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Post treatment conditioning- fixation of CCA

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Introduction

The fixation of chromated copper arsenate (CCA) wood preservative has become an important issue in the operation of treating plants for a number of reasons:

- It is recognised that in the period before all hexavalent chromium (CrVI) in the treating solution injected into wood has been reduced to trivalent chromium (fixed) there is potential for toxic CrVI to move beyond the treating plant boundaries in surface water or ground water. There is also a potential for higher arsenic and copper losses during this period. Fresh treated unfixed wood will also transfer dislodged CrVI and arsenic from the treated wood onto clothing and bare skin of workers, increasing the health risks if handled before fixation is complete.
- The most recent Technical Recommendation Documents - TRD's (Brudermann 1999) recommend that CCA treated wood be tested and determined to be fixed before it is released from unprotected storage;
- In Response to the Strategic Options Process (1999) recommendations on procedures to reduce emissions of CEPA toxic substances – arsenic and hexavalent chromium, the Canadian wood treating industry has agreed to implement the TRD recommendations within 5 years. This implementation includes the recommendation concerning fixation.

The purpose of this paper is to review the important issues around the fixation of CCA at treating plants.

What is CCA fixation?

As soon as the preservative solution is forced into wood, the preservative components (chromium trioxide, copper oxide and arsenic pentoxide) undergo chemical reactions that render them highly insoluble in the wood matrix. The chromium trioxide (chromic acid in solution) drives the fixation process, mainly by its reduction to trivalent chromium, which forms low solubility compounds with arsenic and possibly copper in the wood. During this process, it oxidizes some wood components and causes the pH of the system to rise, assisting the deposition of insoluble compounds and the fixation of copper. These reactions are spontaneous and will occur under all ambient conditions ***EXCEPT,*** when the wood is allowed to dry out completely before the reactions are complete. However, the rates of these reactions decrease greatly as the wood temperature drops.

The speed at which these chemical reactions occur depends on many variables, as discussed below. However, the reaction rate is characterised by a fast "initial" reaction, which renders about 50% of the CCA components unavailable within a few hours. This is followed by a slower "main" reaction period which slows as it nears completion, following first order reaction kinetics, similar to radioactive decay curves (Figure 1).

Another common feature of CCA fixation is that the hexavalent chromium reaction takes much longer to complete than the fixation of copper and arsenic (Figure 1).

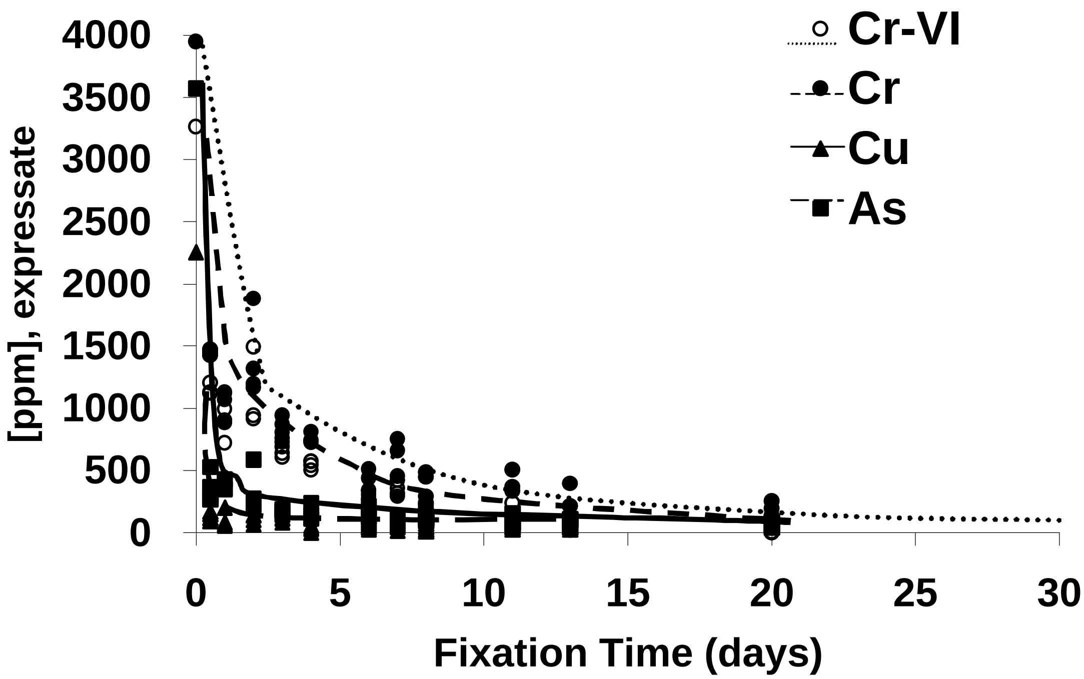


Figure 1: Rate of reaction of CCA components

How is CCA fixation monitored?

