CWPA Proceedings, 2009, 130-141

CURRENT RESEARCH ON WOOD PRESERVATION – UNIVERSITY OF TORONTO

P. Cooper, T. Ung, M.-J. Lee, M. Nejad and G. Zhou
Faculty of Forestry, University of Toronto

Summary

Current research focus and results of studies on wood preservation at the Faculty of Forestry University of Toronto are discussed.

1. Introduction

Wood preservation research at the University of Toronto focuses on environmental impacts of treated wood over the product life cycle, with special emphasis on fixation of preservatives in wood, leaching losses of preservative components in service and management of wastes at the end of the product life cycle. This paper describes current or recently completed projects on ACQ component stabilization, analysis of preservative gradients in treated wood as affected by component, leaching and application of coatings, leaching of preservatives in laboratory tests and natural exposure and extraction of ACQ components from treated wood as a potential method of recycling this material.

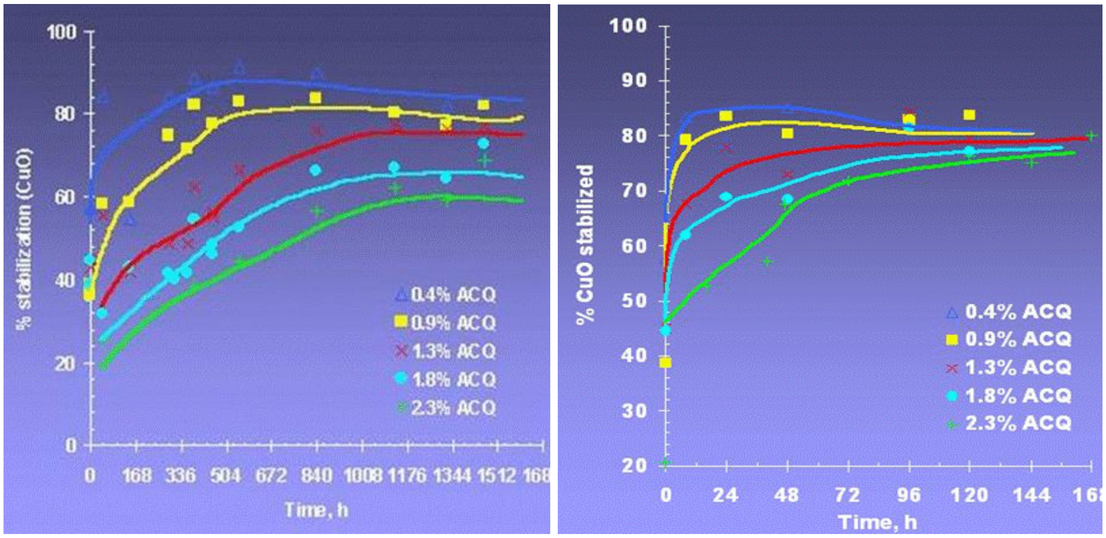
2. Methodology

For each study, methods will be briefly discussed with the results.

3. Results and discussion

3.1 Fixation or stabilization of ACQ

Stabilization of copper, quat and MEA were followed in red pine wood but monitoring the change of component concentration in free solution in wood with time of fixation under non drying conditions. Samples were squeezed at different times to determine the amount of component not yet reacted with wood and the amount fixed or stabilized was determined by comparing this with the original solution strength. A significant amount of copper reacts almost immediately with wood (Figure 1), which we attribute to ion-exchange adsorption to weak acid groups in wood. This is followed by a longer term, temperature-dependent reaction in wood which we attribute to precipitation reactions. It is clear that the rate and total amount stabilized is enhanced by exposing the wood to higher temperatures during fixation. It is also clear that the total proportion of copper stabilized is much higher with lower concentration treatments and the rate is significantly slower as the amount of preservative in the wood increases. As copper stabilization proceeds, the pH of the wood (or of the expressed solution) decreases (Figure 2) and this is believed to drive the precipitation reaction. We observe that the pH decrease is greater for higher temperature stabilization, which could explain the higher degree of stabilization at higher temperature especially for more concentrated solutions (Figure 1a vs 1b).



