moisture content and density of the wood, the interactions between the wood matrix and the preservative, temperature, preservative retention, time and type of wood (heartwood, sapwood, earlywood, and latewood) as well as the concentration of the preservative. Vinden (1984) compared the calculated mathematical models for steady-state and non-steady state diffusion coefficients for copper ions through saturated samples of Scotspine (*Pinus sylvestris*), spruce (*Picea abies*), and birch (*Betula pendula*). His data indicated that the pathway for diffusion was limited to the area of the free water in the lumens, and that that diffusion ceased below the fiber saturation point. He also found that the steady-state diffusion coefficient for spruce air-dried and resaturated

wood was significantly lower than the coefficient for spruce in the green condition. The pathway for diffusion is slowed by pit aspiration (Flynn 1995), highlighting another raw material variable not previously mentioned. Pits aspirate with increased capillary tension caused by the removal of free water in lumens during drying (Siau 1984). Therefore, the coefficients of diffusion differ for green and previously dried wood. Vinden (1984) also found that during the initial or non-steady state diffusion, the coefficient of diffusion will deviate from Fick's law, due to the number of fixation sites within the wood matrix. He found that all the fixation sites, a constant portion of the weight of the wood substance, must be filled before diffusion proceeds. Other researchers have also shown that copper ions fix to the wood matrix (Cooper 1991, Jin and Archer 1991, Bland 1963).

While explainable in mathematical terms, the numerous variables have a significant impact on the retention and penetration of preservatives. Therefore, pilot studies and chemical retention analyses are still needed.

2.5.2. Equipment

Treating by double-diffusion requires that the wood to be soaked in two chemicals sequentially and then wet stacked for a period of time. Depending on the amount and size of the wood to be treated, the double-diffusion method can require fairly simple equipment. Each chemical could be pumped into and out of one treatment tank, or the wood could be moved between two separate tanks. This requires either pumps or the ability to move the wood back and forth between tanks. The material for the tanks can vary from stainless steel to wood with plastic lining, depending on the corrosivity of the chemicals employed. Tank size would depend on the product being produced. Fence posts could be treated upright in a barrel, while decking would have to be fully submerged. Depending on the amount of wood treated per month or the volume of chemicals used per year, containment equipment around the tanks may be necessary (EPA 1996). Depending on species and moisture content, the buoyancy of wood may make hold-down hardware necessary. As with all wood treating methods, equipment is needed to transport the

wood to and from the treating vessel. Personnel protective equipment as mandated by the Material Data Safety Sheets for each chemical and the Occupational Safety and Health Administration is also needed.

2.5.3. Chemical Combinations

Ideally, the two chemicals used in the double-diffusion method will form a precipitate that is highly resistant to leaching and toxic to fungi and termites. In order to be toxic and insoluble after forming a precipitate, salts of very strong acids are used with weakly basic metals (Baechler 1953).

Baechler (1953) initially reacted nickel, zinc, or copper with chromate, fluoride, arsenate, borate, or phosphate. Advantages and disadvantages for each chemical are given in Table 2.1.

Table 2.1. Relative advantages and disadvantages of chemicals used in double-diffusion treatments (Baechler 1953).

Chemical	Advantages	Disadvantages
Copper	More toxic to fungi More economical	More corrosive to tank
Nickel	Less corrosive to tank	Less toxic to fungi Less economical
Zinc	Less corrosive to tank	Less toxic to fungi
Reacting with		
Arsenic	Restricted Use	Restricted Use
Boron		Did not form an insoluble Precipitate with any metal
Chromium	Restricted Use	Restricted Use
Fluoride	Consumers familiar (toothpaste)	Did not form an insoluble Precipitate with nickel or zinc
Phosphorous	Helps fix copper inside wood	Does not contribute to toxicity

Restricted-use is listed as both an advantage and a disadvantage for two chemicals. These chemicals are highly toxic, making personnel training and extra containment equipment essential. The disadvantage would be the costs associated

with the added safety measures. The advantage would be the awareness personnel would gain from training.

Recent efforts to revive double-diffusion as an effective but low cost treatment option for rural areas have focused on sodium fluoride and copper sulfate (Kilborn et al. 2003, Hoffman 2002a,b,c, Reader 2000, and Wheat et al. 1996)

2.5.4. Chemical Labels

Treaters have to legally abide by the wording on the chemical labels. Chemical labels are proprietary to a given company and have either an EPA registration number or NSF-60 certification. Labels contain information on the uses the chemical manufacturer is willing to take liability for, based on past research. It is illegal to use pesticides for non-labeled uses or to use them at levels above or below label recommendations.

The copper sulfate labels from Old Bridge Chemicals Inc. (2000) and Chem One Inc. (2000) have the same wording for use in a wood treatment. Both labels are for peeled, green posts treated "butt end down first in the copper sulfate solution for three days, then butt end down in sodium chromate solution for two days, and finally turn the post upside down in the sodium chromate solution for one additional day"

The label for Blue Viking's Copper Sulfate Instant (Griffin 1997) states that the first solution is a solution of sodium salt or sodium chromate. Therefore, sodium fluoride could be used with this product label. It states that green material is soaked in the sodium solution for up to three days, and then soaked in the Blue Viking Copper Sulfate Instant solution for up to three additional days.

The only registered label found for sodium fluoride states: "For Pesticide Formulation Use: Only in formulation into a fungicide for wood preservation (Osmose 2002)." As the label stands, the term 'formulation' precludes the use of sodium fluoride in double-diffusion. This is because the wood is treated sequentially in the two chemical solutions. Thereby, the formulation of copper fluoride could not occur until after the chemicals are inside the wood matrix.

According to Curtis (2003), Tyonek's Wood Double-Diffusion Treatment Plant in Kenai Borough, Alaska had a sodium fluoride label that included atmospheric pressure immersion. Because the plant is no longer operating, the whereabouts and status of that label are unknown.

Besides the legal issue with using sodium fluoride, there is not enough information on these labels for someone to develop treating schedules based on wood species, retention and penetration.

2.5.5. Preservative Threshold

The minimum amount of preservative needed to prevent wood decay by selected fungi can be determined using AWPA Standard E10-01 Soil-Block Method (AWPA 2001d). The standard treats sapwood test blocks of a non-durable conifer, i.e. southern pine (*Pinus* spp.) or a medium-density angiosperm, i.e. sweetgum (*Liquidambar styraciflua* L.) with different concentrations of the chemical. A minimum of three species each of brown rot and white rot fungi are required when determining thresholds of new preservatives. Depending on the size of the test blocks and fungi used, the incubation period extends from 8 weeks to 24 weeks. The threshold is then calculated by plotting weight lost after incubation against chemical retention to determine the point where fungal induced weight loss ceases. Duncan (1958) reported that the threshold for a given preservative changes with wood species even within a genus, i.e. *Pinus*. Therefore, the wood species used in the soil block test should match the wood species in question for the preservative application.

Baechler and Roth (1956) conducted decay tests using *Neolentinus lepideus*, *Gloeophyllum trabeum*, and *Postia placenta* fungi on 19 mm (3/4-inch) southern pines cubes treated with either copper sulfate, zinc chloride, sodium arsenate, sodium borate, sodium fluoride or sodium dichromate water-borne solutions. The only reference to treating schedules was: "the cubes were treated to refusal with solutions of known concentration". The threshold for copper sulfate and sodium

fluoride are given in Table 2.2. Units were converted from lb/ft^3 to % wt/wt using a specific gravity for southern pine of 0.51 (FPL 1999).

Table 2.2. Threshold concentrations for copper sulfate and sodium fluoride using southern pine sapwood (Baechler and Roth 1956).

Fungus Tested	Retention Threshold Range (%wt/wt)	
	Copper Sulfate	Sodium Fluoride
Neolentinus lepideus	- - 0.59	0.26 - 0.41
Gloeophyllum trabeum	0.94 - 1.31	0.49 - 0.59
Postia placenta	0.96 - 1.67	0.49 - 0.57

It should be noted that these tests were not standardized nor was it stated how the thresholds were determined. Furthermore, because cubes were treated with only one chemical for each decay test, no inferences can be made about the combined fungicidal effect of copper and fluoride. Copper is almost always used with another biocide, i.e. chromated copper arsenate, ammoniacal copper arsenate, copper naphthenate and copper-8-quinolinolate. Cowling (1957) presented threshold values for several preservatives inoculated with 18 wood-destroying fungi, including the three fungi listed in Table 2.2. The threshold reported for copper (as metal) in copper naphthenate was 0.50 % wt/wt. This value may be a more accurate threshold assumption for copper in copper fluoride than those listed in Table 2.2.

Panek (1963) immersed southern yellow pine poles for 15 minutes to four hours in 20 or 30% aqueous ammonium bifluoride. Pole conditions after months of air-seasoning were compared to fluoride retentions. A retention of 0.8 kg/m^3 (0.05 lb/ft^3) was ascertained as an above-ground fluoride threshold for the outer 25 mm (one inch) of southern yellow pine poles. The condition of the poles was rated for one of six categories; no visible stain, light, medium or heavy sapwood stain, incipient decay or decay. For wood with a specific gravity of 0.51, that threshold could be expressed as 0.16 % wt/wt (FPL 1999). Therefore, 0.16 % wt/wt could be

interpreted as an above ground fluoride threshold based on visual inspection of poles not in ground contact.

2.5.6. Previous Studies

Further investigations into the treating of wood using the double-diffusion method were conducted by the USDA Forest Service. The first double-diffusion study (Baechler 1953) resulted from increased interest in treating fence posts for farm use. In 1941, 100 green southern pine posts were treated in copper sulfate followed by sodium arsenate. After treatment, the posts were dried and installed in a fence post plot in the Harrison Experimental Forest in Mississippi. Eleven years later, only one failure occurred and only a few had decay. Five posts have failed after 22 years (Blew and Kulp 1964), and a total of eight posts had failed after 29 years (Gjovik and Davidson 1975). The incomplete copies of these reports did not indicate the service life of untreated southern pine posts in this plot. Because 92% of the treated posts were sound after 32 years of service, it would be safe to say that the double-diffusion method delivered satisfactory amounts of chemical into the wood matrix.

Laboratory tests were also part of Baechler's (1953) initial study. Jack pine posts were treated with copper sulfate, followed by either disodium phosphate or sodium fluoride. Copper sulfate and sodium fluoride absorptions by jack pine posts treated by the double-diffusion process are given in Table 2.3.

Table 2.3. Copper sulfate and sodium fluoride absorptions by jack pine posts treated by the double-diffusion process (Baechler 1953).

Treating Schedule				Chemical Absorption	
Copper Sulfate		Sodium Fluoride		Copper	Sodium
Time	Conc.	Time	Conc.	Sulfate	Fluoride
(days)	(%)	(days)	(%)	(% wt/wt)	(% wt/wt)
1	7.95	4	3.2	1.42	1.04
2	7.95	4	3.2	2.35	0.93
2	7.95	7	3.2	2.16	1.27

Several fence posts were treated by double-diffusion at the Matanuska Experimental Station farm in Palmer, Alaska in the 1954. Species included Alaska- grown white spruce, paper birch (*Betula papyrifera* Marsh), balsam poplar (*Populas balsamifera* L.), and quaking aspen (*Populas tremuloides* Michx.). Posts were treated for three days in 8% copper sulfate solution and then treated for three days in 11% sodium chromate solution. After 32 years in service, 100% of the aspen, balsam poplar and white spruce posts were sound, while only 58% of the paper birch posts were sound. The controls for aspen, balsam poplar, paper birch, and white spruce failed after 9, 4, 7, and 9 years, respectively (Mayer et al. 1995).

Baechler et al. (1959) treated several species of hardwood posts native to the southeast United States. The wood was completely submerged for treatment to replicate larger-scale commercial-type treating, permitting a more efficient utilization of hardwoods than the method of treating upright in a barrel. Treating was conducted at ambient temperature, with only one solution concentration for each chemical used. Treatment times were one-half, one, two, or three days for both tanks. The first tank was zinc sulfate and arsenic acid, while the second tank was sodium chromate. Five posts from each treatment and species group were analyzed for chemical retention and penetration. The remaining 25 posts were installed in a test plot at the Whitehall Experimental Forest in Georgia. Chemical analyses showed that sapwood was much more treatable than heartwood, and that "double-diffusion appears to offer considerable promise." After 29 years in service, only three of 25 pine posts had failed. The overall service lives for white oak, red oak, and yellow-poplar for all of the treatment times combined were 16.3, 16.4, and 16.2 years, respectively (Vick and Baechler 1986).

Twelve species of wood grown in Hawaii were treated by double-diffusion in 1960, as a demonstration of the process for local landowners, salesmen, and industry personnel. At the time, commercially-treated posts were not readily available and this method appeared feasible. Copper sulfate was used as the first solution, followed by sodium chromate. Freshly peeled posts were treated butt

down for three days in each solution, using one barrel for each solution. Discs were cut from the top, middle, and butt after a two-week diffusion period, and analyzed for chemical retention. Analyses showed that the chemical retention for most of the species were within a satisfactory range, based on the desire to retain equal amounts of each chemical. The demonstration showed promise for a commercial double-diffusion treating operation using Hawaiian species (Smith and Baechler 1961).

Baechler (1963) explicitly told farmers "How to treat fence posts by double diffusion." This report recommended sodium fluoride and copper sulfate as the first and second treatment solutions, respectively.

The double-diffusion process was investigated in the late 1960's for its ability to treat Engelmann spruce (*Picea engelmannii*), lodgepole pine (*Pinus contorta*), and Rocky Mountain Douglas-fir (*Pseudotuga menziesii* var. *glauca*) posts. These species resist conventional treatment. One hundred and twenty-six posts of each species were treated using the four treatment combinations given in Table 2.4. Posts were fully submerged in solution for treatment. Sixty posts were analyzed for sapwood thickness, and chemical retention and penetration. The remaining 225 treated posts and 75 untreated posts were installed in a fence post plot at the Central Plains Experimental Range in Colorado (Markstrom et al. 1970).

Table 2.4. Treatment schedule used in a fence post study by Markstrom et al. (1970).

		1st Solution 10 % Copper Sulfate		2nd Solution 13 % Sodium Chromate/ Arsenic Acid	
ID	Pretreatment	Time	Temp	Time	Temp
A	-	1 day	ambient	1 day	Ambient
B	-	3 days	ambient	3 days	Ambient
C	-	8 hrs	200° F	1 day	Ambient
D	Incising	1 day	ambient	1 day	Ambient

Markstrom et al. (1970) found that Engelmann spruce and lodgepole pine could be successfully treated based on the average penetration exceeding 19 mm

(3/4-inch). Full sapwood penetration occurred in Rocky Mountain Douglas-fir, but the average minimum penetration was less than 19 mm for all treatments. They also found that both Engelmann spruce and lodgepole pine could be treated to meet the 6.41 kg/m^3 (0.40 lb/ft^3) of chromated copper arsenate retention specified by AWPA Standard C5-00 fence posts (AWPA 2001c).

Thirty years later, all of the treated posts withstood a 22.7-kg (50-lb) load applied laterally at the top of the post. Untreated posts had service lives of 16, 17 and 9 years for Engelmann spruce, lodegpole pine, and Douglas-fir, respectively. All untreated posts failed at or near the ground line (Markstrom and Gjovik 1999).

By 1985, double-diffusion studies were extended to treating railroad ties in an effort to demonstrate the use of non-pressure processes to treat native Alaskan species. Western hemlock ties and timbers, and Sitka spruce and yellow cedar timbers were in the combinations shown in Table 2.5 (Gjovik 1985).

Table 2.5. Treatment schedule used in the Alaska demonstration project (Gjovik 1985).

