CHARACTERISATION AND WASTE MANAGEMENT OF THE CCA TREATED WOOD ARISING FROM AN INTEGRATED STEELWORKS

By

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A Thesis submitted to the Cardiff University for the Degree of

Doctor of Philosophy

Institute of Sustainability, Energy and Environmental Management,
Cardiff School of Engineering, Cardiff University
January 2014

In loving memories of

Sugandha Vohra

(1992-2012)

Sister and a pure soul

Mangat Ram Raghuyal

(1928-2013)

Grandfather and a wise person

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Abstract

This thesis is concerned with the management of wood waste generated after demolition of a typical 33 year old coke quenching tower from an integrated steelworks. Wood in the coke quenching tower was treated with traditional waterborne preservative, Copper-Chromium-Arsenic (CCA). Due to the growing environmental concern, changes were introduced in the legislation governing the disposal of waste. Hence, the aim of the thesis was to perform a waste management study by investigating CCA treated wood waste and to develop a waste disposal technique.

During the characterisation of the wood waste, elemental analysis was performed to confirm CCA concentration remaining in the treated wood waste. Concentration of CCA elements ranged from 300mg/kg to 10,000mg/kg. The concentration reduced with increase in the years of service life of the treated wood. Leaching tests according to British Standards were performed for different durations from 1 hour to 1 month to determine the leaching behaviour exhibited by the wood. Standard and customised sampling procedures were carried out for leaching tests to study and simulate the loss of CCA from the treated wood during a quenching process. These tests provided a leaching pattern that the loss of CCA follows a trend of As > Cu > Cr which was in agreement with the final concentrations of the quenching tower wood, such that chromium was most resistant to leaching and arsenic was most susceptible to leach. Correlations and linear equations were established between the arsenic-chromium and arsenic-copper leach concentrations. Equations were developed to help in predicting the ratio of leach ability of the CCA elements with respect to each other.

It was also found that the wood from the tower contained a substantial amount of iron which was further investigated. The growth ring analysis showed that iron was mainly deposited on the wood surface. The prime sources of iron were identified to be kish, an air borne particulate matter found in steelworks environment as well as coke and coke ash. Leaching studies performed to determine the leachability of iron showed that there was a potential for iron to restrict the mobility of CCA elements in soil.

A novel three-step chemical extraction method was developed after analysing the sequential analysis performed with different chemical reagents and leaching behaviour of the CCA wood waste. Step one used sodium hydroxide (NaOH) to break down the wood structure by lignin depolymerisation. The use of NaOH provided alkaline conditions and facilitated the process of lignin depolymerisation mainly to release arsenic as water soluble compounds. This was followed by ammonium chloride (NH_4Cl) for release of copper, due to the high affinity of ammonium group to form complexes with copper. Hydrogen peroxide (H_2O_2) was used as a strong oxidising agent and primarily to release the chromium by forming chromium complexes which are readily soluble in water. The effect of the pH, temperature, concentration and order of the reagent to be used were studied. Therefore, CCA wood was subjected to the three-step process, where the order was designed as NaOH followed by NH_4Cl and then H_2O_2 for 1 hour at 100^oC with 1 M, 2 M and 2 M concentration respectively. 98 %, 89 % and 96 % for arsenic, chromium and copper respectively was the extraction percentage achieved by the three step process. The three elements were obtained in a water solution and a dry wood residue. The process showed the potential in an alkaline extraction method with high extraction levels in three hours. The process also provided wood residue with possible uses in paper and pulp industry.

In order to complete the treatment method the CCA elements present in water solution obtained after the three-step extraction process were required to be precipitated. The CCA elements present in water soluble state were precipitated by using an electrocoagulation process. Various parameters were analysed including type of electrodes, a suitable pH range, current, and concentration of the solution to optimise the whole process. The pH of the solution played a vital role in the precipitation of the elements. The pH value was adjusted to 4 in order to achieve the maximum removal potential. The mild steel electrodes were selected over the aluminium. The iron ions released from the mild steel electrodes formed insoluble complexes with the CCA elements in the solution as compared to the soluble aluminium ions. The final process was optimised to 15 minutes of duration using mild steel electrodes and 0.8 A current at room temperature. The solution used for the electrocoagulation was diluted to the factor of 1:5. The full process precipitated about 99 % of CCA elements from water which was filtered and analysed.

Overall, the thesis provided in-depth characterisation of the CCA treated wood waste arising from a steelworks environment. The leaching behaviour and the presence of iron were studied to provide a better understanding for the disposal of such wastes. A chemical extraction method followed by the electrocoagulation for the disposal of CCA treated wood waste provided a foundation for a scaled up treatment method and final disposal of such wastes.

Acknowledgements

I would like to take this opportunity to express gratitude to Professor Tony Griffiths and Mr Julian Steer. This research work is the result of continual help and support provided by Professor Tony Griffiths, mentor and supervisor. I am also grateful to Mr Julian Steer, research associate and friend for his guidance and knowledge provided throughout this study.

I would like to extend my thanks to Tata Steel Europe, Port Talbot Steelworks the help, support and assistance in this research. The co-operation with the Tata steel personnel especially Mr Jon Denley has been unparalleled in providing the vital samples and data required to understand the critical aspect of the research and to achieve the objectives of the research.

Special thanks to Mr Andrew Hopkins for his assistance and contribution particularly ensuring a smooth communication and providing essential networking links.

I would like to thank Cardiff University laboratory co-ordinators Mr Ravi Mitha and Mr Jeff Rowlands for their kind assistance in carrying out various experiments associated with this research.

Thanks to all the staff and friends at Cardiff University for their vital background help, support and assistance in numerous different ways.

Finally I would like to express my sincere gratitude and love to my Mom, Dad and Sis for their full support and encouragement in every aspect of my life.

Table of Contents

List of Figures

List of Table

List of Abbreviations

CCA : Copper Chromium Arsenic

Cu : Copper

Cr : Chromium

As : Arsenic

Fe : Iron

TWW : Treated Wood Waste

BS : British Standard

AWPA : American Wood Protection Association

UK : United Kingdom

WFD : Waste Frame Directive

EU : European Union

EC : European council

EWC : European Waste Catalogue

ICP : Inductively Coupled Plasma

SEM : Scanning Electron Microscope

EDX : Energy dispersive X-Ray

XRD : X-Ray Diffraction

EDR : Electrodialytic Remediation

HCl : Hydrochloric

NaCl : Sodium Chloride

NaOH : Sodium Hydroxide

NH_4Cl : Ammonium Chloride

NH_4OH : Ammonium Hydroxide

H_2O_2 : Hydrogen Peroxide

HFO : Hydrous Ferric Oxide

Chapter 1. Introduction

1.1 Background

For a very long time wood has been a vital material for humans. Wood has been used as fuel, construction, furniture, flooring, art and decorative, musical instruments, sports, marine applications and many industrial uses such as raw material, tools, fences, supports, beams, cooling and quenching towers. However, wood is an organic matter and it will decay and deteriorate over time. There are various factors which are responsible for deterioration of wood including insects, micro-organisms, gases, acids, bases, metals, salts, water and weather conditions such as heat, cold, rain or snow. Hence, the wood was required to undergo preservation in order to retain its strength and properties.

A variety of preservation methods and application techniques have been developed over time. By 1884 a competitive wood preserving industry had been established which led to the development of various preservative salts and treatment methods for preserving wood [1]. By the start of the 20th century, this growing, changing and evolving wood preservation practices led to the advancement of a water-soluble preservative salt which consisted of three heavy metals namely copper, chromium and arsenic (CCA) [1]. Richardson [1] also stated that wood treated with CCA provided excellent protection against most of the fungal and wood-borer deterioration. These formulations of CCA are available in a standardised version by British Standards and American Wood Preserver's Association (AWPA). Pressure treatment processes were used to impregnate wood with the water-borne salts of CCA. This treatment enhanced the service life of the wood by 30 to 50 years [2-4]. The CCA treatment of wood also provided options for painting, with a dry and odourless durable wood. From the 1970's through to 80's the demand of CCA treated wood increased over other types of treatments such as creosotes and pentachlorophenol [1]. The treated wood found its uses across various markets; furniture, play equipment, fencing, decking, utility poles, bridges and industrial applications such as structural fixtures and cooling towers. Though the growth of the CCA production reduced in the 1990's, it was still an important and preferred treatment method in the wood treatment products.

Leaching of three elements copper, chromium and arsenic from in-service CCA treated wood posed health hazards and raised environmental concerns. The severity of these issues increased further with regard to the disposal options of the treated wood. The CCA elements are known to have carcinogenic, mutagenic and teratogenic effects on humans and animals. Plants and aquatic life forms are also at risk from elevated concentration of these elements. With the beginning of the 21st century the Environment Agency and regulatory bodies became more aware and tightened laws and regulations governing the use of CCA preservative. The treatment of new wood with CCA has been banned from the market with only restricted use for professional and industrial purposes only under stringent regulations [5]. The European Directive 2003/2/EC classed the waste arising from a CCA treated wood as hazardous [6].

In the United Kingdom the extensive use of CCA treated wood in 20th century meant that this particular kind of wood has started to come to an end of its useful service life and will begin to appear in the waste stream in steadily increasing quantities. According to a report by Waste Resource and Action Programme [7] about 4.1 million tonnes of wood waste entered the United Kingdom waste stream in 2010. About a quarter of the waste was generated by the demolition activities. There are about 45,000 tonnes of CCA wood waste arising which were used in building and fencing purposes. Murphy RJ [8] have performed a study and predicted that annual CCA treated wood waste in United Kingdom waste stream is expected to keep growing till 2061. CCA wood waste enters the non-hazardous waste stream by several pathways either from construction and demolition debris, Municipal Solid Waste (MSW) or through general industrial waste. Due to the hazardous classification of the CCA treated wood waste and its impacts on the environment, this has caused serious concerns on its disposal. The traditional and generally accepted disposal method of CCA treated wood is landfill or incineration where either of these methods have adverse environmental consequences. Burning or incineration of this wood waste releases highly toxic fumes and smokes into the environment such as arsenic fumes, particulate CCA matter. These resulting chemical compounds from burning are difficult to control whole burning equipment gets contaminated. Incineration of CCA wood waste also results in ash which is highly concentrated with CCA and still requires being disposed. On the other hand if landfilled, then CCA chemicals can leach from wood either unburned or ash. Therefore, landfilling of CCA wood waste inevitably results in contamination of both soil and ground water with toxic CCA pollutants over time. Moreover, landfilling is costly as there is limited space available and it is also not a preferred option because it does not recover any value from the waste.