Because chromium is the last component to be stabilized in treated wood and because it is easy to detect and quantify, most procedures for estimating the extent of CCA fixation analyse for CrVI. The most common procedure cited in AWPA, CSA and the TRD documents is the chromotropic acid test method (AWPA A3/11). This is a spot test that detects very low levels of unreduced chromium. When a drop of chromotropic acid reagent is placed on a core sample or splinter of treated wood, unreduced chromium reacts to give a purple colour at levels of 15 - 50 ppm chromium, corresponding to a chromium fixation status of more than 99 % (Figure 2). More quantitative test procedures have also been developed (e.g. Cooper and Ung 1993) that allow a more accurate estimation of the degree of fixation at any time following treatment. For this procedure, treated borings are placed in a fixed volume of dilute sulfuric acid and diphenylcarbazide reagent is added to develop a purple colour with intensity proportional to the amount of hexavalent chromium. This can be quantified in a visible light spectrometer and the concentration related to the degree of fixation (Figure 3).

Fig. 2: Chromotropic Acid Spot Test for CrVI

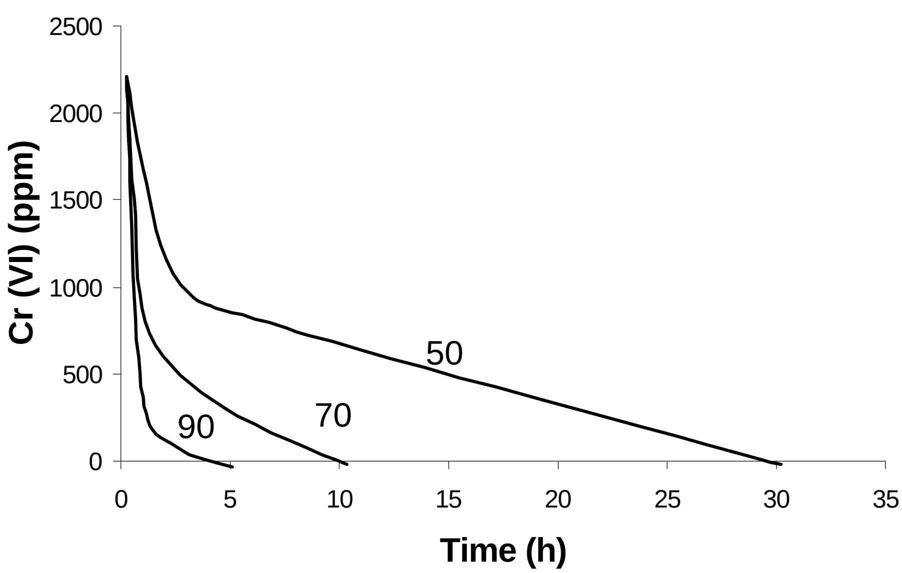
Fig. 3: Quantitative analysis of CrVI

What variables affect CCA fixation?

Wood Temperature

The rate of chromium reduction depends greatly on the wood temperature. At normal summer temperatures, pine species typically require 10-20 days for complete chromium reduction. The time to complete chromium fixation doubles for each decrease in wood temperature of about 7°C (12.5°F). Fixation time can be greatly reduced by subjecting treated wood to high temperature/high humidity fixation conditions in a dry kiln or fixation chamber as seen in Figure 4.

Figure 4: Effect of wood temperature on chromium fixation rate



Wood Moisture content – Drying during fixation

If wood is allowed to dry during the fixation process, the evaporating water reduces the wood temperature to the wet bulb temperature of the atmosphere, significantly retarding the rate of fixation. If wood is allowed to dry to below fibre saturation point moisture content (about 25%) as might occur with shallowly treated spruce or jack pine, the fixation process may be impaired even more (Figure 5). This typically results in high potential for chromium leaching in service.

