

# **FIXATION, PERMANENCY, AND LEACHING OF COPPER CHROME ARSENATE (CCA) WOOD PRESERVATIVES:**

## **AN OVERVIEW OF THEORIES, MECHANISMS, AND IMPLICATIONS**

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### **Abstract**

With regards to Copper-Chromium-Arsenic (CCA) wood preservative chemicals, it is now established that fixation level of the CCA elements is a function of wood species, wood quality, CCA formulation, temperature, time, preservative application method, and conditioning techniques. The amount of Cu, Cr and As leached from CCA-treated wood is known to decrease with increases in the level of fixation. The permanence of a chemical preservative in wood is the single most important factor that determines the effectiveness of the preservative system. Depletion mechanisms that affect all types of wood preservatives include leaching, bleeding, blooming, vaporisation, volatilisation, migration, and biodegradation. Although well understood, the chemical and physical mechanisms involved in the fixation and permanency of CCA elements in wood cell walls, appear to have posed problems not yet resolved

### **Introduction**

The permanence of a chemical preservative in wood is the single most important factor that determines the effectiveness of the preservative system. Depletion mechanisms that affect all types of wood preservatives include leaching, bleeding, blooming, vaporisation, volatilisation, migration, and biodegradation. Whereas solvent and oil-borne preservatives are insoluble and cannot easily be removed from treated wood by water, water-borne preservatives depend on fixation mechanisms to fix and render the preservative elements insoluble to water. Water-borne preservatives may be lost from wood by leaching and blooming; solvent-borne preservatives migrate out of wood mainly by volatilisation, while oil-borne preservatives, like creosote, may be lost through bleeding, volatilisation, and migration and redistribution of components, and creosote fractions that are water soluble, such as tar acids, can be removed from wood by water.

Wood treated to high retentions with CCA may have substantial amounts of unfixed preservative elements in the cell lumens and on the surface of the wood. Such unfixed fractions are easily removed or leached by water. In addition, wood preserving chemicals are known to be subjected to detoxification processes by microorganism, mainly fungi and bacteria (Arsenault, 1973; Sutter and Jones, 1985; Ross, 1986; Collet, 1992; Ruddick, 1992; Illman and Highley, 1996; Clausen, 2000). Leaching only occurs when treated timbers are used in outdoor exposure situations, in wet soils, and in aquatic environments, and information accumulated over the past years have been reviewed by Hingston, Collins, Murphy and Lester, 2001. The objective of treating timber with a chemical

preservative is to protect the timber from biodeteriogens and substantially increase service life. The quality of a preservative that can impart long-term protection is in its ability to remain permanently in the wood. That is not always the case with the majority of commercial wood preservatives, as some of the preservative elements will eventually be leached out of the wood. As the bulk of treated timber around the world is used in outdoor situations, leaching represents two important problems:

1. Depletion of the preservative leaves the wood poorly treated and reduces service life.
2. Preservative elements leached out from wood are toxic and represent environmental risks.

Evaluation of CCA around the world has so far shown good performance, resistance to leaching and long service life of treated timber. However, such evaluations were mainly based on data from selected easy-to-treat softwoods, in which penetration, retention, and fixation of the preservative do not appear to pose problems. However, it has been demonstrated that fixation and leaching varies in different species of timber, and between sapwood and heartwood of the same species (Yamamoto and Rokoba, 1991; Carpenter and Gardner, 1993; Wong and Pearce, 1997; Hashim, Sulaiman, Siev Ching, and Yamamoto, 2001; Taylor and Cooper, 2001; Venkatasamy, 2005). In recent years, leaching of components of CCA (Cu, Cr, and As) from treated wood and possible contamination of soils and ground water has been a subject of concern, and has been widely discussed, (Cooper and Ung, 1992, 1995; Albuquerque, Cragg, and Icely, 1996; Walley, Cobham, and Vinden, 1996a, 1996b, 1996c; Venkatasamy, 1998; Venkatasamy and Okwara, 2003). The subsequent reduction in the effectiveness of the treated wood against decay as a result of leaching, and the ensuing reduction in service life has also been of concern and have been discussed (Venkatasamy, 2002, 2003;). What is becoming of even greater importance is the safe disposal of CCA-treated timbers removed from service, and the environmental and economic implications have been discussed by Deroubaix (1992); Cooper (1993); Stalker, (1993); McQueen, Stevens, and Kamden (1998); Clausen and Smith (1998); and Solo-Gabriele, Townsend, Penha, Tolaymat and Calitu (1999). Cooper (1993) estimated that there would be about 15 million M<sup>3</sup> of treated wood removed from service by 2010 in the USA and Canada alone, 90% of which are CCA-treated. No such information is available for other parts of the world, or for African countries where CCA is heavily used, but the volume is known to be substantial. The cost of safe disposal or preparing CCA-treated wood removed from service for re-use is excessively high.