Possibilities of reuse, reconstituted wood products are other options which can be considered, but the hazards associated with the CCA remain unattended. There are number of studies carried out to understand the leaching behaviour and effects of the CCA elements on the environment. Different materials and methods have been studied and the results obtained vary and in some cases contradicting. But a generalised conclusion has determined that a waste treatment method is required for the CCA wood waste in order to reduce the severity of the arising pollutants to the environment. Thus, remediation of CCA wood waste could reduce the risk threat to the environment and decrease the concern on the health and safety.

There are number of treatment methods that can be used to extract copper, chromium and arsenic from the CCA treated wood waste before the disposal which could reduce its environmental impact. They are mainly categorised as follows:

- Chemical Extraction

  Chemical extraction methods are one of the extensively studied methods. Chemical extraction utilises an array of chemicals and chemical reactions. One of the most common is the acid leaching processes by using citric, oxalic or other mineral acids. The processes could be single or multi-staged which depends on various factors such as type of chemicals and their concentrations.

- Bioremediation

  A number of biological methods have been investigated to extract, treat and finally dispose of the CCA wood waste. These methods involve using copper resistant fungal or bacterial strains. The basic principle used in extraction is by converting the insoluble heavy metals into a soluble form by using acidification with organic acids secreted by the biological organisms [9]. The soluble metal complex can then be leached out of the wood waste.

- Electrolytic methods

  The use of electric current has been widely investigated in the removal of the heavy metals from the CCA wood waste. Processes such as Electrodialytic Remediation (EDR) and electro-kinetic methods are used to extract elements from the wood chips using electric current. In EDR ion exchange membranes are used to separate the pre-soaked wood with water from the electrolyte and current is used as a cleaning agent [10]. The electro-kinetic treatment on the pre-extracted CCA wood waste by using a chemical extraction method has been employed for the disposal of the CCA wood.[11]

- Thermal treatment

  Thermal destruction methods are used to break down the waste wood to obtain energy. This could be achieved mainly by three processes: combustion or incineration, gasification and pyrolysis. These processes are extensively studied to determine the immediate energy generation through combustion or by creating secondary energy carriers through gasification or pyrolysis [12].

Research and development is on-going to develop a more efficient, industrially viable, economic and sustainable method for the disposal of the CCA treated wood waste. This has led to the combination of methods and treatment process of the above mentioned major categories. The generation of more and more CCA waste from all kinds of waste streams is mounting pressure on the waste management community to create a more sustainable disposal option.

A similar pressure is faced by the steel industry which produces a number of waste streams. There are many cooling and quenching towers across long-standing integrated steelworks sites. Large quantities of CCA wood were used in the construction of these towers which are now approaching the end of their service life. One of the major challenges is the disposal of the CCA treated wood waste generated after the demolition of these cooling and quenching towers.

1.2 Aims and objectives

The primary objective of this thesis was to characterise the CCA treated wood waste generated after the demolition of a typical coke quenching tower from an integrated steelworks site. A study of elemental analysis and leaching behaviour will be performed on the wood waste to understand the characteristics exhibited by CCA wood waste. The characterisation will aid to design and evaluate an appropriate waste treatment method and to determine a disposal option in accordance to the current environment regulations.

The principal aims of this thesis are:

- To perform elemental analysis and evaluate the leaching behaviour and characteristics of the CCA wood waste.

- To characterise and identify any specific features of the wood waste from steelworks environment which may hinder waste disposal.
- To develop a waste treatment method to separate or extract CCA elements from wood.

1.3 Thesis structure

The research presented in this thesis is divided over 7 chapters. A background of the wood preservation methods and uses of CCA treated wood is described in **Chapter 1**. This chapter also outlines the disposal issues of this kind of waste and regulations associated with it. The chapter also introduces to the aims and objectives of the research undertaken.

Chapter 2 covers the wood preservation technique, describes the wood treatment methods with CCA. This chapter also details the environment laws and legislations regulating the production, use and disposal of the CCA treated wood.

Chapter 3 reviews various methods of waste treatment techniques.

Chapter 4 details the source of the materials used for the research and provides the background information on the conditions of the CCA wood waste. This chapter also delivers the information on the sample preparation procedures of experiments undertaken for characterisation of CCA wood. The chapter also illustrates the design of the waste treatment process for disposal of the CCA wood.

Chapter 5 discusses the characterisation of the wood which includes the results of elemental analysis and leaching behaviour.

Chapter 6 presents the experimental results of the waste treatment process designed and discusses the disposal options.

Chapter 7 draws the conclusions of the thesis. This chapter highlights findings of the characterisation and waste treatment studies. The chapter provides suggestions and recommendations for the future work.

Chapter 2. **Wood Preservation and Legislation**

2.1 Introduction

This chapter provides the background information on wood and its preservation. The chapter briefly touches on the composition of wood, its structure and properties, need for preservation and different types of preservatives. It then focuses on the study on the particular type of preservative specifically Copper Chromium and Arsenic (CCA), which includes different chemical formulations and provides information on how the market for CCA preservative had previously evolved and standardisation of its formulation. Wood treatment methods used, post-treatment processes and chemical fixation are then highlighted and discussed.

The relation between the treated wood and the environment is then introduced. The toxic nature of CCA preservative has raised concerns regarding the treated wood. The risks and hazards associated with the leaching of chemicals into soil and water which have stimulated the changes in environmental regulations. The chapter describes the environmental laws and legislations which govern the use and treatment of fresh wood as well as mandatory regulations strictly monitoring the market and use of the CCA treated wood.

2.2 Wood

Wood is generally divided into two categories: Hardwood (angiosperms, where the seed is enclosed in the ovary of the flower such as oak and beech) and softwood (Gymnosperms, where the seed is not enclosed in the ovary of the flower such as pine and spruce). The structure of hardwood is more complex and varied than the softwood. However, most of the structural concepts remain similar between the two types. [13].

Here, only softwood is described since it is the important wood type used commercially across the wood preservation industry.

2.2.1 Wood Structure

A tree can be divided into three main parts; top is the crown of leaves, which is supported by the main stem system known as the trunk or bowl which connects the crown to roots in the ground. Wood is the secondary permanent tissue and other than mechanical properties has a range of functions such as conduction of liquids, nutrition and storage in woody plants, i.e. trees and scrubs. A single twig is the simplest form of a trunk which progressively grows over time. Figure 2.1 shows a cross-sectioned grown trunk with pith in the centre and other parts of typical softwood. The wood tissue around the pith is heartwood and is made up of dead cells. The heartwood is surrounded by living cells of sapwood or xylem which are covered by a thin layer of phloem and the protective bark. Sapwood is a band of light coloured wood adjacent to the bark whereas heartwood is the dark coloured wood, found in the interior of the sapwood. The dividing cells between xylem and phloem are known as cambium which is barely visible macroscopically [1].

The basic function of xylem or sapwood tissue is to transfer water and dissolved salts from roots to the crown of the tree where the leaves are, whereas phloem is the tissue responsible for the transfer of the sugars from crown to various parts of the tree. Cambium is a thin layer with formative cells, where cell division occur dividing cells either to the inside to form xylem cells or towards the outside to form phloem cells [14]. Cells formed at the beginning of the growth increment are called ‘earlywood’ whereas the later growth increment forms ‘latewood’ cells [13]. A xylem cell, a tracheid or fibre is formed with a thin cell wall by the polymerisation of sugars into cellulose. Successive layers are built over a primary after a continuous supply of sugars from phloem until the cell structure is complete.

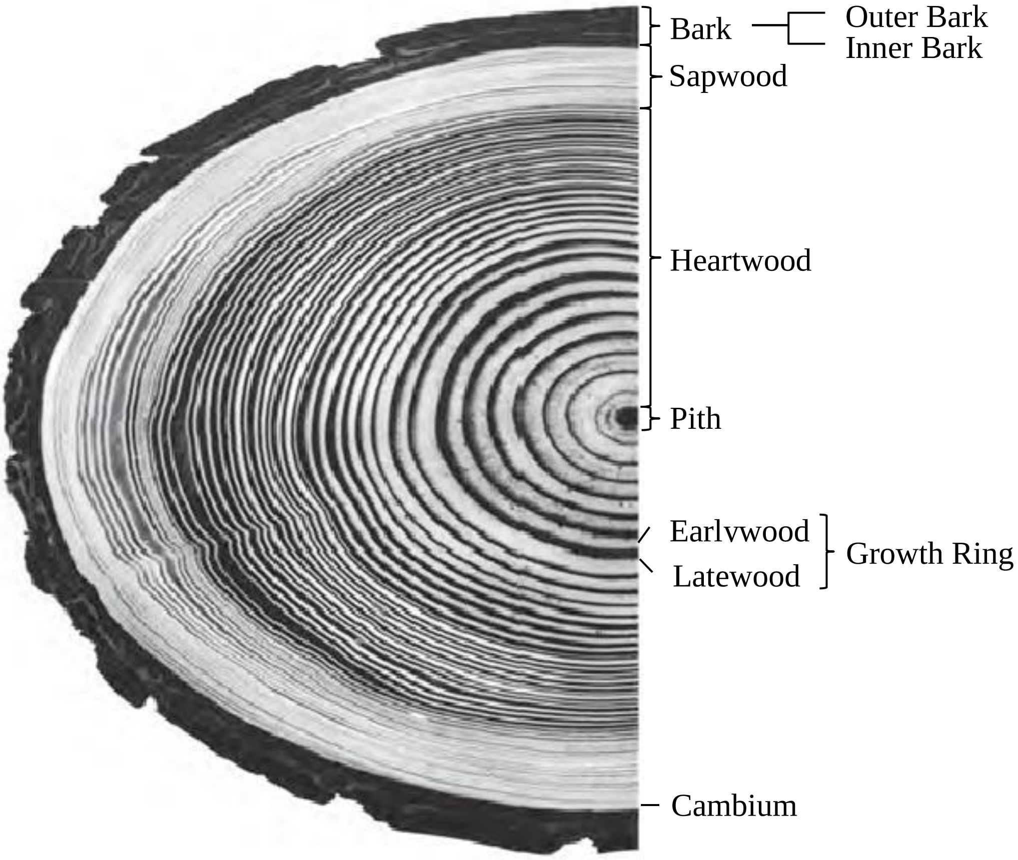


Figure 2.1 Cross-section through a trunk of typical softwood with various wood parts- bark, growth rings, centre pith, sapwood and heartwood [15]

The depth of the sapwood is governed by the availability of the food and oxygen for the living cells; this could be influenced by the seasonal or climatic changes. Furthermore, the growth of cambium and new formative cells leads to the death of the inner layer of the sapwood and conversion into heartwood. A large amount of material gets deposited in the heartwood which reduces its porosity and makes it significantly toxic to fungal and insect attack [1].

