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**Leaching of Heavy Metals from Chromated Copper Arsenate
(CCA) Treated Wood**

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Civil and Environmental Engineering

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Abstract

Leaching of Heavy Metals from Chromated Copper Arsenate (CCA) Treated Wood

Azita H.Moghaddam

Preserved, treated wood is commonly found in solid waste. Among the different types of preserved wood, chromated copper arsenate (CCA) treated wood recently has received much attention due to the scale of usage and its significant role in soil and water contamination. As the ash of CCA treated wood is hazardous, it cannot be burned, and the best available disposal method is thus landfilling. Leaching of the metals from disposed preserved wood in landfills pollutes the soil, water and the environment. The existing literature on leaching of CCA treated wood is reviewed, and several factors affecting leaching of the metals from wood, including pH of the leachant, temperature, the duration of leaching, the type of leachant are discussed. These factors affect each of the metals including chromium, copper and arsenic, differently. Definition and comparison of the effect of these mentioned factors on each preservative metal several experiments were performed. In all experiments ground wood (remaining at the top of sieve No.10) was soaked in leachant (ratio 1:10). The leachants were nitric acid, sulfuric acid and acetic acid (0.1N), having pH values of 3, 4 and 5. They were left in an incubator for 5,10 and 15 days. The temperature of the incubator was set to 15°C for 15 days and then the experiment was repeated for temperatures 25 °C and 35 °C. On the other hand to investigate the biodegradability of the leached wood, unleached wood and

some of the leached wood samples were chosen. The necessary nutrients for growth of fungi and soil were added and the amount of generated CO₂ was measured through the experiment. The results of the experiments showed that sulfuric acid (pH3) is the most effective leachant. Most of the leaching happens in the first 5 days and temperature increases the amount of leached metals. The leached CCA wood is still resistant to biodegradation.

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Table of contents

List of Figures	x
List of Tables	xii
Chapter 1 Introduction	1
1.1 Introduction.....	1
1.2 Objectives.....	4
Chapter 2 Literature Review	5
2.1 Wood	5
2.1.1 Wood structure	5
2.1.2 Chemical composition of the wood cell.....	9
2.2 Biodegradation.....	11
2.2.1 Fungi and how they affect wood.....	11
2.2.2 Fungal effect.....	11
2.2.3 Bacterial effects.....	13
2.2.4 Decay durability of Canadian wood resources.....	13
2.3 Wood preservation.....	15
2.3.1 Thermal Treatment Process.....	15
2.3.2 Pressure treatment.....	16
2.3.3 Canadian wood preservatives.....	18
2.3.4 Wood preservatives' effects.....	18
2.3.5 Canadian treated wood facilities.....	21

2.3.6	The Industry Economy.....	22
2.4	CCA treated wood.....	23
2.4.1	CCA Treatment Process.....	24
2.4.2	CCA fixation.....	28
2.4.3	Factors affecting fixation.....	30
2.5	Leaching.....	32
2.5.1	General remarks.....	32
2.5.2	Physical factors.....	33
2.5.3	Chemical factors.....	36
2.5.4	Speciation.....	37
2.5.4.1	Chromium.....	37
2.5.4.2	Copper.....	39
2.5.4.3	Arsenic.....	41
2.6	Landfills.....	43
2.6.1	Introduction.....	43
2.6.2	Municipal landfill structure	44
Chapter 3	Material and methods.....	48
3.1	Introduction	48
3.2	Materials.....	49
3.2.1	Wood.....	49
3.2.2	Acids.....	50
3.3	Procedure.....	50
3.3.1	Wet digestion.....	51

3.3.1.1	Wet digestion samples.....	51
3.3.1.2	Method.....	52
3.3.2	Dry digestion	52
3.3.3	Microwave digestion.....	55
3.3.4	Leaching method	55
3.3.4.1	The wood preparation	56
3.3.4.2	Leaching solutions.....	56
3.3.4.3	Leaching test.....	57
3.3.5	Leachate digestion.....	59
3.3.6	Biodegradation method.....	60
3.3.6.1	Nutrient preparation:.....	60
3.3.6.2	Test method.....	61
Chapter 4	Results and discussion.....	63
4.1	Equations.....	64
4.2	Leaching results.....	65
4.2.1	Unleached treated wood.....	65
4.2.2	The effect of temperature on leaching.....	67
4.2.2.1	Chromium.....	70
4.2.2.2	Copper.....	71
4.2.2.3	Arsenic.....	72
4.2.3	The effect of pH on leaching.....	73
4.2.3.1	Chromium	75
4.2.3.2	Copper.....	76

4.2.3.3	Arsenic.....	78
4.2.4	Effect of time.....	79
4.2.5	Effect of leachant type.....	84
4.3	Biodegradation results.....	87
4.4	Summary of the results.....	88
Chapter 5	Conclusions.....	97
5.1	Conclusion of this study.....	97
5.2	Future recommendations.....	99
References.....		100

List of Figures

Figure 2.1	Cross section of white oak tree trunk.....	7
Figure 2.2	Typical softwood structure	8
Figure 2.3	Wood cell wall structure.....	9
Figure 2.4	Cellulose structure	10
Figure 2.5	Potential chemical releases from CCA pressure treating plants.....	27
Figure 2.6	The cross section of a municipal solid waste landfill.....	45
Figure 2.7	Storm drainage pipe drain into the ditch.....	46
Figure 2.8	A leachate pond.....	47
Figure 2.9	Methane collection pipe.....	47
Figure 3.1	Leaching containers.....	57
Figure 3.2	Leaching containers.....	58
Figure 3.3	Leachate digestion.....	59
Figure 4.1	Type of sample wood.....	66
Figure 4.2	Effect of temperature on leaching by acetic acid (pH5) during 5 days.....	68
Figure 4.3	Effect of temperature on leaching percentages by acetic acid (pH5) after 5days.....	69
Figure 4.4	Effect of temperature on chromium leaching by acetic acid (pH5).....	70
Figure 4.5	Effect of temperature on copper leaching by acetic acid (pH5).....	71
Figure 4.6	Effect of temperature on arsenic leaching by acetic acid (pH5).....	72
Figure 4.7	Effect of pH on leaching by acetic acid at T=15°C during 5days.....	73
Figure 4.8	Effect of pH on leaching percentages by acetic acid at T=15°C	

	during 5days.....	74
Figure 4.9	Effect of pH on chromium leaching by acetic acid at T=15°C	75
Figure 4.10	Effect of pH on copper leaching by acetic acid at T=15°C.....	77
Figure 4.11	Effect of pH on arsenic leaching by acetic acid at T=15°C.....	78
Figure 4.12	Effect of leaching time by acetic acid (pH 5) at T=15°C.....	79
Figure 4.13	Effect of time on leaching percentages by acetic acid (pH5) at T=15°C.....	80
Figure 4.14	Effect of time on chromium leaching by acetic acid (pH 5).....	81
Figure 4.15	Effect of time on copper leaching by acetic acid (pH5).....	82
Figure 4.16	Effect of time on arsenic leaching by acetic acid (pH5).....	83
Figure 4.17	Effect of type of acid on chromium leaching at T=25°C,15 days.....	84
Figure 4.18	Effect of type of acid on copper leaching at T=25°C,15 days.....	85
Figure 4.19	Effect of type of acid on arsenic leaching at T=25°C,15 days.....	86

List of Tables

Table 2.1	Fungal effect on CCA	12
Table 2.2	Relative decay resistance of heartwood	14
Table 2.3	The number of wood treatment plants in 1995	21
Table 2.4	Composition of three CCA formulations as specified by AWPA Standards.....	26
Table 2.5	Retention levels of CCA active ingredients.....	28
Table 2.6	Leaching hazards for preservative treated wood.....	32
Table 2.7	Factors affecting the leaching of preserved components from wood.....	35
Table 3.1	Ash weight of leached wood at 35°C.....	53
Table 3.2	Ash weight of leached wood at 25°C.....	53
Table 3.3	Ash weight of leached wood at 15°C.....	54
Table 3.4	Ash weight of leached wood by nitric and sulfuric acid.....	54
Table 3.5	Ingredients of used nutrients for biodegradation test.....	61
Table 4.1	The results of titration of NaOH (1N) with HCl (0.1N).....	89
Table 4.2	Results of the leaching tests.....	90
Table 4.3	Results of 5 day leaching tests.....	93
Table 4.4	Unleached wood analysis results.....	94
Table 4.5	Results of 15 day leaching tests.....	95

Chapter 1

Introduction

1.1 Introduction

Today, municipal solid waste management has become an important part of environmental protection activities. In 1999 U.S. produced more than 230,000 million kg of municipal solid waste of which 28% was recycled and the rest was disposed of by landfilling or composting (US. EPA, Office of Solid Waste 1999).

In Canada, even though the population is less, the same problem exists. As there are some limitations for the types of wastes that can be recycled or combusted, landfilling is an important method on municipal and construction debris waste management (Ress, et al., 1998).

Wood is one of the most commonly used building materials in North America. Modern commercial forestry and sawmills mainly are providers of material for the building industry (Sloot et al., 1997). Environmental Protection Agency (EPA) estimated that the largest amount of the 136 million tons of building - related construction debris produced in 1996 was wood (Tom, 2001).

Following wood removal from the forests, several types of deterioration by fungi and insects threaten the untreated wood and reduce the lifetime of the wood and the wooden building materials. These decays increase demand for wood and lead to faster deterioration of wood sources and forests.

Chemicals are thus required to treat the wood to protect wood against bacterial, fungal, and insect attack. This has been practiced for centuries. The practice of treating wood with wood preservatives is intended to enhance wood durability, and thereby increase the life expectancy of wood in service. As an example, untreated timbers used in underground workings of mines could have a lifetime of no greater than two years due to the effect of temperature and moisture. Another example is railroad cross ties used in North America, which would have average life time of five years without treatment (Konasewich and Henning, 1998). however the lifetime of most creosote preserved wood is estimated to be 30 years (Webb, 1990).

Preserved wood is a common part of the solid waste (Tom, 2001). Since the ash of treated wood is hazardous, then the best disposal method of used treated wood is landfilling.

One of the most problematic preserved wood is *Chromated Copper Arsenate (CCA)* treated wood which is used in outdoor facilities, playgrounds, fences and so on and is in direct contact with people. During rain, water penetrates into landfills and causes leaching of wood preservatives (copper, chromium and arsenic) from the disposed *Chromated Copper Arsenate (CCA)* treated wood. The leached metals can pollute underground and drinking water. As the leachate of treated wood in landfills is genotoxic and carcinogenic, the contaminated water is dangerous for human beings and animals and the investigation of leaching and biodegradation of treated wood is an important research.

Recently, a significant amount of arsenic, chromium and copper has been found in children playgrounds in Canada and U.S. and it has received significant attentions (Hauserman,2002). Banning and replacing the CCA treated wood with other preservatives, does not decrease the demands for disposal of existing CCA wood. Landfilling of existing CCA treated wood and its related environmental problems have started and are going to increase. Then it is necessary to know how much of metals leach, which factors affect the leaching process and to find solutions to decrease its damage to the environment.

The existing literature on leaching of CCA treated wood is reviewed, several factors affecting leaching of the metals from wood, including pH of the leachant, temperature, the duration of leaching, the type of leachant are discussed. The effects of sulfuric acid, nitric acid and acetic acid, as three different types of leachants, having pHs of 3.4 and 5, in temperatures 15, 25 and 35 °C over a period of 5,10 and 15 days were investigated.

1.2 Objectives

The objectives of this study are:

- To evaluate the leaching of chromium, copper and arsenic from disposed CCA (*Chromated Copper Arsenate*) treated wood after landfilling.
- To define and to compare the effect of pH, temperature, time and type of acid on their leaching
- And to determine the biodegradability of leached wood.

Chapter 2

Literature Review

2.1 Wood

2.1.1 Wood structure

The three main structural components of trees are: (Kollman and Cote.):

- Roots, which gather water and mineral nutrients and provide firm anchor for all the structure.
- Crown including the leaves and small branches.
- Bole or trunk.

Wood is primarily composed of hollow, elongate, spindle-shaped cells that are arranged parallel to each other along the trunk of a tree. Wood cells are formed in the very thin cambium, between the bark and wood. Cells on the outside of the cambium form the phloem, or inner bark. Cells on the inside form the xylem, or wood. Many more xylem cells than phloem cells are formed (Regis, 1999).

A cross section of a tree (Figure 2.1) shows (from outside to center):

- Bark, which may be divided into dead and living parts. The inner living part (B), which is a thin, carries food from the leaves to the growing parts of the tree. And the outer dead part (A), whose thickness varies greatly with species and age of trees.
- Cambium(C), which forms bark and wood cells.
- Sapwood (D), which contains both living and dead tissue and carries sap from the roots to the leaves.
- Heart-wood (E), which usually consists of inactive cells.
- Pith (F) at the center of tree stem, which is a small core of tissue.
- Branches and twigs.

- Wood rays (G), which are horizontally oriented tissues from pith toward bark, and connect various layers for storage and transfer of food.

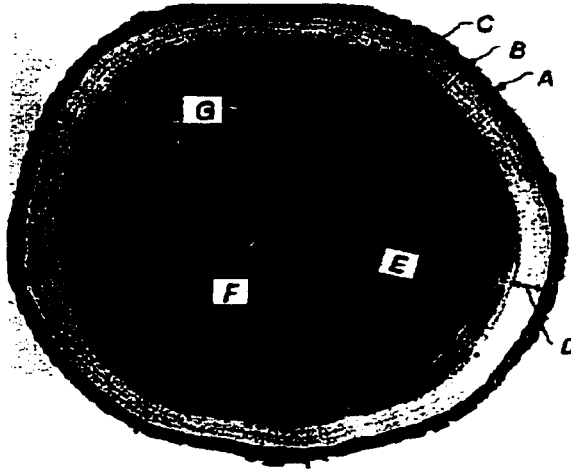


Figure 2.1: Cross section of white oak tree trunk
 (A) outer bark (B) inner bark (C) cambium (D) sapwood
 (E) heartwood (F) pith and (G) wood rays
 Ref. (Regis, 1999)

In softwoods, there are two main types of cells, tracheids and parenchyma. Tracheids are the main part of wood cells, oriented longitudinally with a length of 3-8 mm. The parenchyma, are the cells for storage of food (Regis1999).

Hardwood is more complex than softwood. It consists of inactive cells that do not function in either water conduction or food storage. The main difference is that in hardwood the liquid transport through the vessels but in softwood, through the tracheids. The vessels are composed of short large diameter cells, one on top of another to make a longitudinal channel. Hardwood fibers function only as support and do not conduct water (Regis, 1999).

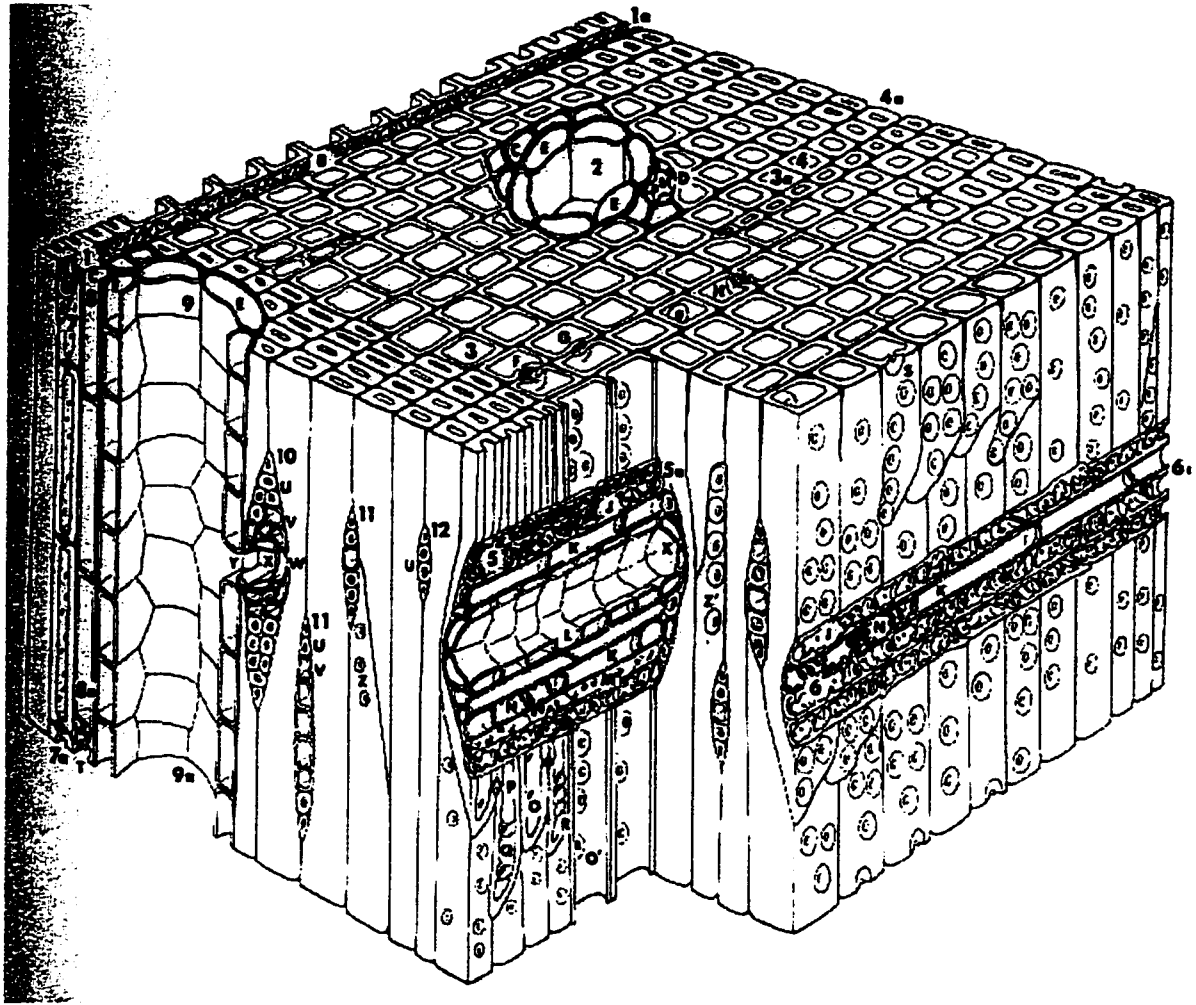


Figure 2.2: Typical softwood structure

(Howard and Manwiller, 1969. From Siau, Transport Process in Wood. Spring.1984)

The wood cell wall is composed of two walls, the primary (P layer) and the secondary layer. The secondary layer made of three layers, S1, S2 and S3 (Butterfield and Meylan, 1980). As the S2 layer is the thickest layer with the highest percentage of lignin, and with respect to physical properties, the S2 layer is the most important layer (Tsoumis, 1992).

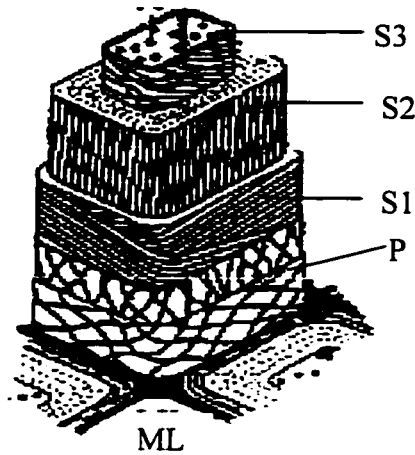


Figure 2.3: wood cell wall structure
ML=middle lamella (mainly lignin); P= primary wall; S1secondary wall;
S2 secondary wall (main body); S3 tertiary wall
Krassig, H.A., 1993.

2.1.2 Chemical composition of the wood cell

Dry wood consists of cellulose, lignin, hemi-celluloses and minor amounts (5% to 10%) of extractives (Regis, 1999).

- Cellulose, the major component, is a linear crystalline polymer of glucose. which constitutes approximately 50% of wood substance by weight. It is present as microfibrils of extended cellulose chains.

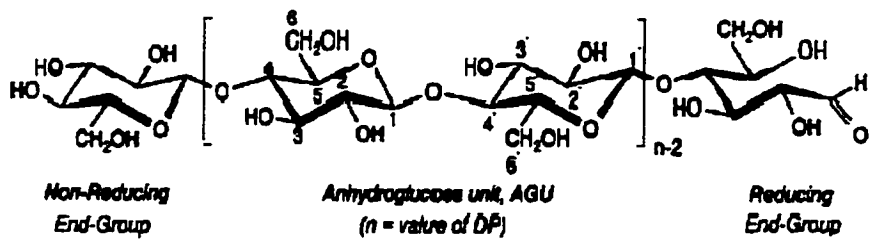


Figure 2.4: Cellulose structure

Krassig, H.A., 1993.

- Lignin is a three-dimensional phenylpropanol polymer, which is often called the cementing agent that binds individual cells together. About 23% to 33% of the wood substance in softwoods and 16% to 25% in hardwoods is lignin. It is concentrated toward outside of the cells and between cells.

The hemicelluloses are branched, low-molecular-weight polymers composed of several different kinds of pentose and hexose sugar monomers. The relative amounts of these sugars are related to the species.

- Extractives are a wide variety of small molecules in wood, which are soluble in organic solvents (Regis, 1999).

2.2 Biodegradation

2.2.1 Fungi and how they affect wood

Fungi are microorganisms that colonize wood. Fungal spores form hyphae, which are thread-like strands. The hyphae grow through wood and produce enzymes, which break down cell constituents and produce bore holes. There are three groups of fungi that affect wood: Mold, Sapstain and Decay fungi. Molds and Sapstain fungi decompose the storage products like fats and sugars in ray cells in sapwood and decay fungi produce enzymes which breakdown the materials that give strength to wood cell walls. All of these groups need water, oxygen, a source of food and temperature (10-32 °C) to colonize (Amburgey , 2000). Before drying and being sterilization, wood is at risk of fungal attack. It should be kept dry until treatment and it is better to process the old stock first.

2.2.2 Fungal effect

Some specific species of fungi can decay the copper based preserved wood (same as CCA treated wood). Most of these fungi are those, which cause brown – rot decay of wood namely the basidiomycetes (Illman and Terry,1996). *Poria cocos*, *P. incrassata* and *P. vailantii* are the brown-rot fungi, which cause CCA treated wood weight loss (Dacosta and Kerruish, 1964). The highest weight loss of southern yellow pine could be caused by isolates of *Meruliporia incrassata* and an isolate of *Antrodia radiculosa*. An

isolate of *Meruliporia incrassata* caused the same weight loss in both treated and untreated yellow pine after 10 weeks (Table 2.1). But only the high level copper sulphate treated wood was decayed, not copper naphthenate or copper-8-quinolinolate treated wood (Illman and Terry, 1996).