(a) (b)

Figure 1. Rate of stabilization of copper in ACQ as affected by solution concentration and temperature (a) 22°C; (b) 50°C

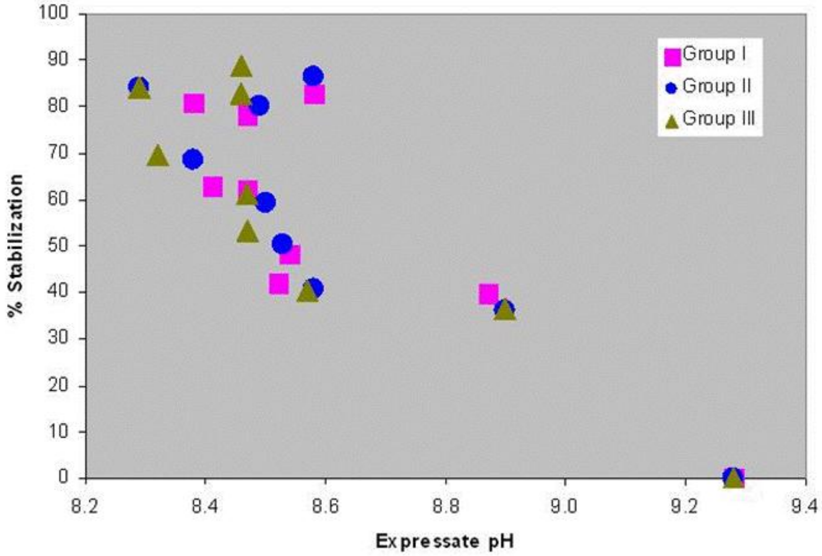


Figure 2. Change in pH of expressed solution as stabilization proceeds

This pH dependence on precipitation can be seen in Figure 3 for a number of solution formulations with varying ratios of Mea to copper acidified by nitric acid. For copper:Mea molar ratios = 1:3.6 (the normal ratio in ACQ treating solutions), precipitation in solution begins at about pH 8.5 and maximizes at about pH 7.5. If higher proportions of Mea are used in the solution, the precipitation begins at a lower pH and is not as complete.

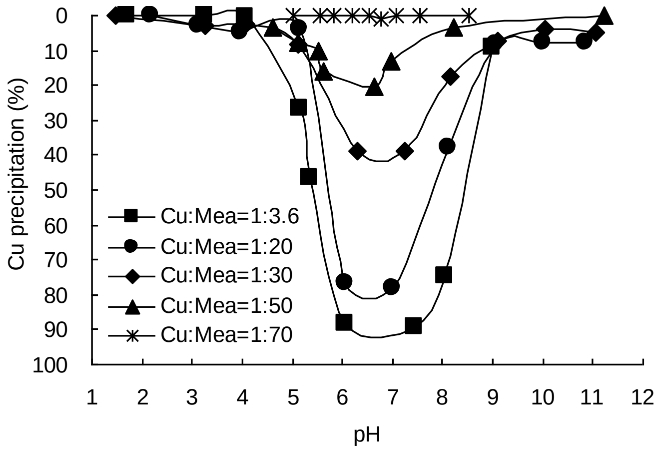
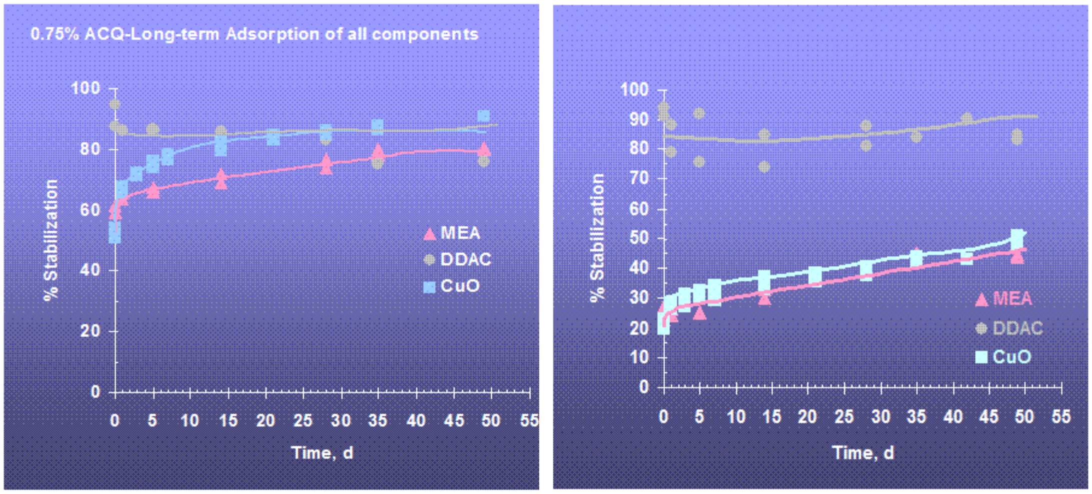


Figure 3. Percent Cu precipitation as affected by Cu to Mea ratios for Cu-Mea solution

When all three components of ACQ are considered (Figure 4) it is clear that the quaternary ammonium compound (DDAC) is rapidly stabilized to a relatively high degree. Copper and Mea appear to co-react in a similar way; as noted above, the degree and rate of reaction are much lower for the higher wood retention.