The annual increment in the growth of wood and its formation on a tree is visible in the shape of rings known as annual growth rings. The width of the growth rings is determined by climate and growth site. The growth rings can help in determining many facts such as the type of wood and also provides possible matches of the species and region. The thickness of these rings varies as a result of seasonal climatic variations. But there are some tropical woods where growth rings are completely absent [14].

2.2.2 Elementary Composition of Wood

There is no difference between the elementary composition of softwood and hardwood or between individual species [13]. Wood is basically composed of carbon, oxygen and hydrogen. Other elements such as nitrogen, calcium, potassium, manganese, magnesium, aluminium, sodium and iron are present as nutrients but at very low concentrations [14]. Table 2.1 shows the primary constituents of wood which are three macromolecular components: cellulose, hemicellulose and lignin. Wood is made up of about 50% of cellulose. Cellulose is a long chain of repeating polymers of glucose. These chains are combined in to bundles which are called microfibrils. Microfibrils are surrounded by a matrix of hemicellulose and lignin. Hemicellulose is also a glucose polymer, but also has other sugars which add to its strength and make it more susceptible to degradation. Lignin is a phenolic component of the wood which imparts rigidity to wood. It is a polymer containing many phenyl propane units. Lignin is most resistant to hydrolysis which makes the wood resistant to degradation and deterioration as compared to other biopolymers.

Table 2.1 Main constituents of softwood of temperate zones [14]

Constituent	Softwood (%)
Cellulose	45-50
Hemicellulose	15-20
Lignin	25-30

2.2.3 Wood Properties

Wood is a porous and hygroscopic material that takes up moisture from the surrounding environment. Moisture exchange between wood and atmosphere depends on relative humidity, temperature of the air and current water level already in the wood. The wood moisture content has effect on various physical properties such as shrinking and swelling, density, electrical, thermal and acoustic properties as well as its mechanical properties. Moisture content also affects wood's reaction towards the biological agents such as decay, fungi, insects, bacteria and marine borers. It also plays a vital role in the technological properties and processing activities of the wood such as machinability, drying, preservative treatment, gluing, coating and consolidation [14].

For a freshly cut wood, moisture is present in the cell cavities as free water and within the cell walls as bound water. Wood gets exposed to the atmosphere, after logging in which pore water is lost, however the bound water remains. This level of the moisture content in the wood is referred to as the fibre saturation point. Moisture content below the fibre saturation point will affect the wood properties, whereas above would make little or no difference to most properties [14]. Moisture content, m, can be classed into three categories.

- m = 0%, oven dry wood achieved after heating the wood in an oven at 105°C until it results in a constant mass,
- m = 25–30%, the fibre saturation point, this value depends on wood species where most of the free water has evaporated but the bound water remains.
- m_{max} the maximum moisture content, when all the pore volume of the wood is completely filled with water. This is also referred to as waterlogged wood.

When oven dried wood is exposed to the atmosphere, it will absorb moisture on and within cell walls as primary sorption sites. Most of the sites will be occupied when the moisture content reaches about 6% based on relative humidity of 30% [14].

The density of a porous material which may contain air, water and salts can change the mass and volume. Density is the weight or mass of wood divided by the volume of the specimen at a given moisture content. Generally, the density measurements for wood are based on oven dry mass as a) oven dry volume, b) Green (fully swollen) volume or c) volume “at test” which is at 12% moisture content. Dry wood on absorbing moisture will increase its mass and volume [13].

2.2.4 Need for Preservation of Wood

Wood is a natural organic material and is susceptible to decay and will deteriorate with time. This gives rise to wood preservation. Hence, it is important to understand the basics of wood degradation and decay agents. There are biological and non-biological agents which are responsible for these processes.

Biological agents require four basic conditions to enable them to act and degrade the wood: i) supply of food, ii) air or oxygen, iii) suitable temperature and iv) water or moisture. The wood destroying biological agents require food as nourishment which is mainly the wood itself. With the help of chemical substances, enzymes and fermentation processes, biota is able to breakdown the wood cells into simpler compounds and utilises the nutrients. Due to the moderate requirement of the air, oxygen is not a limiting factor and is available in ample quantities surrounding the wood in service or storage. Adequate temperature is required for the enzymes produced, to function in a specific temperature range. For most organisms the temperature range is between 0^{o}C to 62^{o}C. Finally the moisture conditions, the many organisms can survive and grow in dry conditions but not on a dry wood. Most organisms use the free water contained in the wood at the fibre saturation point, as highlighted before [16]. Water is used by the organisms for various purposes which include enzyme-mediated hydrolysis, a process to propagate the breakdown of the wood polymers through hydrolysis [17].

On the other hand, non-biological factors such as rain or water from various sources could induce conditions favourable for the biological organisms to thrive. Acids and bases can have a negative effect depending on their type, pH, concentration, exposure duration and temperature. An acid or base attack can lead to hydrolysis of the wood polymers. This could damage the wood properties by causing change in colour, swelling, and/or reduction in mechanical strength. Many inorganic salts in aqueous state form acidic or alkaline solutions which can have similar effects as discussed previously. Crystallisation of salts within the wood structure could lead to mechanical splitting and react with acid groups of wood components. Metals and various gases also have reactions with the wood, but it depends on the wood species, moisture content, environmental conditions and type of metal and gas. There could be other conditions and sources which could lead to the deterioration of wood or may introduce wood degrading factors but this depends on the processes and environment where the wood is to be used [14].

Wood is required to be protected from these decay agents and hence this sparked a need for wood preservation. Wood preservation can be defined as the measure taken to prevent the damage and destruction of wood or wood based materials by decay agents such as fungi, bacteria, marine borers or insects, while retaining its original strength and properties. These measures can be preventive or a control of an active attack [14]. Wood preservation enhances the service life of the wood up to 40 or even 50 years [2-4, 18, 19]. One of the wood preservation methods is treating the wood with chemical preservatives. These chemical preservatives are made of different chemical compounds of elements toxic to a wide range of biological organisms, which essential to their growth but are toxic if present in excess[20]. Fungal and bacterial species differ in their sensitivity towards heavy elements and the respective protection mechanism involved. Toxic heavy elements can inhibit the growth, cause morphological and physiological changes and affect the reproduction of the biota [20]. Addition of use of organic based solvents enhances the properties of the wood which helps it to protect from the non –biological factors such by changing the water repellent properties which reduces the natural affinity of wood for water[21]. This helps economically by reducing the replacement costs and environmentally by reducing the need to harvest large volumes of wood.

2.2.5 Types of Wood Preservatives

According to the British Standard BS1282 [22] the wood preservatives used across United Kingdom are grouped into three categories:

- Tar Oil preservatives (Type TO): these mainly consist of coal tar and generally known as creosotes. These are largely insoluble in water and are highly water repellent. Therefore, this treatment makes the wood resistant to moisture changes and reduces the splitting, cracking or distortion for the wood exposed to weather. But they have a characteristic odour which makes it unfriendly to come in contact with any edible item and is even known to induce smell to other materials in its vicinity. It is also prone to “bleed” from the surface after the treatment especially under hot weather conditions. The wood preserved with this type is also known to leave stains on the objects which come in its contact.
- Organic Solvent preservatives (Type OS): solvents which consist of solutions of one or more fungicides and/or insecticide in an organic solvent which is generally petroleum based white spirit. This type of preservative is flammable and hence is required to dry after which the residual preservative leave the wood’s flammability unchanged. These are considered to be suitable for interior or exterior use. They are generally not corrosive to metals. The active agents used in these formulations include carboxylates of zinc, copper, organoboron ester and tributylin compounds.
- Water-Borne preservatives (Type WB): These are multi-salt and multi-oxide preservatives. They consist of a mixture of inorganic compounds dissolved in water.

Once preservatives are impregnated into the wood, chemical changes occur and the active elements become insoluble in water. Treated wood does not have any odour and can be painted and glued. The prime example of such preservatives is Copper Chromium and Arsenic.

2.3 Copper Chromium and Arsenic

Copper chromium and arsenic (CCA) is a water soluble preservative. CCA has been considered as one of the most effective preservative treatment protecting wood against various biological attacks from fungi, marine borers and other insects. All three elements in the compound CCA play a vital role in the preservation process. Copper is an effective fungicide by interfering with the enzyme reactions of fungi and kills any mold. Arsenic is recognised as an insecticide and also serves as a fungicide for copper tolerant fungi. Chromium is not a proven pesticide but serves the main purposes of strong fixation of copper and arsenic into the wood fibre [23]. A higher percentage of chromium salts is necessary for the fixation of copper and arsenic in wood [24]. Pizzi [25] stated that chromium trioxide improves swelling, water resistance and water repellent characteristics of the treated wood. CCA treated wood is dry, odourless, can be painted and has a very good life span.

2.3.1 CCA Formulations

The development and evolution of today’s water soluble wood preservatives dates back to 1705 when kyanising was proposed, a treatment method of simple immersion of wood in a mercuric chloride solution began. This was later developed into mixed kyanising and deep kyanising by 1924. Simultaneously, the use of fluorides was gaining popularity, following which more and more research led to the development of Wolman salts. Wolman salts contained the formulations of fluorine, chromium, arsenic and phenol compounds and became the base for different types of preservation manufactured [1].

