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CHARACTERIZATION OF ARSENIC, CHROMIUM, AND
COPPER RELEASED FROM CHROMATED COPPER
ARSENATE TYPE C (CCA-C) - TREATED SOUTHERN PINE

presented by

Weining Cui

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CHARACTERIZATION OF ARSENIC, CHROMIUM, AND COPPER RELEASED FROM CHROMATED COPPER ARSENATE TYPE C (CCA-C) - TREATED SOUTHERN PINE

By

Weining Cui

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ABSTRACT

CHARACTERIZATION OF ARSENIC, CHROMIUM, AND COPPER RELEASED FROM CHROMATED COPPER ARSENATE TYPE C (CCA-C) – TREATED SOUTHERN PINE

By

Weining Cui

Toxicological review of arsenic, chromium, and copper indicated that the toxicity of arsenic (As), chromium (Cr), and copper (Cu) is strongly affected by both the exposure level and their oxidation states. Arsenic and the hexavalent form of chromium are known human carcinogen. Trivalent chromium is essential to human health. In a short term low dose exposure, trivalent inorganic arsenic is more potent than pentavalent arsenic.

Commercial chromated copper arsenate type C (CCA), and CCA with water repellent (WR) treated southern pine boards were exposed in the field and the dislodgeable solids were collected on a monthly basis. A method using test tube brush wiping accompanied with water spraying was selected to collect the dislodgeable solids for characterization. Using atomic absorption spectroscopy, As, Cr, and Cu were detected in the solids collected from both CCA and CCA/WR treated wood after an acid digestion. The composition of elemental As, Cr, and Cu in the solids were less than 4 wt.%. Higher amounts of As, Cr, and Cu was collected from the wood surface at the initial stage of field exposure and decreased rapidly after three months. The addition of the water repellent reduced chemical loss from wood at the initiation of field exposure. After 15 months similar levels of As and Cu loss were found in CCA and CCA/WR treated wood. The loss of Cr from CCA/WR treated wood remained lower than that from CCA treated wood.

Environmental scanning electron microscope (ESEM) study indicated that the solids mainly consisted of wood splinters with small chemical deposits. The particle sizes of the chemical deposits were mostly less than 10 μm, the size of wood splinters were between 10 and 100 μm. Energy dispersive x-ray analysis (EDXA) found similar elemental compositions in dislodgeable solids collected from CCA and CCA/WR treated wood. Arsenic, chromium, copper, iron, calcium, potassium, chloride, sulfur, silicon, magnesium, sodium, carbon, and oxygen were detected in the solids. After 7 months of field exposure, contamination by sand or soil in the field was observed in the solids by comparing their x-ray diffractograms before and after a field exposure.

As, Cr, and Cu from the dislodgeable solids partially solubilized in water (pH 3, 4, 5, and 6) during a 168-hour test. The solubilization of As, Cr, and Cu was increased with time, and presented to be pH dependent at various time frame. The addition of a water repellent to CCA wood treatment significantly increased the proportions of As, Cr, and Cu solubilized from the dislodgeable solids. Both As^{V} ($H_2AsO_4^-$) and As^{III} (H_3AsO_3) were solubilized from the dislodgeable solids. As^{V} was the dominant form in water during the first 24 hours. A significant decrease in the proportion of As^{V} and increase in As^{III} were found after 168 hours. Larger amounts of soluble Cr^{VI} was found with the solids from CCA/WR treated wood than those in solids from CCA treated wood.

Both As^{V} and As^{III} were detected in the leachate of CCA-treated wood in a 558-hour leaching. About 70-90% of total arsenic was found as As^{V} and 10-30% as As^{III} in the first 270 hours. The concentrations of total arsenic, As^{V}, and As^{III} presented to be time dependent.

To mum, dad, and my husband Jianguo, for their love, support, and understanding

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Chapter 1.

Introduction

1.1 Overview

Wood has been used in construction for thousands of years. It is susceptible to decay and insect damage in exterior and interior applications. Wood density and mechanical properties are the mostly affected aspects. The average service life of virgin southern yellow pine in above ground application has been estimated at about 13 years in Wisconsin (Highley 1995), and about 10 years in Mississippi (Eslyn and Highley 1976). The extent of damage can be reduced if wood is used in a non-hazardous environment or if appropriate chemicals are used (Smith and Shiau 1998). The introduction of chemicals in wood is called wood preservation. Preserved wood has prolonged service life. Among several types of wood preservatives, chromated copper arsenate (CCA) is one of the most extensively used materials with a track record of more than 60 years (Hingston et al. 2001).

1.2 CCA preservatives

CCA preservative called 'Ascu' was first patented in India in 1933 (Eaton and Hale 1993). Trials carried out during the 1930's and 1940's in India for the treatment of railway sleepers and in the United States for the treatment of poles gave excellent results. CCA wood treatment was first used in Europe in the 1950's. Presently, CCA-treated wood has been widely used for landscape timbers, decks, fences, and fabricated outdoor structures to protect against fungi, insects and marine borers (Eaton and Hale 1993).

CCA mainly consists of arsenic (As), chromium (Cr), and copper (Cu). There are different types of CCA formulations available in market. In Europe, Boliden Mining Co. developed Boliden K33 based on metal oxide, salt-free components in Sweden. Britain's Hickson and Welch Ltd. and Celcure Co. devised salt-type formulations in Britain known as Tanalith C and Celcure A (Eaton and Hale 1993). In the U.S., American Wood Preservers' Association (AWPA 2003) defines CCA types A, B and C based on the relative amounts of oxides (CuO, CrO_3 and As_2O_5) present in the formulation. CCA type C (CCA-C) is the most widely used formulation among the three types of CCA preservatives in the states.

Table 1-1 lists the formulation of CCA type A, B, and C preservatives (AWPA 2003). Potassium dichromate, sodium dichromate, or chromium tiroxide are the major sources of hexavalent chromium; the diavalent copper is prepared from either copper sulfate, basic copper carbonate, cupric oxide or cupric hydroxide. Arsenic pentoxide, arsenic acid, sodium arsenate or pyroarsenate are sources of pentavalent arsenic in the formulation of CCA type C preservatives (AWPA 2003).

The function of copper in wood preservative is to protect against wood decay fungi (Sisler and Cox 1960; Somers 1963). Copper toxicity is mostly attributed to the cupric ion (Cu^{2+}) decomposing hydrogen peroxide (H_2O_2) /oxygen free radical ($O_2^{\cdot-}$) to oxygen gas and formation of hydroxyl radical ($OH^{\cdot}$), and results in uncontrolled oxidation process (Hartmann and Weser 1977; Simpson et al. 1988). The fungicidal property of copper is reported to be dependent on the affinity of Cu^{2+} for different chemical groups in the fungal proteins, particularly thiol groups, which results in the denaturation of fungal proteins and enzymes (Eaton and Hale 1993). Arsenic in CCA acts

Table 1-1. The weight percentage composition of CCA preservatives type A, B and C (AWPA 2003)

Oxide	Type A	Type B	Type C
CuO	18.1	19.6	18.5
CrO_3	65.5	35.3	47.5
As_2O_5	16.4	45.1	34.0

as inhibitors of respiratory pathways for insects and fungi. Arsenate anions can substitute phosphate anions during the formation of high-energy intermediates, adenosine triphosphate (ATP) (Corbett et al. 1984). Chromium in CCA is reduced by wood components thereby causing the copper and arsenic to become insoluble. Chromium (III) arsenate ($CrAsO_4$), chromium (III) hydroxide ($Cr(OH)_3$), and copper (II) - wood carboxylate complexes are the most plausible products of CCA preservative with wood (Bull 2001).

The retention level of CCA preservative in wood with good performance for ground contact application is 6.4 kg/m^3, which is equivalent to 0.40 pound per cubic foot (pcf) CCA oxides, and 4.0 kg/m^3 (0.25 pcf) for above ground usage (AWPA 2003).

1.3 Statistical data on CCA-treated wood

In the past two decades wood treated with CCA has dominated the market of wood preservation, accounting for more than 75% of the total amount of treated wood. The total amount of CCA yearly consumed is estimated at 1.0×10^8 kg compared to the other water-borne preservatives of 1.5×10^6 kg (Connell et al. 1990). According to American Wood Preservers Institute (AWPI 1997), about 79.1% of preserved wood was treated with waterborne preservatives in USA, 1996 (1.3×10^7 m^3 out of 1.7×10^7 m^3). About 6.5×10^6 kg of CCA (oxides, dry basis) was used compared to 1.9×10^6 kg of other waterborne preservatives.

1.4 CCA-treated wood and the environment

The sound performance, relatively low cost, and clean surface of CCA-treated wood distinguish itself from a large variety of other treated wood. However, the potential leaching of arsenic, chromium, and copper from wood in service to the surrounding environment have been monitored from both laboratory accelerated leaching tests (Cooper 1993; Van Eetvelde et al. 1995; Waldron et al. 2003), and in-service treated wood (Jin and Preston 1993; Solo-Gabriele et al. 2003a; Waldron et al. 2003). Elevated levels of arsenic, chromium, and copper in soil have been related to the presence of CCA-treated wood (Suzuki and Sonobe 1993).

Another important issue is the presence of some solid deposits, which might contain arsenic, chromium, and copper on the surface of CCA-treated wood in service. The formation of the dislodgeable solid include an initial loss of surface deposits; the migration of CCA components; the loss of CCA components during wood degradation; mechanic depletion of wood fiber; and the accumulation of dirt and sand etc. during outdoor exposure (Gradient Corporation 2001).

1.5 Current status of CCA-treated wood

Due to the public concerns about potential human exposure to the hazards from CCA-treated wood, especially arsenic and chromium, CCA-treated wood manufactures in the U.S. have made a voluntary decision to withdraw CCA-treated wood from the market available to consumers. This decision was announced by U.S. Environmental Protection Agency (USEPA) on February 12, 2002. Since December 31, 2003, no CCA-treated wood has been manufactured for residential use (USEPA 2002). Public health information regarding arsenic is provided to consumers for each single piece of CCA-treated wood produced before December 31st, 2003, which is currently sold to consumers.

The Canadian Pest Management Regulatory Agency (PMRA) is in collaboration with USEPA to have a re-registration review of CCA. There is no CCA-treated wood available for residential use, similar voluntary label changes has been made in Canada (PMRA 2002).

In Europe, the use of CCA-treated wood has been restricted in Germany, Sweden, Austria, Finland, the Netherlands and Denmark. Labeling with consumer safety information is required. The sale of CCA-treated wood for residential use will be banned by June 30, 2004 in the above mentioned 6 European countries. In the United Kingdom, the Health and Safety Executive recommended continuing use of CCA-treated wood because of the environmental situation, especially the presence of termites (Dang et al. 2003).

Australian Pesticides and Veterinary Medicine Authority (APVMA) has initiated a reconsideration of the registration and associated labeling in CCA-treated wood. A draft report is anticipated by mid-2004 for public comments (Dang et al. 2003).

Additional research on public health risks related to exposure to CCA-treated wood is being carried out in New Zealand. However, the Environmental Risk Management Authority (EMRA) is against a reassessment of registration of CCA (Dang et al. 2003).

1.6 Toxicity of arsenic, chromium, and copper

Humans, especially children may be exposed through direct dermal contact with CCA-treated wood, or through oral ingestion of chemical residues from the touching of the wood surface (McMahon and Chen 2001). The major routes of arsenic, chromium, and copper exposure through the residential use of CCA-treated wood are summarized in Figure 1-1, which include oral ingestion of the dislodgeable solids or the soil contaminated by the leachate of CCA-treated wood, inhalation of small particles in the air, such as contaminated soil, dislodgeable solids/wood sawdust, or dermal contact with the leachate, dislodgeable solids, or the contaminated soil.

Animal studies of some arsenic, chromium and copper compounds have indicated the acute toxicity of arsenic, chromium, and copper is influenced by their oxidation states. In an acute exposure, inorganic trivalent arsenic (As^{III}) is more potent than pentavalent arsenic (As^{V}), hexavalent chromium (Cr^{VI}) is more potent than trivalent chromium (Cr^{III}), and cupric copper (Cu^{II}) is more potent than cuprous copper (Cu^{I}) (Frank and Moxon 1936; Gaines 1960; Tatken and Lewis 1983). Chronic study suggested that Cr^{VI} is "most appropriately designated a known human carcinogen by the inhalation route of exposure" (USEPA 1998a); and Cr^{III} is "essential for lipid, protein, and fat metabolism in animals and humans" (USEPA 1998b). Copper is essential to life, but elevated amount of copper exposure may be associated with the development of diseases such as Wilson's disease (Clarkson 1991).

1.7 Objectives

The potential risk of using CCA-treated wood in residential deck and playsets has been proposed (McMahon and Chen 2001). However, limited information is available on

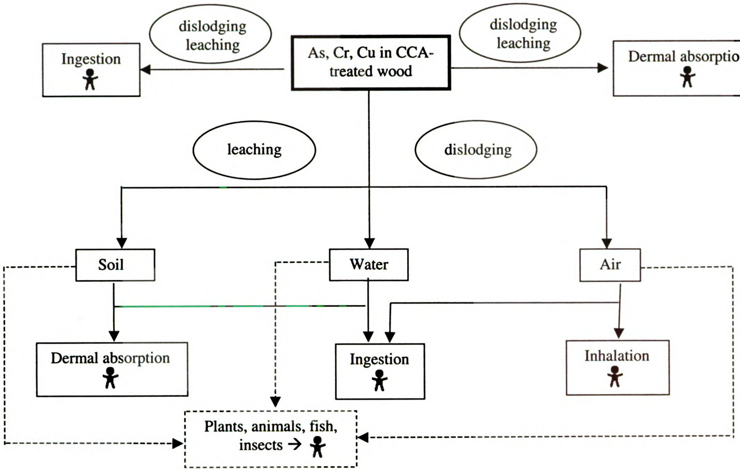

Figure 1-1. CCA exposure through residential use of CCA-treated wood

the nature of the chemicals leached or dislodged from CCA-treated wood. Several risk assessments have been performed based on the hypothesis that the nature of As, Cr, and Cu leaching or dislodging on treated wood surface is similar to that in treated wood (USEPA 2001a; Gradient Corporation 2001; Dang et al. 2003). Such assumptions may under or over estimate the risk associated with CCA-treated wood and its impact on the environment and human health.

The objective of this study was to characterize and identify the chemical nature of solids and liquid that may migrate from CCA-treated wood in service to the surrounding environment. This information is greatly needed to carry out an accurate risk assessment.

Chapter 2

Literature review
- arsenic, chromium, and copper in the environment and their toxicity

2.1 Arsenic

The name arsenic is derived from Greek "arsenikon", which means powerful, strong and potent. Arsenic sulfides were used for medical purpose, such as treatment of ulcers by Hippocrates around 2500 years ago.

Arsenic naturally exists in minerals with more than 60% as inorganic pentavalent arsenic (Onishi 1969). The average value of arsenic concentrations in rocks is reported at 2 mg/kg (O'Neil 1990). Up to 200 mg/kg in phosphate rocks and 900 mg/kg in argillaceous sedimentary rocks have been reported (O'Neil 1990). The presence of arsenic in ground water has been related to arsenic in rocks but the correlation is not clearly established. Two major environmental conditions have been used to explain the solubilization of arsenic in ground water. One is the oxidation of the relatively insoluble arsenic in rock by the introduction of air and aerated water (Mallick and Pajagopal 1995); the other is arsenic eroding from mineral deposits in river and adsorbed onto iron hydroxides to go to the groundwater (Nickson et al. 1998).

2.1.1 Arsenic exposure

Unlike man-made toxicants, arsenic exposure is unavoidable in daily life because of its ubiquitous presence. Major routes of arsenic exposure include inhalation of contaminated soil and dust floating in the air, and oral ingestion of contaminated soil or water.

2.1.1.1 Arsenic in the air

Arsenic concentrations in the air vary with the geological region. Other factors such as land use, and industrial contamination may also affect air quality. Based on the report from the Directorate General for Environment (2000), background arsenic levels are 0.2-1.5 ng/m^3 in rural areas, 0.5-3 ng/m^3 in urban areas, and about 50 ng/m^3 in industrial areas. Up to 1483 ng/m^3 has been reported in Caletones, Chile, near a copper smelter (Romo-Kröger and Llona 1993).

2.1.1.2 Arsenic in water

Arsenic is generally present in inorganic pentavalent form (As^V) in surface water, and inorganic trivalent arsenic (As^{III}) in groundwater (Cherry et al. 1979). In both surface and ground water, the background concentration of arsenic ranges from 1 to 10 μg/l. Elevated concentrations of arsenic in drinking water have been reported in Taiwan, West Bengal, India, Bangladesh, Chile, North Mexico, Argentina, China, USA, Finland, Hungary, Greece and Romania (National Research Council 2001). In the United States, based on USEPA's estimation, about 3.5×10^5 people are exposed to drinking water with more than 50 μg/l of arsenic and about 2.5×10^6 people are consuming drinking water with arsenic level ranges from 25μg/l to 50μg/l (IARC 1987).

2.1.1.3 Arsenic in soil

Arsenic tends to be adsorbed to soil particles (Gomez-Caminero et al. 2001). Less movement of arsenic is observed in clay compared to that in sandy soil (Hiltbold et al. 1974; Elfving et al. 1994). Arsenic concentrations in soils from a non-orchard area in Annapolis valley, USA were reported as ranging from trace level to 7.9 mg/kg (dry weight), while arsenic levels ranged from 9.8-124.4 mg/kg in orchard soil treated with arsenicals (Bishop and Chisholm 1962). In Zimbabwe, up to 9,500 mg/kg of arsenic has been reported in some gold / arsenic mine dumps (Jonnalagadda and Nenzou 1996).

Oxidation, reduction, adsorption, dissolution, precipitation and volatilization of arsenic exist in soil (Bhumbla and Keefer 1994). Arsenate is the dominant form in the porewater of aerobic soils, with small amount of arsenite and monomethylarsonous acid (MMA) (Gomez-Caminero et al. 2001). Arsenate exists as $H_2AsO_4^-$ in an acidic soil condition and $HAsO_4^{2-}$ in an alkaline soil condition. Arsenate and arsenite can be methylated by soil organisms resulting in the production of volatile methylated arsines. It has been reported that about 12% of the arsenic in soil is lost through volatilization (Woolson 1977).

2.1.1.4 Arsenic in food

The average daily dietary ingestion of arsenic varied from 17 to 291 μg depending on the geological region, human age, and dietary habit (Gomez-Caminero et al. 2001), with approximately 25% in inorganic and 75% in organic form (WHO 1996). Fish and meat are the major arsenic sources of human dietary exposure besides drinking water. In Canada, the mean arsenic contents have been reported at 1,600 ng As/g in fish samples, and 24 ng As/g (wet weight) in meat and poultry (Gomez-Caminero et al. 2001). Arsenic may accumulate in some fish species. In a Swedish study, the total arsenic concentrations in brackish-water fish were 200-2,600 ng As/g from an area near a smelter polluted by arsenic, compared with 50-240 ng As/g in the reference fish from an non-contaminated area. About 5-12% of the arsenic was in inorganic form (Norin et al. 1985).

2.1.1.5 Arsenic in plants

Variations in uptake of arsenic, chromium, and copper have been observed with different plants. Study of plants in adjacent to CCA contaminated soil found that the above ground portion of rye grass did not absorb significant amount of arsenic, chromium, or copper; elevated concentrations of the three elements were found in the root portion of rye grass. Radish (analyzed as the complete plants) selectively absorbed more arsenic, but not the other two elements. It was noticed that horsetails (Equisetum) could accumulate all the three elements, but no accumulation was observed with cattails (Typha) (Cooper et al. 1995). A four-year study found that no significant difference existed in the arsenic uptake by banana plants when using CCA-treated eucalypts as the supporting stakes compared to those using untreated wood stakes (Li et al. 2003).

The presence and function of arsenic species in plants is not fully understood. After uptake by cell cultures of the Madagascan periwinkle, methylarsenicals could not be detected by using Nuclear Magnetic Resonance (NMR) (Cullen et al. 1994). Gomez-Caminero et al. (2001) proposed that organic arsenic could be bound to large molecules, possibly to a lipid-soluble species located in plant cell membrane.

2.1.2 Arsenic toxicity

The toxicity of a chemical reagent could be described based on acute exposure (less than 24 hours) or chronic exposure (more than 3 months) (Klaassen and Watkins III 2003).

2.1.2.1 Acute toxicity

Symptoms of arsenic acute toxicity include nausea, vomiting, abdominal pain, watery diarrhea, hypotension, shock, and death (Williams 1999). Medium lethal dose (LD_{50}) is the dosage of chemicals needed to produce death in 50% of treated animals (Klaassen and Watkins 2003). Variations in LD_{50} exist among different chemical forms of arsenic (Table 2-1). Arsenic toxicity is affected by its chemical species. The LD_{50} of sodium arsenite in man is reported at 10 mg/kg, while arsenic trioxide in man is more potent compared to sodium arsenite, which is 1.43 mg/kg (Tatken and Lewis 1983). Inorganic pentavalent arsenic (As^{V}) is less toxic than inorganic trivalent arsenic (As^{III}). The LD_{50} of sodium arsenate is 70 mg/kg compared to that of sodium arsenite at 41 mg/kg in rats (Smyth et al. 1969; Tatken and Lewis 1983).

2.1.2.2 Chronic toxicity

Signs of arsenic chronic toxicity include fatigue, rash, fluid retention gastroenteritis, leukopenia and anemia, sensorimotor peripheral neuropathy, noncirrhotic portal hypertension, and peripheral vascular insufficiency (Novick and Warrell 2000; Abernathy et al. 2003). Chronic exposure to excess amount of inorganic arsenic has been reported in the development of blackfoot disease, hyperpigmentation, keratosis, anemia, leukopenia, diabetes (Chen et al. 1986; Cuzick et al. 1992; Guo et al. 1997; Ferreccio et al. 2000; Chen and Chen 2002; Nakadaira et al. 2002; Chen et al. 2003a, b, c; Guha-Mazumder 2003). However, there is no sufficient data to establish a reliable dose-response relationship of long term - low dose arsenic toxicity mainly because of concomitant exposure to other toxicants, variations in individual human susceptibility,

Table 2-1. LD_{50} values of arsenic, chromium, and copper compounds

Compound	Species	Route of exposure	LD_{50} (mg/kg)	References
arsenate, calcium	rat	oral	298	Gaines, 1960
arsenate, lead	rat	oral	1050	Gaines, 1960
arsenate, sodium	rat	oral	70	Tatken and Lewis, 1983
arsenite, sodium	rat	oral	41	Smyth et al., 1969
arsenite, sodium	man	oral	10	Tatken and Lewis, 1983
arsenite: arsenic trioxide	rat	oral	20	Tatken and Lewis, 1983
arsenite: arsenic trioxide	man	oral	1.43	Tatken and Lewis, 1983
sodium dicromate	mouse	intraperitoneal	32	Tatken and Lewis, 1983
chromium(III) chloride	mouse	intraperitoneal	140	Tatken and Lewis, 1983
copper (II) sulfate	rat	oral	960	Smyth et al. 1969
copper(II) chloride	rat	oral	140	Tatken and Lewis, 1983
copper(I) chloride	rat	oral	265	Tatken and Lewis, 1983

and limited case-specific exposure data in epidemiological study (Wildfang et al. 2001). The lack of animal models limits the understanding of the mechanisms of arsenic toxicity. Reference dose (RfD) is a numerical estimate of a daily oral exposure to the human population that is not likely to cause harmful effects during a lifetime (Klaassen and Watkins 2003). The oral RfD of arsenic is established at 3×10^{-4} mg/kg-day using the thresholds of cellular necrosis (USEPA 1998c) (Table 2-2).

Arsenic is an established human carcinogen. Cancers in skin, lung, and the urinary system, including kidney, bladder, ureter and urethra have been observed upon arsenic exposure (Tseng et al. 1968; Tseng 1977; Morton et al. 1976; Southwick et al. 1981; Chen et al. 1986; Cuzick et al. 1992; Guo et al. 1997; Ferreccio et al. 2000; Chen and Chen 2002; Nakadaira et al. 2002; Chen et al. 2003a, b, c; Guha-Mazumder 2003). Arsenic exposure has also been associated with disease in other internal organs, such as liver cancer but with less convincing evidence (Liu et al. 2002). An increase in the rate of cancer in lung has been observed with occupational exposure to arsenic of smelter workers in Tacoma, WA, Magma, UT, Anaconda, MT, Ronnskar, Sweden, and Saganoseki-Machii, Japan (Enterline and Marsh 1982; Lee-Feldstein 1983; Axelson et al. 1978; Tokudome and Kuratsune 1976; Rencher et al. 1977).

The cancer slope factor via oral exposure to arsenic is determined at 1.5 $(\text{mg/kg-day})^{-1}$ (USEPA 1998c). An updated value at 3.67 $(\text{mg/kg-day})^{-1}$ has been applied in a recent risk assessment for children exposure to CCA-C treated playset decks prepared by USEPA (Dang et al. 2003) (Table 2-2).

2.2 Chromium

The name chromium is derived from Greek "chroma", and means "color".

Chromium is a metal found in natural deposits. There are two commonly existing oxidation states of chromium in the environment: trivalent chromium (Cr^{III}) and hexavalent chromium (Cr^{VI}), which persist in sediments and with high potential of accumulation in biota (Gomez-Caminero et al. 2001). Cr^{III} commonly exists as stable complexes with both organic and inorganic ligands (Hartford 1979). Cr^{VI} exists as oxo species, i.e. CrO_3 and CrO_4^{2-}, which are strong oxidizers (Cotton and Wilkinson 1988). The most common species of Cr^{VI} in solution are hydrogenchromate ($HCrO_4^-$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$). In basic or neutral solution ($pH \geq 7$), chromate is the principle species; while at low pH, dichromate species predominate (USEPA 1998a).

2.2.1 Chromium exposure

Major routes of chromium exposure are through inhalation, oral ingestion and dermal absorption. Humans are subjected to chromium exposure both environmentally and occupationally. The environmental sources mainly include airborne emissions from chemical plants and incineration facilities, road dust from catalytic converter erosion, asbestos brake lining erosion, topsoil, rocks, cement dust, contaminated landfills, and tobacco. Occupational chromium exposure is mainly from leather tanning and textile manufacturing, chrome electroplating, alloy production, welding of alloys or steel, paints, pigments, photoengraving, copier servicing, antifreeze, production of magnetic audio tapes, tattooing, wood preservatives, agricultural fungicides, anti-algae agents, and porcelain / ceramics / glass manufacturing (ATSDR 1993).

Table 2-2. Toxicity values of arsenic, chromium, and copper

Substance	RfD, non-cancer effect			Slope factor, cancer risk
As	3×10^{-4} mg/kg-day, oral			3.67 $(mg/kg/day)^{-1}$
Cr	1.5 mg Cr^{III}/kg-day, oral	3×10^{-3} mg Cr^{VI}/kg-day, oral	2.9×10^{-5} mg Cr^{VI}/kg-day, inhalation	42 $(mg/kg/day)^{-1}$, inhalation Cr^{VI}
Cu	N/A			N/A

2.2.1.1 Chromium in the air

Chromium concentration in ambient air generally ranges from 0.01 to 0.03 μg/m^3 (EAD 2001). Little information is available regarding the nature of chromium species in the air. It is recognized that Cr^0 and Cr^{III} are stable in the environment and do not undergo any interactions intensively (Towill et al. 1978). Cr^{VI} in the air interacts with dust particles to form Cr^{III} (NAS 1974). Chromium in the air may precipitate to the ground. However, particle size smaller than 10 μm may remain in the air and travel with the wind (USEPA 1998a).

2.2.1.2 Chromium in soil and plants

Based on the report from Environmental Assessment Division (EAD 2001), the concentration of naturally occurring chromium in the soil in the United States is reported in the range of 1 to 2,000 ppm, with an average concentration of 54 ppm. It is generally estimated that about 10% to 17% of chromium in soil is Cr^{VI}. Chromium tends to accumulate in clay soil.

2.2.1.3 Chromium in water

Major sources of chromium in aquatic system are from the surface runoff, precipitation from the air, and the release of industrial wastes. Most Cr^{III} end up in the sediments as $Cr_2O_3 \cdot nH_2O$, and Cr^{VI} can be dissolved in aquatic media as a water-soluble complex and persist for a long period (USEPA 1998a). Chromium concentration in drinking water is usually less than 2 μg/l (EAD 2001). Most of the chromium in groundwater is Cr^{VI} (EAD 2001).

2.2.1.4 Chromium in food

Not much information is available on the chemical forms of chromium in food. Based on the data provided by Healthy Eating Club (2003), chromium contents are relatively high in egg yolk (183 μg/100g food) and Brewer's yeast (112 μg/100g food). Chromium concentrations range from 42 to 57 μg/100g food in beef, cheese, liver and wine. Chromium contents in some vegetables are reported between 10 μg/100g food (spinach) and 35 μg/100g food (black pepper).

2.2.2 Chromium toxicity

2.2.2.1 Cr^{III}

Since the 1950's, Cr^{III} has been known as a trace mineral required by human body for insulin to use glucose properly. "Cr^{III} potentiates insulin action in peripheral tissue and is essential for lipid, protein, and fat metabolism in animals and humans" (USEPA 1998b). Chromium deficiency may result in changes in glucose and lipid metabolism, and be associated with maturity-onset diabetes, cardiovascular diseases, and nervous system disorders (Anderson 1993, 1995).

National Research Council (NRC 1989) recommended an estimated safe and adequate daily dietary intake for Cr^{III} of 50-200 μg/day.

2.2.2.2 Cr^{VI}

In vivo reduction of Cr^{VI} to Cr^{III} has been observed in humans and laboratory animals. The reduction agents include gastric juices, ascorbate, and glutathione.

Chromium can be localized in proximal renal tubules within the lysosomes (Suzuki and Fukuda 1990).

2.2.2.2.1 Acute toxicity

Skin irritation, ulceration, and problems in respiration are common symptom of chromium acute toxicity (USEPA 1998a, b). Accidental ingestion of Cr^{VI} may result in metabolic acidosis, acute tubular necrosis, kidney failure, and death (Saryan and Reedy 1988). Liver and other organs may also be damaged (Clarkson 1991).

The lethal dose of sodium dichromate through intravenous injection of several laboratory animals ranges from 37 to 417 mg/kg (animal species not specified). The lethal dose of sodium dichromate to mice is reported at 32 mg/kg (Clarkson 1991). The LD_{50} of chromium (III) chloride in mice is observed at 140 mg/kg (Smyth et al. 1969) (Table 2-1).

2.2.2.2.2 Chronic toxicity

Chronic exposure to Cr^{VI} may result in damage to liver, kidney, lung, circulatory and nerve system. Skin irritation is also frequently observed (Dayal et al. 1995; Bradshaw et al. 1998). The amount of bioavailable chromium through inhalation is affected by the particle size, oxidation states, solubility, activity of alveolar macrophages, and the interaction of chromium with body tissue (USEPA 1998a). Epidemiological studies found there is an increased rate of human lung cancer upon chromium exposure (Davies 1984). Injuries to the skin, nasal and respiration mucous membrane have been noted upon human occupational exposure to hexavalent chromium (Clarkson 1991). Elevated rate of bronchiogenic cancer have been reported with heavy occupational exposure to hexavalent chromium compounds through respiration in Germany, USA, Norway, and the United Kingdom (USEPA 1998a). Development of oral ulcers, diarrhea, abdominal pain, indigestion, vomiting, leukocytosis, and immature neutrophils have been reported with chronic consumption of Cr^{VI} contaminated well water (Cr^{VI} concentration at 20 mg/l) adjacent to a chromium alloy plant (Zhang and Li 1987). Based on the urinary data, intake of Cr^{VI} at more than 0.02 mg/kg-day may result in serious illness; liver damage has been observed of Cr^{VI} intake at 0.04 mg/kg-day (Clarkson 1991).

Table 2-2 summarizes the toxicity values of Cr^{III} and Cr^{VI} provided by Environmental Assessment Division (EAD 2001). The oral RfD of Cr^{III} is 1.5 mg/kg-day, the inhalation RfD of Cr^{VI} is 2.9×10^{-5} mg/kg-day. The slope factor to determine the cancer risk of Cr^{VI} exposure through inhalation is 42 $(mg/kg\text{-}day)^{-1}$.

2.3 Copper

Copper is a natural element found in the earth's crust with an average concentration at 50 μg/kg. The actual quantity of copper varies with geologic region, depending on the amount present in the earth. Copper is found in most plants, animals, surface and ground water.

Copper is involved in the formation of hemoglobin, bones, carbohydrate metabolism, catecholamine biosynthesis, and the cross-linking of collagen, elastin, hair keratin, and balancing the biological environment of the nervous system (Clarkson 1991). It is important for some enzymes such as cytochrome oxidase, tyrosinase, ascorbic acid oxidase, uricase, catalase, and peroxidase to function normally (Clarkson 1991).

Copper is primarily used as metal or alloy in manufacture of wire, pipes, and other metal products; and commonly used in agriculture to treat plants for pest control; in water treatment for algae; as preservatives for wood, leather, and fabrics. Copper is also used in antifouling paints (marine coatings for ships), and a potential replacement for organotins.

2.3.1 Copper exposure

The major human exposure to copper is through inhalation, ingestion of food and water, and dermal contact with copper containing water and soil. Copper from water pipes may be one of the important sources of copper in drinking water.

According to the data from Toxics Release Inventory (TRI 2002), the amount of copper release to the environment in year 2000 was about 4.2×10^6 kg. Among which 12.8% was released to the air, about 0.4% to the water, 0.8% to the ground, and 86.0% to the land. Domestic waste water, combustion process, wood production, phosphate fertilizer production are also important sources of copper release to the environment.

2.3.1.1 Copper in the air

Copper can be emitted into the air mainly from windblown dust. The concentration of copper in the air ranges from 5 to 200 ng/m^3, and up to 5,000 ng/m^3 near copper smelters (ATSDR 2002).

2.3.1.2 Copper in food

Copper contents are high in liver (around 150 μg/g wet in sheep and pork livers), lobster (36.60 μg/g wet), syrup (43.36 μg/g wet), crab and clams (6.08-7.39 μg/g wet), walnuts (6.51 μg/g wet), peas (2.38 μg/g wet) and beans (1.09-3.95 μg/g wet), chili (1.82 μg/g wet), and whole wheat (1.07 μg/g wet) (Brewer 1992).

2.3.1.3 Copper in plants

Copper concentrations in plant tissues are reported in the range of 5 to 20 mg/kg on dry weight basis (Pätsikkä et al. 1998). The bioavailability of copper to plants depends on the presence of ionic copper. Copper based compounds with low water solubility or complexes with substrates in soil or the environment such as humic acid and fulvic acids, or Cu-OH-lignin of peat soils reduce copper availability for "uptake" by plants (Owen 1982). The copper content of wheat increases as it is grown from the north to the south in the U.S., this has been documented at 4.2 μg/g when planted in Oregon, 6.2 μg/g in Oklahoma, 7.8 μg/g in Texas, and 8.7 μg/g in California (Owen 1982). Copper can be stored in the roots of pines and delivered to the shoots when it reaches a certain concentration. Copper concentration is high in cabbage leaves, peony buds, young oat plants and roots of rice plants (Owen 1982).

2.3.1.4 Copper in water

Copper exists in oceans, rivers, lakes and wells with the predominate form being the bivalent oxidation state (Cu^{II}) (ATSDR 2002). The average copper concentration in oceans is reported at 1.2 μg/l. The copper concentration increases with the depth. Copper contents in river water are often higher than that in seawater, which has been reported up to 10 μg/l (Owen 1982). Copper concentrations in tap water vary with the scenario of water exposure to copper tubing and tanks. The copper content is reported at 0.26 μg/ml in the morning and 0.11μg/ml in the evening because of the solubilization of copper from the tubes to water overnight (Owen 1982).

2.3.1.5 Copper in soil

It has been well recognized that copper contents in soil vary and affect the copper content in plants. The copper content in soil has been reported to range from 1 to 4000 μg/g (Owen 1982; IRIS 2003). Soil samples from Wisconsin (USA), African, Ghana, India, and USSR are reported at 20, 68, 21-77, 11-175, and 1-980 μg/g respectively (Brewer 1992).

2.3.2 Copper deficiency in human

Copper deficiency in humans may result in anemia, neutropenia (Montorsi et al. 1975), osteoporosis, pallor, dermatitis, anorexia, diarrhea, hepatomegaly, and slow growth (Hambidge 1977).

The U.S. National Academy of Sciences' Food and Nutrition Board (2003) recommends a daily allowance (RDA) of copper at 0.2 to 0.22 mg for infants, 0.34 to 0.44 mg for children, 0.7-0.9 mg for adults, 1.0 mg for women in pregnancy, and 1.3 mg for women in lactation.

2.3.3 Copper toxicity

Accidental ingestion of samphire, "strongly impregnated with copper" by a 17-year-old girl, was reported to cause abdominal pain, skin rash, followed by severe diarrhea, retching, and green vomitus, and an eventually death (Percival 1785). Symptom of headaches, hypoglycemia, increased heart rate, nausea, inhibition of urine production, anemia, hair loss in women, and damage in brain, liver and kidneys have been observed with high copper exposure. Copper interferes with zinc, which is essential in producing digestive enzymes. Excessive copper in children is associated with hyperactive behavior, ear infections, and learning disorders such as dyslexia (Owen 1981).

Symptoms of violent retching, muscular spams, and collapse are usually observed in copper poisoned animals (Owen 1981). Rats fed with copper sulfate at a dietary level of 25 Cu mg/kg-day for a continuous 4 weeks presented slightly decrease in food intake and growth rate (Clarkson 1991). The food intake and body weight of rats decreased with the increased copper sulfate ($CuSO_4$) content in diet. At dose level of 200 Cu mg/kg-day, rats were observed to eat less than 1/5 of the regular amount of food and die within one week (Clarkson 1991). Pigs fed with $CuSO_4$ in diets at 12.5-21.25 mg Cu/kg-day for 48-79 days showed a gradual development of anemia, jaundice, hepatic necrosis, gastrointestinal hemorrhage, and decreased weight gain (Clarkson 1991).

Lehmann (1897) summarized that the lethal dose of $CuSO_4$ in humans is 7.5g or higher with oral ingestion. Table 2-1 lists the lethal dose values of some copper compounds. The oral LD_{50} of $CuSO_4$ for rats is reported at 960 mg/kg (Smyth et al. 1969), and 87 mg/kg in mice (Jones et al., 1980). The oral LD_{50} of copper (II) chloride in rats is 140 mg/kg and 265 mg/kg for copper (I) chloride (Tatken and Lewis, 1983).

Epidemiological study found that a genetic disorder called Wilson's disease was associated with excess level of copper exposure. Low serum and hair copper levels were found in patients, but high copper levels were present in the liver and brain (Lal and Sourkes 1971; Owen 1974). A remarkable symptom of over exposure to copper resulting in Wilson's disease is blue and brown at the fingernails (Owen 1974). One of the other reported diseases associated with excess level of copper exposure is Parkinson's disease, which affects about 1% of the population over the age of 60 years in the United States (Gorell et al. 1997; Wechsler et al. 1991). The main symptom of Parkinson's disease is a pronounced tremor of the extremities - notably the hands, chin or lips, stiffness or slowness of movement, a shuffling walk, stooped posture, and difficulties in performing simple tasks.

USEPA has not provided specific data on the RfD of copper exposure (IRIS 2003). Copper has not been classified as human carcinogen due to the lack of human data and inadequate of animal data (IRIS 2003).

2.4 Environmental regulation of arsenic, chromium, and copper

2.4.1 National wide

Table 2-3 lists the environmental regulation levels of arsenic, chromium, and copper in the U.S. USEPA set the National Primary Drinking Water Regulations for arsenic, chromium, and copper at 10 μg/l, 100 μg/l, and 1.3 mg/l, respectively.

WHO published the latest edition of arsenic in drinking water regulation level at 10 μg/l with an estimated excess lifetime skin cancer risk at 6×10^{-4} associated with arsenic exposure at this level (WHO 1963).