1st Solution			2nd Solution		
Chemical	Conc.	Temp	Chemical	Conc.	Temp
Sodium Fluoride	4%	ambient	Copper Sulfate	8%	Ambient
Sodium Fluoride	4%	hot	Copper Sulfate	8%	Ambient
Copper Sulfate	8%	ambient	Sodium Chromate/ arsenic acid	11%	Ambient
Copper Sulfate	8%	hot	Sodium Chromate/ arsenic acid	11%	Ambient

The first solution was heated for half of the charges. The goal of heating to 82° to 88° C (180° to 190° F) was unattainable; the actual temperature never exceeded 52° C (125° F). Treating with a heated solution is referred to as the modified double-diffusion process (Gjovik 1985). Forty-eight hemlock ties went into the railroad track near Palmer, AK and are still in the track (Kilborn 2002). The remaining wood was to be analyzed for chemical retention and penetration, but no reports of the results were found.

In an effort to increase retention with the double-diffusion process, the use of ultrasonic energy was investigated. Alaska grown white spruce was treated with approximately 4% sodium fluoride while ultrasonic energy was applied. Wheat et al. (1996) found that using ultrasonic energy during treatment increased chemical retention. However, the second treatment in the double-diffusion process was not used. Therefore, it is not known if the additional chemical uptake would remain in the wood matrix during submersion into the second treatment solution.

In 1995, the Wood in Transportation Program awarded Tyonek Native Corporation a grant to develop a double-diffusion treating facility. The facility would, in turn, utilize locally grown species of wood and provide long-term employment for local residents. Operations began in 1997, by treating wood for a bridge to be built near Fairbanks, Alaska (Russell and Kilborn 1997). Operations ceased shortly thereafter due to lack of infrastructure.

Treating demonstrations using ponderosa pine (*Pinus ponderosa*) posts and poles have also taken place in Colorado, Arizona, and Utah. Posts were treated using sodium fluoride and then copper sulfate. Because these demonstrations were to inform the public of a low cost wood preservation treatment for their refractory species, only one charge of wood was treated at each site. Chemical penetration and retention were not assessed (Reader 2000).

The most recent double diffusion field project took place near Copper Center, Alaska. In order to access proposed agricultural land, the Trans Alaska Pipeline had to be crossed using a bridge. The State of Alaska and Alyeska Pipeline Service opted to used Sitka spruce for the bridge abutments, because wood abutments would not transfer heat to the soil and disturb the permafrost supporting the pipeline. Timbers were treated with heated 4% sodium fluoride and then 10% copper sulfate at (Hoffman 2002a). Samples were treated along with timbers for purpose of analyzing chemical retention and penetration, but no results have been made available at this time.

In the most recent laboratory study on double-diffusion, western hemlock, Sitka spruce, and white spruce railroad ties grown in Alaska were treated with 4% sodium fluoride followed by 8% copper sulfate. Ties were fully immersed for 20, 10, 5 or 2.5 days in each solution. After a two week diffusion period, copper content was analyzed. Fluoride content was estimated from copper content based on a previous study indicating that fluoride was found in excess of copper. Because copper sulfate labels limit treatment time to three days, only the chemical retentions for the 2.5-day treatment are given in Table 2.6. The poster presented for this study did not discuss the implications of the chemical analyses (Kilborn et al. 2003).

Table 2.6. Chemical retentions for Alaskan-grown railroad ties (Kilborn et al. 2003).

Species	MC	Copper		Fluoride (estimated)	
		0-13 mm	13-25 mm	0-13 mm	13-25 mm
	(%)	(% wt/wt)	(% wt/wt)	(% wt/wt)	(% wt/wt)
Sitka spruce	28	0.22	0.06	0.13	0.04
Sitka spruce	34	0.26	0.08	0.15	0.05
Western hemlock	26	0.28	0.06	0.17	0.04
Western hemlock	31	0.48	0.09	0.28	0.05
White spruce	39	0.37	0.08	0.22	0.05
White spruce	32	0.44	0.16	0.26	0.09

Furthermore, it is unknown if decay tests will be performed on these treated ties in order to determine the actual copper and fluoride thresholds needed for service in Alaska.

2.5.7. Gaps in the Literature

While there appear to be many studies treating wood by double-diffusion, several gaps still exist in the literature.

While copper sulfate manufacturers include wood treatment on their label, it is not clear why a maximum treatment time of three days in each solution was selected. It is not clear if a three-day treatment can deliver enough chemical under all conditions of initial moisture content, density, temperature of the wood and/or

solution, and type of wood (species, heartwood, sapwood, earlywood, and latewood). Furthermore, there is no established threshold for copper and fluoride using double-diffusion.

The only report found on the leach resistance of chemical precipitates formed in double-diffusion treatments did not include copper fluoride. The report only included copper arsenate, copper chromate, nickel arsenate, nickel chromate, and magnesium ammonium arsenate (Baechler 1941). It has never been established that copper sulfate forms an insoluble precipitate with sodium fluoride.

Optimum treatment schedules to deliver adequate copper and fluoride retentions into Sitka spruce grown in Alaska, and the optimal length of time for the treated wood to be wet-stacked to facilitate the diffusion remain unknown.

Previous studies were limited to posts, poles, and railroad ties, all of which are likely to have more easily treated sapwood. The treatment times for dimensional lumber that do not contain any sapwood are unknown.

2.6. Analyzing Wood Preservatives

The AWPA has numerous standard methods for analyzing wood preservatives. Two standards relevant to analyzing copper and fluoride are A9-01 Standard method for analysis of treated wood and treating solutions by X-ray spectroscopy and A2-98 Standard methods for analysis of waterborne preservatives and fire-retardant formulations. Standard A9-01 offers a non-destructive analysis for several elements including copper using either energy dispersive or wavelength dispersive X-ray fluorescence spectrometers. Standard A2-98 Method 7 offers a destructive analysis for determination of fluoride using specific ion electrodes. Wood samples have to be processed into a solution before analyzing for fluoride (AWPA 2001a, b).

2.6.1. Analyzing Copper

An energy dispersive X-ray fluorescence analyzer uses the backscatter from an irradiated sample to produce X-rays with different energy signatures. These energy

signatures are segregated into channels and displayed as a spectra. The peak height of the channels is proportional to intensity. Therefore, either copper in solution or in wood could be analyzed. Samples with known amounts of copper are used to calibrate the backscatter detection into the percentage of copper reported (Spectro Instruments 2000).

2.6.2. Analyzing Fluoride

A fluoride electrode with the aid of a reference electrode measures the electrode potential (mV) between the sensing element inside the probe and the solution. The potential depends on the level of free fluoride ions in solution, as measured against a constant reference potential. Fluoride ion activity is directly related to concentration, as long as the background ionic strength is high and constant. Therefore, all sample solutions require that the pH be adjusted between 5.0 and 6.0 and that five mL of Total Ionic Strength Adjustor Buffer (TISAB) III is added. Sample solutions with known amounts of fluoride are used to prepare a standard curve of the electrode potential in parts per million (ppm) (Thermo Orion 2001a,b).

3. OBJECTIVES

The overall objective was to identify suitable treatment time combinations for double-diffusion treatment of Sitka spruce (*Picea sitchensis*) with sodium fluoride and copper sulfate.

Hypothesis 1:

The rates of the solution uptake by the wood will decline to zero within 72 hours.

Because the chemical labels restrict the double-diffusion process to a maximum of three days soaking in each solution, one might conclude that solution absorption reaches a maximum by 72 hours.

Hypothesis 2:

Fluoride and copper will remain in the wood while it is in service.

The double-diffusion method is based on using two chemicals which react inside the wood matrix to form a precipitate that is highly resistant to leaching.

These hypotheses lead to the following objectives:
  a) Examine the rates of solution absorption over time
  b) Assess the potential for selective chemical absorption
  c) Quantify chemical retention after treating
  d) Determine the extent of leaching
  e) Examine the migration of chemicals after a 30-day diffusion period
  f) Examine the distribution of chemicals after leaching.

4. METHODS AND MATERIALS

4.1. Sample preparation

Nominal two-by-six Sitka spruce boards were selected from recently processed lumber at Davidson Industries (Mapleton, OR). Boards were selected on the likelihood of containing heartwood as determined visually by the absence of wane or the presence of pith. Selected boards were sorted by length. Fifteen 2.44-m-long (8-ft.) boards were selected for the first phase of the project. Sixteen 3.66-m-long (12-ft.) boards were selected for the second phase. All boards were brought to OSU. The 3.66-m-long boards were planed on two sides to a thickness of 38 mm (1.5 in.), cut into four 0.91-m-long sections, labeled with a board number, wrapped in plastic and stored at -5° C until needed.

4.1.1. Phase I

The 2.44-m-long boards were planed on two sides to a thickness of 38 mm (1.5 in.), and then a minimum of 150 mm (~6 in.) was cut from each end and discarded. The boards were further shortened if there were indications of end drying, such as splitting. Eleven of the 15 boards were each cut into sixteen 38 X 38 X 130 mm-long clear wood samples. The 11 boards were chosen based on the likelihood that each would yield 16 clear heartwood samples. The samples were numbered and placed immediately into a resealable plastic container to minimize drying.

The transverse faces of each sample were sealed with two coats of a two-part epoxy to limit longitudinal flow and simulate a longer board. In order to minimize moisture loss when coating, samples were stacked and wrapped, leaving only the coated faces exposed. Once the second coat of epoxy was cured, one sample from each board was placed in each of 16 treatment containers.

4.1.2. Phase II

One 0.91-m-long section from each of the sixteen 3.66-m-long boards was allowed to thaw under plastic in a room at 3° C for two days. Eleven of the 16

sections were cut individually into ten 38 X 38 X 130 mm-long clear wood samples. The 11 sections were chosen because they contained enough clear wood to produce ten clear heartwood samples. Each sample was labeled with a board number and placed immediately into a resealable plastic container to minimize drying.

These samples were also end-sealed with epoxy. One sample from each board was placed in each of the ten treatment containers.

4.2. Solution Preparation

Solutions were prepared by adding reagent grade copper sulfate pentahydrate or sodium fluoride to de-ionized water in 5-gallon plastic containers and stirring until the chemical went into solution.

4.2.1. Phase I

A total of 990 g of copper sulfate was dissolved into 15-L of de-ionized water, and 281 g of sodium fluoride was dissolved in 13-L of de-ionized water at 20.5° C to produce 6.19% and 2.12% solutions of copper sulfate and sodium fluoride, respectively. The copper sulfate solution was divided among nine 1.6-L treatment containers. The sodium fluoride solution was divided among seven 1.6-L treatment containers.

4.2.2. Phase II

A total of 924 g of copper sulfate was dissolved into 14-L of de-ionized water, and 308 g of sodium fluoride was dissolved in 14-L of de-ionized water at 26° C to produce 6.19% and 2.15% solutions of copper sulfate and sodium fluoride, respectively. The solutions were then divided among treatment containers as needed.

4.3. Wood Treatment

4.3.1. Phase I

In Phase I, samples were treated with either the copper sulfate or the sodium fluoride treating solution. One end-sealed sample from each board was placed in each of the 16 treatment containers for a total of 11 samples per container. Resealable, 5.5-L plastic containers were used for treating.

Each end-coated sample was weighed before treating. Two plastic spacers were placed in the bottom of the treating container, followed by a horizontal layer of five samples, two more plastic spacers, a horizontal layer of six samples, two plastic spacers, and a lead weight enclosed in plastic. Solution was added until the level exceeded the height of the samples by approximately 6-mm. A 10-mL test tube of solution was drawn from the container and retained for later analysis. The container was sealed with a lid, and then weighed.

This process was repeated for seven containers with sodium fluoride solution and nine containers of copper sulfate solution. A 10-mL test tube of solution was also drawn from the remaining solutions in each of the 5-gallon plastic containers for later analysis.

Samples in the seven containers containing the sodium fluoride solution were treated for 12, 24, 36, 48, 60, 72, or 84 hours. Samples in the nine containers containing the copper sulfate solution were treated for 12, 24, 36, 48, 60, 72, 84, 96, or 108 hours. Once the treatment time was reached, the sealed container was again weighed to check for evaporative loss.

Samples were removed, allowed to drip dry, and weighed. Mass uptake was determined by the difference in sample weight before and after treatment. After all samples were removed, the solution in the container was stirred and a 10-mL test tube of solution was drawn for later analysis.

The samples were cut across their small dimension into three equal sections. The newly exposed end grain would help facilitate drying. The three pieces were

weighed together and placed in the oven at 103° C to dry. After 48 hours, they were weighed again and retained in the event further examination was necessary.

4.3.2. Phase II

Ten containers with 11 samples each were prepared and weighed as in Phase I. Samples in the containers were treated as outlined in Table 4.1. One treatment set was left unsoaked, while another was soaked in de-ionized water for six days.

Table 4.1. Schedule for treatment of Sitka spruce using copper sulfate and/or sodium fluoride.

Treatment		Treatments Time (days)		
Sample ID	Results Code	De-Ionized H2O	Sodium Fluoride Solution	Copper Sulfate Solution
0	Blank	-	-	-
1	DI	6	-	-
2	F0C2	-	-	2
3	F0C3	-	-	3
4	F2C0	-	2	-
5	F2C2	-	2	2
6	F2C3	-	2	3
7	F3C0	-	3	-
8	F3C2	-	3	2
9	F3C3	-	3	3

As in phase I, each sample was weighed before and after soaking in solution. Sealed container weights were checked for evaporative loss.

Phase II samples were cut and processed as shown in Figure 4.1. After treatment, 6-mm of wood with epoxy were removed from one end, and discarded (step B). The next 36-mm wafer was removed, labeled, and dried at 60° C. The 36-mm length was selected because it provided enough wood for analysis. The lower drying temperature was used throughout this phase, in order to reduce sawdust static electricity at the band saw and Wiley mill. The exposed end grain of the sample was re-sealed with epoxy. Once the epoxy cured, the 11 samples within

each treatment were placed in a resealable plastic bag for 30 days at 25°C to 30°C to allow diffusion to occur (step C).

Step:

A 38 X 38 X 130 mm (1.5 x 1.5 x 5 inch) long sample to be treated

B After treating in solutions as specified ▶ | End seal | Dry and retain for analysis | Discard

C Place in resealable plastic bag for 30 days.

D After storing in plastic for 30 days ▶ | End seal | Dry and retain for analysis | Discard

E Dry and condition samples. Leach in de-ionized water for 14 days.

F After leaching for 14 days ▶ | Dry and retain for analysis | Discard

G Discard | Retain for records

Figure 4.1. Pattern used to remove wafers from samples after treating, after a 30-day diffusion period, and after leaching.

At the end of 30 days, 6-mm of wood with epoxy were removed from one end, and discarded. The next 36-mm wafer was removed, labeled, and dried. The exposed end grain of the sample was re-sealed with epoxy (step D).

Once the epoxy cured, samples were dried in the oven at 60° C for 24 hours, and then conditioned under ambient air conditions (25° C and 48% RH) for 72 hours. The samples were placed in containers and subjected to a leaching procedure as described in Standard E11-97 (AWPA 2001e). Samples were soaked in de-ionized water that was changed after 6, 24, 48 and thereafter every 48 hours over a period of 14 days (step E). The leachate was discarded, because the wood samples would be analyzed.

Once the leaching was completed, 6-mm of wood with epoxy were again removed and discarded. The next 36-mm wafer was removed, labeled, and dried (step F). The remaining wood from the original sample was also labeled, dried, and retained (step G).