Table 2.1: Fungal effect on CCA

fungi	weight loss(%)	
	control	CCA treated wood
<i>Merulipolia incrassata</i> (TFFH294)	47.7±2.7	40.2±3.9
<i>Merulipolia incrassata</i> (TFFH296)	15.2±1.6	9.1±4.6
<i>Merulipolia incrassata</i> (MAD-563)	55.5±1.7	9.1±3.2
<i>Antrodia vaillantii</i> (FP-90877-R)	18.0±2.3	6.2±1.5
<i>Antrodia radiculosa</i> (FP-90848)	60.5±2.3	17.2±1.2
<i>Antrodia radiculosa</i> (HHB-11414)	47.2±2.0	3.8±0.8
<i>Poria cocos</i> (90850-s)	62.3±5.3	0±0.1
<i>Poria placenta</i> (MAD-698)	62.3±2.0	0±0.1
<i>Antrodia xantha</i> (LRG-1)	47.6±3.2	0±0
<i>Antrodia sinuosa</i> (LRG-2)	32.1±0.7	0±0
<i>Antrodia sinuosa</i> (LRG-3)	35.1±1.0	0±0
<i>Antrodia sinuosa</i> (LRG-4)	4.2±5.5	0±0
<i>Antrodia sinuosa</i> (LRG-5)	33.3±0.8	0±0

Exposed 10 weeks in soil-block test
Ref. (Illman and Terry, 1996)

2.2.3 Bacterial effects

Under lab conditions, some kinds of bacteria were tested which could decrease the toxic metal from CCA components. These selected bacteria, which grew on nutrient agar containing CCA components were *Pseudomonas putida*, *Bacillus licheniformis*, or *Bacillus coagulans*. The atomic absorption analyses of exposed CCA -treated sawdust to these bacteria after three weeks showed 22% to 46% reduction of copper, 0 to 9% of chromium and 0 to 8% for arsenic, by weight (Cole and Clausen, 1996). Therefore it can be one solution to decrease the heavy metals of disposed treated wood before landfilling.

2.2.4 Decay durability of Canadian wood resources

Wood durability and its ability to resist fungal attacks depends on the wood species. Certain heartwood species, such as western red cedar and oak, are well known for their high durability, but the sapwood is not durable. Table 2.2 contains the durability of some species which grow in Canada (Mullins and Mcknight, 1981).

Table 2.2: Relative decay resistance of heartwood

Resistant or very resistant	Moderately resistant	Slightly resistant or nonresistant
Cedar	Douglas-fir	Alder
Cherry, black	Honeylocust*	Ash
Chestnut, sweet	Larch, western	Basswood
Cypress	Pine, eastern white	Beech
Juniper	Tamarack	Birch
Locust, black		Butternut
Mulberry, red*		Elm
Oak, bur		Hemlock
Oak, white		Hickory
Sassafras		Maple
Walnut, black		Oak, red and black*
Yew, Pacific		Pine (other species)
		Poplar
		Spruce
		Willow

Ref.: (U.S. Dep Agric.,1961)

*These woods have higher decay resistance than most others in their group

2.3 Wood preservation

Wood preservation may be thermal or based on pressure impregnation of wood with chemicals to protect it from fungi, insect or other biological deterioration. The wood treatment depends on the wood type and chemical properties. The chemicals should be toxic for organisms, be able to penetrate the wood and to be fixed on the wood. It should not cause any significant dimensional changes or weaken the wood structure, be safe to handle, as well as economical to use. The odour or colour, paintability, corrosiveness, electrical conductivity and leachability from wood are the other factors that will affect the selection of chemicals (Konasewich and Henning, 1998).

2.3.1 Thermal Treatment Process

The thermal process is applied with PCP (pentachlorophenol) oil solutions, as preservative, to treat dry utilities poles and cross arms of thin sapwood species. Usually, horizontal, rectangular tanks covered by lids are used for treatment. Dry wood is immersed in hot preservative (88 to 113°C) for at least 6 hours (hot bath). Then the hot preservative is quickly replaced by the preservative at ambient temperature, for a minimum of two hours (cold bath). The impregnation of lower ends of the poles (butts) with preservative or pole butt treatment, is carried out in upright cylindrical tanks under the same conditions as the full length treatment. In the next steps, most treatment cycles are followed by a final vacuum to equilibrate internal pressure, remove air and

preservative from the surface fibers of wood and in the case of oil-borne treatments that use elevated temperatures, cool the wood. As the final vacuum step may not be adequate to create clean surfaces for creosote and PCP, the impregnation cycle may be followed by an expansion bath or a final steam cycle, both of which adds a final vacuum step. (In the case of final steam cycle, large volumes of contaminated water will be produced). After being removed from the cylinder, the treated wood is stored on a drip pad until the drippage stops (Brudermann, 1999).

2.3.2 Pressure treatment

The most common treatment includes pressure treatment in which the chemicals are penetrate into the wood under high pressure conditions. The pressure treatment preservatives are grouped into two categories: oilborne and waterborne (Lebow, 1996).

- *Oilborne*: Creosote, pentachlorophenol and copper naphthenate are the common oilborne preservatives.

- *Waterborne*: There are many types of waterborne preservatives for wood used trail, recreational construction and boardwalks such as:
 - *CCA*: Chromated copper arsenate (CCA) has been the most popular wood treatment product. It offers protection from moisture and decaying fungi.

- *Borates*: The toxicity of the chemicals used in wood treatment has promoted researchers to develop less toxic methods such as the use of borates derived from the natural element boron (borax). Borates (from boron) are used in wood treatment in New Zealand and Australia. They offer insect protection and fire retardation benefits to wood. Full-scale commercial introduction of borates in the U.S. awaits resolution of the leaching problem of borates. Since borates are easily soluble in water, thus leave the wood unprotected from decay after a period of time. In a location not exposed to water, they are effective in protecting wood from decay.
- *ACQ*: Ammoniacal copper quaternary (ACQ) is a new wood preservative. This material includes components that are listed in EPA's classification as "General Use" pesticides. This is a less toxic material that CCA performs similarly.

Waterborne preservatives were primarily limited to chromated copper arsenate (CCA), ammoniacal copper arsenate (ACA), borates and ammoniacal copper zinc arsenate (ACZA). However, recently, new waterborne preservatives, based on amine or ammonical copper, have been under consideration by the AWPA same as ammoniacal copper quat (ACQ Type B), alkaline copper quat (ACQ Type D), copper dimethyldithiocarbamate (CDDC), and ammoniacal copper citrate (CC). A formulation under consideration by AWPA for approval in the near future is ammoniacal copper azole (CuAz).

2.3.3 Canadian wood preservatives

The most used preservatives in Canada are (Konasewich and Henning, 1998):

- CCA (chromated copper arsenate). In wood used for fences, lumber for landscaping, foundation and plywood.
- ACA (ammoniacal copper arsenate). Used for poles and landscaping timbers.
- PCP (pentachlorophenol). Used for railway ties and utility poles.
- Creosote. Used for marine pilings, and railway ties and utility poles.

2.3.4 Wood preservatives' effects

- *Pentachlorophenol (PCP)* is a mixture of many related compounds. It contains PCP (85 to 90 percent); 2,3,4,6-tetra chlorophenol (4 to 8 percent), other chlorinated chlorophenols (2 to 6 percent), as well as dioxins and furans (about 0.1 percent). Dioxins and furans are also mixtures of various related compounds. The principal dioxins and furans found in commercial grade PCP have six to eight chlorine atoms present in their structures. The most toxic dioxin and the one of greatest regulatory concern is 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD), which contains four chlorine atoms in its structure. Analysis of commercial PCP produced in the U.S. has not found TCDD. But some wood-preservation methods use PCP at higher temperatures, which may produce traces of TCDD from the PCP itself. Octachloro-dibenzo-p-dioxin (the dioxin containing 8 chlorine atoms) is by far the largest dioxin contaminant, while the most toxic dioxin, TCDD.

occurs only as trace or below detection levels. According to the EPA, octachloro-dibenzo-p-dioxin is about thousand-fold less toxic than TCDD. In any event, EPA recommends that managers of all wood-treating sites which are known to have used PCP should ensure sampling for dioxins and furans at their sites. PCP was formerly one of the most heavily used pesticides in the United States. Today its purchase and use is restricted to certified applicators, and it is used industrially as a wood preservative for power line poles, fence posts, etc. (U.S. Environmental Protection Agency, 1992; U.S. Department of Health & Human Services, 1992; U.S. Environmental Protection Agency, 1995). PCP causes irritation in different parts of human body such as throat, skin, eye and nose. Cancer and birth defects are its effects on lab animals. It is an immediate toxic material to fish and other aquatic organisms and easily absorbed via inhalation, ingestion, and skin and may outgas for up to seven years. It has been shown to cause fetal death, significant liver damage in adults. Polychlorinated-p-dioxins and polychlorinated dibenzofurans, which are impurities in PCP, have long term effects (Environment Canada , 2001; MacMillen, 1995).

- Creosote is a mixture of toxic chemicals such as polyaromatic hydrocarbons, distilled from coal tar, which is a by-product of coke production from high-temperature carbonization of bituminous coal in coking ovens. It is composed of about 85 percent polycyclic aromatic hydrocarbons (PAHs), along with phenolic compounds (about 10 percent) and a variety of other related chemicals (U.S. Environmental Protection Agency, 1992; U.S. Environmental Protection Agency,

1995). It has been in use in the United States since 1889 and is still the treatment of choice for the railroad industry. Since 1986, creosote has been a restricted-use pesticide and is only available to certified applicators (Wilson, 1997). The PAHs contained in creosote are a group of more than hundred related chemicals that are both man-made and naturally occurring. They are found in crude oil, coal, coal tar pitch, as well as road and roofing tar. In pure form a single PAH is usually a white or pale green solid, but they almost always occur as a mixture of PAHs. They have low water solubility, but they can contaminate underground water that comes into contact with soil contaminated by them. They have been found in some U.S. drinking water supplies (U.S. Environmental Protection Agency, 1992). Except naphthalene, PAHs cannot evaporate easily, but most will stick to solid particles in soil. In soil, some of the low molecular weight PAHs can break down in weeks to months, mostly because of microorganisms, although very large PAH molecules are more stable. People living near waste sites contaminated with PAHs may be exposed to them by contact with contaminated air, water, or soil (U.S. Department of Health & Human Services, 1993). Creosote is a colorless to yellowish greasy liquid with a smoky odor and burned taste, which has both immediate and chronic effects and can be carcinogenic (Environment Canada, 2001). It causes skin irritation, cancer and genetic damage: in humans it has been linked to skin cancer and causes eye and skin irritations, dermatitis and burns. It remains potent for years, moving easily through the soil and the skin and lungs of anyone who touches it or breathes its vapors.

- CCA (chromated copper arsenate) and ACA (ammoniacal copper arsenate) are green tinted wood seen in lumber yards, decks, basements. Their compounds have caused cancer, birth defects and genetic mutations in animals, headaches, dizziness and muscle spasms in humans. They cause immediate toxic reactions in fish (MacMillen, 1995).

2.3.5 Canadian treated wood facilities

Table 2.3: The number of wood treatment plants in 1995

Atlantic Region (NS, NB, NF)	4
Quebec Region (QC)	11
Ontario Region (ON)	18
Prairie and Northern region (AB, SK, MB)	14
Pacific and Yukon Region (BC)	17
<hr/>	
Total	64

Reference: Canadian Environmental Protection Act, Strategic Options for the Management of CEPA-Toxic Substances from the Wood Preservation Sector, vol.1. July 1999

Canada is the second largest producer of preserved wood in the world. The Canadian preservative wood industries were started in 1910 (Canadian Environmental Protection Act, 1999). In 1995, there were sixty-four wood treatment plants in Canada. Sixty-one of them were pressure treatment plants, two used both pressure and thermal treatment and one had only thermal facilities. In forty-nine of them, CCA was the only used preservative while PCP and creosote were the sole preservatives in one plant each. Seven of them operated with CCA, PCP; five with CCA, creosote, PCP and one with CCA, ACA, PCP and creosote. Except for Prince Edward Island, all the provinces have this industry. Ontario and British Columbia have the most wood treatment plants (Table 2.3) (Brudermann, 1999).

2.3.6 The Industry Economy

The total installed volume of treated wood products (railway ties, poles, residential lumber, etc.) in 1992 was estimated as 32.11 million cubic meters valued at \$10 billion. It is estimated that in 1995, 1.96 million cubic meters of treated wood were produced, which had a total value of \$ 700 million dollars. There are approximately 1,500 direct and 5000 indirect jobs in the Canadian preservation industries (Canadian Environmental Protection Act, 1999).

Based on 1992 data, the wood preserving industry produced 2 million cubic meters of treated wood with a revenue value of \$547.4 million, only in 1992. Of this production 80% and 20% of the wood was treated with water and oil borne preservatives

respectively. All the oilborne treated products (350,000 cubic meters) were industrial products, such as railway ties, utility poles, industrial construction lumber and timbers, and pilings. Approximately 66.8% of the waterborne treated products were residential lumber products, such as decking, fencing, etc. Of this total production, exports accounted for 160000 cubic meters, or 8.3% of total production, with a revenue value of \$46.4 million. Most of the exports were to the Middle East, Asia and Central America while exports to the USA were less than 20%. During the same period, imports of treated wood originating almost exclusively from the USA totaled 60 thousands cubic meters (Canadian Environmental Protection Act, 1999).

2.4 CCA treated wood

Chromated copper arsenate (CCA) is the major wood preservative, which is used in United States as well as in Canada. CCA is favored for lumber treatment because it is inexpensive, leaves a dry, paintable surface, and binds to become relatively leach-resistant. However, there is increasing concern about potential environmental contamination from leaching of Cu, Cr and As from treated wood in service and from wood removed from service and placed in landfills. The life cycle of treated wood is estimated to be about 25 years; the wood is then discarded as waste. By 1995, more than 90% of 67 million kg of utilized waterborne preservatives was CCA (Solo-Gabriele and Townsend, 1999). The quantity of removed treated wood from services is estimated to increase to 12 million cubic meters by the year 2004 (McQueen and Stevens, 1998) and to 16 million cubic meters by year 2020 (Cooper, 1993).

2.4.1 CCA Treatment Process

To preserve the wood, it is necessary for the chemicals to penetrate into wood deeply (several centimeters). A pressure treatment plant (Figure 2.5) is used to achieve such penetration followed by preservative fixation within wood.

There are several factors that affect the penetration of preservatives into wood such as (Morris, 1996):

- The applied treatment process
- Wood permeability
- Heartwood /sapwood ratio
- Wood moisture content
- Wood quality

Depending on the abovementioned factors, the preservative can either penetrate evenly into the heartwood such as Scots pine or can only be restricted to the surface like Norway spruce (Morris, 1996).

The chemicals, chromated copper arsenate, are normally purchased as a premixed concentrate of 50% to 65% then stored in tanks and diluted with water to a 1.5 % to 4 % strength working solution. Diluted solution is then applied to the wood in pressure cylinders (Konasewich and Henning, 1998).

The CCA treatment is applied by using the “full-cell (Bethell) pressure based process, which was introduced in 1838 and is the only process used for all CCA, ACA and creosote preservative treatments. The process starts by loading the wood, which has been dried in a kiln, into pressure cylinders, which may be up to 45 m long and 2 m in diameter and an initial vacuum for half an hour is applied. While maintaining the vacuum, the preservative solution is admitted to the cylinder at ambient temperature for CCA, ACA (But in the case of oilborne preservatives, they are heated 70 to 90 °C). After filling the cylinders a maximum pressure of 1040 kPa is applied (for either waterborne or oilborne) till all amount of the required solution has been injected to the wood (from 30 minutes to several hours). At that point the pressure is released and the excess preservative is returned to a storage tank for use on subsequent treatments. Usually a final vacuum in the case of CCA and ACA or both an expansion bath and a final vacuum in the case of creosote applies after impregnation stage to remove excess preservative from the wood surface, make wood clean and dry. After pressure treatment the preservative will diffuse from the lumen to the wall matrix of wood cell. The distribution of chemicals in the cell wall matrix which affects the effectiveness of preservation, depends on (Cooper, 1988):

- Wood species
- Cation exchange reactions
- Treating solution pH

The American Wood Preservers’ Association (AWPI) specifies three formulations for CCA (Table 2.4). The differences of the A, B and C types are in the relative proportions

(oxide basis) of chromium, copper, and arsenic. As CCA-C offers the best combination of performance and leach resistance, most of the produced CCA wood is treated with type C of CCA (Tom, 2001). The use of CCA-B is currently confined to field and remedial treatments, and relatively few treaters use CCA-A.

All the components of CCA have important roles in preservative properties. Fixation of CCA is a part of the complex reduction reactions of chromium from the hexavalent to trivalent valence state. These reactions cause insolubility of CCA in the wood, which resists leaching and provides lengthy service. even when the wood is in contact with ground.

Table 2.4: Composition of three CCA formulations as specified by AWPA Standards

Component	Type A (percent)		Type B (percent)		Type C (percent)	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Cr as CrO ₃	59.4	69.3	33	38	44.5	50.5
Cu as CuO	16	20.9	18	22	17	21
As as As ₂ O ₅	14.7	19.7	42	48	30	38

From AWPA 1994

Copper is a very strong fungicide and because of its fungicidal properties and low mammalian toxicity, other waterborne preservatives include copper. Arsenic is an insecticide and helps to protect wood against some copper – tolerant fungi.

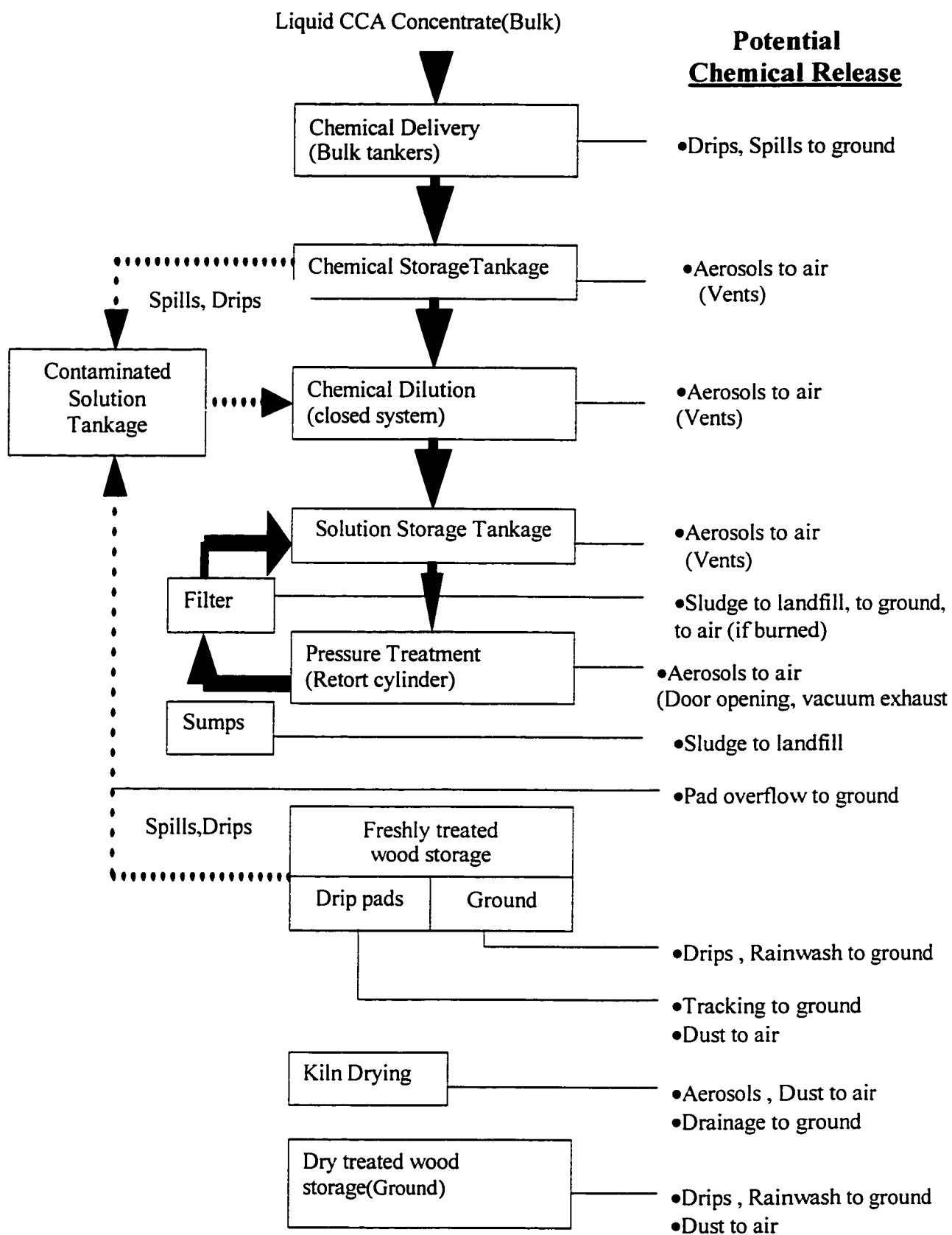


Figure 2.5: Potential chemical release from CCA pressure treating plants (Konasewich and Henning, 1998)

Since preservative composition can affect fixation and thus the leachability of chemicals, the amount of added chemicals to the wood is very important. The retention level and required amount of chemicals vary with the intended use of the product and the place of usage. AWPAs standards list seven amounts of CCA for different usages (Table 2.5).

Table 2.5: Retention levels of CCA active ingredients

Exposure	Retention level (kg/m ³)
Above ground	4
Ground contact	6.4
Poles and foundations	9.6
Land and freshwater piling	12.8 and 16
Sea water application	24 and 40

From AWPAs 1994

2.4.2 CCA fixation

In general, fixation is a series of chemical reactions that reduces the leachability of preservatives during the service. A more appropriate definition of the process can be "the state of the chemical components of the preservative and wood or other substrate when all chemical reactions are complete" (Cooper and Stokes, 1993). Although it may take several weeks or even months for the fixation process to become complete, some of the reactions occur during the first hours and immediately after treatment (Cooper and Ung, 1989; McNamara, 1989).

According to Dahlgren and Hartford (1972) reports concerning extensive tests on wood floor from sapwood of pine and spruce, the fixation had three periods: momentary initial reactions, primary fixation reactions and conversion reactions. It appeared that almost instantaneously, some portions of copper and chromium react with the wood (Dahlgren and Hartford, 1972; Cooper, 1991a; Eadie and Wallace, 1962; Gray and Dickinson, 1988; Forsyth and Morrell, 1990; Levi, 1969; Pizzi, 1982; Rennie, Gray and Dickinson, 1987; Wilson, 1971). Following the initial ion exchange and adsorption reactions, the fixation continues by precipitation reactions or as Dahlgren named the “primary precipitation fixation period”. In this period the chromic acid reduces to trivalent chromium and causes a steady pH increase (Dahlgren and Hartford, 1972; Dahlgren, 1975). According to Dahlgren theory, when the pH of the wood–CCA system reaches a maximum the chromium precipitation is complete and then the primary precipitation period concludes. Some slow reactions may continue for several months as acid and tertiary copper arsenates are converted into basic copper arsenate. During this period the pH of the system varies because of consumption of liberated protons in the reduction of chromates and chromate – wood complexes to trivalent chromium in the form of $\text{Cr}(\text{OH})_3$. Some of this trivalent chromium forms tertiary chromium arsenate with AsO_4 liberated from other reactions. The final equilibrium fixation products as copper fixed to the wood are: CrAsO_4 , $\text{Cu}(\text{OH})\text{CrAsO}_4$, and $\text{Cr}(\text{OH})_3$.