(a) (b)

Figure 4. Rates of stabilization of three ACQ components, Cu, DDAC and Mea (a) wood treated with 0.75% ACQ solution; (b) 2.25% ACQ solution

Wood is weakly acidic in nature having weal acid groups that dissociate between pH 2 and 6 (carboxylic acid groups in hemicelluloses and pectins) and between 8 and 12 (phenol hydroxyl groups of lignin). These groups, if dissociated can ion exchange cationic ions or complex ions. The capacity to adsorb cations (cation exchange capacity – CEC) is expressed here in millimoles/g wood. To study the adsorption mechanism of ACQ components in red pine wood in relation to the CEC of wood, the Na^+ CEC was determined by exposing wood dust to solutions of NaOH adjusted to different pH values with nitric acid. The relationship between adsorption and pH is shown in Figure 5. CEC increased to pH 6, then leveled slightly (carboxlic acids) then increased again to about pH 12 as phenolic groups were exposed.

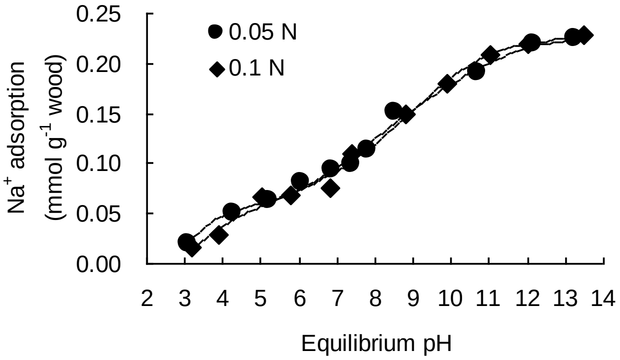


Figure 5. Cation exchange capacity of red pine dust for sodium (Na^+) from $NaOH/HNO_3$ solutions (0.05 N and 0.1 N) as a function of pH

When wood was exposed to Cu-Mea solutions, the copper adsorption followed the CEC curve when the commercial ratio of Cu:Mea = 1:3.6 was used. However, only a narrow pH range could be investigated due to precipitation as pH approached 8. When higher ratios of Mea were evaluated to extend the pH range, copper adsorption decreased at higher pH's (Figure 6). While we are still exploring this effect, we observed that Mea itself (which is protonated or cationic at moderate to low pH's) also adsorbed to wood in close relationship to the CEC of wood (Figure 7). It is possible that under conditions of high Mea content, there is competition for the sites from Mea. Another factor is that at higher pH and Mea content, the proportion of uncharged CuMea complexes increases and if they predominate, the adsorption to wood is decreased.

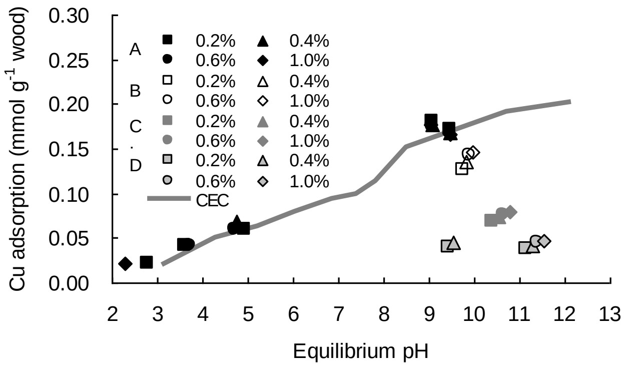


Figure 6. Chemisorption of Cu from different Mea ratios of Cu-Mea in red pine dust and comparison with CEC of red pine. *Note*: In the figure legend A is 1:3.7, B is 1:5, C is 1:10, and D is 1:30 Cu:Mea molar ratio

