

**IMPROVING PENETRATION OF COPPER IN MICRONIZED COPPER AZOLE  
PRESSURETREATED MICHIGAN RED PINE**

By

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## **ABSTRACT**

### **IMPROVING PENETRATION OF COPPER IN MICRONIZED COPPER AZOLE PRESSURE TREATED MICHIGAN RED PINE**

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Michigan red pine *Pinus resinosa* is a critical part of the Great Lakes region lumber industry. The species is used for various applications such as telephone poles, dimensional lumber, decking and various other uses. This species is native to the Great Lakes meaning lower shipping costs and the creation of local jobs. The goal of this study overall was to improve the penetration of MCA pressure treated red pine. Using duration, steaming and penetration enhancers we were able to increase the penetration to allow some samples to pass the AWPAs penetration standard. We found that the average solution uptake of the treated samples was 47% for spring samples, 106% for summer samples and 79% for fall and winter samples. Steaming alone created better penetration than non-steamed samples but with the addition of penetration enhancers we were able to boost the penetration to levels we had not observed with other treatments as indicated above. Penetration enhancers alone greatly increased the penetration but the steaming would allow for a higher moisture content, which in turn swelled the wood allowing PE to aid greater penetration. Anatomically, red pine has issues with high resin content and pit aspiration, which was observed but a conclusion has not been reached as to what causes the pit aspiration or why aspiration is sporadic in red pine samples regardless of drying or treating.

## **DEDICATION**

To my Fiancé Ashlie, my mother Virginia and my entire family for their unwavering support, sacrifices, and confidence.

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## Chapter 1

### Introduction

Michigan red pine *Pinus resinosa* is the species that has built much of Michigan and helped Michiganders in times of despair. In the 1930s with the great depression ongoing and much of upper Michigan's land having being clear-cut or abandoned the Civilian Conservation Corps (CCC) stepped in and put people to work planting red pine plantations in what was once barren land ( Pilon et al. 2006). This was done to restore the forests and to also create jobs when there were few. Today much of the landscape in Michigan is still dotted with red pine plantations and windbreaks placed by the CCC'S. In the 1980s the red pine came of age t harvest and so did technology creating mills that could meet production quotas using moderate sized logs instead of the old growth that the industry had come accustomed to (Pilon et al. 2006).

The trees being harvested today are roughly 55-65 year of age according to a forester for Biewer Lumber in Mcbain Michigan. With today's ever demanding markets for lumber, red pine has become vital because species like southern pine and Jack pine *Pinus banksiana* cannot alone supply the lumber demand the Nation needs. Red pine alone in state and national forests in Michigan make up almost 200,000 acres, which makes this species extremely important to the lumber industry (Pilon et al. 2006).

Since red pine is established on much of the Great Lakes region which is illustrated in Figure 1. With the knowledge of the resource here in Michigan it is necessary to use it to its fullest potential, by using the wood in various products. These products consist of structural lumber in treated and non-treated form telephone poles, woodchips, and various other uses. Treating red pine has become a product that is in the spotlight. Treating red pine can sometimes be associated with gambling since sometimes the species treats well and other times not so well.



**Figure 1:** Red pines geographic distribution (Virginia Tech Forest Resources and Environmental Conservation, 2009) For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis.

Chemical treatment of red pine has greatly changed in the last 10 years due to technological changes and concerns about the safety of chemicals. Today “micronized copper” in a waterborne solution is what has been established to be safer for people and the environment. The micronized shift in chemicals came about due to the voluntary withdrawal of chromated copper arsenate (CCA) which was the chemical of choice until 2003 (Bowyer et al 2007). Today micronized copper azole (MCA) and micronized copper Quaternary (Quat) (MCQ) are the new chemicals that treatment companies have begun treating various species with since CCA is no longer viable for non-industrial use lumber (Osmose Inc.).

The micronized series of copper are better for the environment and are more aesthetically pleasing due to the lighter color/more natural looking treated lumber. The problem that these new micronized chemicals face in treating red pine, known for having a high resin content, and a transition zone that from sapwood to heartwood that is very hard to treat, especially considering that heartwood is almost impossible to treat due to aspirated pits (Wang et al. 1996). The problem with treating red pine is that these aspirated pits are not only in the heartwood but also the sapwood which can slow or stop the penetration of treatment solution into the wood. The combination between high amounts of resin and aspirated pits issues for the treatment companies, which is why this study is needed.

The objectives of the study are;

1. To assess the treatability of red pine treated with MCA while increasing the duration of the treatment.
2. To evaluate the performance of steaming lumber and the use of penetration enhancers added to MCA to aid in increasing the penetration of the treatment solution.
3. To examine the anatomical properties of red pine to view if pits are aspirated.

## **Chapter 2**

### **Literature Review**

#### **2.1.1 Red pine resource**

Red pine is a species of pine that is native to the Northeastern United State, and of high importance to the Great Lakes region. Red pine is known by other names such as Norway pine, Eastern red pine, and pin rouge (Anderson and Moore, 2003). The species occurs in well drained, dry, highly acidic, sandy soils of outwash plains, and gravelly ridges (Barnes and Wagner 1981). The tree is medium sized, and up to twenty-five meters high and seventy five meters in diameter (Farar 1995). The wood is moderately hard and straight grained, and is used for poles, lumber, railway ties, post and pulpwood and other uses (Anderson and Moore, 2003). A key characteristic to red pines use in Michigan is it can grow on sandy soil, thus it was planted as windbreaks and was planted in areas where cash crops were not, especially during the Great Depression.

#### **2.1.2 Properties of red pine**

Red pine is a hard pine, with a density of 26 pcf (AWPA, A12-09). Being of the hard pine family the species is planted for lumber purposes for building structures. The tree itself is large 20-30 m, fast growing and can grow in well drained infertile soils such as sand and outwash plains (Barnes and Wagner, Jr., 2004). The bark is a brown color with a reddish tinge to it and is relatively thick to help fight against fire. The leaves are in clusters of 2 and are 10-17 cm long and are relatively straight (Barnes and Wagner, Jr., 2004). The wood itself has a piney odor, red pine being the strongest odor that is associated with the pine family (Hoadley, 1990). The heartwood is distinct due to the dark brown/red color, while the grain is moderately uneven and transitions from early wood to latewood are abrupt (Hoadley, 1990). Sapwood is a creamy

yellow color while the heartwood is a brownish red color noted earlier. Resin canals are present in the species thus the name *resinosa*. The resin canals are numerous and medium sized compared to other species and evenly distributed throughout the wood (Hoadley, 1990). With resin canals being numerous and throughout wood the pitch needs to be set when the wood is drying in the kiln. Setting the pitch is the process of heating up the lumber to a specified temperature so that the resin will only flow if the temperature rises above the kiln set temperature. If a piece of wood is kiln dried to 120°C the resin will not flow until the temperature of the wood rises above 120°C.

Red pine is sapwood susceptible to sap stain Figure 2. The most significant stain is blue stain. The stain not only discolors infected wood a bluish gray color, but also can reduce the price, due to the wood being used for pulpwood instead of lumber. The fungus can either be transported by air like many fungi or by insects such as beetles. The fungus is most active between 70°F and 90°F but can develop between 40°F and 130°F (Bowe et al., 2005). Blue stain attacks the wood because the fungus needs sugars and starches in the sapwood of the tree to survive (Forest Products Laboratory, 1999). Though blue stain degrades the lumber's aesthetics the stain is good for chemical preservation, especially red pine. This is due to the stain eating away the resin and starches allowing the chemicals to penetrate deeper due to the lack of resin blocking penetration (Figure 2). Though blue stain is problematic the stain can be controlled, temperatures of 150°F are lethal to blue stain, the stain cannot grow in moistures of 20% or less and there are fungicides that can be used along with sealing or coating the logs in a wax barrier (Bowe et al. 2005) (Forest Products Laboratory, 1999). The best solution though is to cut the trees and transport the wood to the mill in a timely manner to decrease the chance of the wood being infected or the stain growing.



**Figure 2:** Treated red pine with 70-80 percent blue stain. The sample was treated with 1 percent MCA solution with less than 20 percent heartwood, treated under pressure for 60 minutes with a maximum pressure of 165 psi.

### 2.1.3 Utilization of red pine

Red pine is a vital resource for building materials in the Great Lakes region. Not only is it used for production purposes like lumber but the bark has occasionally been used to tan leather (Sargent 1961). The species with the higher density is mainly used for structural purposes like 2x4"s, 4x4"s, and 2x6"s but there is a host of other nominal sized lumber that this species is used for. A few construction uses for the timber is ladders, pilings, poles and interior and exterior trim (Barnes and Wagner, Jr. 2004). Red pine is of high importance to Michigan mainly due to the Eastern Upper Peninsula being of the correct conditions to grow high dollar telephone poles. Plus, the species can be used for a multitude of other application or uses such as railroad ties, pulpwood, cabin logs, posts, and fuel (Anderson and Moore, 2003). In addition to the different uses for the timber cost of shipping also comes into play, since the species is native shipping is lower, there is an economic boost due to local jobs and the species can be managed by the people who are local that use and cut the timber, unlike timber that is shipped in from other parts of the



United States. Red pine also has many uses in the treated form especially in decking material, but treated lumber is also used for fencing, decorative outdoor panels, and walkways.

#### **2.1.4 Chemical Preservative treatment**

Wood preservatives have been around since the 17<sup>th</sup> century when settlers came to the new world (Freeman et al. 2003). There has been a need for chemicals because wood is part of the basic building blocks of the United States and many parts of the world. Before steel there was wood and wood continues to be the most cost effective means of building structures even today. Wood is not only renewable but can be shipped to just about anywhere in the world. With the history of chemical treatment of wood ranging back to the 17<sup>th</sup> century there has been many chemicals and treatments used over the years some that were good and some that were not good at all in fact toxic, especially when manufacturing. Creosote has been one of the chemicals that have stood the test of time. Coal-tar creosote was patented in 1836 by Moll and is still used today, where other chemicals have come and gone (Freeman et al. 2003). The first pressure impregnation of chemicals also used creosote, which was developed by John Bethell in 1838 and was known as the Bethell or full cell treatment, which is the basis of chemical treatment today (Freeman et al. 2003).