2.4.3 Factors affecting fixation

Many factors affect the rate and degree of fixation of preservatives like wood properties, treating factors (such as preservative formulation, preservative retention, and processing techniques, as well as post-treatment conditioning factors, such as temperature, humidity, and air flow), and dimensions of the treated product.

1. Wood properties:

Lignin structure and content, extractive content, and pH, are the wood properties that affect fixation.

- pH : The wood's natural pH may affect fixation by altering the amount of hexavalent chromium fixed to the wood. For species with a high pH such as beech (pH =5.6), the fixation process was longer than for more acidic species like ponderosa pine (pH =3.7), as Dahlgren(1975) found in his work with several species of softwoods and hardwoods. The possible reason is that species with low pH tend to precipitate more hexavalent chromium early in fixation (Dahlgren, 1975).
- Lignin type and structure: Chromium and copper compounds form more stable complexes with guaiacyl units of lignin, such as found in

softwoods, than with the syringyl units common in hardwood fibers (Pizzi, 1983) then the type and amount of lignin can also influence fixation.

- Temperature and humidity factors: As the factors that speed drying of wood, make the fixation process faster, then elevated temperature, low humidity, and air flow increase the rate of fixation (Lebow, 1996).

2. Preservative formulation:

Researcher noted that CCA formulations with low proportions of chromium, leach more arsenic and copper (Lebow, 1996).

3. Concentration and retention level:

The preservative concentration affects the pH. Increasing the concentration, decreases the pH of the system and can subsequently accelerate the rate of fixation (Lebow, 1996).

4. Product dimension:

The higher leaching rates have generally resulted from the use of small-sized samples with a high proportions of exposed end-grains.

2.5 Leaching

2.5.1 General remarks

Leachate is the liquid that is produced when rain falls on a landfill or buildings, sinks into the wastes, and picks up chemicals as it seeps downward. In respect to environmental aspects, the leaching of compounds is an important issue for construction materials and their leaching behaviour should be checked during their overall life cycle, from the production time until reuse or disposal.

Table 2.6: Leaching hazards for preservative treated wood

Degree of wetting	Risk of leaching	Typical application
Interior, fully protected from liquid water	No leaching	Framing lumber, joists, flooring
Interior, occasional wetting	No or slight leaching	Sillplates
Exterior, intermittent wetting	Periodic moderate leaching	Windows, fascia boards, decks, fence boards
Exterior, permanent wetting	severe leaching	Wood foundations, utility poles, marine piling, piers, cribs, cooling towers

Ref.(Morris, 1996)

In the late 1980s the treated wood became one of the environmental concerns and because of chemical leaching from disposed or in service preserved wood, the concerns have increased. After treatment there are three stages in the treated wood lifecycle that can be identified (Sloot et al., 1997):

- Storage at the treatment facility
- Actual service (Table 2.6)
- Decommissioning and waste phase

There are several factors, affect leaching of preservatives from wood. According to Sloot (1997) they are classified as three main groups, which are shown in Table 2.7. Physical and chemical factors are discussed in more detail below.

2.5.2 Physical factors

There are some physical processes that the leaching of preserved wood depends on, including (Cooper, 1994):

- Wetting of the treated wood by capillary absorption.
- Diffusion penetration of moisture into the wood.
- Hydrolysis or solution of the components of complexed preservative chemicals.
- Diffusion of the dissolved components to the surface.
- Washing away of the dissolved material.

All the above mentioned processes show the important role of water in leaching from wood. Water acts as a medium for leaching of fixed preservative components in several ways. As the physical nature of the wood affects moisture absorption, hydrolysis and solution of preservative chemicals as well as diffusion of the dissolved material out of wood then the extent of leaching from preserved wood depends on the physical nature of the wood (Table 2.7). For example:

- Permeability affects the preservatives penetration in wood then it might affect the leaching of the chemicals out of the wood (absorption of moisture, diffusion of moisture and dissolution of salts in treated wood).
- High density or low permeability makes wood more resistant to leaching (Sloot et al., 1997).
- Temperature affects diffusion and dissolution, thus it has a significant effect on the leaching.
- The shape, size volume and proportion of the end grain in wood affect leaching. Small sized samples increase the leaching rate because of the high surface area to volume proportion, which increases the rate of wetting and the relative area exposed to the leaching.

- Exposure time is an important factor, it seems that the majority of leaching from treated wood occurs during the initial exposure to the leaching medium.

Table 2.7: Factors affecting the leaching of preserved components from wood

Other relevant factors	Physical factors	Chemical factors
The natural properties of wood (e.g. permeability, pH)	Absorption	pH
Preservative treatment	Diffusion	Ionic strength
Fixation	Dissolution	(Organic)Acids
	Temperature	

Ref (Sloot et al. 1997)

The other physical factors that affects the leaching extent is the way that the wood is exposed to the leaching conditions as described by Cooper (1994). For example:

- Treated wood that is exposed to water or wet soil continually leach more than wood exposed to occasional rainfall.
- A continuous light rainfall causes more leaching than a short heavy rainfall.
- Wood submerged permanently in water leaches more than wood used aboveground (such as fences, boards and decks) and exposed to intermittent rainfall.

- As the vertical exposed wood is subjected mainly to the driving rain from one direction, it leaches less than horizontally applied decking.
- Wood exposed to high rainfall under moderate annual temperature leaches more than wood in colder or drier climates (Cooper, 1994).

2.5.3 Chemical factors

Referring to Table 2.7 there are several chemical factors that affect the leaching.

- pH of surrounding medium affects the leaching rate of preservatives, the acidic condition, as well as alkaline medium (e.g. NaOH) (Cooper, 1991a) can increase the leaching rate.
- Natural pH of wood (between 4.6 to 5.3 depending on species with the extremes of 3-8) is an important factor as it is capable of buffering the acidity of the leachant during acid rain.
- Acid type is important for example use of citric acid causes much higher leaching than sulfuric/nitric acid solution (Cooper, 1991a). The organic acids which can interact with treated wood during service conditions may affect leaching the

chemicals too, for example peaty organic soils or water containing fulvic or humic acid and wood silos containing lactic, formic, acetic and other silage acids.

- The ionic strength of the medium affects the leaching of preservative by increasing the rate of leaching when treated wood is in contact with water having high salt content.
- The degree of fixation of chemicals affects leaching of chemicals from wood.
- An important factor in both the mobility and toxicity of leached preservatives is the form in which the chemicals leave the wood. Although chromium and arsenic may exist in either of two stable valence states (Cr^{+3} , Cr^{+6} , As^{+3} , As^{+5}), however their properties are completely different. Copper remains less stable in the environment in any other form than the +2 valence.

2.5.4 Speciation

2.5.4.1 Chromium

Chromium is the least mobile of the CCA chemicals and its mobility depends on its valency. Trivalent chromium is very reactive with organics and fixes to soil and sediments quickly. Hexavalent chromium is more soluble but less absorbed and the rate of its movement through soil and groundwater is the same (Rouse and Pyrih, 1990). The

valence state of chromium is a function of the oxygen content and redox potential, pH, the presence and type of suspended inorganics and dissolved organics, when it introduced into water and soil (Florence and Batley, 1980).

Hexavalent chromium is the most stable form in equilibrium with atmospheric oxygen when there are no organic compounds in the media (McGrath and Smith, 1990). However, in the presence of organic compounds, Cr (VI) may be reduced to Cr (III) (Cox and Richardson, 1979) same as the reactions take place within treated wood (Lebow, 1996). The laboratory tests have shown that:

- humic acids can reduce Cr(+6) but the reaction does not proceed rapidly under most conditions(Weber, 1988).
- Iron reduces chromium and the reaction depends on the presence of the excess iron (Schroeder and Lee, 1975).
- Sulfides can also reduce chromium and this can be an important process near the sediments and where sulfides are produced by decomposition of organic compounds (Lebow, 1996).
- In soil when there are electron donating compounds the chromium is reduced to trivalent state and this reaction is faster in acid soils (McGrath and Smith, 1990).

- In oxidation water, for example in a rapidly moving stream especially when it is alkaline or hard water, the oxidation process can occur and chromium (+3) oxidise to chromium (+6) (Florence and Batley, 1980).

The resistance of trivalent chromium to leaching or immobility depends on its ability to form inert complexes with organic and inorganic ligands (Bartlett and Kimble, 1976).

As mentioned, both hexavalent and trivalent chromium are stable in the environment. According to Lebow (1997), if chromium leaches from treated wood in the trivalent form, inert complexes with organic and inorganic ligands might be formed and then chromium mobility under these conditions, would be associated to the water soluble complexes or events that move through soil and sediments. If the leached chromium is in the hexavalent form, it can remain in this more soluble, mobile, biologically available state especially in alkaline water (Lebow, 1996).

2.5.4.2 Copper

Unlike chromium, neither the movement and solubility of copper is highly dependent on changing the oxidation state nor are the toxicity and solubility of Cu (I) and Cu (II) widely different from each other. Although Cu (II) is much more stable in most aerated conditions, Cu (I) can exist in saturated soils with water when there is a low

concentration of copper. In the absence of organic and inorganic adsorption agents, water soluble copper is in the forms of $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$, $[\text{Cu}(\text{H}_2\text{O})_5]^{+2}$, CuOH^+ below pH 7 and species $\text{Cu}(\text{OH})_2, \text{CuCO}_3$ at pH greater than 7. Reactions with organic and inorganic compounds affect solubility and the form of copper (Baker, 1990; Parker, 1981; McBride, 1981). For example copper deposited in sediments from pollution sources is usually complexed with organics or precipitated with inorganic oxides (Messure et al., 1991). Copper solubility is greatest at the acid and alkaline extremes and minimum at around pH 7, in most environmental exposures (Baker, 1990; Parker, 1981; McBride, 1981).

Adsorption of copper is a very important factor in determining its mobility and is influenced by pH, amount and type of adsorbents. At low pH, because of proton adsorption, the charge of adsorbents tends to be positive and at high pH they become more negative (James and Barrow, 1981). Adsorption increases with increasing pH and this increases copper precipitation as copper oxides, hydroxides and carbonates at neutral and alkaline pHs (Baker, 1990; McBride, 1981; James and Barrow, 1981).

To be noted that the accumulation of copper in fine sediments can be important when there is CCA treated wood in seawater (Weis and Weis, 1992; Weis et al., 1993). Copper in sediments is not bonded as strongly as chromium (Giblin and Valiela, 1983) and some of deposited copper in sediments may be solubilized under oxidizing conditions, possibly because of the formation of soluble hydroxides and carbonates (Lu and Chen, 1976). But

in reducing environment, the solubility of copper in sediments decreases, possibly through the formation of sulfides (Lu and Chen, 1976).

2.5.4.3 Arsenic

Arsenic is more soluble in water than copper and chromium and is less likely to be adsorbed. Its mobility in the environment can thus be considerable. Like chromium, it exists significantly in two valence states, As (III) and As (V). It almost always forms oxyanions. The trivalent arsenic is much more toxic than pentavalent arsenic and methyl arsenic forms are usually less toxic than the inorganic forms (O'Neill, 1990).

There are many types of microorganisms that change inorganic arsenic to more soluble species. However, their capability in the presence of chromium and copper, has not been confirmed but there is no doubt they affect the mobility and fate of arsenic when arsenic enters the environment. For example, there are some kinds of soil fungi and bacteria that convert arsenic to arsenite (Bautista and Alexander, 1972; Osborne and Ehrlich, 1976) or they can methylate the oxyanions to monomethylarsonic acid, dimethylarsinic acid, trimethylarsenic oxide, trimethylarsine, and dimethylarsine. The methyl-arsines are generally volatilized (O'Neill, 1990; Braman, 1975).

In water, arsenic enters as arsenic acid (As (V)) and by aluminum, mineral clay or iron, precipitate into sediments where it is reduced to trivalent form and methylated by microorganisms. The soluble methylates then move to the water surface, react with

oxygen and the produced oxyanions precipitate again by reactions with inorganic constituents (Ferguson and Gavis, 1972; Wood, 1974). The microorganisms and the involved arsenic species are two factors that affect the biomethylation reactions (O'Neill, 1990; Cheng and Focht, 1979). Some microorganisms can methylate arsenic compounds completely and over a wide range of pH, but some can only methylate specific species and to a lesser degree (O'Neill, 1990). In very wet soils As(III) may be the most stable form, although complexing species and methylating organisms in soil will alter the As(V)/As(III) equilibria (Lebow, 1996). A study of soils in England showed that As (V) made up 90% of soluble arsenic in aerobic soils but only 15-45% of the soluble arsenic in anaerobic, waterlogged soils and in mineralized areas. A small amount of monomethylarsenic acid was found (O'Neill, 1990).

In oxygenated water, inorganic arsenates are the dominant species and arsenites are usually formed in sediments or deep waters (Florence, and Batley, 1980; Ferguson and Gavis, 1972). A study on deep waters below the photic zone, showed the existence of a small amount of organic arsenic. It is suggested that the organic form was produced by plankton in the photic zone. The studies noted that phytoplankton can reduce and methylate up to 50% of As (V) in the media (Sanders and Windom, 1980). The inert organic arsenics may be more toxic than inorganic forms (Riedel et al., 1989). As treated wood is usually placed in shallow water, then there is the probability of reactions by photic zone microorganisms for arsenic leachate of treated wood (Lebow, 1996).

In anaerobic conditions, like seawater sediments. it is favorable for arsenic (V) to be reduced to arsenic (III) (Riedel, et al., 1989). Brannon and Patrick (1987) found that although there were organic forms of As(III) in the sediments of several harbors which they collected, arsenite was the predominant form and even added arsenate to sediments was reduced to trivalent form. Then the solubility and release of arsenic from sediments is related to oxygen content of water. In anaerobic conditions. more arsenic is released. Arsenic can be adsorbed and removed from solution by organic compounds as well as inorganic compounds such as iron, aluminum, calcium and clay which prevent arsenic leaching (Lebow, 1996). The studies show that the released arsenic to environment can be mobile because of the movement of sediments in high water flow. solubility of arsenic species and changing of the species type by microorganisms.

2.6 Landfills

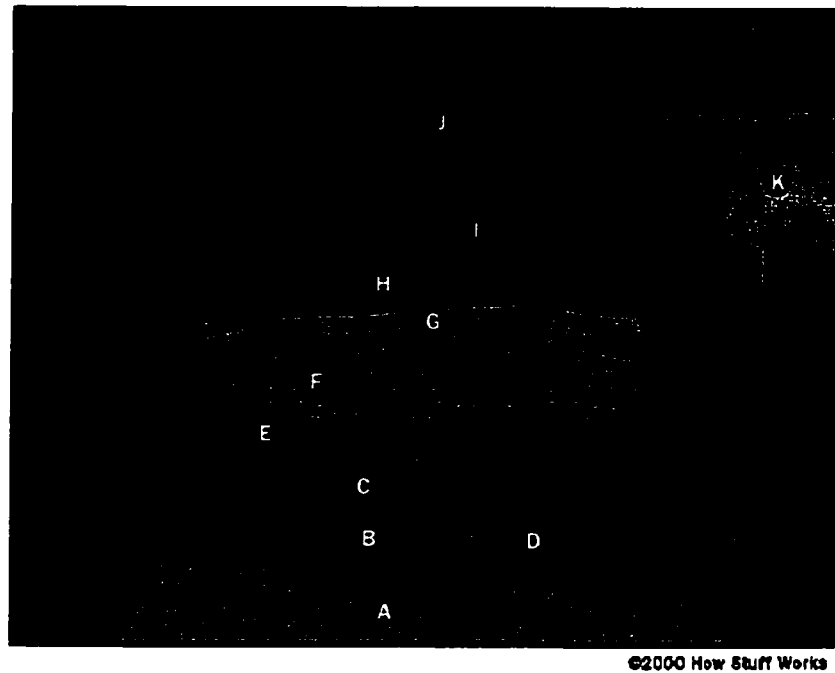
2.6.1 Introduction

Landfill is a built structure in or on the top of the ground to isolate the trash and wastes from the surrounding environment especially groundwater. and keep them dry and not in contact with air. They have bottom liners and daily covering of the soil to complete isolation. In sanitary landfills, the clay liner is used. However, in municipal solid waste (MSW) landfills, the synthetic plastic liner isolates the waste from the surrounding environment (Freudenrich, 2002).

2.6.2 Municipal landfill structure

The main parts of landfills are:

- The bottom liner system is usually of durable synthetic plastic such as polyethylene, high density polyethylene or polyvinylchloride with the 7.62×10^{-5} to 2.54×10^{-4} m (30 to 100 mils) of thickness separates the trash and leachate from the outside soil and groundwater. The plastic layer may be combined with compacted clay soil to make an additional liner or can be surrounded on either side by a fabric geotextile mat for more resistance.
- **Cells** are storages of trashes and are designed for making more space to increase the usable life of landfill, the trashes are compressed by heavy equipment such as tractors, bulldozers, rollers and graders.
- **Storm water drainage system** collects the rain fall on the landfill to keep them as dry as possible and decreases the amount of leachate. The plastic pipes and storm liners conduct the collected water from landfill areas to concrete or gravel lined drainage ditches surrounding the landfill and then to the collection ponds.



- | | |
|----------------------------|------------------|
| Ⓐ Ground Water | Ⓖ Drainage Layer |
| Ⓑ Compacted Clay | Ⓗ Soil Layer |
| Ⓒ Plastic Liner | Ⓘ Old Cells |
| Ⓓ Leachate Collection Pipe | ⓵ New Cells |
| Ⓔ Geotextile Mat | Ⓚ Leachate Pond |
| Ⓛ Gravel | |

Figure 2.6: The cross section of a municipal solid waste landfill.
 (The arrows show the leachate direction)
 Ref. (Freudenrich, 2002)

After settling the solid particles and when the performed tests showed that there is no chemical leachate, the water is pumped off the site (Figure 2.6).

- **Leachate collection system** collects the leachates from the trashes. The perforated pipes through the landfills drain the carried leachate into leachate pipes, which carries the leachate into the collection ponds by gravity or pump. The water in the ponds will be tested for the different chemicals and will be treated as waste or sewage water (Figure 2.6).

- **Methane collection system** collects the methane gas, produced during breaking down of the trash by bacteria under anaerobic conditions of landfills. As methane gas is an explosive gas, embedded pipes within the landfills collect it before venting and burning (Figure 2.9).



Figure 2.7: Storm drainage pipe drain into the ditch
Ref. (Environment Canada, 2001)

- **Cap or covering** covers the top of landfill. Usually each cell is covered by fifteen centimeters of compacted soil every day and finally by finishing the cell. the section is covered by a 1.02×10^{-4} m (40 mil) polyethylene cap, followed by a sixty-one centimeter layer of compacted soil, permanently and then vegetation is planted to prevent the erosion of the soil.

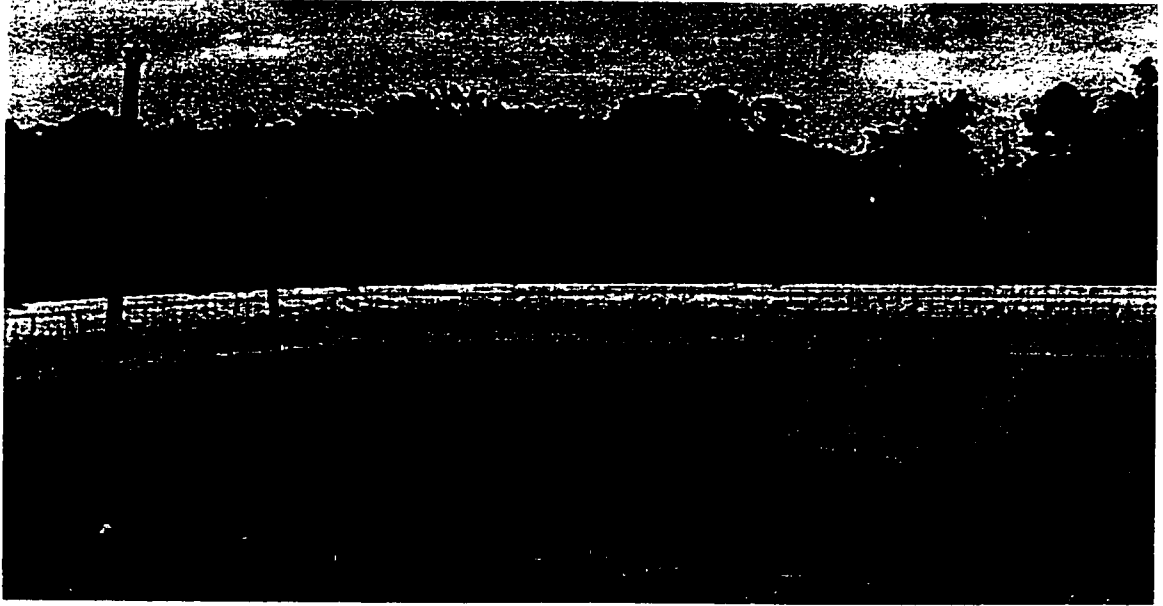


Figure 2.8: A leachate pond
Ref. (Environment Canada, 2001)

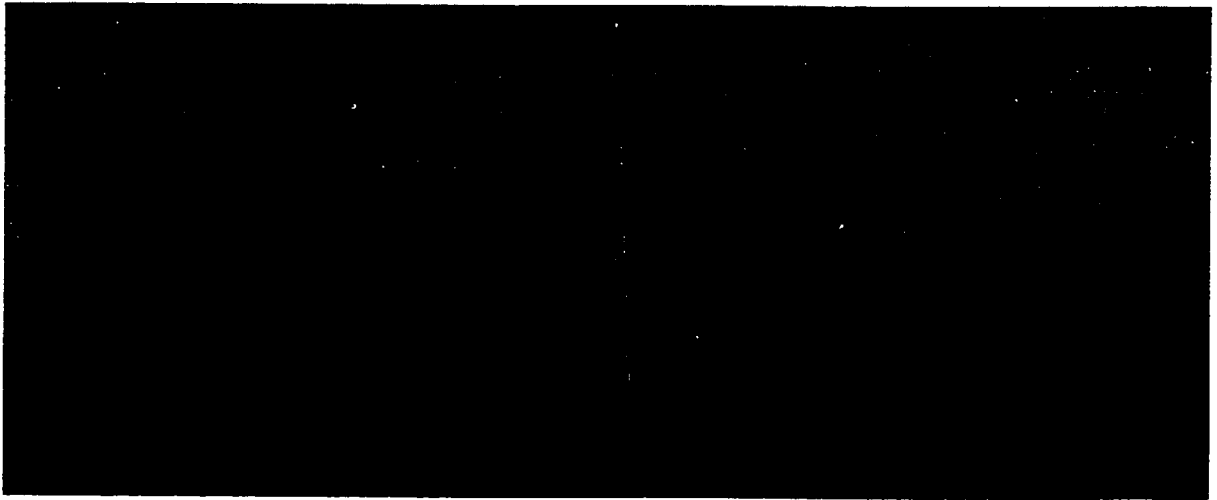


Figure 2.9: Methane collection pipe
Ref.(Environment Canada, 2001)

Chapter 3

Material and methods

3.1 Introduction

The goal of these experiments is to evaluate and compare the effect of time, pH, temperature and the type of acid on leaching of chromium, copper and arsenic from disposed CCA (*Chromated Copper Arsenate*) treated wood, under landfill condition, and to determine the biodegradability of leached wood. The leaching test was based on the *TCLP* (Toxicity Characteristics Leaching Procedure) method (US EPA Method 1311). The wood digestion was based on *Acid Digestion of Sediments, Sludge and Soils* method (US EPA Method 3050B). The leachate digestion was based on the *Nitric acid digestion method*, Method 3030E (Clesceri, 1989).