CCA originated in 1933 when an Indian scientist and timber engineer developed and patented the formulation under the name of Ascu. This was achieved by dissolving 3 parts by weight of copper sulphate, 1 part by weight of arsenic pentoxide and 3-5 parts by weight of potassium dichromate [24].

In the Table 2.2, a comparison between different CCA preservative formulations are highlighted which were developed in different countries. With a variety of formulation ratios, there were various trading names of CCA preservatives such as Celcure, Tanalith, greensalt, Ascu, K33 and CCA. Around 1949, Boliden K33 was introduced in the market of Sweden and Finland with higher levels of arsenic and Osmose K33 in North America. Where Celcure A was introduced and approved in New Zealand in 1959 at about same time Tanalith C was introduced. In 1961 the arsenic content of Tanalith C was changed to 44.1 % and named as Tanalith CA. In 1966, Tanlith NCA was introduced with changed copper levels to achieve a lower retention. In 1969 Celcure AN, a higher copper formulation similar to Tanlith NCA was approved in New Zealand. [1].

Table 2.2 Comparison between various CCA preservative formulations [1]

Preservative Brands	**CuO *(ratio,%)***	**CrO_3 *(ratio,%)***	**As_2O_5 *(ratio,%)***
Tanalith C	18.8	51.9	29.3
Tanalith CA	15.2	40.7	44.1
Tanalith NCA	21.2	34.7	44.0
Celcure A	17.0	45.3	37.8
Celcure AN	22.2	32.0	45.8
Boliden K33	19.6	35.3	45.1

Table 2.3 provide the composition of the preservative based on hydrated salts and Table 2.4 with percentages of oxides of elements to be used as standardised proportions. As the markets flooded with CCA products of various formulations using either salts like potassium

dichromate, copper sulphate and sodium arsenate or oxides like chromic oxide, copper oxide and arsenic pentoxide, the British Standards BS4072 [26] specified the formulation by type 1 and type 2 as two sets for preparing the water solution with different proportion of elements which are based on the hydrated salts or oxides of the CCA elements.

Table 2.3 Nominal and minimum proportions of components in formulations based on hydrated salts [26]

Component	Type 1 Preservative		Type 2 preservative	
	Nominal *% m/m*	Minimum *% m/m*	Nominal *% m/m*	Minimum *% m/m*
Copper (as $CuSO_4.5H_2O$)	32.6	29.5	35.0	31.5
Chromium (as $Na_2Cr_2O_7.2H_2O$)	41.0	37.0	45.0	40.5
Arsenic (as $As_2O_5.2H_2O$)	26.4	23.5	20.0	18.0

Table 2.4 Nominal and minimum proportions of components in formulations based on metals oxides [26]

Component	Type 1 Preservative		Type 2 preservative	
	Nominal *% m/m*	Minimum *% m/m*	Nominal *% m/m*	Minimum *% m/m*
Copper (as CuO)	17.1	15.5	19.1	17.2
Chromium (as CrO_3)	45.3	40.9	51.4	46.3
Arsenic (as As_2O_5)	37.6	33.5	29.5	26.6

Table 2.5 shows the compositions of CCA regulated by the American Wood Protection Association (AWPA) which is followed widely across America and by many other countries. AWPA stated the formulations of CCA on oxide basis with three ratios listed as Type A, B and C under AWPA standard P5-09 [27]. Type A consists of very high chromium with quite low arsenic level and Type B consists of very high arsenic and comparatively low chromium level. Hence, in order to obtain an optimum fixation type C was formulated in 1960s [23]. Type C became the most commonly used in the preservation market as it was considered to

have high fixation characteristics which provided better leach resistance and low corrosion rates [17]

Table 2.5 Composition of CCA Preservative Type A, B and C according to the American Wood Preserver's Association (AWPA) Standard P5-09 [27]

Component	CCA Preservative		
	Type A, %	Type B, %	Type C, %
Copper (as CuO)	18.1	19.6	18.5
Chromium (as CrO_3)	65.5	35.3	47.5
Arsenic (as As_2O_5)	16.4	45.1	34.0

2.3.2 Preservative Treatment

Wood is treated by preparing a CCA preservative solution by using one of the formulations from the standards stated above. The quality of preservative treatment is affected by two parameters: retention and penetration. Retention level (loading) to be achieved is governed according to the environment the wood will serve in. Retention levels are given by mass of CCA preservative per volume of wood. It is stated in mass of the actual CCA formulation (regardless of oxide or salt formulations) per volume of sapwood. The retention levels range from 4 kg/m^3 to 40 kg/m^3 [23]. The net retention depends on the concentration of preservative in solution. The amount of sapwood also determines the penetration levels that will be achieved by the preservatives as heartwood is difficult to penetrate [13].

Wood impregnation can be achieved in a wood treatment plant by loading the wood into a convectional industrial pressure cylinder fitted with air tight locking doors with the help of feed trolleys on rails. Figure 2.2 shows a pressure cylinder loaded with wood for the preservative treatment. The wood to be treated should be of the same species and similar size, and should be loaded in such a way that the solution has free access to all surfaces for the best results as recommended by British Standard BS4072 [26].

Figure 2.2 Convectional pressure cylinder and locking doors with loaded wood for preservative treatment [28]

High vacuum and pressure cycles are used to force the CCA preservative into the wood. British Standard 4072 [26] describes two types of pressure treatment which are the Full cell (Bethel) process and Empty cell (Lowry) process.

Figure 2.3 shows the graphical representation of the Full cell (Bethel) process where wood is loaded in the cylinder and is subjected to an initial vacuum and maintain for a set duration, after which the CCA preservative solution is flooded and before the release of the vacuum. A pressure is then applied for a pre-set duration. Then the cylinder is emptied of preservative solution and a final vacuum is applied. Hence removing the air beforehand flooding facilitates the penetration of preservatives into the wood [26].

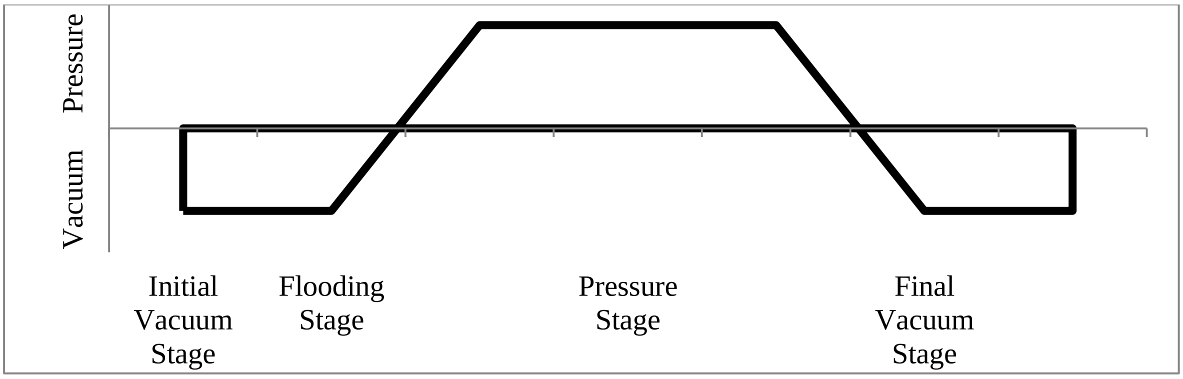


Figure 2.3 Graphical representation of Full Cell (Bethel) process with pressure as positive y-axis and vacuum as negative y-axis, with different stages of the process along x-axis [28]

Figure 2.4 shows the Empty cell (Lowry) process where wood in the cylinder is flooded with the preservative solution without the prior vacuum stage, after which the same pressure and final vacuum stages follow with the removal of the excess solution between the two stages [26]. Due to the absence of the initial vacuum in the empty cell process, the preservative is impregnated into the wood at the expense of trapped air. When the pressure is released and vacuum is applied, trapped air expands and forces the solution from the porous spaces of the wood leaving cell walls coated with preservative [1].

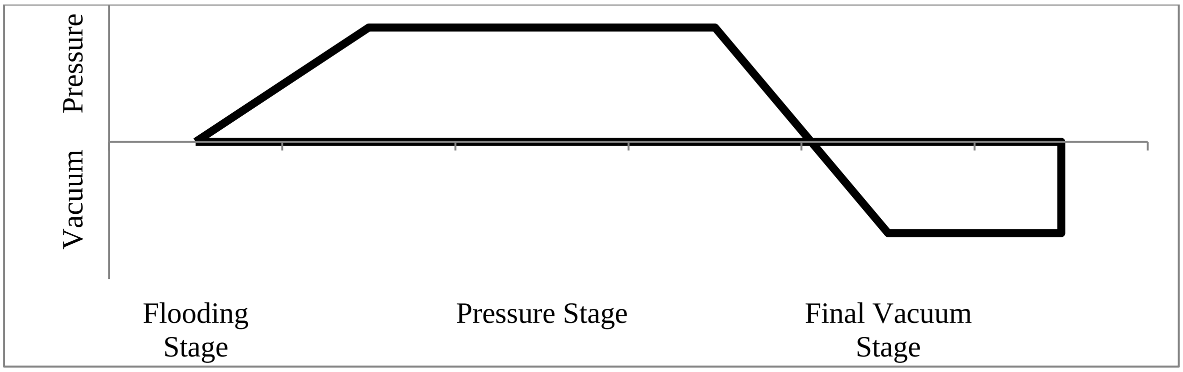


Figure 2.4 Graphical representation of Empty Cell (Lowry) process with pressure as positive y-axis and vacuum as negative y-axis, with different stages of the process along x-axis [28]

2.3.3 Post-Treatment and Chemical Fixation

After the pressure treatment of the wood with CCA preservative, the wood is allowed to dry. Drying allows the CCA components to react with one another as well as the wood; this is termed ‘Fixation’. These chemical reactions result in a change in wood pH and formation of low solubility metal complexes of copper, chromium and arsenic. The rate of fixation can be increased by raising the temperature of the impregnated wood. This is called accelerated fixation and can be carried out by various methods such as steaming or immersion of treated wood in hot water.