Leaching may be defined as the separation of preservative components from woody tissues when passing water through it. Standard test methods have been suggested in order to quantify the release of active ingredients from treated timber into the environment and to interpret the data so obtained (Cooper, 1991; Albuquerque, Cragg and Iceley, 1996; Waldron and Cooper, 2002), and National Standards to that effect are already in force in Western European and North American countries. These are aimed at meeting general safety limits for the environment, and to determine the effects of loss of preservative elements on decay protection of treated wood in service. Leaching of CCA occurs mainly because of unfixed chemicals in the wood. However, not all unleached chemicals are completely fixed and may still have a potential to leach. For this reason, it has been recommended that the standards for assessing environmental contamination due to leaching should use ground water and soil contamination levels as a basis (Lebow, 1996; Barnes and Davies, 1998; Edlund and Nilsson, 1999; Montegi and Inai, 1999). The level should be a leachate figure that is environmentally acceptable, rather than an indication of actual level of fixation of the preservative in the wood. With worldwide use

of CCA, and concern regarding the environmental impact of heavy metals, there has been considerable interest in the permanency of CCA in wood, and rate of fixation as a function of preservative composition, treatment method, fixation regimes, timber species, and the environments in which CCA-treated timbers are used.

As a wood preservative, CCA has been in use since 1938 and has given excellent results as far as protection of timber in aggressive environments is concerned. There are different formulations of CCA and subsequent chemical modifications have aimed at reducing preservative cost and minimizing leachability. The mechanisms responsible for fixation and leaching have not been fully elucidated yet, and the risks that CCA elements may represent to the environment have resulted in the restriction or banning of that preservative in Western Europe and North America. However, CCA is still the preservative of choice in many parts of the world, especially in tropical countries, where a substantial amount of hardwoods is CCA-treated. Information about fixation and leaching of CCA in tropical hardwoods is scanty, but there are indications that the problem may be even more severe than in temperate timbers (Wong and Pearce, 1997; Hashim *et al.*, 2001; Venkatasamy, 2003; Venkatasamy and Okwara, 2003; Venkatasamy, 2005). Efforts to find ways of improving the permanency of CCA in treated wood and minimising leaching to acceptable environmental levels have not been given up yet, as CCA formulations are likely to stay the chemical of choice for many years to come, especially in tropical countries where environmental laws are not rigorous yet, or not strictly enforced.

### **Fixation of CCA in Wood - Mechanisms and Theories**

It is now established that fixation level is a function of wood species, wood quality, CCA formulation, temperature, time, preservative application method, and conditioning techniques. The amount of Cu, Cr and As leached from CCA-treated wood is known to decrease with increases in the level of fixation (Lebow, 1997; Pizzi, 1992; Cooper, McVicar and Ung, 1995). According to Plackett (1983), fixation is a complex process in which the following reactions are thought to occur:

1.  $\text{Cr}^{\text{VI}}$  absorption on cellulose
2.  $\text{Cr}^{\text{VI}}$  reduction to  $\text{Cr}^{\text{III}}$  on cellulose sites
3.  $\text{CuCrO}_4$  formation and complexation with lignin guaiacyl units
4.  $\text{Cr}^{\text{III}}$  complexation as  $\text{CrASO}_4$  with lignin guaiacyl units or precipitation onto cellulose
5.  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCrO}_4^-$  complexation with lignin, followed by  $\text{CrO}_4^{2-}$  complexation with lignin
6.  $\text{Cu}^{2+}$  complexation with lignin and cellulose

It has been shown that once in contact with wood tissues, CCA solutions undergo an extensive increase in pH because of ion exchange and adsorption reactions with the wood (Dahlgren, 1972; Dahlgren and Hartford, 1972; Pizzi, 1992). Some of the early reaction products are unstable and are slowly converted via dissolution into stable compounds. The conversion proceeds by proton liberating and proton consuming reactions over several months. The pH therefore alternatively decreases and increases until the reactions cease. The final equilibrium products has been suggested by Dahlgren (1972) as being Cu fixed by ion exchange,  $\text{CrAsO}_4$ ,  $\text{Cu}(\text{OH})\text{CuAsO}_4$ , and  $\text{Cr}(\text{OH})_3$ . However, the exact proportion of each of these compounds is unclear and probably varies between wood species and preservative concentrations.

According to Pizzi (1982), and Pizzi, Orovan, Sigmin, Jansen and Vogel (1984), three parameters are said to be important during fixation: the temperature of treatment, the initial pH of the treating solution, and concentration of the solution. The rate of fixation accelerates when temperature is increased, and a lowering of the initial pH of the treating solution accelerates it. Initial pH's of 2.4 or lower of treating solutions cause massive

shifts in the distribution of the fixed preservative in favour of holocellulose, and pH's higher than 2.4 cause similar shifts in distribution in favour of lignin. It has been advanced by Pizzi (1982, 1990a, 1990b) that more CCA on holocellulose is equal to better resistance to brown rot and termites. Conversely, fixation of more CCA on lignin (force fixed) is important in preventing or stopping soft rot. The kinetics of fixation of Cu, Cr, and As in wood have been recently discussed in details by Kazi and Cooper (2000) and Kazi, Cooper and Chen (2000).