Wafers were cut on a bandsaw into three sections (Figure 4.2). Two surfaces were discarded to remove the corners of each wafer. Corners may have had more chemical due to having more exposed surface area. The surfaces chosen to be discarded were based on the following criteria: If a visual inspection revealed a color change indicating sapwood, a pitch pocket, or a split that may have facilitated chemical uptake, the wafer was oriented in the bandsaw to remove as much of these zones as possible. If visual inspection revealed a severely asymmetrical penetration pattern, the wafer was oriented in order to keep a more symmetrical penetration pattern for analysis. This typically meant that radial surfaces of flat grain samples were removed. A majority of the samples had growth rings with a small radius of curvature, and therefore cutting orientation did not make a difference.
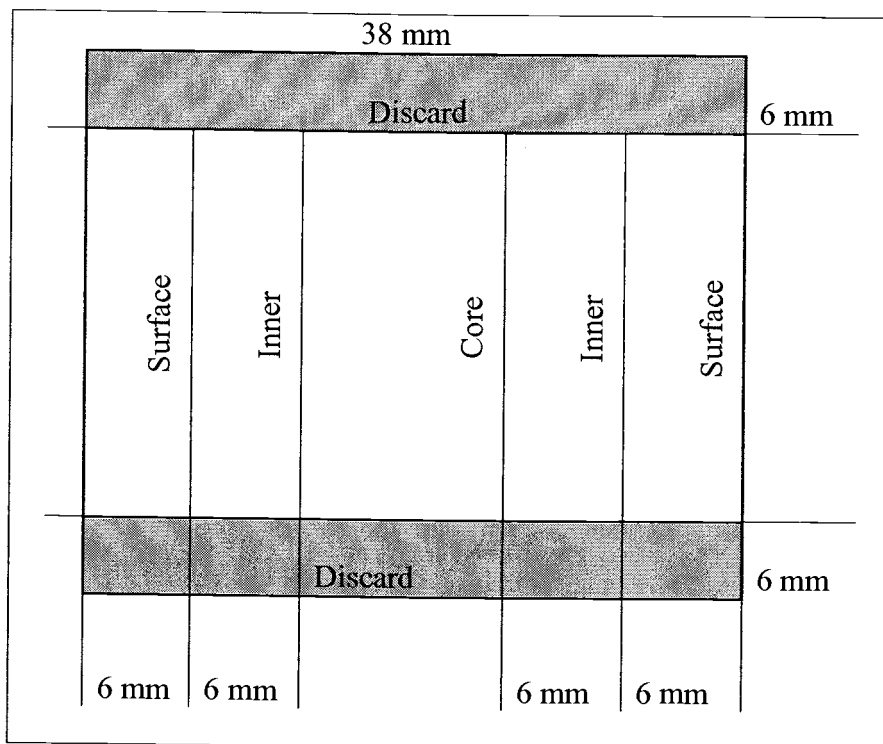
Figure 4.2. Diagram showing how wafers were cut for chemical analysis.

As the wafer was cut, the two surface sections were placed in a resealable plastic bag. Similarly, the two inner sections were placed in another resealable plastic bag. The core was cut into two sections and placed in a third resealable plastic bag.

A Wiley mill with a #20 mesh screen was used to grind these sections into wood dust. The wood in each resealable plastic bag was chopped into four parts to fit into the mill, and ground separately. Care was taken to clean the mill between samples to avoid cross-contamination.

Only the surface sections of the Blanks and DI were ground. Those samples were not subjected to diffusion or leaching periods.

4.4. Copper Analysis

Copper in the solutions and wood dust was analyzed according to procedures described in Standard A9-01 (AWPA 2001b) using a Spectro Titan Energy

Dispersive X-Ray Fluorescence Analyzer. The analyzer was previously calibrated for copper in solution and in wood. Therefore, only a visual inspection and x-ray tube warm up were needed before analyzing the samples cup contents for copper.

4.4.1. Phase I

Solutions taken before and after the wood was treated were diluted by 50% so that the concentrations were within the range for which the analyzer was calibrated. Two mL of solution and two mL of de-ionized water were added to assembled sample cups. A new transfer pipette was used for each solution.

4.4.2. Phase II

Wood dust was carefully poured into assembled sample cups until full. The filled sample cup was placed in an ammunition press and the wood dust was compacted by using approximately 0.4 MPa of pressure. Any stray wood dust was blown off the exterior of the sample cup. The press was wiped with a Kimwipe® after each sample was pressed, and a vacuum was used frequently to keep the area free of wood dust.

4.5. Fluoride Analysis

Fluoride in the solutions and in the wood dust were analyzed using a combination of procedures described in Standard A2-98 Method 7 (AWPA 2001a) and Chen et al. (2003). A Thermo Orion 420A plus Benchtop pH meter was used with a pH probe to determine solution acidity, and a fluoride selective ion probe and reference probe to determine fluoride ion concentration.

4.5.1. Phase I

The before- and after-treatment solutions were diluted one to 1000 wt/vol with de-ionized water and shaken to ensure uniform solution distribution. Five-mL was withdrawn from the volumetric flask into a previously weighed and marked 150-mL wide mouth plastic bottle.

De-ionized water (20-25 g) was added to each bottle to ensure that there was enough fluid to cover the pH probe, then each bottle was swirled for about thirty

seconds prior to the insertion of the pH probe. The pH meter was calibrated prior to each testing session using freshly mixed solutions of known pH. Each solution was adjusted dropwise to a pH between 5.0 and 6.0 using dilute NaOH or $HClO_4$. The probe was rinsed thoroughly with de-ionized water and wiped with a Kimwipe® between bottles. De-ionized water was added to each bottle until the total solution weight was 50 g. Five-mL of Total Ionic Strength Adjustor Buffer (TISAB) III was added to the each 50 g solution to provide sufficient ionic strength for the fluoride and reference probes to function. The electrode potential (mV) of each bottle was then measured using a reference probe and a fluoride selective ion probe. The fluoride in the treatment solutions were quantified by comparison with a standard curve prepared with solutions containing 0, 0.2, 0.4, 0.6, 0.8, 1, 4, or 10 µg/mL fluoride.

The probes were rinsed thoroughly with de-ionized water and wiped with a Kimwipe® between each bottle. Because noise and temperature can interfere with the readings, care was made to take as many fluoride readings as possible in one testing session.

4.5.2. Phase II

One hundred and fifty mg of wood dust were carefully removed from each resealable plastic bag, and placed on wax paper on a scale. The wax paper was then rolled into a funnel and the wood dust transferred to a 25-mL screw cap test tube. Fifteen mL of 0.1 M $HClO_4$ was also added to each test tube using a calibrated pipette. Tubes were placed in a sonicator for three hours at 80°C. After cooling for two to eight hours, 10-mL of the supernatant was withdrawn from each tube into previously-weighed 150-mL wide mouth plastic bottles. The remaining procedure was then the same as in Phase I.

4.6. Data Analyses for Phase I

4.6.1. Solution Uptake

The uptake of solution in kg/m^3 was calculated for each sample by taking the difference in weight from before and after treating in each solution divided by the sample volume. This data was plotted using treatment time as the independent variable and uptake of solution as the dependent variable. The mean uptake of each solution by treatment was calculated and presented in tabular format.

Initial moisture content (%) was calculated for each sample by taking the green weight minus the oven-dry weight and then dividing the difference by the oven-dry weight and multiplying the results by 100. Since end coated samples were in one piece when they were initially weighed, the green weight had to be calculated by subtracting the weight of the end-coating and kerf loss from the before treating weight. The end-coating weight was estimated as a constant one g. Kerf loss was calculated by subtracting sample weight of the three sections before drying from the sample weight after treating. The oven-dry weight was the weight of the samples in three sections after drying. This data was plotted using initial moisture content as the independent variable and uptake of solution as the dependent variable for the purpose of identifying a correlation.

Final moisture content (%) was calculated for each sample by taking the weight after treating minus the oven-dry weight and then dividing the difference by the oven-dry weight and multiplying the results by 100. The mean final moisture content by board was presented in tabular format.

Basic density was calculated for each sample by dividing oven-dry weight by initial volume. This data was plotted using basic density as the independent variable and uptake of solution as the dependent variable for the purpose of identifying a correlation.

Statistical analyses were conducted using S-Plus 6.1 (2002 version). An analysis of variance (ANOVA) was performed for both sodium fluoride and copper sulfate solution uptakes showing the effect of treatment after accounting for board.

A family-wise comparison using the Tukey-Kramer method was automatically chosen by the software, and was also the recommended method for determining which treatments differed from which other treatments (Ramsey and Schafer 2002). Treatment combinations whose 95% confidence intervals did not include zero were flagged as having significantly different means. The results were then used to group treatments with means that were not significantly different with a letter code in a table.

4.6.2. Chemical Content of Solutions

Solutions collected before and after treating were analyzed in triplicate for chemical content and averaged. Copper detected by the x-ray fluorescence analyzer was reported as % wt/wt. Because the solutions were diluted by 50%, analyzer results were multiplied by two. Fluoride analyses were reported in ppm (μg/mL). Because solutions were diluted 1 to 10,000, testing results were numerically equivalent to units of % wt/wt.

Results were plotted using treatment time as the independent variable and change in solution concentration (% wt/wt) as the dependent variable. The change in concentration was calculated using the concentration before treating minus the concentration after treating. Trend lines with equation and R^2-values were applied to each plot to assess the potential for selective absorption.

4.7. Data Analyses for Phase II

4.7.1. Solution Uptake

Solution uptake in kg/m^3 was calculated for each sample by taking the difference in weight from before and after treating in each solution divided by the sample volume. Because samples were soaked sequentially, the sample weight after soaking in the sodium fluoride solution was used as the initial weight for soaking in the copper sulfate solution. This data was plotted using treatment as the independent variable and uptake of solution as the dependent variable.

Abnormally high uptakes were observed for samples from boards 1, 3, and 5 compared to the other eight samples in each treatment (Figure 4.3). It was not until after the first 36 mm wafer was removed and dried, that an abnormal wood color was noticeable in the samples from boards 1, 3, and 5 that were soaked in copper. This abnormal color was identified as decay which, in turn, affected permeability. As a result, samples from boards 1, 3, and 5 were removed from the study.
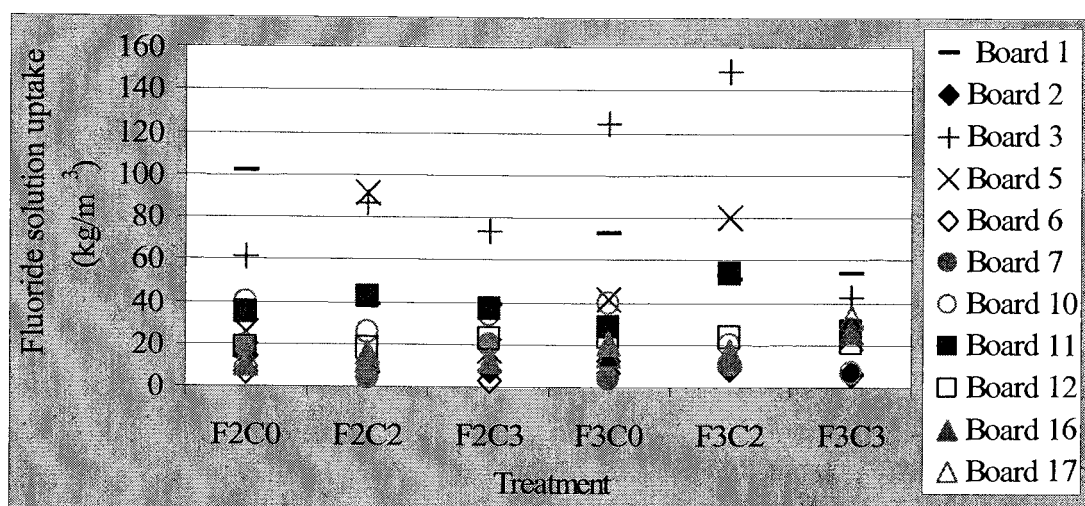
Figure 4.3. Solution uptake for all samples treated in sodium fluoride solution.

The mean and standard error for both sodium fluoride and copper sulfate solution uptake by treatment were calculated and plotted. Standard error is the standard deviation divided by the square root of the sample size. Means were also presented in table format.

Moisture content and density could not be calculated because these samples were processed into wood dust.

Fluoride treatment was the first treatment in this two part process. Therefore, solution uptakes were combined into two groups, two (F2C2 and F2C3) or three (F3C2 and F2C3) days of treatment, for analysis. A standard two-sample t-test, 0.05 level, was used to determine the difference between the two groups. S-Plus 6.1 was used throughout Phase II.

Because samples were treated in sodium fluoride solution and then copper sulfate solution, copper sulfate solution uptakes were grouped by the full treatment code for analysis. Analogous to Phase I, an ANOVA was performed for copper sulfate solution uptake showing the effect of treatment after accounting for board. Again, a family-wise comparison was made using the Tukey-Kramer method, to determine differences among the treatment means at the 0.05 level. Means that were not significantly different were grouped with a letter code in a table.

4.7.2. Chemical Content of Wood Dust

Copper detected by the x-ray fluorescence analyzer was reported as % wt/wt in the wood dust. Fluoride in solution was reported as µg/mL (ppm). A conversion factor of 0.05 was needed to report fluoride in the wood dust in % wt/wt. Assuming one mL equals one g, the conversion factor was calculated using:

$$\frac{50mL_{solution} * X \, \mu g / mL}{0.1g_{wood}} * \frac{10^{-6} \, g}{\mu g} * 100\% = 0.05 X \% \, wt/wt$$

The mean fluoride and copper retentions for each assay zone within a treatment were calculated and plotted.

The three assay zones within a given wafer were averaged in order to report fluoride and copper retention by sample after treating, after a 30-day-diffusion period, and after leaching. These were the values used for analyzing statistical differences among treatments and calculating the mean for each treatment. Means were placed in table format for discussion.

ANOVAs were performed for fluoride and copper retentions showing the effect of treatment after accounting for board. Again, a family-wise comparison was made using the Tukey-Kramer method at 0.05 level. Means that were not significantly different were grouped with a letter code in a table.

The mean and standard error by treatment for both fluoride and copper retentions after treating (T), after a 30-day diffusion period (D), and after leaching (L) were calculated and plotted.

4.8. Quality Control

Several steps were taken throughout this project to ensure integrity of the results. Periodically, samples were re-run for copper content to check analyzer consistency. Several wood dust samples were divided into three sub-samples and extracted for fluoride analyses to check for consistency in preparation. Only the bottle number was known while testing for fluoride, therefore bias was not a factor when recording mV reading. Two sets of independently prepared standard fluoride bottles were used at the beginning of each testing session to check for validity of conversion formula. All data was entered twice and the difference taken, in order to highlight any errors in entering. Finally, calculations were double-checked by major professor.

5. RESULTS AND DISCUSSION

5.1. Phase I

5.1.1. Solution Uptake

More than two thirds of the samples cut from board 1 had a solution uptake greater that 25 kg/m^3, including the sample treated for only 12 hours. It was concluded that board 1 contained decay and these samples were eliminated from analyses.