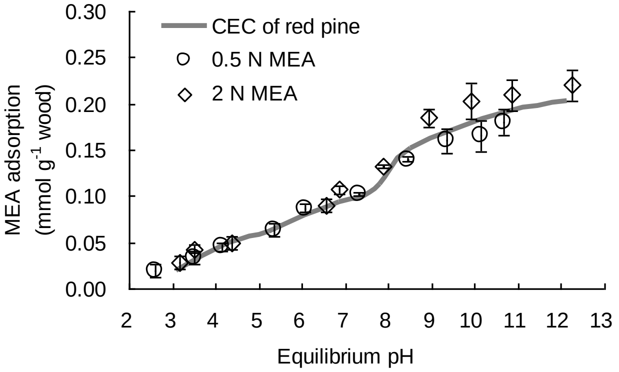


Figure 7. Comparison of Mea adsorption on red pine dust to CEC of red pine dust

The adsorption of quat ADBAC on wood was evaluated at pH 9.5, the normal condition in ACQ treating solution. In this case, the concentration was varied so a sorption isotherm could be developed. After simple washing and without extensive leaching, the ADBAC adsorption was similar to the CEC when exposed to lower quat concentrations, but greatly exceeded the CEC at higher solution concentrations. However, after extensive washing, the levels of retained ADBAC were slightly below the CEC. Quats form aggregates of molecules in solution (micelles) above the critical micelle concentration (CMC) which is lower than typical concentrations in ACQ solutions. Similarly, quats can adsorb on surfaces in two dimensional aggregates,(hemi-micelles) and we propose that this allows the amount adsorbed to exceed the CEC and furthermore, that these aggregates are less stable to leaching and break up leaving a single quat ion adsorbed when exposed to extensive leaching.

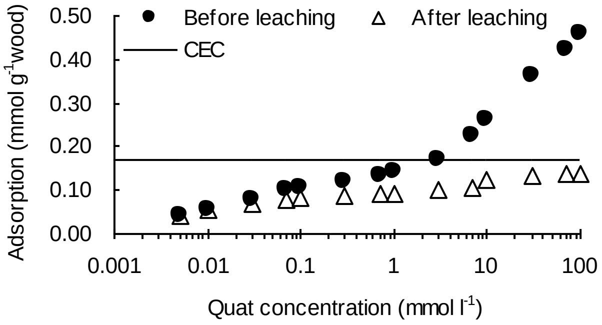


Figure 8. ADBAC adsorption on red pine dust before and after leaching

When copper and quat were exposed to the same wood sample (copper content of the solution was maintained constant at 0.4%), the amount of copper adsorbed declines as the amount of quat adsorbed increase (Figure 9). In fact, the sum of the two components adsorbed was close to the CEC at that pH.

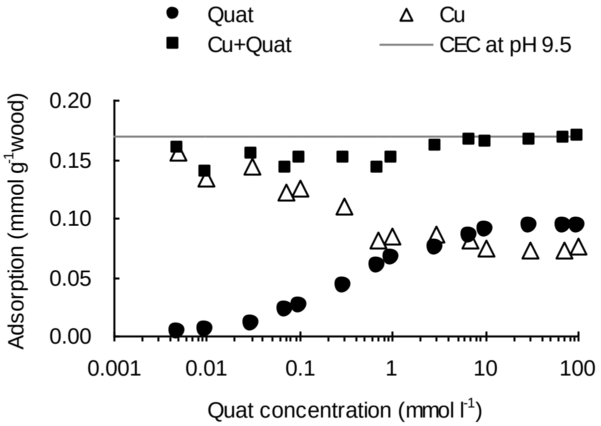
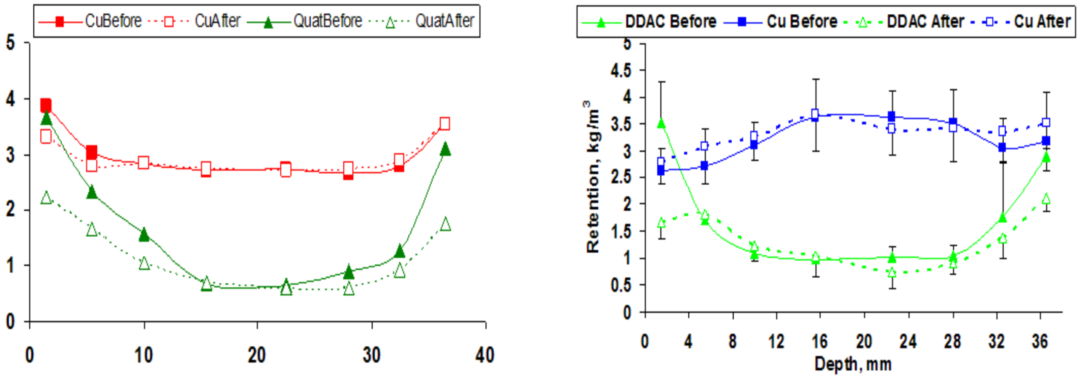


Figure 9. Effect of competition between ADBAC and Cu on equilibrium adsorption of quat at pH 9.5 (a) before leaching (b) after leaching (10 mmol l^{-1} = 0.35 % ADBAC and 0.1 mmol g^{-1} wood = 35 mg g^{-1} wood = 0.64 % Cu and 3.5% ADBAC)

These results suggest that the adsorption of ACQ components is strongly related to the weak acid groups in wood (the CEC) and can all compete for the same sites under certain conditions.