It has also been of concern that fixation mechanisms and theories may not necessarily apply to all species of timber, or sapwood and heartwood of the same species (Yamamoto and Matsuoka, 1989; Carpenter and Gardner, 1993). It has been further established that better fixation is achieved in softwoods compared to hardwoods (Yamamoto and Robra, 1991; Stevanovic-Janesic, Cooper, and Ung, 1997). There is also evidence that fixation varies within and between species of softwoods and hardwoods, the sapwood and heartwood of both softwoods and hardwoods, and water-soluble extractives, common in hardwoods, have been associated with poor fixation (Stevanovic-Janezic, Cooper and Ung, 1997). Pizzi, Conradie, and Bariska (1986), and Pizzi (1992) have established that polyflavonoid tannins, present in some hardwood species (including the eucalypts), may be responsible for poor fixation in these species. Differential retention and fixation of CCA in sapwood and heartwood of some tropical hardwood species have been shown by Wong and Pearce (1997), Hashim *et al.*, (2001), and Venkatasamy (2005). The mechanisms of fixation of CCA are likely to be different in different species, and there may be a necessity for different treatment and fixation regimes for different species of timber.

### **Factors Influencing Leaching**

Preservative salts will leach out of treated wood according to several physical laws. The rate of leaching is concentration-dependent, and follows the laws of mass action. Factors affecting the rate of leaching and the amount of active ingredients leached out of treated wood include both non-environmental and environmental factors.

### **Non Environmental Factors**

#### ***CCA formulation***

Formulations of CCA vary according to the relative percentage amounts of Cu, Cr and As, and performance is said to be related to formulation (Nicholas, 1988; Kim and Kim, 1993; Archer, Chittenden and Preston, 1994). They also vary according to the form of copper used, whether it is in the oxide or salt form. Consequently, leaching rates vary among the different types of CCA available commercially. It has been shown that CCA components are leached more from wood treated with CCA type B compared to CCA type C (Kim and Kim, 1993; Kartal, 1999). This is probably due to the lower amount of chromium, which is the fixative for arsenic and copper, in CCA type B formulations. Kim and Kim (1993) also suggested that arsenic contents as  $As_2O_5$  should not be greater than 66%, compared to chromium contents as  $CrO_3$  in the CCA formulation, in order to prevent leaching of arsenic. It is known that salt formulations of CCA type C show more leaching compared to the oxide formulations. According to Kim and Kim (1993), the reason for this disparity between formulations is yet unknown. It has been demonstrated by these authors that the resistance to leaching is in the sequence of CCA type C (oxide) > CCA type C (salt) > CCA type B (oxide), hence the preference for CCA type C (oxide) in most parts of the world.

### ***Concentration of the preservative***

The concentration of the preservative used is important in achieving the required retentions for specific end uses. Applied at low concentrations, low retentions are achieved and better penetration and fixation are obtained, if applied by pressure. Low concentrations are recommended for timbers used in indoor situations where lower retentions are adequate. Non-pressure techniques are usually adequate for low concentrations and small dimension timbers. With higher concentrations and large dimension timbers, only pressure methods will achieve the required penetration and retention. However, fixation levels may not necessarily depend on concentration. Variations in fixation and leaching of CCA formulations of different concentrations have been studied by Kim and Kim (1993), Connell, Baldwin, and Smith (1995), Cooper, Macvicar, and Ung (1995), and Kartal (1999). Whilst Kim and Kim, Connell *et al.*, and Kartal found better Cr fixation at higher CCA retentions, Cooper *et al.* demonstrated higher levels of leaching of Cu and As at higher concentrations and retentions of the preservative. It is likely that higher concentrations and retentions tend to have higher levels of unfixed chemicals on the surface of the treated timbers and in sites where fixation does not occur. It has also been shown that solution strength and timber species (Wilson, 1971), and temperature and acidity (Van Eetvelde, Orsler, Holland and Stevens, 1995), play important roles in fixation of Cu, Cr, and As.

### ***Method of application***

Method of application of the preservative is known to affect fixation, leaching, and biological performance of CCA-treated timbers. The reasons for such variations have been discussed by Newman and Murphy (1992), and reviewed by Hingston *et al.* (2001). Newman and Murphy (1996) demonstrated such variations in one species tested, Corsican pine. They concluded that treatment method affects microdistribution of CCA elements on the lumen surfaces and within the S<sup>2</sup> cell wall layers. It has also been shown that better penetration, retention and fixation can be achieved by pressure cycling processes (Cobham and Vinden, 1995), and by the more recent multi-phase (MPP) processes (Nasheri, Drysdale, Pearson, and Hedley, 1998), both expensive treatment processes.