To measure copper and chromium, Atomic Absorption (AA) Spectrophotometer (Perkin Elmer Analyst 100) was used and arsenic was measured by Inductively Coupled Plasma

(ICP). Atomic absorption uses the absorption of light to measure the concentration of gas-phase atoms. The light source is usually a hollow-cathode lamp of the element that is being measured. The primary goal of ICP is to get elements to emit characteristic wavelength specific light, which can then be measured.

3.2 Materials

3.2.1 Wood

CCA treated wood is the most frequently used wood, for exterior applications, in Canada. This greenish wood is sold in different renovation stores in different sizes. According to Forintek Canada Corp., the most frequently used Canadian softwood species for exterior applications are:

- Western Red Cedar
- Eastern White Cedar
- Pine (white, Murray, red)
- Douglas fir
- Spruce

The wood samples for these experiments were 2 pieces of 2.5 cm x 15cm x 12.5 cm (1inch x 6 inch x 5 inch) treated wood (the dimensions are inches which is used as wood specification in the store). According to the seller's information (RONA), for this size of wood, they usually use Gray Pine species (To be mentioned that the most disposed wood

are the old preserved wood and the amount of their remain preservatives are less than new wood).

3.2.2 Acids

According to TCLP method the acid used for leaching is acetic acid (0.1N) but as in landfills the buried materials would be exposed to nitric acid and sulfuric acid during acid rains then in these experiments, nitric, sulfuric and acetic acids with pHs 3.4 and 5 are used. Specification of used acids are as follows:

Nitric acid : provided by Fisher Scientific, trade metal grade, 67-71% purified.

Sulfuric acid :provided by Fisher Scientific, reagent A.C.S, 95-98% purified.

Acetic acid : provided by Fisher Biotech, sequencing grade (Aldehyde free), 100% purified.

3.3 Procedure

To evaluate the leaching process in landfills, the leaching tests were performed under the same conditions as landfills. The chosen conditions were:

- Temperatures: 15 °C, 25 °C and 35°C.
- pHs: 3.4 and 5.
- Leaching time: 5 days, 10 days and 15 days.
- Leaching acid: acetic, nitric and sulfuric acid.

3.3.1 Wet digestion

The method was used to prepare leached wood samples, further by Atomic Absorption(AA) or Induced Coupled Plasma (ICP) to be able to measure the amounts of metals remain in wood samples.

3.3.1.1 Wet digestion samples

A wet digestion method is used for wood samples. The organic materials react with nitric acid and leave the flasks as CO₂ and the metals remain in solution to be measured by ICP or AA.

- 3 x 0.5 g unleached wood for wet digestion and one blank.
- 0.5 g of 5 days leached wood by sulfuric acid (pHs=3,4,5), nitric acid (pHs=3,4 and 5), acetic acid (pHs=3,4 and 5) and one blank.
- 3 g of all the leached wood in acetic acid and T=25°C (9 samples), leached wood by nitric acid (0.1N) and sulfuric acid (0.1N) (15 days, 25°C) (6 samples) and one blank.

3.3.1.2 Method

The wood was ground to very fine chips (does not pass through sieve mesh10), dried in a gravimetric oven at 90°C (if the wood was wet, for example after recovering from leachates), weighed and a certain amount of wood (usually 3g) was taken. Concentrated nitric acid (about 70%) was added and the wood was left without any coverage, in nitric acid for several days. A brown, yellowish fume started to release. As the final step, it was put on hot plates until it completely dissolved in nitric acid and no more brown smog was given off. When the digestion finished, 5% nitric acid was added until a certain volume (usually 50mL) was reached. The solution was filtered by a No.41 Whatman filter (if it was required). The samples were later analyzed for arsenic, copper and chromium. Always one flask without any wood was taken as the blank and the same solutions were added to the blank.

3.3.2 Dry digestion

In this method, (usually) 3 grams of very fine ground chips of dry wood were taken in crucibles, burned or charred in Muffle furnace at 450 °C for about 4 hours (it takes about 1 hour for the furnace to reach temperature of 450 °C). The high temperature causes the organic and volatile materials to leave the samples and the metals remain as ashes. After cooling, the ashes were weighed again. 5mL of nitric acid 6N was added to all ashes and put them over hot plates to evaporate the nitric acid. This step was repeated three times. Finally 5 mL of 5% nitric acid was added, the solution was filtered by a No.41 filter and

brought to a certain volume (usually 50 mL) by a 5% nitric acid. All the experiments were performed with the appropriate blanks. The weight of charred ash samples are as follows:

Table 3.1: Ash weight of leached wood at 35°C

T=35°C	5 days	10 days	15 days
pH =3	0.0081g	0.0072g	0.0614g
pH =4	0.0124g	0.0085g	0.0134g
pH =5	0.0236g	0.0274g	0.0245g
Unleached wood = 0.0186g			

Table 3.2: Ash weight of leached wood at 25°C

T=25°C	5 days	10 days	15 days
pH =3	0.0081g	0.0072g	0.0614g
pH =4	0.0124g	0.0085g	0.0134g
pH =5	0.0236g	0.0274g	0.0245g
Unleached wood = 0.0186g			

Table 3.3: Ash weight of leached wood at 15°C

T=15°C	5 days	10 days	15 days
pH =3	0.0071g	0.0074g	0.0065g
pH =4	0.0127g	0.0115g	0.0110g
pH =5	0.0256g	0.0257g	0.0254g
Unleached wood = 0.0158g			

Table 3.4: Ash weight of leached wood by nitric and sulfuric acid

T=25°C	NITRIC ACID	SULFURIC ACID
pH =3	0.0267	0.0293
pH =4	0.0260	0.0298
pH =5	0.0258	0.0308
Unleached wood	0.0169	

However the same amounts of wood were taken but after charring the weight of ashes were different. Arsenic was measured by Inductively Coupled Plasma (ICP), chromium and copper were measured by Atomic Absorption Spectrophotometer (Perkin Elmer Analyst 100). The calculated results based on the weight of ashes showed that compared to the wet digestion, the error of dry digestion method was more, and the results of wet digestion were more reliable.

3.3.3 Microwave digestion

The system was *O.I. Analytical microwave digestion system* (includes microwave and relevant tubes, vessels, vents), which was controlled by relevant software. A sample of 0.5 g of ground tiny chips of wood was soaked in concentrated nitric acid (70%) in microwave special plastic vessels, which are resistant to temperature and pressure, for three days. Then the system tubes and relevant pipes, vents and so on were installed. It took about 30 minutes under maximum pressure of 891 kPa (130 psi). After digestion, analysis for arsenic, chromium and copper was performed.

Compared to wet digestion the results were more consistent but each time, more than 0.5 g of wood could not be used in each vessel according to microwave instruction manual. Since more wood is needed to be digested, the wet digestion was chosen for all the leached and unleached wood samples.

3.3.4 Leaching method

The leaching test used was based on the leaching test TCLP (Toxicity Characteristics Leaching Procedure).

3.3.4.1 The wood preparation

The CCA treated wood was ground (does not pass through sieve mesh10). Ten grams of ground chips of wood were added to 1 liter of solutions to obtain the ratio of 10:1 for all the samples (The suggested ratio of 20:1 by TCLP method was changed to 10:1 to ensure the amounts of leached metals were more than the minimum detection limits of instruments).

3.3.4.2 Leaching solutions

In all the solutions the normality (number of equivalents per liter of solution) of the acid was approximately the same (0.1N) and the pH was adjusted by adding NaOH (1N).

- Acetic acid: 20 mL of acetic acid was added to 3200 mL distilled water and adjusted to different pHs by adding NaOH (1N) and brought to 3.5 liter by distilled water.
 - pH =3: no NaOH was added as the pH of glacial acetic acid was around 3.
 - pH =4: about 50mL of NaOH and 3430mL of distilled water were added.
 - pH =5: about 225mL of NaOH was added (as US EPA Method 1311) and the rest was distilled water.

- Nitric and sulfuric acids: The leaching tests with nitric and sulfuric acids were prepared for 15 days and at $T=25^{\circ}\text{C}$, so one liter and half of solutions was prepared for each pH (1L leachate and about 500 mL as blank).
 - For nitric acid, 9.5 mL of concentrated acid was added to 1 liter of distilled water and adjusted to pHs by NaOH (1N)
 - For sulfuric acid, 4.2 mL of concentrated acid was added to 1 liter of distilled water and adjusted to pHs by NaOH (1N)

3.3.4.3 Leaching test

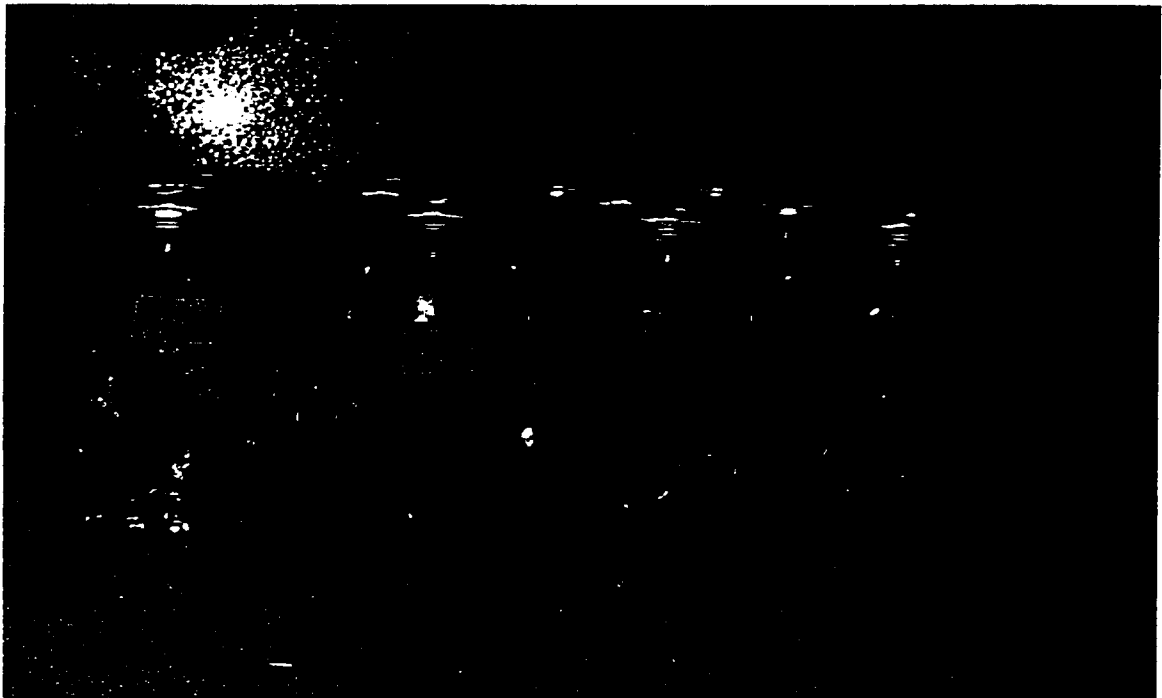


Figure 3.1: Leaching containers

For each pH, four mason jars (1 liter) were used, one as blank and the others for 5 days/ 10days/15days/ tests. Then at each temperature, twelve jars were placed inside the low temperature incubator (Fisher Scientific) and were removed after 5 days, 10days and 15 days (Figure3.1).

The incubator was set to 35°C for the first batch then set to 15 °C and finally set to 25°C, each time for 15 days. During 15 days the mason jars contained of 10g wood and 1liter leaching solution (with pH values 3,4,5) and the blanks (solutions without wood) were placed inside of incubator and after 5 days, 10 days and 15 days the jars were removed, and then wood and leachates were separated by using a Whatman filter No.1.



Figure 3.2: Leaching containers

For each sample the wood was washed by 100 mL of distilled water, transferred to a crucible and dried in the oven (when the difference of weight of wood before and after 1 hour being in the oven, is less than 2% then it is dried). The dried woods were kept in plastic bags and the filtered leachates, were digested .

3.3.5 Leachate digestion

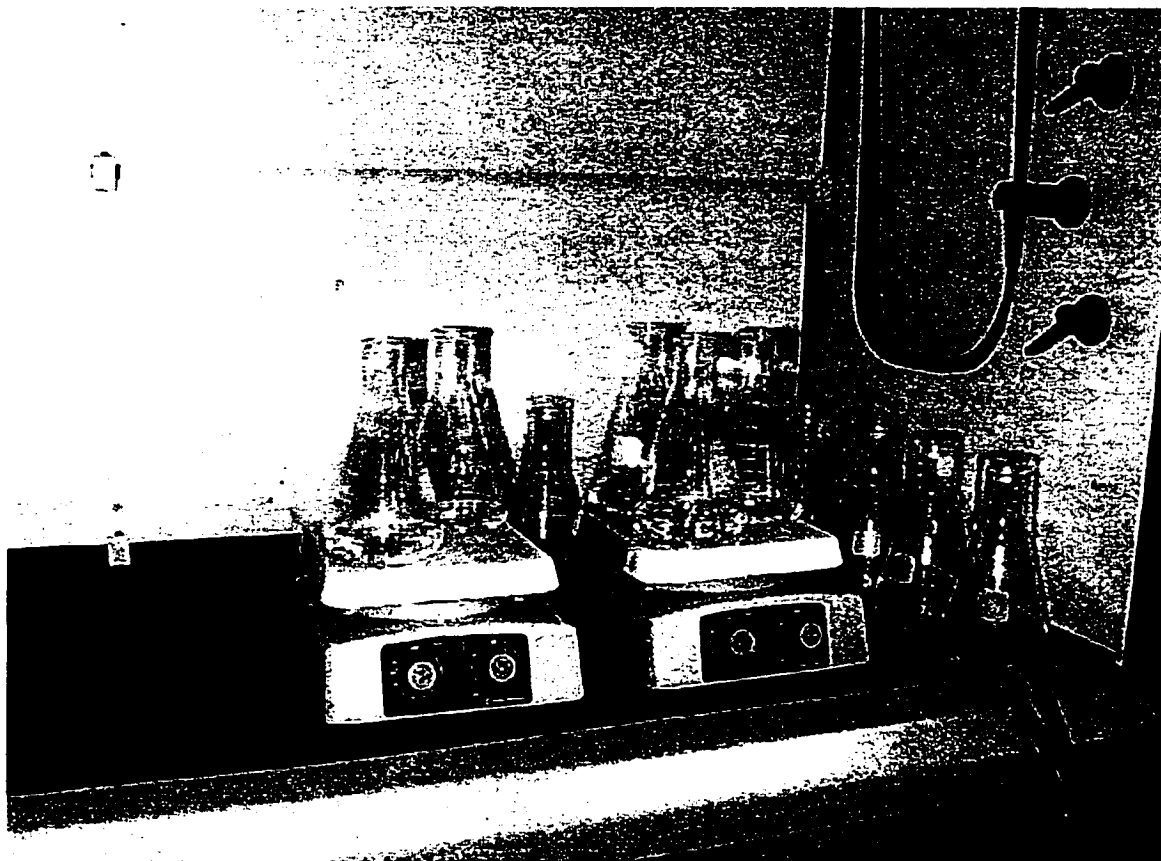


Figure 3.3: Leachate digestion

Twelve flasks of 500 mL were washed with soap, then by chromic acid and then rinsed by water and distilled water and put in oven to be dried. A volume of 40mL of concentrated nitric acid (70%) was added to 200mL of leachates in 500mL flasks. After adding some glass beads, the solutions were heated on hot plates to reach less than 100mL of volume (It took about 12 hours to heat). They were left to cool. Finally the solutions were brought to a volume of 100mL by nitric acid (5%) and were transferred to the plastic bottles.

3.3.6 Biodegradation method

3.3.6.1 Nutrient and media preparation:

- 2.5 mL of nutrients (required minerals for living fungi listed in Table 3.5) were taken and diluted to 50 mL by adding distilled water (20 times dilution or 1:20)
- 0.05 g yeast per 50 mL solution (1g/L)
- 10mg sucrose per 100 mL solution (100 mg/L)
- Soil (0.1g /50 mL)
- pH was adjusted to 5.25 by adding 5M HCl

Table 3.5: Ingredients of used nutrients for biodegradation test

Element	Formula	Quantity (g/kg COD*)
N	$(\text{NH}_4)_2 \text{CO}_3$	84.75
P	$(\text{NH}_4)\text{HPO}_4$	22.50
Vitamins	Yeast extract	150.00
Al	$\text{Al}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$	0.03
Ca	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	10.41
Co	CoCl_2	0.06
Cu	CuCl_3	9.15
Fe	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	7.23
Mg	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	38.45
Mn	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	0.05
Mo	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot \text{H}_2\text{O}$	0.00
Ni	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.03
Zn	ZnCl_2	31.55

COD : chemical oxygen demand

3.3.6.2 Test method:

A sample of 0.5 g of wood was added to plastic tubes, followed by 4 mL of prepared nutrient solution. To keep the wood into solution, paper filter and glass beads and glass wool were added on top of the wood. Small glass tubes containing 5 mL of fresh NaOH (1N) were placed inside of each plastic tube. When the biodegradation starts the CO_2 gas is produced, NaOH would take the produced CO_2 , and then by titration of NaOH with

HCl (0.1N) the amount of produced CO₂ was determined and compared to other tubes. As CO₂ reacts with NaOH and produce H₂CO₃, which decomposes to CO₂ again, barium chloride was added to NaOH exactly before titration to react with H₂CO₃ and not let the H₂CO₃ change to CO₂ again (Harmon, 1992). The titration was prepared every week during one month and each time another fresh NaOH replaced old samples. Five drops of bromothymol blue was added to NaOH as indicator. The color of solution changed from blue to greenish color at the end point of titration.

Table 4.1 contains the amount of consumed HCl for titration. Since HCl and NaOH is a strong acid and base then at the end of titration when there is no CO₂, theoretically the volume of consumed HCl should have been 50mL according to [3.1]. But because there is CO₂ in the air and the container, then the volume of consumed acid even for blank is less than 50mL.

$$\frac{\text{Normality}_{\text{base}} \times \text{Volume}_{\text{base}}}{\text{Normality}_{\text{acid}}} = \text{Volume}_{\text{acid}} \quad [3.1]$$

Chapter 4

Results and Discussion

A series of experiments were performed to determine the leachability of CCA treated wood under various conditions. The results are presented in the following section. The copper and the chromium of all the samples were measured by an Atomic Absorption Spectrophotometer (Perkin Elmer Analyst 100) and the arsenic was measured by Inductively Coupled Plasma (ICP) at the Bodycote Analytical Laboratory (Montreal). Some samples of copper and chromium were also measured by ICP in addition to AA.

According to Lebow (1996), "Although the laboratory studies are useful as comparative tools ,they are not intended to demonstrate the amount of leaching that may occur in service conditions. Many factors that can influence leaching in service are difficult to

simulate in a laboratory; exposure environment, product size and surface area are samples.”

4.1 Equations

Equation 4.1 was used to calculate the amount of arsenic, copper and chromium in the leachate.

$$\begin{aligned}
 & (\text{sample}_{\text{metal}} - \text{blank}) \frac{\text{mg}}{1000\text{mL}} \times (\text{final volume in mL}) \\
 & \times \frac{\text{sample of le achate in m L}}{\text{total le achate in m L}} \times \frac{1}{\text{g wood}} = (\text{metal}) \frac{\text{mg}}{\text{g wood}} \quad [4.1]
 \end{aligned}$$

Equation 4.2 was used to calculate the amount of arsenic, copper and chromium, were remaining in the leached wood.

$$\text{sample}_{\text{metal}} \frac{\text{mg}}{\text{L}} \times \frac{1\text{L}}{1000\text{mL}} \times (\text{final volume in mL}) \times \frac{1}{\text{g wood}} = (\text{metal}) \frac{\text{mg}}{\text{g wood}} \quad [4.2]$$

Equation 4.3, 4.4 and 4.5 were used to calculate the amount of chromium as chromium oxide (III) (CrO_3), copper as copper oxide (CuO) and arsenic as arsenic oxide (III) (As_2O_3):

$$(\text{Cr}) \frac{\text{mg}}{\text{L}} \times \frac{\text{Mw.}(\text{CrO}_3) \text{ g}}{\text{Mw.}(\text{Cr}) \text{ g}} = \frac{\text{mg}(\text{CrO}_3)}{\text{L}} \quad [4.3]$$

$$(\text{Cu}) \frac{\text{mg}}{\text{L}} \times \frac{\text{Mw.}(\text{CuO}) \text{ g}}{\text{Mw.}(\text{Cu}) \text{ g}} = \frac{\text{mg}(\text{CuO})}{\text{L}} \quad [4.4]$$

$$(\text{As}) \frac{\text{mg}}{\text{L}} \times \frac{\text{Mw.}(\text{As}_2\text{O}_3) \text{ g}}{\text{Mw.}(\text{As}) \text{ g}} = \frac{\text{mg}(\text{As}_2\text{O}_3)}{\text{L}} \quad [4.5]$$

4.2 Leaching results

4.2.1 Unleached treated wood

To characterize the type of experimental sample wood, the unleached wood was digested and the amounts of chromium, copper and arsenic were measured. Then the amount of chromium, copper and arsenic were calculated as CrO_3 , CuO and As_2O_3 according to the equations 4.3, 4.4 and 4.5, since the percentages of CCA treated wood types are usually expressed based on the above mentioned formulas in the references. Comparison of the sample wood analysis results with all the three chromated copper arsenate (CCA) wood types (Table 2.4) shows that the sample wood is type C. As mentioned before, of types A, B and C, C is the most common type of CCA treated wood, used outdoors (Figure 4.1).