American Conference of Governmental Industrial Hygienists (ACGIH), National Institute for Occupational Safety and Health (NIOSH), and Occupational Safety and Health Administration (OSHA) also provide occupational regulation levels of arsenic, chromium, and copper in the air (Table 2-3).

2.4.2 Michigan

Table 2-4 summarizes the general cleanup and screening levels of arsenic, chromium, and copper in Michigan (DEQ 2004). The statewide default background levels in soil are 5.8 mg As /kg, 18 Cr^{III} /kg, and 32 mg Cu/kg on dry weight base. The drinking water protection criteria of the three elements in soil are 23 mg As/kg, 1,000,000 mg Cr^{III}/kg, 30 mg Cr^{VI}/kg, and 5,800 mg Cu/kg (dry weight). The direct contact criteria are set at 7.6 mg As/kg, 790,000 mg Cr^{III}/kg, 2,500 mg Cr^{VI}/kg, and 20,000 mg Cu/kg (dry weight). The residential and commercial drinking water criteria are set at 50 μg As/l, 100 μg $Cr^{III/VI}$/l, and 1,000 μg Cu/l.

Table 2-3. National wide environmental regulation of arsenic, chromium, and copper

Hazardous substance	Agency*	Focus	Level
As	USEPA	Drinking water	10 μg As/l
Cr	ACGIH	Air: workplace (8-hr TWA)	10 μg Cr/m^3, insoluble Cr^{VI} 50 μg Cr/m^3, soluble Cr^{VI} 500 μg Cr/m^3, metal and Cr^{III}
	NIOSH	Air: workplace (10-hr TWA)	1 μg Cr/m^3, chromic acid and Cr^{VI} 500 μg Cr/m^3, metal and Cr^{III}
	OSHA	Air: workplace (8-hr TWA)	100 μg CrO_3/m^3, chromic acid and chromate 500 μg Cr/m^3, Cr^{III} 1000 μg Cr/m^3, metal and insoluble salts
	USEPA	Drinking water	100 μg Cr/l
Cu	USEPA	Drinking water	1.3 mg Cu/l
	OSHA	Air: workplace (8-hr TWA)	0.1 mg Cu/m^3, copper fumes 1.0 mg Cu/m^3, copper dusts and mists

*ACGIH: American Conference of Governmental Industrial Hygienists
NIOSH: National Institute for Occupational Safety and Health
OSHA: Occupational Safety and Health Administration
USEPA: The United States Environmental Protection Agency
TWA: time-weighted average

Table 2-4. General cleanup criteria and screening levels of arsenic, chromium, and copper in soil and groundwater, Michigan (DEQ 2004)

Hazardous substance	Soil Residential and commercial, mg/kg dry weight				
	Statewide default background level	Drinking water protection criteria	Groundwater contact protection criteria	Particulate soil inhalation criteria	Direct contact criteria
As	5.8	23	2000	72,000	7.6
Cr^{III}	18	1,000,000	1,000,000	330,000	790,000
Cr^{VI}	NA	30	140,000	260	2,500
Cu	32	5800	1,000,000	130,000	20,000

Hazardous substance	Groundwater Residential and industrial-commercial, $\mu g/l$			
	Residential & commercial drinking water criteria	Industrial & commercial drinking water criteria	Groundwater surface water criteria	Groundwater contact criteria
As	50	50	150	4,300
Cr^{III}	100	100		290,000,000
Cr^{VI}	100	100	11	460,000
Cu	1,000	1,000		7,400,000

Chapter 3

Collection of the Dislodgeable Solids from Chromated Copper Arsenate Treated Southern Pine

3.1 Introduction

The presence of arsenic, chromium, and copper on the surface of chromated copper arsenate (CCA) treated wood has been reported. The amount of arsenic, chromium, and copper present varied with CCA retention in treated wood, the wood species, the method of wood treatment (full cell or empty cell), and the seasoning after the wood treatment (Coggins and Hiscocks 1978, Murphy and Dickinson 1990, and Cooper et al. 1997). CCA components on the wood surface may represent a potential risk to humans and the environment. It is hypothesized that children at playground or decks built up with CCA-treated wood may come in contact with the dislodgeable solids from wood surface. Contamination may occur through skin contact (dermal absorption), hand-to-mouth behavior (oral ingestion) with wood sawdust, soil contaminated with CCA components, and / or water runoff on rainy days.

"Dislodgeable solids" is defined as material that can be removed or may come loose from the surface of CCA-treated wood. The formation of dislodgeable solids involves a series of processes, which include the migration of CCA components from the inner to the outer zone of wood; sludge deposits during CCA wood treatment; sand and dirt introduced during wood handling; the loss of CCA components during wood degradation; and the mechanical depletion of wood splinters, accompanied with the accumulation of dirt, sand, etc. during exterior exposure.

CCA sludges may come from the reduction of hexavalent chromium by interaction with soluble wood extractives or additives such as water repellents during the wood treatment process (Sonti et al. 1987; Pasek and McIntyre 1993; Bull 2000; Stevanovic-Janezic et al. 2001a). The formation of dislodgeable solids on CCA-treated wood surface may also be attributed to wood weathering, which is caused by sunlight, temperature and moisture (Kalnins and Feist 1991), and influenced by wood species (Cui et al. 2004). Studies of CCA fixation in wood revealed that most of the interactions between CCA components and wood are through lignin (Dahlgren and Hartford 1972a, b, c; Pizzi 1982a, b, c). Lignin is photo-degraded and water-soluble quinone-like compounds are formed during wood weathering (Fengel and Wegener 1984). CCA components may come loose from treated wood during the photodegradation of lignin. In formation of dislodgeable solids on the surface of CCA-treated wood may also be caused by the biological activity.

The addition of water repellents (WR) into CCA wood treatment has been applied industrially for years to help improve the dimensional stability of wood. In general, commercial WR used for CCA treatment contains oil, a solvent to reduce the viscosity of the oil, and a surfactant to keep the WR compatible with CCA treating solution (Williams and Feist 1999). WR treatment may reduce the rate of water absorption and desorption by wood, and consequently decrease the changes of moisture content in wood, which reduces wood swelling, shrinking, cracking, and peeling (Zahora 1995).

Several risk assessments associated with contacting CCA-treated wood in playground, deck or other residential use have been conducted (USEAP 2001b; Gradient Corporation 2001; Dang et al. 2003). The cancer risk of arsenic exposure through oral ingestion of the dislodgeable solids and CCA contaminated soil was estimated at 2×10^{-4} by USEPA (2001b), and 1.4×10^{-4} in a recent risk assessment of children exposed to CCA-treated wood in playsets (Dang et al. 2003). However, the cancer risk at 3×10^{-6} provided by Gradient Corporation (2001) is far less than USEPA's estimation. The toxicity of an element is influenced by the route and the amount of exposure. The levels of CCA components that can be dislodged and available on the surface of CCA-treated wood are sources of debate. Several numbers on the amount of arsenic, and chromium that could be collected from the surface of CCA-treated wood were proposed (Stilwell 1999; Maas et al. 2002). These numbers were obtained using several methods to collect and quantify. Little information was given on wood species, the age in service, chemical retention, and details on the method of collection.

In this study we proposed to qualify and quantify the dislodgeable solids that can be removed from the surface of commercial CCA type C (CCA) and CCA/WR southern pine treated at a retention of 6.4 kg/m^3 total oxides. To achieve this goal, the first step was to collect the dislodgeable solids. No standard protocol is available to collect dislodgeable solids from CCA-treated wood. Several methods to collect the dislodgeable solids have been applied and reported: hand wiping, cloth wiping, and paper wiping (Gradient Corporation 2001). We proposed to use three methods to compare the amount of arsenic, chromium, and copper collected: the first method was a glove-on-hand wiping, which consisted of wearing a latex-free nitrile glove on both hands and use the palms to wipe the surface of CCA-treated wood; the second method was to use cellulose filter paper to wipe the board surface; and the third method used a test tube brush to brush wipe a wet board surface. The most appropriate method which was capable of obtaining the largest amount of arsenic, chromium, and copper from the wood surface without changing the chemical nature was selected for further study in order to facilitate characterization of the dislodgeable solids.

CCA and CCA/WR-treated southern pine boards were exposed in the field (above ground). The dislodgeable solids were collected on a monthly basis, to determine the amount of arsenic, chromium, and copper that could be obtained at different stage of exterior exposure. To illustrate the migration/redistribution of arsenic, chromium, and copper in treated wood during the field exposure, and the potential impact on the amount of the three elements collected in the dislodgeable solids, chemical distributions in wood samples with no field exposure and after 15 months of field exposure were analyzed.

Atomic absorption spectroscopy (AA) was used to quantify the amount of arsenic, chromium, and copper in solid samples after an acid digestion. AA analysis is based on the absorption of electromagnetic radiation by atoms or ions. When a sample is atomized at high temperature (e.g. 2100~2400°C for acetylene/air mixture for flame atomic absorption spectroscopy; and 1500-2600°C for samples in a pyrolitically coated graphite tube for graphite furnace atomic absorption spectroscopy), a substantial fraction of the metallic constituents are reduced to gaseous atoms and ionized. The electronic transitions of the outermost electrons yield ultraviolet or visible radiation, which serves as the basis for AA analysis. AA is sensitive means for the quantitative determination of more than 60 metals or metalloid elements.

A flame atomic absorption spectroscopy (FAA) was applied to analyze elemental arsenic, chromium, and copper at parts per million levels (ppm), and a graphite furnace atomic absorption spectroscopy (GFAA) was used to analyze elemental arsenic at parts per billion levels (ppb). The detection limits of arsenic, chromium, and copper by using FAA and the detection limit of arsenic by using GFAA were determined by following a procedure described by Perkin-Elmer (1982). The instrumental detection limit is defined by Delahay (1957) as the lowest concentration of the element that can be clearly differentiated from zero by the instrument at a signal to noise ratio of 2.

3.2 Material and Methods

3.2.1 Dislodgeable solids collection for collection methods comparisons

3.2.1.1 CCA-treated southern pine

CCA-treated southern pine boards used for comparing the dislodgeable solids collection methods were obtained from Osmose, Inc. The boards were removed from an artificial deck built aboveground by Osmose, Inc. in Fayetteville, GA after a 16-month exterior exposure. The initial chemical retention in the wood was labeled at 6.4 kg/m^3. The dimension of each board was 2.5cm × 14cm × 60cm. The weathered surface of the board was used to collect the dislodgeable solids. All the boards had been subjected to an initial test-tube brush wiping before used for the collection method comparisons.

3.2.1.2 Dislodgeable solids collection methods

The collection of dislodgeable solids was performed in the lab at a room temperature of 20°C and relative humidity of 65±5%. Three dislodgeable solids collecting methods were used: a glove-on-hand wiping, a paper wiping, and a test-tube brush wiping. The protocol of each collection method is described as following.

3.2.1.2.1 Glove-on-hand wiping method

The dislodgeable solids were collected by using hand with glove on. Powder and latex free Nitrile-Blue medical examination gloves purchased from Maxxim Medical Inc. MA were used (Item # 484501). The surface area of the hand conducted for the dislodgeable solids collection was about 100 cm^2/hand. The load applied for the wiping (both hands) was measured by using a balance (ACCU-2101, Fisher Scientific). A load of 1000±200 g, which corresponded to a pressure of 5.0±1.0 g/cm^2 was applied for the glove-on-hand wiping. Dry board surface was wiped once along the longest edge starting from one end to the other. It took about 15 seconds to wipe a single board. The gloves were rinsed after each single board wiping with 150 ml deionized (DI) water (pH of 5.6±0.1), and a new pair of gloves was used for each single board. A total of 10 boards with a total surface area of 0.85 m^2 were used for the glove-on-hand wiping. The wash was collected and concentrated. FAA was used to determine the amount of arsenic, chromium, and copper collected.

3.2.1.2.2 Paper wiping method

Dry Whatman #1 filter paper (Whatman International Limited, England) with a surface area of 176 cm^2/piece was used to wipe the wood surface. A total of 10 boards with surface area of 0.85 m^2 were subjected to the paper wiping. One piece of filter paper was used to wipe a single board. Both hands were loaded on the filter paper for the wiping. Each board surface (dry) was wiped once along the longest edge starting from one end to the other. The load applied was 1000±200 g, which corresponded to a pressure of 5.0±1.0 g/cm^2. It took about 15 seconds to wipe a single board. The filter paper was collected and acid digested. Blank filter paper was also digested as the control. The digested samples were analyzed for arsenic, chromium, and copper contents using FAA.

3.2.1.2.3 Test-tube brush wiping method

About 150 ml of deionized (DI) water (pH of 5.6±0.1) was used for each board with a surface area of 0.085 m^2. The board was placed at a 45-degree angle with one end in a polyethylene tray (Rubbermaid). The dimension of the tray was 56 cm × 41 cm × 14 cm. An initial DI water spraying (about 30 ml) was applied to wet the board surface by using a washing bottle (Polyethylene 250ml, VWR 16651-573). The wetted surface was then wiped with a test tube brush (white bristles, fan style tip, 13 cm in length × 3 cm in diameter, VWR 17212-028) from the top to the bottom end along the longest edge of the board. About 30-50 ml of DI water was sprayed on the board surface followed by a test tube brush wiping. Each board was wiped 3-5 times until all the 150 ml DI water was consumed. About 40-60 seconds was used to wipe a single board. The wash from the wiping was collected in the polyethylene tray. The load applied for the brush wiping was 250±30 g. The contacting area between the brush and the board was about 39 cm^2. The pressure applied for the wiping was about 6.4±0.7 g/cm^2.

3.2.1.2.4 Wash concentrating and drying

The wash collected from the glove-on-hand wiping or the test tube brush wiping was filtered through a thin layer of glass wool (Pyrex brand filtering fibers, Owens-Corning Fiberglass Corporation. Catalog No. 3950) placed on a Büchner funnel (glass, 17 cm in diameter) to remove particles larger than 0.5 mm. The wash filtered through the glass wool was collected in a 4-liter Erlenmeyer flask (Pyrex 4L, heavy duty) and stored at 4°C in a refrigerator before further concentration. The wash was concentrated using roto-evaporation (RE 120 & Büchi Rotovapor R-200, Brinkmann Instruments, Inc.). The roto-evaporation was carried out within 24 hours after the wash collection. The roto-evaporation was set at a temperature of 45°C and a vacuum level of 28-30 inch Hg. About 95% of the water was evaporated during the roto-evaporation. The concentrated wash was transferred into a beaker (Griffin glass w/spout, 150 ml capacity, 57 mm × 82 mm, VWR 13912-182) and exposed to the air at a temperature of 20°C and relative humidity of 65±5%. It took approximately 2 days for the concentrated wash to dry. After air drying, solids were collected in a glass bottle (round glass, 60 ml wide mouth, black screw cap w/flat, disc-type polyvinyl liners, VWR 16194-020) tighten with a cap and stored in freezer until further analysis.

3.2.2 Dislodgeable solids collection for characterization

3.2.2.1 CCA and CCA/WR-treated southern pine

Commercial CCA type C (CCA) and CCA with water repellent (CCA/WR) treated southern pine lumbers were purchased from Lowe's in Lansing, Michigan in November, 2001. The lumber was labeled with Georgia-Pacific Co., Atlanta, GA at a chemical retention of 6.4 kg/m^3. According to Georgia-Pacific Co.[1], Chemical Specialties, Inc. is their provider of the WR. The dimensions of the boards were 2.6cm × 15cm × 244cm. Each board was cut into 4 samples of identical size (2.6cm × 15cm × 61cm) to facilitate the handling during the dislodgeable solids collection.

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[1] Information obtained from a telephone conversion with Georgia-Pacific Corporation

An artificial deck was constructed using these CCA or CCA/WR-treated southern pine boards. The deck was loaded at Tree Research Center (TRC), Department of Forestry, Michigan State University, East Lansing, Michigan (Figure 3-1). CCA-treated southern pine boards were isolated from CCA/WR treated boards to prevent possible contamination from each other. The deck was 0.6 m above ground with a total decking area of 7.3 m^2. The seasonal weather report of Lansing, Michigan, USA (42°N 84°W) is illustrated in Figure 3-2.

3.2.2.2 Dislodgeable solids collection from wood exposed in the field

CCA and CCA/WR-treated southern pine boards were collected from TRC once every month during the field exposure trials for the dislodgeable solids collection. Dislodgeable solids were collected from the weathered surface of wood and the collection was performed in the same day when boards were harvested, and returned to the field in the following day. The board surface subjected to dislodgeable solids collection was placed facing the sunshine consistently in the field. The collection schedule was set on the 8th of every month with the exception of rainfalls, the collection schedule was postponed to the next earliest clear day. The collection in the following month followed the regular schedule. Table 3-1 lists the weather information on the day of the solids collection, provided by the database in www.wunderground.com. An initial dislodgeable solids collection was performed in November, 2001 before the field exposure.

3.2.2.3 Arsenic, chromium, and copper distribution in CCA and CCA/WR-treated southern pine with no field exposure and after 15 months of field exposure

Table 3-1. Weather condition on the day of the dislodgeable solid collection

Sampling day	12/9/01	1/8/02	2/8/02	3/10/02	4/10/02	5/10/02	6/8/02	7/10/02	8/8/02
Mean temperature (˚C)	0.5	-4.3	0.0	-7.5	6.0	9.0	19.5	20.0	16.0
Max. temperature (˚C)	4.0	2.0	4.0	-6.0	15.0	15.0	26.0	24.0	24.0
Min. temperature (˚C)	-3.0	-10.6	-4.0	-9.0	-3.0	3.0	13.0	16.0	8.0
Dew point (˚C)	-3.0	-8.5	-3.7	-10.7	-0.1	-1.5	12.9	10.8	11.2
Standard pressure (hPa)	1022.3	-	1018.4	1023.6	1029.9	1022.3	1019.2	1021.9	1025.2
Wind speed (km/h)	10.8	22.2	7.4	36.9	12.0	30.1	10.7	16.0	4.9
Event	Clear	Clear	Clear	Fog	Clear	Clear	Clear	Clear	Clear

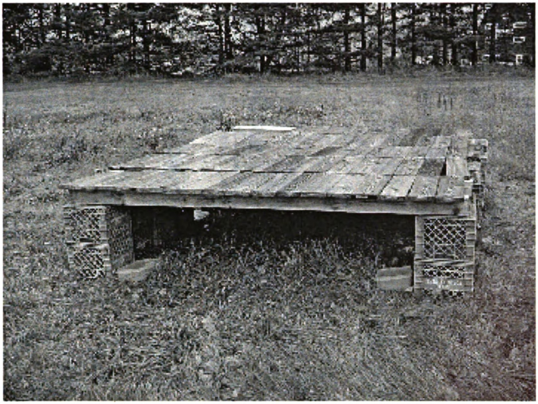


Figure 3-1. Deck built with CCA treated wood

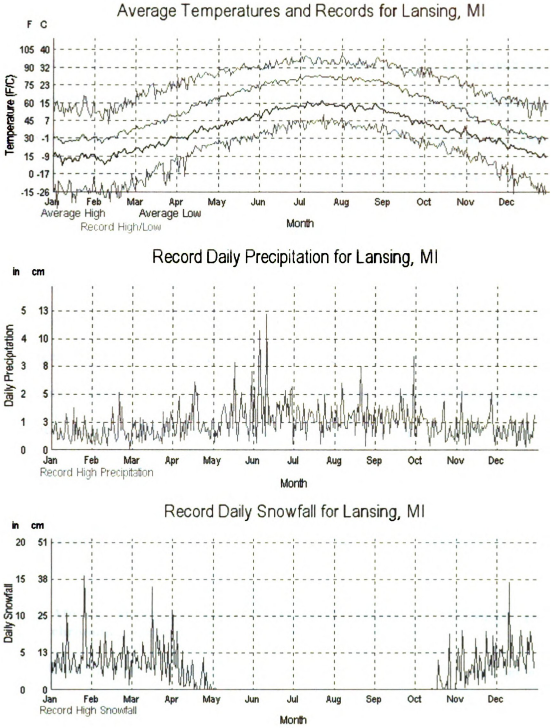


Figure 3-2. Seasonal weather report of Lansing, Michigan, USA (http://www.weatherunderground.com/)

The chemical distributions in CCA and CCA/WR-treated southern pine were analyzed after 15 months of field exposure in TRC, and compared to chemical distributions in wood cut from the same parent board and stored in lab with no field exposure. Wood samples were sectioned into thin layers parallel to the exposed surface. The sectioning schemes are illustrated in Figure 3-3. Arsenic, chromium, and copper in each section were measured individually using FAA after an acid digestion.

3.2.3 Analysis

3.2.3.1 Acid digestion of solid samples

An acid digestion was applied to solid samples such as the treated wood and the dislodgeable solids by following the protocols described in American Wood-Preservers' Association Standard (AWPA 2003): Wet Ashing Procedure for Preparing Wood for Chemical Analysis (A7-93); and Analysis of Treated Wood and Treating Solutions by Atomic Absorption Spectroscopy (A11-93). The reagents used for the acid digestion were nitric acid (A.C.S. Reagent, 68-70%, EM Science) and perchloric acid (A.C.S. Reagent, 70%, Aldrich).

3.2.3.2 Atomic absorption spectroscopy measurement of elemental arsenic, chromium, and copper - FAA and GFAA

Quantification of elemental arsenic, chromium, and copper at parts per million (ppm) level was completed by using Flame Atomic Absorption Spectrophotometer (FAA, Model: Perking Elmer 3110), equipped with an electrodeless discharge lamp (EDL) for arsenic, and hollow cathode lamps for chromium and copper (Perkin Elmer). A graphite furnace atomic absorption spectroscopy (GFAA, AAnalyst 800, Perkin Elmer

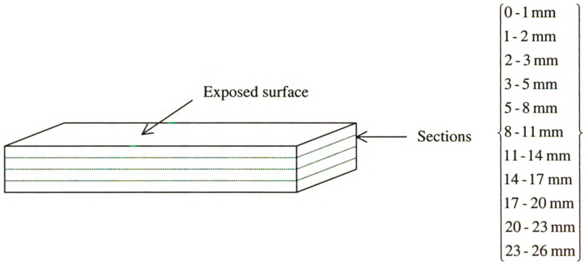


Figure 3-3. The sectioning scheme of CCA and CCA/WR treated southern pine for the chemical redistribution study

Co., CT, USA) equipped with an EDL arsenic lamp was used to quantify arsenic in parts per billion (ppb) level.

The atomic absorption standard solutions of arsenic, chromium, and copper were purchased from Aldrich Chemical Co. The concentrations of elemental arsenic, chromium (VI) and elemental copper in the standard solutions were 990 μg/ml in 2 wt.% potassium hydroxide (KOH), 1005 μg/ml in 1 wt.% hydrochloric acid (HCl), and 1007 μg/ml in 1 wt.% nitric acid (HNO_3), respectively. The solutions used to build the working curve for AA measurement were diluted from the atomic absorption standard solutions by using 2 wt.% KOH for arsenic, 1 wt.% HCl for chromium, and 1 wt.% HNO_3 for copper. Solutions at elemental arsenic concentrations of 0 ppm, 10 ppm, 25 ppm, 50 ppm, and 100 ppm were used to establish the working curve for arsenic analysis. Solutions at 0 ppm, 0.1 ppm, 0.5 ppm, 5 ppm, and 10 ppm of chromium were used to build the working curve for chromium analysis. Concentrations of the solutions used to construct the working curve for copper analysis were 0 ppm, 0.5 ppm, 5 ppm, and 10 ppm.

The concentrations of the solutions used to construct the working curve for arsenic analysis by using GFAA were 0 ppb, 2.5 ppb, 5 ppb, 10 ppb, 25 ppb, 50 ppb, 100 ppb, 150 ppb, and 200 ppb. A matrix modifier was used to reduce the interferences, particularly matrix effects in GFAA analysis. The matrix modifier was prepared by dissolving 0.1g palladium (II) chloride ($PdCl_2$, 99.999%, Aldrich), 10 g citric acid ($(HOC(CO_2H)(CH_2CO_2H)_2$, 99.5%, A.C.S. Reagent, Aldrich), and 0.05 g ammonium tungstate (99.99%, Aldrich) in 10ml hydrochloric acid (HCl, 6N, double distilled, Caledon Laboratory Chemicals), and diluted to 1000 ml using DI water (Flores del Pino 2003).

To determine the detection limits of arsenic, chromium, and copper by using FAA and arsenic by using GFAA, two concentrations of solutions were prepared for each element from the atomic absorption standard solutions according to Perkin-Elmer (1982). The lower concentration standard was approximately 5× the expected detection limit, and the second standard was made twice this concentration: arsenic solution at concentrations of 2.7 ppm and 4.8 ppm, chromium solutions at 0.6 ppm and 1.3 ppm, and copper solutions at 2.6 ppm and 5.2 ppm were prepared to determine the detection limits of arsenic, chromium, and copper, respectively by using FAA. Two arsenic solutions at the concentrations of 2.5 ppb and 5.0 ppb were prepared to determine the detection limits of arsenic by using GFAA. The concentrations of the two solutions of each element were measured by using AA in the sequence of blank, low-concentration solution, blank, high-concentration solution, and repeated the sequence for at least 20 times.

The detection limits of arsenic, chromium, and copper by using FAA, and the detection limit of arsenic by using GFAA were calculated according to Perkin-Elmer (1982) by using Equation 1.

$$\text{detection limit} = \frac{\text{concentration of the solution} \times 2 \text{ standard deviation}}{\text{mean}} \qquad (1)$$

3.2 Results and Discussion

3.3.1 Instrumental detection limits of elemental arsenic, chromium, and copper by using FAA and GFAA

Tables 3-2 and 3-3 list the derivations of the detection limits. The detection limits of arsenic, chromium, and copper by using FAA were determined at 0.6 ppm, 0.02 ppm, and 0.3 ppm, respectively. The detection limit of arsenic by using GFAA was 0.3 ppb.

3.3.2 Comparisons of the dislodgeable solids collecting methods

Table 3-4 lists the FAA analysis results of elemental arsenic, chromium, and copper contents in the dislodgeable solids collected by using the glove-on-hand wiping, the paper wiping, and the test tube brush wiping methods. One-way ANOVA analysis indicated that significant difference existed in the amount of arsenic, chromium, or copper collected by using different collecting method (Appendix 1, 2, and 3).

From a total surface area of 0.85 m^2 of CCA-treated southern pine (Osmose Inc. samples, collected from an artificial deck after field exposure), about 0.13±0.02 mg, 0.24±0.04 mg, and 0.13±0.09 mg of elemental arsenic, chromium, and copper were collected by using the glove-on-hand wiping method. Relatively larger amounts of arsenic, chromium, and copper, at 0.33±0.02 mg, 1.49±0.16 mg, and 0.57±0.05 mg, respectively, were obtained from the same board surface area by using the paper wiping method compared with the glove-on-hand wiping method. The largest quantities of arsenic, chromium, and copper were obtained by using the test tube brush wiping method. About 1.82±0.09 mg of arsenic, 2.45±0.06 mg of chromium, and 0.98±0.12 mg of copper were collected from 0.85 m^2 of board surface.

Similar pressure at 5.0±1.0 g/cm^2 was applied on the board surface by using the glove-on-hand wiping method and the paper wiping method. The surface area of both hands was about 200 cm^2, which was close to the surface area of the filter paper used (176 cm^2). A single wiping was applied by using both collecting methods. The wiping behavior could be described as an "abrasion" of the residuals from the wood surface. The residuals abraded from the wood surface could transfer back to board during the wiping process. The significant difference in the amount of arsenic, chromium, or copper

Table 3-2. **Determination of the detection limits of arsenic, chromium, and copper by** using FAA (Perkin-Elmer 3110)

Statistical analysis	Low-conc. solution			High-conc. solution		
	As	Cr	Cu	As	Cr	Cu
Mean, ppm	2.70	0.61	2.61	4.78	1.32	5.26
Standard error	0.080	0.0090	0.021	0.070	0.0060	0.034
Standard deviation	0.33	0.043	0.098	0.30	0.030	0.16
Count	17	22	22	17	22	22
Detection limit, ppm	0.61	0.014	0.19	0.63	0.023	0.31

Table 3-3. Determination of the detection limit of As by using GFAA (Perkin-Elmer AAnalyst 800)

Statistical analysis	Low-conc. solution	High-conc. solution
	As	As
Mean, ppb	2.46	5.01
Standard error	0.030	0.030
Standard deviation	0.13	0.14
Count	17	17
Detection limit, ppb	0.26	0.28

Table 3-4. Arsenic, chromium, and copper collected from CCA treated southern pine by using the glove-on-hand wiping, the paper wiping, and the test tube brush wiping methods (0.85 m^2, weathered surface)

Collection method	Glove-on-hand wiping	Paper wiping	Test tube brush wiping
Load applied (g)	1000 ± 200	1000 ± 200	250 ± 30
Pressure applied (g/cm^2)	5.0 ± 1.0	5.0 ± 1.0	6.4 ± 0.7
As (mg/m^2)	0.13 ± 0.02	0.33 ± 0.04	1.82 ± 0.09
Cr (mg/m^2)	0.24 ± 0.04	1.49 ± 0.16	2.45 ± 0.05
Cu (mg/m^2)	0.13 ± 0.01	0.57 ± 0.06	0.98 ± 0.12

collected by using the glove-on-hand wiping, and the filter paper wiping could be attributed to the "transfer efficient" - the ratio between the amount of residuals presence on the wood surface and those transferred to the Nitrile-Blue glove or the filter paper. The filter paper tended to "pick up" more residuals compared to the glove. Therefore, the material used for the wiping could affect the amount of chemicals collected.

Compared with the glove-on-hand wiping and the filter paper wiping, a 3-4 times repeated wiping behavior was applied to each single board by using the test tube brush wiping method with a slightly higher pressure applied at 6.7±0.7 g/cm^2. The test tube brush wiping accompanied with water spraying consisted of relatively more activities, which included water absorption by wood, chemicals solubilization and leaching, and an abrasion with the brush bristles. Besides, the running water on the board surface from the water spraying facilitated the collection of the abraded residuals. These were possibilities as to larger amount of residuals were obtained from the board surface compared to the other two methods.

By using a moist polyester wiping, Stilwell (1999) collected about 6.9 mg/m^2 of arsenic from CCA-treated wood (new, sold for playground construction), and 3.5 mg/m^2 of arsenic by using the same collecting method from a in-service playground. Maas et al. (2002) reported the collection of arsenic at 2.3-10.9 mg/m^2 and 2.4-20.3 mg/m^2 of chromium from new boards at chemical retention of 6.4 kg/m^3, and 1.6-4.5 mg/m^2 of arsenic and 2.0-5.0 mg/m^2 of chromium from boards after 6 months of outdoor exposure (Table 3-5). No detailed information on the wiping behavior, such as the pressure applied or the wiping speed was provided from either of these studies. The amounts of arsenic and chromium collected by using the glove-on-hand wiping and the paper wiping were relatively lower compared with Stilwell (1999) and Maas et al. (2002). One of the factors that caused the lower values of arsenic and chromium collected could be attributed to the relatively longer duration of wood exterior exposure (16 months). The amount of arsenic and chromium collected using the test tube brush wiping method was comparable with what has been reported by Stilwell (1999) and Maas et al. (2002).

In order to study the properties of the dislodgeable solids collected, it is critical to avoid altering the nature of the chemicals in the dislodgeable solids. Therefore, the selection of the wiping material, and the collection of the residuals from the wiping material are important to obtain accurate information. In order to collect a relatively larger amount of dislodgeable solids to facilitate further analysis, the test tube brush wiping method was selected in this study.

3.3.3 Dislodgeable solids collected from CCA and CCA/WR-treated southern pine

Table 3-6 presents the elemental arsenic, chromium, and copper contents in the dislodgeable solids collected from CCA or CCA/WR-treated southern pine at different stage in the field study. From a total board surface area of 1.83 m^2, similar mass of dislodgeable solids were obtained from these two types of boards before field exposure. About 0.56 g and 0.62 g of solids were collected from CCA and CCA/WR-treated wood, respectively. FAA analysis found that, the contribution from arsenic, chromium, and copper to the dislodgeable solids was less than 4% in weight. The dislodgeable solids were mainly composed of wood fibers and soil/dust collected from the board surface. The dislodgeable solids collected from CCA-treated wood consisted 1.2% of arsenic, 1.6% of

Table 3-5. Arsenic, chromium, and copper collected from CCA treated wood surface using various methods

Study	Wood samples	Collecting method	As (mg/m^2)	Cr (mg/m^2)	Cu (mg/m^2)
This study	16-month field exposure, chemical retention at 6.4kg/m^3 before the exposure	glove-on-hand wiping	0.13	0.24	0.13
		paper wiping	0.33	1.49	0.57
		test tube brush wiping	1.82	2.45	0.98
Maas et al. 2002	new board, chemical retention at 6.4kg/m^3	laboratory wipes wiping	2.3-10.9	2.4-20.3	-
	6-month exposure, chemical retention at 6.4kg/m^3 before exposure	laboratory wipes wiping	1.6-4.5	2.0-5.0	-
Stilwell 1999	new wood sold for playground construction	moist polyester wipe	6.9	-	-
	playground	moist polyester wipe	3.5	-	-

Table 3-6. Dislodgeable solids collected from CCA or CCA/WR treated southern pine during the field exposure ($1.83m^2$ board surface area)

Board type	Field exposure, month	Dislodgeable solids, weight (g)	Element in the dislodgeable solid, wt. %			Amount of element collected from board surface (mg/m^2)		
			As	Cr	Cu	As	Cr	Cu
CCA	0	0.56	1.2	1.6	0.73	3.7	5.0	2.2
	1	0.17	1.3	1.9	2.9	1.2	1.7	2.7
	2	0.30	0.65	0.88	0.67	1.1	1.4	1.1
	3	0.15	0.41	0.26	0.25	0.33	0.21	0.21
	4	0.14	0.26	0.22	0.26	0.20	0.17	0.20
	5	0.07	0.37	0.39	0.37	0.14	0.15	0.14
	6	0.13	0.15	0.17	0.35	0.11	0.12	0.25
CCA/WR	0	0.62	0.59	0.67	0.55	2.0	2.3	1.9
	1	0.10	0.43	0.36	1.1	0.23	0.20	0.61
	2	0.24	0.32	0.38	0.47	0.42	0.50	0.61
	3	0.16	0.35	0.29	0.29	0.31	0.25	0.25
	4	0.13	0.15	0.13	0.33	0.11	0.10	0.24
	5	0.10	0.24	0.27	0.37	0.13	0.15	0.20
	6	0.12	0.24	0.29	0.34	0.16	0.19	0.22

chromium, and 0.73% of copper. About 50% decrease in the contents of both arsenic and chromium were noticed from dislodgeable solids collected from CCA/WR-treated wood compared to those from CCA-treated wood. About 25% decrease in copper content was found, which was not proportional to the decrease of arsenic or chromium in the solids. With similar mass of dislodgeable solids collected, the decreased arsenic, chromium, and copper contents in dislodgeable solids from CCA/WR-treated wood suggested that water repellent treatment retard the leaching of CCA components instead of the loss of wood fibers.

After one month of field exposure, an 8% increase in arsenic content and an 18% increase in chromium in the dislodgeable solids collected from CCA-treated wood compared with the initial collection were observed. About 300% increase in copper content in the dislodgeable solids after one month of field exposure suggested that the reaction sites of copper in wood could be independent of arsenic or chromium. The addition of WR decreased the depletion of the three elements from wood surface compared with that from wood with no WR treatment. However, there was still a 100% increase in copper content in the dislodgeable solids compared with the initial collection (Table 3-6). These findings are in consistent with the theories of CCA interactions with wood proposed by Pizzi (1982a, b) and Bull (2000, 2001): copper interacts / complexes with wood carboxylate independent of arsenic or chromium, the complex formed is relatively more soluble compared to the fixation product of arsenic and chromium, such as chromium (III) arsenate and chromium (III) hydroxide.

Figure 3-4 illustrates the elemental arsenic, chromium, and copper contents in the dislodgeable solids collected from CCA and CCA/WR-treated southern pine during the field exposure. The largest depletion of arsenic, chromium, and copper was observed at the initial stage of the field exposure. A general decrease of the three elements collected was observed through out the first three months and became stable thereafter. The amount of arsenic, chromium, or copper collected from board surface expressed in mg/m^2 are calculated and listed in Table 3-6. About 3.7 mg/m^2, 5.0 mg/m^2, and 2.2 mg/m^2 of arsenic, chromium, and copper, respectively were collected from CCA-treated wood before the field exposure. About 2.0 mg/m^2, 2.3 mg/m^2, and 1.9 mg/m^2, respectively were collected from CCA-C/WR treated wood before the field exposure. The amount of arsenic, chromium, and copper collected decreased to 0.11 mg/m^2, 0.12 mg/m^2, 0.25 mg/m^2, respectively from CCA-treated southern pine, and 0.16 mg/m^2, 0.19 mg/m^2, and 0.22 mg/m^2 from CCA/WR-treated wood after 6 months of field exposure in TRC.

In Figure 3-4, relatively larger amount of arsenic, chromium, and copper were depleted from CCA-treated wood compared with CCA/WR-treated wood during the first two months of field exposure, minimum difference in the depletion of the three elements was observed thereafter, which suggested the addition of WR to CCA wood treatment reduced the leaching of the three element at the initial stage of field exposure. However, with a prolonged duration of field exposure, WR could be depleted from treated wood or modified caused by the environmental factors such as rainfalls, snow, UV, ect., and resulted in a relatively less significant performance in retarding the leaching of arsenic, chromium, and copper.