Non-pressure methods of application are unlikely to achieve high levels of fixation mainly as result of poor penetration and microdistribution of the preservative. Distribution would be mainly limited to cell lumens. However, since timber treated by non-pressure techniques are strictly for indoor applications, problems of fixation and leaching do not arise. It is also to be noted that investigations have been limited to a few species, mostly sapwood of temperate softwoods and hardwoods. It is yet to be demonstrated how methods of application influence penetration, retention, fixation, and leaching in heartwood of softwoods and hardwoods, and especially sapwood and heartwood of tropical hardwoods.

### ***Retention, fixation level of CCA elements, and fixation method and time***

The retention of a preservative in wood is the most important factor influencing the effectiveness of the preservative system used. Retention at the wood soil-boundary (the fungus front) must be consistently high enough to inhibit fungal colonisation and growth, at the same time protecting against insect attack. According to Nicholas ((1973), when specifying a minimum net retention, the following factors must be considered:

1. The intended use of the timber (indoor, outdoor)
2. Sapwood thickness (in case of envelope treatments)
3. Amount of preservative depletion (fixation level, leaching)
4. The decay hazard (diversity and virulence of biological agents)

5. The preservative distribution gradient in the wood (penetration, microdistribution)
6. The physical character of the preservative
7. Climatic conditions (temperature, rainfall)
8. Exposure conditions (indoor, soil, aquatic, pH)

The retention required immediately after treatment must be the amount needed to protect the timber when in service, plus an amount that would be lost through migration and depletion. As a rule, the higher the retention of active ingredients in wood, the higher the amount of active ingredients in the leachate, simply because high retentions tend to accumulate excess amounts of the preservative at sites where they are not fixed. Permanency is dependent on fixation levels of Cu, Cr, and As, rather than retention alone. Cooper *et al.* (1995), have demonstrated higher leaching of As and Cu in leached water at both high and low retentions when levels of Cr fixation are low, but negligible when fixation is in the region of 99%. These authors also found that leaching in the species tested was invariably lower at low retentions at any fixation level.

Fixation time will depend on fixation techniques used. Fixation at ambient temperature under cover will require that adequate time be allowed to allow fixation to occur, from a few days to a few weeks. Fixation times at ambient temperatures will obviously vary from temperate to tropical regions. Accelerated methods of fixation, such as heat or steam fixation, allow complete fixation of the metal salts within hours to a few days (Anderson, 1989; Kartal, 1999). Storage under cover for a specific period of time may not necessarily result in maximal fixation of the preservative elements. Better fixation are invariably obtained when either heat or steaming is resorted to (Peek and Willeitner, 1988; Anderson, 1989; Connell, Baldwin and Smith, 1995). However, accelerated fixation techniques also add to the cost of treatment, not always attractive to consumers.

#### ***Storage time and conditions of storage after treatment***

As a rule, CAA-treated timber must be kept covered (protected from the weather) until fixation is complete, otherwise preservative components may be leached out even before fixation starts. When storage under cover is not feasible, then the timber should undergo accelerated fixation to prevent leaching in storage or in service. Walley, Cobham, and Vinden (1996) showed that by increasing the fixation time (time kept under cover after treatment), the percent loss of Cr decreases. Wegen and Lucks, (1998) found a similar trend using a bioassay technique where, the longer the treated wood was left in storage prior to immersion in a fish tank, the lower the fish mortality rate observed. Storage conditions must also be appropriate for fixation in terms of such variables as time, temperature, and humidity.

#### ***Size of the timber treated***

The smaller the size of the treated wood, either in laboratory or in field tests, the faster the rate of leaching and the amount of active components leached from it. The work of Yamamoto, Montegi and Inai (1999; 2000) demonstrated how increased surface area to volume ratio in smaller size samples result in more of the preservative elements being leached out per given area, thus resulting in more elements being lost. As an example, Yamamoto *et al.* (2000) demonstrated how rate of leaching from wooden stakes used in horticulture can be much faster than the rate of leaching from telegraphic poles, when both are treated with CCA. For this reason, laboratory tests performed on small samples tend to yield results showing higher values than service situations. However, the bulk of CCA-treated timbers used in outdoor situations are usually of large dimensions and used in

ground contact. It may be assumed that leaching of CCA elements into the environment from such timbers would be slow and sustained, but may be high and rapid if retentions are high and fixation poor, as would be the case if fixation techniques and regimes are not observed.

#### ***Species of timber treated (softwood or hardwood)***

Variations in anatomical structure of wood from species to species have been shown to affect penetration and retention, and therefore leaching rate (Kartal and Lebow, 2002). It has been advanced that the chemical nature of different wood species affects the mode and quality of fixation (Albuquerque and Cragg, 1993; Eglund and Gardner, 1993; Pizzi, 1990a; 1990b). The presence of extractives and differences in lignin types and contents are also known to affect fixation, hence causing differences in leaching. The presence of extractives can also retard the rate of leaching, and tannins have an ability to complex with CCA more readily, thus increasing fixation and reducing leaching, although it leaves other wood components less adequately protected (Pizzi *et al.*, 1984).