3.2 Preservative gradients in treated wood

Since copper and quats of ACQ are both adsorbed to the same sites in wood and quat reacts more quickly and to a higher degree than copper, we expect a significant concentration gradient of both in treated wood, but especially of quat. The copper of micronized systems on the other hand does not react with the wood but we might expect a steep concentration gradient because of screening of the micronized particles as it penetrates the wood structure. 2X6 (38 X 140mm) southern pine treated with ACQ-D and micronized copper quat (MCQ) were exposed horizontally out of doors for approximately 12 months (summer, spring, summer, fall). The samples, leached and unleached were cut in depth layers and the layers analyzed for copper and quat (Figure 10). For ACQ, the copper component was at a higher concentration near the surface. The micronized copper on the other hand was uniform across the section, except for slight depletion near the surface, which we attribute to the fact that the wood was treated with a modified full cell process with a long final vacuum that may have removed copper from the surface. In both formulations, the quat component had a very steep concentration gradient; its average concentration in the outer 3mm was similar to that of copper even though the solution has much higher copper concentration compared to quat. After leaching the copper losses were low (determined by leachate analysis to be about 2.9% for Cu in ACQ and 0.4% for Cu in MCQ). However, the quat component was extensively leached from the surface in both cases (16-20% loss).



(a) (b)

Figure 10. Comparison of copper and quat (DDAC) gradients in southern pine 2 X 6" before and after leaching for ACQ (a) and MCQ (b)

The gradient is highly dependent on the wood species. MCQ gradients in incised lodgepole pine is very steep and similar for both the copper and quat components (Figure 11). In 19mm southern pine samples treated with ACQ and exposed to natural weathering for 3 years, samples protected with a penetrating stain had much lower depletion of copper and quat from the surface compared to uncoated samples (Figure 12)

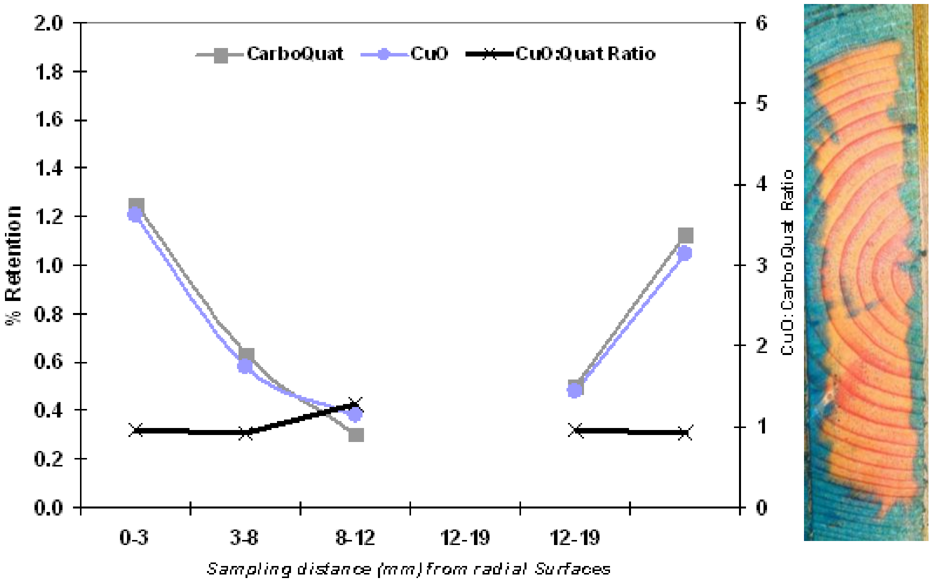
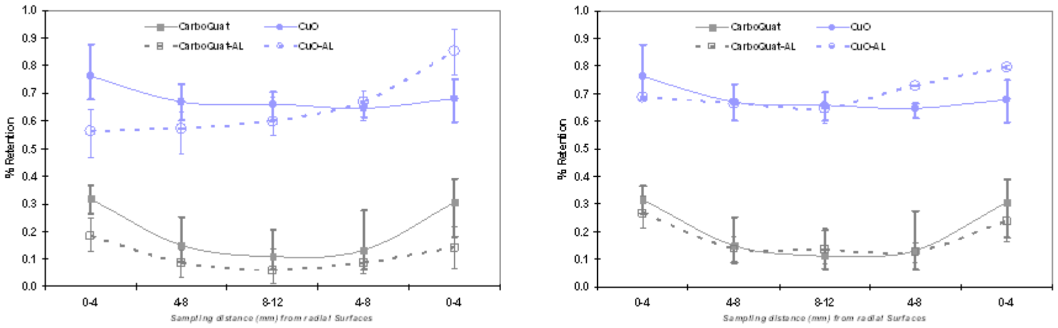