3.3.4 Arsenic, chromium, and copper in CCA and CCA/WR-treated southern pine

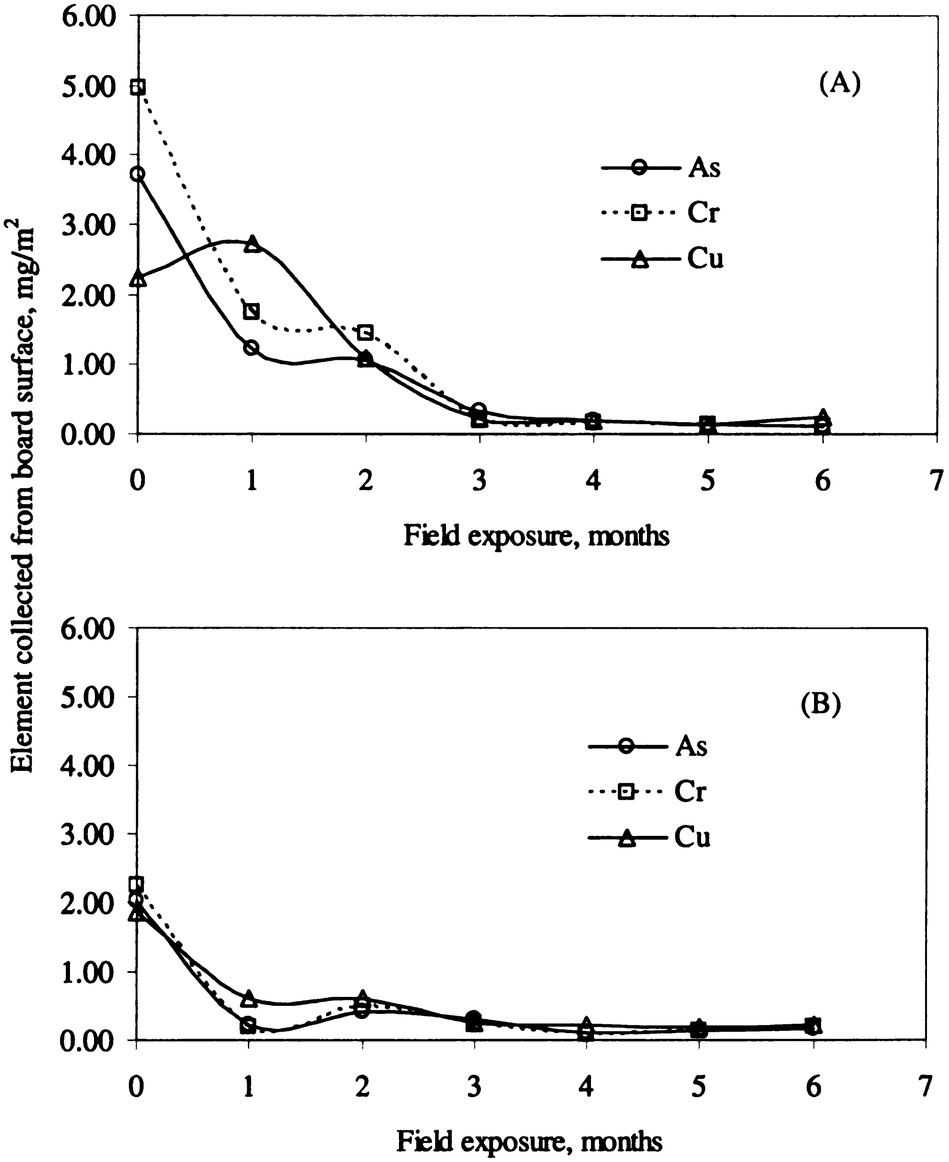


Figure 3-4. Arsenic, chromium, and copper collected from (A) CCA, (B) CCA/WR treated southern pine using DI water during field exposure

3.3.4.1 Arsenic, chromium, and copper in the 1-mm surface layer of CCA and CCA/WR-treated southern pine

Since the dislodgeable solids collection using test tube brush wiping was most related to chemical leaching and "abrasion" of wood fibers on the wood surface layer, arsenic, chromium, and copper retentions in the 1-mm surface layer of the treated wood were analyzed and compared with the three elemental contents in the dislodgeable solids (Table 3-7). Arsenic, chromium, and copper contents in the surface layer of CCA-treated wood were 3.38 mg/g, 6.26 mg/g, and 1.56 mg/g, respectively, and 4.59 mg/g, 9.19 mg/g, and 2.02 mg/g, respectively in the surface layer of CCA/WR-treated wood. The corresponded percentage compositions expressed in oxides were calculated according to the equations listed in Appendix 2 and presented in Table 3-7. The percentage composition of As_2O_5, CrO_3, and CuO was 32.0 : 52.7 : 15.3 in CCA dislodgeable solids and 31.5 : 43.5 : 25.0 in CCA/WR dislodgeable solids. Compared with their percentage composition in the 1-mm surface layer at 27.0 : 62.6 : 10.4 from CCA-treated wood and 25.8 : 64.7 : 9.5 from CCA/WR-treated wood, the percentage composition of arsenic and copper increased while chromium decreased in the dislodgeable solids. The increase in arsenic and copper and decrease in chromium also indicated that the test tube brush wiping collection method was composed of both "abrasion" of fibers on wood surface and the leaching of CCA components. Should the dislodgeable solids have contained only "abraded" wood fibers, similar composition of arsenic, chromium, and copper as those in the surface layer of treated wood would have been expected. The decreased composition of chromium could be attributed to the decreased leaching of chromium after CCA fixation in wood (Cooper 1993; Murphy and Dickinson 1990; Cooper et al. 1997; Kennedy and Palmer 1994; Lahiry 2001; Crawford et al. 2002).

Table 3-7. Comparison of elemental arsenic, chromium, and copper contents in the 1-mm surface layer of CCA treated wood and in the dislodgeable solids

Treatment	Retention in wood (mg/g)			Percentage compositions, $As_2O_5 : CrO_3 : CuO$	
	As	Cr	Cu	1-mm surface layer	Dislodgeable solids
CCA	3.38(0.06)	6.26(0.02)	1.56(0.02)	27.0 : 62.6 : 10.4	32.0 : 52.7 : 15.3
CCA/WR	4.59(0.03)	9.19(0.02)	2.02(0.01)	25.8 : 64.7 : 9.5	31.5 : 43.5 : 25.0

% composition in CCA preservative, AWPA standard ($As_2O_5 : CrO_3 : CuO$): 18.5 : 47.5 : 34.0

Elemental retentions in wood are the average of ten measurement, data in parenthesis are the standard deviations

3.3.5 Chemical redistribution of arsenic, chromium, and copper after 15 months of field exposure

Table 3-8 summarizes arsenic, chromium, and copper contents in CCA or CCA/WR-treated southern pine before and after 15 months of field exposure and the corresponding elemental losses in percentage.

CCA-treated wood consisted of 0.35% of arsenic, 0.76% of chromium, and 0.17% of copper before the field exposure. After 15 months, arsenic, chromium, and copper contents in CCA-treated wood were 0.26%, 0.52%, and 0.13%, respectively. About 24.5% loss in arsenic, 31.9% loss in chromium, and 23.9% loss in copper were observed (Table 3-8).

The initial content of the three elements in CCA/WR-treated wood were 0.42%, 0.81%, and 0.20% for arsenic, chromium, and copper, respectively. After 15 months of field exposure, about 22.3% loss in arsenic, 22.6% loss in chromium, and 22.0% loss in copper were detected (Table 3-8).

The chemical retentions in wood were calculated by using the wood density value at 500 kg/m^3 according to AWPA standard A12 (AWPA 2003) and listed in Table 3-8. The chemical retentions in CCA and CCA/WR-treated wood before the field exposure were at 7.1 kg/m^3 and 8.5 kg/m^3, respectively, and 5.3 kg/m^3 and 6.6 kg/m^3 after 15 months of field exposure. The total chemical losses were 25.3% in CCA-treated southern pine and 22.2% in CCA/WR-treated southern pine.

Similar percentages of arsenic and copper loss at 22.0-24.5% were observed from CCA and CCA/WR-treated southern pine, suggested that the addition of WR to CCA wood treatment did not retard the depletion of arsenic or copper throughout the

Table 3-8. Arsenic, chromium, and copper contents (%) in CCA and CCA/WR treated southern pine before and after 15 months of field exposure

Treatment	Element	Before exposure, %	After exposure, %	Chemical loss, %
CCA*	As	0.35	0.26	24.5
	Cr	0.76	0.52	31.9
	Cu	0.17	0.13	23.8
	Chemical retention, total oxides, kg/m^3	7.1	5.3	25.3
CCA/WR*	As	0.42	0.33	22.3
	Cr	0.81	0.63	22.6
	Cu	0.20	0.15	22.0
	Chemical retention, total oxides, kg/m^3	8.5	6.6	22.2

* The wood density at 500 kg/m^3 was used for the calculation of chemical retentions in wood

15 months of field exposure. However, a decrease of chromium loss from 31.9% in CCA-treated southern pine to 22.6% in CCA/WR-treated southern pine was observed, which indicated that the addition of WR was effective in reducing the loss of chromium within 15 months.

Table 3-9 lists the chemical losses of wood after 15 months of field (TRC) exposure and a study conducted by Jin and Preston (1993). A broad range of chemical loss, at 18.8-72.8% of arsenic, 13.6-23.6% of chromium, and 7.8-27.0% of copper from CCA-treated wood was reported by Jin and Preston (1993) after 12 months of field exposure in Hilo, HI. The wood chemical retentions, wood dimension, and the geological region of the field exposure, and the exposure duration may have affected the results. The levels of arsenic and chromium lost from both CCA and CCA/WR-treated wood were relatively close to wood at chemical retention of 4.0 kg/m^3 observation by Jin and Preston (1993). A 22.0-23.9% of copper loss after TRC exposure was relatively larger than the 7.8% of copper loss at chemical retention of 4.0 kg/m^3 by Jin and Preston (1993).

3.3.6 Arsenic, chromium, and copper redistribution in CCA and CCA/WR-treated southern pine in field exposure

The redistribution of a chemical in wood is defined as the changes in chemical distribution pattern in wood. The chemical redistribution of arsenic, chromium, and copper in CCA and CCA/WR treated southern pine in a 15-month field exposure is plotted in Figures 3-5 and 3-6. The distributions of earlywood and latewood in wood samples used to study the redistribution pattern are marked in the legend in each figure.

After 15 months of field exposure, arsenic, chromium, and copper contents decreased in the weathered face of CCA-treated southern pine. The largest decreases in

Table 3-9. Arsenic, chromium, and copper losses after field exposure - comparisons of values from this study and Jin and Preston (1993)

Study	Above ground	Wood dimension	Chemical retention, total oxides, kg/m^3	As loss, %	Cr loss, %	Cu loss, %
This study	15 months, East Lansing, MI	0.026×0.15×0.61m	7.5	24.5	31.9	23.9
			9.1/WR	22.3	22.6	22.0
Jin and Preston (1993)	12 months, Hilo, HI	0.9×0.9×1m	1.0	72.8	23.6	27.0
			2.0	40.1	17.8	13.1
			4.0	18.8	13.6	7.8

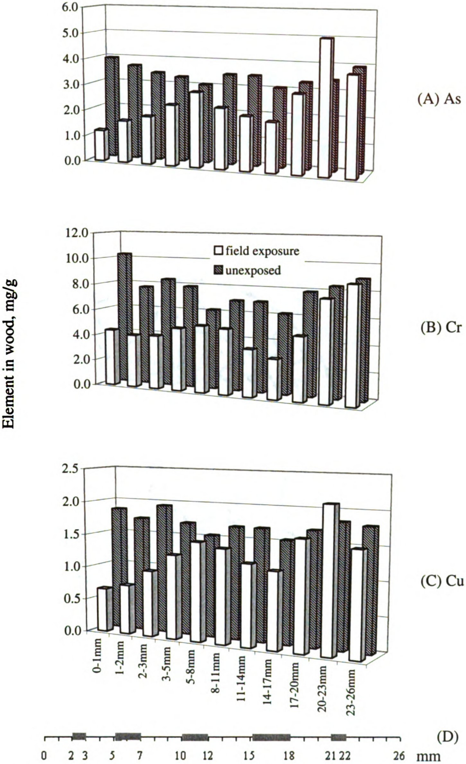


Figure 3-5. (A) As, (B) Cr, (C) Cu distribution in CCA treated southern pine with no field exposure and after 15-month of field exposure, and (D) the earlywood and latewood distributions in wood sections, ┬┬┬ earlywood, ▬ latewood

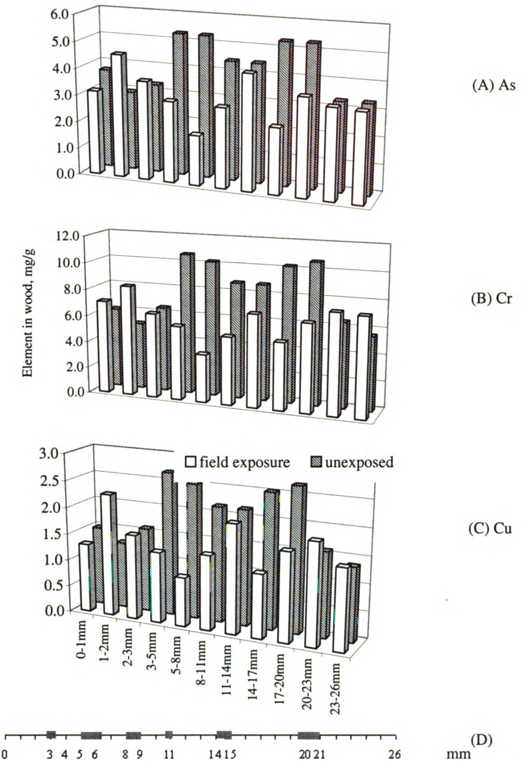


Figure 3-6. (A) As, (B) Cr, (C) Cu distribution in CCA/WR treated southern pine with no field exposure and after 15-month of field exposure, and (D) the earlywood and latewood distributions in wood sections, ┬┬┬ earlywood, ▬ latewood

arsenic, chromium, and copper were observed in the top 1-mm section of the weathered surface, with about 75% decrease in arsenic and about 60% decrease in both chromium and copper, which was partially attributed to the chemical leaching and the collection of the dislodgeable solids. The metallic components of CCA could migrate from the top toward the bottom side. This was demonstrated by larger depletions of arsenic, chromium, and copper from the weathered side of wood, the gradually less depletion from the bottom (unweathered) side, and the increased arsenic, chromium and copper content in the 20-23 mm section. The migration of the metallic components in wood may be caused by the weather conditions. During rainfalls or during the melting of snow, large amount of water was absorbed by the wood. The mobile arsenic, chromium, and copper could move with the water flow following an "up-to-down" pattern caused by gravity. The 5-8-mm wood section was mostly latewood, higher in density and more hydrophobic. Therefore, a "jammed" water movement resulted in a relatively less chemical depletion.

The redistribution patterns of arsenic, chromium, and copper in CCA/WR-treated southern pine after 15 months of field exposure were different from those in CCA-treated wood (Figure 3-6). The chemical loss of arsenic, chromium, and copper in the top 3-mm sections of CCA/WR-treated southern pine was not as severe as those in CCA-treated wood. Increases of arsenic, chromium, and copper in the 1-2 mm section were observed. The highest chemical depletion was found in the 3-8 mm and the 14-20 mm sections. The chemical retentions in the unweathered side remained close to those with no field exposure. The chemical redistribution pattern in CCA/WR-treated wood could be described as a depletion "from inner to peripheral zone" pattern. The chemical redistribution pattern in CCA/WR-treated wood could be attributed the introduction of water repellent, which consisted of paraffin wax and increased the hydrophobisity of wood. Less water was absorbed during the period of rainfall, but once absorbed, the water stayed longer in wood. The migration of arsenic, chromium, and copper with the water evaporation from the inner sections to the peripheral zone became important, and resulted in larger depletion of arsenic, chromium, and copper in the core.

3.4 Conclusions

The amount of arsenic, chromium, and copper collected from the board surface of CCA-treated wood was significantly influenced by the collection methods such as a glove-on-hand wiping, a paper wiping, or a test tube brush wiping method. Largest quantities of arsenic, chromium, and copper were obtained by using the test tube brush wiping method.

The compositions of elemental arsenic, chromium, and copper in the dislodgeable solids collected from CCA and CCA/WR-treated southern pine were less than 4%. Larger amounts of arsenic, chromium, and copper were collected from the board surface at the initial stage of field exposure and decreased rapidly after three months.

The addition of water repellent reduced the chemical losses at the initial stage of wood exterior exposure. After 15 months, similar levels of arsenic and copper loss were found in CCA and CCA/WR-treated wood. The loss of chromium from CCA/WR-treated southern pine remained lower than that from CCA-treated wood.

Different chemical redistribution patterns were observed with CCA or CCA/WR-treated southern pine after 15 months of field exposure. The largest depletion of arsenic, chromium, and copper was noticed on the weathered surface of CCA-treated wood, while the largest chemical depletion was noticed in the inner zone rather than the peripheral region of CCA/WR-treated wood. Arsenic, chromium, and copper level in the unexposed side of CCA and CCA/WR-treated wood remained stable.

Chapter 4

Environmental Scanning Electron Microscope and X-ray Diffractometry Characterization of the Dislodgeable Solids

4.1 Introduction

Data from atomic absorption spectroscopy analysis of the dislodgeable solids collected from chromated copper arsenate type C (CCA) and chromated copper arsenate type C with water repellent (CCA/WR) treated southern pine indicated that less than 4% of the solids consist of arsenic, chromium, and copper. The nature of the remaining 96% was unknown.

Environmental scanning electron microscope (ESEM) is a useful technique to collect information on the topography, morphology, microstructure, and elemental composition of a specimen (Schalek and Drzal 2000). The advantage of ESEM compared to traditional scanning electron microscope (SEM) is that ESEM works under controlled environmental conditions and requires no conductive coating on the specimen. This makes it possible to examine specimens in their natural state under a vacuum of less than 50 Torr (6650 Pa).

X-ray energy dispersive spectroscopy (EDS) uses silicon doped with lithium as a detector. The interaction between the energetic monochromatic electrons from an impinging electron beam and the electrons in the atoms of the specimen results in the generation of X-rays. The generated X-rays impinge on the silicon detector surface. The penetration depth of the X-ray into the silicon is directly related to the energy of the X-rays. EDS permits detection of elements ranging from carbon (Z=6) to bismuth (Z=83) at chamber pressures of 2-10 Torr (665-1330 Pa) of water vapor.

Environmental scanning electron microscope equipped with X-ray energy dispersive spectroscopy (ESEM-EDS) has been previously used to reveal the macrodistribution of preservative in treated wood (Dawson-Andoh and Kamdem 1998; Kamdem et al. 1998; Rosenqvist 1999). However, little information on crystalline properties could be provided by ESEM.

X-ray diffractometry (XRD) is a useful technique to study compounds with ordered structures. When X-ray beam traverses the crystallite, the beam light was reflected from interplanar spacing of the particles at a certain direction. The identification of chemical compounds is based upon the position of the reflected lines (in terms of θ or 2θ) (Skoog 1984; Klug and Alexander 1954). The uniqueness of an X-ray diffraction pattern for each crystalline substance makes XRD a convenient and practical means for the qualitative identification of crystalline compounds. However, the XRD peak intensity of the crystalline component in a given sample is influenced by percentage composition and the density of the crystallite in its matrix, and its particle size. The XRD peak may not be identifiable if the composition of the crystallite is too low in its matrix or the particle size is smaller than the instrument detection limit.

XRD technique has been used to elucidate the nature of crystallite in treated wood. Gallacher et al. (1995) identified the crystal formation of copper dimethyldithiocarbamate (CDDC) in CDDC treated wood using XRD. Sutter et al. (1983) confirmed the formation of copper oxalate in copper treated wood by copper tolerant fungi. Kamdem et al. (1998) identified the formation of cuprous oxide (Cu_2O) in copper naphthenate treated southern pine after a post-treatment steaming.

ESEM-EDS analysis was employed in this study to examine the topography and chemical composition of the disoldgeable solids. XRD was used to investigate any possible crystalline information presented in the dislodgeable solids collected from CCA and CCA/WR treated southern pine.

4.2 Instrumental analysis

4.2.1 ESEM-EDS

The dislodgeable solids collected before and after 7 months of field exposure from both CCA and CCA/WR treated southern pine were used for ESEM-EDS analysis to reveal the topography and the particle size, as well as the chemical composition of the dislodgeable solids.

The ESEM-EDS analysis was performed using an ElectroScan 2020 outfitted with a LaB6 filament. The ESEM was equipped with a Link ISIS system that had an energy resolution of 130 eV and an image resolution of 5-7 nm. An Oxford Si(Li) detector utilizes an Atmospheric Thin Window (ATW) that X-ray mapping allowed the determination of imaging the chemical composition of a specimen.

All the dislodgeable solids were imaged at an accelerating energy of 20 Torr, a water-vapor pressure of 2.0 Torr, at magnifications of 300× and 1000×. The EDS measurements were completed using the bullet detector with a working distance of 19 mm at a 30° takeoff angle.

4.2.2 XRD

The XRD patterns of the dislodgeable solids were collected and compared with their parent boards, the corresponded water leachate, and the main ingredients of CCA preservatives, to investigate any crystalline correlation among these samples.

4.2.2.1 Sample preparation

XRD diffractograms of the dislodgeable solids were collected directly with no further preparation. The dislodgeable solids were obtained from CCA and CCA/WR treated southern pine boards before and after 7 months of field exposure (Tree Research Center, Michigan State University, East Lansing, Michigan). The collection of the dislodgeable solids has been described in Chapter 3.

Commercial CCA and CCA/WR treated southern pine lumbers (Georgia-Pacific Corporation, Atlanta, GA) were purchased from Lowe's. The chemical retention of the lumber was 6.4 kg/m^3 on the label. The dimension of the boards was 2.6cm × 15cm × 244cm. The surface of wood with no field exposure, and the weathered surface of wood exposed in the field were used to obtain the XRD patterns. Wood samples were microtomed into thin slices (about 200 μm).

Untreated southern pine powder was prepared from defect free sapwood of kiln dried southern pine with no field exposure. Wood was ground and passed through a sieve at a size of 40 mesh.

Solids from the leachates were prepared from commercial CCA and CCA/WR treated southern pine. The treated wood was ground into powder using a hammer mill. About 100 ml of Deionized (DI) water was mixed with 20 g of CCA or CCA/WR treated southern pine powder and stirred for 6 hours at room temperature. The leachate was then filtered through a 0.45-μm filter unit (Millex-HA, Millipore Corporation, MA, USA) driven with a 20-ml syringe (Becton Dickinson & Co., part No. 301625) to remove the wood powder. The leachate after the filtration was concentrated by using roto-evaporation (RE 120 & Büchi Rotovapor R-200, Brinkmann Instruments, Inc.). The concentrated leachate was air dried and used to collect XRD diffractogram.

CCA preservative was prepared by using freeze-drying of CCA stock solution obtained from Osmose, Inc. at a concentration of 9.4% total oxides.

The XRD patterns of CCA main ingredients including arsenic (V) oxide (As_2O_5, 99.99+%, Aldrich), chromium (VI) oxide (CrO_3, 98%, ACS Reagent, Aldrich), copper (II) oxide (CuO, ACS Reagent, 99+%, Aldrich) were collected with no further preparation.

The XRD diagram of sand (SiO_2, 50-70 mesh, Aldrich) was also collected directly.

4.2.2.2 XRD diffractogram collection

During the XRD diffractogram collection, samples were mounted to a sample holder using double sided tape. The diffractogram was obtained by running a Rigaku XRD diffractometer using Cu Kα radiation of λ equal to 1.5418 Å, and a voltage of 45 kV at 100 mA. Diffraction patterns were collected using DD and DS slot widths of 0.5°. The diffraction angle (2θ) was measured from 5° to 65° at a speed of 2°/minute. The detection limit with a typical background at 200 counts was approximately 0.2% in weight composition and 100 Å in particle size.

4.3 Results and Discussion

4.3.1 ESEM-EDS

Figures 4-1 and 4-2 present the ESEM images of the dislodgeable solids collected from CCA or CCA/WR treated southern pine before and after 7 months of field exposure, respectively. A typical pattern of small particles randomly distributed was observed with all the dislodgeable solids examined. Particles with length ranging from 10 to 100 μm were labeled "large", and "small" for those with length less than 10 μm.

In Figures 4-1A, the small particles were attributed to chemical deposits from CCA treatment, and the large particles were wood splinters collected from the surface of CCA-treated wood.

After 7 months of field exposure, the small particles were still observable at 300× or higher magnifications (Figures 4-1B). However, unlike the typical long, narrow shaped larger particles in the dislodgeable solids before the field exposure (Figures 4-1A), the pattern of the large particles was not uniform after the field exposure. The disappearance of the characteristic pattern of wood splinters was attributed to the photodegradation of wood during exterior exposure (Kalnins and Feist 1991).

Figures 4-2A and 4-2B are the images of the dislodgeable solids collected from CCA/WR treated southern pine before and after the field exposure, respectively. The disappearance of the characteristic pattern of wood splinters in the dislodgeable solids from CCA/WR treated wood after the field exposure was also observed.

EDS spectrum of the dislodgeable solids collected from CCA or CCA/WR treated southern pine at 300× magnification are illustrated in Figures 4-3 and 4-4. The elemental compositions of the dislodgeable solids from CCA and CCA/WR treated southern pine

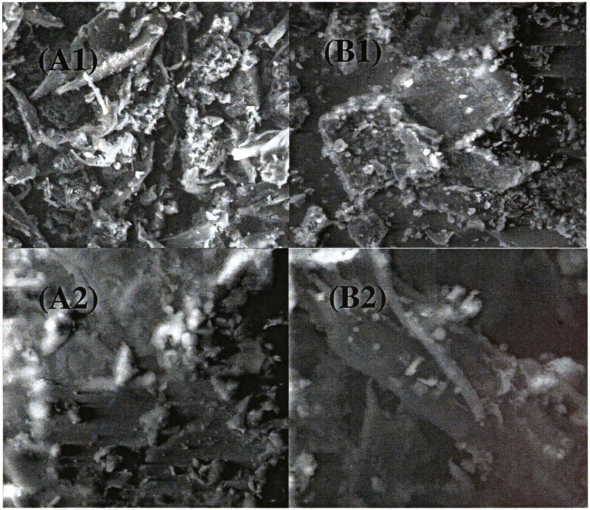


Figure 4-1. ESEM images of dislodgeable solids collected from CCA treated southern pine, (A) before field exposure at (1) 300×, (2) 1000× magnifications; and (B) after field exposure at (1) 300×, (2) 1000× magnifications

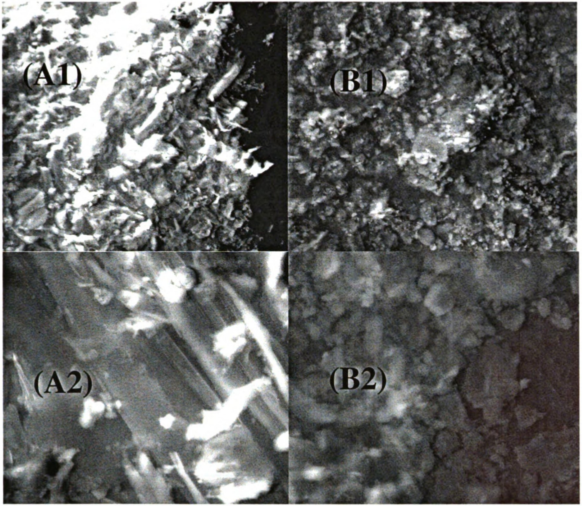


Figure 4-2. ESEM images of dislodgeable solids collected from CCA/WR treated southern pine, (A) before field exposure at (1) 300×, (2) 1000× magnifications; and (B) after field exposure at (1) 300×, (2) 1000× magnifications

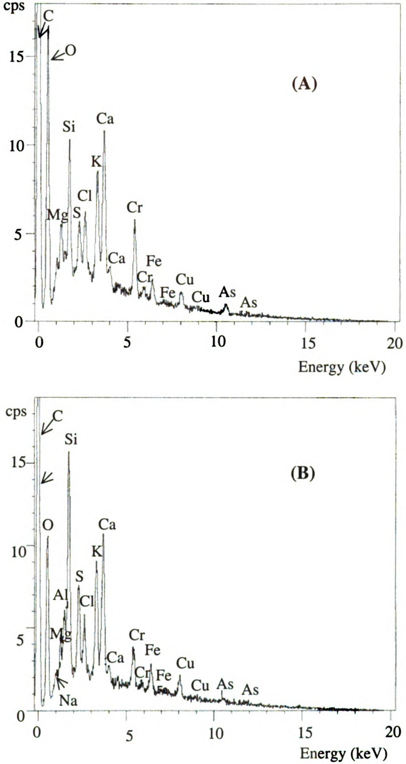


Figure 4-3. EDS spectrum of the dislodgeable solids collected from CCA treated southern pine, (A) before the filed exposure, (B) after 7 months of field exposure

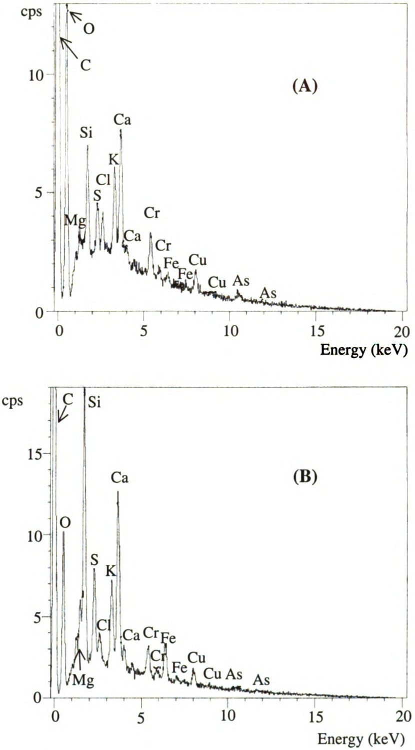


Figure 4-4. EDS spectrum of the dislodgeable solids collected from CCA/WR treated southern pine, (A) before the filed exposure, (B) after 7 months of field exposure

were qualitatively similar. The EDS peaks of arsenic, chromium, and copper were identified in the entire spectrum collected. This consistent presence of arsenic, chromium, and copper in the dislodgeable solids was attributed to CCA wood treatment. Besides these three elements, iron, calcium, potassium, chloride, sulfur, silicon, magnesium, sodium, carbon, and oxygen were also found in dislodgeable solids collected from both CCA and CCA/WR treated wood. Calcium, potassium, magnesium, sodium, carbon, and oxygen may come from the wood components (Fengel and Wegener 1984). Calcium, magnesium, silicon and aluminum may also come from airborne soil. Sulfur could come from the air pollution, such as the release of sulfur dioxide (SO_2) during coal burning and come done out of the atmosphere by rain. Iron and chloride may come from the contamination during wood industrial treatment.

The relatively strong signal of both carbon and oxygen suggested the presence of organic material. Since CCA preservatives are composed of non-carbon based inorganic chemicals (AWPA 2003), this organic material present in the dislodgeable solids could be attributed to the collection of wood material. This hypothesis was supported by observations from ESEM study.

After 7 months of field exposure, an addition of aluminum was found in the dislodgeable solids collected from both CCA and CCA/WR treated wood (Figures 4-3B and 4-4B). Significant increase in the peak intensities of silicon, sulfur, and decrease in the peak intensity of chromium were also observed after the field exposure. The presence of aluminum in field (TRC) soil has been demonstrated in a previous soil analysis by Crawford et al. (2002). This addition of aluminum and the increment of silicon could be attributed to the accumulation of soil on wood surface during the field exposure and consequently collected in the dislodgeable solids. Another alternative for the silicon source could come from the glassware used during the dislodgeable solids collection. The increased peak intensity of sulfur could be attributed to the air pollution, or the presence of biological organisms on the wood surface. The decreased peak intensity of chromium is in consistent with atomic absorption spectroscopy analysis (Chapter 3), which indicated that chromium content in the dislodgeable solids decreased after the field exposure.

4.3.2 XRD

4.3.2.1 Wood

XRD patterns of untreated southern pine powder and CCA-treated southern pine before and after field exposure are illustrated in Figure 4-5. Two broad peaks from cellulose exist in the 2θ angle between 10° and 25° (Kamdem et al. 1998). This typical cellulose pattern is attributed to the $101, 10\bar{1}$, 002 and 040 reflections of cellulose I (Fengel and Wegener 1983). Cellulose I patterns presented in untreated southern pine (Figure 4-5C), CCA-treated southern pine before and after the field exposure (Figure 4-5A, B). No significant modification in the XRD patterns was observed after CCA treatment and the field exposure compared with untreated southern pine.

This characteristic pattern from cellulose I was also observed with CCA/WR treated southern pine before the field exposure (Figure 4-6A, B). No other significant peak information was observed throughout the rest of the diffraction angle (2θ at 25° to 65°).

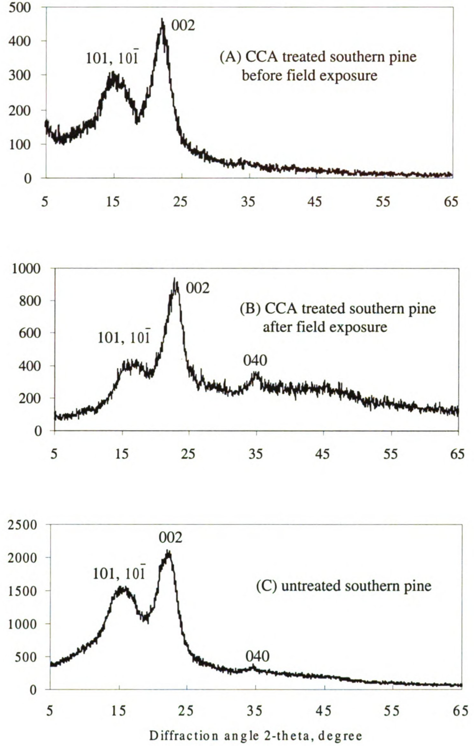


Figure 4-5. XRD diagrams, (A) CCA treated southern pine before field exposure, (B) CCA-C treated southern pine after field exposure, (C) untreated southern pine

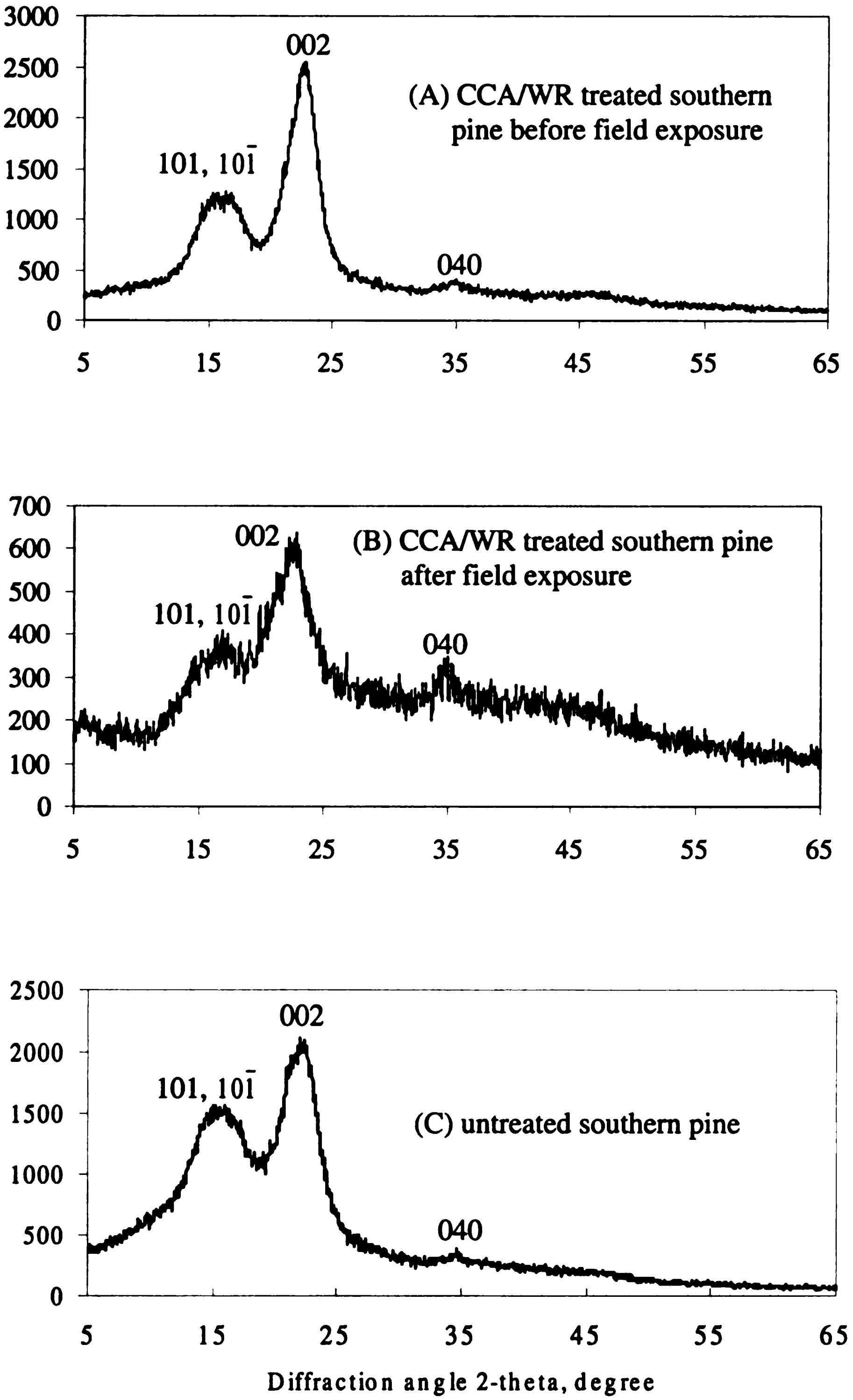


Figure 4-6. XRD diagrams, (A) CCA/WR treated southern pine before field exposure, (B) CCA/WR treated southern pine after field exposure, (C) untreated southern pine

4.3.2.2 Dislodgeable solids

The diffractograms of the dislodgeable solids collected from CCA and CCA/WR treated southern pine before the field exposure are presented in Figures 4-7A and 4-8A. Two broad peaks between 10° and 25° were identifiable, which are attributed to the $101, 10\bar{1}$, and 002 reflection from cellulose I. This was an indication of the presence of wood material in the dislodgeable solids, which was also evidenced in the ESEM observation. After 7 months of field exposure, this cellulose pattern disappeared in the dislodgeable solids (Figures 4-7B and 4-8B). This could be attributed to the decrease of wood material in the dislodgeable solids or the deformation of cellulose I lattice during wood weathering (Kalnins and Feist 1991).

Two peaks at 2θ angle of 20.5° and 26.2° consistently presented in the dislodgeable solids from wood before and after the field exposure (Figures 4-7A, B and 4-8A, B). These two peaks are attributed to the presence of sand (SiO_2) (Figures 4-7C and 4-8C), which may come from contamination during industrial wood treatment and / or the surrounding environment during the field exposure.

4.3.2.3 Solids from the leachate and CCA main ingredients

XRD diffractograms of the solids dried up from CCA and CCA/WR treated southern pine leachates are illustrated in Figure 4-9. No identifiable crystalline information was obtained, which suggested that the solids from leachates were either amorphous or the crystallite size formed after a roto-evaporation were smaller than the detection limit at 100 Å.