The majority of softwoods, with the exception of some known refractive species, are known to be generally easy to treat, especially when treatment aims at achieving a sapwood envelope, or total sapwood penetration. It has been established that sapwood is easier to treat in most species, both softwood and hardwood. However, the heartwood of both softwoods and heartwoods usually pose treatment and fixation problems (Yamamoto and Rokoba, 1991).

#### ***Proportion of heartwood to sapwood***

Although scanty, there is now enough evidence as to differential retention and fixation of CCA in sapwood and heartwood of both softwoods and hardwoods. That may not be of concern where an envelope treatment is the objective of preservation, and the sapwood thickness is adequate to satisfy treatment standards. Some species, especially hardwood species, have narrow sapwood bands and to satisfy treatment requirements part or the whole of the heartwood have to be also treated. Given short service lives achieved by CCA-treated eucalyptus utility poles in Kenya, Venkatasamy (2002) suggested that apart from sapwood, heartwood of the portion of poles in contact with the ground should also be adequately treated, since the heartwood of that species is only moderately durable. However, appropriate treatment and conditioning schedules will remain a problem to be resolved, since sapwood and heartwood behave differently in terms of permeability, thus influencing penetration, retention, and fixation in the majority of commercial species.

What has become of concern in recent years is the probability that there may be problems in achieving high fixation of CCA in commercial tropical hardwood species, and the possibility of differential fixation in sapwood and heartwood of tropical hardwoods (Wong and Pearce, 1997; Hashim *et al.* 2001; Venkatasamy, 2002; 2003; 2005). A substantial amount of CCA-treated hardwood utility poles is used in ground contact in tropical countries around the world, and CCA-treated sawn material containing both sapwood and heartwood are used exposed to the weather, in soil contact, and in aquatic situations. There are reasons to believe that environmental contamination and economic losses are high in such countries. However, differential penetration, retention, and fixation is a problem that has to be further investigated, as available information is limited to a few species from a few countries.

#### ***Preparation of the wood prior to preservation***

Before treatment, wood must be seasoned to the appropriate moisture content ideal for impregnation by CCA. Removal of water from the lumen and inter and intra-cellular

spaces leaves voids for easier penetration of the chemical. A better penetration and retention of chemicals will increase the degree of fixation of CCA elements in the wood. This will in effect reduce the amount of leaching of CCA components when the wood is exposed to a moist environment. There may also be other requirements (especially for refractory species), such as incising, kerfing, centre boring, steaming prior to treatment, ponding, biological or chemical pre-treatment, or other techniques of physically preparing the timber to achieve better penetration, retention, and fixation. There is evidence of better penetration when refractory timbers are incised (Venkatasamy, 2003; Richards, 1993), ponded (Dunleavy and Fogarty, 1971; Kobayashi and Imamura, 1995), subjected to fungal or bacterial treatment (Nicholas and Thomas, 1968a; Rosner, Messner, Tucker, and Bruce, 1998; Kobayashi, Iida, Imamura and Wanatabe, 1998), chemically pre-conditioned (Nicholas, 1977; Nijdam, Lehman and Keey, 2001), or steamed (Nicholas and Thomas, 1968b; Rowell, 1985; Kanagawa, Okuyama, and Hattori, 1988). However, information as to whether fixation is at the same time improved and leaching reduced is lacking.

#### ***Presence of deterioration in the wood before treatment***

Wood with some degree of fungal decay before treatment has increased permeability of the rays, resulting in higher retentions, but poorer fixation, and greater losses through leaching, since moisture movement in and out of the cells would be greater. Venkatasamy (2003) advanced that intermittent volumetric swelling and moisture movement in CCA-treated timbers in service may accelerate leaching. Fungal decay also depletes either cellulose or lignin, or both in wood, and that affects fixation negatively. In envelope treatments, there may be a possibility of fungal colonisation of the heartwood of the timber prior to treatment, especially by heartrot fungi. Since the preservative will not reach the colonised areas, fungi will continue to proliferate and, apart from hollowing the treated timber, may also detoxify preservative elements, which will lead to higher leaching of preservative components and reduced service life.

#### ***Time, duration, and conditions of leaching***

In general, the relationship between leaching and exposure time is an exponentially decreasing function represented by ( $y=bc^{-ax}$ ).

Where

y = the amount of CCA leached.

x = time.

a, b and c being constants.

This has been primarily attributed by Coggins and Hiscocks (1987), Homan, Millitz, and Lewis (1993) and Choi, Ruddick and Morris (2004) to the more readily leachable CCA elements found as surface deposits, and removed from the surface of treated wood during the initial stages of leaching, and also due to post fixation processes. Hence, the longer the leaching time, the lower the amount of leached elements and the rate of leaching.