The solution uptake by treatment time and board number for the samples treated in sodium fluoride and copper sulfate solutions are shown in Figures 5.1 and 5.2, respectively. Solution uptake and variability generally increase over time. The polynomials used to model both solution uptakes over time were poorly correlated (R^2<0.20) due to board variation.
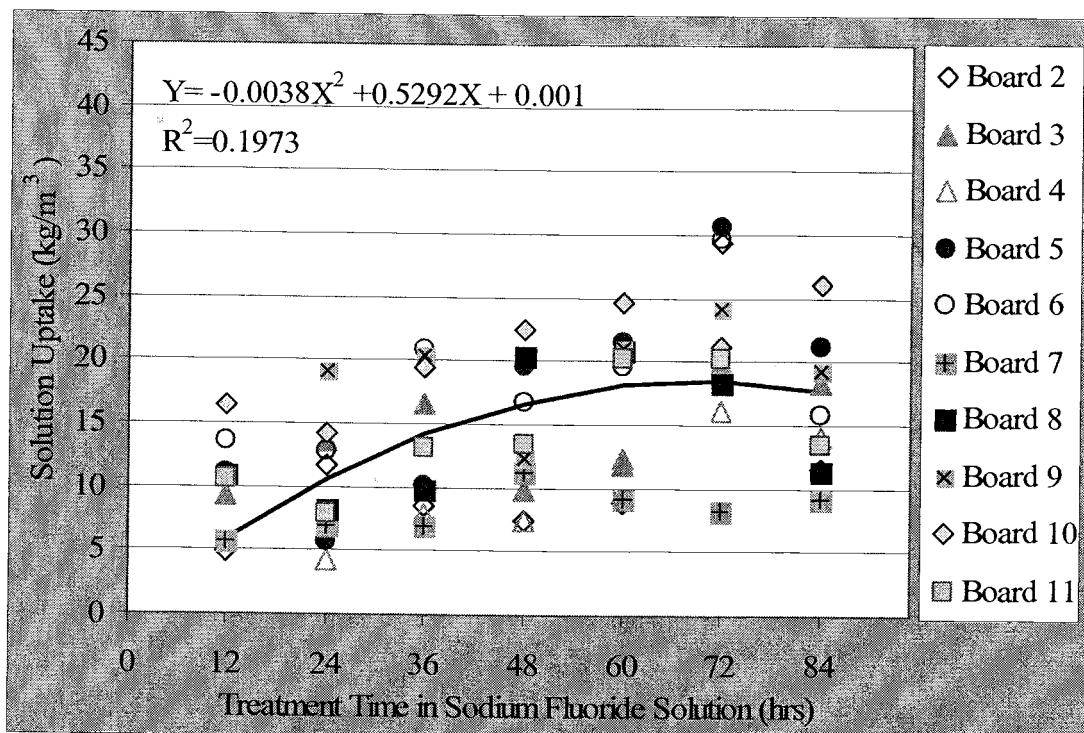
Figure 5.1. Solution uptake for samples treated in sodium fluoride solution for 12 to 72 hours.
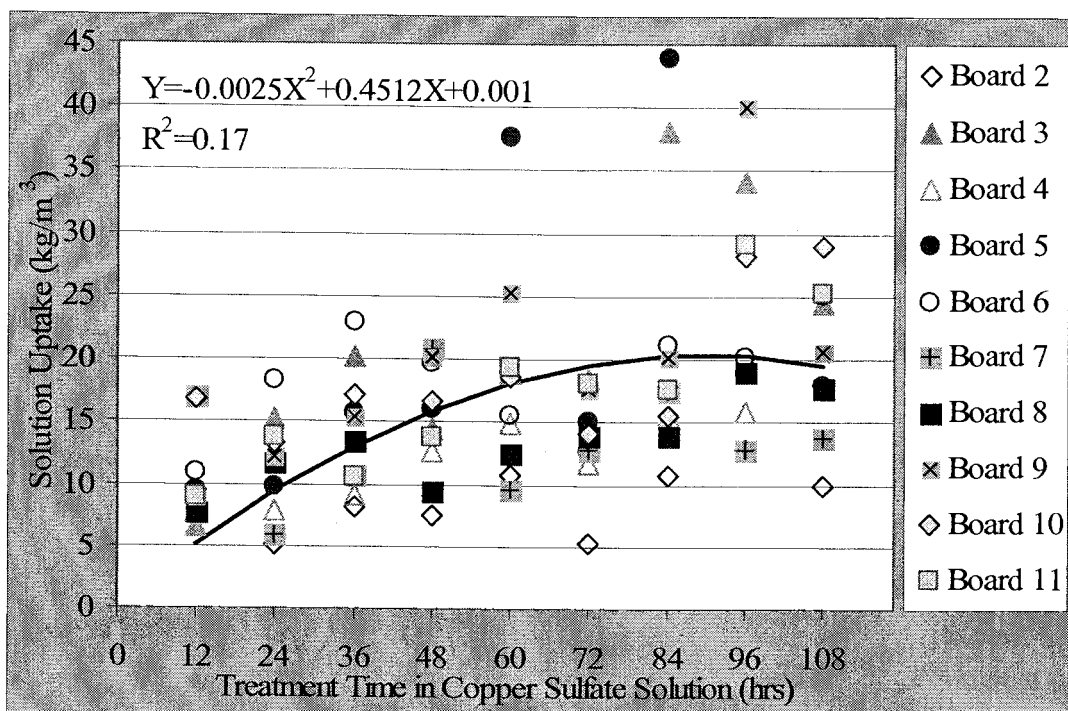
Figure 5.2. Solution uptake for samples treated in copper sulfate solution for 12 to 108 hours.

ANOVA tables for fluoride and copper sulfate solution uptakes are given in Tables 5.1 and 5.2, respectively. Both tables show that treatment and board had significant effects on solution uptake.

Table 5.1. ANOVA table for sodium fluoride solution uptake using treatment and board as independent variables.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	6	970.11	161.69	10.4	<0.0001
Board	9	970.07	107.79	6.9	<0.0001
Residuals	54	839.01	15.54		

Table 5.2. ANOVA table for copper sulfate solution uptake using treatment and board as independent variables.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	8	1624.13	203.02	6.8	<0.0001
Board	9	1422.01	158.00	5.3	<0.0001
Residuals	72	2138.23	29.70		

The results of a Tukey-Kramer test for statistically significant differences in means among treatments are shown in Table 5.3, as well as the mean solution uptakes. Solution uptakes for either solution were not significantly different for most times greater than 36 hours. Therefore, field tests designed to find the optimum treatment time should focus on treatment times between 36 hours and 72 hours. Seventy-two hours is the maximum treatment time on the copper sulfate label for wood treatment.

Table 5.3. Mean solution uptakes for samples treated for various times in sodium fluoride or copper sulfate solutions.[a]

Treatment Time (hrs)	Mean Sodium Fluoride Solution Uptake (kg/m^3)				Mean Copper Sulfate Solution Uptake (kg/m^3)			
12	10.27 A				10.34 a			
24	10.43 A				11.3	a	b	
36	13.35 A	B			14.33	a	b	c
48	14.08 A	B			15.11	a	b	c
60	16.98	B	C		18.29		b	c	d
72	21.77		C		13.97	a	b	c
84	16.01	B			21.4			c	d
96					23.11				d
108					20.16			c	d

[a]Means with the same letter are not significantly different at 0.05 level.

Mean solution uptake did not always increase with treatment time (Table 5.3), probably due to the natural variability within a board. A closer look at Figures 5.1 and 5.2 showed that samples from the same board did not always have the same ranking of solution uptake for each treatment. For example, a sample from board 11 had a higher sodium fluoride solution uptake than a sample from board 8 after treating for 36 hours, but the results were reversed after 48 hours of treating (Figure 5.1).

The natural variability in uptake within each board, led to the examination of the initial wood moisture content and density effect on solution uptake (Figures 5.3 and 5.4). Initial moisture content and density were poorly correlated with uptake
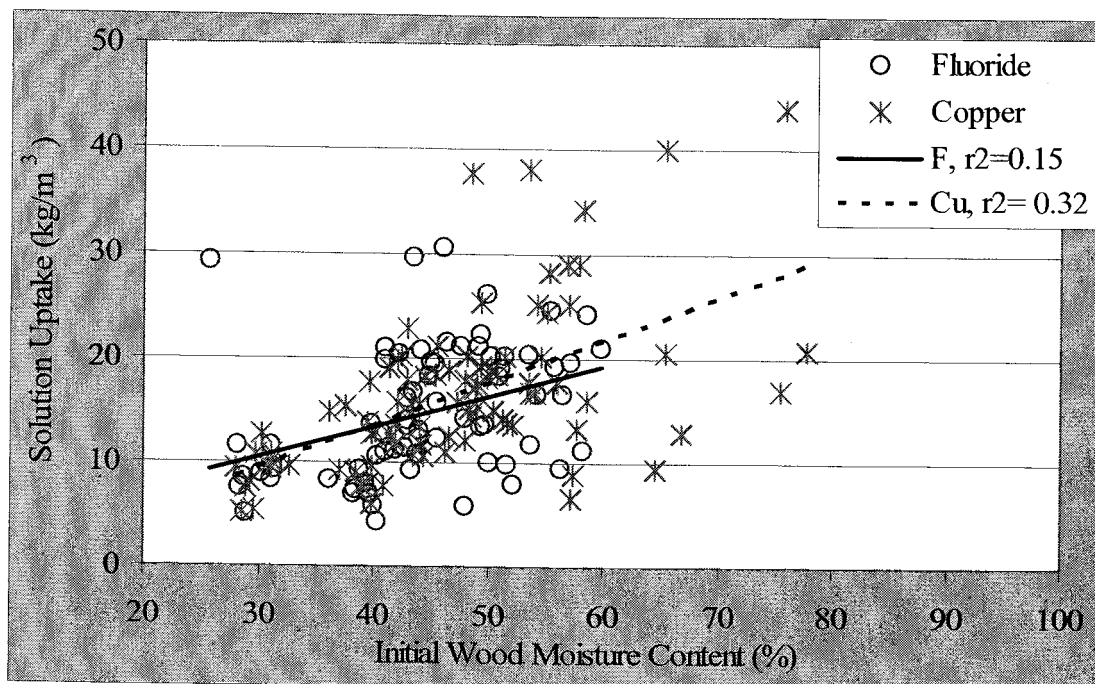
Figure 5.3. Solution uptakes of copper sulfate and sodium fluoride as a function of initial wood moisture content.
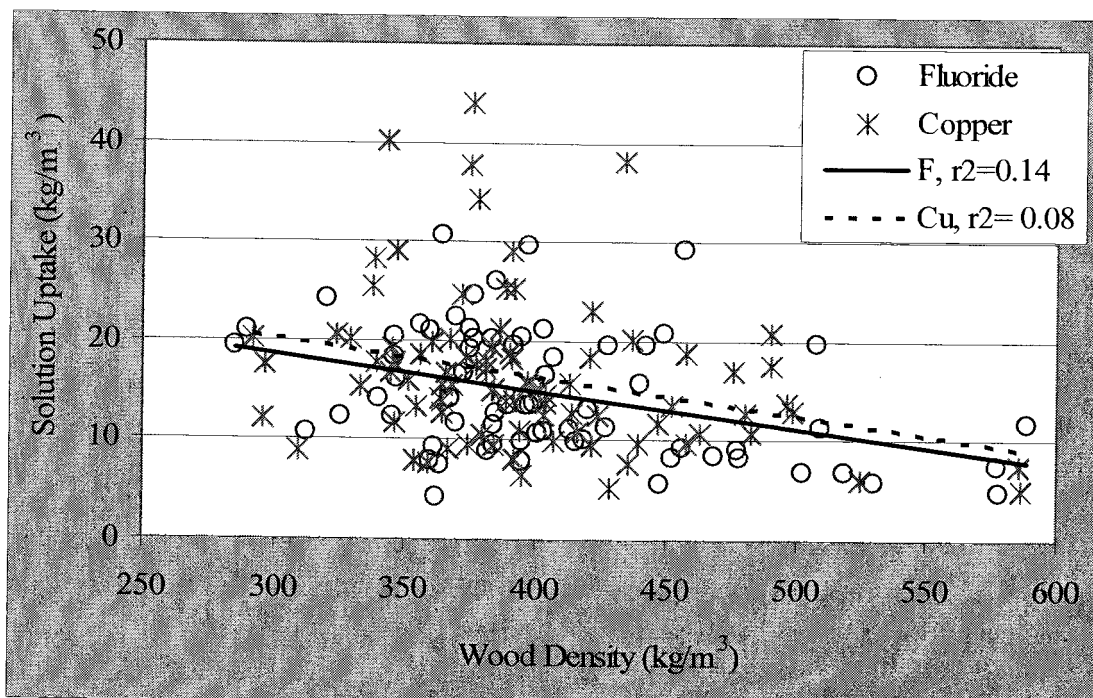
Figure 5.4. Solution uptakes of copper sulfate and sodium fluoride as a function of wood density.

of either solution ($R^2 < 0.33$). Wide variation above and below the trend line made it difficult to detect any relationship, but the slopes of the trend lines indicate general uptake trends with changes in moisture content or density.

There were slight trends for the solution uptake to increase with initial wood moisture content and decrease with wood density (Figures 5.3 and 5.4). Wood samples with lower moisture contents may contain more aspirated pits than higher moisture content samples due to drying or heartwood formation. Aspirated or closed pits reduce pathways for free water to flow within the wood matrix (Flynn 1995, Siau 1984). Therefore, it is understandable that solution uptake increased as the moisture content increased from 25% to 80% moisture content. The rate of solution uptake for moisture contents greater than 80% is not known. Void space decreases with increased moisture content and bulk flow of the solution would probably also be inhibited.

Higher density wood has more cell wall material and less space for free water relative to less dense samples. Therefore, it is understandable that solution uptake may decrease with increasing density.

It may also be important to note that the trend line for both solutions in Figures 5.3 and 5.4 were in close proximity to each other. This means that the solution type, copper sulfate or sodium fluoride, has no effect on solution uptake for wood that has not been previously treated.

The mean initial moisture content, final moisture content, density and solution uptakes by board are also given (Table 5.4). The mean initial moisture content by board ranged from 29 to 53%, while mean density by board ranged from 320 to 490 kg/m^3. Moisture content increased 6 to 11% after treating depending on the board. The increase in moisture content represents bulk flow of solution into the wood matrix during treatment.

Table 5.4. Mean initial moisture content, density, and solution uptakes in Sitka spruce boards treated by the double-diffusion process.