Today most chemical treatment companies still use pressure to impregnate or treat wood but the chemicals have changed. Now with the ever present carbon exchange and global warming, chemists and chemical companies alike are looking for safer and all around better chemicals to treat lumber. Most solutions currently are aqueous copper based solutions, the two copper forms being used in the United States is “soluble copper (Typically amine based) or more recently particulate or “micronized” copper based biocides” (Zahora 2011). Currently, there are 5

primary chemicals that are being used (Table 1). These chemicals are all in use currently with chromated copper arsenate (CCA) being in limited use. The limited use of CCA is due to a voluntary withdrawal from the residential use in December of 2003 because of health risks (EPA 2011). With the withdrawal of CCA from residential markets the other 4 chemicals have seen a rise in use especially since a study done in 2000 by the Southern Forest Products Association found that CCA treated 80% of residential use lumber (Freeman et al. 2003). With this knowledge MCA, MCQ, CA, and ACQ are all competing to take CCA's place.

**Table 1:** Five common treatment preservatives that are currently being used to treat and protect conifer species.

Chemical Preservative	Full Name	Organics	Current Status
MCA	Micronized Copper Azole	Azole	In use
MCQ	Micronized Copper Quaternary	Quaternary	In use
ACQ	Alkaline Copper Quaternary	Quaternary and Ammonia or Amine	In use
CA	Copper Azole	Azole	In use
CCA	Chromated Copper Arsenic		Limited use in USA

### 2.1.5 Performance of treated conifers

It is well established that all wood is different, wood is not like steel, where we know the exact chemical make-up and how much of a certain chemical or element is in the sample or piece. All wood has similar characteristics but all species differ. Some species have more resin than other, which causes treatment parameters to change and some species do not treat well at all, while others have natural decay resistance. Red pine, southern pine, and Jack pine are three species that are from the same family (pinaceae) and genus (*Pinus*), but are all a little different from each other and treat differently. The problem that plagues treatment companies is pit aspiration which will be gone over more extensively in the Microscopy chapter, but when a pit is

aspirated or closed off, the wood is resistant to penetration by protective chemicals whether it is creosote or waterborne preservatives (Bowyer et al. 2007). With this in mind, the goal for treating conifers is to limit the closing of the cells, with changes in chemicals, treatment parameters and kiln drying. Figure 4 portrays how two species, southern pine and red pine, react to the same treatment differently. Southern pine usually treats very well, treating 80% or more of the sapwood, while red pine is vary sporadic, and most times luck to reach the AWP standard of treating 80% or more sapwood (AWPA A3-08). The goal when treating conifers is to know which parameters need to be adjusted for each species, and if these parameters are correct most species with treat well.



**Figure 3:** Southern pine wood (left) exhibits excellent MCA penetration by the presence of the blue indicator copper dye. Red pine wood (right) shows significantly lesser penetration by MCA. (30 min. initial/final vacuums, 60 min. pressure duration)

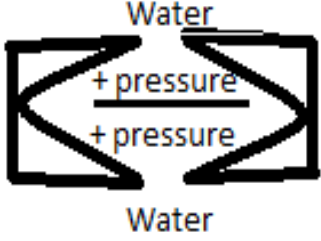
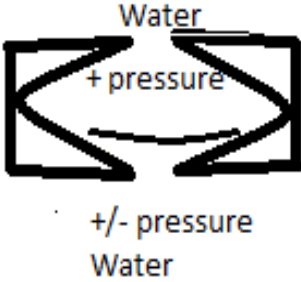
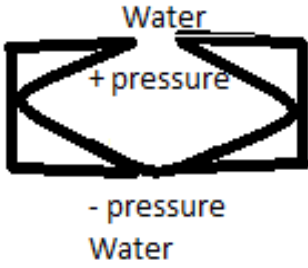
## **Chapter 3**

### **A few anatomical properties of red pine**

#### **3.1 Introduction**

##### **3.1.1 Anatomical properties**

The flow of fluids through softwoods like red pine is done through tracheids. Tracheids are long slender cells that make up 90-95 % of the volume of softwood and are 25-45  $\mu\text{m}$  in diameter and 3-4 mm in length (Bowyer et al. 2007). Imagine a tracheid looking like a soft drink straw that is closed by pinching both ends (Bowyer et al. 2007). The walls of the tracheid are composed of pits that allow fluids to flow laterally from longitudinal tracheid to tracheid. A pit by definition is a gap or recess in the secondary cell wall, together with its external closing membrane (Siau 1971). The pit is believed to be the main problem in pressure treating lumber, due to the membrane being closed off or the pit being aspirated. An aspirated pit is a pit that has had the torus move to one side so that it is being held tightly to the aperture due to pressure or a pressure change (Siau 1971). A change in pressure on one side of the torus is all it takes to aspirate that pit which can be caused by drying or any number of changes that the wood undergoes once cut (Bowyer et al. 2007). Figure 4 is a depiction of how the pit aspirates and the little change in pressure it takes to move the torus.

	<p>The pit is open allowing flow around the torus, due to the water pressure being the same on either side of the pit.</p>
	<p>The torus is shifting from positive pressure to negative pressure. The pit is not aspirated fully aspirated</p>
	<p>Torus has been shifted by the pressure difference, thus the pit is aspirated. The shifting of the torus was due to the pressure differenced on either side of the pit.</p>

**Figure 4:** Depiction of the pit aspiration of softwood tracheids

Once the pit aspirates, chemicals will not be able to flow through the pit and will have to find an open pit to continue the flow from tracheid to tracheid. It is thought that once a pit is aspirated, it is apparently a permanent condition (Jane et al. 1970).

The other anatomical structure that limits chemical penetration is resin canals. Resin canals are tubular passageways lined with living parenchyma cells, which extrude resin or pitch into the canals, which the tree uses as a defense/healing mechanism (Hoadley 1992). The resin is problematic first because the pitch needs to be set for the wood to be used as lumber but when the tree is cut, the resin fills many of the canals as a defense mechanism noted earlier. With the canals being full of resin and the pits being aspirated, treating this species becomes a difficulty depending on the degree to which these mechanisms are enacted, and every tree is different. Some species have resin few resin canals and some have many, and unfortunately *Pinus resinosa* has quite a few that are throughout the entire wood structure, meaning they are evenly dispersed.

## **3.2 Materials and Methods**

### **3.2.1 Confocal laser scanning microscopy (CLSM)**

The Zeiss 5 Pascal confocal laser scanning microscope proved fruitful in observing pits and tracheids. We found that the best picture quality of pits was from using the reflected laser light. The samples were cut to approximately 10mm by 10 mm by 1mm thick in the radial direction. Neither chemicals nor water was used in sample preparation due to changing the sample and perhaps aspirating more pits. Images were collected with using a 50x EC EpiPlan (NA0.7) objective, and reflected laser light was recorded from the surface of the wood samples using the 488nm Argon laser for illumination and a 475-525nm band pass filter for isolation of the laser line (Frame 2011). Confocal images were recorded at 1 micron increments through the Z-thickness and Maximum Intensity Projection was used to generate the through-focus projection for each image (Frame 2011).

### **3.2.2 Scanning electron microscopy (SEM)**

The JSM-6400 SEM was used because of the clarity of the images that can be obtained and the magnification abilities of the microscope. The samples were 4mm by 4mm by 3mm, and were coated using a carbon coater. Samples were all prepared using a razor, for clean and precise cuts. The SEM produces quality images by using electrons. Specifically an electron beam that is projected over the sample where an interaction occurs producing secondary electrons that escape the surface, which are collected by the Everhart-Thornley detector and converted to image by the cathode-ray tube (Flegler et al. 1993). The problem we encountered was that the samples were charging, even when gold coating and carbon coating were used. We found the carbon coating to work the best but the images were not satisfactory due to the inability for proper sample preparation due to chemicals altering the resin and the pits. We were able to obtain a couple quality images, Figure 5 being the best before the electron beam distorted the sample. More work would be beneficial for another project, but we found the CLSM, to be the best for the time and money allotted for this project.

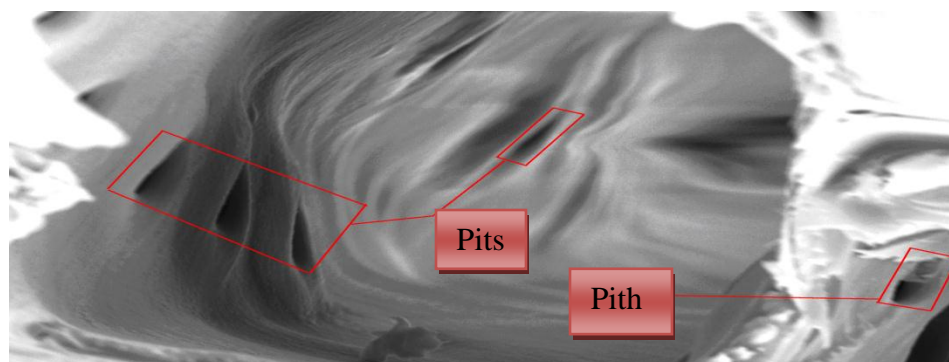
### **3.3 Results and Discussion**

#### **3.3.1 Microscopic features of red pine**

The SEM in the beginning of this study looked to be the way to observe the anatomical structure of red pine. The problems we soon encountered were we were not able to chemically prepare the samples as the standard calls for and we also receive high amounts of charging on the samples. Figure 4 is the depiction of the inside of a longitudinal tracheid cell kiln dried red pine at 3600 magnification, which looks unobstructed but further analysis is needed. Further analysis is needed for two reasons. First the sample preparation resulted in poor quality images due to the tearing of the cells and the cut being of the transverse surface instead of the radial surface. Future