#### **Environmental Factors**

##### ***Amount of rainfall (volume of leach water)***

The volume of water used for rainfall-simulated testing has been found to affect the amount of preservative elements lost through leaching. Walley, Cobham, and Vinden (1996a) have shown that the percentage of chromium leached increases with rainfall volume over a period of 10 days in a simulated rainfall test. Their results reflect the situation in actual field situations. Treated wood used in the ground or above ground in areas with high precipitation will undergo higher levels of leaching. However, the volume



of leach water in the form of rain varies with geographical regions. Heavier precipitations over short periods of time are common in tropical regions. Low fixation of CCA elements in treated timbers in such regions will invariably result in high leaching over short periods of time, greater environmental contamination, short service lives, and substantial economic losses. The temperature of the precipitation, cooler in temperate countries, and warm in tropical regions, will also affect the rate of leaching, since temperature of leach water is also known to accelerate leaching of CCA elements (Van Eetvelde, Homan, Millitz and Stevens, 1995; Taylor and Cooper, 2001).

***Agitation of surrounding water (leach water)***

Loss of metal components of CCA is aggravated by stirring or movement of leach water. According to Van Eetvelde, Orsler, Holland and Millitz, (1995), Breslin and Adler-Ivanbrook (1998) and Brown and Eaton (2000) stirring or movement of the leach water strongly aggravates leaching resulting in greater quantities of metal elements being lost from treated timber. This is because the static saturation zone adjacent to the wood surface is disturbed, creating a concentration gradient; hence more elements can be lost from the wood. Many aquatic applications of structural timbers are associated with slow running waters, or tidal movements. Under these conditions, a slow but sustained change in water movement adjacent to the treated wood surface may take place leading to sustained leaching near the saturation zone and the wood surface. Leaching in dynamic environments as rivers, estuaries and the sea, and the ensuing environmental implications have been discussed by Brooks (1996), Marchal and Martin (1998), and Brown and Eaton (2002).

***Acidity or alkalinity (pH) of leaching water or soil***

It has been shown that the amount of CCA elements leached from treated wood increases with increases in acidity of the leaching solutions, regardless of CCA type and target retention (Kim and Kim, 1993; Venkatasamy, 2002, Venkatasamy and Okwara, 2003). Acidified water at pH 3.0 or below will preferentially leach more Cu than As, while As is more preferentially leached at pH 4.0 or above. Considerable losses of all CCA components will occur from CCA-treated wood if exposed to a solution of pH 2.0 and below.

The work of Cooper (1991), Kim and Kim (1993), Venkatasamy (2002) and Venkatasamy and Okwara (2003) demonstrated a consistent effect of pH on the amount of CCA components leached. However, these results were derived from laboratory tests using accelerated leaching regimes. For application to actual field situations, field tests in areas that receive acid rain, or have acidic or alkaline soils have to be performed to investigate actual leaching characteristics of CCA treated wood in service. Industrial emissions have a tendency to modify the pH of rainfall and it has been proposed that acid rain increases leaching of CCA elements (Murphy and Dickinson, 1990). High hazard conditions have been associated with acidic soils and it has been shown that leaching is invariably higher in acidic soils by Wang, Nicholas, Sites, and Pettry (1998) and Venkatasamy and Okwara (2003). Seawater has a pH of approximately 8.4 and CCA-treated timbers exposed in seawater may not suffer from excessive leaching due to pH alone. Strong acid and alkaline conditions are not likely to occur in practice, although the results of laboratory experiments provide valuable information on the influence of pH on losses of CCA elements. The increase in loss of elements at higher acidity levels may be explained by the chemical exchange reactions involved. Increased acidity provides more hydrogen ions that act in the ion exchange reactions taking place at the acid adsorption points on wood cell walls.

### ***Presence of organic acids in leach water***

The normally leach resistance of CCA can be compromised by exposing wood to organic matter in soils, such as in horticultural soils and composts (Cooper and Ung, 1992, 1995; Cooper, Jeremic, Taylor and Ung, 2000). In addition to pH, the presence of organic buffers in soil may influence leaching and migration of CCA components. A study carried out by Hudson and Murphy (1997) under different pH conditions to determine the effect of organic buffers (organic components containing multi-dentate ligands), demonstrated that CCA components were leached more in the presence of such buffers than at low pH conditions alone. Copper was preferentially leached in the presence of organic buffers, and arsenic was leached the most under acidic conditions. Similarly, in a study by Cooper and Ung (1995), CCA-treated blocks exposed to vegetable compost matter in a bin for one year were more highly depleted of all CCA components compared to similar blocks submerged in water, buried in soil or exposed to weathering. Copper was the most severely depleted element, while Chromium was least depleted. The relative mass balance of Cu in the wood exposed to vegetable compost for 3 years greatly reduced compared to unleached wood, showing that it is preferentially extracted by the compost environment. Losses of Cr were lower compared to those of Cu, while those of As were intermediate to those of Cu and As. In consideration of high Cu depletions and loss in protection, CCA-treated wood is not recommended for use in the fabrication of compost bins, or as horticultural posts and poles.