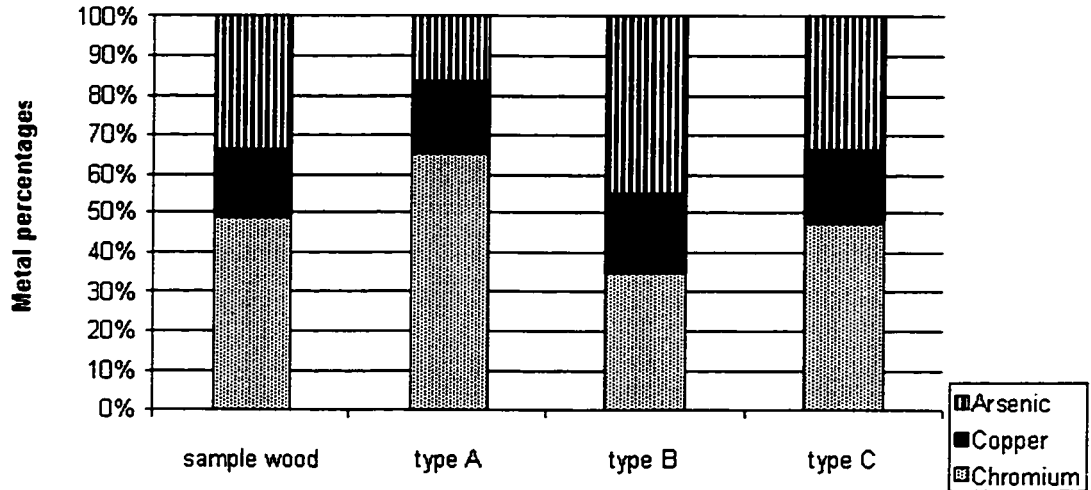


Figure 4.1: Type of sample wood

As the ratio of preservative components in CCA formulations is crucial to allow rapid and complete fixation (Hingston et al., 1999), the type of preserved wood is an important factor on wood leachability. The major difference between different types of CCA is the amount of chromium and arsenic; copper does not vary a lot. Type A is high in chromium and type B is rich in arsenic (Table 2.4), but type C is by far the most common type which have been used as it has the best leach resistance and field efficacy (Ibach,1999). According to Pizzi (1982) the ratio of As/Cu determines the fixation rate; increasing arsenic slows the fixation reactions and increasing copper stimulates them. With increased arsenic, more chromium arsenate are formed and less hexavalent chromium as HCrO_4 is available for rapid complexation with lignin but increased copper makes more hexavalent chromium as CuCrO_4 (Lebow,1996). As a consequence of this variation in different formulations, early leaching studies generated variable results, with arsenic

often proving to be the most leached element, presumably due to insufficient chromium available for fixation (Fahlstrom et al.,1967). Type C was chosen by AWPA technical committees to encourage a single standard for CCA (Ibach,1999).

4.2.2 The effect of temperature on leaching

Figures 4.2 and 4.3 show the effect of temperature on the leaching of the chromium, copper and arsenic by acetic acid (pH 5) after 5 days. To obtain the results for Figure 4.2, three 10 gram samples of ground wood (does not pass through sieve mesh 10) were soaked in 1L bottles, full of acetic acid (pH 5) at temperatures 15°C, 25°C and 35°C for 5 days. Arsenic, chromium and copper were measured for each sample. Then the ratio of each metal in each sample to the total amount of metal in unleached treated wood ,was calculated and is presented in Figure 4.3.

According Figure 4.2, the effect of temperature on leaching of chromium is less than its effect on copper and arsenic. Arsenic is less resistant to leaching when the temperature changes. It seems that the effect of temperature on chromium is a little different from the others. Copper and arsenic leached more, by increasing the temperature but chromium leaching decreases a little when temperature increases from 15°C to 25°C and increases by increasing the temperature from 25°C to 35°C.

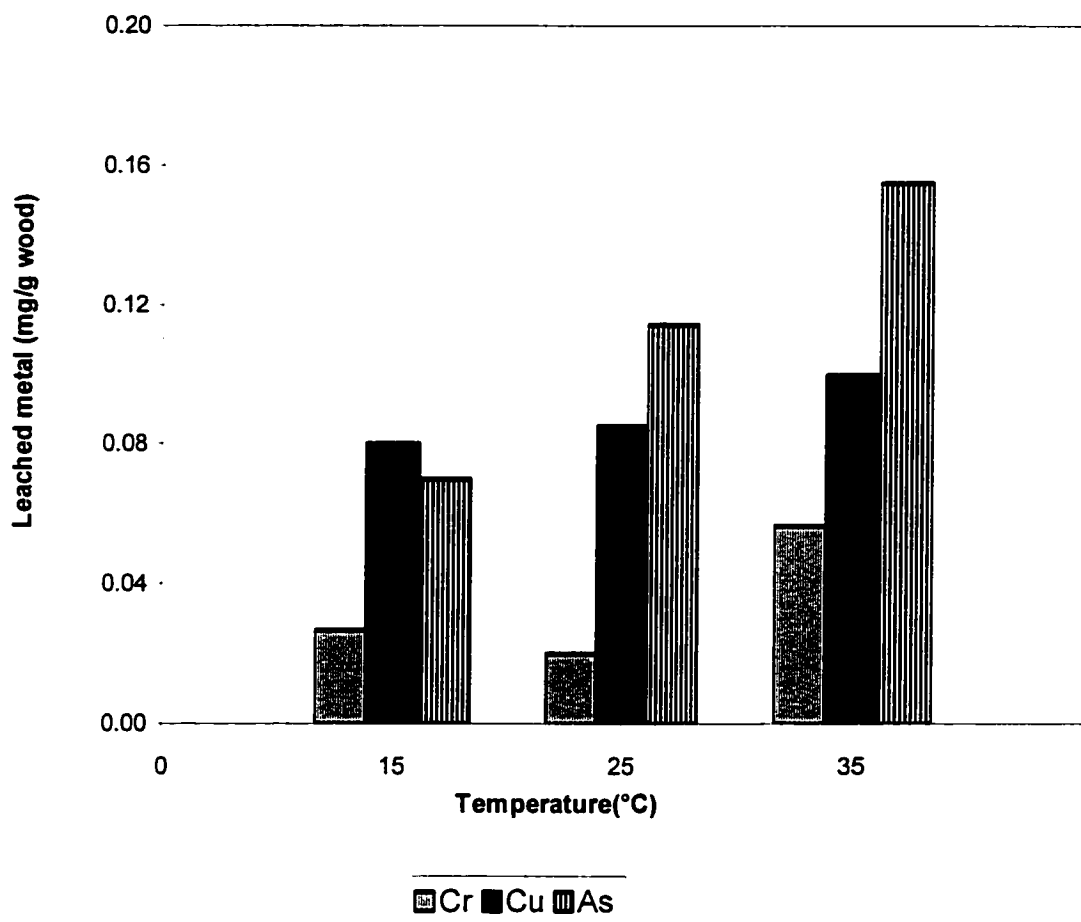


Figure 4.2: Effect of temperature on leaching by acetic acid (pH 5) during 5 days

The reason why pH=5 and 5 days leaching was chosen, was to decrease the effects of pH and time on leaching so that temperature would be the dominant factor for correct comparison and deduction. Figure 4.3 confirms that arsenic is the least resistant metal to the leaching when the temperature increases and chromium is the most.

The results of leaching tests show that, copper and then arsenic leach much more than chromium (Hingston et al.2001) and as it was mentioned earlier the speciation of metals is an important factor for leaching. But there is little research about the speciation of CCA leachates (Albuquerque and Cragg, 1995).

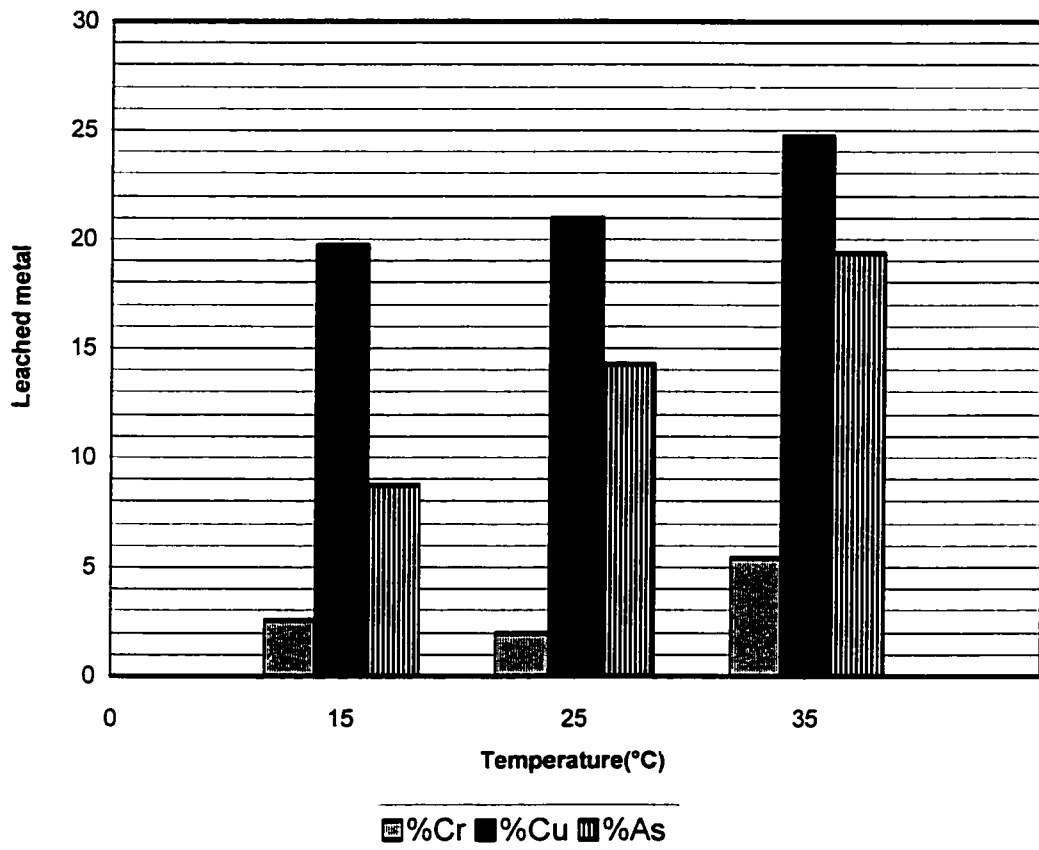


Figure 4.3: Effect of temperature on leaching percentages by acetic acid (pH5) after 5 days

4.2.2.1 Chromium

To investigate the effect of temperature on chromium more precisely, three 10 gram samples of ground (does not pass through sieve mesh 10) treated wood were soaked in three 1L bottles full of acetic acid (pH 5) for 5, 10 and 15 days at $T=15^{\circ}\text{C}$. Then the same experiments were performed but at $T=25^{\circ}\text{C}$ and $T=35^{\circ}\text{C}$ instead of $T=15^{\circ}\text{C}$ and finally the amount of chromium was measured for all nine samples. Figure 4.4 is the result of these performed experiments. Again, this experiment confirms that at 25°C , chromium leaches less than 15°C but at 35°C it increases. Figure 4.4 shows, increasing the temperature makes much chromium leach before 15 days.

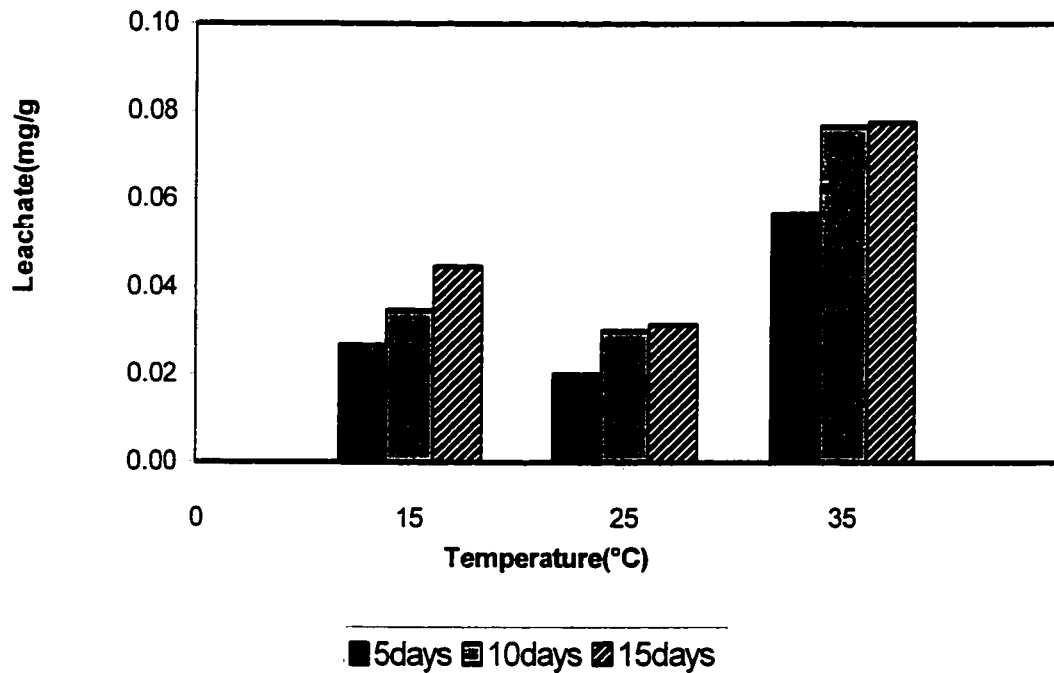


Figure 4.4: Effect of temperature on chromium leaching by acetic acid (pH 5)

4.2.2.2 Copper

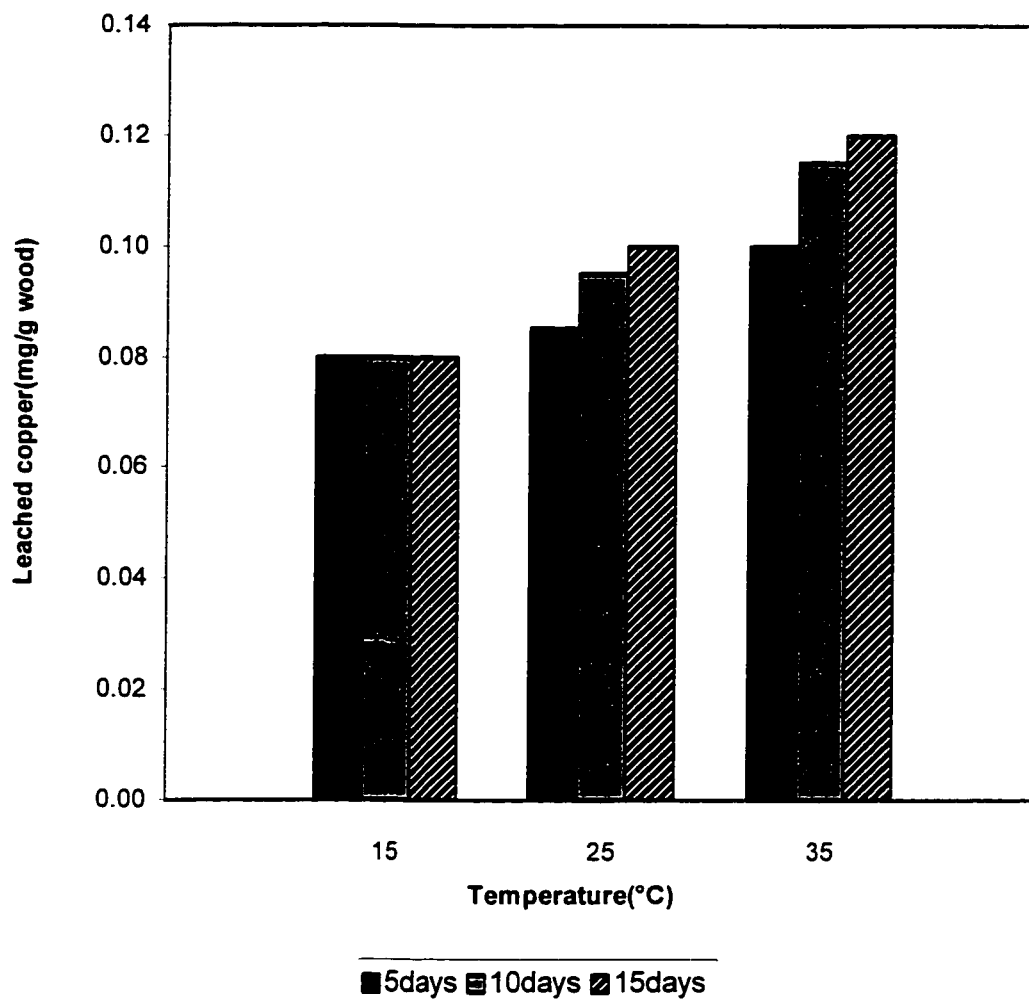


Figure 4.5: Effect of temperature on copper leaching by acetic acid (pH 5)

To find the effect of temperature on copper, the amount of copper was measured in all the same nine samples analyzed for chromium. Figure 4.5 shows that, for lower temperatures

there is no significant difference between the amount of leaching after 5 days at 15 °C. However, by increasing the temperature, copper leaches more and the effect of time on copper increases.

4.2.2.3 Arsenic

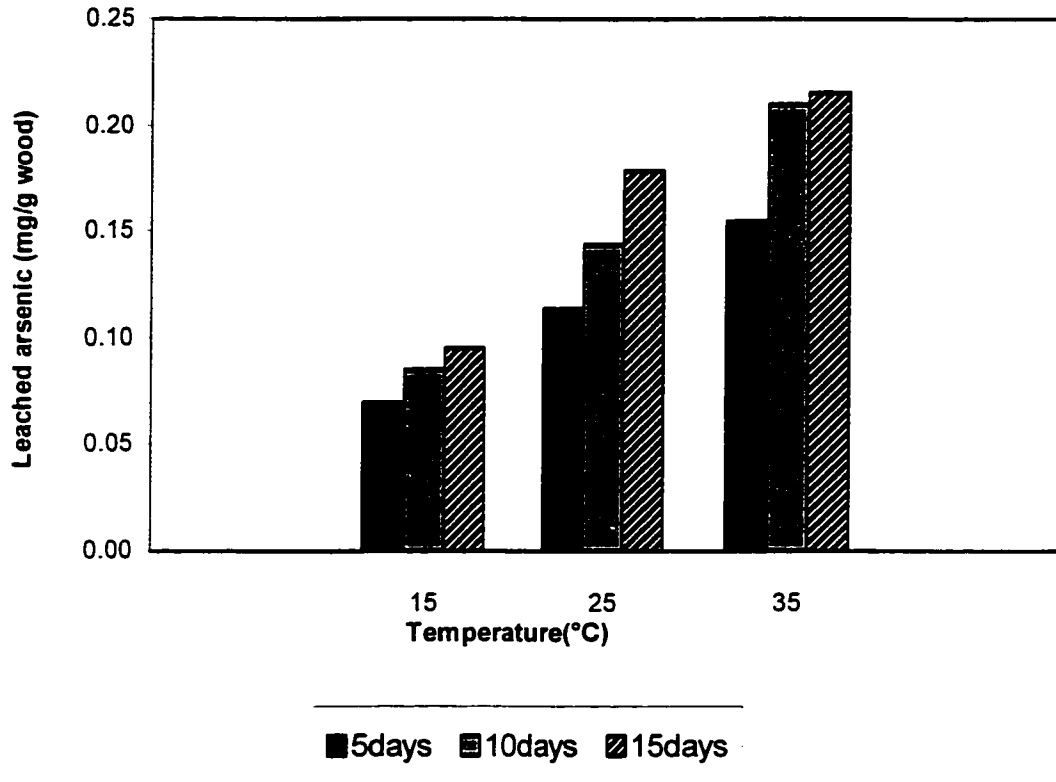


Figure 4.6: Effect of temperature on arsenic leaching by acetic acid (pH 5)

The measured amount of arsenic in all the nine samples leached by acetic acid (pH5) during 5,10 and 15 days. at temperatures 15, 25 and 35°C (Figure 4.6) show that not only

the leaching of arsenic increases by increasing the temperature but it is almost a linear function of temperature with time as a constant.

4.2.3 The effect of pH on leaching

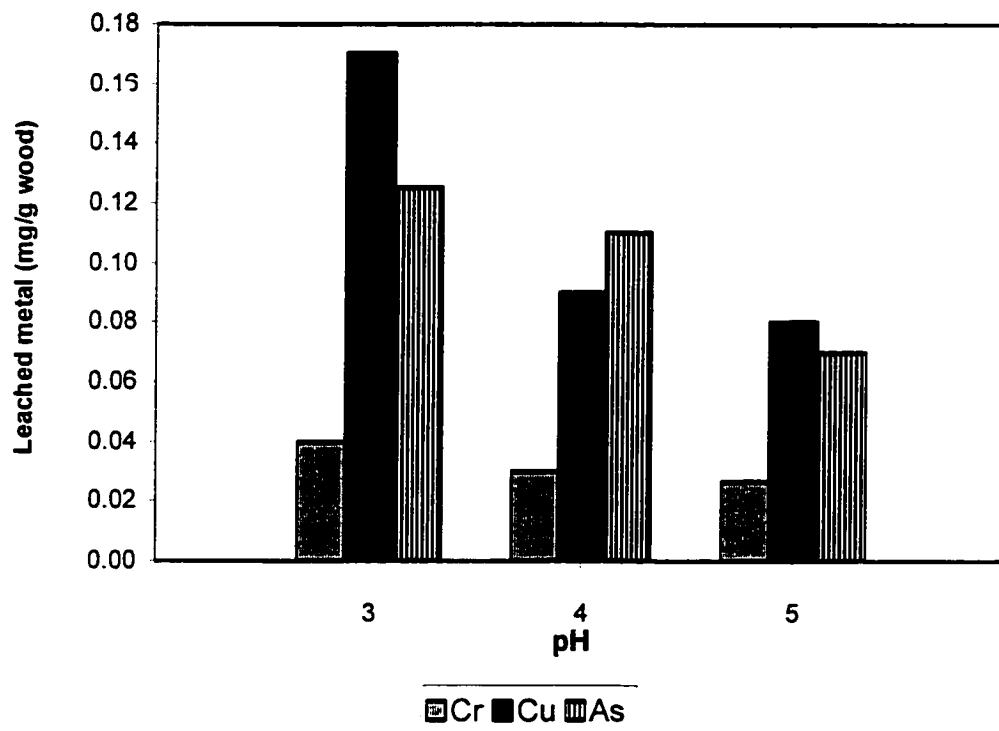


Figure 4.7: Effect of pH on leaching by acetic acid at T=15°C during 5 days

Figure 4.7 shows the effect of pH on the leaching of the chromium, copper and arsenic by acetic acid, at 15°C after 5 days. To obtain the results for Figure 4.7, three samples of ground wood (does not pass through sieve mesh 10) were soaked in mason jars containing 1L acetic acid with pH values of 3,4 and 5 at temperature 15°C for 5 days. Arsenic, chromium and copper were measured for each sample. Then the ratio of each

metal in each sample to the total amount of metal in unleached treated wood, was calculated as shown in Figure 4.8.