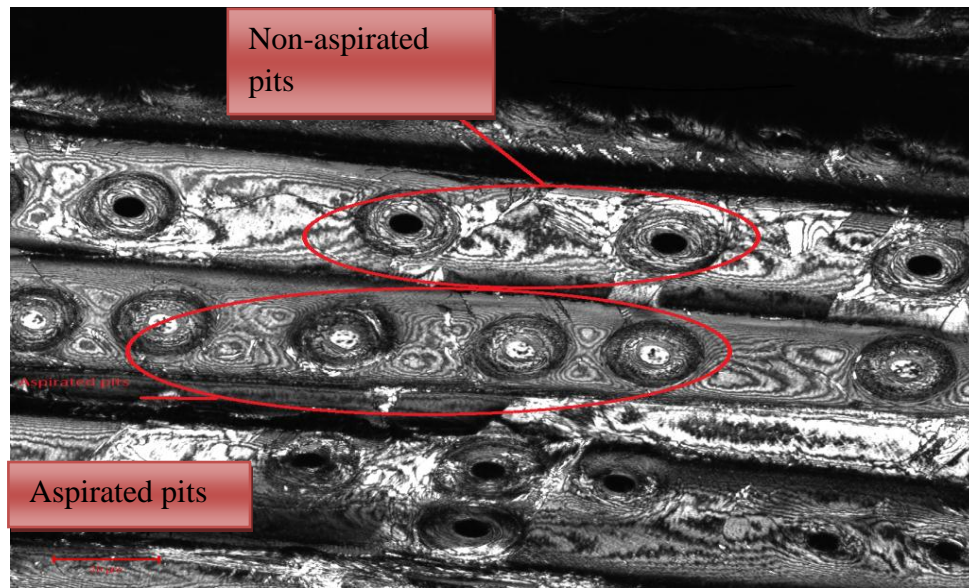
studies may want to cut according to the radial and the tangential views to aid in finding if the pits are aspirated or open according to the methods that were used by (Dute et al. 2010).

The CLSM was very helpful in looking at the pits; the key will be in future studies to allow a study that focuses only on the structure of red pine. We found that some pits were open and others were closed. It did not seem to matter if the samples were of treated or untreated early wood (Figures 7-8) we saw both aspirated and non-aspirated pits. The latewood did show more aspirated pits but more work needs to be done to have conclusive results (Figure 9). What we say is that green wood that is wood that has not been kiln dried seemed to have the most open, non-aspirated pits. We also found it easier to find pits on these samples, whether that be because of our limited sample number and time using the microscope, we are not sure. The one aspect of this study that we are sure of is that more work needs to be done in the future on the CLSM to view the pit structure in all samples of treated, untreated, and kiln dried lumber. We were able to see that some samples pits were non-aspirated which is why in some samples we observed greater penetration, but more work needs to be done especially a study documenting the before and after of kiln drying wood.

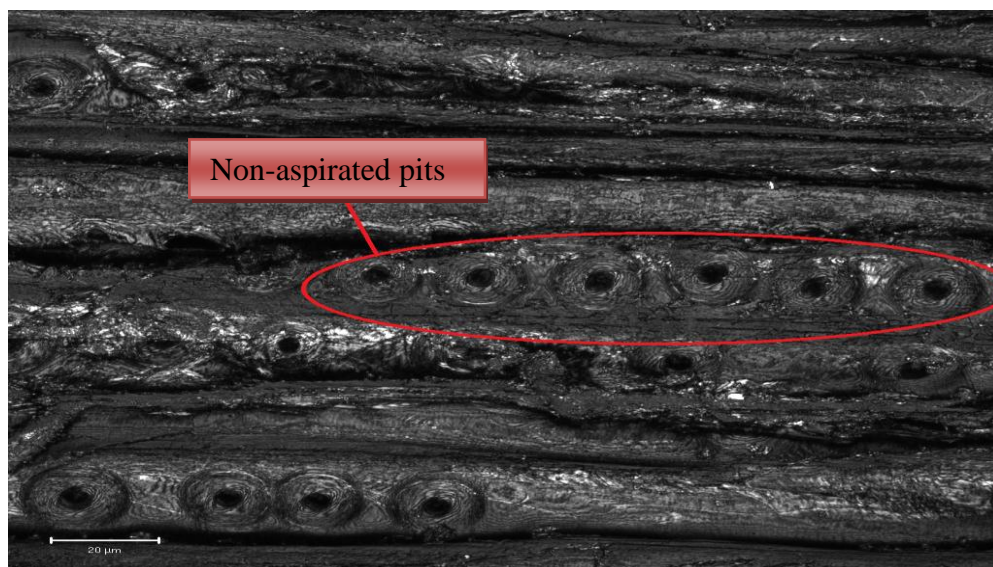


**Figure 5:** Inside the longitudinal Tracheid of kiln dried red pine. The magnification was 3600x taken using 6400 SEM. On the left side of the wall one can see the pits of the sample.

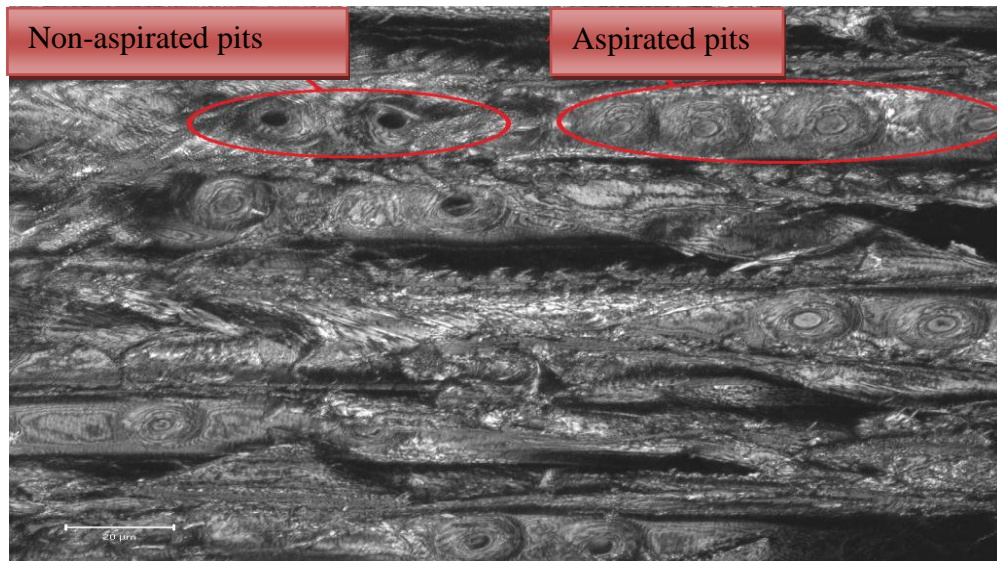




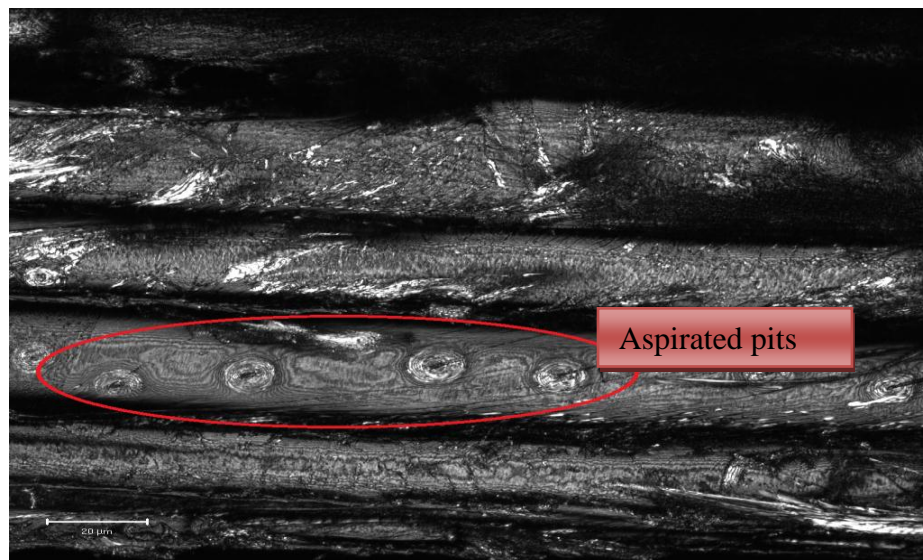
**Figure 6:** Untreated green sample of red pine sapwood; roughly half pits are open, and half are not. Closed pits appear to be filled “White color”. Picture was taken using reflected light. Scale bar: 20  $\mu$ m



**Figure 7:** Untreated early wood “sapwood” All pits appears to be open. Picture was taken using reflected light. Scale bar: 20  $\mu$ m



**Figure 8:** Treated early wood “sapwood”. Some of the pits appear open while others appear closed. Picture was taken using reflected light. Scale bar: 20 μm



**Figure 9:** Treated latewood “sapwood” sample of kiln dried red pine. Pits appear to be all closed in the picture. Picture was taken using reflected light. Scale bar: 20 μ

## **Chapter 4**

### **Pressure treatment of spring wood**

#### **4.1 Introduction**

During different seasons the moisture, growing conditions, and temperature change in trees. These changes during the season affect the growth cycles in the wood which is why there are ring from the stresses during the summer months to the prime growing environment the spring brings. In knowing the differences in the seasons we wanted looked at the four different seasons. Spring season was used to begin, this experiment. The spring samples were all gathered from Biewer Lumbers sawmill in McBain, MI, which is where all the wood from this study was procured. Spring wood, which in the study was from the end of April, was observed to be full of water due to the higher precipitation that comes with Michigan springs.

#### **4.2 Materials and Methods**

##### **4.2.1 Procurement of Lumber**

All lumber for the study was procured from Biewer Lumber sawmill, in McBain, Michigan (Biewer Lumber 2009-2011). The red pine ranged in age from 50 to 55 years old and was from the North eastern area of Lower Michigan. Logs were cut and on the landing from 1 to 5 days maximum, before being shipped to the McBain sawmill. Generally the logs were in the log yard less than a week depending on when the manager could allow the study logs to be cut in the sawmill. After the log was cut to lumber the wood went into the drying kiln to be dried and then graded (Figure 10). Kiln drying methods and specific temperatures were not noted due to confidentiality agreements with the study and we did not want the parameters changed since this was a study about how to improve pressurize chemical treatment of red pine. Jack pine used in

the study was also procured the same way as red pine. The lumber was picked up for the study within one week of the lumber coming out of the kiln and planed. The lumber was transported from McBain to the Natural Resources Building in East Lansing, Michigan, within 3 hours of the samples being loaded on the truck. The samples were then cut to 17.25" and placed in one of two chest freezers in the lab to control the moisture content. The exception was the summer wood for the study, these samples moisture content was very low in the 9-12 % MC so the decision was made that keeping the samples at room temperature 70 degrees Fahrenheit, since the temperature at the time of procurement was around 70 degrees Fahrenheit the wood was already at an equilibrium moisture content (EMC).