The conditions of precipitation of metals changes, when the wood is introduced into a pure preservative solution. Bull [29] stated that the inorganic chemistry of CCA is driven by the reaction of chromate with wood.

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

The pH values increase to a maximum during the main fixation period when the absorption of chromic acid in the wood takes place. The increase in pH is due to the consumption of hydrogen ions as stated by Bull [29]. The pH fluctuates until the final phase of reaction and conversion is completed, after which the pH reaches the final value [30]. Though depending on the CCA formulation different pH values have been recorded, such that according to Bull [31] due to the strong polymerisation of chromium (III) arsenate a critical pH of 2.3 or less was found. Whereas, Dahlgren [32] recorded pH up to 5.5 in wood during the CCA treatment using different formulations.

The interaction between the CCA components and wood as described by Pizzi [33] is that the main precipitation and fixation period can be divided as three reaction zones which are different phases of when reaction occurs. The first reaction zone was adsorption of Cr^{6+} on cellulose and dichromate ($Cr_2O_7^{2-}$) form lignin complexes. In the second zone, chromate ($HCrO_4^-$) forms lignin complexes and the third zone is mainly the reduction of Cr^{6+} to Cr^{3+} on cellulose sites. Pizzi [33] stated following as the end products formed by CCA and wood interactions after the wood preservative treatment:

- $CuCrO_4$ form stable lignin complexes.
- $CrAsO_4$ form lignin complexes and inorganic precipitates on cellulose sites.
- $Cr_2(OH)_4CrO_4$ forms inorganic precipitates on cellulose
- $HCrO_4^-$ forms lignin complexes
- Cu^{2+} ions form lignin and cellulose complexes and also physically adsorbed on wood.

According to a comparative study by Christensen [23] the fixation theories by Bull [29], Dahlgren [30] and Pizzi [25] agree that Cr^{6+} is reduced to Cr^{3+} and is the driving force for CCA fixation in wood. But the theories disagree on the fact that is Cr^{6+} present in the fixed wood or not.

Bull [29] stated that no Cr^{6+} is present in fully fixed wood whereas Dahlgren [30] suggested that Cr^{6+} may be present in freshly treated wood, but gets converted into stable Cr^{3+} compounds during storage at ordinary temperatures after some months.

But Pizzi [33] stated that amount of Cr^{6+} present in the treated wood depends on the relative proportions of copper and arsenic to the amount of chromium present. Cr^{6+} is totally and irreversibly fixed in the wood and hence, cannot readily leach. However, Cr^{3+} can leach but slowly with arsenic. If the concentration of copper is increased or concentration of arsenic is decreased in the preservative then it will result in the formation of more irreversibly fixed Cr^{6+} and less of arsenic in $CrAsO_4$ which would result in low insecticide protect for wood. If the concentrations of copper is decreased or arsenic is increased in the preservative then less irreversibly fixed Cr^{6+} and more of $CrAsO_4$ will be formed providing higher protection. However, this chromium in Cr^{3+} will slowly leach out from treated wood over time with arsenic.

2.4 Preserved Wood and Environment

The CCA treated wood with fixed chromium, copper and arsenic compounds within the wood and enhanced service life is introduced in the market and ready for the use. But the treated wood and its preservative components have great environmental influence and each metal (copper, chromium and arsenic) has raised environmental concerns. There are various ways by which the exposure to the three CCA metals can increase in the environment.

2.4.1 In-Service Concerns

While the CCA treated wood is in-service, there are concerns of slowly losing the CCA elements from the wood. CCA can enter the environment through various routes while the wood is in-service. Biological route where Epibiota or fouling community such as green algae, are the organisms found living on the surface of treated wood especially in marine wood products. With the help of enzymes and proteins, these organisms have the first hand uptake of the CCA elements. It has been found that organisms can have up to four times the concentration of copper, twice the chromium and five times the arsenic than rocks and sediments from the similar environment. This leads CCA elements to enter the food chain as these algae are consumed by the grazing snails, further increasing the concentration of CCA even to lethal effects and pass the toxic elements to crabs and further up the chain [34]. As well as direct contact with CCA treated wood is known to dislodge CCA elements from wood to organisms [35].

Leaching of the metals from the in-service wood is inevitable and can enter the water table or soil even with the best fixated CCA treated wood, ultimately raising environmental concerns. There are various factors which are responsible for the leaching of the CCA elements [36], these are;

- Physical factors
    - Wood species
    - Shape, size and surface area of the wood product
    - Exposure
    - Weather conditions such as light or heavy rainfall
- Chemical factors
    - pH of the soil and natural pH of the wood
    - Degree of fixated CCA elements in the wood.
    - pH of rain water such as acid rain
    - Surrounding temperature
    - Salinity in the environment

Leaching of the CCA elements also depend on other factors such as biological media present which help the leaching process by releasing enzymes and protein. The abrasive working conditions of the treated wood products such as marine applications and cooling towers gets exposed to more favourable leaching conditions. Ultimately, these CCA components get released in the environment and contaminate soil, the water table and finally enter the food chain.

2.4.2 Chromium Concerns

Chromium in the oxidation state of Cr^{3+} has low toxicity, but Cr^{6+} has high toxicity due to strong oxidation characteristics and permeability through biological membranes. Excessive exposure to chromium can produce an allergic skin sensitisation reaction, severe nasal irritation, scarring and damage to the lungs, liver and kidney. Cr^{6+} compounds have shown a strong indication of causing human lung cancer. However, Cr^{3+} is also known to cause cancer of the respiratory tract. Cr^{6+} has also shown mutagenic characteristics in bacteria and caused chromosome aberrations in mammalian cells. It may also cause birth defects and is known to have affected fertility in animals [37].

Hazards associated with the chemical CrO_3 used are T+ which is very toxic, O oxidising and N – Dangerous for the environment. On the Risk phrases (R), it is rated as R50/53 which means it is very toxic to aquatic organisms and may cause long term adverse effects in the aquatic environment. Furthermore R48/23 toxic danger of serious damage to health by prolonged exposure through inhalation. This material and its container must be disposed as hazardous waste due to safety concerns.

2.4.3 Arsenic Concerns

Exposure to arsenic compounds results in hyper pigmentation of the skin and hyperkeratosis of the skin as well as dermatitis of both primary irritation and sensitisation types. Acute inhalation can result in irritation of upper respiratory tract, even leading to ulceration and perforation of nasal septum. Symptoms of acute arsenic poisoning include burning lips, constriction of throat, abdominal pain, severe nausea, projectile vomiting, and profuse diarrhoea. Other toxic effects on the liver, blood-forming organs, central and peripheral nervous systems and cardiovascular systems may appear. Inorganic arsenic can produce lung, skin and lymphatic cancer with long term exposure. Teratogenic effects of soluble arsenic compounds at high doses have been recorded in hamsters, rats and mice [37].

Arsenic is used as As_2O_5 with hazards like T – Toxic, and N – Dangerous for the environment. The risk and safety associated with this chemical are R45 which may cause cancer and R23/25 is toxic by inhalation and if swallowed, with S60 as safety concern regarding its disposal as hazardous waste.

2.4.4 Copper Concerns

Though copper is an essential element for living organisms, it can be highly toxic to aquatic organisms even at low concentrations. Therefore, the CCA treated wood products being used in marine applications raises concerns for the aquatic environment. Copper in the free ion state is most toxic. Water alkalinity and hardness contribute towards a reduction in toxicity. Organism size also influences the toxicity and bioaccumulation [38].

Hazards associated with copper as CuO are XN – Harmful and N – Dangerous for the environment, particularly for aquatic environment. The risks and safety issues are R22 as it may harmful if swallowed and R50 which states that it is very toxic to aquatic organisms. S24/25 states that contact with skin and eyes should be avoided and S29 associated with copper states that it should not be disposed through the drains.

2.4.5 Disposal Concerns

Traditionally, treated wood gets mixed with construction and demolition waste and remains undetected. In a study by Jacobi [39] at a recycling facility in Florida, at least 10% by weight of treated wood waste was found in construction and demolition waste. From the analysis of wood waste 77% by weight was CCA wood and the rest was treated with other copper based preservatives. This waste is either landfilled or is destined to a generally accepted method of incineration. But there were concerns associated with both the disposal methods. The incinerated or thermal destruction provides significant reduction in waste volume with recovery of energy. But the ash generated is considered as hazardous due to the high metal content. Arsenic compounds are volatile and requires additional set up and modifications for capturing and monitoring the air emissions. For landfill disposal, the CCA solution can leach from the unburned wood or as ash in quantities which exceed the regulatory thresholds. Also, hazardous landfill sites have high disposal costs with a very limited landfill space and no recovery value [12].

2.5 Legislations

In the European Union (EU), laws (Regulations, Directives and Decisions) take precedence over national law and are binding on national authorities. EU Directives lay down certain end results that must be achieved in every Member State. National authorities have to adapt their laws to meet these goals, but are free to decide how to do so. Regulations are the most direct form of EU law where they have a binding legal force throughout the member states and national governments do not have to take actions themselves to implement EU regulations. Regulations are different from Directives which are addressed to national authorities, who must then take action to make them part of national law, and decisions [40].

2.5.1 European Commission

There are several directives that standardise the legislations governing the wood preservation industry with in the Europe. These documents include:

- *Biocidal Products Directive (98/8/EC)* is a Directive enacted on 16th February 1998 and related to the placing of biocidal products on the market. It can be defined as any substance that is considered to be a biocidal product which is used to destroy, deter, render harmless, prevent action of or exert a controlling effect on any harmful organism by chemical or biological means. Biocidal products are divided into four main groups and 23 product types which are regulated by the EU under this Directive. Wood preservatives fall in the group two ‘Preservatives’ and product type 8 [41].
- *European Commission’s (EC) White Paper (COM [2001] 88 final)* is a strategy on future chemical policy in the community presented by the Commission on 27 February 2001 with an overriding goal of sustainable development. Commission defined the political objective as the protection of human health and promotion of non-toxic environment. It proposes the maintenance and enhancement of the

competitiveness of the EU chemical industry by stimulating innovation and preventing the fragmentation of the internal market. This document proposes that existing and new substances should be revised for a more effective and efficient system. This system is abbreviated as REACH and stands for **R**egistration, **E**valuation and **A**uthorisation of **CH**emicals. It was estimated that about 80% of the substances would require registration and systematic evaluation shows that 70% of the new substances are classified as dangerous (e.g. carcinogenic, toxic, sensitising, irritant or dangerous for the environment). Hence, the biocides used in wood preservative formulations or as additives evaluated under Biocidal Products Directive (98/8/EC) will be subjected to the REACH [42].