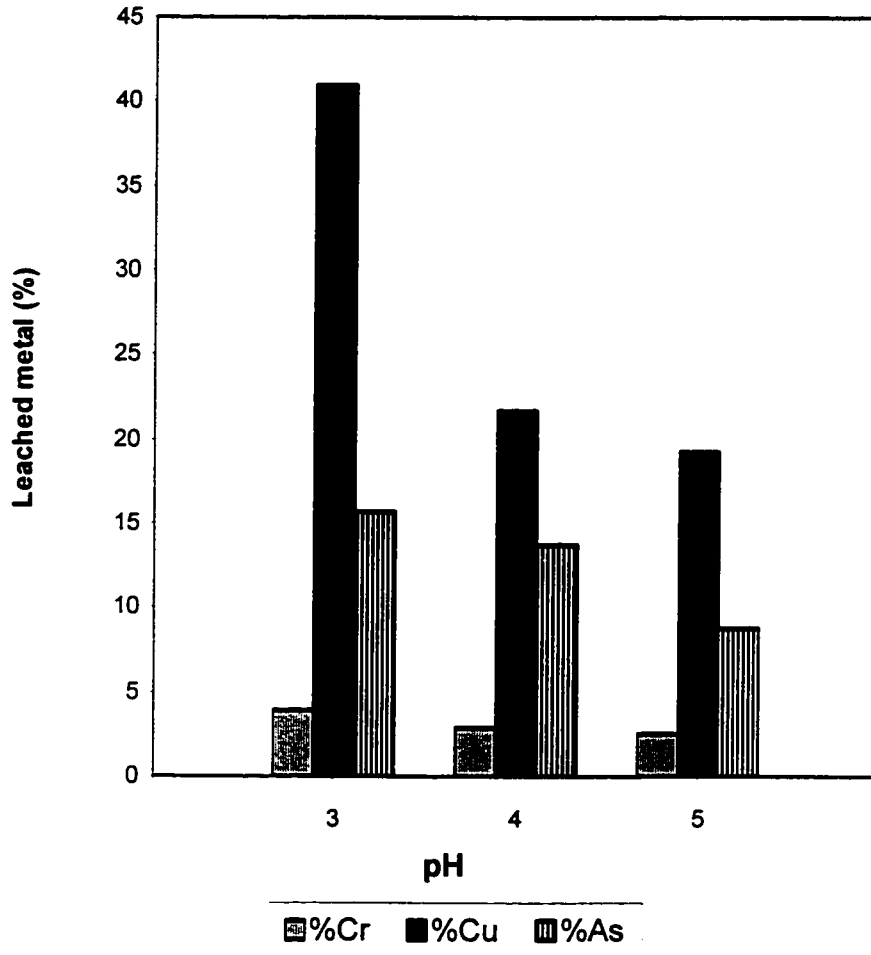


Figure 4.8: Effect of pH on leaching percentages by acetic acid at T=15°C during 5 days

According to Figure 4.7, the most leaching for all the metals occurs at pH 3. Increasing the pH, causes less leaching for all the metals. Comparing the results based on the ratio of

the leachants to the total amount of metal in unleached wood (Figure 4.8). confirms that copper is the least resistant metal to the leaching when the pH increases and chromium is the most.

4.2.3.1 Chromium

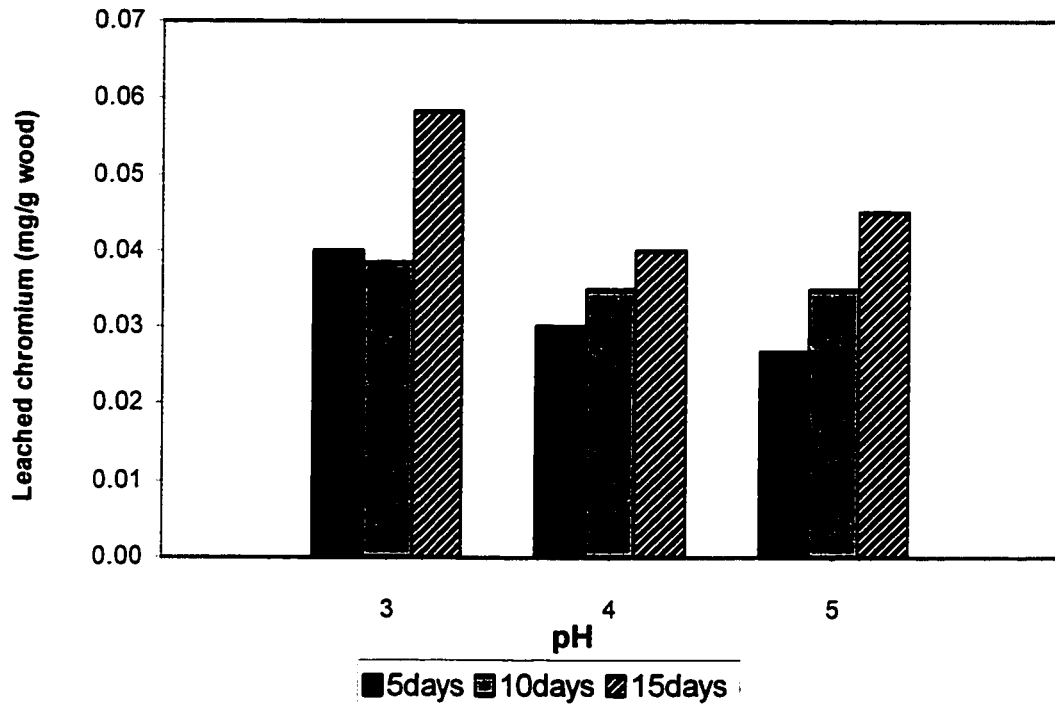


Figure 4.9: Effect of pH on chromium leaching by acetic acid at T=15°C

To investigate the effect of pH on chromium more precisely, three samples of ground treated wood soaked in 1L acetic acid (pH 3) at T=15°C for 5,10 and 15 days. The same experiments were then performed by acetic acid at pH 4 and pH 5. The amount of chromium was measured in all nine mentioned samples. Figure 4.9 is the result of these

performed experiments. Acetic acid (pH 3), causes chromium to leach much more than at pH 4 and pH 5 (Figure 4.9) at all the 5, 10 and 15 day tests. Comparing the rate of leaching at pH 3, there is no significant difference between leaching at pH 4 and pH 5.

According to Florence and Batley (1980), the valence of chromium when introduced into soil or water, is a function of some factors and pH is one of these factors. As mobility and leaching of metals is related to their form, then the pH will affect the leaching rate of chromium. Referring to obtained results, it is recommended, for leaching less chromium, the pH should not be around pH 3. A pH of 4 is the best alternative.

4.2.3.2 Copper

To find the effect of pH on copper leaching, the amount of copper was measured in all nine samples analyzed for chromium. Since at $T=15^{\circ}\text{C}$ the temperature effect on leaching is the least in comparison to 25°C and 35°C , the tests were performed at $T=15^{\circ}\text{C}$ to investigate the effect of pH. Increasing pH, from 3 to pH 4 decreases the amount of leached copper considerably but there is no significant difference between leaching of copper at pH 4 and pH 5. Therefore, to leach less copper, both pH 4 and pH 5 can be recommended (Figure 4.10).

According to Lebow (1996), pH affects the inorganic and organic adsorption of copper and as the adsorption is important in determining copper mobility then pH affects the copper leaching. At low pH, the adsorbents charge tends to be positive because of proton adsorption and at high pH the adsorbents become more negatively charged (James and

Barrow, 1981). Consequently, adsorption generally increases with increasing pH (Baker,1990; James and Barrow . 1981; McBride, 1981). If organic and inorganic adsorption agents are not present, the water-soluble copper is primarily in the forms of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, $\text{Cu}(\text{H}_2\text{O})_5^{2+}$ CuOH^+ below pH 7 and $\text{Cu}(\text{OH})_2$, CuCO_3 at pHs greater than 7.

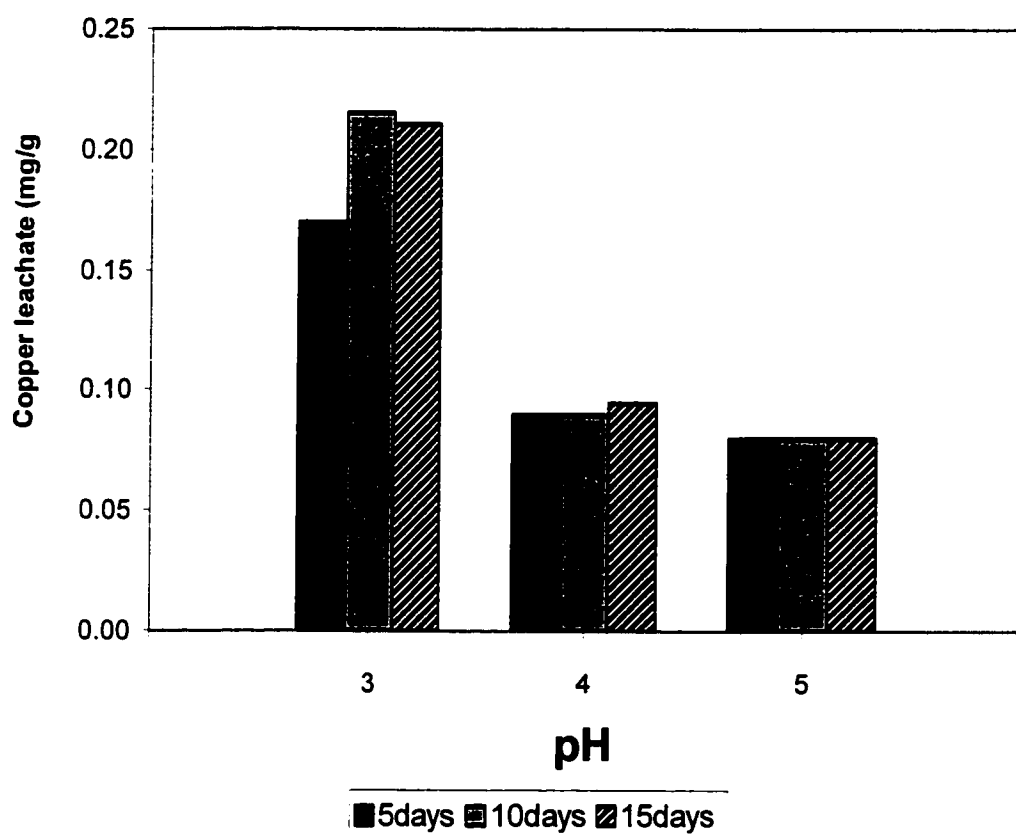


Figure 4.10: Effect of pH on copper leaching by acetic acid at T=15°C

4.2.3.3 Arsenic

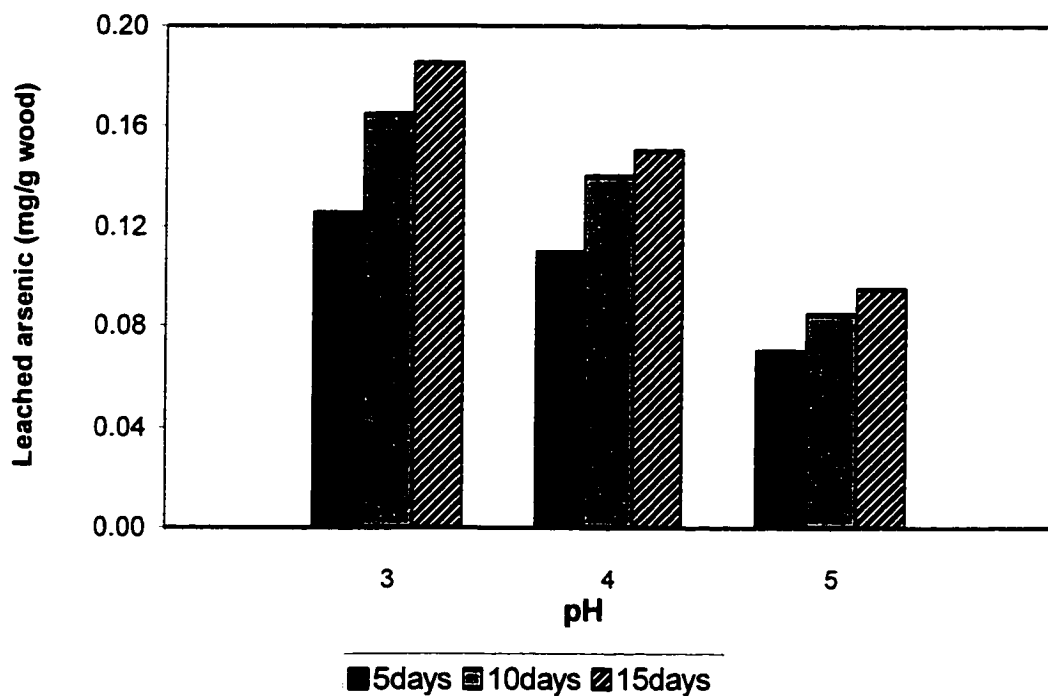


Figure 4.11: Effect of pH on arsenic leaching by acetic acid at T=15°C

The measured amount of arsenic in all the nine samples leached by acetic acid at pH 3, 4 and 5 (Figure 4.11) shows the effects of pH on leaching of arsenic by acetic acid at T=15°C in 5, 10 and 15 days. By increasing pH, the amount of leached arsenic decreases. This relationship is much more linear than for copper and chromium leaching. Therefore the most leaching for arsenic occurs at pH 3 and the least at pH 5. For less leaching the pH should be kept high.

According to Lebow (1996) for inorganic species, the equilibria between arsenic acid (H_3AsO_4 , As(V)) and arsenous acid (H_3AsO_3 , As(III)) are related to pH and redox potential (Eh). Between pH values of 4 and 8, As (III) can be the most stable form if the Eh is below 300 mV at pH4 and below 100 mV at pH8. At higher Eh values and up to pH7, H_2AsO_4^- will be more stable.

4.2.4 Effect of time

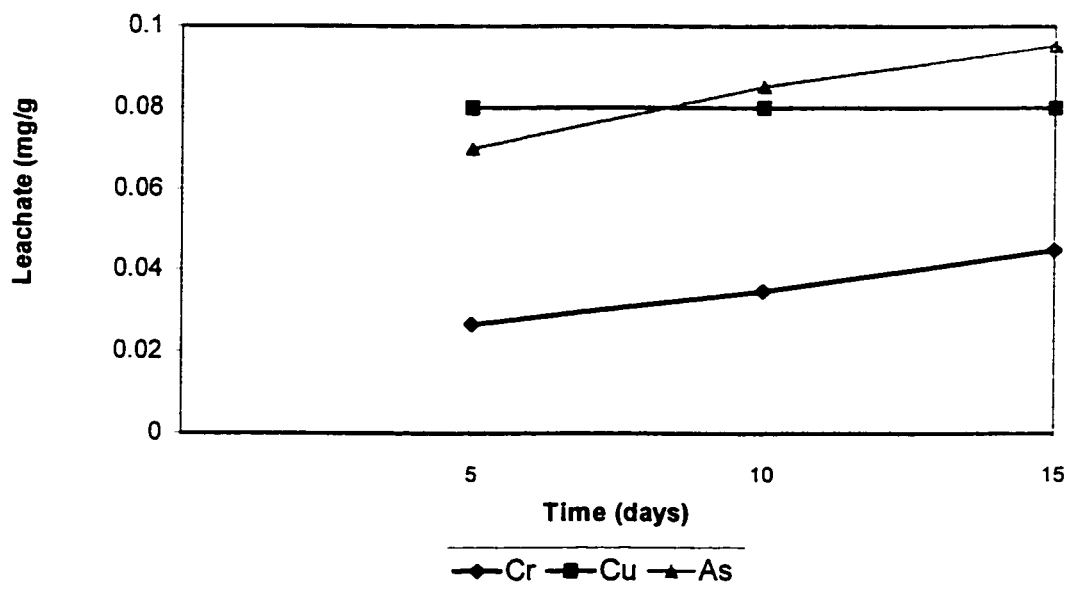


Figure 4.12: Effect of leaching time by acetic acid (pH 5) at T=15°C

Three 10 gram samples of ground wood were soaked in three 1L bottles contain acetic acid (pH 5) for 5,10 and 15 days. The amounts of chromium, copper and arsenic of the

samples were measured. Based on the performed tests, Figure 4.12 was obtained. The results show that after 5 days of leaching, copper does not leach anymore (Figure 4.12) but the leaching of chromium and arsenic is still occurring over time. Figure 4.13 confirms that, most of the metals leach during the first 5 days and the rate of leaching decreases significantly after 5 days. These results can be confirmed by the similar results of other researchers.

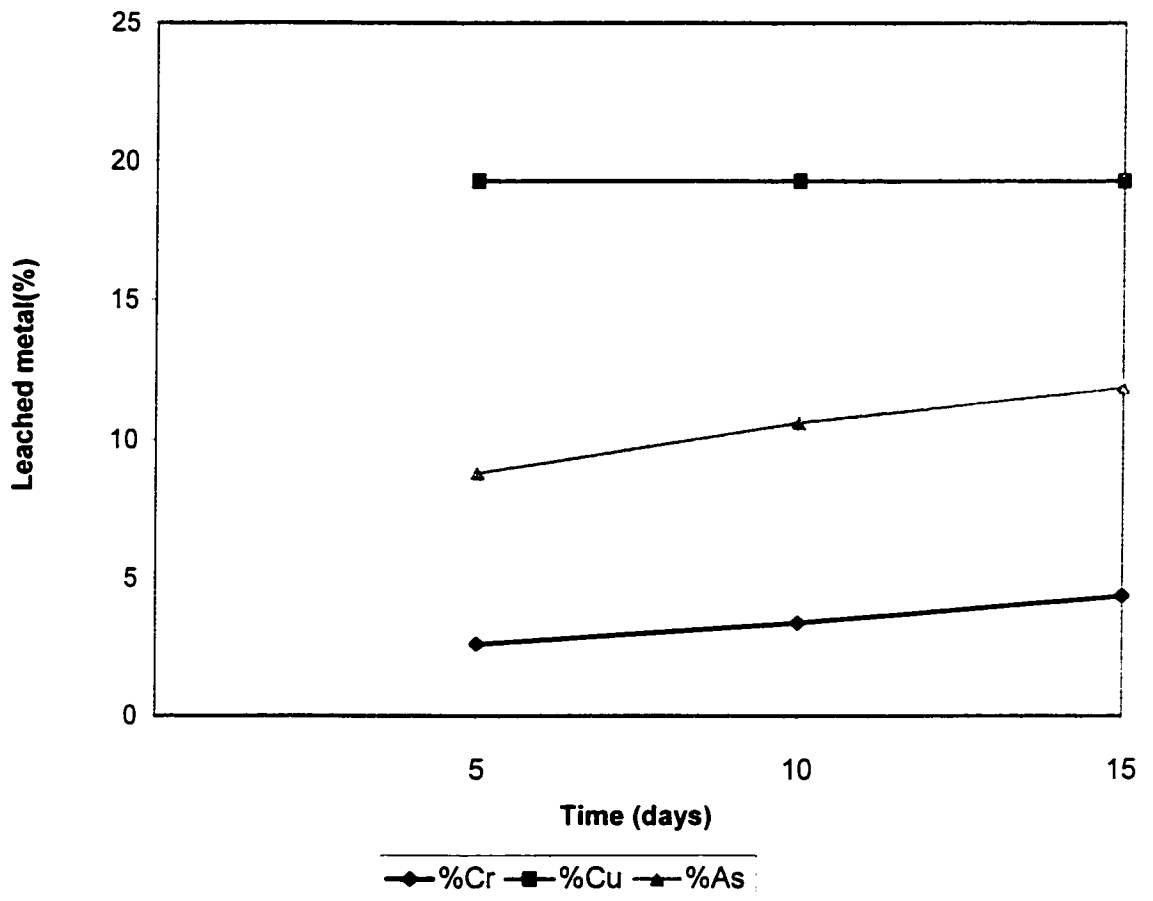


Figure 4.13: Effect of time on leaching percentages by acetic acid (pH 5) at T=15°C

According to Lebow (1996) the majority of leaching occurs upon the initial moments of preserved wood contact with the leaching medium. Although the overall amount of leached components is relatively small, an initial wave of readily available and unfixed or poorly fixed components is transported from the wood, followed by a rapid decline to a more stable leaching rate (Bergholm 1992; Evans 1987; Fahlstorm et al. 1967; Fowlie et al. 1990; Merkle et al. 1993; Teichman and Monkan 1996). As most of leaching occurs initially, then the products have not leached within the first years are not likely to leach more in future (Lebow,1996).

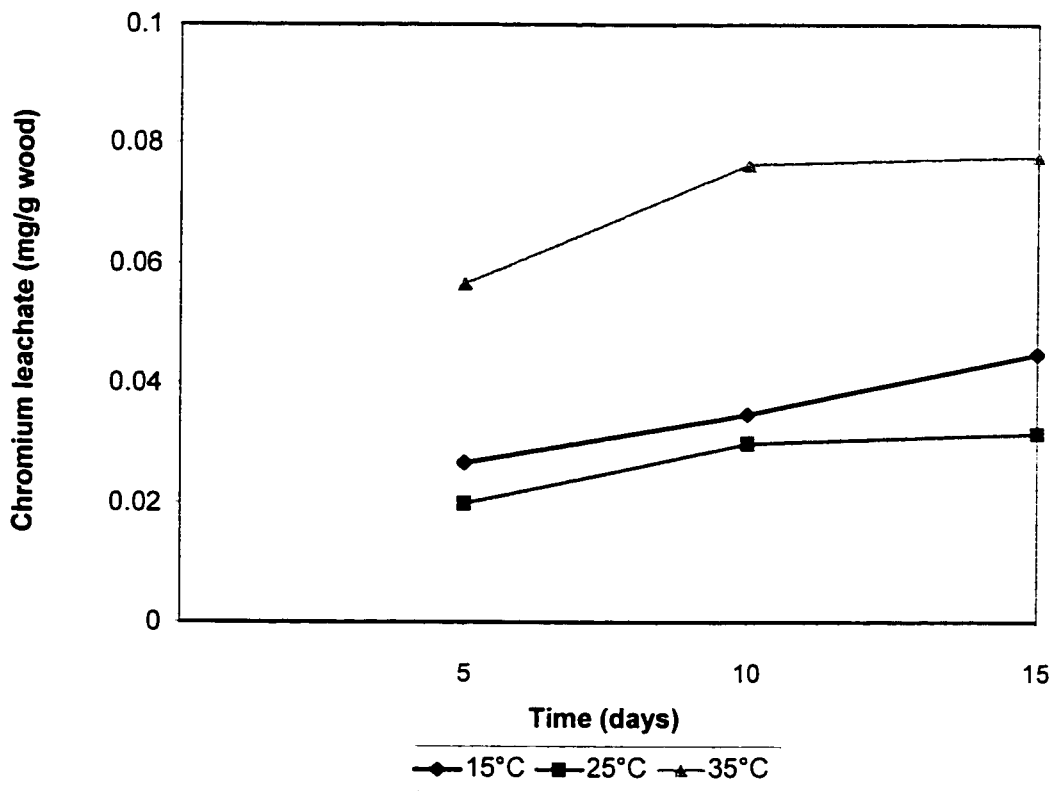


Figure 4.14: Effect of time on chromium leaching by acetic acid (pH 5)

To know more specifically about the effect of time on leaching of chromium, copper and arsenic, three 10gram samples of ground wood (does not pass through sieve mesh 10) were soaked in three 1L bottles containing acetic acid at pH 5 for 5,10 and 15 days. The amounts of chromium, copper and arsenic were measured. Based on these results, the graphs of Figures 4.14, 4.15 and 4.16 were obtained.