However the southern pine in the study was procured in the study from Biewer Lumber but it was cut and shipped in from sawmills in the Southern United State, due to the native area of southern pine being not native to the Great Lakes region. To know the specifics of where the lumber came from was not available since we were not working with these mills and southern pine is known to treat well, which is why it was a control in certain treatments.



**Figure 10:** Graded and stamped kiln dried red pine that was used in this study, all lumber was graded and kiln dried by Biewer Lumber, McBain Michigan.

#### **4.2.2 Wood samples**

The red pine samples were gathered from Biewer Lumbers sawmill in Mcbain, MI. The lumber was from the upper northeast area of Lower Michigan, as was all samples for this study. The lumber was trucked in to Michigan State within one week from the moment the lumber came out of the kilns and cut to nominal 2"x4"x8' and 10' (5.1 x 10.2 cm x 2.4 and 3.1 M) lengths. The Lumber was then kiln dried according to Biewer Lumbers standards, but not noted due to confidentiality. The lumber was then unpacked, loaded in a pickup truck and driven the 2.5 h to Michigan State University, East Lansing, MI. Boards were marked and cut to 17.5" (44.4cm) lengths and stored in Freezers to preserve the moisture content, until a later date for treatment.

#### **4.2.3 Pre- treatment Moisture content**

Samples were cut to 16" (40.6 cm) and the remaining 1" (2.54cm) samples were oven dried according to ASTM standard D4442-07 (ASTM 2009). Samples were then allowed to reach room temperature over 12 hours, while being stored in a conditioning room at 70-80°F (21-27°C) and 50-60% humidity. Samples were not end sealed in this case to view maximum penetration, from all surfaces.

#### **4.2.4 Pressure treatment**

Samples were all treated in the treatment tank that was 12" diameter that was 16.5" long (Figure11) using 1% Cu MCA solution. The tank is filled with solution via initial vacuum ranging from 20-25"Hg, when vacuum is diminished solution is then pumped into cylinder via, pressurized liquid transfer pump. A valve located at the top of the cylinder indicates when solution has filled the tank along with weighing the solution before and after tank filling. Tank is



then pressurized for 1-2 h depending on the schedule, and in a couple cases the tank was refilled after 30 or 45 min.”, half the treatment duration” to view if adding solution helped penetration. The Maximum continuous pressure reached was 180 psi and the minimum pressure was 160 psi. Following positive pressurization period the samples were subjected to a final vacuum (20-25” Hg) to withdraw free solution in wood and follow industrial practices, that are used to reduce weight for shipping costs. Following treatment samples were weighed, and allowed to dry for 24 h before samples were cut in half longitudinally, and sprayed with heartwood/sapwood indicator “reddish color” and copper indicator “bluish color” (AWPA M2-07)(AWPA A3-08).



**Figure 11:** Treatment tank used for all treatments for the entire experiment. Tank is 12” x16” and can handle pressures above 200 psi.

#### 4.3 Results and Discussion

The spring treatments consisted of treating red pine samples with MCA in a 1% Cu concentration (Cu/Az = 96:4). The goal of this cycle of treatments was to view if changes in treatment cycles improved the penetration. That is we changed the duration of the cycles and

refilled the tank half way through the treatment process. This means that we refilled the tank at 30 min. for a 60 min. duration and 45 min. for 90 min. duration (Figures 12 and 15). The remaining samples were then treated without refilling the tank halfway through the treatment (Figures 13, 14, and 16). The reason behind experimenting with refilling the tank was that perhaps after the first half of the treatment some samples were not submerged in solution. This however was not the case by looking at figures 12 “refilled” and 13 “non-refilled”, since both treatments did not treat well and both still have sporadic penetration through what cells were open, in fact by observations the non-refill samples of board I treated better. In addition, the remaining treatments Figures 14-16, did not show any observable improvement in penetration, whether the treatment had a tank refill or did not have a tank refill.

The only observable detail was that when penetration was observed to increase, also did the uptake as in Figures 13 and 17. When looking at the graph of Figure 17 and the pictures of the samples one can view that uptake does correspond to increase in penetration in most observable cases. However, in the spring treatments we did not view a difference with the moisture contents affecting the penetration, though almost all samples were around the 15% moisture content.

What we can gather from this information is that there may be an increase in penetration with increasing the duration, but nothing that stands out as an achievement. We know that refilling the makes little to no change in penetration. The main difference that seems to affect penetration is the wood samples themselves. This could be due to different drying conditions, as in different locations in the pack being dried, receiving different drying temperature. The reason behind this is that when drying lumber, one has to account for wood being a superb insulator, so samples or boards on the inside of a lumber package may not be receiving the same temperatures

as the lumber on the outside of the pack. A future study would need to be done with a temperature probe to observe and record the differences in moisture and temperature associated with the location of the lumber in the pack or in the kiln. The problem was that with this study all the kiln drying methods and temperatures are trade secrets for each company, and thus we were not able to examine drying techniques and temperatures.



**Figure 12:** Spring kiln dried samples treated for 90 min. with tank refill at 45 min. Initial and final vacuum 30 min.





**Figure 13:** Spring kiln dried samples treated for 90 min. without tank refill. Initial and final vacuum 30 min.



**Figure 14:** Spring kiln dried samples treated for 60 min. without tank refill. Initial and final vacuum 30 min.

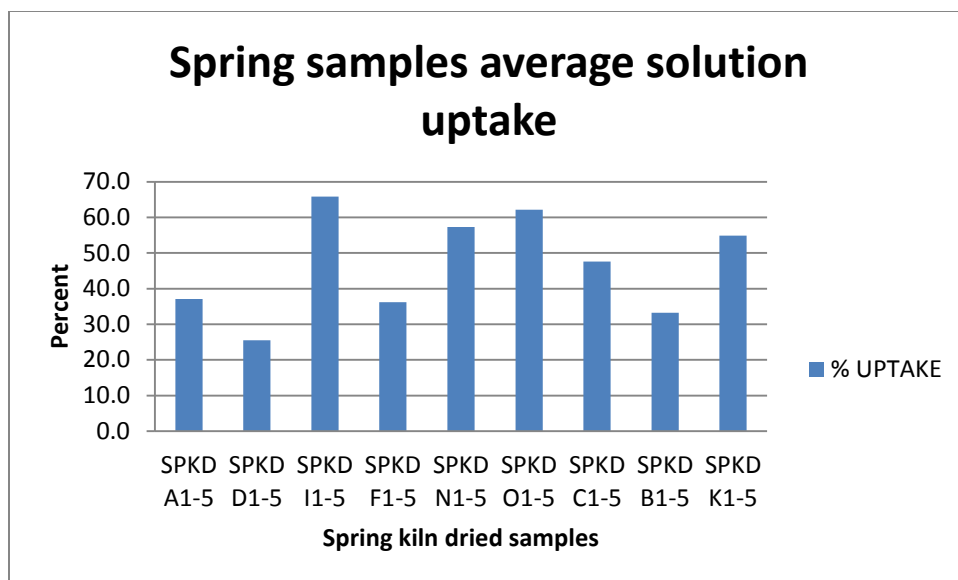




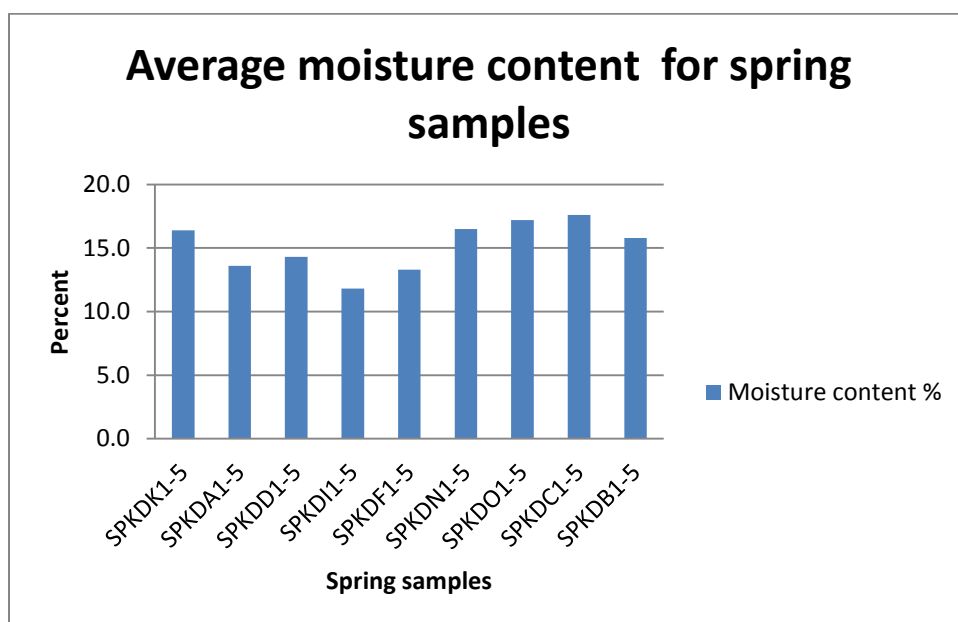
**Figure 15:** Spring kiln dried samples treated for 60 min. with tank refill at 30 min. Initial and final vacuum 30 min.



**Figure 16:** Spring kiln dried samples treated for 90 min. without tank refill. Initial and final vacuum 30 min.



**Figure 17:** This graph indicates the average percent solution uptake for each set of samples, a set of samples as in A1-A5 is samples all from one board.



**Figure 18:** This graph indicates the average moisture content for each set of samples, a set of samples as in A1-A5 is samples all from one board.