- *Commission Regulation (EC) No 2031/2003* is a second phase of the 10 year work programme of Directive 98/8/EC. This regulation details the rules to review the safety of biocides. This regulation requires environmental and health hazards of all the existing biocidal substances to be review at the EU level. This review process includes all wood preservative formulations [43].
- *Marketing and Use Directive 2003/2/EC* is the tenth amendment of the ouncil Directive 76/769/EEC which is primarily aimed on the restriction of the marketing and use of arsenic as a dangerous substance. This Directive highlights the risk posed to human health from the disposal of CCA treated wood waste. It also identifies the risk associated with the aquatic environment. These substances are considered as carcinogenic and genotoxic in nature, with an advice to consider no threshold limits for carcinogenic effects. Thus the CCA treated wood waste wood has been classified as Hazardous waste. The Directive also states that the wood preservatives are to be evaluated as a priority in the review programme under the Directive 98/8/EC. The

Directive did not place any requirements for the removal of CCA treated wood currently in use or in service [6].

The European Waste Catalogue (EWC) is a list of codes to be provided in the Duty of Care Notices or waste transfer notes used by the waste management companies, carriers, producers and to report volumes received or treated to the governing agency such as Environment Agency. EWC contains 20 chapters that are based upon the source that generated the waste or upon the type of waste. EWC is a set of six digit code in pairs where first pair identifies the chapter; next pair identifies the sub chapters contained in the stated chapter. The final pair relates directly to the waste forming a unique six digit code. This six digit code is called an entry and there are three types of entries stated in the [44]

- Absolute entries

  The waste under this code is automatically considered as hazardous. These entries are marked with an asterisk (*) and are not required to assess the composition of the waste as these possess one or more hazardous properties. These are colour-coded with Red and are marked with ‘A’ in the EWC document.

- Mirror entries

  As some waste are considered to have potential to be either hazardous or not, depending on if they contain dangerous substances. Hence mirror entries can be hazardous marked with an asterisk (*) or an alternative non-hazardous waste without an asterisk. These entries are colour-coded with Blue and are marked with ‘M’.

Following are the six digit codes according to the EWC 2002 relevant to the wood waste dealt in this study.

03 02 01*	non-halogenated organic wood preservatives	A
03 02 02*	organochlorinated wood preservatives	A
03 02 03*	organometallic wood preservatives	A
03 02 04*	inorganic wood preservatives	A
03 02 05*	other wood preservatives containing dangerous substances	M
17 02 04*	glass, plastic and wood containing or contaminated with dangerous substances	M
19 12 06*	wastes from waste management facilities, off-site waste water treatment **plants** - wood containing dangerous substances	M
20 01 37*	municipal wastes (household waste and similar commercial, industrial and institutional wastes) including separately collected fractions - wood containing dangerous substances	M

The Statutory Instruments 2003/3274 [5] of UK legislation provided regulations on the Environmental Protection (control of dangerous substances). This legislation also adapted the European Commission Directive 2003/2/EC. The legislation includes restrictions on the use of arsenic compounds and treated wood. CCA treated wood must be individually labelled “for professional and industrial installation and use only”. It also clearly defines that the waste generated by CCA treated wood will be deemed as hazardous.

Summary

The structure of wood and its properties provided a basic understanding of the wood anatomy. This included wood composition and different parts of wood at cellular level. The need for preservation and information on the wood degrading agents which lead to the destruction of the wood were discussed. Different types of preservatives available, specifically CCA preservative, were introduced. A background on the development and standardisation of the formulation of CCA preservative salts and wood preservation method followed by the fixation process provided an understanding of the chemical changes involved in a CCA treated wood. This formed a base of the knowledge for the characterisation of the CCA treated wood waste by understanding the functions of CCA components and their interaction with the wood and its parts.

Various environmental concerns associated with CCA treated wood were discussed and the evolutionary changes in the laws and legislation governing the wood preservation industry. The understanding of these regulations on the CCA preservative, its treatment and the treated wood itself has provided a framework which is necessary to deal with the waste generated from the CCA treated wood.

Chapter 3. **Waste Management and Waste Disposal Techniques**

3.1 Introduction

This chapter covers the legislation governing the aspects of waste management and its disposal. The chapter discusses the waste prevention followed by waste recovery and then disposal options defined as waste hierarchy according to the European Waste Framework Directive (WFD). Then the vital statistical data are highlighted regarding the use of CCA preservative in different parts of the world including a prediction on quantity of treated wood waste generated up to the year 2060. These data show the importance of the need of waste management and available disposal options for the CCA treated wood at the end of its service life.

CCA treated wood as a waste is then discussed which is followed by a discussion on the preventive methods available to reduce the consumption of this preservative. Reuse and recycling options for potential treated wood waste entering the waste stream are then considered. Landfill as a disposal option for hazardous waste is described according to the Environment Agency. The studies and research on the landfill and leaching of CCA treated wood are highlighted and discussed.

The chapter then describes the treatments and destruction techniques studied to reduce or extract the concentration of CCA components from the wood waste before recycling or disposal. These processes or treatments include various techniques such as bioremediation, Electrodialytic Remediation (EDR), chemical extraction or thermal treatments.

3.2 Waste Management

Directive 2008/98/EC is a guidance document on waste and repealing directives which is also known as the Waste Framework Directive or WFD. This document establishes the legislative framework for the handling of waste in the community. It defines key concepts of the waste, recovery, disposal and essential requirements for waste management [45]. Directorate General Environment [46] issued a guidance document on the interpretation of key provisions of WFD.

- ‘Waste’ can be defined as ‘any substance or object which the holder discards or intends or is required to discard’ [46].
- It also defines the concept of ‘discard’ as provided by the Court of Justice of the European Union (CJEU) such that discard applies to both recovery or disposal of waste or discard can involve a positive, negative or neutral commercial value or discard can be intentional/ deliberate voluntary or accidental by the holder or can happen without the their knowledge and there is no influence of storage on the status of the waste[46].

In the European waste policies and legislation the waste hierarchy is the most important aspect and it serves the primary principle to minimise the adverse environmental effects from waste and, to increase and optimise resource efficiency in waste management policy [46]. The waste hierarchy is a generalised method of prioritising the order of what is constituted as the best overall environmental option in waste legislation and policy with justified technical feasibility, economic viability and environmental protection [45]. Figure 3.1 shows the waste hierarchy in order of priority with the prevention of waste on the top and disposal option at the bottom with recovery options in the middle. Certain processes in the hierarchy can produce residues, which in turn should be managed in accordance with the hierarchy.

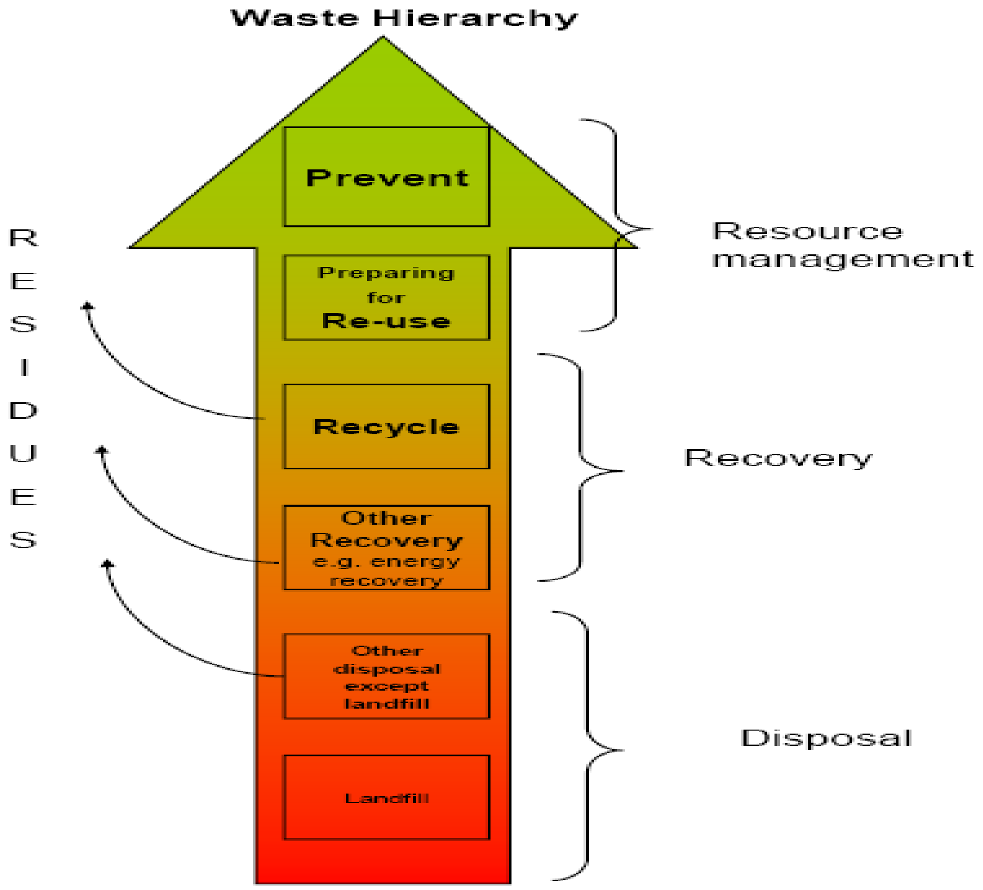


Figure 3.1 The waste hierarchy for hazardous waste management [47]

In the order of priority the waste hierarchy described by the Directive 2008/98/EC [45] is:

- Prevention:

  This includes the measures that are taken before a substance, material or product has become waste that either will reduce the quantity of waste including through the reuse of the product or by increasing the life span of products, or by reducing the adverse impacts of the generated waste on environment and human health, or by reducing the content of harmful substances in material or products;

- Preparing for Re-use:

  This is the process of checking, cleaning or repairing recovery operations, by which the product or component of the product that has become waste is prepared such that it can be re-used without any pre-processing. ‘Prepare for Re-use’ differs from the ‘Re-use’ as the product in question is already declared as waste according to the definition of waste and certain operations are required to undertake for it to be re-used. Whereas Re-use means any operation by which the product was not waste and is used again for the same purpose for which it was originally meant;

- Recycling:

  It is any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. This includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations. Therefore, waste material is processed by changing its physical and chemical properties so that it can be used again in the same or other applications. Thus recycling includes any physical, chemical or biological treatment leading to a material which no longer a waste [46].