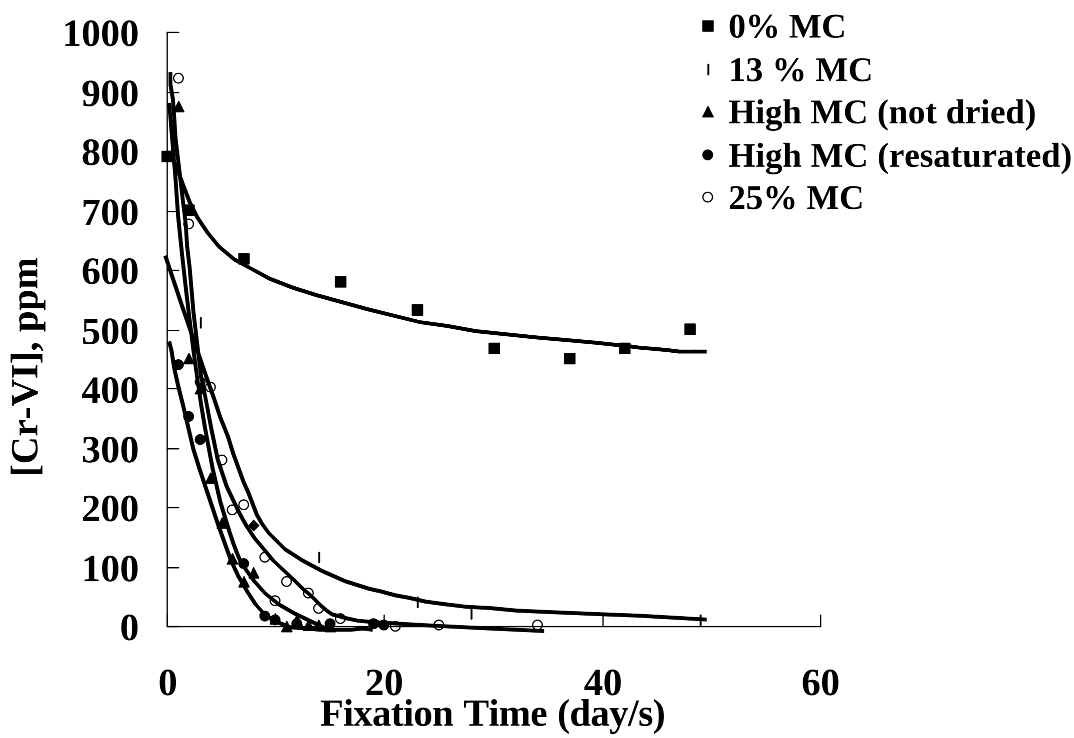


Figure 5: Effect of wood moisture content on chromium fixation

IT IS ESSENTIAL THAT DRYING OF WOOD DURING FIXATION BE MINIMIZED!

Achieving "surface dry" material should only be a goal after the chromium reduction reactions are complete.

Wood species and sapwood/heartwood

The chemical components and especially extractives vary significantly among wood species and between sapwood and heartwood. Also, wood density varies greatly. Both density and chemical composition of wood have large effects on the rate at which chromium is reduced in wood. Generally, dense species, such as maple, oak and beech have rapid rates of chromium fixation as seen in Figure 6, while low density hardwoods such as aspen and basswood fix slowly. Generally, woods with rapid fixation rates have poor quality arsenic fixation as seen in Figure 7.

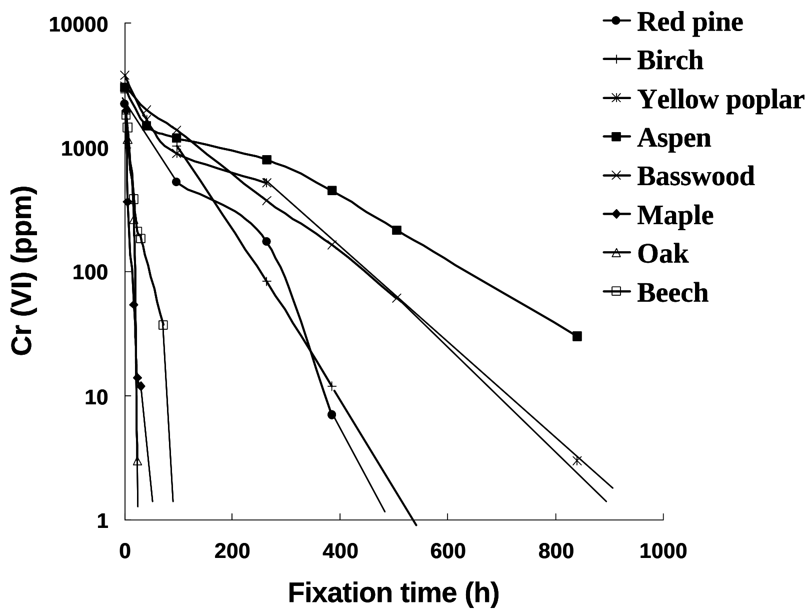


Figure 7: Effect of wood species on rate of chromium fixation at 21°C (Stevanovic-Janezic et al (2000)