## **Chapter 5**

### **Penetration and retention of red pine summer wood (steaming)**

#### **5.1 Introduction**

Moisture plays an important role in the treatment of lumber. Moisture content is “the quantity of moisture in wood expressed as a percentage of the oven dry weight” (Siau 1971). From the moment the tree is cut moisture is being lost to the surrounding environment. The first that is lost is free water; this is free water which is stored in the lumen. The other form of moisture that is present in wood is bound water; this is water that is in the cell wall. Bound water is” limited to approximately 30 percent of oven dry weight of the wood” (Siau 1971). For the lumber companies these two sources of water in wood can present problems, because the wood needs to be dried for shipping and structural purposes, but if the wood is dried too fast or slow, the wood can be difficult to chemically treat and the lumber can become unstable, warping. The problem is that to chemically treat lumber the wood must have a moisture content below the fiber saturation point (FSP) so that chemicals can enter the cells. What this means is that the lumen is empty so water can be absorbed, but the cell walls are saturated at FSP ( Bowyer et al. 2007). Most Micronized solutions are water borne as previously noted; meaning if the lumber is below FSP the wood is more easily treated due to the ability to absorb water. The goal when treating lumber is to have a moisture content in the area of 15-20% moisture, this way the wood is not completely dry but not saturated, allowing the optimal condition for chemical uptake.

The equilibrium moisture content (EMC) is the bound water moisture content, meaning that the moisture content is at equilibrium with the surrounding environment (Siau 1971). The EMC means that the moisture content of wood is always changing, meaning, if wood is stored dry indoors versus wet outdoors, and the wood outdoors will have the higher EMC. When

treating lumber it is extremely important to keep track of temperature, storage of lumber, and humidity, because the EMC is always changing and if the EMC becomes too low it becomes increasingly more difficult to treat as is wood with very high moisture higher than the FSP. The formula used to calculate moisture content is very important and is something everyone working in the wood industry must know.

$$\text{Percent Moisture Content} = [(\text{weight with water} - \text{oven dry weight}) / \text{oven dry weight}] \times 100$$

## **5.2 Materials and Methods**

### **5.2.1 Wood samples**

In September of 2009 we received our summer wood for treatment, the problem that was not known at the time, was that the lumbers moisture content was too low, below 12% which we would learn is too low for quality pressure treatments . This was solved when procuring other lumber by talking directly with foresters to know when the lumber will be available, to ensure the highest moisture content possible. As before the samples were procured from Biewer Lumbers sawmill in McBain MI and cut to the exact specifications as spring wood with the exception of the samples not being frozen. The lumber was then stored at 70°F on racks, for treatment at a later date since moisture would change little due to outdoor temperatures being equivalent to indoor temperatures.

### **5.2.2 Pre-treatment steaming and end sealing**

After not meeting the AWPAs penetration standard in many of the springwood samples with higher moisture contents and not having the ability to obtain new samples since summer season was over we decided to try and raise the moisture content. The moisture content was

raised by steaming the wood samples, using an autoclave. The samples were steamed at 180°F to 200°F for one hour, in the autoclave, and then allowed to cool to touch. This was done because at these temperatures the polymerized resins will begin to flow once again and allow water to penetrate the lumen and cells raising the moisture content and hopefully opening up cells to allow for improved penetration. Once samples were cooled, the samples were end sealed with a marine grade epoxy and placed in the conditioning room at 70-80°F (21-27°C) and 50-60% humidity for 24 hours to set the epoxy and the samples were then treated. Samples were end sealed to observe if steaming was increasing penetration through the tangential and radial surfaces and to mimic the treatment of longer lumber in industrial applications.

### **5.2.3 Pressure treatment**

The copper concentration of MCA for the summer samples was around 0.80%, which was lowered due to industrial standards also lowering, since this study is intended to help the industry we changed our concentrations when they did, since our solution came from industry treatment plants. A performance enhancer (PE) was also added to aid in penetration, which was Quaternary or Quat. The Quat was added to aid in breaking down the resins that had polymerized while during the industrial high temperature kiln drying. The concentration was .5lbs to 55lbs (0.9%). The 16" samples were placed into the 12"x 16.5" treatment tank filled with solution using the same process as spring samples and treated for a total of 3h. A 30 min initial vacuum for tank filling, (20-25 in Hg) followed by 120 min positive pressure(180 psi) and a 30 min final Vacuum for recycling solution was used once again (20-25 in Hg). Following treatment samples were weighed, and allowed to dry for 24 h before samples were cut in half longitudinally, and sprayed with Heartwood/sapwood indicator "reddish color" and copper indicator "bluish color" (AWPA M2-07)(AWPA A3-08).



### 5.3 Results and Discussion

The moisture content of the samples after receiving the one hour steam cycle rose to roughly 20% (Figure 22). Raising the moisture content noticeably improved penetration compared to the samples previous moisture content in the range below 12 percent moisture. The explanation behind why the samples penetration improved could be for a few reasons, as in moving the resin, swelling the wood, and bringing the wood samples back to a higher EMC. The steam also made the resin that was plasticized it into a polymer that is not completely solid allowing the high pressure associated with treatment to move the solution where it was once blocked before.

The most likely explanation is that the steam creates swelling in the wood. The swelling of the samples means that all the checks, cracks, and defects in the wood would open larger than when the sample had a lower moisture content. The swelling would allow the solution to penetrate through the cracks and areas of the wood that were once smaller.

To aid the steaming Quat was used and also aided in improving penetration. Quat is used in soaps, in this case we were supplied with 47% Quat, but in soap applications the concentration is much lower, sometimes around 1%. The goal was to view if the Quat would break down the resins as soap does, to allow solution to penetrate deeper. After looking at samples like Figures 19 and 20, it is easy to see that the steaming and Quat are aiding in penetration, but more work needs to be done to view the maximum amount of Quat and temperature/ duration of steam creates the best penetration without degrading the wood.

However with steaming alone as Figure 21 indicated greatly improved penetration of MCA solution into samples. The question that we were left with was that was steaming alone

solely increasing the penetration or was the PE that we added increasing the penetration, or both. After viewing the uptake graph (Figure 23) we for the most part viewed higher average amounts of solution uptake in samples that were treated with PE and steam, but the observations made on Figure 21 indicate that the penetration is on par with PE and steam treated samples viewed in Figure 19. So with this in mind we aimed at observing if treating samples solely with PE's would in fact mimic what we saw in steamed samples with PE added or would the results differ.



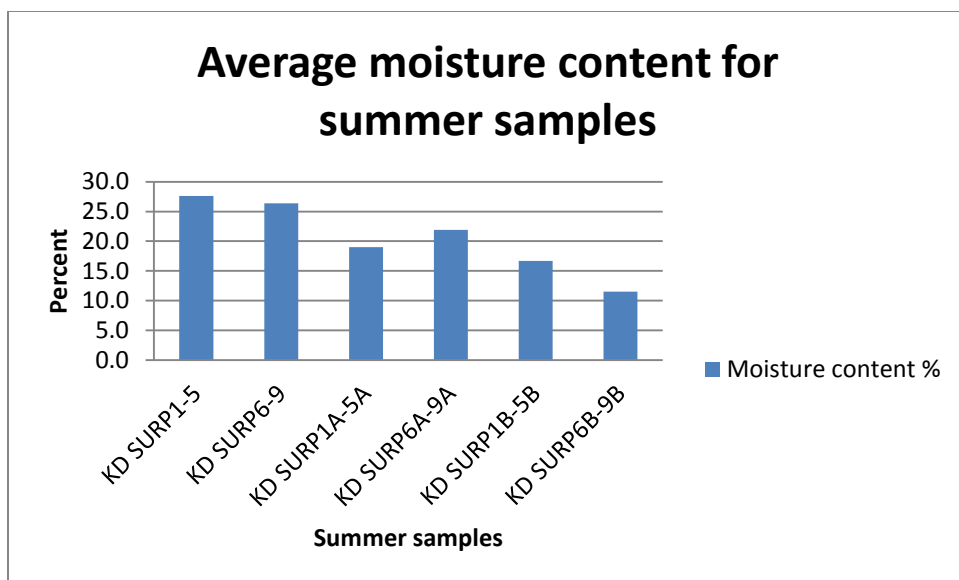
**Figure 19:** Kiln dried summer wood, which was subjected to 1 h of steaming and treated with MCA and Quat PE.



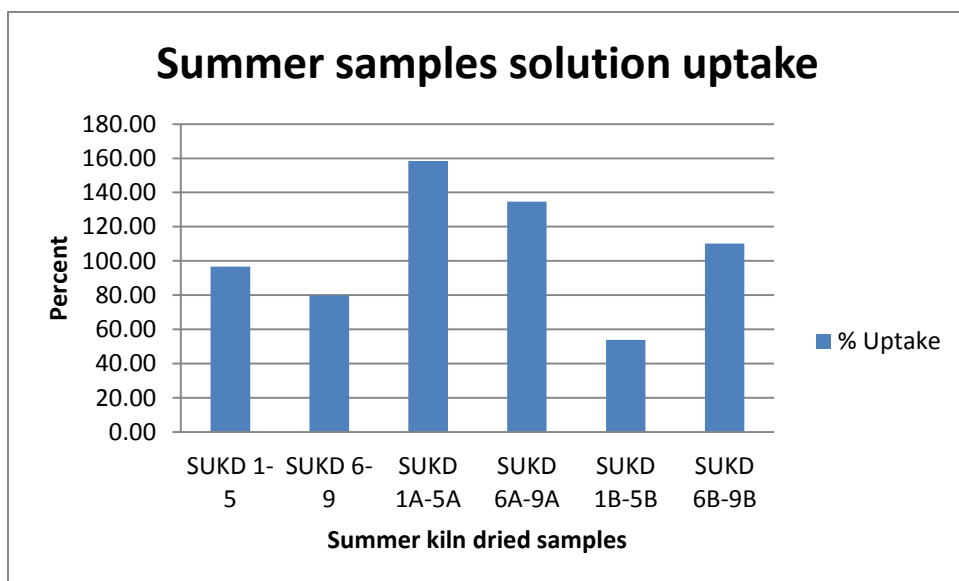
**Figure 20:** Kiln dried summer wood, which was subjected to 1 h of steaming and treated with MCA and Quat PE.