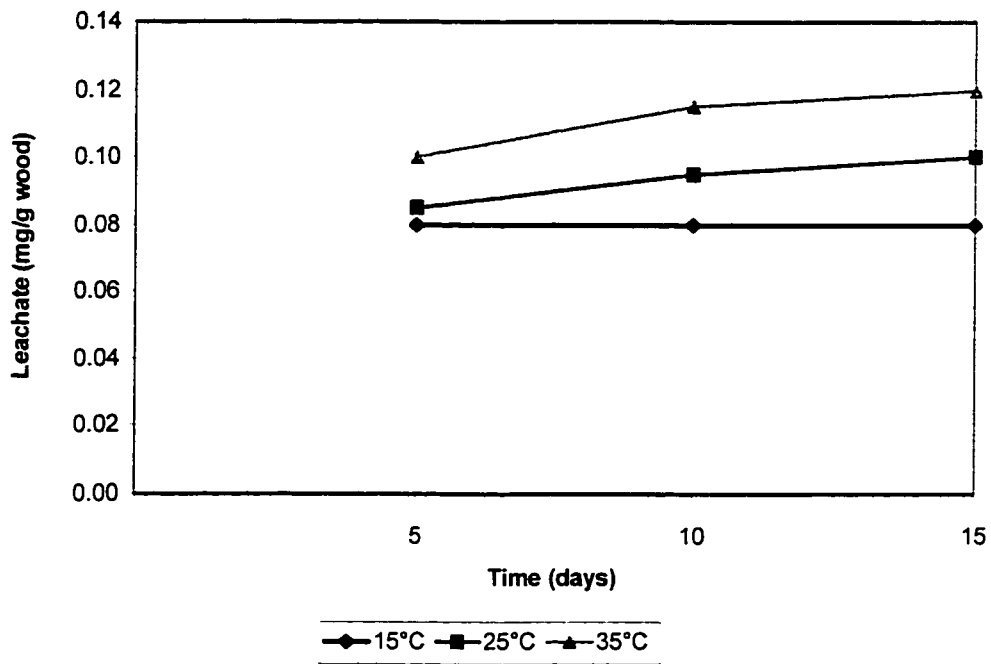


Figure 4.15: Effect of time on copper leaching by acetic acid (pH 5)

Figure 4.14 shows that at lower temperatures, the leaching of chromium is a linear function of time but increasing temperature makes it nonlinear. It means that increasing

temperature makes all the chromium leach in shorter time and there would not be any more leaching. Then at higher temperatures, the fast drainage of leachant may not be a good solution for decreasing the amount of leached chromium. Figure 4.15 shows at 15°C, after 5 days copper does not leach anymore. In a spreadsheet-based computer model based on Putt (1993) results and using non-linear regression techniques, the leached concentration of copper from CCA treated marine structures was predicted by equation [4.6] (Hingston et al. 2001).

$$(\text{Cu loss}) \frac{\mu\text{g}}{\text{cm}^2 \text{day}} = 3.566e^{-0.048 \times \text{time}(\text{day})} \quad [4.6]$$

Increasing the time causes more arsenic to leach (Figure 4.16).

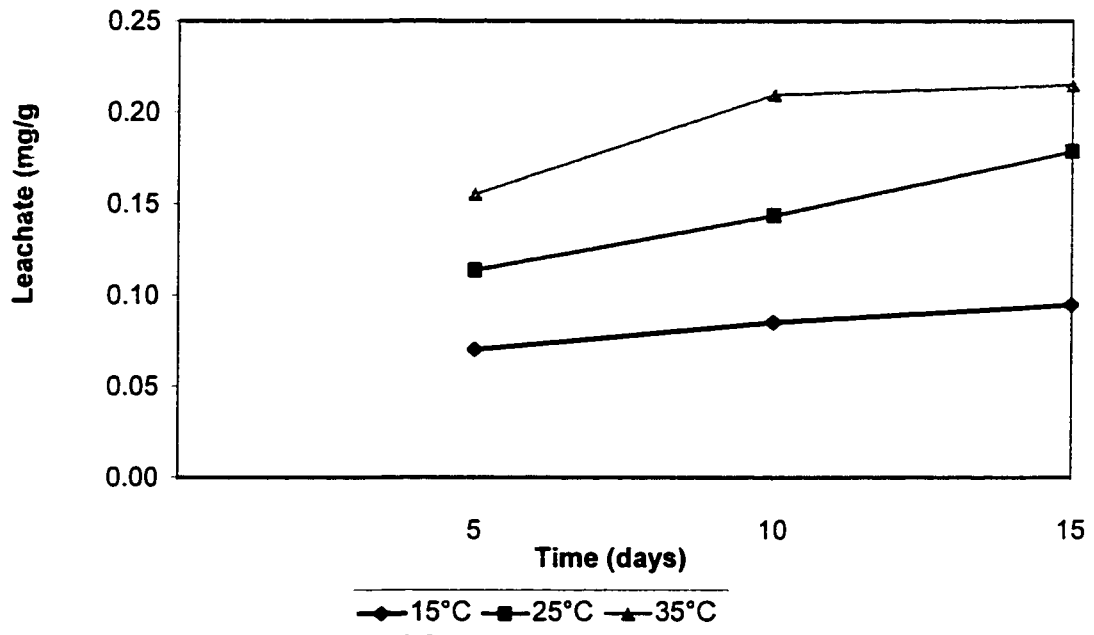


Figure 4.16: Effect of time on arsenic leaching by acetic acid (pH 5)

4.2.5 Effect of leachant type

To investigate the effects of types of acid, 0.5 gram samples of ground wood (that does not pass through sieve mesh10) were soaked in 50mL tubes containing acetic acid (pH 3, 4 and 5), sulfuric acid (pH 3, 4 and 5) and nitric acid (pH 3,4 and 5). All samples were left at $T=25^{\circ}\text{C}$ for 15 days. To show reproducibility, three identical samples were prepared for each test. The same test was performed under same condition but 10gram of wood in 1L of leachant. The amounts of chromium, copper and arsenic in the leachates of

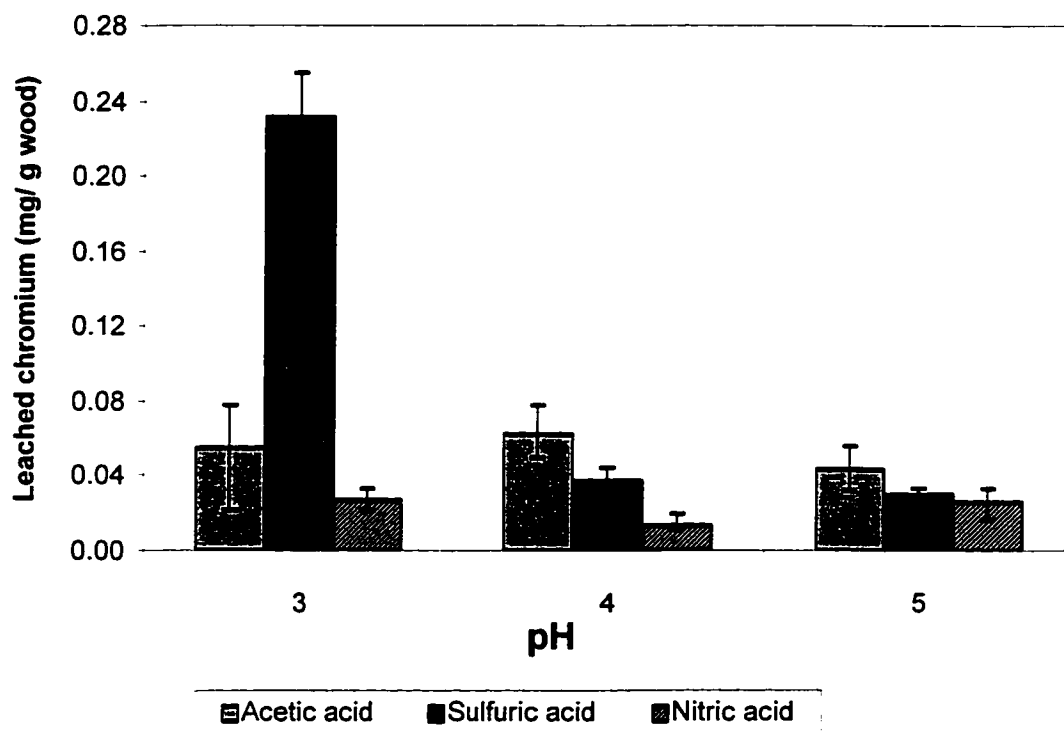


Figure 4.17: Effect of type of acid on chromium leaching at $T=25^{\circ}\text{C}$, 15 days

the samples were measured. The bars on each column (Figure 4.17,4.18,4.19) show the maximum and minimum amount of every result series, while the columns show the average.

The results of the performed experiments show that sulfuric acid at pH 3, makes a high amount of chromium leach (Figure 4.17) and its effect on leaching is incomparable to sulfuric acid with pH values of 4 and 5, nitric and acetic acid. Acetic acid makes more chromium leach in comparison to nitric acid for all pH values.

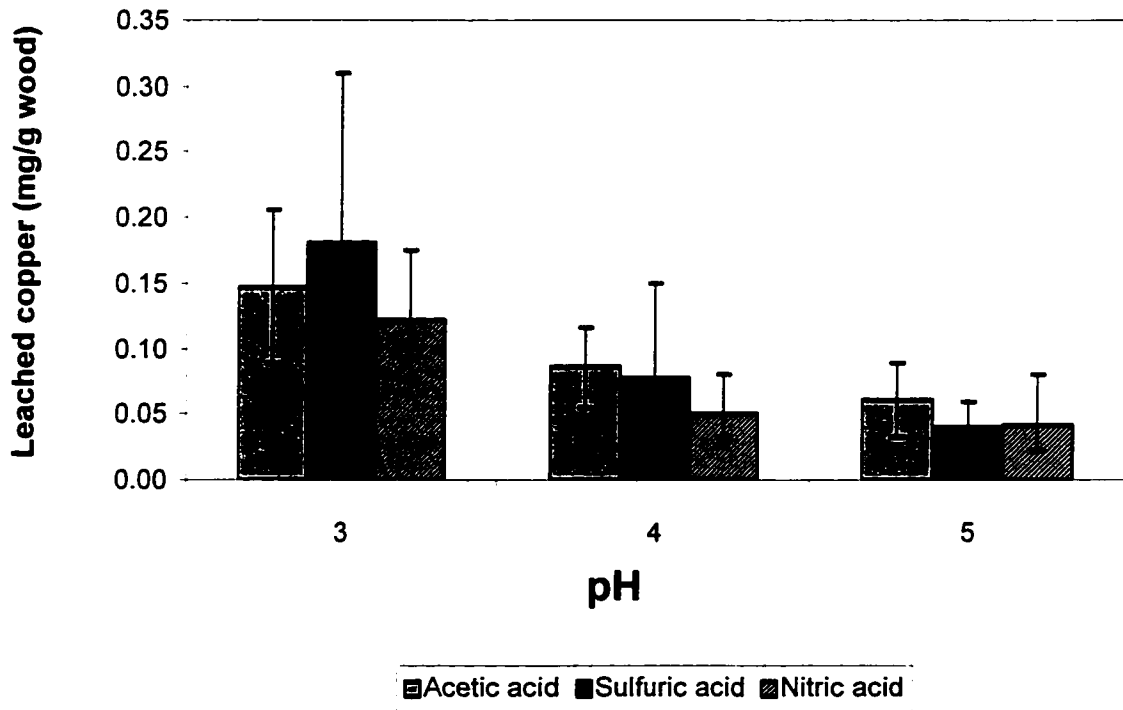


Figure 4.18: Effect of type of acid on copper leaching at T=25°C,15 days

According to Van Eetvelde and others (1998), the influence of increased acidity is explained due to the role of the additional hydrogen ions acting in the acid ion exchange reactions at the acid adsorption points on wood cell walls.

Sulfuric, nitric and acetic acids make more copper leach at pH 3 compared to pH 4 and 5. Among them, sulfuric acid causes the most leaching and nitric makes the least copper leaching (Figure 4.18).

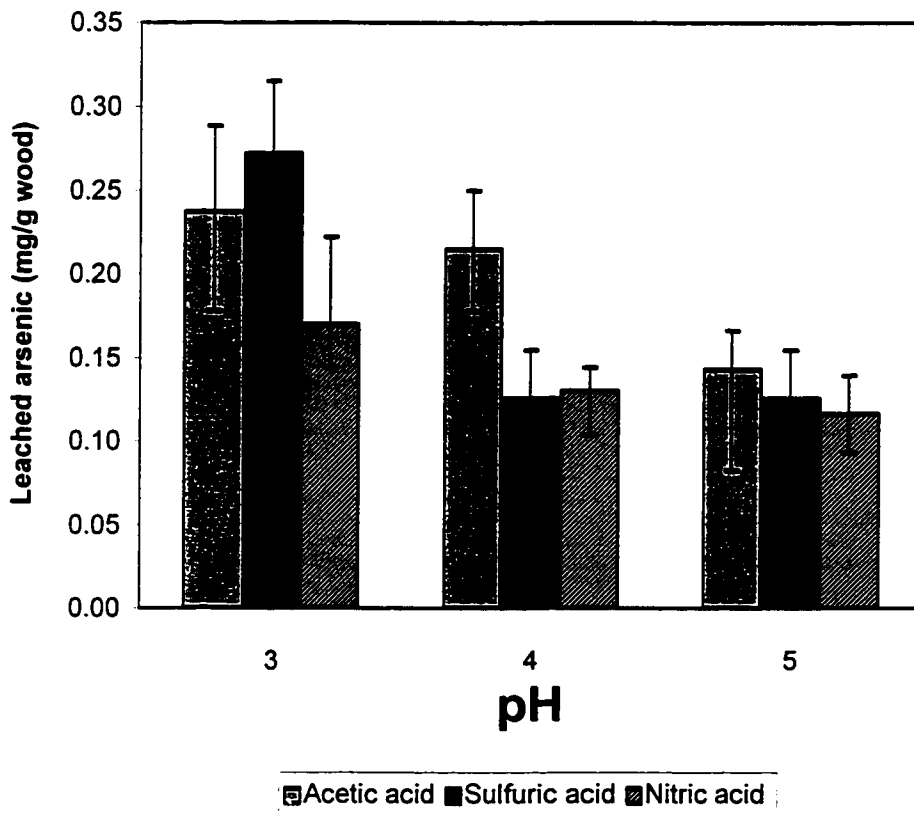


Figure 4.19: Effect of type of acid on arsenic leaching at T=25°C, 15 days

At pH 3, almost all the acids make arsenic leach more, but the most leaching occurs by sulfuric acid (Figure 4.19). Nitric acid (pH 5) causes the least amount of arsenic to leach. Opposite to pH4 and 5, sulfuric acid causes less leaching of arsenic compared to Acetic acid.

In brief, it seems that sulfuric acid (pH 3) is the most effective solution for the leaching of chromium, copper and arsenic. It can be the most problematic and critical leachant for those landfills containing CCA treated wood. Then it is recommended that, landfills should not be built in the regions where the sulfuric acid rain risk is high and the pH of soil is low.

4.3 Biodegradation results

To investigate the biodegradability of CCA treated wood 0.5g of 15 day leached wood by acetic acid, sulfuric acid, nitric acid having pH values of 3, 4 and 5 and 0.5 gram of unleached wood were chosen as the samples. The necessary nutrients for fungi growth and soil as the source of microorganisms were added (Table 3.5), a tube containing 5 mL fresh NaOH was placed inside the biodegradation tubes. For almost 1.5 months the NaOH of each tube was titrated by HCl. None of the nine samples started to biodegrade during this six week period. If there was any biodegradation and consequently, CO₂ generation, then the amount of consumed HCl should have decreased significantly. Adding some glucose to control tube and consuming more HCl to titrate it, showed that microorganisms were active. As the microorganisms in the blank sample (only contained

soil and not wood) were active and usually natural wood starts to biodegrade after one month, this experiment shows that even leached treated woods are still resistant to biodegradation.

4.4 Summary of the results

Table 4.1 contains the results of 5 weeks titration. It shows the volume of consumed HCl (0.1N) for titration 5 mL NaOH (1N) which indicates CO₂ production. Table 4.2 contains the results of leaching tests. They are the amount of metals in 100mL of final solution (10g ground wood soaked in 1000mL of leachant.200 mL of leachate was taken and evaporated to 100mL during digestion). Table 4.3 contains the results of 5 day leaching tests. They are the amount of metals in 50mL of final solution (0.5g wood soaked in 50mL of leachant). Table 4.4 contains the amount of metals in 0.5 g of wood, which was digested and the volume was brought to 25mL. To show the reproducibility of the results the triple leaching tests were performed by soaking 0.5g of CCA wood samples in 50mL of different type of acids having different pH values in 25°C. Table 4.5 contains the amount of metals in 45mL of leachate.

Table 4.1: The results of titration of NaOH (1N) with HCl (0.1N)

Samples	Consumed HCl (mL)				
	week 1	week 2	week3	week4	week5
Blank	44.4	46.5	46.9	46.5	45.9
unleached wood	45.8	45.9	47	46.1	45.6
Acetic acid, pH=3, 25 °C, 15 days	42.9	44.7	45.3	45	46.4
Acetic acid, pH=4, 25 °C, 15 days	43.2	45	44.7	44.8	44.5
Acetic acid, pH=5, 25 °C, 15 days	42.4	42	43.5	43.3	44.8
Nitric acid, pH=3, 25 °C, 15 days	42.6	45.3	45.6	45.5	46.7
Nitric acid, pH=4, 25 °C, 15 days	43.2	45.1	44.4	42.3	42.2
Nitric acid, pH=5, 25 °C, 15 days	44.2	45.1	45.5	45	46.4
Sulfuric acid, pH=3, 25 °C, 15 days	44.2	45.1	45.1	46.5	45.9
Sulfuric acid, pH=4, 25 °C, 15 days	42.9	44.9	45.2	46.5	46.1
Sulfuric acid, pH=5, 25 °C, 15 days	44.2	45	44.8	46.9	46.5

Table 4.2: Results of the leaching tests

Leachate	Chromium (ppm)	Copper (ppm)	Arsenic (ppm)
Acetic acid , 15 °C , pH3 , Blank	0.47	0.00	0.00
Acetic acid , 15 °C , pH3 , 5 days	1.27	3.40	2.50
Acetic acid , 15 °C , pH3 , 10 days	1.23	4.30	3.30
Acetic acid , 15 °C , pH3 , 15 days	1.63	4.20	3.70
Acetic acid , 15 °C , pH4 , Blank	0.53	0.00	0.00
Acetic acid , 15 °C , pH4 , 5 days	1.13	1.80	2.20
Acetic acid , 15 °C , pH4 , 10 days	1.23	1.80	2.80
Acetic acid , 15 °C , pH4 , 15 days	1.33	1.90	3.00
Acetic acid , 15 °C , pH5 , Blank	0.63	0.00	0.00
Acetic acid , 15 °C , pH5 , 5 days	1.17	1.60	1.40
Acetic acid , 15 °C , pH5 , 10 days	1.33	1.60	1.70
Acetic acid , 15 °C , pH5 , 15 days	1.53	1.60	1.90
Acetic acid , 25 °C , pH3 , Blank	1.00	0.00	0.01

Table 4.2: Results of the leaching tests

Leachate	Chromium (ppm)	Copper (ppm)	Arsenic (ppm)
Acetic acid ,25 °C , pH3 , 5 days	0.87	3.60	3.00
Acetic acid ,25 °C , pH3 , 10 days	1.57	4.40	4.20
Acetic acid , 25 °C , pH3 , 15 days	1.43	4.00	4.90
Acetic acid , 25 °C , pH4 , Blank	0.33	0.00	0.01
Acetic acid , 25 °C , pH4 , 5 days	0.83	2.00	3.40
Acetic acid , 25 °C , pH4 , 10 days	1.10	2.30	4.50
Acetic acid , 25 °C , pH4 , 15 days	1.33	2.20	5.00
Acetic acid , 25 °C , pH5 , Blank	0.20	0.00	0.02
Acetic acid , 25 °C , pH5 , 5 days	0.60	1.70	2.30
Acetic acid , 25 °C , pH5 , 10 days	0.80	1.90	2.90
Acetic acid , 25 °C , pH5 , 15 days	0.83	2.00	3.60
Acetic acid , 35 °C , pH3 , Blank	0.07	0.00	0.01
Acetic acid , 35 °C , pH3 , 5 days	1.07	4.20	4.50
Acetic acid , 35 °C , pH3 , 10 days	1.27	4.90	5.70
Acetic acid , 35 °C , pH3 , 15 days	1.17	4.20	5.50
Acetic acid , 35 °C , pH4 , Blank	-0.20	0.00	0.00
Acetic acid , 35 °C , pH4 , 5 days	0.63	2.60	4.90

Continued

Table 4.2: Results of the leaching tests

Leachate	Chromium (ppm)	Copper (ppm)	Arsenic (ppm)
Acetic Acid , 35 °C , pH4 , 10 days	1.13	2.40	5.90
Acetic Acid , 35 °C , pH4 , 15days	1.43	2.80	6.40
Acetic acid , 35 °C , pH5 , Blank	0.37	0.00	0.00
Acetic acid , 35 °C , pH5 , 5 days	1.50	2.00	3.10
Acetic acid , 35 °C , pH5 , 10 days	1.90	2.30	4.20
Acetic acid , 35 °C , pH5 , 15 days	1.57	2.10	4.30
Sulfuric acid , 25 °C , pH3 , Blank	0.87	0.00	0.00
Sulfuric acid , 25 °C , pH3 , 15 days	5.80	6.20	6.30
Sulfuric acid , 25 °C , pH4 , Blank	0.97	-0.10	0.00
Sulfuric acid , 25 °C , pH4 , 15 days	1.73	2.90	3.10
Sulfuric acid , 25 °C , pH5 , Blank	0.77	-0.10	0.00
Sulfuric acid , 25 °C , pH5 , 15 days	1.40	1.10	2.80
Nitric acid 25 °C , pH3 , Blank	0.67	0.00	0.00
Nitric acid 25 °C , pH3 , 15 days	1.07	3.50	3.20