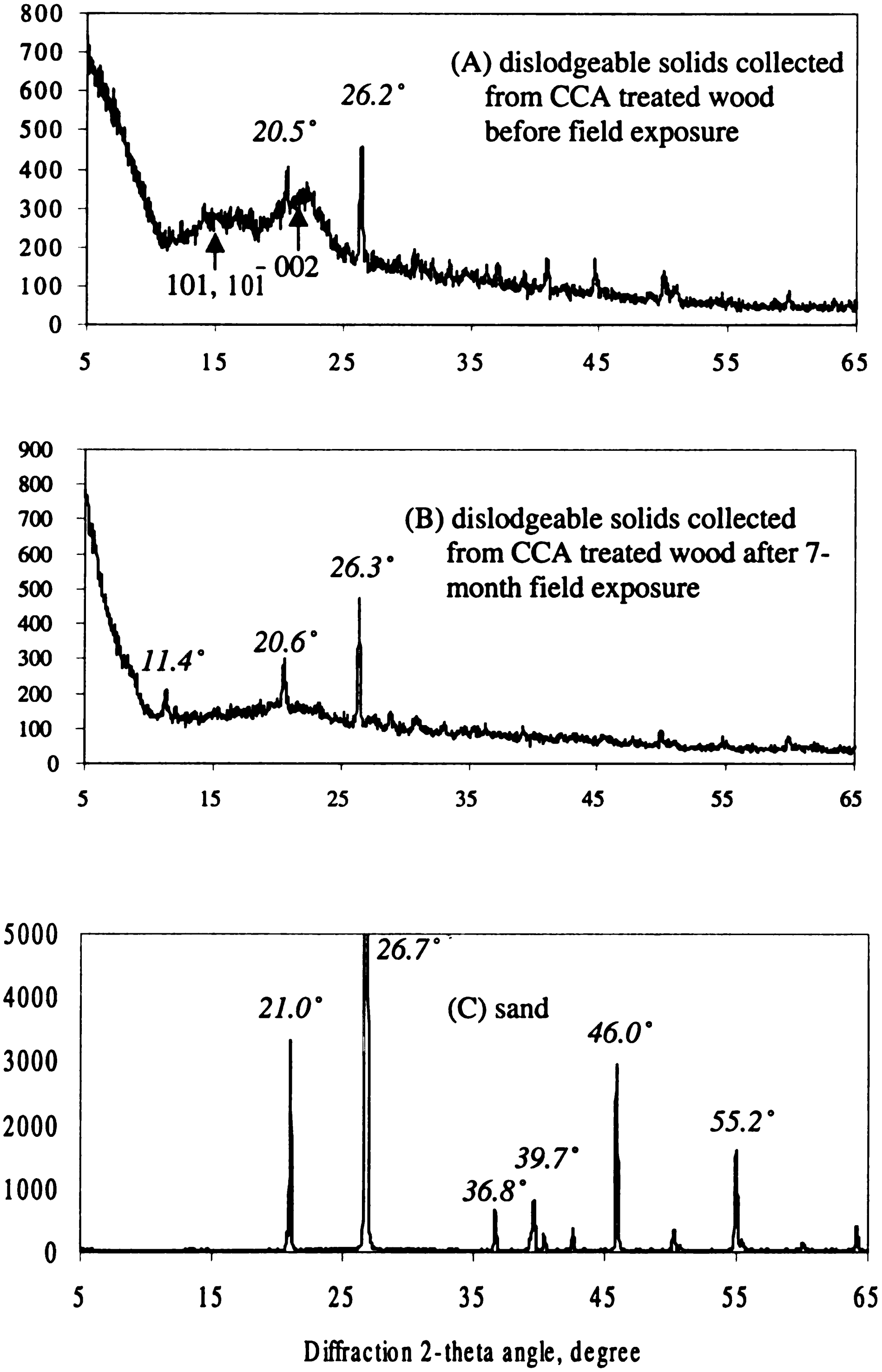


Figure 4-7. XRD diagram of the dislodgeable solids collected from the surface of CCA treated southern pine: (a) before field exposure, (b) after 7 months of field exposure, (c) sand

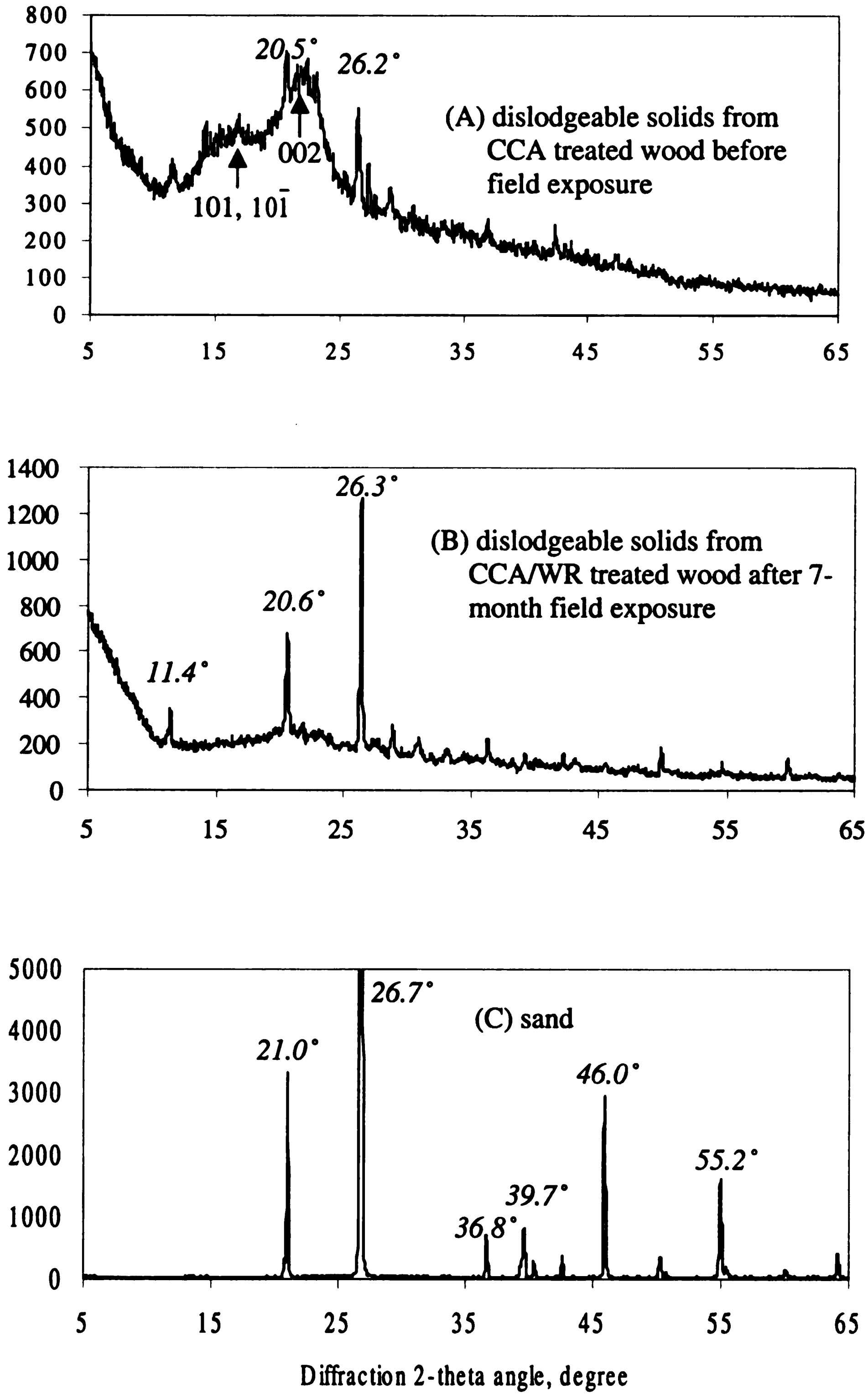
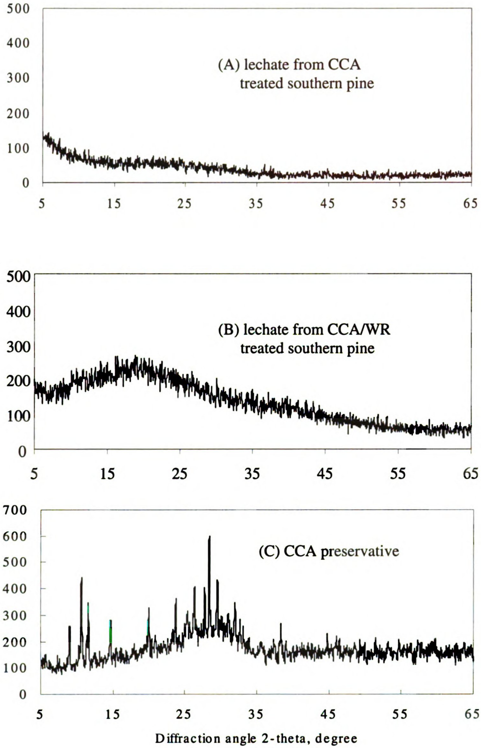


Figure 4-8. XRD diagram of the dislodgeable solids collected from the surface of CCA/WR treated southern pine: (A) before field exposure, (B) after 7 months of field exposure, (C) sand


(A) lechate from CCA treated southern pine

(B) lechate from CCA/WR treated southern pine

(C) CCA preservative

Figure 4-9. XRD diagrams, (A) solids from CCA treated southern pine leachate, (B) solids from CCA/WR treated southern pine leachate, (C) CCA preservative

Industrially, CCA preservative is prepared by adding chromium (VI) trioxide to water to form chromic or dichromic acid, and solid copper oxide to form a copper dichromate solution; arsenic pentoxide is added as solution of arsenic acid. The preservative is a mixture of ions that could form a mixture of copper dichromate, copper arsenate, etc. After CCA wood treatment, a series of interactions could be carried out between CCA components and wood, results in the reduction of Cr^{VI}, and the formation of chromium (III) arsenate / hydroxide, and complex between chromium, copper and wood (Bull 2001). Figure 4-10 illustrates the XRD patterns of the main ingredients of CCA preservative: CuO, CrO_3, and As_2O_5. No crystalline information could be observed with As_2O_5 (Figure 4-10C). Peaks at 32.5°, 35.3°, 38.8°, and 48.8° from CuO (Figure 4-10A), peak at 59.1° from CrO_3 (Figure 4-10B) could not be identified from either CCA-treated wood (Figures 4-5 and 4-6) or the dislodgeable solids (Figures 4-7 and 4-8), which suggested that after CCA wood treatment, there is no presence of CuO, CrO_3, and /or As_2O_5 in treated wood.

4.4 Conclusions

The dislodgeable solids mainly consisted of wood splinters with small chemical deposits distributed in wood matrix. The particle sizes of the chemical deposits were mostly less than 10 μm, and the wood splinters between 10 and 100 μm. After the field exposure, the crystalline lattice of cellulose I in wood was destroyed.

Similar elemental compositions were found in the dislodgeable solids collected from CCA and CCA/WR treated southern pine. Arsenic, chromium, copper, iron,

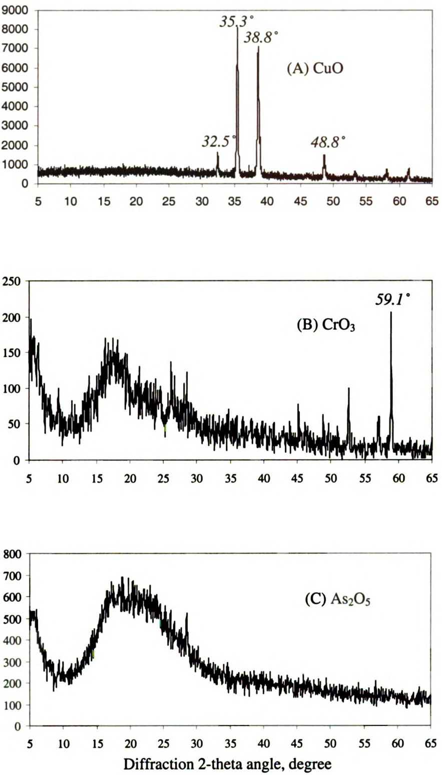


Figure 4-10. XRD diagrams of CCA main ingredients, (A) CuO, (B) CrO_3, (C) As_2O_5

potassium, chloride, sulfur, silicon, magnesium, sodium, carbon, and oxygen were detected in the dislodgeable solids from wood before the field exposure. After 7 months of field exposure, contamination of sand or soil from the surrounding environment was observed with the dislodgeable solids.

Chapter 5

Solubilization of Arsenic, chromium, and Copper from the Dislodgeable Solids

5.1 Introduction

Human exposure to arsenic and chromium through the use of chromated copper arsenate (CCA) treated wood is considered a potential risk of human health (McMahon and Chen 2001). Study of the dislodgeable solids collected from the surface of CCA-treated southern pine boards found that, the dislodgeable solids mainly consisted of wood splinters with less than 4 wt.% of total arsenic, chromium, and copper. In residential exposure to CCA-treated wood, oral ingestion of the dislodgeable solids through a hand-to-mouth behavior, typically found in children, can be one of the main routes of exposure to arsenic, chromium, and copper. In an exterior exposure, chemicals dislodged from CCA-treated wood could partially solubilize during a rainfall. A direct dermal contact with the contaminated rainfalls can be another important route of exposure to arsenic, chromium, and copper.

The toxicity of arsenic, chromium, and copper varies with the chemical forms (Tatken and Lewis 1983). Simple hydrated metal ions are considered to be the most toxic, while strong complexes and species associated with colloidal particles are usually assumed to be less toxic (Russeva 1995). The water solubility of arsenic compounds influences their bioavailability. The absorption of arsenic in a water-soluble form through the gastrointestinal tract is generally assumed to be nearly complete (Campbell 1995). Arsenic in water-insoluble forms may be incompletely absorbed (McMahon and Chen 2001). The toxicity of arsenic and chromium is strongly affected by their oxidation states.

In a short term and large dose exposure, inorganic pentavalent arsenic (As^V) is less potent than inorganic trivalent arsenic (As^{III}); hexavalent chromium (Cr^{VI}) has been recognized as a carcinogen while trivalent chromium (Cr^{III}) is human essential (Schroeder and Balassa 1966; Hughes et al. 1994; Healy et al. 1998).

The objective of this study is to characterize the solubilization of arsenic, chromium, and copper from the dislodgeable solids collected on the surface of CCA type C (CCA) and CCA type C with water repellent (CCA/WR) treated southern pine boards, and to speciate the chromium and arsenic solubilzed.

5.2 Arsenic speciation

In documented studies, arsenic leaching of CCA-treated wood is generally reported in total amount with little information on the species. No standard method of arsenic speciation in CCA-treated wood is available from American Wood Preservers' Association (AWPA 2003). In recent years, there are several studies conducted to speciate arsenic from CCA-treated wood. Nygren and Nilsson (1993) used a selective solvent extraction coupled with atomic absorption spectroscopy (AA) to study arsenic species in CCA-treated wood, and found more than 99.5% of total arsenic was As^V, with less than 0.5% of total arsenic as As^{III}. Information on the extraction efficiency and stability of arsenic species during the extraction was not provided. Hingston (2003) published a paper describing the use of differential pulse polarography to speciate the species of arsenic in leachate of CCA-treated wood, and found less than 10% of total arsenic was As^{III}. Solo-Gabriele et al. (2003b) reported the speciation of arsenic in the leachate of CCA-treated wood removed from service by using high performance liquid chromatography coupled with hydride generation atomic fluorescence spectrometry (HPLC-HG-AFS). It was reported that As^{III} ranged from 0 to 51% of total arsenic in the leachate from various treated wood samples.

Most of the studies associated with arsenic speciation are conducted with liquid or aqueous phase solution. The history of arsenic speciation in water could be traced back to year 1775. The reduction of arsenic to volatile arsine (AsH_3) was classified as a "hydride generation" analytical method (Partington 1962). As^V and As^{III} were determined using hydride generation reactions by varying the pH of the solution (Cullen et al. 1994). The documented speciation methods of arsenic in water and biological samples include: sequential spectrophotometric determination of As^V and As^{III} by controlling the pH of the reduction solution, which is appropriate for determination of 2-40 μg of each arsenic species (Howard and Arab-Zavar 1980); solvent extraction combined with neutron activation with a detection limit of 10^{-2} μg/l described by several authors (Yasui et al. 1978; Mok et al. 1986); colorimetric detection of the colored complex formed between arsine and silver diethyldithiocarbamate with a detection limit of 40 μg/l used by Irgolic (1994); high-performance liquid chromatography equipped with inductively coupled plasma and atomic emission spectrometry (HPLC-ICP-AES) and / or mass spectrometry (HPLC-ICP-MS) were also used to speciate arsenic and the detection limits were at subnanogram level (Monplaisir et al. 1994).

An ion-exchange chromatography method of arsenic speciation in water was developed and reported by Flores del Pino (2003). This method was employed in this study to speciate arsenic solubilzed from the dislodgeable solids. The chemical structures of As^V and As^{III} are presented in Figure 5-1. The conversion between As^{III} and As^V is

Arsenate (As^{V})

Arsenite (As^{III})

Figure 5-1. Structure of arsenate and arsenite influenced by the redox potential (Eh) and pH of the matrix. The Eh-pH diagram of different arsenic species at 25°C and at pressure of one atmosphere is illustrated in Figure 5-2 (Ferguson and Gavis 1972). The Eh-pH correlation between various arsenic species suggests that pH modification of a matrix can be used to change the ionized and neutral forms of arsenic without altering their oxidation states. This principle was used to separate As^{III} from As^{V} using pH and ion-exchange chromatography.

5.3 Chromium speciation

After CCA treatment, a series of interactions may carry out, mainly between arsenic, chromium, copper, and wood components. Chromium in CCA-treated wood is mainly Cr^{III}, due to the reduction of Cr^{VI} after fixation (Cooper and Ung 1993). Bull (2000, 2001) pointed out that three major fixation products could exist in CCA-treated wood: chromium (III) arsenate ($CrAsO_4$), chromium (III) hydroxide ($Cr(OH)_3$), and copper complexing with wood components. Cr^{VI} could also be reduced to Cr^{III} through the interaction with some functional groups of lignin or the lignin fraction. The reduction of Cr^{VI} is used as an indication of CCA fixation in wood. If fixation is not complete, relatively large amount of Cr^{VI} would be present in treated wood and ready to leach (Chen et al. 1994; Cooper et al. 1994).

A colorimetric method using the complexing between Cr^{VI} and 1, 5 diphenylcarbazide was employed to determine the amount of Cr^{VI} solubilized from the dislodgeable solids.

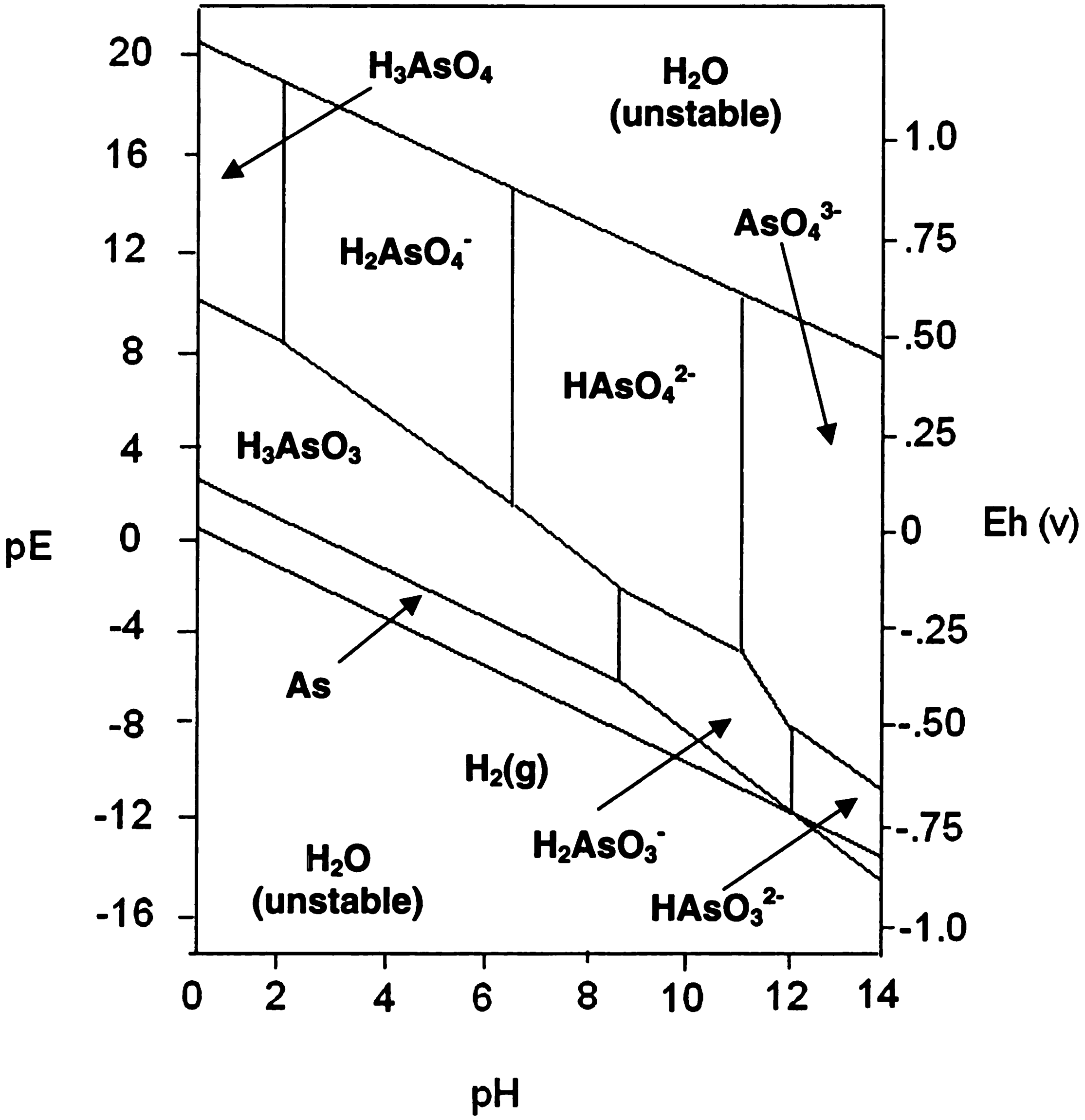


Figure 5-2. pE-pH diagram for the As-H_2O system at 25°C with total As species of 50 ppb

5.4 Material and Methods

5.4.1 Dislodgeable solids solubility study protocol

A laboratory method was developed to characterize the solubilization of arsenic, chromium, and copper from the dislodgeable solids at various test durations and pH of the water matrix. The dislodgeable solids collected from CCA-treated southern pine (dislodgeable solids CCA), or CCA/WR-treated southern pine (dislodgeable solids CCA/WR) before the field exposure were used in this study. The collection of the dislodgeable solids has been described in Chapter 3. Arsenic, chromium, and copper contents in dislodgeable solids CCA were 1.2%, 1.6%, and 0.73% in weight, respectively; and 0.59%, 0.67%, and 0.73%, respectively in dislodgeable solids CCA/WR.

Figure 5-3 presents the protocol of the solubilization study. About 10 mg of the dislodgeable solids were weighed using a digital balance (accuracy: 0.001 g, Mettler AE200, Mettler Instrument AG, Switzerland) and mixed with 13.0 ml of dissolving water in a 15-ml centrifuge tube (Polypropylene, Sterile, VWR 21008-678). About 360 mg of dislodgeable solids were used to prepare 36 centrifuge tubes. A total of 72 tubes were prepared: 36 from dislodgeable solids CCA and 36 from dislodgeable solids CCA/WR. The 36 tubes containing each type of dislodgeable solids were divided into four groups. In each of the 9 tubes 13.0 ml of deionized (DI) water at pH 3, 4, 5, or 6 was added. The pH of the DI water was adjusted using sulfuric acid and measured by a pH meter (Consort P601 from Scientific Instrument, Inc.) equipped with a pH electrode (Cole-Parmer Instrument Co. Catalog number 5990-65). The centrifuge tubes were fitted with screw caps, to limit water evaporation and air exposure. The suspension in the centrifuge

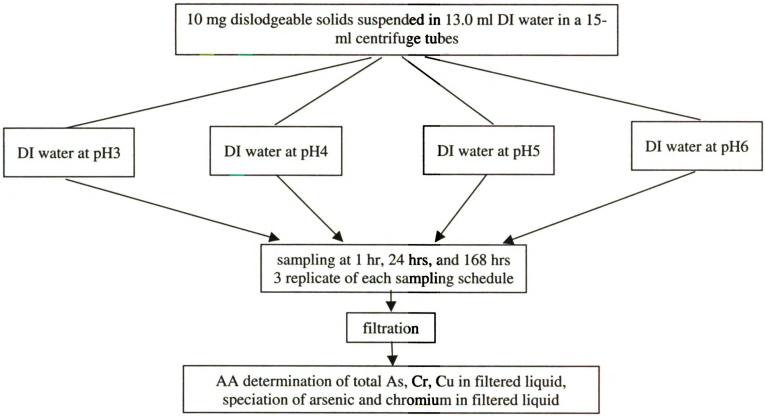


Figure 5-3. Protocol of the dislodgeable solids solubilization study

tube was shaken using a mechanical mixer (Thermolyne Model 37615, Barnstead / Thermolyne, Iowa, USA) at room temperature. Three tubes at each pH were collected after 1, 24, and 168 hours.

The suspension was filtered through a 0.45-µm filter unit (Millex-HA, Millipore Co., Cat. No. SLHA025OS) driven with a 20-ml syringe (Becton Dickinson & Co., Part No. 301625). The filtered liquid was collected in a clean 15-ml centrifuge tube for further analysis. About 8 ml of the filtered liquid was used to determine the total chromium and copper, about 4 ml used for chromium speciation, and another 1.0 ml for total arsenic determination and arsenic speciation.

Figure 5-4 illustrates the procedure of total arsenic, chromium, copper analysis, and the speciation of arsenic and chromium.

5.4.2 Total arsenic, chromium, and copper solubilized from the dislodgeable solids

Total arsenic, chromium, and copper solubilized from the dislodgeable solids in water were measured using atomic absorption spectrometry (AA). A graphite furnace atomic absorption spectroscopy (GFAA, AAnalyst 800, Perkin Elmer Co.) equipped with an EDL arsenic lamp was employed to determine arsenic concentration at parts per billion level (ppb). A flame atomic absorption spectrophotometer (FAA, Model: Perking Elmer 3110), equipped with an EDL arsenic lamp, and hollow cathode lamps for chromium and copper (from Perkin Elmer) was used to determine arsenic, chromium and copper concentrations in parts per million level (ppm). The preparation of the standard solutions to obtain the working curve of each element for AA analysis has been described in the experimental section of Chapter 3.

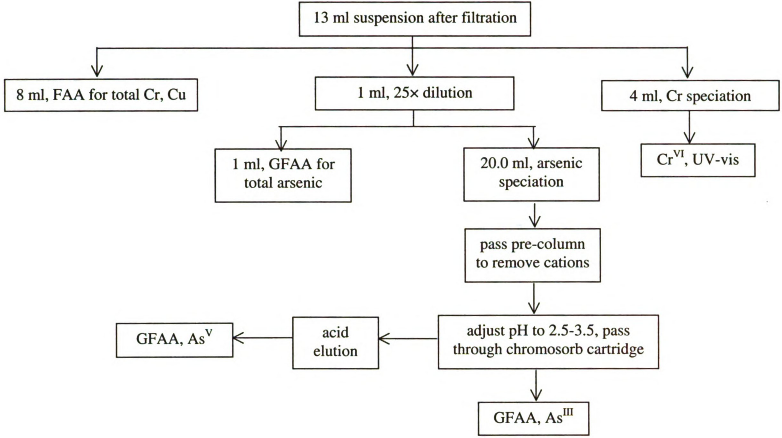


Figure 5-4. Determination of total arsenic, chromium, copper solubilized from the dislodgeable solids and the speciation of arsenic and chromium in water

Samples subjected to GFAA determination of arsenic were prepared after 25-fold dilution from the initial filtered liquid. About 1 ml of the diluted solution was used to determine the total arsenic, and 20.0 ml of the diluted solution for arsenic speciation.

5.4.3 Speciation of arsenic solubilized from the dislodgeable solids - selective ion-exchange measurement of As^V and As^{III}

5.4.3.1 Procedure of As^V and As^{III} speciation

Arsenic speciation was performed immediately after the sampling to limit possible oxidation or reduction of arsenic. Figure 5-5 illustrates the pre-column and the modified chromosorb cartridge used for arsenic speciation. Cation exchange resins with mesh size ranging from 50 to 100 were packed in a 1-ml syringe (Becton Dickinson 309602 NH 17530). The cation exchange capacity of this pre-column was 2 meq/g. The resin was pre-wetted with DI water before use. The pre-column was connected to a vacuum pump under a vacuum level of 10 in Hg (3.4×10^4 Pa). The 20.0 ml diluted solution passed through the pre-column (cation-exchange) at a flow rate of 1 ml/minute. The function of the pre-column was to eliminate the potential interference of cations before arsenic speciation, such as copper (Cu^{2+}) from CCA.

The pH of the solution passing through the pre-column was adjusted to 2.5-3.5 by using 1.0N of hydrochloric acid (HCl) and / or 0.1N of aqueous ammonium hydroxide (NH_4OH) before the separation of As^V and As^{III}. The pH of the solution was measured by using a pH meter (Consort P601 from Scientific Instrument, Inc.). The separation of As^V and As^{III} was performed by passing the solution through a modified chromosorb cartridge, which was a silanized diatomaceous earth with dioctyltin dichloride ($(C_8H_{17})_2SnCl_2$) that preferentially absorb As^V. As^V in an ionized form was absorbed on

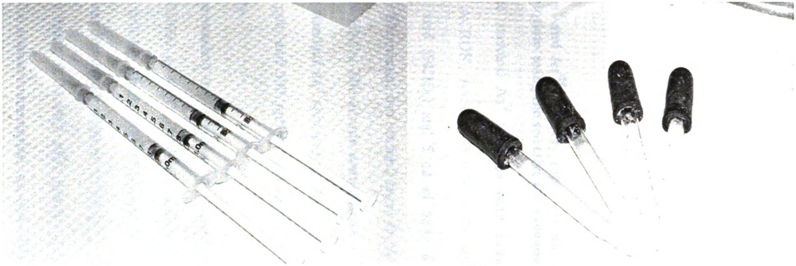

(A)
(B)

Figure 5-5. Cartridges used for arsenic speciation: (A) pre-column, (B) modified chromosorb cartridge the modified chromosorb in the cartridge and As^{III} in its neutral form was found in the effluent. The As^{V} trapped in the modified chromosorb cartridge was desorbed by using 0.5N of HCl. The solution passing through the cartridge contained As^{III}, the elution washed out from the cartridge consisted of As^{V}, and the initial liquid collected were analyzed by using GFAA to determine the contents of As^{III}, As^{V}, and total arsenic, respectively.

5.4.3.2. As^{V} and As^{III} recovery rate - arsenic speciation of standard As^{V} and As^{III} solutions using the selective ion-exchange method

The standard As^{V} solutions were prepared from arsenic pentoxide (As_2O_5, 99.999%, ACROS). About 0.05 g of As_2O_5 was weighed and solubilized in 2 ml of perchloric acid ($HClO_4$) and 5 ml of nitric acid (HNO_3, double distilled, Caledon Laboratory Chemicals), and set for 2 hours for the solubilization before diluted to 500 ml using 0.1N HNO_3. The arsenic concentration was measured at 65.2 ppm (mg/l) using FAA. The standard As^{V} solutions at concentrations of 5 ppb (µg/l), 10 ppb, 50 ppb, 100 ppb, 300 ppb, and 500 ppb were diluted from the initial solution using 0.1N HNO_3 accordingly.

The standard As^{III} solution was prepared according to Chen et al. (2002). Arsenic trioxide (0.0660 g, As_2O_3, 99.995%, Aldrich) was weighed using a digital balance (accuracy: 0.001 g, Mettler AE200, Mettler Instrument AG, Switzerland). This 0.0660 g of As_2O_3 was dissolved in 1000 ml of NaOH solution (0.1N) and acidified to pH between 2.5-3.5 by using 0.1N HCl (6N, double distilled, Caledon Laboratory Chemicals) titration. The arsenic concentration was measured at 49.98 ppm using FAA. The standard

As^{III} solutions at the concentrations of 5 ppb, 10 ppb, 50 ppb, 100 ppb, 300 ppb, and 500 ppb were diluted from the initial solution accordingly using 0.1N HCl.

The concentrations of both As^{V} and As^{III} standard solutions prepared were measured by using GFAA. These standard solutions were analyzed using the selective ion-exchange arsenic speciation method. The recovery rate of As^{V} or As^{III} was defined as the ratio between the amount of As^{V} (or As^{III}) detected after the speciation to the known amount of As^{V} (or As^{III}) in the standard solution. The recovery rate of As^{V} or As^{III} was used as an indicator of the efficiency of As^{V} or As^{III} that could be detected by using this selective ion-exchange method.

5.4.4 Ultraviolet visible (UV-vis) spectroscopy analysis of hexavalent chromium (Cr^{VI}) in water

Cr^{VI} in water was determined by using a colorimetric method described by Cooper and Ung (1993). The standard solutions were prepared by diluting Cr^{VI} standard solution (1000 ppm, Atomic absorption standard, Aldrich) using 0.5N sulfuric acid (H_2SO_4) (A.C.S. Reagent, 98%, J.T. Baker). The concentrations of the standard solutions were 0 ppm, 0.2 ppm, 0.4 ppm, 0.6 ppm, 0.8 ppm, and 1.0 ppm. A 2.5 wt.% 1, 5-diphenylcarbazide solution was used as an indicator. The 1, 5-diphenylcarbazide solution was prepared by dissolving 2.5 g of 1, 5-diphenylcarbazide (A.C.S. Reagent, Aldrich) in 100 ml mixture of acetone (A.C.S. Reagent, J.T. Baker) and DI water (v/v: 1:1). The UV-vis absorbance of the colored complex formed between Cr^{VI} and 1, 5-diphenylcarbazide was measured at 540 nm by using UV-visible (UV-vis) spectrophotometer (DU 640B, Beckman Co.). The Cr^{VI} working curve was obtained by plotting the visible absorbance of Cr^{VI}-diphenylcarbazide complex against the corresponding chromium (Cr^{VI}) concentrations determined by using FAA.

5.4.5 Statistic analysis

One-way ANOVA analysis (Jandel SigmaStat Version 2.0, Jandel Co.) using all pairwise multiple comparison tests (Tukey Test) at the significant level of 0.05 was performed, to analyze significant difference between the percentage of arsenic, chromium, or copper solubilized from the dislodgeable solids influenced by the pH (pH 3, 4, 5 or 6) of water, the test duration (1, 24, or 168 hours), or the addition of water repellent to CCA wood treatment.

5.5 Results and discussion

5.5.1 Speciation of chromium solubilized from the dislodgeable solids

The working curve for Cr^{VI} analysis using the 1, 5-diphenylcarbazide method is plotted in Figure 5-6. A linear correlation ($R^2 = 0.99$) was found between the UV absorbance of Cr^{VI}-diphenylcarbazide complex and the concentration of Cr^{VI} between 0 to 1 ppm.

Table 5-1 lists the concentrations of Cr^{VI} solubilized from 0.010 g of dislodgeable solids CCA or dislodgeable solids CCA/WR in the 13.0 ml water. The corresponded percentages of Cr^{VI} solubilized from the dislodgeable solids are calculated using Equation 1 and also reported in Table 5-1. These percentage values were obtained after dividing the amount of Cr^{VI} present in water by the total chromium in the dislodgeable solids.

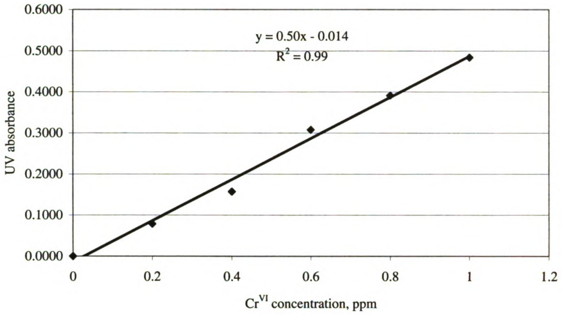


Figure 5-6. Working curve for Cr^{VI} analysis by using UV-vis spectrometry

Table 5-1. Concentration of Cr^{VI} in dissolving water (pH 3, 4, 5, and 6) and the corresponded percentage (%) of Cr^{VI} in total chromium from the dislodgeable solids

Test duration, hours	pH	dislodgeable solids CCA		dislodgeable solids CCA/WR	
		concentration of Cr^{VI} solubilized from dislodgeable solids, ppm	Cr^{VI}_{sol} in total Cr from dislodgeable solids, %	concentration of Cr^{VI} solubilized from dislodgeable solids, ppm	Cr^{VI}_{sol} in total Cr from dislodgeable solids, %
1	3	0.159 (0.002)*	1.29 (0.01)	0.348 (0.210)	2.82 (1.70)
	4	0.112 (0.002)	0.91 (0.02)	0.307 (0.002)	2.49 (0.02)
	5	0.127 (0.002)	1.03 (0.02)	0.249 (0.014)	2.02 (0.11)
	6	0.090 (0.001)	0.73 (0.01)	0.137 (0.002)	1.11 (0.02)
24	3	0.311 (0.002)	2.53 (0.02)	0.479 (0.001)	3.89 (0.00)
	4	0.196 (0.002)	1.59 (0.01)	0.435 (0.003)	3.53 (0.02)
	5	0.185 (0.000)	1.50 (0.00)	0.401 (0.002)	3.25 (0.01)
	6	0.138 (0.001)	1.12 (0.00)	0.365 (0.001)	2.96 (0.00)
168	3	0.517 (0.001)	4.20 (0.01)	0.699 (0.005)	5.68 (0.04)
	4	0.355 (0.005)	2.88 (0.04)	0.618 (0.003)	5.02 (0.02)
	5	0.184 (0.001)	1.49 (0.01)	0.471 (0.001)	3.82 (0.00)
	6	0.159 (0.001)	1.29 (0.00)	0.417 (0.003)	3.39 (0.03)

* data are mean of three replicate, values in parenthesis are the standard deviation of the mean

element solubilized (%)

$$= \frac{\text{concentration of elemental species in water (mg/l)} \times 0.0131}{0.010\text{g dislodgeable solids} \times \text{total element in dislodgeable solids (\%)}} \times 100\% \qquad (1)$$

In dislodgeable solids CCA, by varying the pH of the water from 6 to 3, about 0.09 ppm to 0.16 ppm of Cr^{VI} was found in water during the first hour, which corresponded to 0.7-1.3% of total chromium in the solids. After 24 hours, about 1.1-2.5% of total chromium in the solids was detected as Cr^{VI} in water. A maximum value of 4.2% was found in water at pH 3 after 168 hours.

In dislodgeable solids CCA/WR, by decreasing the pH of water from 6 to 3, the concentrations of Cr^{VI} increased from 0.14 ppm to 0.35 ppm in the first hour, from 0.37 ppm to 0.48 ppm after 24 hours, and from 0.42 ppm to 0.70 ppm after 168 hours.

One-way ANOVA analysis suggested that significant difference existed in the percentage of Cr^{VI} solubilized from dislodgeable solids CCA and dislodgeable solids CCA/WR throughout the 168-hour test duration (Appendix 3 Tables 1-3). Relatively larger percentage of Cr^{VI} was found with dislodgeable solids CCA/WR (Table 5-1) resulted from a relatively incomplete CCA fixation in CCA/WR-treated wood, which could mainly be attributed to the presence of water repellent. The UltraWood water repellent used in this commercial CCA/WR-treated wood was a paraffin wax and surfactant based emulsion[2]. The main function of water repellent is to reduce the water absorption and desorption, and therefore improve the dimensional stability of wood products (Williams and Feist 1999; Zahora 1995).

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[2] Information obtained from CSI, Inc., provider of Ultrawood WR used for this commercial CCA wood treatment

After CCA treatment, CCA components penetrate into the cell wall of tracheids, and preferentially react with guaiacyl lignin (Petty and Preston 1968; Newman and Murphy 1996). With the presence of water repellent it takes longer period for water to evaporate from wood, thus interferes the interactions between CCA components and wood, e.g. the precipitation and / or complexing between copper and lignin, and reduction of Cr^{VI} to Cr^{III} by the primary alcohol groups in lignin (Pizzi 1982a, b, c; Bull 2001). A lagged CCA fixation resulted in relatively large amounts of unfixed CCA components in wood ready to leach out (Cooper et al. 1994).

Statistical analysis also suggested that the solubilization of Cr^{VI} from both dislodgeable solids CCA and dislodgeable solids CCA/WR are time and pH dependent (Appendix 3 Tables 4-7). An increased amount of soluble Cr^{VI} was observed with the increased test duration and water acidity (Figures 5-7 and 5-8).

5.5.2 Water soluble arsenic, chromium, and copper in the dislodgeable solids

The working curve used for GFAA arsenic analysis is illustrated in Figure 5-9, which is the plot of the signal from GFAA versus the concentration of arsenic in the standard solution. A linear correlationship with a R^2 of 0.99 was found at arsenic concentration from 0 to 200 ppb.

Table 5-2 lists the percentage of total arsenic, chromium, and copper solubilized in water (pH 3-6) from dislodgeable solids CCA or dislodgeable solids CCA/WR at test durations of 1, 24, and 168 hours.