Board	Initial MC (%)	Final MC (%)	Density (kg/m^3)	Sodium Fluoride Solution Uptake (kg/m^3)	Copper Sulfate Solution Uptake (kg/m^3)
2	29	35	468	11.73	8.85
3	52	61	400	14.19	21.14
4	40	47	357	10.19	12.56
5	53	62	401	17.1	21.26
6	44	53	402	18.41	17.71
7	46	52	490	8.21	13.43
8	40	47	403	14.26	13.28
9	53	64	320	18.13	20.02
10	51	60	370	20.63	18.83
11	49	57	390	14.13	17.39

5.1.2. Chemical Content of Solutions

The change in solution concentration by treatment time is given in Figures 5.5 and 5.6. Initial treatment solutions were identical because they were prepared in a large container and then distributed among treatments. Any changes in concentration following treatment should reflect selective sorption by the wood.

$$y = 0.0007x + 0.0067$$
$$R^2 = 0.75$$
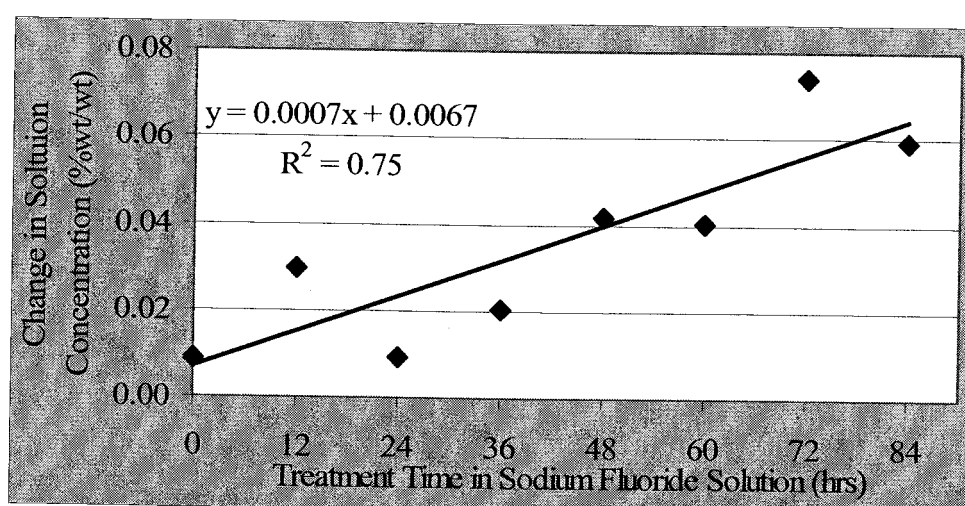
Figure 5.5. The effect of treatment time on the change in fluoride concentration in the sodium fluoride treating solution.
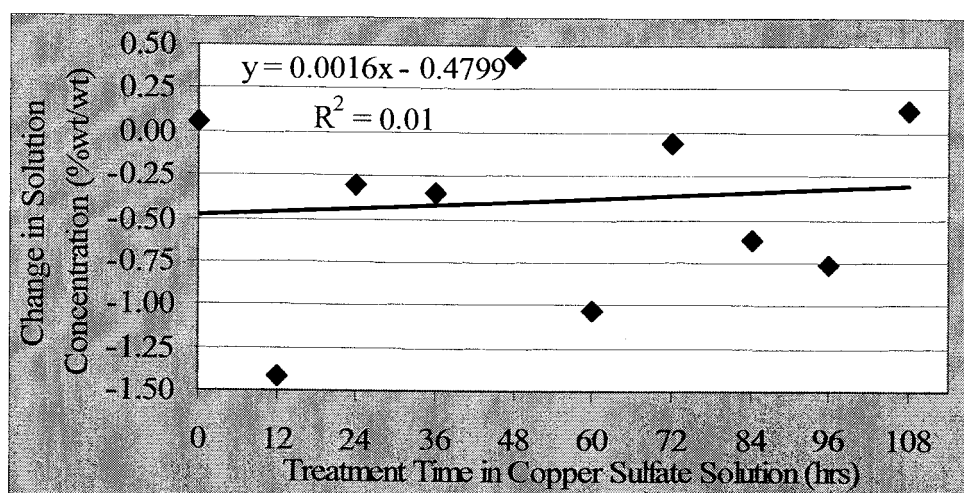
Figure 5.6. The effect of treatment time on the change in copper concentration in the copper sulfate treating solution.

There was a strong correlation ($R^2 = 0.75$) between the change in fluoride concentration and treatment time (Figure 5.5). Therefore, the slope of that trend line was used to conclude that selective fluoride absorption had occurred. This could be an issue on a production scale where the solution is reused. Fluoride concentration changed 0.0007 % wt/wt every hour, which would produce a decrease in solution concentration of 0.05% every 72 hours of treatment. Because the initial solution concentration was only 2.1%, the solution lost 2.4% of its original strength every 72 hours. Sodium fluoride would have to be added to the tank before using the solution again, regardless of whether or not additional solution is needed to cover the next charge of wood.

Changes in copper sulfate solution concentration were poorly correlated with treatment time ($R^2 = 0.01$) (Figure 5.6). Therefore, there was not enough evidence to determine if selective copper absorption had occurred.

5.2. Phase II

5.2.1. Solution Uptake

Mean solution uptakes and standard errors by treatment are shown in Figures 5.7 and 5.8. The treatment code on the abscissa refers to the treatment time in days

for each chemical. For example, F2C0 means a two-day treatment in sodium fluoride solution with no copper sulfate treatment. Treatment means were calculated using only eight samples per treatment. Samples cut from boards 1, 3, and 5 were removed from analysis. It was not until after samples were treated in the copper sulfate solution and dried that decay was noticeable in these boards.
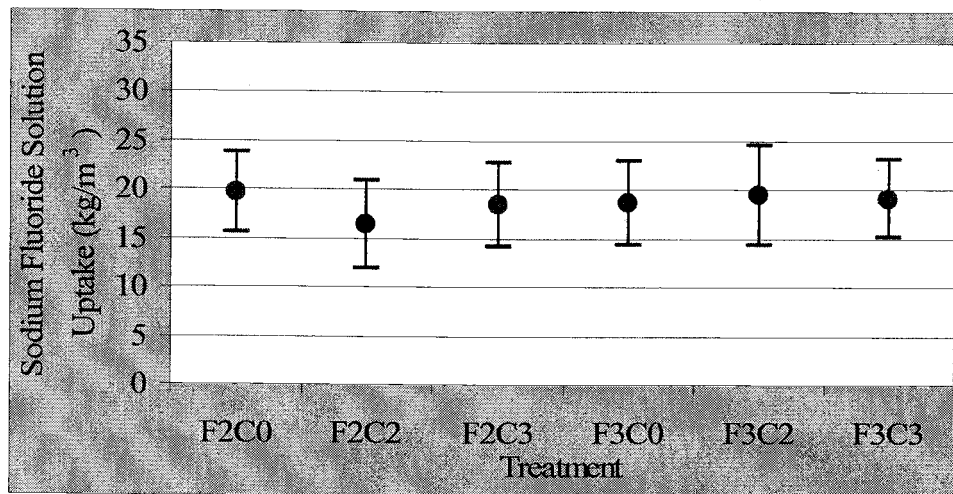
Figure 5.7. Mean solution uptake for Sitka spruce samples treated for selected time periods in sodium fluoride solution (bars represent standard error).
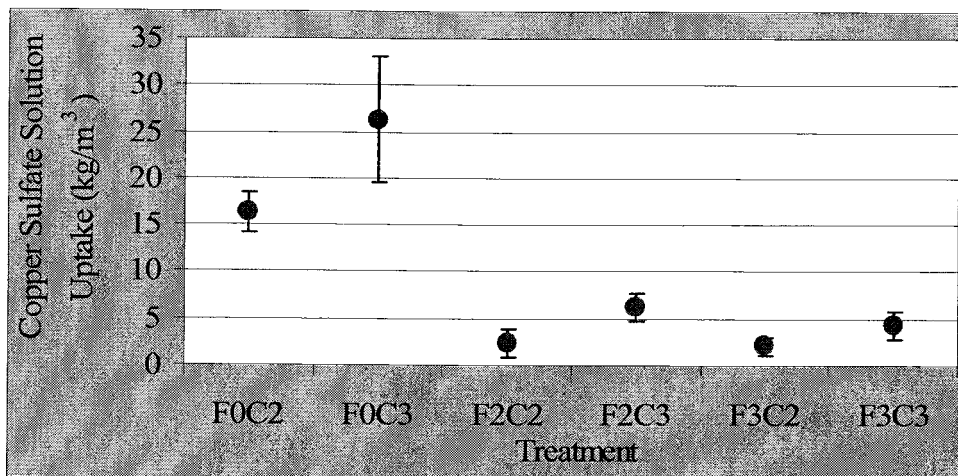
Figure 5.8. Mean solution uptake for Sitka spruce samples treated for selected time periods in copper sulfate solution (bars represent standard error). Note treating in copper sulfate solution followed treatment in sodium fluoride solution.

For statistical analysis, sodium fluoride solution uptakes were combined into two groups, two (F2C2 and F2C3) or three (F3C2 and F3C3) days of treatment. The mean uptakes for F2 and F3 were 18.9 and 19.1 kg/m^3, respectively. A standard two-sample t-test revealed that there was no significant difference between the two groups (p-value = 0.78, 95% CI = -7.856 to 5.926). While these mean uptakes are slightly different than those found in Phase I (Table 5.3), these results do reinforce the conclusion that there is little difference between two and three days of treating in the sodium fluoride solution. The differences in mean uptakes between Phase I and Phase II could be a result of the natural variability of wood, the effect of storing Phase II boards in the freezer, or from using a very limited number of samples per treatment.

Because samples were treated in the sodium fluoride solution and then the copper sulfate solution, the full treatment code was used in analyzing copper sulfate solution uptakes. Referring to error bars in Figure 5.8, samples that did not receive treatment is sodium fluoride solution had a noticeably greater uptake than samples that did receive a treatment in sodium fluoride solution. This was due to the available void space within the wood for the bulk flow of solution. Therefore, two ANOVAs were performed; with and without sodium fluoride treatment (F0C2 and F0C3). The ANOVA tables for copper sulfate solution uptake (Tables 5.5 and 5.6), indicate that both treatment and board had a significant effect on solution uptake. This was consistent with Phase I results (Table 5.2).

Table 5.5. ANOVA table for copper sulfate solution uptake using treatment and board as independent variables.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	5	3746.41	749.28	14.86	<0.0001
Board	7	1489.49	212.78	4.22	0.0018
Residuals	35	1764.67	50.42		

Table 5.6 ANOVA table for copper sulfate solution uptake using treatment and board as independent variables without treatments F0C2 and F0C3.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	3	91.9	30.63	3.80	0.0254
Board	7	262.9	37.55	4.66	0.0028
Residuals	21	169.3	8.06		

The results of a Tukey-Kramer test for statistically significant differences in mean copper sulfate solution uptake among treatments (with F0C2 and F0C3) are shown with uppercase letters in Table 5.7. Samples treated in sodium fluoride solution before treating in copper sulfate solution did have a significantly lower mean uptake of copper sulfate solution compared to samples not previously treated in the sodium fluoride solution (F0C2 and F0C3). This was because samples not treated in sodium fluoride solution still had a lot of free space for the bulk flow of solution into the wood matrix. Conversely, samples treated in sodium fluoride solution had less free space, and therefore, noticeably less bulk flow of solution into the wood matrix.

Table 5.7. Mean copper sulfate solution uptake of Sitka spruce samples treated using the double-diffusion process.[a][b]

	Mean Copper Solution Uptake (kg/m^3)	Tukey-Kramer Results			
Treatment		With		Without	
		F0C2 and F0C3			
F0C2	16.27	B		- -	
F0C3	26.23		C	- -	
F2C2	2.38	A		a	b
F2C3	6.30	A	B		b
F3C2	2.09	A		a	
F3C3	4.34	A		a	b

[a]Note samples previously treated in sodium fluoride solution as depicted in treatment code.
[b]Means with the same letter are not significantly different at 0.05 level.

The results of the Tukey-Kramer test for statistically significant differences between means, without F0C2 and F0C3 treatments (Table 5.6), are shown as

lowercase letters in Table 5.7. Only F2C3 was significantly different from F3C2 at the 0.05 level. While not always significantly different, the mean uptakes of copper sulfate solution more that doubled from two days to three days. This doubling should be considered when managing the amount of solution required to cover the wood in a larger tank.

5.2.2. Chemical Retention in the Wood Samples

The mean and standard error bars for chemical retention after treating (T), after a 30-day diffusion period (D), and after leaching (L) by treatment are shown in Figures 5.9 and 5.10. The treatment code on the abscissa refers to the treatment time in days for each chemical and when the samples were analyzed. Blank and DI were controls used to measure background chemical levels in the wood and in de-ionized water, respectively.
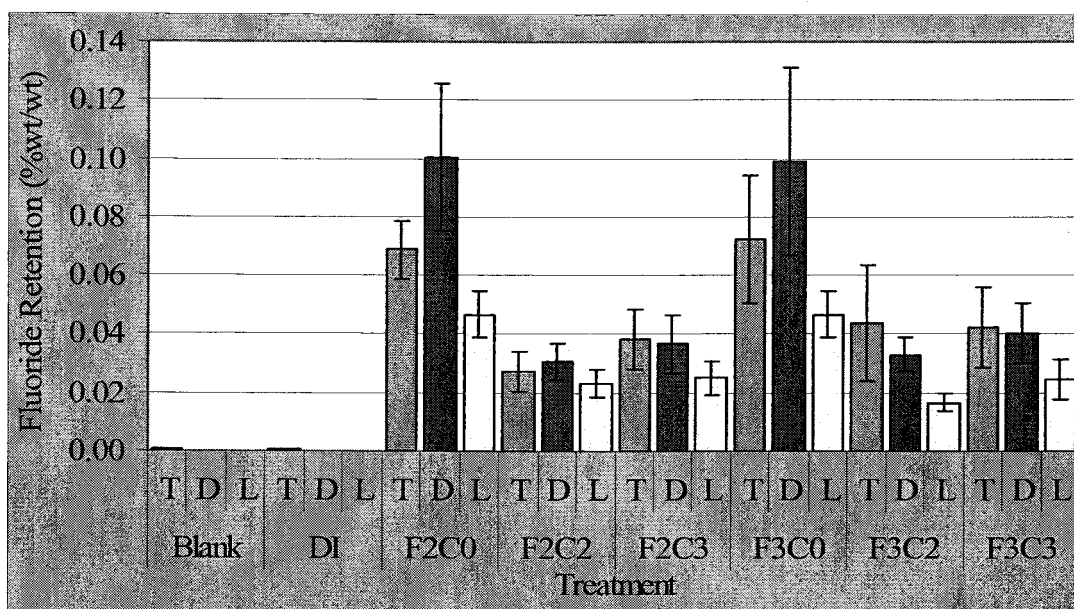
Figure 5.9. Means and standard errors for fluoride retention after treating (T), after a 30-day diffusion period (D), and after leaching (L).
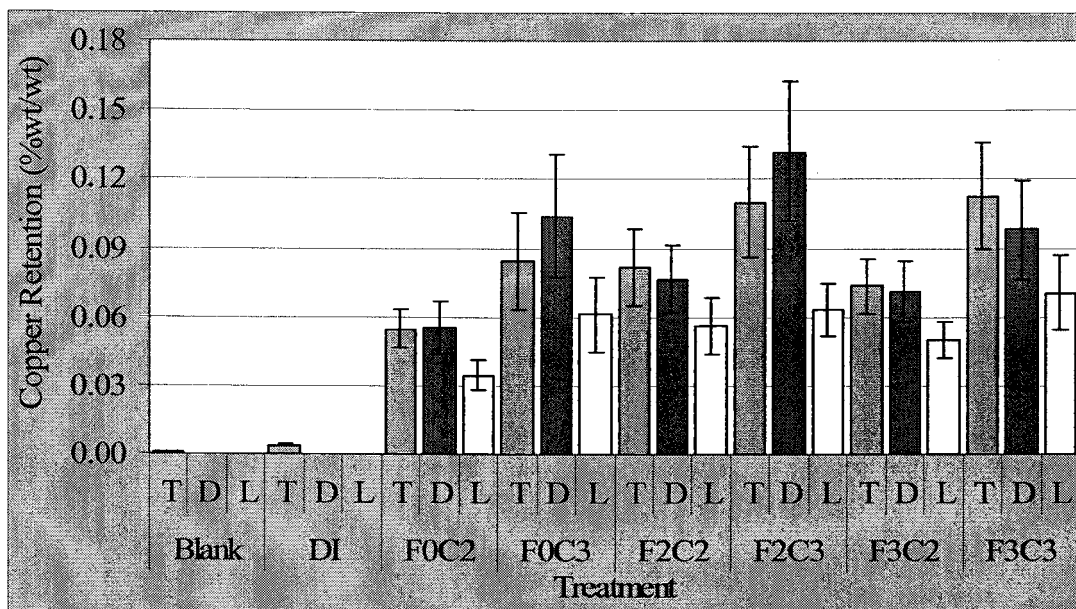
Figure 5.10. Means and standard errors for copper retention after treating (T), after a 30-day diffusion period (D), and after leaching (L).

5.2.2.1 After Treating

While the controls, Blank and DI, were analyzed for background fluoride and copper retentions, they were not included in the following statistical analyses. Samples from both control treatments had less than 0.01 % wt/wt of either of fluoride or copper.

The ANOVA tables for fluoride and copper retentions after treating showing the effect of treatment and board are given in Tables 5.8 and 5.9, respectively. Treatment did not have a significant effect on either fluoride or copper retention.