Table 4.2: Results of the leaching tests

Leachate	Chromium (ppm)	Copper (ppm)	Arsenic (ppm)
Nitric acid , 25 °C , pH4 , Blank	0.67	-0.10	0.00
Nitric acid , 25 °C , pH , 15 days	1.07	1.50	2.60
Nitric acid , 25 °C , pH5, Blank	0.43	0.00	0.00
Nitric acid , 25 °C , pH5, 15 days	0.77	1.60	2.80

Table 4.3: Results of 5 day leaching tests

Leachate	Chromium (ppm)	Copper (ppm)	Arsenic (ppm)
Acetic acid (35 °C , pH3 , 5 days)	0.70	1.70	2.00
Acetic acid (35 °C , pH4 , 5 days)	0.70	0.90	1.50
Acetic acid (35 °C , pH5 , 5 days)	0.50	0.90	1.20

Continued

Table 4.3: Results of 5 day leaching tests

Leachate	Chromium (ppm)	Copper (ppm)	Arsenic (ppm)
Sulfuric acid , 35 °C , pH3 , 5 days	2.30	2.80	2.30
Sulfuric acid , 35 °C , pH4 , 5 days	0.50	1.00	1.10
Sulfuric acid , 35 °C , pH5 , 5 days	0.40	0.60	0.93
Nitric acid , 35 °C , pH3 , 5 days	0.70	2.30	1.70
Nitric acid , 35 °C , pH4 , 5 days	0.20	0.60	0.85
Nitric acid , 35 °C , pH5 , 5 days	0.30	0.70	1.10

Table 4.4: Unleached wood analysis results

	chromium (ppm)	copper (ppm)	arsenic (ppm)
unleached wood	15.0	8.1	16.0

Table 4.5: Results of 15 day leaching tests

Leachate	Chromium (ppm)	Copper (ppm)	Arsenic (ppm)
Nitric Acid , 25 °C , pH3 , Blank	0.00	0.00	0.00
Nitric Acid , 25 °C , pH3 , 15 days	0.20	0.70	1.30
Nitric Acid , 25 °C , pH3 , 15 days	0.30	0.80	1.40
Nitric Acid , 25 °C , pH3 , 15 days	0.30	1.30	2.00
Nitric Acid , 25 °C , pH4 , Blank	-0.10	0.00	0.00
Nitric Acid , 25 °C , pH4 , 15 days	0.00	0.40	1.30
Nitric Acid , 25 °C , pH4 , 15 days	0.00	0.40	1.30
Nitric Acid , 25 °C , pH4 , 15 days	0.00	0.30	0.93
Nitric Acid , 25 °C , pH5 , Blank	-0.20	0.00	0.00
Nitric Acid , 25 °C , pH5 , 15 days	0.10	0.30	1.10
Nitric Acid , 25 °C , pH5 , 15 days	0.10	0.30	1.00
Nitric Acid , 25 °C , pH5 , 15 days	0.00	0.20	0.84
Acetic Acid , 25 °C , pH3 , Blank	-0.10	0.00	0.00
Acetic Acid , 25 °C , pH3 , 15 days	1.00	1.60	2.60
Acetic Acid , 25 °C , pH3 , 15 days	0.50	0.80	1.60
Acetic Acid , 25 °C , pH3 , 15 days	0.60	1.10	2.20

Continued

Table 4.5: Results of 15 day leaching tests

Leachate	Chromium (ppm)	Copper (ppm)	Arsenic (ppm)
Acetic Acid , 25 °C , pH4 , Blank	-0.10	0.00	0.00
Acetic Acid , 25 °C , pH4 , 15 days	0.40	0.50	1.60
Acetic Acid , 25 °C , pH4 , 15 days	0.50	0.60	1.90
Acetic Acid , 25 °C , pH4 , 15 days	0.60	1.00	2.00
Acetic Acid , 25 °C , pH5 , Blank	-0.10	0.00	0.00
Acetic Acid , 25 °C , pH5 , 15 days	0.40	0.40	1.30
Acetic Acid , 25 °C , pH5 , 15 days	0.40	0.60	1.50
Acetic Acid , 25 °C , pH5 , 15 days	0.20	0.30	0.74
Sulfuric Acid , 25°C, pH3, BLANK	-0.10	0.00	0.01
Sulfuric Acid , 25°C, pH3, 15 days	2.20	1.50	2.80
Sulfuric Acid , 25°C, pH3, 15 days	1.60	1.00	2.00
Sulfuric Acid , 25°C, pH3, 15 days	2.00	1.20	2.20
Sulfuric Acid , 25°C, pH4, BLANK	-0.20	0.00	0.00
Sulfuric Acid , 25°C, pH4, 15 days	0.10	0.30	1.10
Sulfuric Acid , 25°C, pH4, 15 days	0.10	0.30	1.00
Sulfuric Acid , 25°C, pH4, 15 days	0.00	0.20	0.84
Sulfuric Acid , 25°C, pH5, BLANK	-0.10	0.00	0.00
Sulfuric Acid , 25°C, pH5, 15 days	1.00	1.60	2.60
Sulfuric Acid , 25°C, pH5, 15 days	0.50	0.80	1.60
Sulfuric Acid , 25°C, pH5, 15 days	0.60	1.10	2.20

Chapter 5

Conclusions

5.1 Conclusion of this study

The aim of this study was to investigate the effects of different factors on leaching of chromium, copper and arsenic from disposed chromated copper arsenate (CCA) treated wood, in landfills.

The results of this study shows:

- There is the risk of soil, water and environmental contamination by chromium, copper and arsenic, wherever the chromated copper arsenate treated wood is buried. The more that is buried, the higher contamination.

- As it was expected chromium was leached the least despite being present in the greatest proportion.
- In those areas, where the region is exposed to sulfuric acid rain, pH of 3, there are a high risk of leaching of chromium, copper and arsenic. If the landfills are built in these areas high level of soil and groundwater contamination would happen.
- As the underground temperature in landfills increases, the amount of leached metals is higher.
- The highest amount of leaching happens during the first 5 days of leaching.
- The buried treated wood can't be biodegraded by microorganisms at the same rate as untreated wood.
- As a solution, it is better to perform some preprocessing steps to take the metals out of wood and make wood leach, before landfilling.
- The landfills should be built in the areas where the soil pH is high and the soil is less penetratable and the underground temperature is low.
- The landfills should be resistant to the leaching and have liner and leachate collection systems.

5.2 Future recommendations

The following recommendations can be made.

- Investigating the effect of particle size on leaching
- Investigating the effect of type of wood on leaching
- Performing the leaching test for the intervals less than 5 days
- Performing longer biodegradation tests
- Performing biodegradation tests for the same type of wood but untreated
- Finding methods to make treated wood leach before landfilling

References

- Albuquerque, R.M., Cragg, S.M., 1995. Evaluation of impact of CCA treated wood on the marine environment (IRG/WP 95-50040). The International Research Group on Wood Preservation, Stockholm.
- Amburgey, T.L. Fungi and Their Effects on Untreated Wood Products, Mississippi State University, AWWPA Newslines, February 2000.
- AWPA, 1994. Book of standards. Woodstock, MD: American Wood Preservers' Association.
- Baker, D.E., 1990. Copper. In: Alloway, B.J., ed. Heavy metals in soils. New York: John Wiley and Sons.
- Bartlett, R.J.; Kimble J.M., 1976. Behaviour of chromium in soils. III. Oxidation. Journal of Environmental Quality. 5:379-386
- Bautista, E.M.; Alexander, M. 1972. Reduction of inorganic compounds by soil microorganisms. Soil Science American Proceedings.36: 918-920.
- Bergholm, J. 1992. Leakage of arsenic, copper and chromium from preserved wooden chips deposited in soil. An eleven year old field experiment. Rep. 166. Stockholm, Sweden: Swedish Wood Preservation Institute.
- Braman, R.S. 1975. Arsenic in the environment. In: Woolson, E.A., ed. Arsenical pesticides, ACS symposium series 7. Washington, DC: American Chemical Society: 108-123.
- Brannon, J.M.; Patrick, W.H., Jr., 1987. Fixation, transformation, and mobilization of arsenic in sediments. Environmental Science and Technology. 21:450-459.
- Brudermann, G.E. Recommendations for the Design and Operation of Wood Preservation Facilities, Frido Consulting For Environment Canada, National Office of Pollution Prevention, and Canadian Institute of Treated Wood, March 1999.

Butterfield, B.G. and B.A. Meylan. (1980). Three dimensional structure of wood. An ultrastructural approach. London, New York; Chapman and Hall, 99 pp.

Canadian Environmental Protection Act, Strategic Options for the Management of CEPA-Toxic Substances from the Wood Preservation Sector, vol.1, July 1999.

Cheng, C.N.; Focht, D.D. 1979. Production of arsine and methylarsines in soil and culture. *Applied and Environmental Microbiology*. 9:494-498.

Clesceri, L.S.; Greenberg, A.E.; Trussell, R.R. Standard methods for the examination of water and wastewater, 17th ed., 1989

Cole, F.A. and Clausen, C.A.. Bacterial biodegradation of CCA- treated waste wood, Clark Atlanta Univ., Atlanta, Ga.; and Research Microbiologist, USDA Forest Service, Forest Prod. Lab., Madison, Wis.

Cole, F.A.; Clausen, C.A., 1996. Bacterial biodegradation of CCA- treated waste wood. Proceedings of Forest Products Society Conference on the Use of Recycled Wood and Paper in Building Application, 1996 September 9. Madison, WI, PP.201-204.

Cooper, P.A. ; Ung, T. 1989. Moderate temperature fixation of CCA –C. IRG/WP.3522. 20TH annual meeting, Finland. Stockholm, Sweden: International Research Group.

Cooper, P.A. 1991a. Cation exchange adsorption of copper on wood. *Wood Protection*. 1(1):30-32.

Cooper, P.A., 1988. Diffusion and interaction of components of water-born preservatives in the wood cell wall. IRG/WP/3474.

Cooper, P.A., 1994. Leaching of CCA : Is it a problem? In “Environmental considerations in the manufacture, use, and disposal of CCA-C from jack pine sapwood in compost. *Forest Products Journal* 41(1), pp. 57-59.

Cooper, P.A., 1993. Disposal of treated wood removed from service: the issues ,In: Proceedings, Environmental Considerations in Manufacture, Use and Disposal of

Preservative Treated Wood. Madison, WI, USA: Carolinas-Chesapeake Section. Forest Products Society, pp. 85-90.

Cooper, P.A.; Stokes, D. 1993. Leaching characteristics and fixation of copper dimethyldithiocarbamate treated wood. In: Proceedings, American Wood Preservers' Association; 89: 192-203.

Cox, T.R.G.; Richardson, B.A. 1979. Chromium in wood preservation; health and environmental aspects. *International Journal of Wood Preservation*. 1(1): 27-32

Dacosta, E.W.B. and Kerruish R.M., The tolerance of *Poria* species to copper-based wood preservatives. *Forest Products Journal*(1964). 14:106-112.

Dahlgren, S.E. 1975. Kinetics and mechanism of fixation of preservatives. Part V. Effect of wood species and preservative composition on leaching during storage. *Holzforschung*. 29: 84-95.

Dahlgren, S.E.; Hartford, W.H. 1972. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part I. pH behaviour and general aspects of fixation. Part II. Fixation of Boliden K33. Part III. Fixation of Tanalith C and comparison of different preservatives. *Holzforschung*. 26: 62-69, 105-113, and 142-149.

Dahlgren, S.E. 1972. The course of fixation of Cu-Cr-As wood preservatives. Record Annual Convention British Wood Preservers' Association; 109-128.

Eadie, J.; Wallace, E.M. 1962. Some observations on the fixation of copper and arsenic in *Pinus sylvestris* sapwood. *Institute of Wood Science*. 10:56-65.

Elder, T. Introduction to Wood Science, chapter 3, pp.41-56, 2002.
<http://www.forestry.auburn.edu/elder/fp339/ch3/ch3.html>

Evans, F.G. 1987. Leaching from CCA-impregnated wood to food, drinking water and silage. IRG/WP/3433. Stockholm, Sweden: International Research Group.

Environment Canada. Wood preservatives - an overview. The role of wood preservatives, May 2001.
<http://www.ns.ec.gc.ca/epb/factsheets/pesticides/wood.html>

Fahlstrom, G.B., Gunning, P.E., Carlsin, J.A., 1967. Chrome arsenate wood preservatives: a study of the influent composition on leachability. *Forest Products Journal* 17, 17-2.

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

Florence, T.M.; Batley, G.E. 1980. Chemical speciation natural waters. *CRC Critical Reviews in Analytical Chemistry*. 9: 219-296.

Forsyth, P.G.; Morrell, J.J. 1990. Hexavalent chromium reduction on CCA treated sawdust. *Forest Products Journal*. 40(6):48-50.

Fowlie, D.A.; Prestron, A.F.; Zahora, A.R. 1990. Additives: an example of their influence on the performance and properties of CCA treated Southern Pine lumber. In: *Proceedings, American Wood Preservers' Association*; 86: 11-21.

Freudenrich, C.C. How landfills work: parts of landfill?, 2002
<http://www.howstuffworks.com/landfill6.htm>

Freudenrich, C.C. How landfills work: What is a landfill?, 2002
<http://www.howstuffworks.com/landfill3.htm>

Giblin, A.E.; Valiela, I. 1983. The fate of metals introduced into a New England salt marsh. *Water, Air and Soil Pollution*. 20:81-98

Gray, S.M.; Dickinson, D.J. 1988. The role of copper in fixed waterborne preservatives. *Record Annual Convention British Wood Preservers' Association*; 65-77.

Harmon, M.E. Long term experiments on log decomposition at the H.J. Andrews experimental forest. *USDA general technical report PNW-280*. September 1992.

Hauserman, J. Study finds wood leaking arsenic. *St. Petersburg Times*; St. Petersburg, Fla.; Aug 29, 2002;

Hingston, J.A.; Collins, C.D.; Murphy, R.J.; Lester, J.N. Leaching of chromated copper arsenate wood preservatives: a review. *Environmental pollution* 111(2001) 53-66.

Ibach, R.E. Wood preservation (Ch14). Forest Products Laboratory. 1999. Wood handbook--Wood as an engineering material. Gen. Tech. Rep. FPL-GTR-113. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.

Illman, B. L. and Terry, L. Highley, Fungal degradation of wood treated with metal-based preservatives, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, U.S.A,1996.

James, R.O.; Barrow, N.J. 1981. In: Lonegran, J.F. and others, eds. Copper in soil and plants. New York: Academic Press: 47-68

Kollman,F.P.P; Cote, Jr.W.A. Principles of wood science and technology:I. solid wood.1984

Konasewich, D.E.; Henning, F.A. Chromated Copper Arsenate Wood Preservation facilities, Environment Canada, Report EPS 2 /WP/3, April1998.

Krassig, H.A., Polymer Monographs, Vol 2, Elsevier Press, New York, NY,1993.

Lebow, S. Leaching of wood preservative components and their mobility in the environment, United States Department of Agriculture, General Technical Report FPL-GTR-93, 1996.

Levi, M.P. 1969. The mechanism of action of copper-chrome-arsenate preservatives against wood –destroying fungi. Record Annual Convention British Wood Preservers' Association; 113-127.

Lu, J.C.S.; Chen, K.Y. 1976. Migration of trace metals in interfaces of seawater and polluted surficial sediment. *Environmental Science and Technology*. 11: 174-182

MacMillen, A. Treated Wood: Is it Safe?, Oregon Public Networking 1995.
<http://www.efn.org/~andrewm/hhd/wood.html>

McBride, M.B., 1981. Forms and distribution of copper in solid and solution phases of soil. In: Loneragan, J.F.; and Academic Press: 25-45

McGrath, S.P.; Smith, S. 1990. Chromium and nickel, In: Alloway, B.J., ed. Heavy metals in soils. New York: John Wiley and Sons: 125-150.

McNamara, W.S. 1989. CCA fixation experiments – part I. IRG/WP/3504, Stockholm, Sweden: International Research Group.

McQueen, J.; Stevens, J., 1998. Disposal of CCA treated wood. Forest Products Journal 48 (11/12), 86 -90.

Merkle, P.; Gallagher, D.L.; Solberg, T.N. 1993. Leaching rates, metals distribution and chemistry of CCA-treated lumber: Implications for water quality modeling. In: Proceedings, Forest Products Society symposium on environmental considerations in the use of pressure treated wood; Richmond, VA.

Messure, K.; Martin, R.E.; Fish, W. 1991. Identification of copper contamination in sediments by a microscale partial extraction technique. Journal of Environmental Quality. 20:114-118

Morris, P.I., 1996. Towards a unified international hazard class system. IRG / WP / 96-20081.

Mullins, E.J. and McKnight, T.S. Canadian woods, third ed. Minister of Supply and Services, Canada 1981

O'Neill, P. 1990. Arsenic. In: Alloway, B.J., ed. Heavy metals in soils. New York: John Wiley and Sons: 83-99.

Osborne, F.H.; Ehrlich, H.L. 1976. Oxidation of arsenite by a soil isolate of *Alcaligenes*. Journal of Applied Bacteriology. 41: 295-305

Parker, A.J. 1981. In: Loneragan, J.F. and others, eds. Copper in soils and plants. New York: Academic Press: 1-22.

Pizzi, A.,1983. Practical consequences of the clarification of the chemical mechanism of CCA fixation to wood. IRG/WP/3220. In: Proceedings, 16th annual meeting, Australia. Stockholm, Sweden: International Research Group.

Pizzi, A.1982. The chemistry and kinetic behaviour of Cu-Cr-As/B wood preservatives. II. Fixation of the Cu/Cr system on wood .III. Fixation of the Cr/As system on wood .IV. Fixation of CCA to wood. Journal of Polymer Science. Chemistry Ed. 20:707-724,725-738,739-764.

Putt, A.F., 1993. Sediment bound CCA-C leachate 10 day repeated exposure toxicity to *Amplisca abdita* under static conditions. Springborn Laboratories Inc., Warehan, MA, USA.

Regis B. Miller, Structure of Wood (Ch2), Forest Products Laboratory. 1999. Wood handbook--Wood as an engineering material. Gen. Tech. Rep. FPL-GTR-113. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.

Rennie, P.M.S.; Gray, S.M.; Dickinson, D.J. 1987.Copper based waterborne preservatives: Copper adsorption in relation to performance against soft rot. IRG/WP/3452. Stockholm, Sweden: International Research group.

Ress, B.B.; Calvert, P.P.; Pettigrew, C.A. and Barlaz, M.A. Testing Anaerobic Biodegradability of Polymers in a Laboratory-Scale Simulated Landfill, Environ Science & Technology, Vol. 32, No.6, 1998, 821- 827.

Riedel, G.F.; Sanders, J.G.; Osman, R.W., 1989. The role of three species of benthic invertebrates in the transport of arsenic from contaminated estuarine sediment. Journal of Experimental Marine Biology and Ecology. 134 : 143-155.

Rouse, J.V.; Pyrih, R.Z.,1990. In place clean -up of heavy metal contamination of soil and ground water at wood preservation sites. In: Proceedings, American Wood Preservers' Association;86:215-220.

Sanders, J.G.; Windom, H.L.,1980. The uptake and reduction of arsenic species by marine algae. Estuaruarine and Coastal Marine Science. 10:555-567.

Schroeder, D.C.; Lee, G.F.1975. Potential transformation of chromium in natural waters. *Water, Air, and soil Pollution*. 4(3/4):355-365

Sloot, H.A.van der; Heasman, L., Quevauviller, PH., Harmonization of leaching extraction tests, 1997.

Solo-Gabriele, H. and Townsend, T., Disposal – end management of CCA – treated wood 95th Annual Meeting of the American Wood Preservers' Association, 1999May 16-19 Ft.Lauderdale, Florida , 95,pp. 65-73.

Teichman, T.; Monkan, J.L. 1966. An investigation of inorganic wood preservatives. Part I. The stability to extraction of arsenic impregnated wood. *Holzforschung*. 20(4): 125–127.

Tom, P., Good wood gone bad, *Waste Age* vol. 32 No. 8, August 2001, 36-51.

Tsoumis, G. (1992). *Science and technology of wood; structure, properties, utilisation*. New York: Van Nostrand Reinhold: London; Chapman and Hall, 494 pp.

U.S. Department of Agriculture, Forest Services, Forest Prod. Lab. Tech. Note 229, May 1961.

U.S. Department of Health & Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. "Toxicological Profile for Pentachlorophenol," draft, Atlanta, GA, October 1992.

U.S. Department of Health & Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, "Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs)," draft, Atlanta, GA, October 1993.

U.S. Environmental Protection Agency, Office of Research and Development, Contaminants and Remedial Options at Wood Preserving Sites, prepared by Foster Wheeler Enviresponse, Inc., EPA/600/R-92/182 (Washington, DC: October 1992).

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, "Presumptive Remedies for Soils, Sediments, and Sludges at Wood Treater Sites," EPA/540/F-95/006, PB 95-963410 (Draft), Washington, DC: May 1995.

Van Eetvelde, G.; Stevens, M.; Mahieu, F., Wegen, H.W.; Platen, A., 1998. An appraisal of methods for environmental testing of leachates from salt treated wood, part 1 (IRG/WP 98-50115). The International Research Group on Wood Preservation, Stockholm.

Webb, David A. Wood preservative treatments for crossties and potential future treatments. The Railway Tie Association Annual Meeting ,Birmingham, Alabama, October 10-12,1990

Weber, J.H. 1988. Binding and transport of metals by humic materials. In: Frimmel ,F.H.;Christman, R.F., eds. Humic substances and their role in the environment. New York: John Wiley and Sons:: 165-178.

Weis, J.S.; Weis P.1992. Transfer of contaminants from CCA-treated lumber to aquatic biota.. *Journal of Experimental Marine Biology and Ecology*.161: 189-199.

Weis, P.; Weis J.S.; and procter,1993. Copper, chromium and arsenic in estuarine sediments adjacent to wood treated with chromated copper arsenate. *Estuarine, Coastal and Shelf Science*. 36: 71-79.

Wilson, A. 1971. The effects of temperature, solution strength, and timber species on the rate of fixation of a copper-chrome-arsenate wood preservative. *Institute of Wood Science*. 5(6): 36-40.

Wilson, A., Disposal: The Achilles' Heel of CCA-Treated Wood, *Environment Building News, Feature Articles, Volume 6, No. 3, March 1997*.

Wood, J.M. 1974. Biological cycles for toxic elements in the environment. *Science*. 183: 1049-1052.