- Other Recovery:

  It is any operation meeting the definition for ‘recovery’ under the WFD but failing to comply with the specific requirements for preparation for re-use or for recycling [46].

- Disposal:

  These are any operations which are not recovery even where the operation has as a secondary consequence the reclamation of substances or energy. These include landfilling, incinerations and backfilling (which do not meet recovery requirements).

Under the WFD, ‘Recovery’ comprises of the sub categories of preparing for re-use, recycling and other recovery operations. Recovery is defined by the WFD [45] as any operation which achieves its results by utilising waste as replacement of other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in a plant or in a wider economy. Recovery and disposal are defined as opposite terms such that disposal operations are based on getting rid of the waste as a result of waste management, whereas in recovery operations waste is served to a useful purpose of fulfilling a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy as described in Article 3(15) of WFD [45].

The guidelines by Directorate General Environment [46] also described the concept of ‘End of Waste’ incorporated by WFD such that substances or objects which met the waste definition can achieve a non-waste status and fall outside the scope of waste legislation, after undergoing a recovery operation (including recycling) such that waste no longer involves waste related risks and is ready to be used as a raw material in other processes.

Article 18 of WFD [45] clearly stated a ban on mixing of hazardous waste with member states to take the necessary measures to ensure that hazardous waste is not mixed, either with other categories of hazardous waste or with other wastes, substances or materials. Dilution of the hazardous waste is also considered as mixing of waste. The mixing of hazardous waste can be undertaken if all three preconditions set out by the WFD are met, such that

- Mixing operation is carried out by an establishment or undertaking which has obtained all relevant permits from competent authority and follow the safety and precautionary measures to be taken, monitoring, control operations, closure and after-care provisions as necessary.

- Mixing will not lead to the increase in the adverse impact of waste management on human health and environment. This includes the risk posed to water, soil, air, plants and animals.
- The mixing operation makes use of best available techniques.

3.3 Statistical Data of CCA Wood

Wood treated with CCA has a service life of 30 to 50 years considering the level of fixation, quality and grade of the treated wood [2-4, 18] as well as the service conditions such as in fresh and marine waters are considered to be 30 and 15 years respectively [19]. In the early 1970s the demand of CCA treated wood increased across various wood products. The odourless and paintable dry surface gave this type of treated wood an advantage over the creosotes and pentachlorophenol-treated wood and through 1980s to 1990s CCA continued to be an important chemical in the wood preservation industry [17]. By 2002, it was estimated that the world-wide wood preservation industry was treating about 30 million m^3 of wood each year consuming about 500,000 tonnes of preservative chemical, out of which two thirds was CCA [48].

Murphy RJ [8] predicted that the amount of annual CCA treated wood waste generated in the United Kingdom was 62,000 m^3 in 2004 and the amount in the waste stream is expected to grow to 100,000 m^3 by 2020 and 870,000 m^3 by 2061.

Within 15 countries of the European Union (EU) about 18million m^3 of pressure treated wood is produced annually for various uses [17]. In Germany and France, the total amount of wood waste generated is about 3-4 million tons per year, of which 2.1-2.4 million tons of waste is deemed as toxic [49]. In Denmark, the estimated amount of treated wood removed from service increased from 17,000 tons in 1992 to 100,000 tons a year by 2010 [23]. In the present decade, Norway has about 200,000 tons of preserved wood waste which is estimated to increase to more than 1.6 million tons by year 2041-2050 [23].

By 1995, in the United States of America (USA) about 67,000 tons of water-borne preservatives were utilised, out of which more than 90 % was CCA [50]. Approximately 17 million m^3 of CCA treated wood was generated annually in the USA [51]. In 1990, the estimated total volume of treated wood removed from service was about 18 million m^3 and the volume changed to 9 million m^3 in 2000 then to 15 million m^3 in 2010. It is estimated that 18 million m^3 by 2020 where 90% of wood removed from service in USA will be CCA treated [52].

In Canada the total production of treated wood was 3.5 million m^3 out of which 83 % was water-borne, mainly CCA [3]. It is predicted that the annual amount for ‘out of service’ CCA treated wood would be 2 million m^3 by the year 2020 of which more than 90 % will be coming from residential construction [53].

In Japan the volume of CCA preservative treated wood produced in 1996 was around 300,000 m^3, but the production has gradually reduced and stopped in 2003. However, due to the extensive use and predicting the long life cycle of the preserved wood with average service of 25 years, it is speculated that there will be a steady rise in the quantity of CCA treated wood waste. In 2003, the CCA wood waste was about 200,000 m^3 [54].

As of 2004, there were about 125 CCA treatment plants in Australia. Total treated wood production in Australia was about 1 to 1.3 million m^3 with about 70 % to 80 % of CCA treated wood using about 8,000 tons of CCA actives of which mostly were oxides formulations [17].

Currently for countries like India and Korea, Townsend [17] concluded that there are no known initiatives to restrict the CCA treated wood and its use. Rather, it is likely to increase the production of this type of preservation method.

It is inevitable that the wood treated with the preservatives will come to an end of its service life. Therefore, it can be expected that the percentage of the CCA treated wood in global wood waste will increase over the coming years which is demonstrated in Table 3.1 with the quantity of the treated wood waste produced over the past years and predicted substantial volumes of treated wood in waste across various countries in the world. The quantities represented are in volumes as well as by weight; this is due to the reason that the wood waste is reported according to industrial standards rather than the International standards. The variation is also due to the reporting of the units followed by different countries in waste reporting. The unknown wood types and densities conversion to one unit was not possible.

Table 3.1 Amount of treated wood produced by various countries across the world and compared with predicted quantities of treated wood waste generated by respective countries

Country	Volume of preserved wood production predicted (year)	Volume of Preserved wood waste generation predicted (year)
European Union*	18,000,000 (Annual)	n/a
United Kingdom*	n/a	870,000 (2061)
Germany and France†	n/a	2,400,000 (Annual)
Denmark†	17,000 (1992)	100,000 (2010)
Norway†	200,000 (2004)	1,600,000 (2041-2050)
Australia*	1,000,000 – 1,300,000 (2004)	n/a
Canada*	3,500,000	2,000,000 (2020)
Japan*	300,000 (1996)	200,000 (2003)
United States of America*	17,000,000 (1996)	18,000,000 (2020)

* Quantities represented by volume and measured in cubic metres (m^3)

† Quantities represented by weight and measured in tons

3.4 CCA Treated Wood as Waste

It is estimated that wood waste is mainly generated by five sectors; construction where wood waste is derived from the new buildings and demolition where the wood waste is removed from the buildings. Refurbishments generate wood waste derived from the removal and replacement of internal fittings. End of life furniture produces furniture which has been sent for disposal by the present owner and wooden packaging waste also sent for disposal by its current owners [55]. These wood waste accounts for 5.5 million tons per year in the UK. Only 9.6 % of this wood waste is re-used compared to 25.4 % recycled and 64.5 % sent to landfill or incinerated without energy recovery [56].

Figure 3.2 shows the trend of the hazardous waste from 2000-2008 where in 2008 over 6.6 million tons of hazardous wastes were sent for disposal and recovery in England and Wales. The amount of hazardous waste sent to landfill increased by 26 % to over 1 million tonnes, with recycling and reuse showing a decrease of 6 % in 2008 [47].

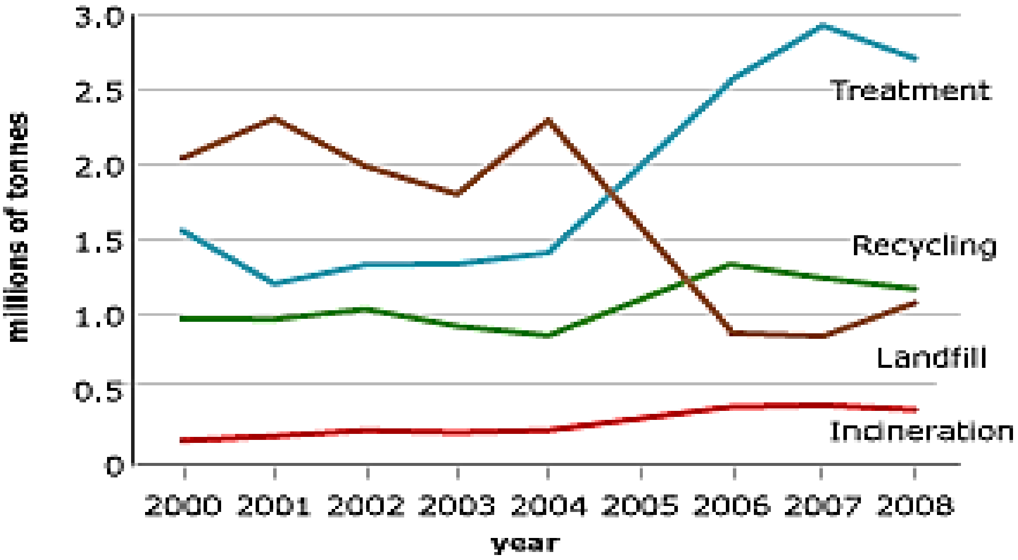


Figure 3.2 Trends in hazardous waste management for England and Wales from 2000-2008 [47]

According to a report by the Waste Resource and Action Programme [7] about 4.1 million tons of wood waste entered the United Kingdom waste stream in 2010. About a quarter of the waste was generated by the demolition activities. There is about 45,000 tons of CCA wood waste arising which were used in building and fencing purposes.