### ***Soil types and effects of inorganic salts***

Important characteristics of soils, from the standpoint of decay hazards, are degrees of acidity or alkalinity, moisture contents, microbial populations, soil ionic status, and soil organic matter. Highly acidic soils are known to cause more leaching of metal elements from wood in service. It has been demonstrated by Warner (1990) that soil pH of 3.5 and below may cause as much as 100% of leaching, whereas at pH 8.5, leaching can be as low as 9%. Acid soils have a greater proportion of fungi to bacteria and actinomycetes than neutral soils. Fungi prefer a pH of 4.0 to 5.0, bacteria 6.0 to 8.0 and actinomycetes 7 to 7.5. Apart from their association with wood decay, fungi and bacteria are also known to detoxify heavy metals, including Cu, Cr, and As in CCA formulations. The pH of soils is not static and is subject to changes. Some fungi have the ability to change the pH of soil to one that suits them within 2-3 weeks (Arsenault, 1973). The amount of moisture in soil not only affects the rate of leaching, but also the density of populations of bacteria and fungi. Treated wood in waterlogged (anaerobic) soils will lose active ingredients due to leaching, but not through the activities of microorganisms. Negligible leaching is expected to occur in dry sandy soils. However, in moist soils with abundant organic matter, leaching and microbial detoxification of preservative elements may occur concurrently.

It has been suggested that the performance of CCA-treated wood is dependant upon the ionic status of the soil solutions and also the mechanism whereby soil ions may migrate in and out of wood with changes in soil and wood moisture contents (Plackett, 1984; Archer and Jin, 1994). Wood in soils containing high concentrations of calcium, magnesium, potassium, or phosphorous may be more susceptible to copper leaching than wood in soils of lower ionic status. In horticultural and calcareous soils, calcium salts may be at concentrations sufficient to cause enhanced copper leaching (Plackett, 1984). Leaching trials carried out have indicated that free  $\text{Ca(OH)}_2$  could leach copper, chrome and arsenic from CCA-treated wood and possibly sequester copper making it unavailable as a toxicant to invading fungi (Vinden, Levy, and Dickinson, 1983). The works of Wang

*et al.* (1998), Schultz *et al.* (2002) and Venkatasamy and Okwara (2003), further demonstrate the combined influences of soil properties and soil pH on leaching of CCA elements from wood.

#### ***Temperature of leach water***

It has been demonstrated by Van Eetvelde, Homan, Millitz, and Stevens (1995), that leaching of CCA elements from test specimens at 20°C, the standard laboratory conditions temperature, is more severe than leaching at 8°C. The same authors also showed that a combination of high temperature and leach water acidity enhances the release of CCA elements from treated test specimens. In natural conditions of exposure, both acidity and temperature may vary. In alkaline soils of temperate regions, where soil or water temperatures are relatively low round the year, leaching of CCA elements from timbers in service can be expected to be low, whereas in acidic soils in tropical countries, where such temperatures can be relatively high with significant fluctuations, leaching may be excessively high. Apart from temperature of leach water, a combination of other problems associated with poor fixation in tropical hardwoods may further accentuate levels of leaching in tropical soils. Low temperatures around the year in temperate countries may be one of the reasons for better performance of CCA-treated timbers in these countries.

#### **Environmental Implications of Leaching**

Studies on fixation of CCA elements in treated wood has been a subject of investigation for over two decades in Europe and N. America, and risks to the natural environment established. Enough information has accumulated to justify the removal of CCA from use in these parts of the world (Begholm, 1990; Hudson and Murphy, 1997; Brooks, 1996; Wang *et al.*, 1998; Brown and Eaton, 2000; Lee and Son, 2001; Crumiere, Son and Kennedy, 2002). It is not quite clear whether the decision was based on the urgent need to protect the environment from contamination by toxic chemicals alone, or the inability to economically achieve 99.99% fixation of the preservative salts in all species and types of timbers treated, or both. Whilst it has been demonstrated that 99.99% fixation can be achieved in small specimens of a few selected species, it is not known whether the same can be achieved in industrial situations for all species and types of timber without excessively increasing the cost of treatment. Laboratory tests are performed under strictly controlled conditions whilst industrial treatment is based on schedules.

Similar studies have been scanty in tropical and sub-tropical countries, where a substantial amount of CCA-treated timbers is used in outdoor situations. There is now enough evidence that CCA elements leached from treated timbers find their way into soils, ground water, and aquatic systems, and may eventually get into the food chain (Evans, 1987). Heavy metal salts are known to be persistent in the environment. Although there is evidence of microbial detoxification of these elements by natural populations of bacteria and fungi, such processes are slow. That is by no means a warranty that all the chemicals leached will be taken care of by these microorganisms fast enough to justify allowing further uncontrolled leaching of CCA elements into the environment. Since CCA will remain a popular wood preservative in tropical countries, there is an urgent need to find out whether fixation levels that ensure minimal leaching can be achieved in tropical timber species, and whether leaching of CCA elements into the environment is a current environmental risk that has been allowed to go unnoticed for too long (Venkatasamy, 2002; 2003).