Table 5.8. ANOVA table for fluoride retention after treating.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	5	0.013	0.003	2.16	0.082
Board	7	0.031	0.004	3.73	0.004
Residuals	35	0.042	0.001		

Table 5.9. ANOVA table for copper retention after treating.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	5	0.020	0.004	2.04	0.097
Board	7	0.049	0.007	3.64	0.005
Residuals	35	0.068	0.002		

Because treatment did not have a significant effect on retention, no significantly different treatment combinations would be identified in the Tukey-Kramer test, as shown in Table 5.10. The mean fluoride and copper retention by assay zone are also given in Table 5.10 and discussed in Section 5.2.2.4.

Table 5.10. Mean chemical retentions by assay zone after treating.[a]

	Chemical retention (% wt/wt) by assay zone								
	0 to 6 mm		6 to 12 mm		12 to 18 mm		0 to 18 mm		
Treatment	F	Cu	F	Cu	F	Cu	F	Cu	
F0C2		0.15		0.01		0.00		0.05	a
F0C3		0.23		0.01		0.01		0.08	a
F2C0	0.17		0.03		0.01		0.07 A		
F2C2	0.05	0.24	0.02	0.00	0.02	0.01	0.03 A	0.08	a
F2C3	0.07	0.29	0.02	0.01	0.02	0.03	0.04 A	0.11	a
F3C0	0.20		0.01		0.01		0.07 A		
F3C2	0.06	0.21	0.05	0.01	0.02	0.00	0.04 A	0.07	a
F3C3	0.08	0.33	0.04	0.01	0.02	0.00	0.04 A	0.11	a

[a]Means with the same letter are not significantly different at 0.05 level.

Referring to Figure 5.9 and Table 5.10, mean fluoride retention from two days to three days of treating did not differ by more than 0.01 % wt/wt. Therefore, a third day of treating in sodium fluoride solution may not be necessary in a large-scale production. This is also evident in Figure 5.7. While mean fluoride retention was not significantly different among samples treated in sodium fluoride solution, there was a trend for a higher mean retention in samples not subsequently soaked in copper sulfate solution (F2C0 and F3C0). It could be concluded that some of the fluoride left the wood matrix and entered the copper sulfate solution during

treating. Therefore, investigations into improving fluoride retention should not be assessed without sequentially treating in copper sulfate solution.

Referring to Figure 5.10 and Table 5.10, there was a trend for samples treated in copper sulfate solution for two days (F0C2, F2C2, and F3C2) to have a higher mean copper retention if they were also treated in sodium fluoride. The same held true for samples treated in copper sulfate solution for three days. The higher copper retentions after treating in sodium fluoride solution may help explain why Blue Viking's Copper Sulfate Instant chemical label required copper sulfate solution to be the 2nd half of the treatment (Griffin 1997).

More importantly, copper sulfate solution uptake (Figure 5.8) should not be used to assess copper retention. Prior absorption of solution from the sodium fluoride treatment can limit uptake of the second solution but not copper sulfate diffusion.

It is also important to remember that retentions given in Table 4.10 are the results treating Sitka spruce heartwood samples in solutions of 2.1% sodium fluoride and 6.2% copper sulfate. Therefore, results were, as expected, lower than retentions discussed in the Literature Review (Tables 2.3 and 2.6.)

5.2.2.2 After a 30-Day Diffusion Period

The ANOVA tables for fluoride and copper retentions after a 30-day diffusion period showing the effect of treatment and board are given in Tables 5.11 and 5.12, respectively. Both treatment and board had a significant effect on the chemical retention after a 30-day diffusion period.

Table 5.11. ANOVA table for fluoride retention after 30-day diffusion period.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	5	0.045	0.009	5.29	0.001
Board	7	0.049	0.007	4.11	0.002
Residuals	35	0.059	0.002		

Table 5.12. ANOVA table for copper retention after 30-day diffusion period.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	5	0.03	0.006	2.90	0.027
Board	7	0.073	0.01	5.04	0.001
Residuals	35	0.073	0.002		

The results of a Tukey-Kramer test for statistically significant differences in means among treatments after a 30-day diffusion period are shown in Table 5.13. The mean fluoride and copper retentions by assay zone are also given.

Table 5.13. Mean chemical retentions by assay zone after a 30-day diffusion period.

	Chemical retention (% wt/wt) by assay zone									
	0 to 6 mm		6 to 12 mm		12 to 18 mm		0 to 18 mm			
Treatment	F	Cu	F	Cu	F	Cu	F		Cu	
F0C2		0.15		0.01		0.00			0.05 a	
F0C3		0.23		0.01		0.01			0.08 a	b
F2C0	0.14		0.09		0.07		0.10 A			
F2C2	0.04	0.24	0.03	0.00	0.02	0.01	0.03	B	0.08 a	b
F2C3	0.05	0.29	0.03	0.01	0.03	0.03	0.04	B	0.11	b
F3C0	0.14		0.09		0.07		0.10 A			
F3C2	0.04	0.21	0.03	0.01	0.03	0.00	0.03	B	0.07 a	b
F3C3	0.05	0.33	0.04	0.01	0.04	0.00	0.04 A	B	0.11 a	b

[a] Means with the same letter are not significantly different at 0.05 level.

Referring to Figure 5.9 and Table 5.13, the mean fluoride retention for samples not treated in the copper sulfate solution (F2C0 and F3C0) were significantly greater than those that did receive copper sulfate solution. Again, it could be concluded that some of the fluoride left the wood matrix and entered the copper sulfate solution during treating.

Referring to Figure 5.10 and Table 5.13, only the mean copper retention from F0C2 was significantly different from treatment F2C3. Due to rounding, F3C3 appears to have the same mean retention as treatment F2C3. Yet, treatment F3C3 was not identified as being significantly different from treatment F0C2. Again, samples that were treated in copper sulfate solution for two days (F0C2, F2C2, and

F3C2) had a higher mean copper retention if they were initially treated in sodium fluoride. The same held true for samples treated in copper sulfate solution for three days. This may be due to increased moisture content of the samples or the pH of fluoride affecting permeability.

Referring to Tables 5.8 through 5.13, it was expected that the mean fluoride and copper retentions after treating and after the 30-day diffusion period would be the same. Yet, mean fluoride retentions for F2C0 and F3C0 were greater after the 30-day diffusion period. One explanation is that the adjacent wafers cut from the samples (Figure 4.1) had differences in permeability due to the natural variability of wood. Another explanation is that once the solution made its way into the wood matrix, longitudinal flow enhanced diffusion. The middle length of the sample may have benefited from longitudinal flow, which in turn, became the wafer analyzed after the 30-day diffusion period. The values in the ANOVA tables are also different as a result of sample variations. This is seen in the after-treating and after-a-30-day-diffusion-period error bars of Figures 5.9 and 5.10.

5.2.2.3 After Leaching

The ANOVA tables for fluoride and copper retentions after leaching showing the effect of treatment and board are given in Tables 5.14 and 5.15, respectively. Treatment and board did not have a significant effect on the chemical retention after leaching.

Table 5.14. ANOVA table for fluoride retention after leaching.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	5	0.003	0.001	0.60	0.70
Board	7	0.011	0.002	1.62	0.16
Residuals	35	0.035	0.001		

Table 5.15. ANOVA table for copper retention after leaching.

	d.f.	Sum of Sq	Mean Sq	F Value	Pr(F)
Treatment	5	0.005	0.001	0.87	0.51
Board	7	0.017	0.002	2.18	0.06
Residuals	35	0.038	0.001		

Because treatment did not have a significant effect on retention, no treatment combinations were significantly different from another treatment, as shown in Table 5.16. The mean fluoride and copper retention by assay zone are also given.

Table 5.16. Mean chemical retentions by assay zone after leaching.

	Chemical retention (% wt/wt) by assay zone								
	0 to 6 mm		6 to 12 mm		12 to 18 mm		0 to 18 mm		
Treatment	F	Cu	F	Cu	F	Cu	F		Cu
F0C2		0.09		0.01		0.00			0.03 a
F0C3		0.14		0.03		0.02			0.06 a
F2C0	0.05		0.05		0.05		0.05 A		
F2C2	0.02	0.13	0.02	0.02	0.02	0.02	0.02 A		0.06 a
F2C3	0.03	0.15	0.02	0.03	0.02	0.02	0.03 A		0.06 a
F3C0	0.05		0.05		0.04		0.05 A		
F3C2	0.02	0.13	0.02	0.02	0.01	0.01	0.02 A		0.05 a
F3C3	0.03	0.16	0.03	0.03	0.03	0.04	0.02 A		0.07 a

[a]Means with the same letter are not significantly different at 0.05 level.

Referring to Figures 5.9 and Table 5.16, even after leaching, there was still a trend for the mean fluoride retention to be higher in treatments not treated in the copper sulfate solution (F2C0 and F3C0). Because there is no evidence that fluoride fixes to the wood matrix (Becker 1976) and there was no copper present to form a precipitate, most of the fluoride was expected to leach from the wood.

Referring to Figures 5.10 and Table 5.16, there was no statistical difference in the mean copper retentions among treatments after leaching. Length of treatment did not affect chemical retention after leaching for two weeks in water.

The percent change in mean chemical retentions after leaching is given in Table 5.17. A two-sample t-test for each treatment was conducted using the after-treating retention and after-leaching retention. P-values and confidence intervals are also given in Table 5.17. Statistically, there was no significant loss of either chemical after leaching, compared to initial retention. Refer to Figures 5.9 and 5.10 for a visual comparison. However, the amount of chemical lost was a

substantial portion of what was present in the wood, suggesting that some fluoride and copper may leach while in service. Therefore, end-use applications must be considered in order to determine approximate service-life of the treated wood as well as the hazards posed to the environment from leached chemicals.

Table 5.17. Percentage of chemical leached from Sitka spruce after a 14 day leaching period.

	Comparing After-Treating and After-Leaching Retentions[a]						
	Fluoride			Copper			
Treatment	Loss (%)	P-value	Confidence Interval		Loss (%)	P-value	Confidence Interval	
F0C2					37	0.08	0.00 - 0.00
F0C3					27	0.40	-0.03 - 0.08
F2C0	32	0.10	0.00 - 0.05				
F2C2	15	0.63	-0.01 - 0.02	31	0.24	-0.02 - 0.70
F2C3	34	0.28	-0.01 - 0.04	43	0.10	-0.01 - 0.10
F3C0	36	0.28	-0.02 - 0.08				
F3C2	62	0.19	-0.02 - 0.07	32	0.15	-0.01 - 0.06
F3C3	42	0.27	-0.02 - 0.05	37	0.16	-0.02 - 0.10

[a]Two-sample t-test, 14 d.f., 0.05 level.

5.2.2.4 By Assay Zone

Mean fluoride and copper retentions by assay zones given in Tables 5.10, 5.13, and 5.16 are also shown in Figures 5.11 and 5.12. The three assay zones, surface, inner, and core, represent wood 0 to 6 mm, 6 to 12 mm, and 12 to 18 mm from the surface, respectively.
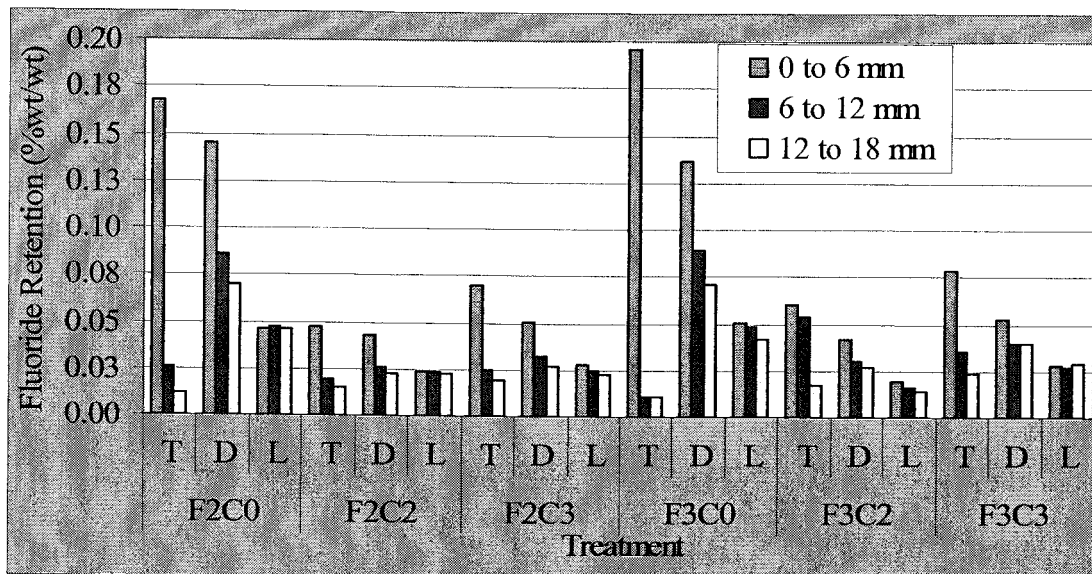
Figure 5.11. Mean fluoride retention by assay zone after treating (T), after a 30-day diffusion period (D), and after leaching (L).
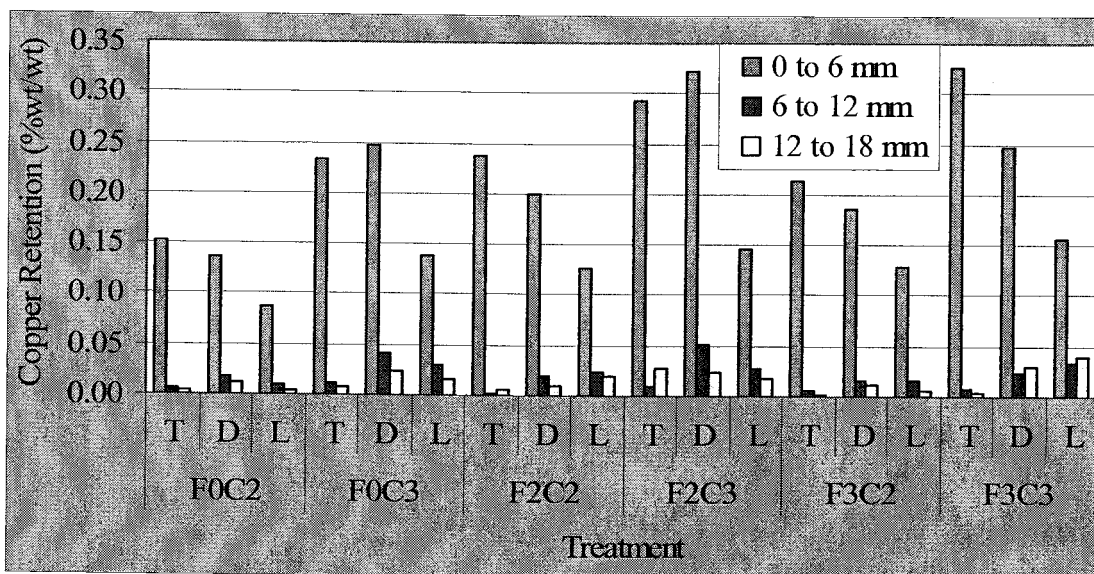
Figure 5.12. Mean copper retention by assay zone after treating (T), after a 30-day diffusion period (D), and after leaching (L).

There was more fluoride and copper in the first 6 mm than in the other two assay zones after treating, reflecting the tendency for chemical to be concentrated near the wood surface. There was a noticeable migration of fluoride into the 6 to 12 and 12 to 18 mm zones after a 30-day-diffusion period. There was little

evidence of copper migration. This could be due to the size of fluoride ions, which are smaller than copper ions and therefore, more mobile (Vinden 1984). After leaching, the fluoride content was fairly uniform among the assay zones. This could be due to the lack of fluoride fixation to the wood matrix. Yet, copper content was still noticeably higher in the 0 to 6 mm zone, possibly due to copper binding to the wood matrix (Bland 1963, Cooper 1991, Jin and Archer 1991).