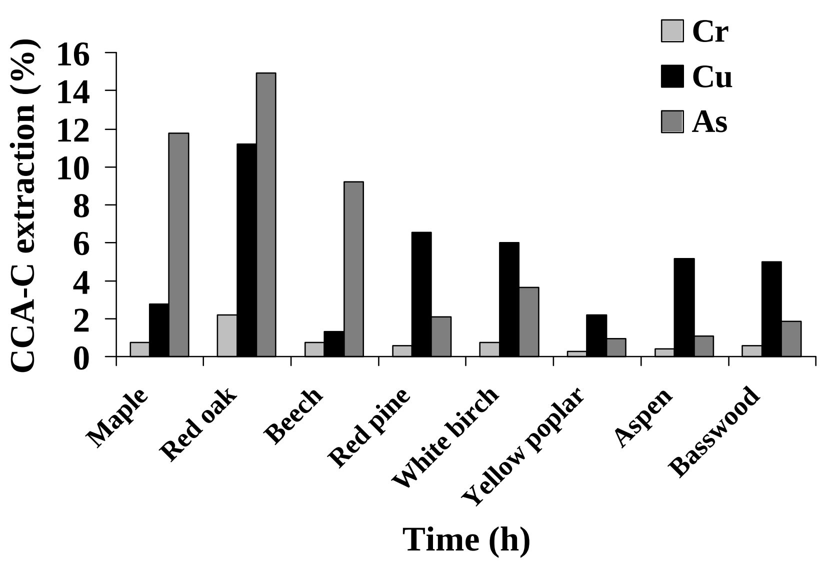


Figure 8: Relative leaching of CCA components from different species (AWPA E11 leaching test) Stevanovic-Janezic et al (2001)

There are differences in fixation rates among softwood species as well, as shown in Figure 8. In most species, chromium is reduced faster in heartwood than in sapwood (Figures 8 and 9).

CCA solution concentration (retention in wood)
Chromium reduction or fixation is greatly retarded when high concentration CCA treating solutions are used.

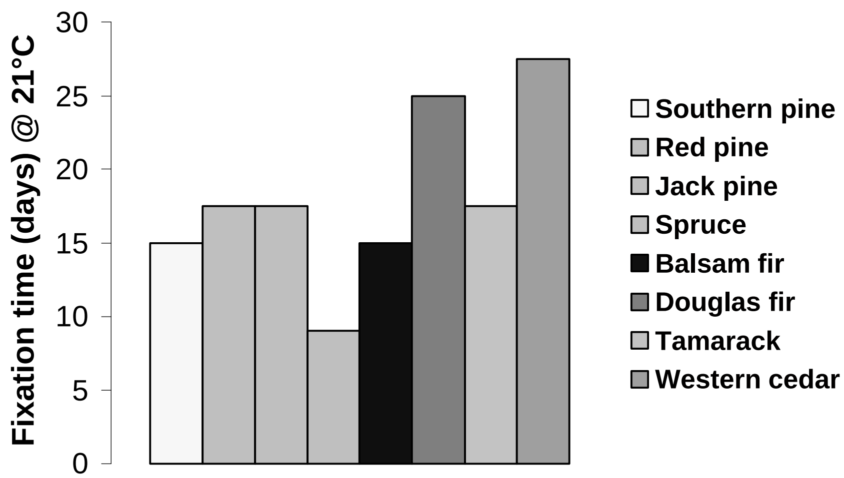


Figure 8: CCA fixation rate at 21°C in sapwood of several softwood species

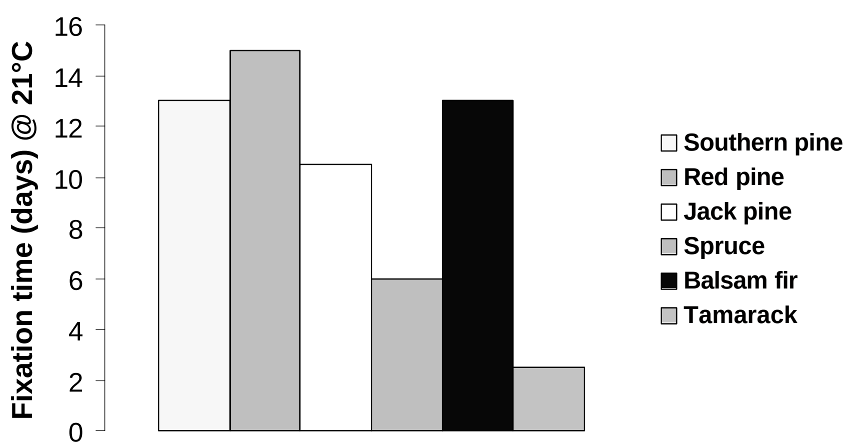


Figure 9: CCA fixation rate at 21°C in heartwood of several softwood species

What are the implications of producing incompletely fixed wood?