**Figure 21:** Kiln dried summer wood, which was subjected to 1 h of steaming, treated with MCA without Quat PE added.



**Figure 22:** Average moisture content of summer samples that were steamed for 1 h in autoclave.



**Figure 23:** Average amount of solution uptake in steamed summer samples.

## **Chapter 6**

### **Pressure treatment of fall and winter wood with penetration enhancers added**

#### **6.1 Introduction**

The goal of the fall and winter treatments was to experiment solely with penetration enhancing chemicals such as Quat and sodium phosphate. This was done due to not being able to experiment with drying standards and because an additive would be easy to implement into industrial practices if proved beneficial. Michigan winters can be very tough on all living organisms including trees, but with cold temperatures comes freezing, which helps preserve the moisture content when a tree is cut into logs, but increases drying times and sometimes temperatures. The winter can also be a trying time for chemical treatment companies because wood needs to be unfrozen to properly chemically treat. With the knowledge that fall and winter wood is usually the hardest to treat, due to lack of blue stain and higher drying temperatures, we wanted to continue using the Quat that aided in improving summer wood samples penetration. We also wanted to experiment with amine salts, due to the high cost of Quat to view if this PE would improve penetration, as Quat did in the summer samples.

#### **6.2 Materials and Methods**

##### **6.2.1 Wood samples**

Samples were gathered from Biewer Lumbers sawmill in Mcbain, MI. Winter and fall samples were picked up at the same time, in mid-December 2010. The fall samples were from late November 2010 and thus had been cut for 2 weeks, but due to the cold temperatures the wood was at near freezing conditions resulting in little moisture loss for the fall wood. Lumber was again procured according to the same methods as spring wood and frozen when cut to 17.5" lengths. The samples were then cut 24h prior to treatment to 16" lengths for treatment and end

sealed, which is why samples were cut 24h before due to epoxy setting time. Also at the time of cutting the samples a sample was taken and oven dried for moisture, as we did with previous treatments.

### **6.2.2 Penetration enhancer additives**

In the past treatments we looked at changing treatment parameters, but in some cases companies cannot change their parameters due to cost, which is why we aimed at penetration enhancers. After viewing the results from Quat and steaming the samples we wanted to see what Quat could do without steam. We also added sodium phosphates to our PE experiment as a more inexpensive option, if the salts did work. As stated earlier, Quat is an additive to soap, Quat is not breaks the resin down, it is a lubricant, due to the viscosity. The idea behind adding Quat is that it not only breaks down resins to allow deeper penetration but it also binds the resin acids that in many cases inhibits the copper from penetrating deeper. This is the reasoning behind the salts, is that the salts would perhaps aid in the binding or bonding with the resin acids that tend to filter out the copper. We believed that if we can add a chemical that will readily bond with the resin acids that the copper may be able to penetrate deeper than when there is no PE added.

### **6.2.3 Pressure treatment**

The duration did not change from the summer treatments; we decided to keep with 2 h duration, due to the results from summer treatments. The same 12" diameter tank pictured in Figure 11 was used. The pressure for all the treatments was in the area of 180 psi and the initial and final vacuum was in the area of 25"Hg. The biggest change was adding only PE for these treatments, since our MCA concentration of copper was still around 0.80% (0.799% actual). The Quat for all the fall and winter treatments was a concentration of 0.9% and the two different

concentrations of sodium phosphates were 0.0004 and 0.0008 percent concentrations. The PE was added before each treatment and thoroughly mixed using an electric mixer. Following treatment samples were weighed, and allowed to dry for 24 h before samples were cut in half longitudinally, and sprayed with heartwood/sapwood indicator “reddish color” and copper indicator “bluish color” (AWPA M2-07)(AWPA A3-08).

### **6.3 Results and Discussion**

To say the least we saw improvements over our original spring treatments. The Quat additive greatly improved observable penetration. We observed results similar to that of the summer treatments with steam added. Figure 24 and 25 indicate the quality of penetration that we could never achieve with only using MCA without additives or changes to drying. We still have a little ways to go to achieve perfect penetration, penetration better than 80 percent in sapwood. As far as the sodium phosphates, figure 27 indicates that we did see some improvements in penetration over some spring samples but more research needs to be done. Figures 26 and 27 indicate that by doubling the concentration we also saw better penetration. In looking at the increasing in penetration with concentration, perhaps if the concentration is increased penetration would also increase. The problem that we had was that time, funds, and the amount of the salt we had was limited due to this being a small trial. By looking at the moisture contents, (Figure 28) we see that the average moisture contents was around 15%, so we knew that we were in the moisture content that is optimal for treating, the problem was that the uptake (Figure 29) did not match the moisture content as what we saw in past treatments. This could be due to a number of reasons, heartwood, being the main cause. Heartwood being in the center of

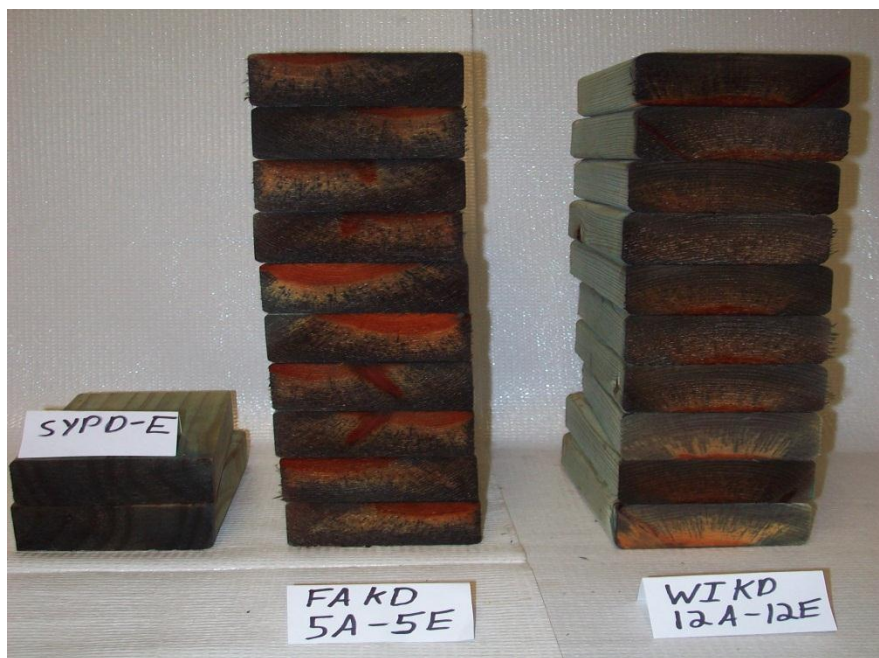
the tree is made up of thick walled cells, but is more prone to aspirated pits, which is why heartwood can be almost impossible to achieve any penetration at times. We do know that the sodium phosphates for the most part were not as successful at increasing penetration and uptake. We did view and increase in uptake with the increasing amount of salts added from 0.0004 to 0.0008 percent, which is positive.

However, we did not a large noticeable difference between the summer and winter and fall samples being for the most part above 80%. This means that the steam 1h steam and the concentration of PE could be increased to view an increase in penetration, or that PE alone may be that main factor in increasing penetration, which is why we decided to do a small study for the AWPA discussed in the next chapter. What we did achieve was an increase in penetration adding the PE, what we have not achieved in a “Home Run”, that is there still needs to be work done with steaming and PE concentrations.





**Figure 24:** Fall and winter kiln dried samples treated for 2 h with 0.5lbs Quat PE added to MCA solution.



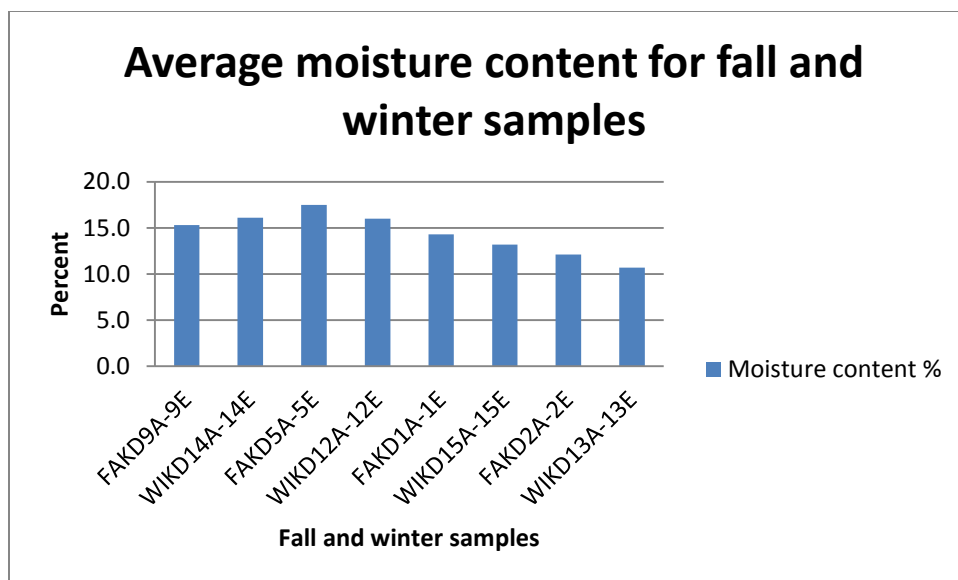
**Figure 25:** Fall and winter kiln dried samples treated for 2 h with 0.5lbs Quat PE added to MCA solution.