More important is the safe disposal of CCA-treated timbers removed from service. Deroubaix, 1992; Pasek and McIntyre, 1993; McQueen *et al.*, 1998; Solo-Gabrielle *et al.*, 1999). Cooper (1993) estimated that about 13 million M<sup>3</sup> of CCA-treated wood will be

removed from service in the USA and Canada by 2010. Assuming retentions of 15Kg/M<sup>3</sup> in these timbers, 195,000 tons of CCA risk finding a way into the environment in that part of the world alone. There are no similar data for Europe and the rest of the world, but it can be assumed that the amount of CCA that finds its way into the environment annually must be too high to be acceptable. Reducing leaching to minimal acceptable levels by ensuring fixation of 99.99% at treatment plants has not been feasible so far. In both Europe and North America, legislations have been put in place for treated timbers removed from service to be either safely disposed of in landfills or re-used with or without initial removal of the preservative, both expensive. There have been efforts to look into ways of re-use (Kampden and Munson, 1996). However, any product made from CCA-treated timbers will eventually find a way back into the environment, upon removal from service. Other options include removal of the preservative by mechanical and chemical methods, or biological detoxification (Clausen and Smith, 1998), both in the experimental stages, and unlikely to be financially feasible. The option of landfill will remain feasible until environmental legislations declare it as an environmental risk too. Removal of CCA from the market appears to have been the only sound solution in several countries and others should follow.

### **Economic Consequence of Leaching**

Apart from the risks that leaching of CCA from treated wood in service represents to the environment, depletion of the preservative also results in substantial economic losses. The aim of chemical treatment of timber is to extend service lives, especially in such aggressive environments as soils. Treated poles and posts of non-durable species used in ground contact are expected to have minimum service lives of over 30 years, and as wood preserving chemicals and techniques of application are improved, service lives are expected to reach up to 60 years. In Kenya, service lives of barely 15 years are common for CCA-treated poles and posts, a reflection on poor treatment, low fixation of CCA elements, and high leaching (Venkatasamy, 2002, 2003; Venkatasamy and Okwara, 2003). The recent findings that CCA elements cannot be totally fixed in all species of timber and are prone to leaching have also cast doubts as to the efficacy of that preservative.

It is unlikely that problems associated with poor fixation and leaching of CCA in many timber species would be resolved in the near future. Data on economic losses due to premature failure, or reduced service lives of CCA-treated timbers as a result of poor fixation and excessive leaching is lacking. Short service lives of 5-15 years of CCA-treated eucalyptus utility poles have been reported in Kenya (Venkatasamy, 2000). The observations of Murira (1983) gave an indication of substantial monetary losses resulting from poor treatment and probably excessive leaching in utility poles in Tanzania. Problems associated with softrot in CCA-treated utility poles and constant replacements in Australia is well recognised, and higher retentions (40Kg/M<sup>3</sup>) recommended by Leightley and Norton (1983) did not substantially improve service lives. Such high retentions may lead to better control of softrot fungi, but may also result in poorer fixation of CCA elements, higher leaching, and increased environmental contamination. It is likely that reduced service lives around the world because poor fixation and excessive leaching may be substantial and unnecessarily high in monetary terms. Reduced service lives lead to two other problems: increased amounts of treated timbers to be safely disposed of, and increased demands on forests.

### **Discussion and Conclusions**

The chemical and physical mechanisms involved in the fixation and permanency of CCA elements in wood cell walls, although well understood, appear to have posed problems not

yet resolved. Fixation of 99.9% of all elements can be successfully achieved through proper conditioning techniques, assuming that no other extraneous substances that will interfere with the chemistry of fixation are present in the treated wood. That would be possible if wood were to be composed of cellulose, hemicelluloses and lignin alone. The composition of wood differs from species to species, from sapwood to heartwood of the same species, and may also differ from country to country within the same species, at different times of the year, and at different felling times.

There are no indications of any immediate changeover from CCA to safer wood preservatives in tropical countries, where a substantial amount of tropical hardwoods achieving poor fixation, high leaching, and short service lives are put in service every year. The concern shown by researchers and environmentalists in Europe and N. America has been lacking in tropical countries. Studies on fixation of CCA in tropical hardwoods, the bulk of treated material in tropical countries, have been slow, and limited information available. However, there have been reports of short service lives of CCA-treated timbers used in outdoor situations from several tropical countries. The information is yet too scanty or incomplete to arouse concern. It is therefore likely that CCA will remain the preservative of choice for many years to come in most tropical countries. Damage to the environment, monetary losses through short service lives, constant replacements and unnecessary pressures on forests will continue.

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