Figure 11. Comparison of copper and quat (DDAC) gradients in incised lodgepole pine



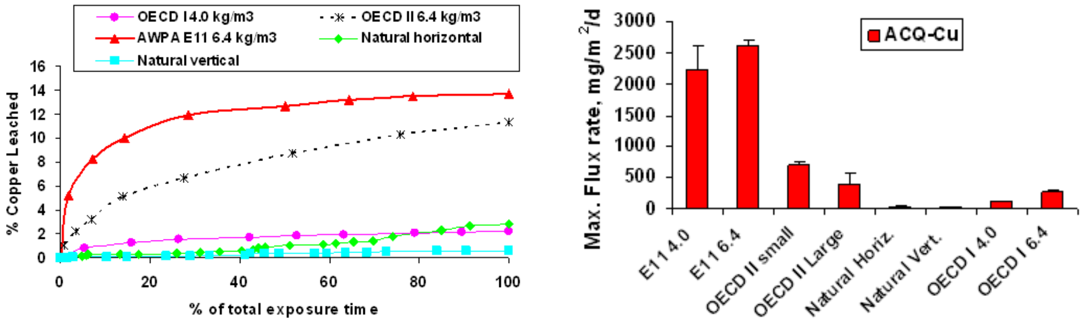
(a) (b)

Figure 12. Comparison of copper and quat (DDAC) gradients in 19mm ACQ-treated southern pine exposed to 3 years weathering (a) uncoated (b) penetrating stain

3.3 Preservative leaching

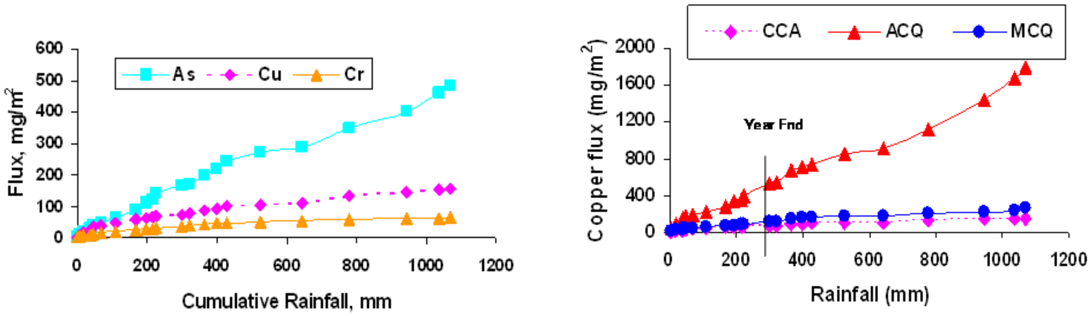
Wood samples treated with CCA, ACQ and MCQ were evaluated for leaching characteristics by a number of laboratory tests and horizontal and vertical natural exposure tests (Figure 13). Leaching parameters were much higher for small scale laboratory testing as expected (Figure 14). For natural weathering exposure, copper leaching was lower for CCA and MCQ compared to ACQ (Figure 15).

Figure 14. Horizontal and vertical configuration of samples exposed to 12 months natural weathering



(a) **(b)**

Figure 15. Comparison of leaching parameters among test protocols (a) % leached over the test duration (b) maximum rate of release during the test (mg/m^2/day)



(a) (b)

Figure 16. Comparison of component leaching during exterior horizontal exposure (a) CCA (b) Copper in CCA, ACQ and MCQ

3.4 Evaluating of penetrating stains on wood

Five commercial stains were evaluated for their effects on preservative leaching and other performance properties on southern pine wood. Surface analysis techniques were used to quantify film layer thickness and checking development on weathered surfaces (Figure 15). Coating film thickness varied significantly from stain to stain and this affected performance such as leaching characteristics.