5.3. Quality Control

Several steps were taken throughout this project to ensure the integrity of the results and to assess measurement errors.

5.3.1. Copper Analysis

Unlike fluoride testing, the wood dust was analyzed directly for copper content. Only one person poured and pressed all the samples for copper analysis to minimize variability in the procedure. Analyzer error in measuring the copper content in wood dust was estimated as follows. The copper contents for ten samples left in the machine and analyzed three times each are shown in Table 5.18. A, B and C represent the same compressed wood dust analyzed three times. With the exception of the first sample, the standard deviation was 0.00.

Table 5.18. Copper content (% wt/wt) in ten wood dust samples analyzed in triplicate by X-ray fluorescence spectroscopy.

Sample	Replication			Mean	Std Dev
	A	B	C		
1	0.5	0.5	0.46	0.49	0.02
2	0.11	0.11	0.11	0.11	0.00
3	0.65	0.64	0.64	0.64	0.00
4	0.21	0.21	0.21	0.21	0.00
5	0.16	0.16	0.16	0.16	0.00
6	0.48	0.48	0.48	0.48	0.00
7	0.48	0.48	0.48	0.48	0.00
8	0.63	0.63	0.63	0.63	0.00
9	0.18	0.18	0.18	0.18	0.00
10	0.29	0.29	0.29	0.29	0.00

5.3.2. Fluoride Analysis

Errors in fluoride measurements had many possible sources, such as preparing testing solution from wood dust, and quantifying the fluoride amount using a standard curve.

Preparing a solution from wood dust was a labor intensive process. Therefore, four wood dust samples were tested in triplicate through the process to check for consistency. Fluoride concentrations in the wood dust for the replicates A, B, C are shown in Table 5.19. The standard deviation was 0.00, meaning the preparation process was consistent enough not to make a difference in fluoride content results.

Table 5.19. Fluoride content (% wt/wt) in four wood samples extracted and analyzed in triplicate.

Sample	Replication			Mean	Std Dev
	A	B	C		
T9 B 2 S	0.037	0.037	0.038	0.037	0.000
T9 B10 S	0.039	0.035	0.035	0.036	0.002
L5 B 2 S	0.018	0.017	0.017	0.017	0.001
L5 B11 S	0.038	0.038	0.033	0.037	0.003

Fluoride concentrations were quantified by comparison with two individually prepared sets of fluoride standards. Both sets were measured at the beginning of each testing session. If either set produced a calibration curve with a R^2-value less than 0.985, that set was disposed of and re-prepared before any unknowns were measured. An example of the curves produced at the beginning of each testing session is given in Figure 5.13. Note that the two trend lines can not be visually separated.
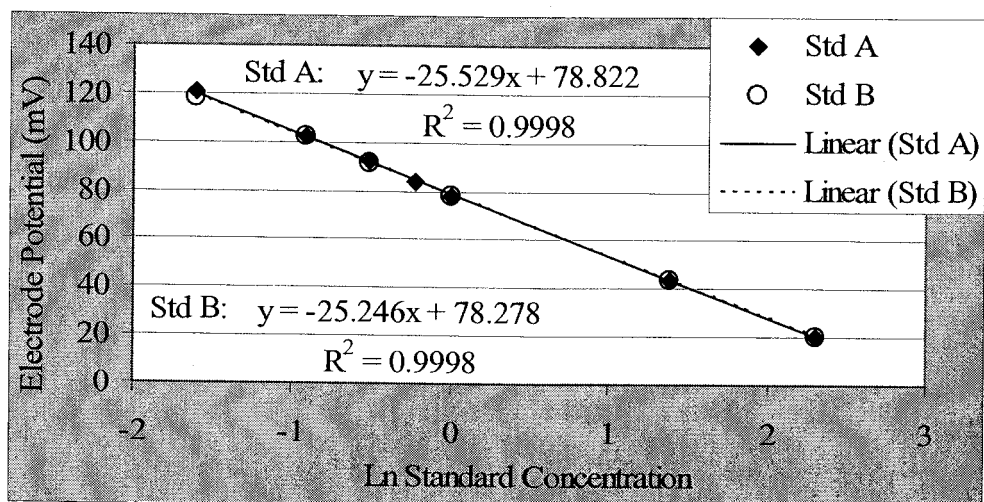
Figure 5.13. Standard curves for two individually prepared sets of fluoride standards.

6. CONCLUSION

There was considerable variability in solution uptake and chemical retention among the wood samples. This was due to the natural variation in wood properties.

When samples were treated with only one solution (Phase I), the type of solution, sodium fluoride and copper sulfate, did not have an effect on uptake. The solution uptake was not statistically different for most of the treatment times greater than 36 hours. Therefore, there was not enough evidence to reject that the rates of the solution uptake by the wood will decline to zero within 72 hours. There was a slight trend for solution uptake to increase with initial wood moisture content and decrease with wood density. There was enough evidence to conclude that selective fluoride absorption from the solution to the wood occurred, however, there was insufficient evidence of selective absorption for copper.

When samples were treated in the sodium fluoride solution followed by the copper sulfate solution (Phase II), some of the sodium fluoride leached into the copper sulfate solution. Therefore, fluoride retention should not be assessed without sequentially treating in the copper sulfate solution. Because copper sulfate solution uptake was confounded by loss of sodium fluoride, copper sulfate solution uptake should also not be used to assess chemical retention. While not statistically significant, copper retention increased from two to three days of treatment. Copper retention was greater samples initially treated in sodium fluoride solution.

Fluoride was more mobile than copper during the 30-day diffusion period and during leaching. Most of the copper stayed in the outer six-mm of the wood matrix during the 30-day diffusion period.

There was not enough evidence to reject that the fluoride and copper will remain in the wood while it is in service, even though 15% to 62% of the fluoride and copper initially deposited in the samples was lost during leaching. The potential impacts of these losses on the surrounding environment merit further study.

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APPENDIX

Table A.1. Phase I solution uptakes, moisture contents, and densities.

Treatment (hrs)	Bd	Fluoride Solution Uptake (kg/m³)	MC %	Density (kg/m³)	Treatment (hrs)	Bd	Copper Solution Uptake (kg/m³)	MC %	Density (kg/m³)
12	2	4.936	29	578	12	2	9.384	28	384
12	3	9.384	56	384	12	3	6.509	57	395
12	4	9.276	39	361	12	4	7.757	41	359
12	5	11.066	58	413	12	5	9.384	64	374
12	6	13.561	40	398	12	6	10.957	46	417
12	7	5.750	40	530	12	7	16.924	75	476
12	8	10.903	41	403	12	8	7.757	39	436
12	9	10.740	44	313	12	9	8.896	57	309
12	10	16.490	54	404	12	10	16.816	54	366
12	11	10.632	40	401	12	11	9.005	38	367
24	2	11.608	28	589	24	2	5.099	29	586
24	3	13.615	50	399	24	3	15.134	48	384
24	4	4.285	40	362	24	4	7.811	40	354
24	5	5.696	48	447	24	5	9.710	40	439
24	6	12.802	41	385	24	6	18.335	44	421
24	7	6.943	38	518	24	7	5.967	40	525
24	8	8.191	36	478	24	8	11.663	42	447
24	9	19.094	51	375	24	9	12.097	48	296
24	10	14.158	48	368	24	10	13.344	58	355
24	11	7.865	52	395	24	11	13.832	52	389
36	2	8.462	29	468	36	2	8.137	29	392
36	3	16.599	56	371	36	3	20.125	55	437
36	4	7.920	39	360	36	4	9.167	37	366
36	5	10.090	50	418	36	5	15.677	47	414
36	6	20.776	44	449	36	6	22.945	43	421
36	7	6.889	40	503	36	7	10.740	43	483
36	8	9.818	31	415	36	8	13.507	44	452
36	9	20.396	54	346	36	9	15.297	49	333
36	10	19.474	45	428	36	10	17.141	49	381
36	11	13.073	44	420	36	11	10.523	44	380
48	2	7.432	28	577	48	2	7.486	29	586
48	3	9.818	52	395	48	3	14.429	49	404
48	4	7.377	39	364	48	4	12.693	40	365

Table A.1. Phase I solution uptakes, moisture contents, and densities (cont.).

Treatment (hrs)	Bd	Fluoride Solution Uptake (kg/m³)	MC %	Density (kg/m³)	Treatment (hrs)	Bd	Copper Solution Uptake (kg/m³)	MC %	Density (kg/m³)
48	5	19.582	57	392	48	5	16.002	59	397
48	6	16.762	43	373	48	6	19.745	42	361
48	7	11.229	42	509	48	7	20.830	78	490
48	8	20.396	42	395	48	8	9.384	31	422
48	9	12.314	46	325	48	9	20.125	52	329
48	10	22.403	49	370	48	10	16.653	54	344
48	11	13.453	49	396	48	11	13.724	52	404
60	2	8.842	30	382	60	2	10.795	30	394
60	3	11.771	54	370	60	3	18.823	50	390
60	4	12.314	44	345	60	4	14.863	36	384
60	5	21.535	46	356	60	5	37.646	48	375
60	6	19.528	45	442	60	6	15.568	44	397
60	7	9.222	31	456	60	7	9.601	33	457
60	8	20.884	41	360	60	8	12.422	42	424
60	9	20.938	60	289	60	9	25.332	49	338
60	10	24.573	55	377	60	10	18.552	45	356
60	11	20.179	50	376	60	11	19.311	49	383
72	2	29.292	26	457	72	2	5.316	30	428
72	3	19.854	41	508	72	3	18.389	51	374
72	4	16.111	43	347	72	4	11.717	44	346
72	5	30.648	46	365	72	5	15.080	50	401
72	6	29.672	43	397	72	6	12.585	47	403
72	7	8.245	31	452	72	7	12.802	67	480
72	8	18.280	45	346	72	8	13.941	39	364
72	9	24.193	59	321	72	9	17.630	56	296
72	10	21.210	48	375	72	10	14.158	51	364
72	11	20.233	51	383	72	11	18.118	50	391
84	2	11.554	31	384	84	2	10.740	31	462
84	3	18.280	51	407	84	3	38.134	54	434
84	4	14.049	43	340	84	4	15.460	38	364
84	5	21.101	49	404	84	5	43.884	76	376
84	6	15.785	46	440	84	6	21.101	46	386

Table A.1. Phase I solution uptakes, moisture contents, and densities (cont.).

Treatment (hrs)	Bd	Fluoride Solution Uptake (kg/m^3)	MC %	Density (kg/m^3)	Treatment (hrs)	Bd	Copper Solution Uptake (kg/m^3)	MC %	Density (kg/m^3)
84	7	9.167	43	477	84	7	17.467	49	490
84	8	11.337	43	427	84	8	13.941	39	392
84	9	19.257	56	285	84	9	20.125	43	292
84	10	26.092	50	385	84	10	15.568	43	368
84	11	13.453	43	390	84	11	17.630	54	378
					96	2	12.747	30	414
					96	3	34.174	58	378
					96	4	15.839	42	351
					96	5	18.823	47	458
					96	6	20.179	48	368
					96	7	12.856	40	499
					96	8	19.094	41	346
					96	9	40.033	65	343
					96	10	28.261	55	339
					96	11	29.129	57	391
					108	2	9.927	31	407
					108	3	24.519	55	372
					108	4	17.738	40	346
					108	5	25.115	54	389
					108	6	17.955	48	381
					108	7	13.724	42	497
					108	8	17.792	43	339
					108	9	20.613	65	324
					108	10	28.967	58	347
					108	11	25.224	57	392

Table A.2. Phase I solution concentrations.

Treatment	Fluoride Concentration		Treatment	Copper Concentration	
	Before	After		Before	After
(hrs)	(% wt/wt)	(% wt/wt)	(hrs)	(% wt/wt)	(% wt/wt)
0	0.98	0.96	0	6.68	6.86
0	0.98	0.97	0	6.56	6.42
0	0.97	0.97	0	6.44	6.24
12	0.96	0.93	12	6.48	8.32
12	0.96	0.93	12	6.16	7.50
12	0.96	0.93	12	6.06	7.14
24	0.91	0.90	24	6.84	7.32
24	0.91	0.90	24	6.68	6.94
24	0.91	0.90	24	6.56	6.74
36	0.93	0.91	36	6.88	7.54
36	0.93	0.91	36	6.80	7.00
36	0.93	0.91	36	6.48	6.68
48	0.94	0.89	48	6.84	6.44
48	0.94	0.90	48	6.52	6.08
48	0.94	0.90	48	6.34	5.90
60	0.93	0.89	60	6.12	7.44
60	0.93	0.89	60	5.98	6.94
60	0.93	0.89	60	5.86	6.68
72	0.94	0.87	72	6.50	6.88
72	0.94	0.87	72	6.24	6.28
72	0.94	0.87	72	6.16	5.92
84	0.94	0.88	84	6.90	7.68
84	0.94	0.88	84	6.64	7.26
84	0.94	0.88	84	6.56	7.04
			96	6.30	7.04
			96	6.30	7.10
			96	6.38	7.12
			108	6.86	6.86
			108	6.62	6.48
			108	6.54	6.30

Table A.3 Phase II solution uptakes.

Treatment Code	Bd	Fluoride Soln. Uptake (kg/m³)	Copper Soln. Uptake (kg/m³)	Treatment Code	Bd	Fluoride Soln. Uptake (kg/m³)	Copper Soln. Uptake (kg/m³)
F0C2	1		68.72	F2C2	1	39.06	8.23
F0C2	2		16.35	F2C2	2	6.24	-1.04
F0C2	3		167.30	F2C2	3	86.57	19.24
F0C2	5		44.36	F2C2	5	91.46	14.01
F0C2	6		8.23	F2C2	6	6.29	0.38
F0C2	7		8.50	F2C2	7	3.42	-1.31
F0C2	10		18.42	F2C2	10	25.39	9.05
F0C2	11		25.94	F2C2	11	42.26	9.05
F0C2	12		20.98	F2C2	12	18.01	1.96
F0C2	16		14.77	F2C2	16	15.57	0.44
F0C2	17		17.00	F2C2	17	13.45	0.49
F0C3	1		215.64	F2C3	1	38.24	12.75
F0C3	2		24.80	F2C3	2	7.11	3.81
F0C3	3		230.41	F2C3	3	73.50	18.75
F0C3	5		20.00	F2C3	5	16.54	5.34
F0C3	6		11.77	F2C3	6	2.87	3.00
F0C3	7		12.37	F2C3	7	19.47	5.89
F0C3	10		39.78	F2C3	10	33.47	13.19
F0C3	11		67.85	F2C3	11	36.34	13.08
F0C3	12		19.18	F2C3	12	23.00	4.36
F0C3	16		21.36	F2C3	16	12.21	3.11
F0C3	17		12.75	F2C3	17	12.48	3.98
F2C0	1	101.38		F3C0	1	72.15	
F2C0	2	13.89		F3C0	2	12.10	
F2C0	3	61.51		F3C0	3	124.38	
F2C0	5	25.22		F3C0	5	41.06	
F2C0	6	6.62		F3C0	6	6.35	
F2C0	7	19.15		F3C0	7	3.63	
F2C0	10	39.16		F3C0	10	39.76	
F2C0	11	34.99		F3C0	11	28.10	
F2C0	12	17.74		F3C0	12	23.11	
F2C0	16	10.58		F3C0	16	21.05	
F2C0	17	14.48		F3C0	17	14.75	

Table A.3 Phase II solution uptakes (cont.).