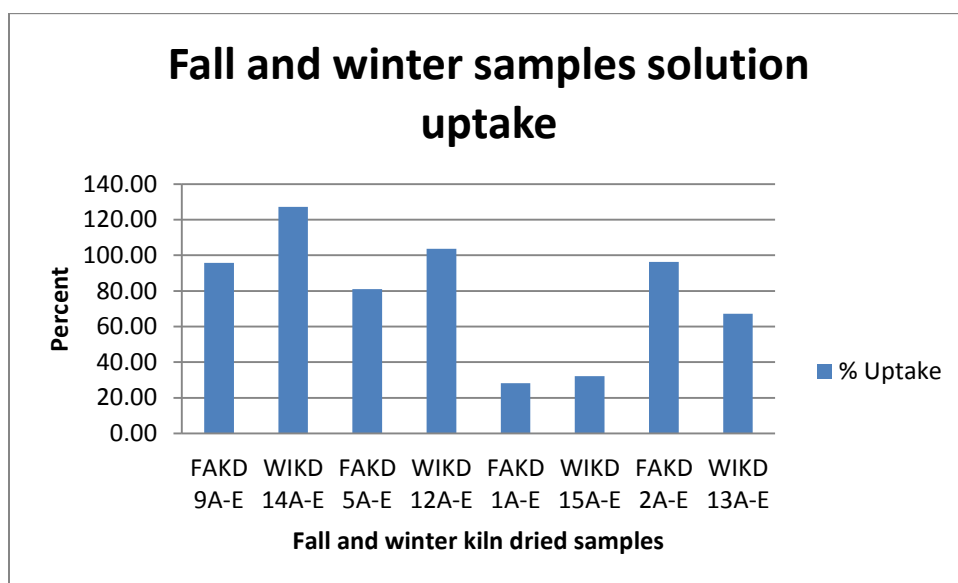
**Figure 26:** Fall and winter kiln dried samples treated for 2 h with 0.0004% Sodium phosphate PE added to MCA solution.



**Figure 27:** Fall and winter kiln dried samples treated for 2 h with 0.0008% Sodium phosphate PE added to MCA solution.



**Figure 28:** Average kiln dried fall and winter samples moisture contents.



**Figure 29:** Average fall and winter kiln dried samples solution uptake.

## **Chapter 7**

### **Pressure treating with MCA and DDAC penetration enhancer (AWPA)**

#### **7.1 Introduction**

The basis behind this mini study was to present that data for an AWPA poster competition. The overall reason though was to view if increasing the concentration of Quat (PE), in MCA would yield deeper penetration into out treated samples. We know that adding a PE helps with penetration but would more PE increase the penetration, this was the question we were out to prove, at least in a small experiment. The goal was to view 3 species southern pine, red pine and Jack pine, which are all species that are used in the lumber industry, especially the great lakes region. We knew that southern pine treated very well, usually better than 80 sapwood penetration, and we knew that Jack pine is extremely hard to treat due to the heartwood content the species is known for. That being said, red pine was our middle of the road species, treatable but can be troublesome at times.

#### **7.2 Materials and methods**

##### **7.2.1 Wood samples**

Wood samples were once again gathered from Biewer Lumbers sawmill in Mcbain, Michigan. The samples this time around were nominal 2"x6"x8' boards due to short notice on the study and samples being readily available in 2x6. Once samples were brought to Michigan State, East Lansing Michigan, the wood was cut into 17.5" lengths and frozen, due to treatment chemicals no being available. Once chemicals were available samples were thawed, and cut to 16" lengths and end sealed once again to mimic treating larger boards. Boards were cut and

numbered according to board as other treatments and in this case species were mixed for treatment because the goal was to view how increasing concentrations affected penetration in each species.

### **7.2.2 Quat additive**

We used the same 47% concentrations of Quaternary as before, to add to our MCA solutions in increasing strengths. The MCA solution had a 0.80% copper concentrations and Copper to azole ratio of 96:4. We treated our MCA only boards for 1,2, and 3 hours to have a basis as to how MCA treated wood does, using only MCA and increasing the duration as we did in the spring samples. Then we used the remaining samples from each board for our PE experiment. The concentrations were 5%, 1%, and 2% PE added to MCA.

### **7.2.3 Pressure treatment**

The treatment procedure mimicked all the other treatments that we did. We used the same green12” diameter treatment tank as the other treatments and filled that tank completely full. The biggest difference was that for non PE MCA treatments we increased our pressure treatment duration from 1h to 2h to 3h, for one to view the best treatment duration, and also to view how increasing duration, affects penetration. For the MCA with PE we kept the duration set at 2h, because from observations and past treatments 2h seemed to be equal or a little less than the 3h treatment, but the 3h treatment penetration increase was negligible in our view. The pressures were in the range of 25 in Hg for the initial and final vacuum, while the positive pressure was in the range of 180 psi. Following treatment samples were weighed, and allowed to dry for 24 h before samples were cut in half longitudinally, and sprayed with heartwood/sapwood indicator “reddish color” and copper indicator “bluish color” (AWPA M2-07)(AWPA A3-08).

### 7.3 Results and discussion

Even before this study from treating experience both industrially and experimentally we knew that southern pine would treat the best, in all cases, since there is less resin in southern pine than red pine, and southern pine has a record of treating well. With this in mind we treated southern pine with MCA and as Figure 30 illustrates we easily penetrated most if not all the sapwood in all three durations 1,2,and 3 h. Knowing this we knew that the PE would keep with this standard of quality penetration, which Figure 31 indicates better than satisfactory penetration. We did see a change however in uptake from MCA to MCA with PE, in fact we viewed an increase in uptake in samples treated with PE (Figures 36 and 37). Which can be good or bad, it is good that we are allowing more penetration of chemicals but bad due to increasing weight when MCA treated southern pine is already treating very well.

Next we treated Jack pine; the problem from the start is that Jack pine is notorious for high amounts of heartwood, which in the treatment world we know as almost being impervious to solution penetration. The problem was that the lumber we were given for the study had high amount of heartwood and even when sorting the lumber to better match the southern pine and red pine we were unable to find samples of only heartwood(Figures 32 and 33). What we did find was that we penetrated the sapwood and thus the wood samples would pass the AWP standard for penetrating 80% or more sapwood (Figures 32 and 33) (AWPA A3-08). The low numbers in the uptake of MCA with PE treatment was due to the high amount of sapwood (Figure 37). Plus, by looking at Figure 36 it is easy to view how heartwood affected penetration, in looking at how the samples boards differ in heartwood in Figure 32.

Since this study was all about red pine, we saved the most positive or influential improvements adding PE gained last. We not only viewed increases in penetration with increasing the amount of PE added we also viewed a higher and constant uptake from sample to samples in MCA with PE (Figure 36 and 37). This is due to the PE allowing improved penetration in all samples and also the samples having little to no heartwood. The most interesting data or observation was the with increasing the amount of PE from 0.5% to 2%, we also viewed an increase in penetration in both boards from left to right in Figure 35, MCA with PE added. This shows that indeed the Quaternary is aiding in penetration and breaking down the resins. The question for further studies will be how much PE should be added before we view decreases in perhaps structure or what is the maximum effective amount of PE that should be used to treat the sapwood of red pine or other species. We know that MCA alone does not always treat red pine well as Figure 34 indicates, and we also know that duration does help, in allowing the solution to penetrate deeper. The problem with treating red pine with MCA alone is that there is sporadic penetration meaning, it cannot be for the most part predicted, which results in problems for some chemical treatment companies and creates problems for quality control. MCA is a great treatment chemical that treats many species extremely well and is much friendlier for the environment; as far as red pine goes MCQ will perhaps be the micronized chemical for the future treatment of red pine, but time, treatment methods and additives will dictate this.





**Figure 30:** Southern pine samples treated with MCA. The top two samples of each column are of the same board as is the bottom two samples. Treatment duration is increasing from one hour to three hours from the left column to the right column.



**Figure 31:** Southern pine samples treated with MCA with PE added. The top two samples of each column are of the same board as is the bottom two samples. Treatment duration was set at 2 h with PE concentrations increasing from 0.5 %, 1 %, and 2 % from the left column to the right.





**Figure 32:** Jack pine samples treated with MCA. The top two samples of each column are of the same board as is the bottom two samples. Treatment duration is increasing from one hour to three hours from the left column to the right column.



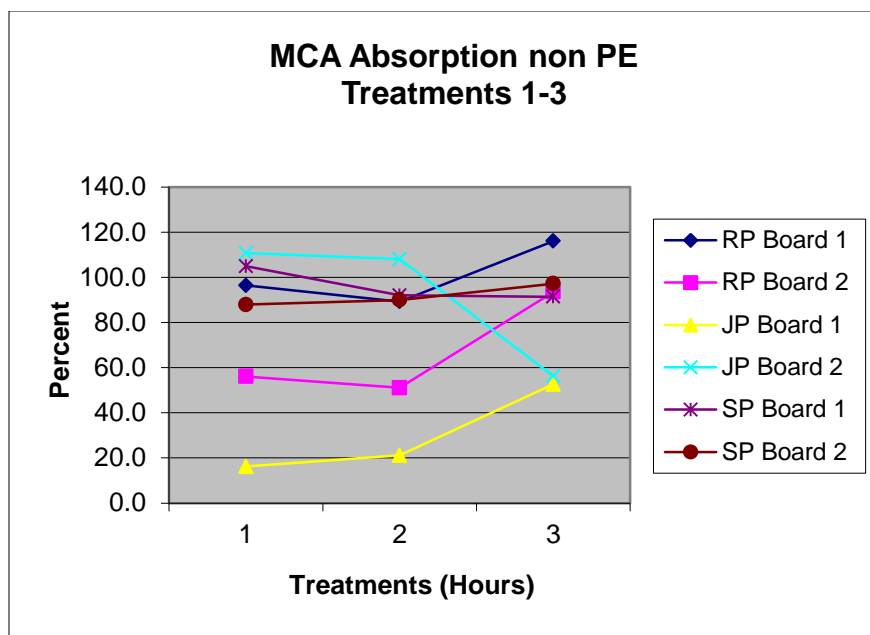
**Figure 33:** Jack pine samples treated with MCA with PE added. The top two samples of each column are of the same board as is the bottom two samples. Treatment duration was set at 2h with PE concentrations increasing from 0.5 %, 1 %, and 2 % from the left column to the right.