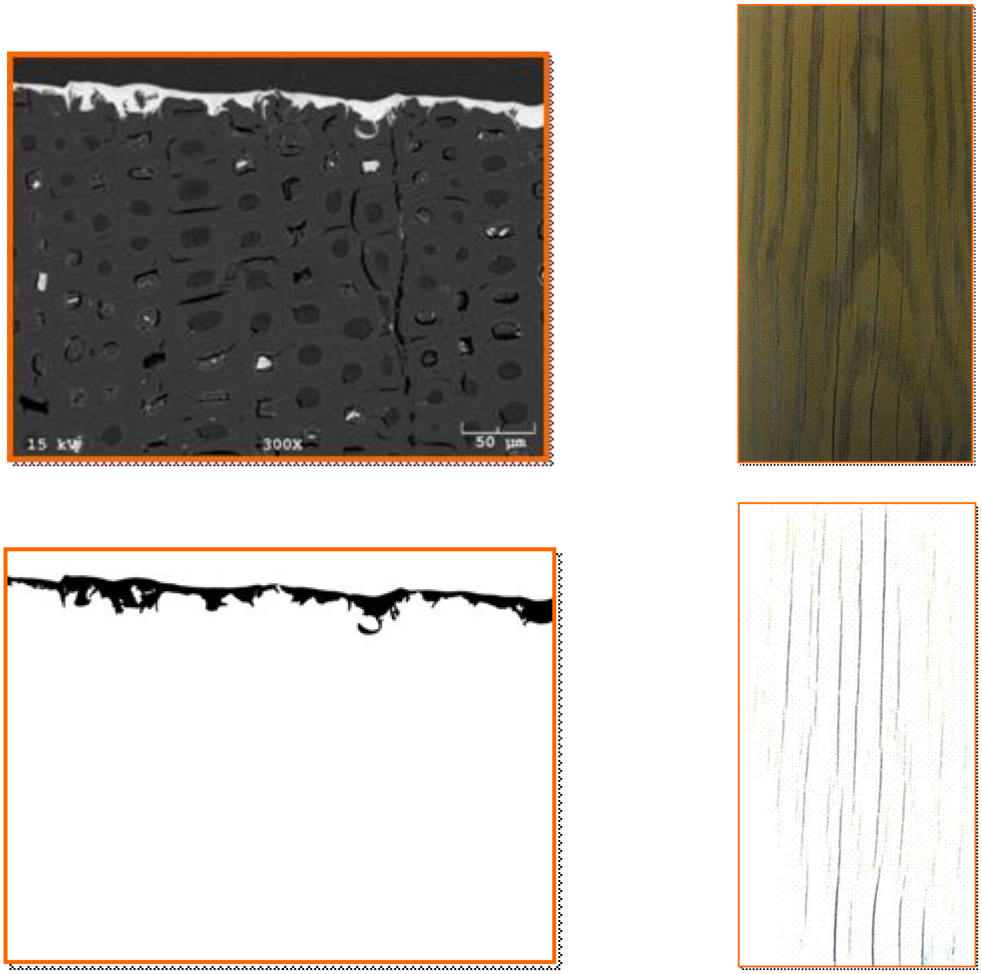
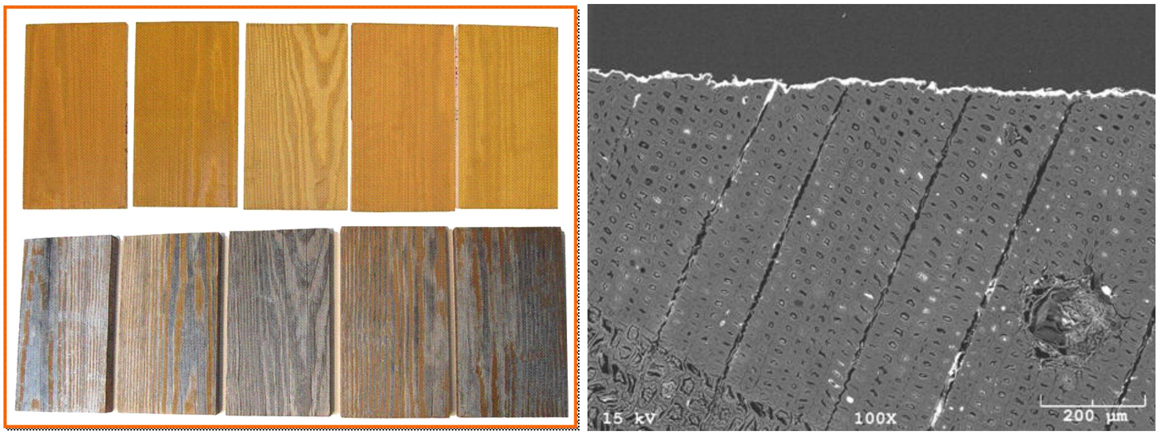


Figure 15. Quantification of film thickness and checking on coated samples by image analysis

After 3 years weathering, the coatings were significantly degraded (Figure 16a). Flat sawn boards developed fine checks along the rays (Figure16b).