The CCA components remain more available for leaching and dislodging until fixation is complete. As stated above, chromium is the last component to stabilize in wood. Thus. chromium (hexavalent) remains available for leaching (Figure 10) much longer than arsenic (Figure 11) and copper. A high degree of chromium reduction is needed to avoid significant leaching of CrVI. Generally high temperature fixation results in fast chromium reduction on the surface so the effect is less critical for high T fixation, as seen in Figure 10.

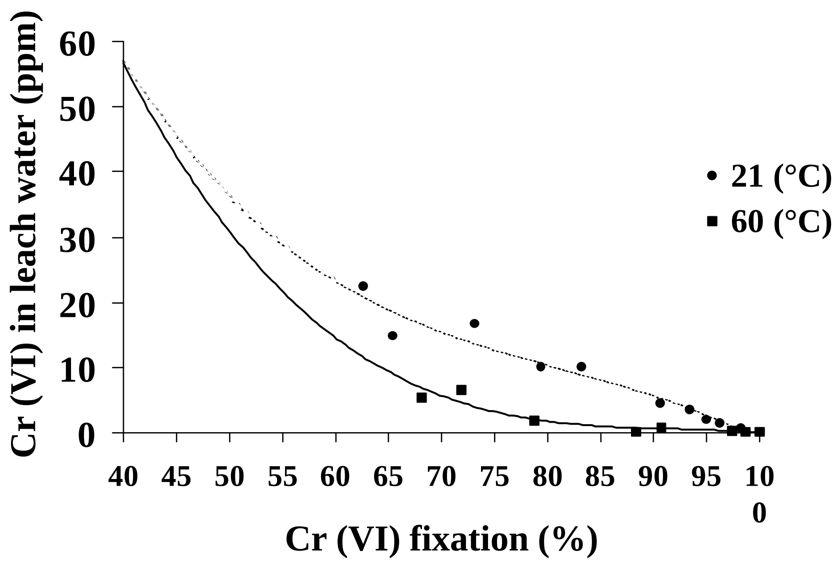


Figure 10: Relative leaching of hexavalent chromium at different stages of chromium fixation (Cooper et al 1996)

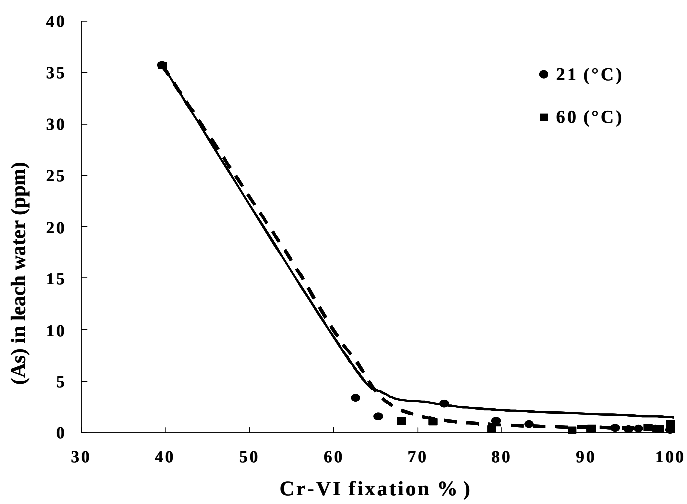


Figure 11: Relative leaching of arsenic at different stages of chromium fixation (Cooper et al 1996)

The surface dislodgeability of CCA components from incompletely fixed wood follows a different pattern. The amounts dislodged by a kimwipe wipe test on wet wood is shown in Figure 12. The arsenic and copper levels reach a constant value at 70 – 80 % chromium fixation, as observed above for leaching, while chromium dislodged levels drop to very low values while there are still large amounts of unreduced chromium in the wood. It appears that the surface fixation of the chromium is very high, resulting in little available hexavalent chromium on the surface even though levels are high inside the wood.