Treatment Code	Bd	Fluoride Soln. Uptake (kg/m^3)	Copper Soln. Uptake (kg/m^3)
F3C2	1	50.83	7.63
F3C2	2	8.52	1.25
F3C2	3	149.01	49.26
F3C2	5	80.12	16.35
F3C2	6	9.76	1.85
F3C2	7	10.04	-0.76
F3C2	10	20.07	1.91
F3C2	11	53.27	8.56
F3C2	12	23.16	2.13
F3C2	16	13.94	1.74
F3C2	17	16.65	0.05
F3C3	1	53.92	15.80
F3C3	2	6.46	1.85
F3C3	3	42.74	14.88
F3C3	5	23.54	4.74
F3C3	6	5.86	-1.74
F3C3	7	27.23	5.12
F3C3	10	7.00	1.53
F3C3	11	26.15	9.70
F3C3	12	21.10	3.49
F3C3	16	26.04	4.09
F3C3	17	33.25	10.68

Table A.4. Phase II chemical retentions.

Treatment	Bd	Assay	After Treating (T)		After 30 Days (D)		After Leaching(L)	
			Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)
Blank	2	S	0.00	0.00				
Blank	6	S	0.00	0.00				
Blank	7	S	0.00	0.00				
Blank	10	S	0.00	0.00				
Blank	11	S	0.00	0.00				
Blank	12	S	0.00	0.00				
Blank	16	S	0.00	0.00				
Blank	17	S	0.00	0.00				
DI	2	S	0.00	0.00				
DI	6	S	0.00	0.00				
DI	7	S	0.00	0.01				
DI	10	S	0.00	0.00				
DI	11	S	0.00	0.01				
DI	12	S	0.00	0.00				
DI	16	S	0.00	0.00				
DI	17	S	0.00	0.00				
F0C2	2	S	0.11		0.06		0.08	
F0C2	2	I	0.00		0.01		0.00	
F0C2	2	C	0.00		0.02		0.00	
F0C2	6	S	0.13		0.08		0.08	
F0C2	6	I	0.00		0.01		0.01	
F0C2	6	C	0.00		0.00		0.00	
F0C2	7	S	0.07		0.07		0.03	
F0C2	7	I	0.00		0.00		0.03	
F0C2	7	C	0.00		0.00		0.00	
F0C2	10	S	0.17		0.24		0.06	
F0C2	10	I	0.01		0.02		0.00	
F0C2	10	C	0.01		0.00		0.00	
F0C2	11	S	0.25		0.25		0.18	
F0C2	11	I	0.02		0.04		0.03	
F0C2	11	C	0.01		0.05		0.03	

Table A.4. Phase II chemical retentions (cont.).

| Treatment | Bd | Assay | After Treating (T) | | After 30 Days (D) | | After Leaching(L) | |
			Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)
F0C2	12	S	0.14		0.11		0.08	
F0C2	12	I	0.00		0.00		0.00	
F0C2	12	C	0.00		0.00		0.00	
F0C2	16	S	0.12		0.18		0.12	
F0C2	16	I	0.00		0.03		0.00	
F0C2	16	C	0.00		0.00		0.00	
F0C2	17	S	0.24		0.10		0.07	
F0C2	17	I	0.00		0.03		0.01	
F0C2	17	C	0.01		0.02		0.01	
F0C3	2	S	0.24		0.16		0.07	
F0C3	2	I	0.01		0.04		0.00	
F0C3	2	C	0.00		0.05		0.00	
F0C3	6	S	0.08		0.18		0.07	
F0C3	6	I	0.01		0.01		0.00	
F0C3	6	C	0.00		0.02		0.00	
F0C3	7	S	0.11		0.33		0.12	
F0C3	7	I	0.00		0.03		0.01	
F0C3	7	C	0.00		0.00		0.00	
F0C3	10	S	0.58		0.58		0.26	
F0C3	10	I	0.01		0.10		0.07	
F0C3	10	C	0.01		0.04		0.06	
F0C3	11	S	0.38		0.36		0.22	
F0C3	11	I	0.05		0.14		0.13	
F0C3	11	C	0.04		0.06		0.06	
F0C3	12	S	0.16		0.12		0.07	
F0C3	12	I	0.00		0.00		0.00	
F0C3	12	C	0.00		0.00		0.00	
F0C3	16	S	0.16		0.18		0.17	
F0C3	16	I	0.00		0.00		0.00	
F0C3	16	C	0.00		0.00		0.00	

Table A.4. Phase II chemical retentions (cont.).

Treatment	Bd	Assay	After Treating (T)		After 30 Days (D)		After Leaching (L)	
			Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)
F0C3	17	S		0.16		0.07		0.13
F0C3	17	I		0.01		0.01		0.02
F0C3	17	C		0.01		0.01		0.01
F2C0	2	S	0.15		0.06		0.03	
F2C0	2	I	0.00		0.04		0.02	
F2C0	2	C	0.01		0.03		0.03	
F2C0	6	S	0.13		0.09		0.05	
F2C0	6	I	0.01		0.06		0.05	
F2C0	6	C	0.01		0.04		0.03	
F2C0	7	S	0.27		0.21		0.07	
F2C0	7	I	0.01		0.13		0.06	
F2C0	7	C	0.01		0.09		0.07	
F2C0	10	S	0.26		0.41		0.08	
F2C0	10	I	0.02		0.16		0.08	
F2C0	10	C	0.01		0.16		0.07	
F2C0	11	S	0.21		0.16		0.08	
F2C0	11	I	0.02		0.15		0.08	
F2C0	11	C	0.04		0.13		0.08	
F2C0	12	S	0.10		0.05		0.02	
F2C0	12	I	0.01		0.03		0.02	
F2C0	12	C	0.01		0.03		0.02	
F2C0	16	S	0.10		0.06		0.03	
F2C0	16	I	0.01		0.05		0.04	
F2C0	16	C	0.01		0.04		0.03	
F2C0	17	S	0.13		0.11		0.02	
F2C0	17	I	0.12		0.08		0.03	
F2C0	17	C	0.01		0.05		0.03	
F2C2	2	S	0.03	0.12	0.03	0.10	0.02	0.06
F2C2	2	I	0.00	0.00	0.01	0.00	0.02	0.00
F2C2	2	C	0.01	0.00	0.01	0.00	0.01	0.00

Table A.4. Phase II chemical retentions (cont.).

Treatment	Bd	Assay	After Treating (T)		After 30 Days (D)		After Leaching(L)	
			Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)
F2C2	6	S	0.06	0.17	0.06	0.18	0.03	0.12
F2C2	6	I	0.01	0.00	0.02	0.00	0.02	0.00
F2C2	6	C	0.01	0.00	0.01	0.00	0.01	0.00
F2C2	7	S	0.04	0.14	0.06	0.12	0.00	0.00
F2C2	7	I	0.01	0.00	0.01	0.00	0.01	0.00
F2C2	7	C	0.01	0.00	0.01	0.00	0.03	0.06
F2C2	10	S	0.10	0.39	0.06	0.30	0.05	0.28
F2C2	10	I	0.04	0.01	0.05	0.04	0.05	0.07
F2C2	10	C	0.02	0.00	0.05	0.01	0.04	0.01
F2C2	11	S	0.09	0.47	0.05	0.31	0.03	0.14
F2C2	11	I	0.05	0.00	0.06	0.07	0.04	0.08
F2C2	11	C	0.05	0.03	0.08	0.06	0.05	0.06
F2C2	12	S	0.03	0.14	0.03	0.16	0.01	0.11
F2C2	12	I	0.01	0.00	0.01	0.00	0.01	0.00
F2C2	12	C	0.01	0.00	0.01	0.00	0.01	0.00
F2C2	16	S	0.03	0.18	0.03	0.19	0.02	0.15
F2C2	16	I	0.01	0.00	0.02	0.01	0.01	0.00
F2C2	16	C	0.01	0.00	0.02	0.00	0.01	0.00
F2C2	17	S	0.00	0.29	0.04	0.25	0.02	0.15
F2C2	17	I	0.02	0.00	0.03	0.03	0.02	0.03
F2C2	17	C	0.01	0.01	0.01	0.00	0.02	0.00
F2C3	2	S	0.02	0.11	0.02	0.20	0.01	0.05
F2C3	2	I	0.01	0.00	0.01	0.00	0.01	0.03
F2C3	2	C	0.01	0.01	0.01	0.00	0.00	0.00
F2C3	6	S	0.03	0.16	0.03	0.26	0.02	0.08
F2C3	6	I	0.02	0.01	0.02	0.02	0.02	0.01
F2C3	6	C	0.01	0.01	0.01	0.00	0.02	0.02
F2C3	7	S	0.12	0.48	0.09	0.45	0.04	0.16
F2C3	7	I	0.05	0.00	0.05	0.08	0.03	0.03
F2C3	7	C	0.02	0.00	0.05	0.06	0.03	0.02

Table A.4. Phase II chemical retentions (cont.).

Treatment	Bd	Assay	After Treating (T)		After 30 Days (D)		After Leaching(L)	
			Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)
F2C3	10	S	0.20	0.48	0.10	0.67	0.05	0.29
F2C3	10	I	0.04	0.00	0.09	0.16	0.06	0.08
F2C3	10	C	0.04	0.00	0.08	0.06	0.06	0.03
F2C3	11	S	0.08	0.63	0.06	0.44	0.03	0.21
F2C3	11	I	0.05	0.01	0.05	0.09	0.04	0.03
F2C3	11	C	0.03	0.01	0.04	0.04	0.04	0.04
F2C3	12	S	0.03	0.18	0.03	0.22	0.01	0.14
F2C3	12	I	0.01	0.03	0.01	0.00	0.01	0.00
F2C3	12	C	0.02	0.15	0.00	0.00	0.00	0.01
F2C3	16	S	0.05	0.29	0.03	0.15	0.02	0.14
F2C3	16	I	0.01	0.00	0.01	0.02	0.01	0.01
F2C3	16	C	0.01	0.00	0.01	0.01	0.01	0.01
F2C3	17	S	0.04	0.00	0.04	0.18	0.03	0.10
F2C3	17	I	0.01	0.01	0.02	0.04	0.03	0.03
F2C3	17	C	0.02	0.04	0.01	0.01	0.02	0.02
F3C0	2	S	0.04		0.06		0.03	
F3C0	2	I	0.00		0.03		0.03	
F3C0	2	C	0.00		0.02		0.02	
F3C0	6	S	0.14		0.07		0.05	
F3C0	6	I	0.01		0.04		0.05	
F3C0	6	C	0.00		0.04		0.04	
F3C0	7	S	0.10		0.09		0.06	
F3C0	7	I	0.00		0.04		0.02	
F3C0	7	C	0.00		0.02		0.01	
F3C0	10	S	0.56		0.39		0.08	
F3C0	10	I	0.02		0.27		0.08	
F3C0	10	C	0.02		0.21		0.08	
F3C0	11	S	0.34		0.21		0.07	
F3C0	11	I	0.03		0.17		0.08	
F3C0	11	C	0.03		0.18		0.08	

Table A.4. Phase II chemical retentions (cont.).

Treatment	Bd	Assay	After Treating (T)		After 30 Days (D)		After Leaching(L)	
			Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)
F3C0	12	S	0.09		0.06		0.03	
F3C0	12	I	0.01		0.03		0.03	
F3C0	12	C	0.01		0.03		0.03	
F3C0	16	S	0.15		0.10		0.04	
F3C0	16	I	0.01		0.06		0.04	
F3C0	16	C	0.01		0.05		0.04	
F3C0	17	S	0.13		0.11		0.04	
F3C0	17	I	0.01		0.06		0.05	
F3C0	17	C	0.02		0.04		0.04	
F3C2	2	S	0.03	0.14	0.02	0.08	0.02	0.05
F3C2	2	I	0.01	0.00	0.01	0.00	0.01	0.00
F3C2	2	C	0.01	0.00	0.01	0.00	0.01	0.00
F3C2	6	S	0.06	0.20	0.05	0.12	0.04	0.12
F3C2	6	I	0.01	0.00	0.03	0.00	0.02	0.01
F3C2	6	C	0.01	0.00	0.02	0.01	0.03	0.01
F3C2	7	S	0.08	0.15	0.07	0.14	0.02	0.14
F3C2	7	I	0.01	0.00	0.03	0.02	0.02	0.01
F3C2	7	C	0.01	0.00	0.03	0.02	0.01	0.00
F3C2	10	S	0.04	0.20	0.03	0.27	0.02	0.16
F3C2	10	I	0.03	0.01	0.03	0.01	0.02	0.07
F3C2	10	C	0.02	0.00	0.02	0.00	0.02	0.03
F3C2	11	S	0.18	0.42	0.07	0.29	0.00	
F3C2	11	I	0.30	0.02	0.07	0.06	0.00	
F3C2	11	C	0.06	0.00	0.07	0.05	0.00	
F3C2	12	S	0.03	0.13	0.03	0.15	0.01	0.09
F3C2	12	I	0.01	0.00	0.02	0.00	0.01	0.00
F3C2	12	C	0.01	0.00	0.02	0.00	0.01	0.00
F3C2	16	S	0.04	0.19	0.04	0.15	0.02	0.19
F3C2	16	I	0.02	0.00	0.02	0.00	0.03	0.01
F3C2	16	C	0.02	0.00	0.02	0.00	0.01	0.00

Table A.4. Phase II chemical retentions (cont.).

Treatment	Bd	Assay	After Treating (T)		After 30 Days (D)		After Leaching(L)	
			Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)	Fluoride (% wt/wt)	Copper (% wt/wt)
F3C2	17	S	0.04	0.27	0.03	0.28	0.02	0.15
F3C2	17	I	0.03	0.01	0.03	0.02	0.02	0.00
F3C2	17	C	0.01	0.00	0.04	0.01	0.01	0.00
F3C3	2	S	0.04	0.19	0.02	0.09	0.01	0.05
F3C3	2	I	0.01	0.01	0.02	0.01	0.01	0.00
F3C3	2	C	0.01	0.00	0.02	0.01	0.01	0.00
F3C3	6	S	0.04	0.11	0.04	0.15	0.00	0.00
F3C3	6	I	0.01	0.00	0.03	0.01	0.01	0.00
F3C3	6	C	0.01	0.00	0.03	0.01	0.03	0.15
F3C3	7	S	0.19	0.69	0.12	0.48	0.06	0.27
F3C3	7	I	0.11	0.01	0.07	0.04	0.06	0.11
F3C3	7	C	0.05	0.01	0.09	0.10	0.07	0.06
F3C3	10	S	0.04	0.15	0.03	0.16	0.02	0.10
F3C3	10	I	0.02	0.00	0.02	0.00	0.01	0.00
F3C3	10	C	0.01	0.00	0.01	0.01	0.01	0.00
F3C3	11	S	0.08	0.40	0.06	0.33	0.04	0.22
F3C3	11	I	0.05	0.02	0.06	0.05	0.05	0.08
F3C3	11	C	0.05	0.01	0.06	0.03	0.05	0.07
F3C3	12	S	0.03	0.30	0.03	0.15	0.02	0.11
F3C3	12	I	0.02	0.01	0.02	0.00	0.01	0.00
F3C3	12	C	0.01	0.00	0.02	0.00	0.01	0.00
F3C3	16	S	0.04	0.27	0.04	0.26	0.02	0.25
F3C3	16	I	0.01	0.01	0.03	0.00	0.02	0.01
F3C3	16	C	0.01	0.01	0.02	0.01	0.01	0.00
F3C3	17	S	0.18	0.50	0.09	0.36	0.04	0.25
F3C3	17	I	0.06	0.01	0.07	0.07	0.05	0.07
F3C3	17	C	0.05	0.00	0.07	0.07	0.05	0.05