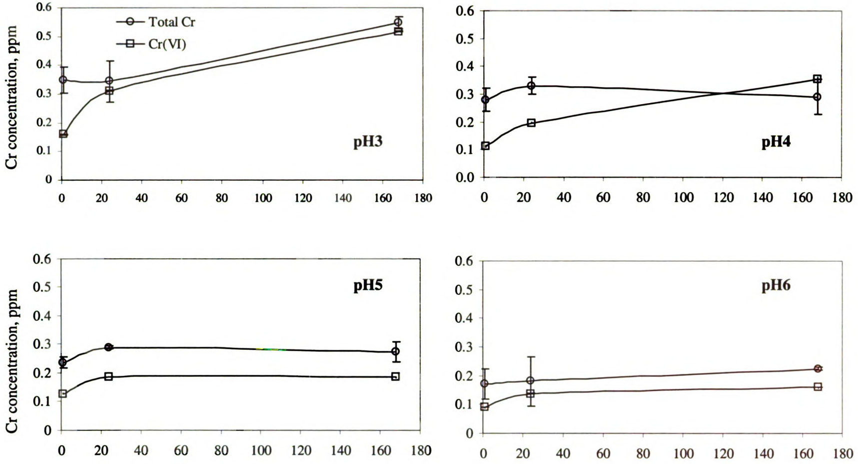

Figure 5-7. Soluble Cr^{VI} and total chromium in dislodgeable solids collected from CCA treated wood

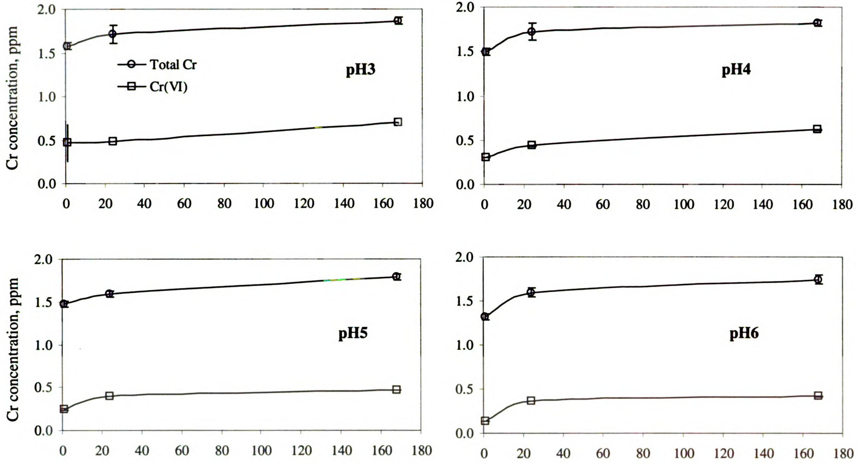

Figure 5-8. Soluble Cr^{VI} and total chromium in dislodgeable solids collected from CCA/WR treated wood

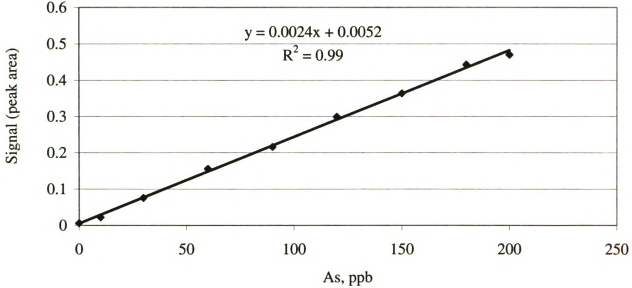

Figure 5-9. Working curve of elemental arsenic determination by using GFAA

Table 5-2. Percentage (%) of soluble arsenic, chromium, and copper in total arsenic, chromium, and copper form the dislodgeable solids

Element dissolved, %		dislodgeable solids CCA solubilization**			dislodgeable solids CCA/WR solubilization***		
	pH	1 hour	24 hours	168 hours	1 hour	24 hours	168 hours
As	3	4.91(0.01)*	6.72(0.15)	9.57(2.09)	14.38(0.54)	21.22(0.23)	26.79(0.77)
	4	4.80(0.04)	5.86(1.42)	9.83(0.04)	14.92(0.15)	18.63(0.54)	25.25(1.00)
	5	4.67(1.61)	9.71(3.08)	11.33(3.61)	16.01(0.31)	19.06(0.15)	24.50(1.14)
	6	3.91(0.01)	6.55(0.11)	8.93(0.04)	15.56(0.08)	18.73(0.54)	27.01(0.62)
Cr	3	2.80(0.37)	2.76(0.57)	4.39(0.17)	30.85(0.80)	33.42(2.05)	36.45(0.79)
	4	2.24(0.34)	2.65(0.24)	2.33(0.50)	29.27(0.85)	33.65(1.81)	35.47(0.66)
	5	1.89(0.16)	2.72(0.71)	2.20(0.28)	28.83(0.68)	31.00(0.68)	35.05(0.67)
	6	1.37(0.43)	1.45(0.69)	1.80(0.04)	25.74(0.73)	31.13(1.00)	34.09(1.09)
Cu	3	6.42(0.33)	8.20(0.37)	18.71(0.88)	17.73(0.65)	32.80(1.14)	33.97(1.27)
	4	5.07(0.23)	5.76(0.24)	12.06(0.46)	14.12(3.98)	18.12(3.61)	26.87(5.30)
	5	4.38(0.08)	5.72(0.22)	5.53(0.23)	14.36(2.09)	21.30(0.53)	30.60(0.96)
	6	4.18(0.17)	4.81(0.19)	4.30(0.16)	12.90(0.74)	20.76(0.68)	28.19(0.91)

*data are mean of three replicate, values in parenthesis are the standard deviation of the mean

** % of total element in dislodgeable solids CCA: As: 1.2%, Cr: 1.6%, Cu: 0.73%,

*** % of total element in dislodgeable solids CCA/WR: As: 0.59%, Cr: 0.67%, Cu: 0.55%.

5.5.2.1 Influence of water repellent on the solubilization of total arsenic, chromium, and copper

Throughout the 168-hour test duration, about 4% to 10% of total arsenic and 4% to 19% of total copper in dislodgeable solids CCA was solubilized. The percentage of chromium solubilized was the least of the three elements, ranging from 1.4% to 4.4% of total chromium in the dislodgeable solids (Table 5-2).

About 14% to 27% of total arsenic and 13% to 34% of total copper were solubilized from dislodgeable solids CCA/WR. Unlike what was observed with dislodgeable solids CCA, the proportion of chromium solubilized from dislodgeable solids CCA/WR was the highest of the three elements. About 26% to 37% of the total chromium was found in water.

One-way ANOVA analysis suggested that, the percentage of total arsenic, chromium, and copper solubilized from dislodgeable solids CCA/WR were significantly larger than those from dislodgeable solids CCA (Appendix 3 Tables 8 to 16). The interference of water repellent with CCA fixation was demonstrated by the increased levels of soluble total arsenic, chromium, and copper from dislodgeable solids CCA/WR compared with those from dislodgeable solids CCA (Figures 5-10, 5-11, and 5-12).

5.5.2.2 Influence of test duration on the solubilization of total arsenic, chromium, and copper

In dislodgeable solids CCA, about 3.5±0.5%, 7.0±1.0%, and 9.0±1.0% of total arsenic was solubilized after 1 hour, 24 hours, and 168 hours, respectively. Similar levels of chromium at 3.0±1.5% were solubilized throughout the 168-hour test. The percentage

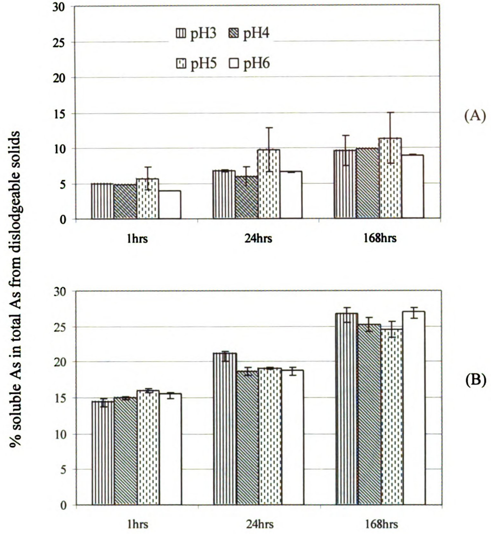

Figure 5-10. Percentages of total arsenic solubilized from the dislodgeable solids,
(A) dislodgeable solids from CCA treated wood,
(B) dislodgeable solids from CCA/WR treated wood

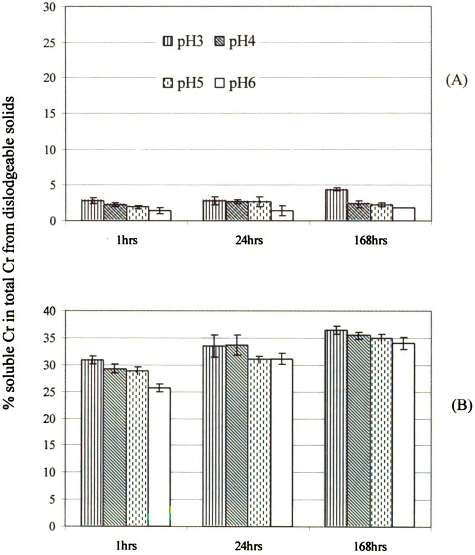

Figure 5-11. Percentages of chromium solubilized from the dislodgeable solids,
(A) dislodgeable solids from CCA treated wood,
(B) dislodgeable solids from CCA/WR treated wood

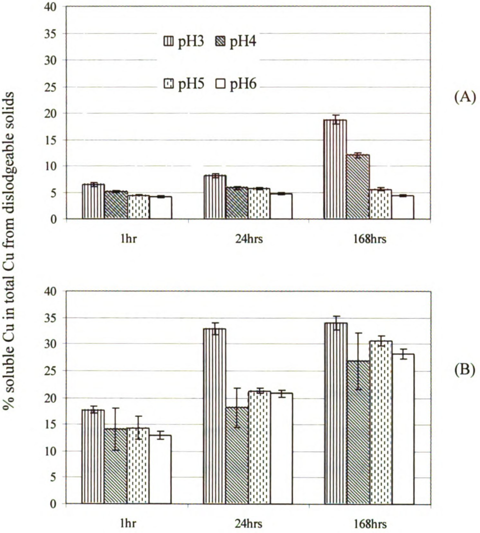

Figure 5-12. Percentages of total copper solubilized from the dislodgeable solids, (A) dislodgeable solids from CCA treated wood, (B) dislodgeable solids from CCA/WR treated wood

of copper solubilized increased from 4% to 19% from 1 hour to 168 hours (Table 5-2). One-way ANOVA analysis found that, the solubilization of arsenic was significantly influenced by the test duration at pH 6 (Appendix 3 Table 17). An increase in the percentage of arsenic solubilized was observed with increased test duration (Figure 5-10A). Data groups at pH 3, 4, and 5 failed to pass the normality test. No statistical report was further performed. The solubilization of chromium presented to be less time dependent at pH 4, 5, and 6. At pH 3, the solubilization of chromium was significantly influenced by time (Appendix 3 Table 18). An increase of chromium solubilized was observed with increased test duration (Figure 5-11A). The percentage of copper solubilized was time dependent at pH 5 and 6 (Appendix 3 Table 19), and increased with test duration (Figure 5-12A). Data groups at pH 3 and 4 failed to pass the normality test. No statistical evaluation was reported.

In dislodgeable solids CCA/WR, about 15.0±1.0% of total arsenic was found in water during the first hour. The amount of water soluble arsenic increased to 19.5±1.5% after 24 hours, and 25.5±1.5% after 168 hours. About 28.0±3.0%, 32.5±1.5%, and 35.0±1.0% of water soluble chromium were found at 1-hour, 24-hour, and 168-hour test durations, respectively. The percentage of copper solubilized from dislodgeable solids CCA/WR was 15.0±3.0%, 27.0±6.0%, and 31.0±3.0% after 1 hour, 24 hours, and 168 hours, respectively (Table 5-2). One-way ANOVA analysis suggested that, the solubilization of the three elements in dislodgeable solids CCA/WR was time sensitive (Appendix 3 Tables 20, 21 and 22). The percentage of arsenic, chromium, and copper solubilized from dislodgeable solids CCA/WR generally increased with the test duration (Figures 5-10B, 5-11B, and 5-12B).

This solubilization-time relationship suggested that the dissolving of arsenic, chromium, and copper from the dislodgeable solids was not equilibrated in most test conditions by varying the duration from 1 to 168 hours and pH from 6 to 3.

5.5.2.3 Influence of pH on the solubilization of total arsenic, chromium, and copper

Significant difference in the percentage of chromium solubilized from dislodgeable solids CCA was found in the 1-hour water matrix at various pH (Appendix 3 Tables 23). The increased amount of water soluble chromium at lower pH could possibly be attributed to the dissociation of chromium fixation products, such as chromium arsenate ($CrAsO_4$) and/or chromium hydroxide ($Cr(OH)_3$) as proposed in Equations 2 and 3. The ionized form of chromium is relatively higher in water solubility.

$$CrAsO_4 + 2H^+ \rightarrow Cr^{3+} + H_2AsO_4^- \quad (2)$$

$$Cr(OH)_3 + 3H^+ \rightarrow Cr^{3+} + 3H_2O \quad (3)$$

No pH dependency was found in the solubilization of chromium after 24 hours, which suggested the dissociation of $CrAsO_4$ or $Cr(OH)_3$ was less to negligible after 24 hours.

The percentage of copper solubilized from dislodgeable solids CCA was influenced by pH at 1-hour and 24-hour test durations (Appendix 3 Table 24), which could also be attributed to the interaction between H^+ and copper compounds or copper complex with wood components proposed by Bull (2000, 2001), resulted in the release of copper ions in water.

The solubilization of arsenic, chromium, and copper from dislodgeable solids CCA/WR was also influenced by pH, which increased with the decreasing pH values.

The impact from pH was observed with arsenic at all the three time intervals (Appendix 3 Table 25). Chromium was found to be pH dependent during the first hour. No significant difference was found after 24 hours (Appendix 3 Table 26). The percentage of copper solubilized was not significantly affected by the pH during the first hour. Significant difference existed after 24 hours (Appendix 3 Table 27). These observations may also be explained by the dissociation of CCA fixation products at low pH, and resulted in the release of soluble arsenic, chromium, and copper in water. The pH dependency of chromium within 1-hour test duration, and after 24 hours for copper from both dislodgeable solids CCA and dislodgeable solids CCA/WR suggested that the dissociation of copper and chromium could be carried out individually. Chromium fixation products could be dissociated during the first hour, which was demonstrated by the pH dependency of chromium within one hour test duration. The physical dissolving of unfixed copper in wood dominated during the first hour, which was found to be less pH dependent. In prolonged test duration, this physical dissolving became less significant. The dissociation of copper fixation products became important. This observation was in agreement with Pizzi (1982a,b,c) and Bull (2001), who proposed copper could be fixed in CCA-treated wood independent from chromium or arsenic.

5.5.3 Proportions of water soluble arsenic, chromium, and copper in the dislodgeable solids

Table 5-3 lists the weight percentage of water soluble arsenic, chromium, and copper in the dislodgeable solids, which was derived from Table 5-2. By varying the pH of the water matrix in the first hour of the test, the proportions of water soluble arsenic, chromium, and copper corresponded to about 0.05%, 0.03±0.01%, and 0.03±0.01% in

Table 5-3. Weight percentage of soluble As, Cr, and Cu in the dislodgeable solids and the corresponded atomic ration of As: Cr: Cu

solids	test duration	element	pH 3			pH 4			pH 5			pH 6		
			wt.%*	mole-% ×1000**	ratio ***	wt.%	mole-% ×1000	ratio	wt.%	mole-% ×1000	ratio	wt.%	mole-% ×1000	ratio
dislodgeable solids, CCA	1hr	As	0.059	0.787	1.07	0.058	0.771	1.32	0.056	0.745	1.48	0.047	0.626	1.30
		Cr	0.045	0.862	1.17	0.036	0.689	1.18	0.030	0.582	1.15	0.022	0.422	0.88
		Cu	0.047	0.738	1.00	0.037	0.583	1.00	0.032	0.504	1.00	0.031	0.481	1.00
	24hrs	As	0.081	1.075	1.14	0.070	0.940	1.42	0.095	1.270	1.93	0.079	1.049	1.90
		Cr	0.044	0.849	0.90	0.042	0.815	1.23	0.037	0.711	1.08	0.023	0.446	0.81
		Cu	0.060	0.943	1.00	0.042	0.662	1.00	0.042	0.658	1.00	0.035	0.553	1.00
	168hrs	As	0.115	1.533	0.71	0.118	1.575	1.14	0.111	1.482	2.33	0.107	1.431	2.89
		Cr	0.070	1.351	0.63	0.037	0.717	0.52	0.035	0.677	1.06	0.029	0.554	1.12
		Cu	0.137	2.151	1.00	0.088	1.386	1.00	0.040	0.636	1.00	0.031	0.494	1.00
dislodgeable solids, CCA/WR	1hr	As	0.085	1.132	0.74	0.088	1.175	0.76	0.094	1.260	0.90	0.092	1.226	1.10
		Cr	0.207	3.975	2.59	0.196	3.771	2.43	0.193	3.715	2.65	0.172	3.317	2.97
		Cu	0.098	1.536	1.00	0.099	1.554	1.00	0.089	1.401	1.00	0.071	1.117	1.00
	24hrs	As	0.125	1.672	0.59	0.110	1.467	0.78	0.112	1.501	0.81	0.111	1.475	0.82
		Cr	0.224	4.306	1.52	0.225	4.336	2.32	0.208	3.994	2.17	0.209	4.011	2.23
		Cu	0.180	2.841	1.00	0.119	1.871	1.00	0.117	1.845	1.00	0.114	1.798	1.00
	168hrs	As	0.158	2.110	0.72	0.149	1.993	0.72	0.145	1.935	0.73	0.159	2.127	0.87
		Cr	0.244	4.570	1.60	0.238	4.570	1.65	0.235	4.516	1.70	0.228	4.392	1.80
		Cu	0.187	2.942	1.00	0.176	2.775	1.00	0.168	2.650	1.00	0.155	2.442	1.00

*wt.% = % of soluble element in total element × % of total element in the dislodgeable solids,
where % of soluble element in total element is listed in Table 5-2,
% of total element in dislodgeable solids CCA: As: 1.2%, Cr: 1.6%, Cu: 0.73%;
% of total element in dislodgeable solids CCA/WR: As: 0.59%, Cr: 0.67%, Cu: 0.55%.

**mole-%×1000 = wt.% /M.W. × 1000, where M.W. of As: 74.9, Cr: 52.0, Cu: 63.5

*** CCA-C ratio: As: 1.27, Cr: 2.04, Cu: 1.00 (AWPA 2003) weight of the total dislodgeable solids CCA, respectively. After 24 hours, the proportions of soluble arsenic, chromium, and copper corresponded to 0.09±0.01%, 0.03±0.01%, and 0.05±0.01% % of the dislodgeable solids CCA, respectively. These values increased to about 0.11%, 0.05±0.02%, and 0.03% to 0.14% for soluble arsenic, chromium, and copper, respectively after 168 hours. The atomic ratio of As : Cr : Cu was in the range of 0.7-2.9 : 0.5-1.2 : 1.0. Compared with the atomic ratio of As : Cr : Cu at 1.27 : 2.04 : 1.00 in CCA-C preservative (AWPA 2003), the decrease in the proportion of chromium was noticed, which suggested the formation of chromium fixation products with low water solubility.

Relatively larger proportion of soluble arsenic, chromium, and copper was found in dislodgeable solids CCA/WR. During the first hour, the amounts of water soluble arsenic, chromium, and copper corresponded to about 0.09%, 0.19±0.02%, and 0.08±0.02% of the total dislodgeable solids. After 24 hours, the percentages of soluble arsenic, chromium, and copper increased to 0.12%, 0.22%, and 0.16±0.03%, respectively. About 0.16% of the solids was found as soluble arsenic, about 0.24% as soluble chromium, and 0.18±0.02% as soluble copper after 168 hours. The atomic ratio of soluble As : Cr : Cu in dislodgeable solids CCA/WR was in the range 0.59-1.10 : 1.5-4.0 : 1.0. Compared with the ratios of soluble As : Cr : Cu in dislodgeable solids CCA, an increase in the proportion of soluble chromium was observed, which suggested that, relatively larger proportion of chromium was not fixed in CCA/WR-treated wood. This also explained the increased percentage of soluble arsenic, chromium, and copper in total arsenic, chromium, and copper from dislodgeable solids CCA/WR compared with those from dislodgeable solids CCA.

5.5.4 Speciation of arsenic solubilized from the dislodgeable solids

5.5.3.1 As^V and As^{III} recovery rate - arsenic speciation of standard As^V and As^{III} solutions

The recovery rates after arsenic speciation of As^V and As^{III} standard solutions are listed in Table 5-4. More than 94% of As^V was recovered after the speciation of As^V standard solutions from 5 ppb to 500 ppb. The concentration of As^{III} found in As^V standard solutions was below the detection limit of 0.3 ppb by using GFAA. The recovery rate of As^{III} after the speciation of As^{III} standard solutions at the concentrations from 5 ppb to 100 ppb was between 74% and 85%. With increased As^{III} concentration from 100 ppb to 500 ppb, As^{III} recovery rate increased from 85% to 99%. This increased As^{III} recovery rate was attributed to the increased stability of As^{III} at higher concentrations. Manning and Goldberg (1997) and Gallagher et al. (2001) reported that more As^{III} could be oxidized to As^V in open air at lower concentrations, and this tendency decreases with the increase of As^{III} concentrations. This phenomenon could be explained by the thermodynamic principles using actual reversible potential of arsenic. At 298.15 K (25°C), the half reaction of arsenic in water and its standard electrode potential (E^0) are listed as following (Wilson 1974):

$$H_3AsO_4 + 2H^+ + 2e^- = H_3AsO_3 + H_2O \qquad E_{AsO_4^{3-}/AsO_3^{3-}} = 0.559\ volt$$

The actual reversible potential $E_{AsO_4^{3-}/AsO_3^{3-}}$ could be expressed by using Nernst equation (Equation 4).

$$E_{AsO_4^{3-}/AsO_3^{3-}} = E^0{}_{AsO_4^{3-}/AsO_3^{3-}} - \frac{0.059}{2}\log\frac{[H_3AsO_3]}{[H_3AsO_4]} \tag{4}$$

Table 5-4. Arsenic speciation of standard As^{V} and As^{III} solutions

Standard solutions	As^{V} standard solution				As^{III} standard solution			
	Total As	As^{V}	As^{III}	Recovery rate, As^{V} (%)	Total As	As^{III}	As^{V}	Recovery rate, As^{III} (%)
5ppb	4.5(0.1)*	4.5(0.1)	0.1(0.1)	100.0	4.3(0.1)	3.2(0.1)	1.0(0.3)	74.4
10ppb	14.3(0.2)	14.3(0.7)	0.2(0.1)	100.0	8.7(0.1)	7.0(0.3)	0.9(0.3)	80.5
50ppb	48.6(1.9)	50.7(1.7)	0.3(0.1)	104.3	46.3(0.2)	36.9(3.4)	1.5(0.4)	79.7
100ppb	119.6(1.6)	116.9(3.8)	0.1(0.2)	97.7	109.0(0.1)	93.1(4.6)	2.6(0.2)	85.4
300ppb	281.6(0.2)	265.7(1.3)	0.2(0.1)	94.4	297.2(1.0)	291.3(1.1)	2.6(0.4)	98.0
500ppb	520.4(0.8)	516.9(13.4)	0.1(0.0)	99.3	504.8(1.4)	502.3(1.3)	3.7(0.2)	99.5

*data are mean of three replicate, values in parenthesis are the standard deviation

Where the higher $E_{AsO_4^{3-}/AsO_3^{3-}}$ value, the stronger tendency of As^{III} (H_3AsO_3) to be oxidized. With a fixed value of $E^0_{AsO_4^{3-}/AsO_3^{3-}}$, $E_{AsO_4^{3-}/AsO_3^{3-}}$ in Equation 4 decreases with the increase of As^{III} concentration. Consequently the formation of H_3AsO_4 (As^V) is less favored.

5.5.3.2 Speciation of arsenic solubilized from the dislodgeable solids

Results from the speciation of arsenic solubilized from the dislodgeable solids in the water matrix are listed in Table 5-5. In the first hour samples from dislodgeable solids CCA, the concentration of As^V was 365±15 ppb in water at pH 6 to 3. As^V concentrations ranged from 473 ppb to 483 ppb in the 24-hour samples, and from 410 ppb to 564 ppb after 168 hours. One-way ANOVA analysis indicated that the solubilization of As^V in dislodgeable solids CCA appeared to be pH dependent after 24 hours (Appendix 3 Table 28). This suggested that As^V solubilized in the first hour could mostly be attributed to large volume of physical dissolving of unfixed arsenic rather than the fixed products, which are low in water solubility and sensitive to low pH.

The concentration of As^{III} from dislodgeable solids CCA was less than 50 ppb within the first 24 hours. After 168 hours, As^{III} increased to 360±40 ppb. As^{III} concentration was significantly influenced by the pH in the 1-hour samples, which increased with the acidity of water. No significant difference was observed with As^{III} in the 24-hour samples (Appendix 3 Table 28). Data of As^{III} after 168 hours failed to pass the normality test.

Table 5-5. Speciation of arsenic solubilized from the dislodgeable solids

Test duration, hrs	pH	Arsenic species in water, ppb					
		dislodgeable solids CCA			dislodgeable solids CCA/WR		
		As^V	As^{III}	Total As	As^V	As^{III}	Total As
1	3	383.6 (8.4)*	37.4(3.5)	465.0(0.0)	460.1(26.0)	173.7(19.4)	660.0(24.8)
	4	384.3(26.2)	38.8(1.9)	454.0(3.5)	477.2(33.5)	146.8(1.8)	686.0(7.1)
	5	377.0(4.7)	31.3(1.8)	440.0(1.8)	455.3(53.5)	136.2(5.3)	735.0(14.1)
	6	351.4(3.5)	31.3(1.8)	370.0(0.0)	434.5(130.3)	122.4(3.6)	715.0(3.5)
24	3	562.1(8.1)	38.8(5.2)	635.0(14.1)	793.5(73.9)	160.5(10.6)	975.0(10.6)
	4	483.3(20.7)	37.5(7.2)	555.0(134.4)	714.8(42.3)	153.9(8.8)	855.0(24.8)
	5	617.3(40.2)	46.3(12.4)	749.0(10.6)	730.9(26.7)	141.3(1.8)	875.0(7.1)
	6	472.5(32.5)	43.8(19.3)	619.0(10.6)	628.9(68.0)	151.0(1.8)	860.0(24.8)
168	3	563.7(20.6)	355.1(3.6)	905.0(198.0)	743.6(100.3)	439.7(7.1)	1230.0(35.4)
	4	435.2(33.5)	322.5(28.8)	930.0(3.5)	799.6(99.5)	405.4(127.3)	1159.0(46.0)
	5	410.4(2.4)	408.8(8.8)	875.0(0.0)	672.7(51.8)	363.8(12.4)	1125.0(53.0)
	6	488.0(57.8)	333.8(1.8)	845.0(3.5)	721.2(27.8)	430.0(0.1)	1240.0(28.3)

* values are mean of three replicate, values in parenthesis are the standard deviation of the mean

For dislodgeable solids CCA/WR, As^V concentration in water was 455±25 ppb in the first hour, and 710±80 ppb after 24 hours. As^V concentrations after 168 hours were similar to those at the 24-hour test duration. Unlike the pH dependency of As^V solubilized from dislodgeable solids CCA, As^V from dislodgeable solids CCA/WR did not appear to be pH sensitive (Appendix 3 Table 29). This suggested that large proportions of As^V solubilized from dislodgeable solids CCA/WR could be attributed to the physical dissolving of unfixed As^V, with less proportion of arsenic fixation products such as $CrAsO_4$. This also indicated an incomplete CCA fixation in CCA/WR-treated wood.

During the first 24 hours, As^{III} concentrations in water fell between 120 ppb to 170 ppb from dislodgeable solids CCA/WR, which was higher that those from dislodgeable solids CCA. After 168 hours, As^{III} concentrations increased to 400±40 ppb, which was significantly higher than those in the 1-hour and the 24-hour samples (Appendix 3 Table 30).

One-way ANOVA analysis also found that the addition of water repellent to CCA wood treatment significantly influenced the concentrations of As^V (or As^{III}) solubilized (Appendix 3 Tables 31 to 36). The amount of As^V or As^{III} solubilized from dislodgeable solids CCA/WR was generally larger than those from dislodgeable solids CCA and suggested an incomplete CCA fixation in wood with the presence of water repellent.

The distribution of As^V and As^{III} as well as the arsenic recovery rate in terms of the amount of As^V and As^{III} detected as a proportion of total arsenic in water are derived from Table 5-5 and listed in Table 5-6. About 76% to 95% of total arsenic present in

Table 5-6. Distribution of arsenic species solubilized from the dislodgeable solids

Test duration, hrs	pH	dislodgeable solids CCA			dislodgeable solids CCA/WR		
		$\frac{As^{V}_{sol}}{total\ As_{sol}}$, %	$\frac{As^{III}_{sol}}{total\ As_{sol}}$, %	$\frac{As^{V}_{sol} + As^{III}_{sol}}{total\ As_{sol}}$, %	$\frac{As^{V}_{sol}}{total\ As_{sol}}$, %	$\frac{As^{V}_{sol}}{total\ As_{sol}}$, %	$\frac{As^{V}_{sol} + As^{III}_{sol}}{total\ As_{sol}}$, %
1	3	82.5	8.1	90.6	69.7	26.3	96.0
	4	84.5	8.5	93.0	69.6	21.4	91.0
	5	85.7	7.1	92.8	61.9	18.5	84.5
	6	95.0	8.5	103.4	60.8	17.1	77.9
24	3	88.5	6.1	94.6	81.4	16.4	97.8
	4	87.1	6.8	93.9	83.6	18.0	101.6
	5	82.3	6.2	88.5	83.5	16.1	99.7
	6	76.2	7.1	83.3	73.1	17.6	90.7
168	3	62.3	39.2	101.5	60.5	35.8	96.2
	4	47.0	34.7	81.5	68.9	34.9	103.8
	5	46.9	46.7	93.6	59.8	32.3	92.1
	6	57.8	39.5	97.2	58.2	34.7	92.8

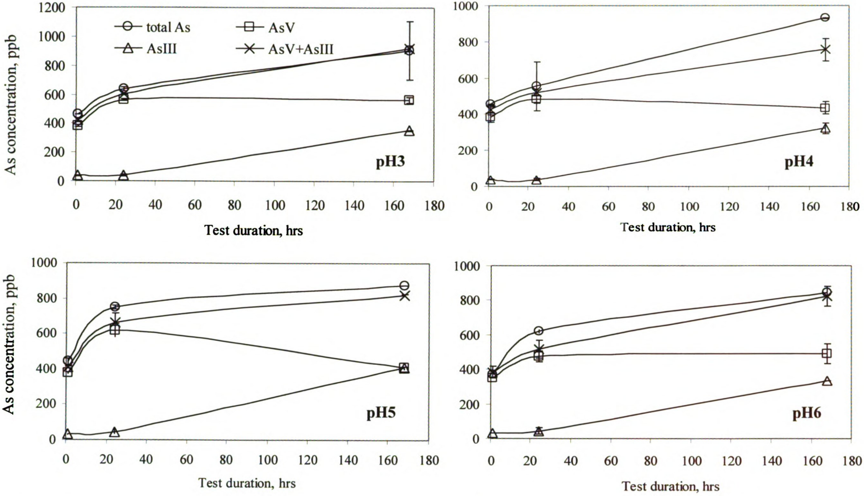

Figure 5-13. Soluble As^{III}, As^{V}, total As, and the sum of As^{III} and As^{V} in dislodgeable solids collected from CCA treated wood

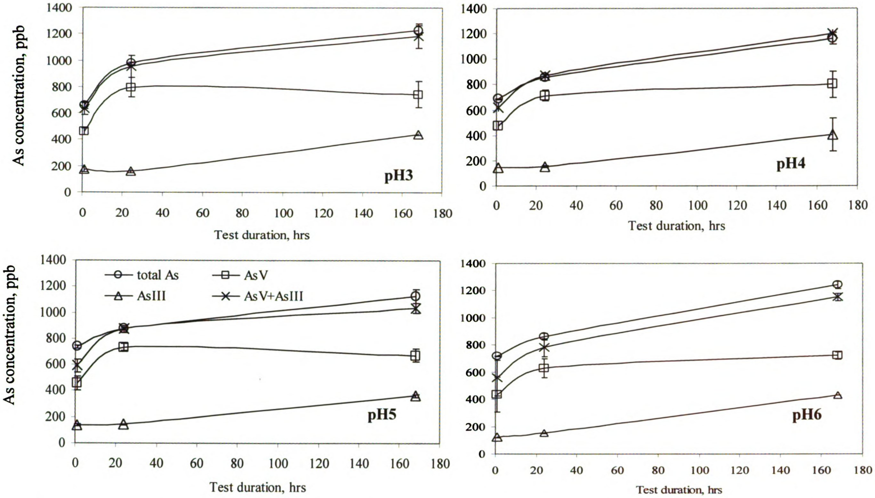

Figure 5-14. Soluble As^{III}, As^{V}, total As, and the sum of As^{III} and As^{V} in dislodgeable solids collected from CCA/WR treated wood

water was found as As^V in the 1st hour and the 24th hour, and 6% to 9% as As^{III} from dislodgeable solids CCA. The proportion of As^{III} increased to 41±6% after 168 hours. Similar phenomenon was observed with dislodgeable solids CCA/WR. About 77±7% of arsenic in water was As^V, and 22±6% was As^{III} during the first 24 hours. As^V decreased to 64±6%, and As^{III} increased to 34±2% after 168 hours. Figures 5-13 and 5-14 illustrate the concentrations of As^V, As^{III}, the sum of As^V and As^{III}, and total arsenic in water from dislodgeable solids CCA and dislodgeable solids CCA/WR. A consistent increase in the concentration of total arsenic was observed throughout the 168-hour test duration. As^V concentration increased during the first 24 hours and became stable or even some decrease in water matrix at pH 4 and 5 from 24 to 168 hours. On the other hand, As^{III} concentrations remained constant in the first 24 hours and increased from 24 hours to 168 hours. The curve of the sum of As^V and As^{III} were close to the curve of total arsenic, which suggested that As^V and As^{III} were the major arsenic species solubilized from dislodgeable solids CCA and dislodgeable solids CCA/WR.

5.5.3.3 Questions raised and future work recommended

The water solubility of As^{III} compounds is about 4 to 10 folds higher than that of As^V compounds (Federal Remediation Technologies Roundtable 2004). As^{III} has a greater potential to leach than As^V (Mok and Wai 1994). Therefore, larger proportions of As^{III} would be expected at the initial stage of the solubilization test if present in the dislodgeable solids. The increased amount of As^{III} from 24 to 168 hours is suspected to come from the reduction of As^V during the solubilization process, rather than a release of As^{III} from the dislodgeable solids. The mechanism of As^V reduction in this situation is not clear. The involvement of microbiological activity is highly suspected (Ahmann et al. 1994; Laverman et al. 1995; Newman et al. 1998; Cánovas et al. 2003).

The percentage of the sum of As^V and As^{III} to total arsenic in water ranged from 83% to 103% (Table 5-6). This 20% variation between the sum of As^V and As^{III}, and the total arsenic in water indicated the presence of errors during arsenic speciation, possibly an incomplete elution of As^V from the modified chromosorb cartridge or the present of arsenic species other than As^V or As^{III}.

5.6 Conclusions

Arsenic, chromium, and copper partially solubilized from dislodgeable solids CCA and dislodgeable solids CCA/WR in a 168-hour test. The amount of arsenic, chromium, and copper solubilized generally increased with the test duration from 1 hour to 168 hours. The solubilization of chromium was influenced by pH during the first hour of the test. Copper showed pH dependency in the first 24 hours from dislodgeable solids CCA and after 24 hours in dislodgeable solids CCA/WR. Arsenic in dislodgeable solids CCA/WR was pH dependent throughout the 168-hour test duration.

The addition of water repellent to CCA wood treatment significantly increased the proportions of arsenic, chromium, and copper solubilized from the dislodgeable solids. Larger amount of soluble Cr^{VI} were found with dislodgeable solids CCA/WR than dislodgeable solids CCA.

Both As^V and As^{III} were found in the water matrix. As^V was the dominant form during the first 24 hours. Significant decrease in the proportions of As^V and increase in

As^{III} were found after 168 hours from both dislodgeable solids CCA and dislodgeable solids CCA/WR.

Chapter 6

Speciation of Arsenic in the Leachate of Chromated Copper Arsenate (CCA) Treated Southern Pine

6.1 Introduction

Toxicity of arsenic and chromium is strongly influenced by their oxidation states. Inorganic trivalent arsenic (As^{III}) is more potent than inorganic pentavalent arsenic (As^{V}) in an acute exposure; hexavalent chromium (Cr^{VI}) has been recognized as a carcinogen while trivalent chromium (Cr^{III}) is essential to human health (Schroeder and Balassa 1966; Hughes et al. 1994; Healy et al. 1998).

Copper, chromium, and arsenic have been frequently reported to leach from chromated copper arsenate (CCA) treated wood. A general finding is that arsenic leaches the most while chromium tends to be fixed in wood (Jin and Preston 1993; Kennedy and Palmer 1994; Cooper et al. 1997; Yamamoto et al. 2000; Venkatasamy 2002). Trivalent chromium is the major chromium species found in the leachate of CCA-treated wood after the fixation (Cooper and Ung 1993; Kennedy and Palmer 1994; Cooper et al 1994 1997).

Information on arsenic speciation related to CCA-treated wood is limited. There are several studies carried out to speciate arsenic from CCA-treated wood in recent years. By using a selective solvent extraction coupled with atomic absorption spectroscopy (AA), Nygren and Nilsson (1993) reported that less than 0.5% of the total arsenic was As^{III} in commercially CCA-treated wood. Hingston et al. (2003) reported that less than 10% of total arsenic in leachate of CCA-treated wood was As^{III} by using differential pulse polarography for arsenic speciation. Using high performance liquid chromatography coupled with hydride generation atomic fluorescence spectrometry (HPLC-HG-AFS), Solo-Gabriele et al. (2003) found up to 50% of total arsenic in CCA leachate was As^{III}. Various studies using different arsenic speciation methods have generated a larger variety of data.

The objective of this study is to apply a newly developed selective ion-exchange chromatography method to speciate arsenic, and to gain insight of arsenic species in the leachate of CCA-treated wood.

6.2 Material and Methods

6.2.1 Commercially prepared CCA-treated southern pine

Commercially CCA-treated southern pine boards were purchased from a hardware store located in Lansing, Michigan. The board was labeled at a chemical retention of 6.4 kg/m^3. Defect free cubes measuring 19 mm in edges were cut from these boards and stored in a conditioning room maintained at 20°C and 65% relative humidity (RH) for one week before the leaching test. Cubes with similar weight were selected for further testing.

6.2.2 Laboratory prepared CCA-treated southern pine

Cubes measuring 19 mm in edges were cut from defect-free kiln-dried sapwood boards of southern pine and stored in a conditioning room maintained at 65% relative humidity (RH) and 20°C (68°F) until the blocks reached a constant moisture content of 10.50 ± 0.75%.

6.2.3 CCA treating solution and wood treatment

A 1% CCA treating solutions were prepared by diluting 9.4% CCA type C stock solution received from Osmose, Inc. using deionized (DI) water. The concentrations of CCA treating solutions were expressed in weight percentage of total oxides for copper, chromium, and arsenic, as CuO, As_2O_5, and CrO_3, respectively. The elemental copper, chromium, and arsenic concentrations in the solutions were analyzed using Flame Atomic absorption spectrometry.

A 1-liter stainless steel treating tank was used for wood treatment. A total of 20 southern pine blocks were full cell pressure treated. The treating process included an 84.6-kPa (30″ Hg) vacuum for 30 minutes followed by a 1240-kPa (180-psi) pressure for 1 hour with no final vacuum applied. Wood samples were wrapped in plastic bags and stored in the dark at 20°C (68°F) for 7 days after removed from the treating tank. The treated blocks were then set unwrapped in a conditioning room at 65% relative humidity (RH) and 20°C (68°F) for another 3 weeks before further test.

6.2.4 Chemical retentions in CCA-treated wood

The retention of arsenic, chromium, and copper in treated cubes were evaluated by using chemical analysis protocols A7-93 and A11-93 described in American Wood-Preservers' Association Standard (AWPA 2003).

6.2.5 Laboratory accelerated leaching test

The laboratory accelerated leaching test of both commercially and laboratory CCA-treated wood was conducted according to AWPA standard E11-97 (AWPA 2003) with some modification as described below: six cubes from each treatment were submerged in 300 ml of deionized (DI) water in an Erlenmeyer flask and magnetic stirred with magnetic stirring at room temperature. The flask was covered with parafilm to prevent possible evaporation. The leachate was removed and replaced with fresh DI water after 6, 24, and every 48 hours thereafter up to a total of 558 hours.