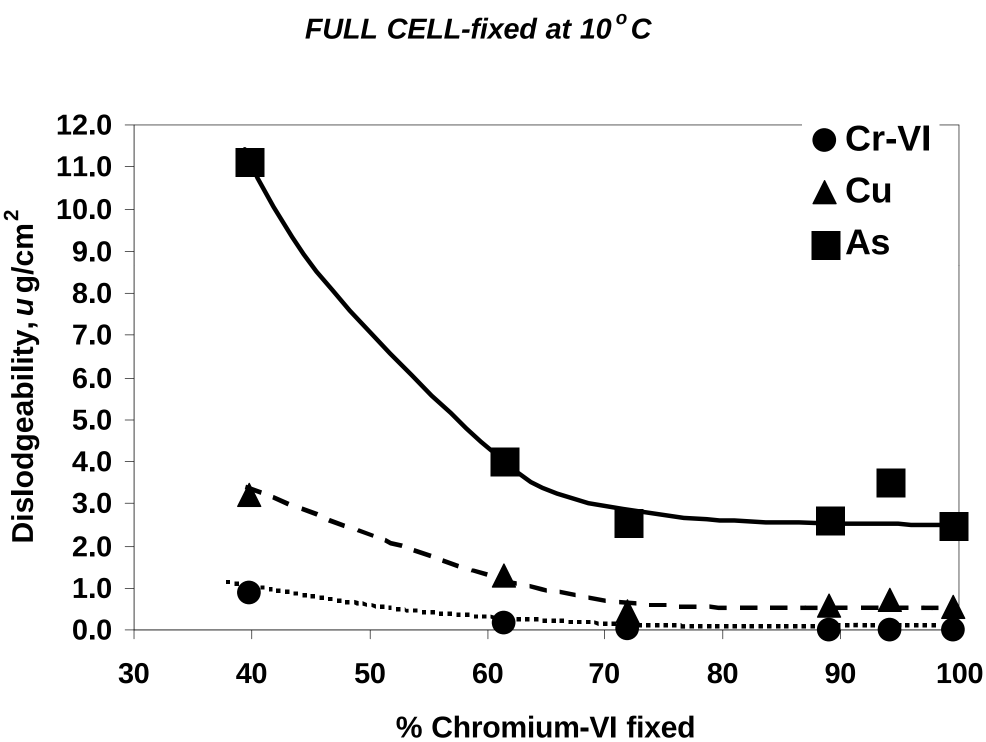


Figure 12: Effect of level of hexavalent chromium fixation on surface dislodgeability of CCA components (kimwipe test)

What are the implications of surface deposits from sludging and how can they be avoided?

Sludging in CCA treatment is caused by Cr(VI) reduction by wood extractives and other solution contaminants outside the timber. There is an important difference, however. The concentration of copper in sludge is much lower than in treated wood and in fact sludge is mainly chromium arsenates. Thus if there are surface deposits on wood, there will be higher exposure to arsenic both in leachates and in material dislodged during handling. This poses increased health and environmental risks at the plant site and at the point of use of the product, if not removed by power spraying.

There are several types and causes of these sludges. Some of the material collected from storage tanks is highly contaminated sawdust and dirt generated at the plant site or brought in with the wood. Other deposits are associated with wood sugars and other extractives dissolved from the wood during the treating process; the generation of this material is aggravated by high solution temperatures, empty cell processes and treatment of wet wood. We have some evidence that other sludges (seen as surface deposits on the wood) develop as a result of accelerated fixation processes from thermal expansion of treating solution and from wicking of solution to the surface if drying is permitted during the fixation process. CCA additives such as polyethylene glycol (to soften pole surfaces), water repellent wax additives and colorants also destabilize CCA solutions. They are best controlled by keeping the treating solution as clean and cool as possible and by using up aged solution or solution with additives as quickly as possible. If accelerated fixation is used, it is important that the wood be heated slowly and under saturated humidity conditions to avoid solution wicking to the surface.

Take home messages

- It is relatively easy to monitor fixation at the treating plant to ensure that unfixed wood does not contaminate the yard or endanger users;
- The rate of CCA fixation can be accelerated greatly by increasing the wood temperature;
- However, it is essential that the wood not be allowed to dry during fixation;
- SURFACE DRY ≠ FIXED
- Wood species and type of wood (sapwood/heartwood) has a large effect on rate of fixation; this must be considered when monitoring the fixation of charges – fixation must be followed in the slowest fixing wood in the charge.

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