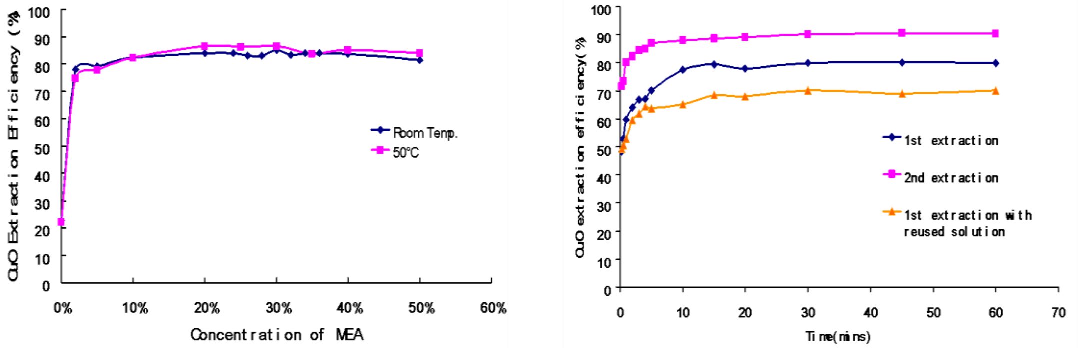
(a) (b)

Figure 16: (a) appearance of samples before and after 3 years natural exposure (b) section of coated sample after 3 years weathering

3.5 Extraction of preservative components for recycling

In a collaborative project with INRS (Quebec) we are investigating the extraction of spent CCA-treated wood with sulfuric acid as a low cost efficient process. The study also investigates recovery of metals and composting etc. of wood residue. Another approach is to extract components for reuse as treating solution, for example oxidation of CCA treated wood (CrVI) and use of monoethanolamine (Mea) for copper amine based preservatives. In both cases, the extracted solution should be reusable for treating wood. Some preliminary results of Mea extraction of ACQ treated wood are shown in Figure 17. Extraction of copper by Mea is as effective at room temperature as at 50°C and independent of Mea concentration (Figure 17a). Repeated extractions improve the extraction and extracting solutions can be reused (Figure 17b).

Mea also effectively extracted the quat component (Figure 19) as long as repeated extractions are applied.



(a) (b)

Figure 17. Mea extraction of copper from ACQ treated wood (a) effect of T and [C] (b) effect of repeated extractions and reuse of solution.

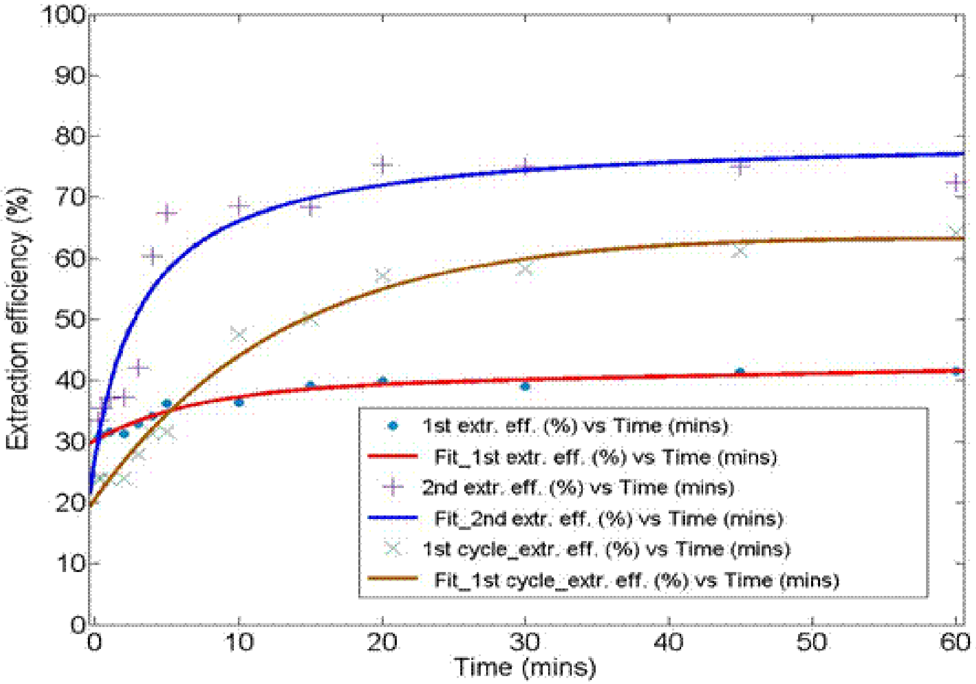


Figure 18. Mea extraction of quat from ACQ treated wood as affected by repeated extractions and reuse of solution.

4. Acknowledgements

We appreciate the funding support for the described work from NSERC, NRCan (Value to Wood) and Timber Specialties Ltd. and the technical support and advice from Paul Morris of FPInnovations and colleagues at INRS.