6.2.6 Atomic absorption spectroscopy (AA) measurement of arsenic, chromium, and copper

Quantification of elemental arsenic, chromium, and copper was completed by using flame atomic absorption spectrophotometer (FAA, Perking Elmer 3110), equipped with an electrodeless discharge lamp (EDL) for arsenic, and hollow cathode lamps for chromium and copper (Perkin Elmer) at parts per million (ppm) level. A graphite furnace atomic absorption spectroscopy (GFAA, Perkin Elmer AAnalyst 800) equipped with an EDL arsenic lamp was used to quantify arsenic at parts per billion (ppb) level. Arsenic, chromium, or copper solutions used to construct the working curves for AA measurements were diluted from atomic absorption standard solutions purchased from Aldrich Chemical Co. The preparation of the standard solutions to obtain the working curve of each element has been described in the experimental section of Chapter 3. A matrix modifier was used to reduce the interferences from matrix effects during GFAA measurement of arsenic. The preparation of the modifier was previously described (Flores del Pino 2003). The instrumental detection limits were 0.6 ppm for arsenic, 0.02 ppm for chromium, and 0.3 ppm for copper with FAA, and 0.3 ppb for arsenic with GFAA.

6.2.7 Speciation of Cr^{VI} in the leachate

Cr^{VI} in water was determined by using a colorimetric method described by Cooper and Ung (1993). Chromium solutions with concentrations from 0 to 1.0 ppm were prepared by diluting Cr^{VI} standard solution (1000ppm, Atomic absorption standard, Aldrich) using 0.5N sulfuric acid. Diphenylcarbazide solution was used as an indicator, and was prepared by dissolving 2.5 g of 1, 5-diphenylcarbazide (A.C.S. Reagent, Aldrich) in 100 ml mixture of acetone and DI water (v/v: 1:1). The visible absorbance of the complex formed between Cr^{VI} and 1, 5-diphenylcarbazide at room temperature was measured at 540 nm using ultraviolet-visible (UV-vis) spectrophotometer (DU 640B, Beckman Co.). The Cr^{VI} working curve was obtained by plotting a linear regression between the absorbance of Cr^{VI}-diphenylcarbazide complex and the corresponding Cr^{VI} concentrations as determined by AA. Cr^{VI} in the leachate was measured directly with no further preparation.

6.2.8 Speciation of arsenic in the leachate

As^{V} and As^{III} have been reported as time dependent, As^{III} could be oxidized to As^{V} in an open air (Manning and Goldberg 1997; Cánovas 2003). The isolation of As^{V} and As^{III} was performed within 10 minutes after each leachate collection in order to limit possible changes in arsenic oxidation states. A cation exchange pre-column and a modified chromosorb column were used to speciate arsenic. The pre-column was prepared by packing 0.6 g of cation exchange resin with capacity of 2 meq/g into a 1-ml syringe from Becton Dickinson. The modified chromosorb in the column consisted of a silanized diatomaceous earth with dioctyltin dichloride ($(C_8H_{17})_2SnCl_2$). The leachate was diluted 50 folds to satisfy the ion-exchange capacity of the columns based on preliminary test. A total of 20.0 ml of the diluted leachate was passed through the pre-column at a flow rate of 1 ml/min. The pre-column was used to eliminate or reduce potential interference of cations such as copper (Cu^{2+}) present in the leachate during arsenic speciation. The pH of the solution eluted from the pre-column was adjusted to 2.5-3.5 using 1.0N hydrochloric acid (HCl). As^{V} and As^{III} was separated by passing the pH-adjusted solution through modified chromosorb column capable of retaining ionized As^{V}. As^{III} in its neutral form was not retained and present in the eluant. As^{V} trapped in the modified chromosorb column was desorbed by using 0.5N HCl. The solution passing through the column containing As^{III}, the elution washed out from the column consisting of As^{V}, and the initial leachate after 50-fold dilution were analyzed by using GFAA to quantify As^{III}, As^{V}, and total arsenic, respectively.

6.2.9 Statistic analysis

One-way ANOVA analysis (Jandel SigmaStat Version 2.0, Jandel Co.) using all pairwise multiple comparison tests (Tukey Test) at the significant level of 0.05 was performed, to determine if significant difference existed in the concentration of total arsenic, As^{V} or As^{III} leached at various leaching durations (0-6 hours, 6-30 hours, 30-78 hours, 78-126 hours, 126-174 hours, 174-222 hours, 222-270 hours, and 270-318 hours).

6.3 Results and discussion

6.3.1 Elemental arsenic, chromium, and copper in the treating solutions and treated wood

Table 6-1 lists the weight of the southern pine blocks before (Wi) and after (Wa) CCA treatments. The weight gain of each block after CCA treatment was calculated using Equation 1. Blocks with similar values of weight gain (about 150%) were selected for the leaching test.

$$\text{weight gain}, \% = \frac{\text{Wa} - \text{Wi}}{\text{Wi}} \times 100\% \qquad (1)$$

The percentage of elemental arsenic, chromium, and copper in CCA-treated wood are listed in Table 6-2. Arsenic, chromium, and copper retentions in wood were found at 0.23%, 0.46% and 0.13%, respectively in commercially CCA-treated wood, and 0.32%, 0.62%, and 0.17%, respectively in laboratory treated wood. Retentions of the corresponding oxides in kg/m^3 were calculated by using a density of 500 kg/m^3 for southern pine. The chemical retentions expressed in total oxides were 4.8 kg/m^{-3} in commercially CCA-treated wood and 6.6 kg/m^{-3} in laboratory treated wood.

6.3.2 Cr^{VI} and elemental arsenic, chromium, and copper in the leachate of CCA-treated wood

It is reported that in CCA treated wood, a series of interactions may occur between arsenic, chromium, copper, and wood components, resulting in the formation of chromium (III) arsenate, chromium (III) hydroxide, and complex between copper, chromium and wood components (Bull 2001). The reduction of Cr^{VI} to Cr^{III} has been widely used as indication of CCA fixation in wood (Cooper and Ung 1993; Cooper et al 1994). Figure 6-1 illustrates the cumulative concentrations of total chromium and Cr^{VI} in the leachate from commercially or laboratory CCA-treated wood. The reduced amount of Cr^{VI} present in CCA treated wood after fixation is assumed to be converted to Cr^{III}. After

Table 6-1. Weight gain of southern pine blocks after CCA treatment and the selection of treated blocks for the leaching test

sample ID	Wi	Wa	weight gain, %	comments
1	3.44	8.47	146	
2	3.44	7.84	128	
3	3.44	8.62	151	*
4	3.44	8.03	133	
5	3.44	8.50	147	
6	3.44	8.11	136	
7	3.44	8.67	152	*
8	3.44	8.53	148	
9	3.44	8.07	135	
10	3.44	8.09	135	
11	3.44	8.64	151	*
12	3.44	8.76	155	*
13	3.44	8.68	152	*
14	3.45	8.63	150	
15	3.43	8.42	145	
16	3.45	8.18	137	
17	3.45	8.57	148	
18	3.46	8.52	146	
19	3.46	8.73	152	*
20	3.46	8.22	138	

Wi: weight before the treatment; Wa: weight after the treatment;
*** blocks selected for the leaching test**

Table 6-2. Arsenic, chromium, and copper in CCA-treated wood

CCA-treated wood	%			Retention, kg/m^3			
	As	Cr	Cu	As_2O_5	CrO_3	CuO	Total oxides
Commercially treated wood	0.23	0.46	0.13	1.76	2.21	0.81	4.79
Laboratory treated wood	0.32	0.62	0.17	2.45	3.08	1.06	6.59

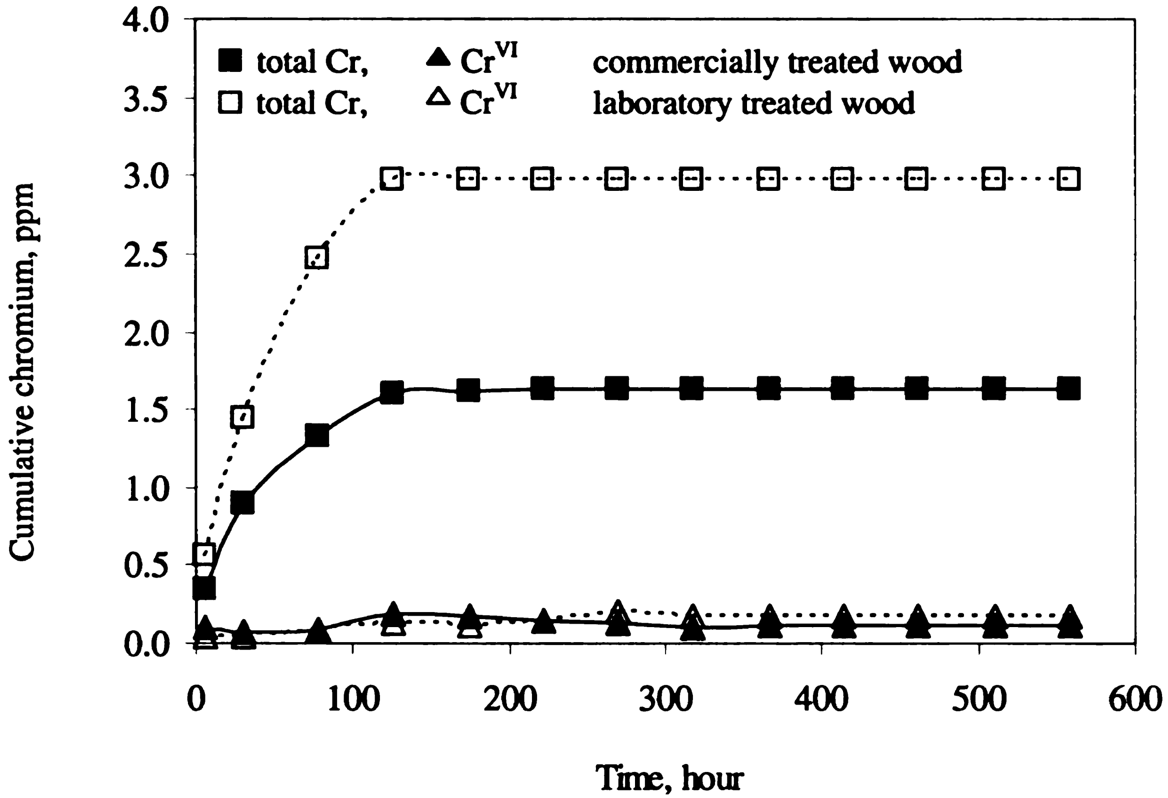

Figure 6-1. Cumulative Cr^{VI} in the leachate of commercially and laboratory treated wood

30 hours of leaching, less than 10% of the total chromium was found as Cr^{VI}; this relatively low level of Cr^{VI} suggests a nearly complete CCA fixation in commercially and in laboratory CCA-treated wood.

The cumulative amounts of arsenic, chromium, and copper in leachate were calculated and illustrated in Figure 6-2. Arsenic was the element with the highest amount in the leachate followed by copper and chromium. This is in agreement with the findings by Jin and Preston (1993) and Kennedy and Collins (2001). A plateau was reached for chromium after 174 hours and for copper after 366 hours, indicating that the leaching of chromium and copper was nearly completed after 174 hours and 366 hours, respectively. Additional leaching of arsenic continued throughout the test. After 558 hours, similar amount of arsenic was leached from commercially and laboratory treated wood, at 13.15 mg and 13.17 mg, respectively. A total of 0.49 mg of chromium and 1.76 mg of copper were leached from commercially treated wood; about 0.89 mg of chromium and 2.38 mg of copper from laboratory treated cubes. Relatively larger amount of chromium and copper were leached from laboratory treated wood than commercially treated, which was attributed to the higher chemical retention resulted from a better penetration of CCA treating solution into small cubes during the laboratory wood treatment.

Table 6-3 lists the percentages of arsenic, chromium, and copper leached from both commercially and laboratory CCA-treated cubes at each time interval during the leaching test. After 558 hours, a total of 6.31% and 6.77% of copper were lost through leaching from commercially and laboratory CCA-treated cubes, respectively. Relatively less proportions of chromium were leached. About 0.51% of chromium was lost from commercially treated cubes, and about 0.69% from laboratory treated cubes. The largest

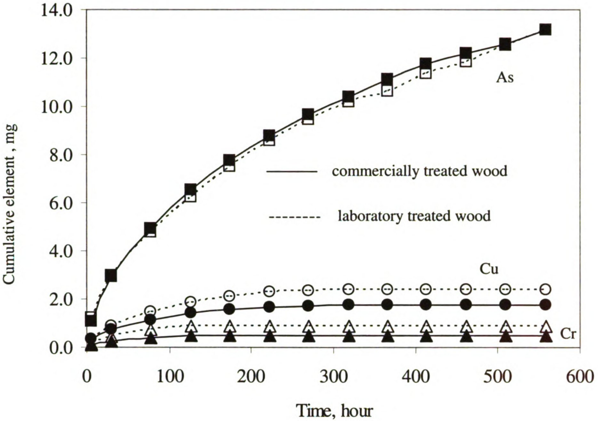

Figure 6-2. Cumulative element from commercially and laboratory CCA-treated southern pine cubes in a 558-hour leaching test

Table 6-3. Percentage* of leached element in CCA-treated cubes in a 558-hour leaching

Leaching duration, h	As		Cr		Cu	
	Commercially treated cubes	Laboratory treated cubes	Commercially treated cubes	Laboratory treated cubes	Commercially treated cubes	Laboratory treated cubes
0 - 6	2.25	1.86	0.11	0.13	1.30	0.92
6 - 30	3.91	2.60	0.17	0.20	1.41	1.53
30 - 78	4.22	2.76	0.14	0.24	1.40	1.67
78 - 126	3.37	2.20	0.09	0.12	0.93	1.10
126 - 174	2.64	1.91	0.00	0.00	0.53	0.71
174 - 222	2.11	1.57	0.00	0.00	0.40	0.54
222 - 270	1.84	1.35	0.00	0.00	0.23	0.20
270 - 318	1.61	1.10	0.00	0.00	0.08	0.05
318 - 366	1.49	1.03	0.00	0.00	0.03	0.05
366 - 414	1.36	1.05	0.00	0.00	0.00	0.00
414 - 462	1.34	1.17	0.00	0.00	0.00	0.00
462 - 510	1.21	0.98	0.00	0.00	0.00	0.00
510 - 558	1.24	0.98	0.00	0.00	0.00	0.00
total	28.59	20.56	0.51	0.69	6.31	6.77

* percentage of element leached in initial amount in wood after treatment

proportion of leaching was found with arsenic at 28.59% and 20.56%, respectively from commercially and laboratory CCA-treated cubes.

The reduction of Cr^{VI} to Cr^{III} in CCA-treated wood is generally used as an indication of CCA fixation (Cooper and Ung 1993; Kennedy and Palmer 1994; Cooper et al 1994 1997). However, the continuous release of arsenic from CCA-treated cubes during the 558-hour test suggested that arsenic should also be considered in the evaluation of CCA fixation in treated wood. Since arsenic toxicity is influenced by its oxidation states, monitoring its species in the leachate is paramount information in human health and environmental risk assessment.

6.3.3 Speciation of arsenic in the leachate

The leaching rates of As^V, As^{III}, and total arsenic (μg/h) were plotted as functions of time in Figure 6-3. The highest leaching rate was found at the initial stage of the test and decreased with prolonged test duration. In the first 6 hours, the average leaching rate of total arsenic was 177.8 μg/h from commercially CCA-treated cubes, among which, 110.5 μg/h was attributed to As^V and 53.6 μg/h to As^{III}. The leaching rate of total arsenic, As^V, and As^{III} in the leachate collected from laboratory treated cubes were 205.9 μg/h, 176.9 μg/h, and 28.8 μg/h, respectively. About 12.3 μg/h of total arsenic, 9.4 μg/h of As^V, and 2.9 μg/h of As^{III} were detected in the leachate of commercially treated cubes from the last collection (510-558 hours interval); about 13.5 μg/h, 9.9 μg/h of As^V, and 3.2 μg/h of As^{III} were leached from laboratory treated cubes. Similar amount of arsenic was leached from commercially and laboratory treated wood.

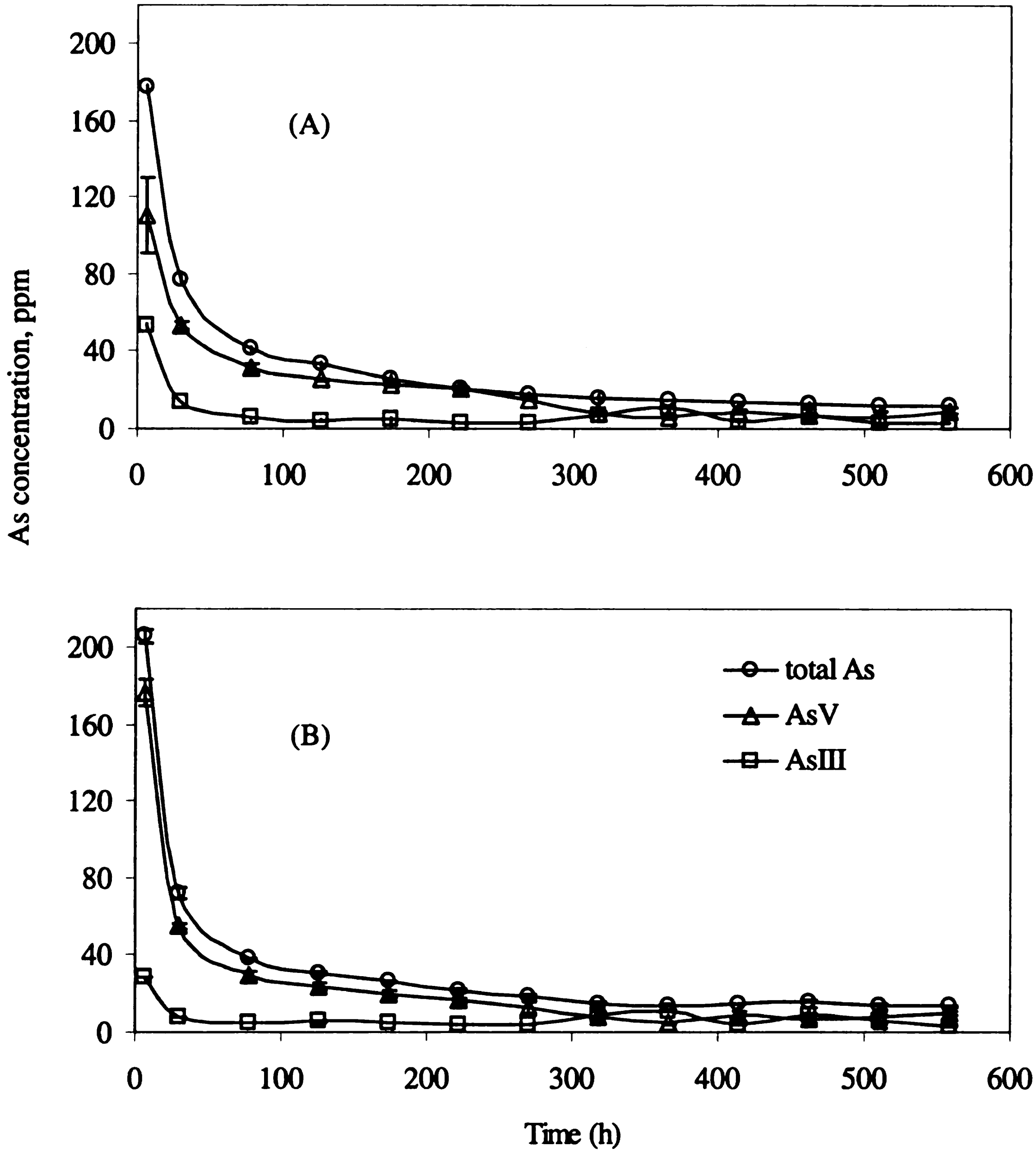

Figure 6-3. Leaching rate of As^V, As^{III} and total As from (A) commercially, and (B) laboratory treated wood

The proportions of As^V and As^{III} in total arsenic presented in each leachate are listed in Table 6-4. The proportions of As^V were relatively larger than those of As^{III} during the first 270 hours: about 62.2-99.5% of total arsenic in the leachate of commercially CCA-treated cubes was found as As^V, and 13.1-30.2% was As^{III}; about 69.5-86.0% of the total arsenic in the leachate of laboratory treated cubes was found as As^V, and 10.9-19.8% was As^{III}. The sum of As^V and As^{III} as a proportion of total arsenic in each leachate are also listed in Table 6-4. About 102±13% of total arsenic in leachate from the first 270 hours was found as As^V and As^{III}, which suggested that As^V and As^{III} were the major arsenic species in the leachate of CCA-treated southern pine. After 270 hours, relatively larger standard deviations in data groups were noticed.

Tables 6-5 and 6-6 list the result from one-way ANOVA analysis of arsenic concentrations in leachate collected at various time interval. Statistical analysis suggested that the concentrations of total arsenic, As^V, and As^{III} were significantly influence by the leaching duration in the first 270 hours leaching. Significant difference was observed within most of the treatment groups. Exceptions were found in total arsenic between the 6-30 hours and the 78-126 hours from commercially CCA-treated wood (Table 6-5), the 6-30 hours and the 30-78 hours from laboratory treated wood (Table 6-6). No statistical difference was found in the concentration of As^V between the 78-126 hours and the 6-30 hours / the 126-174 hours, the 126-174 hours and the 174-222 hours leachates of commercially treated wood (Table 6-5); the 0-6 hours and the 78-126 hours, the 6-30 hours and the 30-78 hours / the 78-126 hours, the 126-174 hours and the 78-126 hours / the 174-222 hours, the 174-222 hours and the 222-270 hours leachates of laboratory treated wood (Table 6-6). Exceptions were also observed in As^{III} between the 174-222

Table 6-4. Percentage of As^V and As^{III} in the leachate from CCA-treated cubes

Leaching duration, hour	Commercially CCA-treated cubes*			Laboratory CCA-treated cubes*		
	$\frac{As^V}{total\ As}$, %	$\frac{As^{III}}{total\ As}$, %	$\frac{As^V + As^{III}}{total\ As}$, %	$\frac{As^V}{total\ As}$, %	$\frac{As^{III}}{total\ As}$, %	$\frac{As^V + As^{III}}{total\ As}$, %
0 - 6	62.2(11.2)	30.2(0.5)	92.4(11.1)	86.0(3.9)	14.0(0.2)	100.0(4.0)
6 - 30	69.3(1.9)	18.1(0.1)	87.4(1.9)	76.6(2.3)	10.9(0.0)	87.5(2.3)
30 - 78	75.2(3.3)	13.3(0.3)	88.4(3.2)	78.0(6.3)	12.8(0.9)	90.8(7.2)
78 - 126	76.7(2.7)	13.1(0.3)	89.8(2.9)	76.7(6.4)	18.3(0.9)	95.0(7.3)
126 - 174	87.1(4.5)	17.9(8.1)	105.0(11.0)	74.5(7.0)	19.8(0.6)	94.3(7.5)
174 - 222	99.5(2.1)	15.7(0.6)	115.2(1.8)	76.1(8.1)	19.2(1.2)	95.3(8.9)
222 - 270	83.3(1.3)	17.3(0.1)	100.6(1.3)	69.5(19.6)	19.7(1.2)	89.2(20.8)
270 - 318	49.9(6.3)	43.1(21.1)	93.0(27.3)	50.0(0.8)	59.9(8.0)	109.9(7.3)
318 - 366	40.0(8.9)	70.4(8.3)	110.3(17.0)	79.7(3.4)	32.5(1.5)	112.2(4.8)
366 - 414	69.3(3.3)	26.7(4.1)	96.0(6.1)	60.4(17.1)	27.7(2.8)	88.1(16.6)
414 - 462	25.6(0.4)	52.9(25.9)	78.5(25.4)	56.2(22.6)	44.6(19.8)	100.7(2.8)
462 - 510	60.6(22.6)	47.8(38.5)	108.5(54.9)	54.9(17.4)	41.3(29.9)	96.2(12.7)
510 - 558	76.5(9.7)	24.0(0.3)	100.4(9.4)	73.5(10.0)	24.0(3.2)	97.5(11.9)

*Data are mean of three replicate, values in parenthesis are the standard deviation

Table 6-5. One-way ANOVA analysis of significant difference of total arsenic, As^V, and As^{III} in leachate of commercially CCA-treated wood collected at various time interval

leachate	1st*			2nd*			3rd*			4th*			5th*			6th*			7th*		
	a**	b**	c**	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
1st*				+	+	+	+	+	+	+	+	+	+	+		+	+	+	+	-	+
2nd*	+	+	+				+	+	+	-	-	+	+	+		+	+	+	+	+	+
3rd*	+	+	+	+	+	+				+	+	+	+	+		+	+	+	+	+	+
4th*	+	+	+	-	-	+	+	+	+				+	-		+	+	+	+	+	+
5th*	+	+		+	+		+	+		+	-					+	-		+	+	
6th*	+	+	+	+	+	+	+	+	+	+	+	+	+	-					+	+	-
7th*	+	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+	-			

*1st: 0-6 hours; 2nd: 6-30 hours; 3rd: 30-78 hours; 4th: 78-126 hours; 5th: 126-174 hours; 6th: 174-222 hours; 7th: 222-270 hours

**a: total arsenic; b: As^V; c: As^{III}

+: significant difference

- : no significant difference

Table 6-6. One-way ANOVA analysis of significant difference of total arsenic, As^{V}, and As^{III} in leachate of laboratory CCA-treated wood collected at various time interval

leachate	1st*			2nd*			3rd*			4th*			5th*			6th*			7th*		
	a**	b**	c**	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
1st*				+	+	+	+	+	+	+	-	+	-	-	+	+	+	+	+	+	-
2nd*	+	+	-				-	-	+	+	-	+	+	+	+	+	+	-	+	+	-
3rd*	+	+	+	-	-	+				+	+	+	+	+	-	+	+	+	+	+	+
4th*	+	-	+	+	-	+	+	+	+				+	-	-	+	+	+	+	+	+
5th*	-	-	+	+	+	+	+	+	-	+	-	-				+	-	+	+	+	+
6th*	+	+	+	+	+	-	+	+	+	+	+	+	+	-	+				+	-	-
7th*	+	+	-	+	+	-	+	+	+	+	+	+	+	+	+	+	-	-			

*1st: 0-6 hours; 2nd: 6-30 hours; 3rd: 30-78 hours; 4th: 78-126 hours; 5th: 126-174 hours; 6th: 174-222 hours; 7th: 222-270 hours

**a: total arsenic; b: As^{V}; c: As^{III}

+: significant difference

- : no significant difference

hours and the 222-270 hours leachates of commercially treated wood (Table 6-5), and the 0-6 hours and the 6-30 hours / the 222-270 hours, the 6-30 hours and the 174-222 hours / the 222-270 hours, the 30-78 hours and the 126-174 hours, the 78-126 hours and the 126-174 hours, and the 174-222 hours and the 222-270 hours (Table 6-6).

Relatively larger standard deviation existed in the results of arsenic speciation of the leachate collected after 270 hours. No statistic conclusion was drawn.

The detection of As^V and As^{III} in leachate of CCA-treated wood has been reported by several researchers (Table 6-7). By using a sequential solvent extraction with HCl and toluene, Nygren and Nilsson (1993) reported that more than 99.5% of total arsenic was As^V and less than 0.5% was As^{III} in commercially CCA type B treated wood. Hingston et al. (2003) leached CCA-treated southern pine cubes with artificial sea water and found 2.9-8.6% of total arsenic in the leachate was As^{III} by using a differential pulse polarography. Unlike the consistent low level of As^{III} reported by Hingston et al. (2003), Solo-Gabriele et al. (2003) reported a broad range of As^{III} in the leachate collected with CCA-treated wood removed from a playground after 14 years of service. By varying the pH of leaching water from 1.3 to 12.8, up to 51% of total arsenic was found as As^{III} using HPLC-HG-AFS. However, the time issue involved in arsenic speciation was not specified in these studies.

As^{III} in the leachate was attributed to the reduction of As^V. The mechanism of As^V reduction in CCA-treated wood is not clear. The involvement of microorganism is highly suspected (Ahmann et al. 1994; Cánovas 2003). Factors such as chemical retention in wood, the environmental condition, and wood species may possibly influence the

Table 6-7. Comparison of arsenic speciation in CCA treated wood

Study	Sample	method	Results
This study	Leachate from commercial and lab prepared CCA-treated southern pine (AWPA E-11 test)	Selective ion-exchange chromatography	As^{V}: 50-90 % of total arsenic As^{III}: 10-50 % of total arsenic
Nygren and Nilsson 1993	Commercial CCA-B treated lumber (Cu: 0.5%, Cr: 0.7%, As: 1.0% in wood)	Sequential solvent extraction using 9N HCl and toluene coupled with GFAA	$As^{V} > 99.5\%$, $As^{III} < 0.5\%$ of total arsenic
Hingston 2003	Southern pine blocks treated with 6.9% CCA solution, leached with artificial sea water for 16, 44, and 164 hours	Differential pulse polarography	As^{III}: 2.9-8.6% of total arsenic
Solo-Gabriele et al. 2003	Leachate from CCA treated wood removed from playground after 14 years of service	Wood leached with water at pH 1.3 -12.8, HPLC-HG-AFS	As^{V}: 48-100% of total arsenic As^{III}: 1-51% of total arsenic

microbial activity. Further investigations in As^V reduction in leachate of CCA-treated wood is highly expected.

6.4 Conclusions

Both arsenic and chromium were used to indicate CCA fixation in commercially and laboratory CCA-treated southern pine in a 558-hour leaching. The largest amount of leaching was found with arsenic followed by copper. The leaching of chromium and copper was nearly complete after 174 hours and 366 hours, respectively. Consistent leaching of arsenic was observed throughout the 558-hour test from both commercially and laboratory CCA-treated southern pine. A total of 24.6±4.0% of arsenic, 0.6±0.1% of chromium, and 6.5±0.2% of copper were leached from commercially and laboratory CCA-treated wood. Less than 10% of total chromium in the leachate was found as Cr^{VI}. Both As^V and As^{III} were detected in the leachate. In the first 270 hours, about 70-90% of total arsenic in the leachate was found as As^V and 10-30% as As^{III}. The concentrations of total arsenic, As^V, and As^{III} were influenced by the leaching duration.

Chapter 7

Conclusions

Arsenic, chromium, and copper could dislodge on the surface of commercial chromated copper arsenate type C (CCA), and CCA with water repellent (CCA/WR) treated southern pine boards.

The amounts of arsenic, chromium, and copper obtained in the dislodgeable solids from the board surface of CCA-treated wood are influenced by the collection methods. Largest amount of arsenic, chromium, and copper could be collected by using a test tube brush wiping method, compared with those collected using a glove-on-hand wiping method, or a paper wiping method. The amount of arsenic, chromium, and copper collected from CCA-treated wood surface by using the test tube brush wiping method was about 10 folds higher than those collected by using the glove-on-hand wiping method.

The amount of arsenic, chromium, and copper collected from CCA-treated wood surface before a field exposure was higher than those collected from board surface after a field exposure; the addition of water repellent to CCA wood treatment reduced the amount of arsenic, chromium, and copper collected from boards in the first 2 months of field exposure, similar amounts of arsenic, chromium, or copper were collected from CCA and CCA/WR-treated wood after 3-4 months.

The dislodgeable solids collected from CCA and CCA/WR-treated southern pine mainly consisted of wood splinters with small chemical deposits randomly distributed in the wood matrix. The amount of arsenic, chromium, and copper formed less than 4 wt.%

of the dislodgeable solids. The particle sizes of the chemical deposits were mostly less than 10 μm, and between 10 and 100 μm for the wood splinters. The elemental compositions in dislodgeable solids collected from CCA and CCA/WR-treated wood include arsenic, chromium, copper, iron, calcium, potassium, chloride, sulfur, silicon, magnesium, sodium, carbon, and oxygen were detected in the solids. After 7 months of field exposure, the deformation of cellulose in the dislodgeable solids caused by wood weathering was observed using environmental scanning electron microscope (ESEM) and X-ray diffractometry (XRD). The accumulation of sand or soil from the surrounding environment on the board surface and consequently collected in the dislodgeable solids by comparing their x-ray diffractograms before and after the field exposure.

Study of the solubilization of dislodgeable solids collected from CCA and CCA/WR-treated wood before the field exposure found that arsenic, chromium, and copper partially solubilized from the dislodgeable solids in water at pH 3, 4, 5, and 6. The amount of arsenic, chromium, and copper solubilized generally increased with time. The solubilization of chromium was influenced by pH during the first hour of the test. Copper presented pH dependency in the first 24 hours from dislodgeable solids collected with CCA-treated wood and after 24 hours from solids collected with CCA/WR-treated wood. Arsenic in the solids collected with CCA/WR-treated wood appeared to be pH dependent throughout the 168-hour test duration. The addition of a water repellent to CCA wood treatment significantly increased the proportions of arsenic, chromium, and copper solubilized from the dislodgeable solids.

Both As^{V} ($H_2AsO_4^-$) and As^{III} (H_3AsO_3) were solubilized from the dislodgeable solids. As^{V} was the dominant form in water during the first 24 hours. A significant decrease in the proportion of As^{V} and increase in As^{III} were found after 168 hours. A significant increase in the proportion of As^{III} in total arsenic was observed in a prolonged test duration from 24 hours to 168 hours. Larger proportions of soluble Cr^{VI} was found with the solids from CCA/WR-treated wood than those from solids collected with CCA-treated wood.

Speciation of arsenic in the leachate of CCA-treated wood found the presence of both As^{V} and As^{III} during a 558-hour leaching. In the first 270 hours, about 70-90% of total arsenic in the leachate was found as As^{V} and 10-30% as As^{III}. The concentrations of total arsenic, As^{V}, and As^{III} presented to be time dependent in leachate collected at some time intervals.

APPENDICES

ACRONYMS in Appendices

SD	standard deviation
SEM	standard error of the mean
DF	degree of freedom
SS	sum of squares
MS	mean squares
F	F statistic
P	P value

Appendix 1

Table 1. One-way ANOVA analysis of the amount of arsenic obtained by using the hand wiping, the paper wiping, and the test tube brush wiping methods

Group	Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference (P<0.05)**
Hand wiping	0.566	0.890	0.132	0.023	0.013	Between treatments	2	0.024	0.012	32.1	<0.001	Paper As vs Brush As; Paper As vs. Hand As
Paper wiping			0.239	0.023	0.013	residual	6	0.002	0.000			
Brush wiping			0.127	0.009	0.005	total	8	0.026				

* Mean of 3 replicate

** Statistical analysis shows that the amount of arsenic obtained from dislodgeable solids collected on the surface of CCA treated wood, vary significantly with the collecting methods, between the paper wiping and hand or brush wiping.

Table 2. One-way ANOVA analysis of the amount of chromium obtained by using the hand wiping, the paper wiping, and the test tube brush wiping methods

Group	Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference (P<0.05)**
Hand wiping	0.556	0.523	0.330	0.036	0.021	Between treatments	2	2.238	1.119	112.9	<0.001	Paper Cr vs Brush Cr; Paper Cr vs. Hand Cr
Paper wiping			1.486	0.157	0.091	residual	6	0.060	0.010			
Brush wiping			0.567	0.061	0.035	total	8	2.298				

* Mean of 3 replicate

**Statistical analysis shows that the amount of chromium obtained from dislodgeable solids collected on the surface of CCA treated wood, vary significantly with the collecting methods, between the paper wiping and hand or brush wiping.

Table 3. One-way ANOVA analysis of the amount of copper obtained by using the hand wiping, the paper wiping, and the test tube brush wiping methods

Group	Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ($P<0.05$)**
Hand wiping	0.807	0.466	1.823	0.087	0.050	Between treatments	2	3.263	1.631	211.6	<0.001	Paper Cu vs Brush Cu;
Paper wiping			2.452	0.046	0.027	residual	6	0.046	0.008			Paper Cuvs. Hand Cu;
Brush wiping			0.982	0.116	0.067	total	8	3.309				Hand Cu vs. Brush Cu

* Mean of 3 replicate

**Statistical analysis shows that the amount of copper obtained from dislodgeable solids collected on the surface of CCA treated wood, vary significantly with the collecting methods, among the paper wiping, hand wiping, and brush wiping.

Appendix 2. Calculation, percentage compositions of As_2O_5, CrO_3, and CuO in total oxides in CCA treated wood or dislodgeable solids

$$\%\ \text{composition of } As_2O_5 = \frac{\dfrac{\text{elemental As content} \times \text{M.W.} As_2O_5}{\text{M.W. As} \times 2}}{\dfrac{\text{elemental As content} \times \text{M.W.} As_2O_5}{\text{M.W. As} \times 2} + \dfrac{\text{elemental Cr content} \times \text{M.W.} CrO_3}{\text{M.W. Cr}} + \dfrac{\text{elemental Cu content} \times \text{M.W. CuO}}{\text{M.W. Cu}}} \times 100\%$$

$$\%\ \text{composition of } CrO_5 = \frac{\dfrac{\text{elemental Cr content} \times \text{M.W.} CrO_3}{\text{M.W.} Cr}}{\dfrac{\text{elemental As content} \times \text{M.W.} As_2O_5}{\text{M.W. As} \times 2} + \dfrac{\text{elemental Cr content} \times \text{M.W.} CrO_3}{\text{M.W. Cr}} + \dfrac{\text{elemental Cu content} \times \text{M.W. CuO}}{\text{M.W. Cu}}} \times 100\%$$

$$\%\ \text{composition of CuO} = \frac{\dfrac{\text{elemental Cu content} \times \text{M.W. CuO}}{\text{M.W. Cu}}}{\dfrac{\text{elemental As content} \times \text{M.W.} As_2O_5}{\text{M.W. As} \times 2} + \dfrac{\text{elemental Cr content} \times \text{M.W.} CrO_3}{\text{M.W. Cr}} + \dfrac{\text{elemental Cu content} \times \text{M.W. CuO}}{\text{M.W. Cu}}} \times 100\%$$

M.W.: molecular weight (g/mole), As: 74.9, As_2O_5: 229.8; Cr: 52.0, CrO_3: 100.0; Cu: 63.5, CuO: 79.5;
As content, Cr content, and Cr content in the wood could be in the unit of mg/g or %;
As content, Cr content, and Cr content in the dislodgeable solids could be in the unit of mg/g, %, or mg/m^2.

Appendix 3

Table 1. One-way ANOVA tests - influence of WR on the proportion of Cr^{VI} solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 1- hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH4	6.3-1E	7.7-1E	9.1-1E	1.8-2E	1.0-2E	between treatment	1	3.8	3.8	1.1+ 4E	< 1-3E	yes
			2.5	2.0-2E	1.1-2E	residual	4	1.0- 3E	0.0			
			-	-	-	total	5	3.8				
pH6	7.7-1E	3.3-1E	7.3-1E	1.1-2E	6.5-3E	between treatment	1	2.2- 1E	2.2- 1E	9.8+ 2E	< 1-3E	yes
			1.1	1.8-2E	1.0-2E	residual	4	1.0- 3E	0.0			
			-	-	-	total	5	2.2- 1E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of Cr^{VI} solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 1- hour test duration, vary significantly with the addition of WR. The concentration of Cr^{VI} increases with the addition of WR.

Appendix 3

Table 2. One-way ANOVA tests - influence of WR on the proportion of Cr^{VI} solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 24- hour test duration

Group	Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH4	3.9-1E	7.3-1E	1.6	1.3-2E	8.0-3E	between treatment	1	5.6	5.6	1.8+4E	< 1-3E	yes
			3.5	2.2-2E	1.3-2E	residual	4	1.0-3E	0.0			
			-	-	-	total	5	5.6				
pH5	4.6-1E	1.5-1E	1.5	3.0-3E	2.0-3E	between treatment	1	4.6	4.6	4.0+4E	< 1-3E	yes
			3.3	1.5-2E	9.0-3E	residual	4	0.0	0.0			
			-	-	-	total	5	4.6				
pH6	6.2-1E	1.0-1E	1.1	9.0-3E	5.0-3E	between treatment	1	5.1	5.1	9.7+4E	< 1-3E	yes
			3.0	6.0-3E	3.0-3E	residual	4	0.0	0.0			
			-	-	-	total	5	5.1				

* Mean of 3 replicate

**Statistical analysis shows that the amount of Cr^{VI} solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 24- hour test duration, vary significantly with the addition of WR. The concentration of Cr^{VI} increases with the addition of WR.