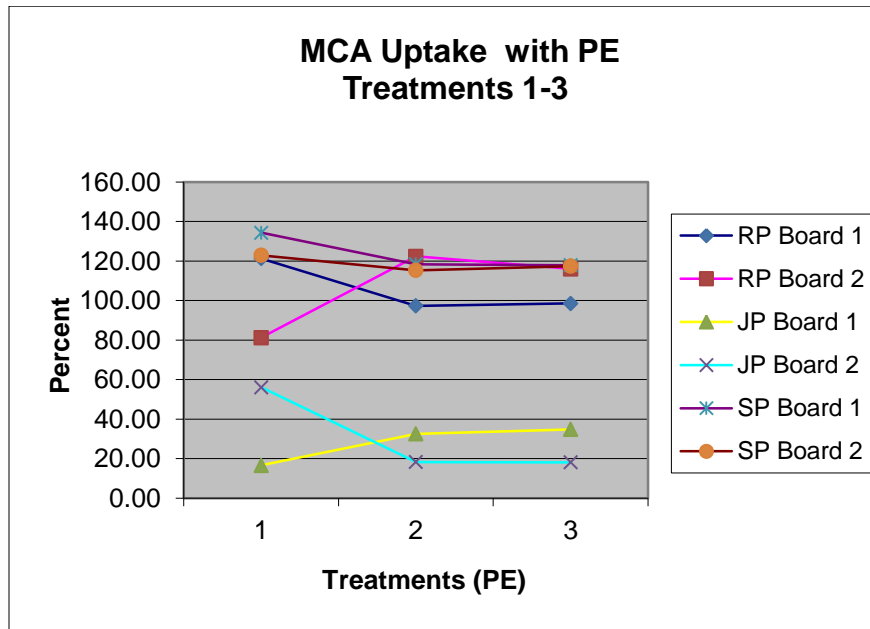
**Figure 34:** Red pine samples treated with MCA. The top two samples of each column are of the same board as is the bottom two samples. Treatment duration is increasing from one hour to three hours from the left column to the right column.



**Figure 35:** Red pine samples treated with MCA with PE added. The top two samples of each column are of the same board as is the bottom two samples. Treatment duration was set at 2 h with PE concentrations increasing from 0.5 %, 1 %, and 2 % from the left column to the right.



**Figure 36:** Absorption of pine species treated with MCA without PE. Board 1 indicates the top two samples in a column while board 2 indicated the bottom two samples in the above figures. RP = Red pine JP = Jack pine SP = Southern pine



**Figure 37:** Absorption of pine species treated with MCA with PE added, with two hour treatment time. Board 1 indicates the top two samples in a column while board 2 indicated the bottom two samples in the above figures. RP = Red pine JP = Jack pine SP = Southern pine

## Chapter 8

### Conclusion

Using CLSM and SEM microscopes we were able to view both open and closed pits. The images that we gathered did not show enough evidence on our part to know if what may be causing pit aspiration or why some pits appear aspirated while a row next to the aspirated pits appear to be non-aspirated. We learned that the CLSM is highly valuable in viewing samples that cannot be altered, but future SEM studies using other techniques may also be fruitful.

The spring treatments taught us that increasing the duration and refilling the tank half way through the pressure treatment may have yielded small increases in penetration but not the answer that we were looking for and not the solution to the industries problem. We found from all the treatments combined that 2h was the optimal treatment time. This time gave the solution proper time to penetrate and even an hour about 2h yielded little to no change in penetration. After treatment of all 4 seasons using various methods and chemicals, we did not observe definitive differences. This could be due to industry drying standards and it could also be due to the smaller scale of this study. We do know that blue stain greatly influences the ease of chemical treatment during the summer months, which is why some treatment companies may say that summer wood tends to treat easier. Secondly, the wood during the winter is frozen in certain parts of the Great Lakes Region, which in some instances causes the temperature and duration of kiln drying lumber to increase, thus placing causing higher differences in pressure/moisture in wood causing perhaps more aspirated pits. We believe the biggest opponent to increasing or decreasing penetration may be in the drying process, whether that be duration, temperature, or the final moisture of the wood upon exiting the kiln.

Chemical solutions may be the easiest way to influence changes in penetration. Our constant chemical throughout this experiment was MCA. MCA treats many species well mainly southern pine, where most in no all treated southern pine passed the AWP standard for sapwood penetration, but the problem is that every species is not the same even if they are in the same genus or family (AWPA, A3-08). MCA did treat some samples of red pine well but the treatments were not predictable, the entire basis of this study was to find a predictable treatment for red pine, on that the industry could use with confidence. Penetration enhancers gave us a partial answer to what the industry and what we were looking for. We found that PE increased our uptake and penetration, especially with increasing the amounts of PE added from 0.5% to 2.0%. The problem was that still in some samples PE did not give us the predictable and quality treatment that we wanted.

PE and steam was the best combination for treating red pine with MCA or MCQ that we found. The high temperature steam “around 200 °F” allowed the wood to swell which opened the wood and cells to allow the solution to penetrate. Steam and MCQ was our best combination for improving penetration because the steam moved and cracked the plasticized resin, while the Quaternary broke down the now penetrated resins allowing deeper penetration in most if not all treated samples. The combination of steam and MCQ gave us the combination that we had been looking for. It also was a partial solution that the industry was looking for since they also tried the MCQ after our increases observed in lab.

Steam however may be the magic wand if you will that the industry is looking for because any sample or piece of wood can be steamed and treated with any chemical a company desires. We observed that steam improved penetration with both MCA and MCQ, but steam could also be helpful in treating other species and could be used with other chemicals. Steam

also may allow sawmills to still use high temperature fast drying methods but allow treatment companies the ability now to penetrate woods such as red pine or Jack pine that were considered more difficult to treat.

Above all this research has opened up new methods to treat red pine. Companies have already adopted some of our treatment methods and ideas. The main goal of this research was to improve the penetration of red pine which we did. Though we improved the penetration, there is still room for improvements and further testing needs to be done. What this study has done is open the doors on treating red pine, we know that there are options now and it is a matter of time and funding to find the correct combinations to have red pine treatment perfection.

## LITERATURE CITED

## Literature Cited

- Anderson, M.K. and L.M. Moore. 2003. United States Department of Agriculture, plan guide: Red pine *Pinus resinosa*. USDA NRCS National Plant Data Center. Available at: <http://plants.usda.gov>
- ASTM Book of Standards. 2009. Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-Base Materials, West Conshohocken, PA  
Available at: <http://www.astm.org/search/standards-search.html?query=d4442-07&searchType=standards-full>
- AWPA Book of Standards. 2009. American Wood Protection Association. Birmingham, Alabama. Available at: [www.awpa.com/standards/updates.asp](http://www.awpa.com/standards/updates.asp)
- Barnes, B.V. and W.H. Warren, Jr. 1981 Michigan trees. The University of Michigan Press. Ann Arbor, Michigan.
- Barnes, B.V. and W.H. Warren, Jr. 2004. Michigan Trees: A guide to the trees of the Great Lakes Region. Revised and updated. The University of Michigan Press. Ann Arbor, Michigan. P. 92.
- Bowe, S., S. Hubbard, T. Mace, J. Koning, and J. Cummings Carlson. 2005. Blue Stain: is it coloring your bottom line red? DNR Publication and University of Wisconsin extension. Wisconsin.
- Bowyer, J.L., R. Shmulsky, and J.G. Haygreen. 2007. Forest Products and wood science. Fifth edition. Blackwell Publishing. Ames, Iowa.
- Dirr, M.A. 1990. Manual of woody landscape plants: their identification, ornamental, characteristics, culture, propagation, and uses. fourth edition. Stipes Publishing Co., Champaign, Illinois.
- Dute, R., D. Rabaey, J. Allison, & S. Jansen. 2010. Torus-bearing pit membranes in species of *Osmanthus*. International Association of Wood Anatomists Journal 31:217-226.
- Farrar, J.L. 1995. Trees of the northern United States and Canada. Iowa State University Press, Ames, Iowa.



- Frame, M. 2011. Center for advanced microscopy (CLSM).Michigan State University. East Lansing, Michigan.
- Freeman, M.H., T.F. Shupe, R.P. Vlosky, and H.M. Barnes. 2003. Past, present, and the future of the wood preservation industry. *Forest Products Journal*. Vol. 53, No. 10. pp. 8-15.
- Flegler, S.L., J.W. Heckman, and K.L. Klomparens. 1993.Scanning And Transmission Electron Microscopy An Introduction. Oxford University Press., Inc., New York, New York.
- Forest Products Laboratory. 1999. Wood handbook—Wood as an engineering material. Gen. Tech. Rep. FPL–GTR–113. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory. 463 p.
- Hoadley, B.R. 1990. Identifying wood: Accurate results with simple tools. First edition. The Taunton Press, Inc. Newtown, Connecticut.
- Hoadley, B.R. 1992. Understanding wood: a craftsman’s guide to wood technology. Eighth printing. The Taunton Press, Inc. Newtown, Connecticut.
- Jane, F., W, K. Wilson, and D.J.B. White. 1970. The structure of wood. Adam and Charles Black Publishers Ltd. London, England.
- Osmose, Inc. 1016 Everee Inn Road, Griffin, Georgia 30224
- Pilon, J., J. Bielecki, R. Doepker, F. Krist, and L. Pedersen. 2006. Guidelines for Michigan Red pine management based on ecosystem management principles for state forestland in Michigan. Michigan Department of Natural Resources statewide council.
- Sargent, C.S. 1961. Manual of the trees of North America. Vol. 1. Docer Publications, Inc., New York, New York.
- Siau, J.F. 1971. Flow in wood. First edition. Syracuse University Press. Syracuse, New York.
- Virginia Tech. 2009. *Pinus resinosa* Fact Sheet. Department of Forest Resources and Environmental Conservation. Available at:  
<http://www.cnr.vt.edu/DENDRO/DENDROLOGY/syllabus/factsheet.cfm?ID=110>
- Wang, J. Z. and R. DeGroot. 1996. Treatability and Durability of Heartwood. Available at: [www.reeis.usda.gov/web/crisprojectpages/219807.html](http://www.reeis.usda.gov/web/crisprojectpages/219807.html) (verified November 3, 2009)
- Zahora, A. 2011. Further studies of the distribution of copper in treated wood using an XRF microscope technique. Viance R&D Technology Center. Charlotte, North Carolina.