Appendix 3

Table 3. One-way ANOVA tests - influence of WR on the proportion of Cr^{VI} solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 168- hour test duration

Group	Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	3.8-1E	1.3-1E	4.2	1.0-2E	6.0-3E	between treatment	1	3. 3	3.3	4.0+3E	<1-3E	yes
			5.7	3.9-2E	2.3-2E	residual	4	3.0-3E	1.0-3E			
			-	-	-	total	5	3.3				
pH4	5.7-1E	4.3-1E	2.9	3.8-2E	2.2-2E	between treatment	1	6.9	6.9	6.9+3E	<1-3E	yes
			5.0	2.3-2E	1.3-2E	residual	4	4.0-3E	1.0-3E			
			-	-	-	total	5	6.9				
pH5	4.9-1E	2.9-1E	1.5	1.1-2E	7.0-3E	between treatment	1	8.1	8.1	8.3+4E	<1-3E	yes
			3.8	8.0-3E	5.0-3E	residual	4	0.0	0.0			
			-	-	-	total	5	8.1				
pH6	2.8-1E	1.9-1E	1.3	5.0-3E	3.0-3E	between treatment	1	6.6	6.6	1.6+4E	<1-3E	yes
			3.4	2.8-2E	1.6-2E	residual	4	2.0-3E	0.0			
			-	-	-	total	5	6.6				

* Mean of 3 replicate

**Statistical analysis shows that the amount of Cr^{VI} solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 168- hour test duration, vary significantly with the addition of WR. The concentration of Cr^{VI} increases with the addition of WR.

Appendix 3

Table 4. One-way ANOVA tests - influence of test duration on Cr^{VI} solubilized from dislodgeable solids collected with CCA treated southern pine

Group		Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH 3	1hr	5.8-1E	5.4-1E	1.6-1E	1.8-3E	1.0-3E	between treatment	2	1.9-1E	1.0-1E	3.3 +4E	< 1-3E	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			3.1-1E	2.0-3E	1.2-3E	residual	6	1.8-5E	0.0			
	168hrs			5.2-1E	1.3-3E	7.4-4E	total	8	1.9-1E				
pH 4	1hr	6.8-1E	2.8-1E	1.1-1E	2.2-3E	1.3-3E	between treatment	2	0.9-2E	0.0	4.6 +3E	< 1-3E	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			2.0-1E	1.6-3E	9.3-4E	residual	6	5.9-5E	0.0			
	168hrs			3.6-1E	4.7-3E	2.7-3E	total	8	0.9-2E				
pH 6	1hr	8.1-1E	4.4-1E	9.0-2E	1.4-3E	8.1-4E	between treatment	2	7.5-3E	0.0	3.3 +4E	< 1-3E	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			1.4-1E	1.1-3E	6.1-4E	residual	6	6.9-6E	0.0			
	168hrs			1.6-1E	6.1-4E	3.5-4E	total	8	7.5-4E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of Cr^{VI} solubilized in water from dislodgeable solids collected on the surface of CCA-treated wood, vary significantly with the duration of the solubility test at pH 3, 4, and 6. The concentration of Cr^{VI} increases with the test duration.

Appendix 3

Table 5. One-way ANOVA tests - influence of pH on Cr^{VI} solubilized from dislodgeable solids collected with CCA treated southern pine

Group		Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
1hr	pH3	8.0-1E	3.9-1E	1.6-1E	1.8-3E	1.0-3E	between treatment	3	7.6-3E	2.5-3E	6.4+2E	< 1-3E	pH3 vs. pH6 pH3 vs. pH4 pH3 vs. pH5 pH5 vs. pH6 pH5 vs. pH4 pH4 vs. pH6
	pH4			1.1-1E	2.2-3E	1.3-3E							
	pH5			1.3-1E	2.4-3E	1.4-3E	residual	8	3.2-5E	4.0-6E			
	pH6			9.0-2E	1.4-3E	8.1-4E	total	11	7.7-3E				
24 hrs	pH3	4.4-1E	1.2-1E	3.1-1E	2.0-3E	1.2-3E	between treatment	3	4.9-2E	1.6-2E	8.3+3E	< 1-3E	pH3 vs. pH6 pH3 vs. pH4 pH3 vs. pH5 pH5 vs. pH6 pH5 vs. pH4 pH4 vs. pH6
	pH4			2.0-1E	1.6-3E	9.3-4E			1.6-5E	2.0-6E			
	pH5			1.9-1E	4.0-4E	2.3-4E	residual	8	4.9-2E				
	pH6			1.4-1E	1.1-3E	6.1-4E	total	11					
168 hrs	pH3	1.2-1E	1.4-1E	5.2-1E	1.3-3E	7.4-4E	between treatment	3	2.5-E	8.3-2E	1.3+4E	< 1-3E	pH3 vs. pH6 pH3 vs. pH4 pH3 vs. pH5 pH5 vs.pH6 pH5 vs. pH4 pH4 vs. pH6
	pH4			3.6-1E	4.7-3E	7.4-4E							
	pH5			1.8-1E	1.4-3E	2.7-3E	residual	8	5.2-5E	6.5-6E			
	pH6			1.6-1E	6.1-4E	8.1-4E	total	11	2.5-E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of Cr^{VI} solubilized in water from dislodgeable solids collected on the surface of CCA-treated wood, vary significantly with the pH of water. The concentration of Cr^{VI} increases with the water acidity.

Appendix 3

Table 6. One-way ANOVA tests - influence of pH on Cr^{VI} solubilized from dislodgeable solids collected with CCA/WR treated southern pine

	group	Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
pH 4	1hr	5.8-1E	9.6-1E	3.1-1E	2.4-3E	1.4-3E	between treatment	2	1.5-1E	7.3-2E	1.1+4E	<1-3E	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1 hr
	24hrs			4.4-1E	2.7-3E	1.5-3E	residual	6	4.1-5E	6.9-6E			
	168hrs			6.2-1E	2.8-3E	1.6-3E	total	8	1.5-1E				
pH 6	1hr	2.8-1E	5.1-1E	1.4-1E	2.2-3E	1.3-3E	between treatment	2	1.3-1E	6.7-2E	1.1+4E	<1-3E	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1 hr
	24hrs			3.7-1E	6.9-4E	4.0-4E	residual	6	3.5-5E	5.9-6E			
	168hrs			4.2-1E	3.5-3E	2.0-3E	total	8	1.3-1E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of Cr^{VI} solubilized in water from dislodgeable solids collected on the surface of CCA-treated wood, vary significantly with the duration of the solubility test at pH 4 and 6. The concentration of Cr^{VI} increases with the duration of the solubility.

Appendix 3

Table 7. One-way ANOVA tests - influence of pH on Cr^{VI} solubilized from dislodgeable solids from CCA-C/WR southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of Variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
24 hrs	pH3	5.7-1E	6.2-1E	4.8-1E	6.1-4E	3.5-4E	between treatment	3	2.1-2E	7.0-3E	2.5+3E	< 1-3E	pH3 vs. pH6 pH3 vs. pH5 pH4 vs. pH6 pH5 vs. pH6 pH4 vs. pH5 pH3 vs. pH4
	pH4			4.4-1E	2.7-3E	1.5-3E							
	pH5			4.0-1E	1.8-3E	1.1-3E	residual	8	2.3-5E				
	pH6			3.7-1E	6.9-4E	4.0-4E	total	11	2.1-2E				
168 hrs	pH3	6.5-1E	1.8-1E	7.0-1E	4.8-3E	2.8-3E	between treatment	3	1.5-1E	5.1-2E	4.6+3E	< 1-3E	pH3 vs. pH6 pH3 vs. pH5 pH4 vs. pH6 pH5 vs. pH6 pH4 vs. pH5 pH3 vs. pH4
	pH4			6.2-1E	2.8-3E	1.6-3E							
	pH5			4.7-1E	1.0-3E	5.8-4E	residual	8	8.9-5E	1.1-5E			
	pH6			4.2-1E	3.5-3E	2.0-3E	total	11					

* Mean of 3 replicate

**Statistical analysis shows that the amount of Cr^{VI} solubilized in water from dislodgeable solids collected on the surface of CCA/WR treated wood, vary significantly with the pH of water at 24- and 168-hour test duration. The concentration of Cr^{VI} increases with the duration of the solubility.

Appendix 3

Table 8. One-way ANOVA tests - influence of WR on total arsenic solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 1 hour test duration

Group	Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH4	2.1-1E	1.0	4.8	4.0-2E	2.0-2E	between treatment	1	1.5+2E	1.5+2E	1.2+4E	< 1-3E	yes
			1.5+1E	1.6-1E	9.0-2E	residual	4	5.0-2E	1.0-2E			
			-	-	-	total	5	1.5+2E				
pH5	4.5-1E	0.5-1E	4.7	1.9-1E	9.0-2E	between treatment	1	1.6+2E	1.6+2E		< 1-3E	yes
			1.6+1E	3.1-1E	1.7-1E	residual	4	5.3	1.3	1.2+2E		
			-	-	-	total	5	1.7+2E				
pH6	8.0-2E	1.0	3.9	0.0	3.0-3E	between treatment	1	2.0+2E	2.0+2E	7.1+4E	< 1-3E	yes
			1.6+1E	8.0-2E	4.0-2E	residual	4	1.0-2E	3.0-2E			
			-	-	-	total	5	2.0-2E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of arsenic solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 1-hour test duration, vary significantly with the addition of WR. The concentration of arsenic increases with the addition of WR.

Appendix 3

Table 9. One-way ANOVA tests - influence of WR on total arsenic solubilized from dislodgeable solids collected with CCA-C and CCA-C/WR treated southern pine at 24-hour test duration

Group	Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	3.4-1E	7.9-1E	6.7	1.5-1E	9.0-2E	between treatment	1	3.2+2E	3.2+2E	8.3+3E	< 1-3E	yes
			2.1+1E	2.3-1E	1.3-1E	residual	4	2.0-1E	4.0-2E			
			-	-	-	total	5	3.2+2E				
pH5	9.0-2E	4.1-2E	7.9	1.1-1E	1.8	between treatment	1	1.3+2E	1.3+2E	2.8+1E	< 1-3E	yes
			1.9+1E	1.5-1E	9.0-2E	residual	4	1.9+1E	4.8			
			-	-	-	total	5	1.5+2E				
pH6	3.0-2E	8.0-2E	6.6	1.1-1E	6.0-2E	between treatment	1	6.3+2E	6.3+2E	3.2+3E	< 1-3E	yes
			1.9+1E	5.4-1E	4.0-1E	residual	4	8.0-1E	2.0-1E			
			-	-	-	total	5	6.3+2E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of arsenic soluble in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 24-hour test duration, vary significantly with the addition of WR. The concentration of arsenic increases with the addition of WR.

Appendix 3

Table 10. One-way ANOVA tests - influence of WR on total arsenic solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 168-hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	6.9-1E	1.5-1E	9.6	2.1	1.2	between treatment	1	4.5+2E	4.5+2 E	1.8+ 2E	< 1-3E	yes
			2.7+1E	0.8	4.5-1E	residual	4	9.9	2.5			
			-	-	-	total	5	4.5+2E				
pH4	7.0-2E	6.0-2E	9.8	4.0-2E	2.0-2E	between treatment	1	3.6+2E	3.6+2 E	7.1+ 2E	< 1-3E	yes
			2.5+1E	1.0	5.8-1E	residual	4	2.0	0.5			
			-	-	-	total	5	3.6+2E				
pH5	4.4-1E	1.0	9.3	0.0	0.0	between treatment	1	2.6+2E	2.6+2 E	3.6+ 1E	4-3E	yes
			2.5+1E	1.2	6.6-1E	residual	4	2.9+1E	7.2			
			-	-	-	total	5	2.9+2E				
pH6	1.0-1E	6.0-2E	8.9	4.0-2E	2.0-2E	between treatment	1	4.9+2E	4.9+2 E	2.6+ 3E	< 1-3E	yes
			2.7+1E	6.2-1E	3.6-1E	residual	4	8.0-1E	2.0-1E			
			-	-	-	total	5	4.9+2E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of arsenic solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 168-hour test duration, vary significantly with the addition of WR. The concentration of arsenic increases with the addition of WR.

Appendix 3

Table 11. One-way ANOVA tests - influence of WR on total chromium solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 1-hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	7.7-1E	2.3-1E	2.8	3.7-1E	2.2-1E	between treatment	1	1.2+3E	1.2+3E	3.0+3E	< 1-3E	yes
			3.1+1E	8.0-1E	4.7-1E	residual	4	1.6	4.0-1E			
			-	-	-	total	5	1.2+3E				
pH4	2.5-1E	2.8-1E	2.2	3.4-1E	2.0-1E	between treatment	1	1.1+3E	1.1+3E	2.6+3E	< 1-3E	yes
			2.9+1E	8.5-1E	4.9-1E	residual	4	1.7	4.0-1E			
			-	-	-	total	5	1.1+3E				
pH5	4.0-1E	5.1-1E	1.9	1.6-1E	9.0-2E	between treatment	1	1.1+3E	1.1+3E	4.4+3E	< 1-3E	yes
			2.8+1E	6.8-1E	3.9-2E	residual	4	1.0	2.0-1E			
			-	-	-	total	5	1.1+3E				
pH6	8.0-2E	1.0	1.4	4.3-1E	2.5-1E	between treatment	1	8.9+2E	8.9+2E	2.5+3E	< 1-3E	yes
			2.6+1E	7.3-1E	4.2-1E	residual	4	1.4	0.4			
			-	-	-	total	5	8.9+2E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of chromium solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 1-hour test duration, vary significantly with the addition of WR. The concentration of chromium increases with the addition of WR.

Appendix 3

Table 12. One-way ANOVA tests - influence of WR on total chromium solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 24-hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
pH3	3.0-1E	4.4-1E	2.8	5.7 -1E	3.3-1E	between treatment	1	1.4+3E	1.4+3E	6.2+2E	< 1-3E	yes
			3.3+1E	2.1	1.2	residual	4	9.1	2.3			
			-	-	-	total	5	1.4+3E				
pH5	5.0-1E	9.5-1E	2.3	7.1 -1E	4.1-1E	between treatment	1	1.2+3E	1.2+3E	2.5+3E	< 1-3E	yes
			3.1+1E	6.8 -1E	3.9-1E	residual	4	1.9	0.5			
			-	-	-	total	5	1.2+3E				
pH6	6.6-1E	6.9-1E	1.5	6.9 -1E	4.0-1E	between treatment	1	1.3+3E	1.3+3E	1.8+3E	< 1-3E	yes
			3.1+1E	1.0	5.8-1E	residual	4	2.9	0.7			
			-	-	-	total	5	1.3+3E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of chromium soluble in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 24-hour test duration, vary significantly with the addition of WR. The concentration of chromium increases with the addition of WR.

Appendix 3

Table 13. One-way ANOVA tests - influence of WR on total chromium solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 168-hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	5.1-1E	3.9-1E	4.4	1.7-1E	1.0-1E	between treatment	1	1.5+3E	1.5+ 3E	4.7+ 3E	<1-3E	yes
			3.6+1E	7.9-1E	4.6-1E	residual	4	1.3	0.3			
			-	-	-	total	5	1.5+3E				
pH4	5.5-1E	4.8-1E	2.3	4.0-2E	2.9-1E	between treatment	1	1.6+3E	1.6+ 3E	4.8+ 3E	<1-3E	yes
			3.5+1E	6.6-1E	3.8-1E	residual	4	1.4	0.3			
			-	-	-	total	5	1.6+3E				
pH5	5.3-1E	4.9-1E	2.2	2.8-1E	1.6-1E	between treatment	1	1.6+3E	1.6+ 3E	6.2+ 3E	<1-3E	yes
			3.5+1E	6.7-1E	3.9-1E	residual	4	1.1	0.3			
			-	-	-	total	5	1.6+3E				
pH6	7.7-1E	8.0-2E	1.5	6.9-1E	4.0-1E	between treatment	1	1.3+3E	1.3+ 3E	1.8+ 3E	<1-3E	yes
			3.1+1E	6.8-1E	5.8-1E	residual	4	2.9	0.7			
			-	-	-	total	5	1.3+3E				

* Mean of 3 replicate

**Statistical analysis shows that the amount of chromium soluble in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 168-hour test duration, vary significantly with the addition of WR. The concentration of chromium increases with the addition of WR.

Appendix 3

Table 14. One-way ANOVA tests - influence of WR on total copper solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 1-hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	0.77	0.08	6.42	0.33	0.19	between treatment	1	192.0	192.0	732.0	<0.001	yes
			17.73	0.65	0.37	residual	4	1.0	0.3			
			-	-	-	total	5	193.0				
pH4	0.10	0.40	5.07	0.23	0.13	between treatment	1	122.8	122.8	15.4	<0.001	yes
			17.94	0.73	0.43	residual	4	31.8	8.0			
			-	-	-	total	5	154.6				
pH5	0.08	0.18	4.38	0.08	0.05	between treatment	1	149.3	149.3	68.1	<0.001	yes
			16.17	0.53	0.21	residual	4	8.8	2.2			
			-	-	-	total	5	158.1				
pH6	0.53	0.29	4.18	0.17	0.10	between treatment	1	114.1	114.1	398.9	<0.001	yes
			12.90	0.74	0.43	residual	4	1.1	0.3			
			-	-	-	total	5	115.2				

* Mean of 3 replicate

**Statistical analysis shows that the amount of copper soluble in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 1-hour test duration, vary significantly with the addition of WR. The concentration of copper increases with the addition of WR.

Appendix 3

Table 15. One-way ANOVA tests - influence of WR on total copper solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 24-hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
pH3	0.47	0.31	8.20	0.37	0.21	between treatment	1	907.7	907.7	1252.1	<0.001	yes
			32.80	1.14	0.66	residual	4	2.9	0.7			
			-	-	-	total	5	910.6				
pH4	0.10	0.41	5.76	0.24	0.14	between treatment	1	229.4	229.4	35.0	0.004	yes
			21.60	0.63	0.34	residual	4	26.2	6.6			
			-	-	-	total	5	255.6				
pH5	0.49	0.13	5.72	0.22	0.13	between treatment	1	364.1	364.1	2190.0	<0.001	yes
			21.30	0.53	0.31	residual	4	0.7	0.2			
			-	-	-	total	5	364.8				

* Mean of 3 replicate

**Statistical analysis shows that the amount of copper soluble in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 24-hour test duration, vary significantly with the addition of WR. The concentration of copper increases with the addition of WR.

Appendix 3

Table 16. One-way ANOVA tests - influence of WR on total copper solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 168-hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** ($P<0.05$)
pH3	0.67	0.11	18.71	0.88	0.51	between treatment	1	349.1	349.1	291.7	<0.001	yes
			33.97	1.27	0.74	residual	4	4.8	1.2			
			-	-	-	total	5	353.9				
pH4	0.14	0.39	12.06	0.46	0.27	between treatment	1	329.2	329.2	23.2	0.009	yes
			32.04	0.96	0.62	residual	4	56.7	14.2			
			-	-	-	total	5					
pH6	0.36	0.12	4.30	0.16	0.09	between treatment	1	856.1	856.1	2009.7	<0.001	yes
			28.19	0.91	0.53	residual	4	1.7	0.4			
			-	-	-	total	5	857.8				

* Mean of 3 replicate

**Statistical analysis shows that the amount of copper soluble in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 168-hour test duration, vary significantly with the addition of WR. The concentration of copper increases with the addition of WR.

Appendix 3

Table 17. One-way ANOVA tests - influence of test duration on total arsenic solubilized from dislodgeable solids collected with CCA treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
pH 6	1hr	0.15	0.13	3.9	0.01	0.00	between treatment	2	37.7	18.9	4141.5	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			6.6	0.11	0.06	residual	6	0.03	0.00			
	168hrs			8.9	0.04	0.02	total	8	37.8				

* Mean of 3 replicate

**Statistical analysis shows that the amount of arsenic solubilized in water from dislodgeable solids collected on the surface of CCA treated wood, vary significantly with the duration of the solubility test. The concentration of arsenic increases with the test duration.

Appendix 3

Table 18. One-way ANOVA tests - influence of test duration on total chromium solubilized from dislodgeable solids collected with CCA treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SE M	Source of variation	DF	SS	MS	F	P	Significant difference** ($P<0.05$)
pH3	1hr	0.40	0.72	2.80	0.37	0.22	between treatment	2	5.19	2.59	15.86	0.004	168hrs vs. 24hrs 168hrs vs. 1hrs
	24hrs			2.76	0.57	0.33	residual	6	0.98	0.16			
	168hrs			4.39	0.17	0.10	total	8	6.17				
pH4	1hr	0.25	0.48	2.24	0.34	0.20	between treatment	2	0.27	0.14	0.97	0.43	No significant difference exists
	24hrs			2.65	0.24	0.14	residual	6	0.84	0.14			
	168hrs			2.33	0.50	0.29	total	8	1.11				
pH5	1hr	0.30	0.63	1.89	0.16	0.09	between treatment	2	1.05	0.53	2.57	0.16	No significant difference exists
	24hrs			2.72	0.71	0.41	residual	6	1.22	0.20			
	168hrs			2.20	0.28	0.16	total	8	2.27				
pH6	1hr	0.09	0.57	1.37	0.43	0.25	between treatment	2	0.32	0.16	0.74	0.517	No significant difference exists
	24hrs			1.45	0.69	0.40	residual	6	1.32	0.22			
	168hrs			1.80	0.04	0.02	total	8	1.64				

* Mean of 3 replicate

**Statistical analysis shows that the amount of chromium soluble in water from dislodgeable solids collected on the surface of CCA treated wood, vary significantly with the duration of the solubility test at pH3. The concentration of chromium increases with the test duration. No significant difference exists at pH 4, 5, or 6.

Appendix 3

Table 19. One-way ANOVA tests - influence of test duration on total copper solubilized from dislodgeable solids collected with CCA treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
pH5	1hr	0.77	0.14	4.38	0.08	0.05	between treatment	2	3.14	1.57	43.98		24hrs vs. 1hr 168hrs vs. 1hr
	24hrs			5.72	0.22	0.13	residual	6	0.21	0.04			
	168hrs			5.53	0.23	0.13	total	8	3.36				
pH6	1hr	0.68	0.85	4.18	0.17	0.10	between treatment	2	0.67	0.33	11.35	0.009	24hrs vs. 1hr 24hrs vs. 168hrs
	24hrs			4.81	0.19	0.11	residual	6	0.18	0.03			
	168hrs			4.30	0.16	0.09	total	8	0.84				

* Mean of 3 replicate

**Statistical analysis shows that the amount of copper solubilized in water from dislodgeable solids collected on the surface of CCA treated wood, vary significantly with the duration of the solubility test at pH 5 and 6. The concentration of copper increases with the test duration.

Appendix 3

Table 20. One-way ANOVA tests - influence of test duration on total arsenic solubilized from dislodgeable solids collected with CCA/WR treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
pH3	1hr	0.53	0.22	14.4	0.5	0.3	between treatment	2	231.8	115.9	368.5	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			21.2	0.2	0.1	residual	6	1.9	0.3			
	168hrs			26.8	0.8	0.5	total	8	0.8				
pH4	1hr	0.39	0.09	14.9	0.2	0.1	between treatment	2	164.3	82.1	186.8	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			18.6	0.5	0.3	residual	6	2.6	0.4			
	168hrs			25.3	1.0	0.6	total	8	166.9	104.9			
pH6	1hr	0.39	0.11	15.6	0.1	0.0	between treatment	2	209.7	0.2	466.3	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			18.7	0.5	0.3	residual	6	1.4				
	168hrs			27.0	0.6	0.4	total	8	211.1				

* Mean of 3 replicate

**Statistical analysis shows that the amount of arsenic soluble in water from dislodgeable solids collected on the surface of CCA/WR treated wood, vary significantly with the test duration at pH 4, 5 and 6. The concentration of arsenic increases with the duration of the solubility test.

Appendix 3

Table 21. One-way ANOVA tests - influence of test duration on total chromium solubilized from dislodgeable solids collected with CCA/WR treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	1hr	0.26	0.61	30.9	0.8	0.5	between treatment	2	47.2	23.6	12.9	0.007	168hrs vs. 1hr
	24hrs			33.4	2.1	1.2	residual	6	11.0	1.8			
	168hrs			36.5	0.8	0.5	total	8	58.1				
pH4	1hr	0.33	0.06	29.3	0.9	0.5	between treatment	2	60.9	30.4	20.7		168hrs vs. 1hr
	24hrs			33.7	1.8	1.0	residual	6	8.8	1.5			
	168hrs			35.5	0.7	0.4	total	8	69.7				
pH5	1hr	0.29	0.99	28.8	0.7	0.4	between treatment	2	59.7	29.9	65.3	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			31.0	0.7	0.4	residual	6	2.8	0.5			
	168hrs			35.1	0.7	0.4	total	8	62.5				
pH6	1hr	0.24	0.93	25.7	0.7	0.4	between treatment	2	107.3	53.7	59.0	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			31.1	1.0	0.6	residual	6	5.5	0.9			
	168hrs			34.1	1.1	0.6	total	8	112.8				

* Mean of 3 replicate

**Statistical analysis shows that the amount of chromium solubilized in water from dislodgeable solids collected on the surface of CCA/WR treated wood, vary significantly with the test duration. The concentration of chromium increases with the test duration.

Appendix 3

Table 22. One-way ANOVA tests - influence of test duration on total copper solubilized from dislodgeable solids collected with CCA/WR treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH 3	1hr	0.49	0.45	17.7	0.7	0.4	between treatment	2	491.9	245.9	220.3	<0.001	168hrs vs. 1hr 24hrs vs. 1hr
	24hrs			32.8	1.1	0.7	residual	6	6.7	1.2			
	168hrs			34.0	1.3	0.7	total	8	498.6				
pH 5	1hr	0.72	0.29	17.9	0.7	1.2	between treatment	2	398.4	199.2	106.9	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			21.3	0.5	0.3	residual	6	11.2	1.9			
	168hrs			30.6	1.0	0.6	total	8	409.6				
pH 6	1hr	0.72	0.84	12.9	0.7	0.4	between treatment	2	350.6	175.3	287.0	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1hr
	24hrs			20.8	0.7	0.4	residual	6	3.7	0.6			
	168hrs			28.2	0.9	0.5	total	8	354.3				

* Mean of 3 replicate

**Statistical analysis shows that the amount of copper solubilized in water from dislodgeable solids collected on the surface of CCA/WR treated wood, vary significantly with the test duration at pH 3, 5, and 6. The concentration of copper increases with the test duration.

Appendix 3

Table 23. One-way ANOVA tests - influence of pH on total chromium solubilized from dislodgeable solids collected with CCA treated southern pine

Group		Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
1hr	pH3	0.75	0.84	2.8	0.4	0.2	between treatment	3	3.3	1.1	9.4	0.01	pH3 vs. pH6 pH3 vs. pH5
	pH4			2.2	0.3	0.2							
	pH5			1.9	0.2	0.1	residual	8	0.9	0.1			
	pH6			1.4	0.4	0.3	total	11	4.2				
24 hrs	pH3	0.39	0.91	2.8	0.6	0.3	between treatment	3	3.6	1.2	3.6	0.01	No significant difference exists
	pH4			2.7	0.2	0.1							
	pH5			2.7	0.7	0.4	residual	8	2.7	0.3	0.1		
	pH6			1.5	0.7	0.4	total	11	6.3				

* Mean of 3 replicate

**Statistical analysis shows that the amount of chromium solubilized in water from dislodgeable solids collected on the surface of CCA treated wood, vary significantly with the pH of water at 1-hour test duration. The concentration of chromium increases with the test duration. No significant difference exists at 24-hour test duration.

Appendix 3

Table 24. One-way ANOVA tests - influence of pH on total copper solubilized from dislodgeable solids collected with CCA treated southern pine

Group		Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
1hr	pH3	0.44	0.08	6.4	0.3	0.2	between treatment	3	9.2	3.1	63.1	<0.001	pH3 vs. pH6 pH3 vs. pH5 pH3 vs. pH4 pH4 vs. pH6 pH4 vs. pH5
	pH4			5.1	0.2	0.1							
	pH5			4.4	0.1	0.1	residual	8	0.4	0.1			
	pH6			4.2	0.2	0.1	total	11	9.6				
24 hrs	pH3	0.64	0.53	8.2	0.4	0.2	between treatment	3	19.0	6.4	92.5	<0.001	pH3 vs. pH6 pH3 vs. pH5 pH3 vs. pH4 pH4 vs. pH6 pH5 vs. pH6
	pH4			5.8	0.2	0.1							
	pH5			5.7	0.2	0.1	residual	8	0.6	0.1			
	pH6			4.8	0.2	0.1	total	11	19.6				

* Mean of 3 replicate

**Statistical analysis shows that the amount of copper solubilized in water from dislodgeable solids collected on the surface of CCA treated wood, vary significantly with the pH of water at 1-hour and 24-hour test durations. The concentration of copper increases with the acidity of water.

Appendix 3

Table 25. One-way ANOVA tests - influence of pH on total arsenic solubilized from dislodgeable solids collected with CCA/WR treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of Variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
1hr	pH3	0.45	0.29	14.4	0.5	0.3	between treatment	3	4.6	1.5	14.8	<0.001	pH5 vs. pH3 pH5 vs. pH4 pH6 vs. pH3
	pH4			14.9	0.2	0.1							
	pH5			16.0	0.3	0.2	residual	8	0.8	0.1			
	pH6			15.6	0.1	0.0	total	11	5.4				
24 hrs	pH3	0.22	0.25	21.2	0.2	0.1	between treatment	3	13.5	4.5	27.2	<0.001	pH3 vs. pH4 pH3 vs. pH6 pH3 vs. pH5
	pH4			18.6	0.5	0.3							
	pH5			19.1	0.2	0.1	residual	8	1.3	0.2			
	pH6			18.7	0.5	0.3	total	11	14.8				
168 hrs	pH3	0.77	0.20	26.8	0.8	0.5	between treatment	3	13.2	4.4	5.4	0.03	pH6 vs. pH5
	pH4			25.3	1.0	0.6							
	pH5			24.6	1.2	0.7	residual	8	6.6	0.8			
	pH6			27.0	0.6	0.4	total	11	19.8				

* Mean of 3 replicate

**Statistical analysis shows that the amount of arsenic solubilized in water from dislodgeable solids collected on the surface of CCA/WR treated wood, vary significantly with the pH of water. The concentration of arsenic increases with the acidity of water.

Appendix 3

Table 26. One-way ANOVA tests - influence of pH on total chromium solubilized from dislodgeable solids collected with CCA/WR treated southern pine

Group		Normality test, P	Variance test, P	Mean	SD	SEM	Source of Variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
1hr	pH3	0.29	0.91	30.9	0.8	0.5	between treatment	3	41.2	13.7	23.2	<0.001	pH3 vs. pH6 pH3 vs. pH5 pH4 vs. pH6 pH5 vs. pH6
	pH4			29.3	0.9	0.5							
	pH5			28.8	0.7	0.4	residual	8	4.7	0.6			
	pH6			25.7	0.7	0.4	total	11	45.9				
24 hrs	pH3	0.70	0.61	33.4	2.1	1.2	between treatment	3	18.4	6.1	2.7	0.11	No significant difference exists
	pH4			33.7	1.8	1.0							
	pH5			31.0	0.7	0.4	residual	8	17.9	2.2			
	pH6			31.1	1.0	0.9	total	11	36.2				
168 hrs	pH3	0.14	0.91	36.5	0.8	0.5	between treatment	3	8.7	2.9	4.3	0.04	pH3 vs. pH6
	pH4			35.5	0.7	0.4							
	pH5			35.1	0.7	0.4	residual	8	5.4	0.7			
	pH6			34.1	1.1	0.6	total	11	14.1				

* Mean of 3 replicate

**Statistical analysis shows that the amount of chromium solubilized in water from dislodgeable solids collected on the surface of CCA/WR treated wood, vary significantly with the pH of water in 1-hour and 168-hour test duration. The concentration of chromium increases with the acidity of water. No significant difference exists at 24-hour test duration.

Appendix 3

Table 27. One-way ANOVA tests - influence of pH on total copper solubilized from dislodgeable solids collected with CCA/WR treated southern pine

Group		Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
1hr	pH3	0.25	0.61	17.7	0.7	0.4	between treatment	3	38.6	12.9	2.4	0.14	No significant difference exists
	pH4			17.9	0.7	0.3							
	pH5			16.2	0.5	0.2	residual	8	42.4	5.3			
	pH6			12.9	0.7	0.4	total	11	81.0				
24 hrs	pH3	0.07	0.59	32.8	1.1	0.7	between treatment	3	382.5	127.5	33.8	<0.001	pH3 vs. pH4 pH3 vs. pH6 pH3 vs. pH5
	pH4			21.6	0.6	0.3							
	pH5			21.3	0.5	0.3	residual	8	30.2	3.8			
	pH6			20.8	0.7	0.4	total	11	412.7				

* Mean of 3 replicate

**Statistical analysis shows that the amount of copper solubilized in water from dislodgeable solids collected on the surface of CCA/WR treated wood, vary significantly with the pH of water in 24-hour test duration. The concentration of copper increases with the acidity of water. No significant difference exists at 1-hour test duration.

Appendix 3

Table 28. One-way ANOVA tests - influence of pH on As^{V} and As^{III} solubilized from dislodgeable solids collected with CCA treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
1hr	$pH3As^{V}$	0.14	0.07	383.6	8.3	4.8	between treatment	3	2128.6	709.5	3.6	0.066	No significant difference exists
	$pH4As^{V}$			384.3	26.3	15.1							
	$pH5As^{V}$			377.0	4.7	2.7	residual	8	1582.9	197.9			
	$pH6As^{V}$			351.4	3.5	1.9	total	11	3711.5				
24 hrs	$pH3As^{V}$	0.70	0.36	562.1	8.1	4.6	between	3	42227.7	14075.9	17.8	<0.001	pH5 vs. pH6
	$pH4As^{V}$			483.3	20.6	11.9			6333.7	791.7			pH5 vs. pH4
	$pH5As^{V}$			617.4	40.1	23.2	residual	8	48561.4				pH3 vs. pH6
	$pH6As^{V}$			472.5	32.3	18.8	total	11					pH3 vs. pH4
168 hrs	$pH3As^{V}$	0.09	0.08	563.7	20.6	11.9	between treatment	3	41399.6	13799.8	11.3	0.003	pH3 vs. pH5 pH3 vs. pH4
	$pH4As^{V}$			435.2	33.4	19.4							
	$pH5As^{V}$			410.4	2.4	1.4	residual	8	9795.2	1224.4			
	$pH6As^{V}$			488.0	57.8	33.4	total	11	51194.8				
1hr	$pH3As^{III}$	0.66	0.65	37.5	3.5	2.0	between treatment	3	143.0	47.7	8.7	0.007	pH4 vs. pH5 pH4 vs. pH6 pH3 vs. pH5
	$pH4As^{III}$			38.8	1.8	1.1							
	$pH5As^{III}$			31.3	1.8	1.0	residual	8	43.7	5.5			
	$pH6As^{III}$			31.3	1.8	1.0	total	11	186.7				
24 hrs	$pH3As^{III}$	0.58	0.64	38.8	5.3	3.0	between treatment	3	153.1	51.0	0.3	0.799	No significant difference exists
	$pH4As^{III}$			37.5	7.1	4.1							
	$pH5As^{III}$			46.3	12.4	7.1	residual	8	1209.0	151.1			
	$pH6As^{III}$			43.8	19.4	11.2	total	11	1362.1				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^{V} solubilized in water from dislodgeable solids collected with CCA treated wood, vary significantly with the pH of water in 24- and 168-hour test duration. The amount of As^{III} dissolved vary significantly with the pH of water in 1-hour test duration The concentration of As^{V} or As^{III} increases with the test duration.

Appendix 3

Table 29. One-way ANOVA tests - influence of pH on As^V solubilized from dislodgeable solids collected with CCA/WR treated southern pine

Group		Normality test, P	Variance test, P	Mean*	SD	SEM	Source of Variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
1hr	pH3	0.42	0.30	460.1	26.0	15.0	between treatment	3	2771.2	923.7	0.17	0.913	No significant difference exists
	pH4			477.2	33.4	19.3							
	pH5			455.2	53.4	30.9	residual	8	43303.6	5415.9			
	pH6			434.6	130.	75.2	total	11	46074.8				
24 hrs	pH3	0.11	0.64	793.5	73.9	42.7	between treatment	3	41453.4	13817.8	4.39	0.042	pH3 vs. pH6
	pH4			714.6	42.2	24.4							
	pH5			731.0	26.7	15.4	residual	8	25191.4	3148.9			
	pH6			628.9	67.8	39.3	total	11	66644.8				
168 hrs	pH3	0.61	0.06	743.7	100.	57.9	between treatment	3	24909.2	8303.1	1.42	0.31	No significant difference exists
	pH4			799.6	99.8	57.4							
	pH5			672.7	51.9	29.9	residual	8	46851.4	5856.4			
	pH6			721.2	27.8	16.1	total	11	71760.6				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^V solubilized in water from dislodgeable solids collected with CCA/WR treated wood, vary significantly with the pH of water in 24-hour test duration. The concentration of As^V increases with water acidity. No significant difference exists at 1-hour or 168-hour test duration.

Appendix 3

Table 30. One-way ANOVA tests - influence of test duration on As^{III} solubilized from dislodgeable solids collected with CCA/WR treated southern pine

Group		Normality test, P	Variance test, P	Mean *	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
pH 3	1hr	0.79	0.23	173.8	19.4	11.2	between treatment	2	148863	74432	414	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs
	24hrs			160.0	10.6	6.2	residual	6	1078	180			
	168hrs			440.0	7.1	4.1	total	8	149941				
pH 5	1hr	0.21	0.14	136.3	5.3	3.1	between treatment	2	101334	50667	814	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs
	24hrs			141.3	1.8	1.0	residual	6	373	62			
	168hrs			363.8	12.4	7.2	total	8	101707				
pH 6	1hr	0.07	0.10	122.5	3.5	2.1	between treatment	2	173277	86638	15724	<0.001	168hrs vs. 1hr 168hrs vs. 24hrs 24hrs vs. 1 hr
	24hrs			151.0	1.8	1.0	residual	6	33	6			
	168hrs			430.0	0.0	0.0	total	8	173310				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^{III} dissolved in water from dislodgeable solids collected on the surface of CCA/WR treated wood, vary significantly with the test duration at pH 3, 5, and 6. The concentration of As^{III} increases with the duration of the solubility.

Appendix 3

Table 31. One-way ANOVA tests - influence of WR on As^V solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 1- hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** ($P<0.05$)
pH4	0.63	0.43	384	26.3	15.1	between treatment	1	12955	12955	14	0.019	yes
			477	33.4	19.3	residual	4	3621	905			
			-	-	-	total	5	16576				
pH5	0.06	0.22	351	3.5	2.0	between treatment	1	10334	10334	1.2	0.332	no
			435	130	75.2	residual	4	33996	8499			
			-	-	-	total	5	44330				
pH6	0.21	0.08	562	8.1	4.6	between treatment	1	80203	80203	29	0.006	yes
			794	74	42.7	residual	4	11062	2766			
			-	-	-	total	5	91265				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^V solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 1- hour test duration, vary significantly with the addition of WR. The concentration of As^V increases with the addition of WR.

Appendix 3

Table 32. One-way ANOVA tests - influence of WR on As^{V} solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 24- hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** ($P<0.05$)
pH3	0.21	0.08	562	8	5	between treatment	1	80203	80203	29	0.006	yes
			794	74	43	residual	4	11062	2766			
			-	-	-	total	5	91265				
pH4	0.61	0.45	483	20	12	between treatment	1	80250	80250	72	0.001	yes
			715	42	24	residual	4	4440	1110			
			-	-	-	total	5	84690				
pH5	0.77	0.36	617	40	23	between treatment	1	19346	19346	17	0.015	yes
			731	27	15	residual	4	4661	1165			
			-	-	-	total	5	24007				
pH6	0.16	0.58	473	33	19	between treatment	1	36676	36676	13	0.023	yes
			629	68	39	residual	4	11362	2841			
			-	-	-	total	5	48038				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^{V} solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 24- hour test duration, vary significantly with the addition of WR. The concentration of As^{V} increases with the addition of WR.

Appendix 3

Table 33. One-way ANOVA tests - influence of water repellent on As^V solubilized from dislodgeable solids collected with CCA-C and CCA-C/WR treated southern pine at 168- hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference ** (P<0.05)
pH5	0.09	0.12	410	2	1	between treatment	1	103281	103281	77	<0.001	yes
			673	52	30	residual	4	5387	1347			
			-	-	-	total	5	108668				
pH6	0.20	0.36	488	58	33	between treatment	1	81597	81597	40	0.003	yes
			721	28	16	residual	4	8240	2060			
			-	-	-	total	5	89836				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^V solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 168- hour test duration, vary significantly with the addition of WR. The concentration of As^V increases with the addition of WR.

Appendix 3

Table 34. One-way ANOVA tests - influence of WR on As^{III} solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 1- hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	0.27	0.11	38	4	2	between treatment	1	27853	27853	144	<0.001	yes
			174	19	11	residual	4	774	193			
			-	-	-	total	5	28626				
pH4	0.66	1.00	39	2	1	between treatment	1	17496	17496	5249	<0.001	yes
			146	2	1	residual	4	13	3			
			-	-	-	total	5	17509				
pH5	0.32	0.55	31	2	1	between treatment	1	16506	16506	1047	<0.001	yes
			136	5	3	residual	4	63	16			
			-	-	-	total	5	16569				
pH6	0.76	0.11	31	2	1	between treatment	1	12449	12449	1505	<0.001	yes
			122	4	2	residual	4	33	8			
			-	-	-	total	5	12482				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^{III} solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 1- hour test duration, vary significantly with the addition of WR. The concentration of As^{III} increases with the addition of WR.

Appendix 3

Table 35. One-way ANOVA tests - influence of water repellent on As^{III} solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 24- hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** (P<0.05)
pH3	0.53	0.07	39	5	3	between treatment	1	22240	22241	317	<0.001	yes
			160	11	6	residual	4	281	70			
			-	-	-	total	5	22521				
pH4	0.73	0.31	38	7	4	between treatment	1	20323	20323	319	<0.001	yes
			154	9	5	residual	4	255	64			
			-	-	-	total	5	20578				
pH6	0.14	0.38	44	19	11	between treatment	1	17259	17259	92	<0.001	yes
			151	2	1	residual	4	753	188			
			-	-	-	total	5	18012				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^{III} solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 24- hour test duration, vary significantly with the addition of WR. The concentration of As^{III} increases with the addition of WR.

Appendix 3

Table 36. One-way ANOVA tests - influence of water repellent on As^{III} solubilized from dislodgeable solids collected with CCA and CCA/WR treated southern pine at 168- hour test duration

Group	Normality test, P	Variance test, P	Mean*	SD	SEM	Source of variation	DF	SS	MS	F	P	Significant difference** ($P<0.05$)
pH3	0.41	0.56	355	4	2	between treatment	1	10736	10736	339	<0.001	yes
			440	7	4	residual	4	127	32			
			-	-	-	total	5	10862				
pH4	0.51	0.23	323	28	17	between treatment	1	10317	10317	1	0.333	no
			405	127	74	residual	4	34057	8514			
			-	-	-	total	5	44374				
pH5	0.47	0.37	409	9	8	between treatment	1	3038	3036	26	0.007	yes
			364	12	7	residual	4	464	116			
			-	-	-	total	5	3502				
pH6	0.07	1.00	334	2	1	between treatment	1	13901	13901	8780	<0.001	yes
			430	0	0	residual	4	6	2			
			-	-	-	total	5	13907				

* Mean of 3 replicate

**Statistical analysis shows that the amount of As^{III} solubilized in water from dislodgeable solids collected on the surface of CCA and CCA/WR treated wood at 168- hour test duration, vary significantly with the addition of WR. The concentration of As^{III} increases with the addition of WR.

Bibliography

Abernathy, C.O., D.J. Thomas, and R.L. Calderon. 2003. Health effects and risk assessment of arsenic. J. Nutr. 133: 1536-1538.

Agency for Toxic Substances and Disease Registry (ATSDR). 1993. Agency for toxic substances and disease registry toxicological profile for chromium. U.S. Department of Health and Human Services, Public Health Service Report # TP-92/08.

Agency for Toxic Substances and Disease Registry (ATSDR). 2002. Toxicological profile for copper. Draft for public comments, US department of health and services. Public health services: 286pp.

Ahmann, D. A.L. Roberts, L.R. Krumholz, and F.M.M. Morel. 1994. Microbe grows by reducing arsenic. Nature. 351: 750.

Alexander, D.L. and P.A. Cooper. 1993. Effects of temperature and humidity on CCA-C fixation in pine sapwood. Wood Protection. 2(2): 1-7.

American Wood Preservers' Association. 2003. Book of standards. Granbury, TX.

American Wood Preservers Institute (AWPI) 1997. The 1996 Wood Preserving industry Production Statistical Report. Virginia.

Anderson, R.A. 1993. Recent advances in the clinical and biological effects of chromium deficiency. Prog. Clin. Biol. Res. 380: 221-234.

Anderson, R.A. 1995. Chromium and parenteral nutrition. Nutrition. 11(1 suppl.): 83-86.

Axelson, O., E. Dahlgren, C.D. Jansson, and S.O. Rehnlund. 1978. Arsenic exposure and mortality: A case referent study from a Swedish copper smelter. Br. J. Ind. Med. 35(8-15).

Bhumbla, D.K. and R.F. Keefer. 1994. Arsenic mobilization and bioavailability in soils. In: Arsenic in the environment: Part I: Cycling and characterization. John Wiley & Sons. New York. 51-82.

Bishop, R.F. and D. Chisholm. 1962. Arsenic accumulation in Annapolis valley orchard soils. Can. J. Soil Sci. 42: 77-80.

Bradshaw, L.M. Fishwick, D. Slater, T. Pearce, and N. 1998. Chronic bronchitis, work related respiratory symptoms, and pulmonary function in welders in New Zealand. Occup. Environ. Med. 55(3): 150-4.

Brewer, G. 1992. Wilson Disease. Medicine. 71: 139.

Bull, D.C. 2000. The chemistry of chromated copper arsenate I. Characterization of timber treatment plant chemical sludge. Wood Sci. and Tech. 34. 367-376.

Bull, D.C. 2001. The chemistry of chromated copper arsenate II. Preservative-wood interactions. Wood Sci. and Tech. 34. 459-466.

Campbell, P.G.C. 1995. Metal speciation and bioavailability in aquatic systems. Eds. Tessier A., Tumer D.R. John & Wiley. Chichester.

Cánovas, D., R. Mukhopadhyay, B.P. Rosen, and V. de Lorenzo. 2003. Arsenate transport and reduction in the hyper-tolerant fungus Aspergillus sp. P37. Environmental Microbiology. 5(11): 1087-1093.

Chen, W. and J. Chen. 2002. Nested case-control study of lung cancer in four Chinese tin mines. Occup. Environ. Med. 59(2): 113-118.

Chen, C.J., Y.C. Chuang, S.L. You, T.M. Lin, and H.Y. Wu. 1986. A retrospective study on malignant neoplasms of bladder, lung, and liver in blackfoot disease endemic area in Taiwan. Br. J. Cancer. 53: 399-405.

Chen, J., M. Kaldas, Y.T. Ung, and P.A. Cooper. 1994. Heat transfer and wood moisture effects in moderate temperature fixation of CCA treated wood. IRG document. IRG/WP/94-40022

Chen, Y.-C., C.J. Amarasiriwardena, Y.-M. Hsueh, and D.C. Christiani. 2002. Stability of arsenic species and insoluble arsenic in human urine. Cancer Epidemiology, Biomarker & Prevention. 11: 1427-1433.

Chen, G.Q., L. Zhou, M. Styblo, F. Walton, Y. Jing, R. Weinberg, Z. Chen, and S. Waxman. 2003a. Methylated metabolites of arsenic trioxide are more potent than arsenic trioxide as apoptotic but not differentiation inducers in leukemia and lymphoma cells. Cancer Res. 63(8): 1853-1859.

Chen, Y.C., H.J. Su, Y.L. Guo, Y.M. Hsueh, T.J. Smith, L.M. Ryan, M.S. Lee, and D.C. Christiani. 2003b. Arsenic methylation and bladder cancer risk in Taiwan. Cancer Causes Control. 14(4): 303-310.

Chen, Y.C., Y.L. Guo, H.J. Su, Y.M. Hsueh, T.J. Smith, L.M. Ryan, M.S. Lee, S.C. Chao, J.Y. Lee, and D.C. Christiani. 2003c. Arsenic methylation and skin cancer risk in southwestern Taiwan. J. Occup. Environ. Med. 45(3): 241-248.

Cherry, J.A., A.U. Shaikh, D.E. Tallman, and R.V. Nicholson. 1979. Arsenic species as an indicator of redox conditions in groundwater. J. Hydrol. 43: 373-392.

Clarkson, T.W. 1991. Inorganic and organometal pesticides. Handbook of Pesticide Toxicology. Academic Press. New York. Pp 497-583.

Coggins, C. R. and P. Hiscocks. 1978. Chromium on the surface of CCA-treated wood. IRG document. IRG 78-386.

Connell, M., J.A. Cornfield, and G.A. Williams. 1990. A new preservative - a double edged sword. IRG document. IRG/WP/3573.

Cooper, P.A. and Y.T. Ung. 1992. Leaching of CCA-C from Jack pine sapwood in composts. For. Prod. J. 42(9): 57-59.

Cooper, P.A. 1993. Leaching of CCA: Is it a problem? Disposal of treated wood removed from service: this issues. In: Environmental Considerations in the Manufacture, Use, and Disposal of Preservative-Treated Wood. Proc. 7323. For. Prod. Soc., Madison, Wis. Pp 45.

Cooper, P.A. and Y.T. Ung. 1993. A simple quantitative measure of CCA fixation. For. Prod. J. 43(5): 19-20.

Cooper, P.A., Y.T. Ung, and G. Zanjani. 1994. Comparison of methods for monitoring CCA fixation. IRG document. IRG/WP 94-40023.

Cooper, P.A., E. Jasonek, and J.-P. Aucoin. 1995. Plant uptake of CCA components from contaminated soil. IRG document. IRG/WP 95-50043.

Cooper, P.A., T. Ung, and R. MacVicar. 1997. Effect of water repellents on leaching of CCA from treated fence and deck units - An update. IRG document. IRG/WP97-50086.

Corbett, J.R., K. Wright, and A.C. Baillie. 1984. The biochemical mode of action of pesticides. 2nd Ed. Academic Press. London.

Cotton, F.A. and G. Wilkinson. 1988. Advanced Inorganic Chemistry. . John Wiley & Sons. Pp 755-775.

Crawford, D., R. Fox, P. Kamdem, S. Lebow, D. Nicholas, D. Pettry, T. Schultz, L. Sites, and R. Ziobro. 2002. Laboratory studies of CCA-C leaching: influence of wood and soil properties on extent of arsenic and copper depletion. IRG document. IRG/WP 02-50186.

Cui, W., D. P. Kamdem, and T. Rypstra. 2004. Diffuse reflectance infrared fourier transform spectroscopy (drift) and color changes of artificial weathered wood. Wood and Fiber Science. In press.

Cullen, W.R., H. Li, K.J.R. G. Hewitt, and N. Zalunardo. 1994. Identification of extracellular arsenical metabolites in the growth medium of the microorganisms

Apiotrichum humicola and *Scopulariopsis brevicaulis*. Appl. Organimet. Chem. 8: 303-311.

Cuzick, J., P. Sasieni, and S. Evans. 1992. Ingested arsenic, keratoses, and bladder cancer. Am. J. Epidemiol. 136(4): 417-421.

Dahlgren, S.E. and W.H. Hartford. 1972a. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part I. pH behavior and general aspects of fixation. Holzforschung. 26(2): 62-69.

Dahlgren, S.E. and W.H. Hartford. 1972b. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part II. Fixation of Boliden K33. Holzforschung. 26(3): 105-113.

Dahlgren, S.E. and W.H. Hartford. 1972c. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part III. Fixation of Tanalith C and comparison of different preservatives. Holzforschung. 26(4): 142-149.

Dang, W., J. Chen, M. Mottle, L. Phillips, P. Wood, S. McCarthy, R. Lee, M. Helmke, M. Nelson, and K. Coon. 2003. A probabilistic risk assessment for children who contact CCA-treated playsets and decks. Draft preliminary report, Nov. 10, 2003. (under EPA review) (Internet) http://www.epa.gov/scipoly/sap/2003/december3/shedsprobabalisticriskassessmentnov03.pdf.

Davies, J.M. 1984. Lung cancer mortality among workers making lead chromate and zinc chromate pigments at three English factories. Br. J Ind. Med. 41: 158-169.

Dawson-Andoh, B.E. and D.P. Kamdem. 1998. Application of environmental Scanning Microscopy to the study of macrodistribution of copper in copper naphthenate treated hardwoods. Holzforschung. 52: 603-606.

Dayal, H. Gupta, S. Trieff, N. Maierson, D. Reich, and D. 1995. Symptom clusters in a community with chronic exposure to chemicals in two superfund sites. Arch. Environ. Health. 50(2): 108-11.

Delahay, P. 1957. Instrumental analysis. New York, Macmillan. 384 p.

Department of Environmental Quality (DEQ). 2004. Administrative Rules for Part 201, Environmental Remediation, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended. (Internet). http://www.michigan.gov/deq/0,1607,7-135-3311_4109_9846-58095--,00.html

Directorate General For Environment (DGE). 2000. Ambient air pollution by As, Cd and Ni compounds. Position paper. Final version, October 2000. Brussels, European Commission DG Environment.

Eaton, R.A. and M.D.C. Hale. 1993. Wood Decay, pests and protection. Chapman & Hall. London, New York. Pp: 320-326.

Elfving, D.C., K.R. Wilson, J.G. Ebel, K.L. Manzell, W.H. Gutenmann, and D.J. Lisk. 1994. Migration of lead and arsenic in old orchard soils in the Georgian Bay region of Ontario. Chemosphere. 29(2): 407-413.

Enterline, P.E. and G.M. Marsh. 1982. Cancer among workers exposed to arsenic and other substances in a copper smelter. Am. J. Epidemiol. 116(6): 895-911.

Environmental Assessment Division (EAD). 2001. Chromium. Human Health Fact Sheet. ANL. November 2001.

Eslyn, W.E. and T.L. Highley. 1976. Decay resistance and susceptibility of sapwood of fifteen tree species. Phytopathology. 66: 1010-1017.

Federal Remediation Technologies Roundtable. 2004. (Internet). http://www.frtr.gov/ matrix2/section1/toc.html

Fengel, D. and G. Wegener. 1984. Wood chemistry ultrastructure reactions. Walter de Gruyter. Berlin, New York. Pp: 359.

Ferguson, J.F. and J. Gavis. 1972. A review of the arsenic cycle in natural waters. Water Res. 6: 1259-1274.

Ferreccio, C., C. Gonzalez, V. Milosavjlevic, G. Marshall, A.M. Sancha, and A.H. Smith. 2000. Lung cancer and arsenic concentrations in drinking water in Chile. Epidemiology. 11(6): 673-679.

Flores del Pino, L. 2003. Development of an Arsenic Speciation Method for Drinking Water and its Application to Human Health and Risk Assessment. Ph.D. Dissertation, Michigan State University. Pp 63-79.

Gaines, T.B. 1960. The acute toxicity of pesticides to rats. Toxicol. Appl. Pharmacol. 2: 88-99.

Gallacher, A.C., C.R. McIntyre, M.H. Freeman, D.K Stokes and W.B. Smith. 1995. Standard and new analytical techniques for CDDC preserved wood analysis. Proc. Amer. Wood-Preservers' Assoc. 91: 194-199.

Gallagher, P.A., C.A. Schwegel, X. Wei, and J.T. Creed. 2001. Speciation and preservation of inorganic arsenic in drinking water sources using EDTA with IC separation and ICP-MS detection. J. Environ. Monit. 3(4): 371-376.

Gomez-Caminero, A., P. Howe, M. Hughes, E. Kenyon, D.R. Lewis, M. Morre, J. Ng, A. Aitio, and G. Becking. 2001. Environmental Health Criteria 224, Arsenic and Arsenic Compounds. 2nd. National Academy Press. 257 p.

Gorell, J.M., C.C. Johnson, B.A. Rybicki, E.L. Peterson, G.X. Kortsha, G.G. Brown, and R.J. Richardson. 1997. Occupational exposures to metals as risk factors for Parkinson's disease. Neurology. 48(3): 650-658.

Gradient Corporation. 2001. Evaluation of human health risk from exposure to arsenic associated with CCA-treated wood. Prepared for Arch Wood protection, Inc., and Osmose, Inc.

Guha-Mazumder, D.N. 2003. Chronic arsenic toxicity: clinical features, epidemiology, and treatment: experience in West Bengal. J. Environ. Sci. Health. Part A. Tox. Hazard Subst. Environ. Eng. 38(1): 141-163.

Gunther, M.R., P. M. Hanna, R.P. Mason, and M.S. Cohen. 1995. Hydroxyl radical formation from cuprous ion and hydrogen peroxide: A spin-trapping study. Archives of Biochemistry and Biophysics. 316(1): 515-522.

Guo, H.R., H.S. Chiang, H. Hu, S.R. Lipsitz, and R.R. Monson. 1997. Arsenic in drinking water and incidence of urinary cancers. Epidemiology. 8(5): 545-550.

Hambidge, K.M.D. 1977. The role of zinc and other trace metals in pediatric nutrition and health. Ped. Clin. N. Amer. 24: 95-106.

Hartmann, H.-J. and U. Weser. 1977. Copper-thionein from fetal bovine liver. Biochim. Biophys. Acta. 491:211

Hartford, W.H. 1979. Chromium compounds. In: Kirk-Othmer encyclopedia of chemical technology. John Wiley and Sons. Inc. New York. Pp 82-120.

Healthy Eating Club. 2003. Chromium (internet). http://www.healthyeatingclub.com/ info/books-phds /books/foodfacts/htm l/data /data5m.html

Healy, S.M., R.A. Zakharyan, and H.V. Aposhian. 1997. Enzymatic methylation of arsenic compounds: IV. In vitro and in vivo deficiency of the methylation of arsenic and monomethylarsonic acid in the guinea pig. Mutat. Res. 386: 229 - 239.

Healy, S.M., E.A. Casarez, F. Ayala-Fierro, and V. Aposhian. 1998. Enzymatic methylation of atsenic compounds. V. Arsenite methyltransferase activity in Tissues of mice. Toxicol. Appl. Pharmacol. 148: 65-70.

Highley, T.L. 1995. Comparative durability of untreated wood in use above ground. International Biodeterioration & Biodegradation. 35(4): 409-419.

Hiltbold, A.E., B.F. Hajek, and G.A. Buchanan. 1974. Distribution of arsenic in soil profiles after repeated applications of MSMA. Weed Sci. 22(3): 272-275.

Hingston, J.A., C.D. Collins, R.J. Murphy, and J.N. Lester. 2001. Leaching of chromated copper arsenate wood preservatives: a review. Environ. Pollut. 111: 53-66.

Hingston, J.A., J. Moore, R.J. Murphy, J.N. Lester, and C.D. Collins. 2003. Speciation of Cr and As leachates from CCA treated wood by differential pulse polarography. Holzforschung. 57: 597-601

Howard, A.G. and M.H. Arab-Zavar. 1980. Sequential spectrophotometric determination of inorganic arsenic(III) and arsenic(V) species. Analyst. 105: 338-343.

Hughes, M.F., M. Menache, and D.J. Thompson. 1994. Dose-dependent disposition of sodium arsenate in mice following acute oral exposure. Fund. Appl. Toxic. 22: 80-89.

International Agency for Research on Cancer (IARC). 1987. Monographs on the evaluation of carcinogenic risks to humans. Overall evaluation of carcinogenicity: an updating of the IARC monographs. Vol. 1-42. International Agency for Research on Cancer. Lyon.

Integrated Risk Information system (IRIS). 2003. Arsenic, inorganic (CASRN 7440-38-2). Copper (CASRN 7440-50-8). U.S. Environmental Protection Agency. 1998.

Irgolic, K.J. 1994. Determination of total arsenic and arsenic compounds in drinking water. In: Arsenic: exposure and health. C.R. Cothern. Science and Technology Letters. Northwood, U.K. Pp 51-56.

Jin, L. and A.F. Preston. 1993. Depletion of preservatives from treated wood: results from laboratory, fungus cellar and field tests. IRG document. IRG/WP93-50001-07.

Jonnalagadda, S.B. and G. Nenzou. 1996. Studies on arsenic rich mine dumps: I. Effect on the surface soil. J. Environ. Sci. Health. A31(8): 1909-1915.

Kalnins, M.A. and C.W. Feist. 1991. Increase in the wettability of wood with weathering. Forest Prod. J. 43 (2): 55-57.

Kamdem, D.P., J. Zhang, and M.H. Freeman. 1998. The effect of post-steaming on copper naphthenate treated southern Pine. Wood Fiber Sci. 30(2): 210-217.

Kennedy, M.J. and P.A. Collins. 2001. Leaching of preservative components from pine decking treated with CCA and copper azole, and interactions of leachates with soils. IRG document. IRG/WP 01-50171.

Kennedy, M.J. and G. Palmer. 1994. Leaching of copper, chromium and arsenic from CCA-treated slash pine heartwood. IRG document. IRG/WP 94-50020.

Klaassen, C.D. and J.B. Watkins III. (eds). 2003. Essentials of toxicology. McGraw-Hill Medical Publishing Division. New York. P8, p47.

Klug, H.P and L.E. Alexander. 1954. X-ray diffraction procedures for polycrystalline and amorphous materials. John Wiley and Sons Inc. New York, NY.

Lahiry, A.K. 2001. An environmental aspect relating to leachability of CCA from hardwood and softwood poles in Bangladash. IRG document. IRG/WP 01-50167.

Lal, S. and T.L. Sourkes. 1971. Deposition of copper in rat tissue - the effect to dose and duration of administration of copper sulfate. Toxicol. Appl. Pharmacol. 20: 269-283.

Laverman, A.M., J.S. Blum, J.K. Schaefer, E.J.P. Phillips, D.R. Loveley, and R.S. Oremalnd. 1995. Growth of strain SES-3 with arsenate and other diverse electron acceptors. Appl. Environ. Microbiol. 61: 3556-3561.

Lee-Feldstein, A. 1983. Arsenic and respiratory cancer in man: Follow-up of an occupational study. In: Arsenic: Industrial, Biomedical, and Environmental Perspectives,. W. Lederer and R. Fensterheim. Van Nostrand Reinhold. New York.

Lehmann, K.B.W. 1897. Hygienische studien über kupfer. VI. Die Wirkung des Kupfers auf den Menschen. Arch. F. Hygiene. 31: 279-309.

Li, Z., H. Su, and L. Liang. 2003. Do CCA treated support stakes cause increased arsenic level in crops? IRG document. IRG/WP 03-50204.

Liu, J., B. Zheng, H.V. Aposhian, Y. Y. Zhou, M.L. Chen, A. Zhang, and M.P. Waalkes. 2002. Environ. Health. Perspect. 110(2): 119 -122.

Mallick, S. and J.R. Rajagopal. 1995. The mischief of oxygen on groundwater. Post conference report: expert's opinions, recommendations and future planning for groundwater problem of West Bengal. SOES. JU, Calcuta, India. Cited in British Geological Survey Mott MacDonald Ltd (UK). 1999.

Manning, B.A. and S. Goldberg. 1997. Adsorption and stability of arsenic(III) at the clay mineral-water interface. Environ. Sci. Technol. 31(7): 2005-2011.

Maas, R.P., S.C. Patch, A.M. Stork, J.F. Berkowitz, and G.A. Stork. 2002. Release of total chromium, chromium VI nad total arsenic from new and aged pressure treated lumber. Technical reoprt 02-093.16pp.

McMahon, T.F. and J. Chen. 2001. Hazard identification and toxicology endpoint selection for inorganic arsenic and inorganic chromium, FIFRA Scientific Advisory Panel Background Document.

Mok, W.M., N.K. Shah, and C.M. Wai. 1986. Extraction of arsenic(III) and arsenic(V) from natural waters for neutron activation analysis. Anal. Chem. 58: 110-113.

Mok, W.-M., and C.M. Wai. 1994. Mobilization of arsenic in contaminated river waters. In: Arsenic in the environment: part I: cycling. J.O. Nriagu (ed.). Vol. 26. John Wiley & Sons, Inc. New York, NY.

Monplaisir, G.M., T. Lei, and W.D. Marshall. 1994. Performance of a novel silica T-tube interface. Anal. Chem. 66: 3533-3539.

Montorsi, W., F. Annoni, S.B. Doldi, R. Germiniani, and F. Longoni. 1975. Concentration plasmatique du zinc et du cuivre après court-circuit intestinal. Nouv. Presse. Med. 4: 1734.

Morton, W., G. Starr, D. Pohl, J. Stoner, S. Wagner, and P. Weswig. 1976. Skin cancer and water arsenic in Lane County, Oregon. Cancer. 37: 2523-2532.

Murphy, R.J. and D.J. Dickinson. 1990. The effect of acid rain on CCA treated timber. IRG document. IRG/WP90-3579.

Nakadaira, H., K. Endoh, M. Katagiri, and M. Yamamoto. 2002. Elevated mortality from lung cancer associated with arsenic exposure for a limited duration. J. Occup. Environ. Med. 44(3): 291-299.

National Academy of Sciences (NAS). 1974. Medical and biological effects of environmental pollutants: chromium. Washington, DC. National Academy Press.

National Research Council (NRC). 1989. Recommended dietary allowances. 10th ed. Washington, DC. National Academy of Sciences. Pp 241-243.

National Research Council (NRC). 2001. Arsenic in Drinking Water. 2001 update. Subcommittee to update the 1999 arsenic in drinking water report. Committee on Toxicology Board on Environmental Studies and Toxicology, Division on Earth and Life Studies, National Research Council. National Academy Press. Washington, D.C. 307p.

Newman, P.R. and R.J. Murphy. 1996. Variation on biological performance of CCA caused by preservative application method. IRG document. IRG/WP/96-40072.

Newman, D.K., D. Ahmann, and F.M.M. Morel. 1998. A brief review of dissimilatory arsenate reduction. Geomicrobiology Journal. 15: 255-268.

Nickson, R., J.M. MacArthur, W.G. Burgess, K.M. Ahmed, P. Ravenscroft, and M. Rahman. 1998. Arsenic poisoning in Bangladesh groundwater. Nature. 395: 338.

Norin, H., M. Vahter, A. Christakopoulos, and M. Sanström. 1985. Concentration of inorganic and total arsenic in fish from industrially polluted water. Chemosphere. 14(3/4): 325-334.

Novick, S.C. and R.P.Warrell. Jr. 2000. Arsenicals in hematologic cancers. Semin. Oncol. 27(5): 495-501.

Nygren, O. and A.A. Nilsson. 1993. Determination and speciation of chromium, copper and arsenic in wood and dust from CCA-impregnated timber. Aualusis. 21: 83-89.

O'Neil, P. 1990. Arsenic. In: Heavy metals in soils. B.J. Alloway. Blackie and Sons. Glasgow. Pp 83-99.

Onishi, H. 1969. Arsenic. In: Handbook of Geochemistry. K.H. Wedepohl. Springer. New York. II-2.

Onken, B.M., and D.C. Adriano. 1997. Arsenic availability in soil with time under saturated and subsaturated conditions. Soil Sci. Soc. Am. J. 61: 746-752.

Owen, J.C.A. 1982. Biological Aspects of Copper. Occurrence, Assay and Interrelationships. Copper in Biology and Medicine Series. Noyes Publications. Park Ridge, New Jersey. Pp 1-23.

Partington, J.R. 1962. VI. Chemistry in Scandinavia. II. Scheele. In: A history of chemistry. Macmillan. London. 3: 205-234.

Pasek E.A., and C.R. McIntyre. 1993. Treatment and recycle of CCA hazardous wastes. IRG document. IRD/WP93-50007.

Pätsikkä, E., E.-M. Aro, and E. Tyystjarvi. 1998. Increase in the quantum yield of photoinhibition contributes to copper toxicity in vivo. Plant Physiology. 117: 619-627.

Percival, T. 1785. A history of the fatal effects of pickles impregnated with copper; together with observation on that mineral poison. Med. Trans. Roy. Coll. Physicians. London. 3: 80-95.

Perkin-Elmer. 1982. Analytical methods for atomic absorption spectrophotometry. Perkin-Elmer Corporation. Norwalk, Connecticut. Pp 8.1-8.2.

Pest Management Regulatory Agency (PMRA). 2002. Re-evaluation note - chromated copper arsenate (CCA). (Internet). http://www.hc-sc.gc.ca/pmra-arla/english/pdf/rev/rev2002-03-e.pdf.

Petty, J.A. and R.D. Preston. 1968. Electron probe microanalysis of metals in cell walls of conifer wood treated with preservatives. Holzforschung. 22(6): 174-177.

Pizzi, A. 1982a. The chemistry and kinetic behavior of Cu-Cr-As /B wood preservatives. III. Fixation of the Cu/Cr system on wood. J. Polym. Sci.: Polym. Chem. Ed. 20: 725-738.

Pizzi, A. 1982b. The chemistry and kinetic behavior of Cu-Cr-As /B wood preservatives. Part 4. Fixation of CCA to wood. J. Polym. Sci.: Polym. Chem. Ed. 20: 739-764.

Pizzi, A. 1982c. The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives. II. Fixation of the Cu/Cr system on wood. J. Polym. Sci.: Polym. Chem. Ed. 20(3): 707-724.

Pizzi, A., W.E. Conradie, and M. Bariska. 1986. Polyflavanoid Tannis-From Cause of CCA Soft-rot Failure to the "Missing Link" lignin and Microdistribution Theories. IRG document. IRG/WP/3359.

Rencher, A.C., M.W. Carter, and D.W. McKee. 1977. A retrospective epidemiological study of mortality at a large western copper smelter. J. Occup. Med. 19(11): 754-758.

Romo-Kröger, C.M. and F. Llona. 1993. A case of atomspheric contamination at the slopes of the Los Andes mountain range. Atoms. Environ. 27A(3): 401-404.

Russeva, E. 1995. Speciation analysis-pecularities and requirements. Anal. Lab. 4(3): 143-148.

Rosenqvist, M. 1999. Localization of wood improvement compounds by microautoradiography and ESEM. Holzforschung. 53: 648-654.

Ryan, K.G. and D.V. Plackett. 1987. The Interaction of Polyflavanoid Tannins with CCA in *Pinus radiata*. IRG document. IRG/WP/3422.

Saryan, L.A. and M. Reedy. 1988. Chromium determinations in a case of chromic acid ingestion. J. Anal. Toxicol. 12: 162-164.

Schroeder, H.A. and J.J. Balassa. 1966. Abnormal trace metals in man: arsenic. J. Chronic Dis. 19: 85-106.

Schalek, R.L. and L.T. Drzal. 2000. Characterization of advanced materials using an environmental ESM. J. of Advanced Material.32(2): 32-38.

Simpson, J.A., K.H. Cheeseman, S.E. Smith, and R.T. Dean. 1988. Free-radical Generation by Copper ions and Hydrogen Peroxide Stimulation by Hepes Buffer. Biochem. J. 254:519-523.

Sisler, H.D. and C.E. Cox. 1960. Physiology of fungitoxicity. Academic Press. New York.

Skoog, D.A. 1984. Principles of Instrumental Analysis. 3rd Ed. Saunders College Publishing. Philadelphia, New York, Chicago, San Francisco, Montreal, Toronto, London, Sydney, Tokyo. 23-24.

Smith, R.L. and R.J. Shiau. 1998. An industry evaluation of the reuse, recycling, and reduction of spent CCA wood products. For. Prod. J. 48(2): 44-48.

Smyth, H.F.J., C.P. Carpenter, C.S. Well, U.C. Pozzani, J.A. Striegel, and J.S. Nycum. 1969. Range-finding toxicity data: list VII. Am. Ind. Hyg. Assoc. J. 30: 470-476.

Solo-Gabriele, H.M., T.G. Townsend, and J. Schert. 2003a. Environmental impacts of CCA-treated wood: a summary from seven years of study focusing on the U.S. Florida environment. IRG/WP 03-50205. The International Research Group On Wood Preservation. Brisbane, Austialia. 13p.

Solo-Gabriele, H., T. Townsend, J.-K. Song, J. Jambeck, B. Dubey, Y.-C. Yang, and Y. Cai. 2003b. Arsenic and chromium speciation of leachates from CCA-treated wood. Florida center for solid and hazardous waste management. Report # 03-07.

Somers, E. 1963. The uptake of copper by fungal cells. Ann. Appl. Bio. 51: 425-437.

Sonti, V.R., S. Sonti, and B. Chatterjee. 1987. A study of salt imbalances observed in recycled copper/chrome/arsenic preservative solutions in commercial practice. IRG document. IRG/WP 3461.

Southwick, J., A. Western, and M. Beck. 1981. Community health associated with arsenic in drinking water in Millard County, Utah. Health Effects Research Laboratory, Cincinnati, OH. EPA-600/1-81-064.

Stevanovie-Janezie, T., P.A. Cooper, and Y.T. Ung. 2000. Chromated copper arsenate preservative treatment of north American hardwoods. Part 1. CCA fixation performance. Holzforschung. 54(6): 577-584.

Stevanovie-Janezie, T., P.A. Cooper, and Y.T. Ung. 2001a. Characteristics of sludges produced by destabilization of CCA preservative solutions. Holzforschung. 55(5): 471-477.

Stevanovie-Janezie, T., P.A. Cooper, and Y.T. Ung. 2001b. Chromated copper arsenate preservative treatment of north American hardwoods. Part 2.: CCA leaching performance. Holzforschung. 55(1): 7-12.

Stilwell D. 1999. Arsenic in pressure treated wood. (internet). http://www.caes. state. ct. us/PlantScienceDay/1999PSD/arsenic99.htm

Styblo, M., D. Z., I. Jaspers, S. Lin, and D.J. Thomas. 2002. The role of biomethylation in toxicity and carcinogenicity of arsenic: a research update. Environ. Health Perspect. 110 Suppl. 5: 767-771.

Sutter, H.P., E.B.G. Jones, and O. Walchli. 1983. The mechanism of copper tolerance in *Poria placenta* (Fr.) Cke. and *Poria vaillantii* (Pers.) Fr. Material und Organismen. 18: 241-262.

Suzuki, Y. and K. Fukuda. 1990. Reduction of hexavalent chromium by ascorbic acid and glutathione with special reference to the rat lung. Arch Toxicol. 64: 169-176.

Suzuki, K. and H. Sonobe. 1993. The results of detection on CCA components of the soil contacted with CCA treated woods - a trial study for the availability of the burial methods as a disposal CCA treated wood waste. IRG document. IRG/WP 93-50005.

Tatken, R.L. and R.J. Lewis Sr. (Eds.). 1983. Registry of Toxic Effect of Chemical Substances. 1981-82 Edition. Vol. 1. U.S. Department of Health and Human Services. Public Health Service. Centers for Disease Control. National Institute for Occupational Safety and Health. Cincinnati, OH.

Tokudome, S. and M. Kuratsune. 1976. A cohort study on mortality from cancer and other causes among workers at a metal refinery. Int. J. Cancer. 17: 310-317.

Towill, L.E., C.R. Shriner, and E.A. J.S. Drury. 1978. Reviews of the environmental effects of pollutants. III. Chromium. Prepared by the Health Effects Research Laboratory, Office of Research and Development. U.S. Environmental Protection Agency. Report No. ORNL/EIS-80. EPA 600/1-78-023. NTIS PB 282796. Cincinnati, OH.

Toxic Release Inventory (TRI). 2002. TRI explorer: providing access to EPA's toxics release inventory data. U.S. Environmental Protection Agency. April 24, 2002.

Tseng, W.P., H.M. Chu, S.W. How, J.M. Fong, C.S. Lin, and S. Yeh. 1968. Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan. J. Natl. Cancer. Inst. 40(3): 453-463.

Tseng, W.P. 1977. Effects and dose-response relationships of skin cancer and blackfoot disease with arsenic. Environ. Health Perspect. 19: 109-119.

United States Environmental Protection Agency (USEPA). 1998a. Toxicological review of hexavalent chromium. In support of summary information on the integrated risk information system (IRIS). Washington, DC.70p.

United States Environmental Protection Agency (USEPA). 1998b. Toxicological review of trivalent chromium. In support of summary information on the integrated risk information system (IRIS). Washington, DC. 44p.

United States Environmental Protection Agency (USEPA). 1998c. Integrated risk information system datasheet: Arsenic, inorganic (CASRN 7440-38-2). (Internet). http://www.epa.gov/iris/subst/0278.htm

United States Environmental Protection Agency (USEPA). 2001a. FIFRA Scientific Advisory Panel Meeting Report No. 2001-12. Washington, D.C. 63p.

United States Environmental Protection Agency (USEPA). 2001b. Protocol for: Sampling for residues of arsenic, chromium, and copper in substrates (soil/buffering materials) beneath/adjacent to chromated copper arsenate (CCA) – treated playground equipment. Modification of OPPTS Guidelines: OPPTS 875.1100 (Terrestrial Field Dissipation). Study sponsor and Coordinators. Office of Pesticide Program (OPP) Consumer Product Safety Commission (CPSC). 24p.

United States Environmental Protection Agency (USEPA). 2002. EPA newsroom: Whitman Announces Transition from Consumer Use of Treated Wood Containing Arsenic. (Internet). http://www.epa.gov/epahome/headline_021202.htm.

Van Eetvelde, G., R. Orsler, H. G., and M. Stevens. 1995. Effect of leaching temperature and water acidity on the loss of metal elements from CCA treated timber in aquatic applications, Part 1: Laboratiry scale investigation. IRG document. IRG /WP 95-50046.

Waldron, L., Y.T. Ung, and P.A. Cooper. 2003. Leaching of inorganic wood preservatives - investigating the relationship between leachability, dissociation characteristics and long-tern leaching potential. IRG document. IRG/WP 03-50199.

Wildfang, E., T.R. Radabaugh, and H.V. Aposhian. 2001. Enzymatic methylation of arsenic compounds. IX. Liver arsenic methyltransferase and arsenate reductase activities in primates. Toxicology. 168: 213-221.

Williams, S.R. 1999. Arsenic. In: Poisoning and drug overdose. Olson, K.R. (ed). 3rd ed. Appleton & Lange. Stamford, Connecticut. P95.

Williams, R.S. and W.C. Feist. 1999. Water repellents and water-repellent preservatives for wood. United States Department of Agriculture. Forest Service. For. Prod. Lab. General Technical Report FPL-GTR-109. 14p.

Wilson, L.E. 1974. Introductory Quantitative Analysis. Charles E. Merrill Publishing Co. Columbus, Ohio.

Woolson, E.A. 1977. Fate of arsenicals in different environmental substrates. Environ. Health Perspect. 19: 73-81.

World Health Organization (WHO). 1963. International Standards for Drinking-water , Second edition

World Health Organization (WHO). 1996. Guidelines for drinking-water quality. 2nd ed. Vol. 2. Health criteria and other supporting information. Geneva, World Health Organization, pp: 156-167.

Yasui, A., C. Tsutsumi, and S. Toda. 1978. Selective determination of inorganic arsenic (III), (V) and organic arsenic in biological materials by solvent extraction - atomic absorption spectrophotometry. Agric. Biol. Chem. 42(11): 2139-2145.

Zahora, A.R. 1995. Comparative field performance of CCA and CCA-water repellent treated southern pine lumber. IRG document. IRG/WP 95-30089.

Zhang, J. and X. Li. 1987. Chromium pollution of soil and water in Jinzhou. J. Clin Prevent Med. 21: 262-264.