As described in Chapter 2, legislation has clearly defined the status of waste arising from CCA treated wood as hazardous material. According to the European Waste Catalogue the waste from the wood with dangerous substances are allocated six digit code of 17 02 04* mirror entry. The British Wood Preserving and Damp-Proofing Association [57] concluded that treated wood waste with the retention of CCA preservative at 4 kg/m^3 will be deemed as hazardous.

Successful methods of waste management will have an effect in three principal areas [17]:

a) Conserving both public and private softwood forests,
b) Reducing the area of public and private land utilisation for landfills, and
c) Providing new economic opportunities via the creation of recycling businesses.

3.4.1 Prevention of CCA Treated Wood Waste

In the guidelines of Directive 2008/98/EC by Directorate General Environment [46] that technical ‘Prevention’ is not a waste management operation because it concerns with substances or objects before they become waste. Hence, the obligations under waste management legislation do not apply, whereas reducing the amount of waste can be called as the quantitative waste prevention. The restricted use on the new CCA treated wood, declaration of the waste as hazardous and spreading awareness regarding the environmental impacts and dangers posed to human, plants and animals has led to the reduction in the use of this kind of treated wood. The changes in the legislations and view point towards CCA have led to an increased research and development in the wood preservation market. These include arsenic-free preservatives such as acid copper chromate (ACC), alkaline copper quat (ACQ), copper azole, copper citrate (CC), copper dimethyldithiocarbamate (CDDC), and copper HDO (CX-A). Most of the preservatives are copper based which is the primary biocide. These preservatives are reported to have lower toxicity and are lesser likely to cause concerns for the residential applications. The concentration used and retention levels for these preservatives are to be determined by the type of application and use [58]. However, the heavy amount of CCA treated wood historically used will inevitably be entering the waste stream in the near future. These wastes arising across the globe are required to be managed. The next level of hierarchy is preparing the waste for re-use.

3.4.2 Re-use of CCA Treated Wood Waste

The CCA treated wood can be re-used as it is, in the garden borders, posts fences, land piling, retaining walls or it can be prepared for re-use by sawing in to smaller pieces for fitting and retaining components in various wood products. But due to the strict regulations and considering the risk assessments, the applications identified for which CCA treated wood would be inappropriate are [56];

- Residential or domestic constructions;
- Any application where there is repeated risk of skin contact;
- Marine waters;
- Agricultural purposes other than for livestock fence posts and permitted structural use;
- Any application where the treated wood may come into contact with intermediate or finished products intended for human and/or animal consumption.

Irle [56] concluded that there is a high potential of CCA treated wood to be re-used for industrial purposes only and not for domestic applications.

There are also various barriers in preparing the wood waste for reuse as wood waste is required to be re-sawn and cut into smaller pieces as wood is a bulky material and inefficient to be transported. The generation of sawdust with a CCA presence makes it a health hazard [12]. There are high costs associated with the wood dismantled as it is usually contaminated with nails and other fasteners, which lowers the wood quality and limits its applications. Costs of handling, sorting, transportation and storage also increase due to the presence of CCA which requires the operator to carry out relevant risk assessments and use of protective equipment at all times [12].

3.4.3 Recycling of CCA Treated Wood Waste

There is a potential in the recycling of the CCA treated wood waste such as utilising the waste wood as raw material for the manufacturing of composite wood products. These products include a number of varieties and have varied characteristics to suit today's market demands. The treated wood waste may be chipped or pulped to add to the feedstock of the wood composite production. Utilising CCA wood waste in to wood composites has seen a mixed opinion either on the grounds of material properties and quality of products or environmental and economic concerns. Though recycling would ease the pressure on the waste management of the treated wood, lower the forest harvesting needs and act as a new inexpensive raw material resource for the wood composite. But this has also raised concerns that toxic fumes and airborne particles might be released by cutting and machining these wood products containing CCA metals. Hazardous materials will become further dispersed in the environment as they enter new products, and at the end of life, disposal to landfill may only be deferred rather than avoided [56].

There have been various studies to explore the use of CCA treated wood waste in wood composites, These are;

- ***Particleboard or chipboard***, a wood based panel product with wood chips or particles mixed with a synthetic resin adhesive. In a study performed by Kartal [59] on leach ability of CCA elements from Particleboard-CCA wood with phenol formaldehyde resin, it was concluded that relatively high leaching concentrations of arsenic were found, whereas for chromium and copper concentrations were comparable and insignificant respectively when compared with CCA treated wood particles.

  On the other hand the particleboard with CCA wood showed acceptable mechanical properties if an appropriate type and amount of thermoset resin such as phenol formaldehyde is used [17]. Kamdem [60] established that particleboard prepared with urea formaldehyde resin leached out more CCA components than particleboard prepared with phenol formaldehyde resin.

- ***Wood–cement composite***, another potential for the recycling of the wood waste is by making products suitable for exposed structural applications. Zhou [61] carried out a study on different wood cement ratio using Portland cement and wood particles from CCA wood removed from service to understand the mechanical and physical properties. Optimum results were obtained for bending strength, internal bonding strength and dimensional stability in agreement with published work on cement-bonded particleboard. In the further work on wood-cement Gong [62] with the ratio of cement to wood of 1.0 and 1.5 by weight, wood cement particle composite was found to have capability to absorb energy based on the significant non-linearity in load-deformation curves. Compressive strength of the composites was comparable to normal concrete material, and toughness index and strain at peak load were 7 times and 10 times than normal concrete. Composite material also demonstrated the ability to sustain large plastic deformations which implies that it can be used for the applications with energy dissipation requirements.

Townsend [17] stated that the levels of arsenic and copper leached from the wood-cement composites contained recycled CCA treated wood particles were not detectable. But chromium was found to leach at 3 % within 28 days out of which 60-70 % was hexavalent chromium.

- ***Wood plastics composites***, recycling the CCA treated wood flour or fibre with plastics could be a method of reducing waste stream. Wood plastics prepared by compression moulding of CCA wood particles at 3 % moisture content and High Density Polyethylene (HDPE). Wood plastics with heat diffused CCA showed increased strength properties, anti-photo-degradation and decay resistance [63].

  Laboratory based leaching tests showed that copper, chromium and arsenic leached at concentrations of 7 mg/kg, 11 mg/kg and 12 mg/kg respectively. The arsenic concentration was relatively high compared to the drinking water limit of 0.0010 mg/kg. Hence, the wood-plastics were suggested to be used for applications with minimum human exposure [63].

- ***Other applications,*** the CCA treated wood can also be considered for recycling in applications such as wet processed-fibreboards, medium-density fibreboards, flakeboards and oriented strand board. However, the decay hazard for these products is too low to be justified for the use of CCA treated wood as CCA would complicate the clean-up of process water and induce unnecessary environmental concerns, as well as introduce work related hazards. Also some of the products such as oriented strand boards are of high quality flakes, whereas the presence of CCA would lower all properties substantially [12].

The use of waste wood was proposed to be used in applications such as mulches, animal bedding and compost. Relatively high concentrations of CCA elements in the treated wood will exceed the recommended exposure limit of less than 0.1 % CCA due to the risk associated with the exposure to arsenic in such applications. Moreover, the increased surface area of the treated wood will increase the leaching of heavy metals. CCA treated wood in these applications will lead to the spreading of these toxic elements in the environment making them untraceable [12, 56].

3.4.4 Landfill as Disposal Option

The main aim of the legislations is to reduce the reliance on the landfill for the hazardous waste which is advised to be used only if no better options are available for the recovery or other disposal methods [47]. Landfill is considered as the last resort for the disposal options and in the waste management hierarchy. Incineration is also described as one of the disposal options but it will be discussed in the thermal treatments section of Chapter 3.

In the United Kingdom, landfills for hazardous waste have stringent requirements on the lining and capping, so that they can accept the wastes with higher leaching potential [64]. Hazardous waste landfill appears to be sufficient for current need with some seven dedicated hazardous waste landfills in England providing a disposal option for a wide range of hazardous wastes. There are also a number of separate cells in non-hazardous landfill for stable non-reactive hazardous waste and for asbestos. Current void capacity in dedicated hazardous waste landfills is estimated to be 19 million m^3. Some of the facilities have time limited planning permissions which may require extension in due course [47].

However, the landfill space should be considered as limited. There are stringent technical requirements that apply to the hazardous waste landfill in order to discourage the hazardous waste to be destined to landfill. This is managed through the Waste Acceptance Criteria (WAC) under the European Council Decision 2003/33/EC [47]. The 3 step procedure to be followed to ensure the landfill of hazardous waste in accordance to the legislation and regulations by the Environment Agency UK [64]:

- **Level 1: Basic Characterisation.** Before the landfill, the waste is required to be characterised. This will determine composition and properties of the waste.
- **Level 2: Compliance Testing.** Periodic checks required for regular arising wastes. This is to ensure the properties and composition is not changed.
- **Level 3: On-site Verification.** Checking of waste on delivery to landfill to ensure the waste was not contaminated during storage or transportation.

The basic characterisation is the first step in the acceptance procedure and constitutes a full characterisation of the waste. It determines the key variables in the waste. These are the properties that determine the potential for environmental impact or harm to health and may affect waste classification. These variables form the parameters to be assessed in level 2 and level 3 checking and establish the frequency of the checks. These variables include type and origin, composition, consistency, leachability and other properties which may help to understand the behaviour of waste in landfills. A full characterisation should include all the necessary information for a safe disposal of the waste for a long term [64].

Table 3.2 shows the leaching limits values for the granular waste, calculated for a liquid to solid ratio (L/S) = 2 l/kg and 10 l/kg such that waste can be acceptable at the landfills. These tests should be performed on dry substances.

Table 3.2 Leaching limit values for the criteria for waste acceptable at landfills for hazardous waste [65]

Component	L/S = 2 l/kg mg/kg of dry substance	L/S = 10 l/kg mg/kg dry substance
As	6	25
Cr	25	70
Cu	50	100

Various tests are performed on the CCA treated wood either to predict and understand the leaching behaviour exhibited by the waste in the landfills or to simulate leaching conditions in a lysimeter (leaching column) to consider correct choice and conditions for landfill.

As large amounts of CCA components remain in the treated wood waste which may cause significant damage to the environment and prove to be hazardous even in small percentages. Townsend [66] describes the two main objectives of leaching by evaluating the loss of preservatives from the treated wood products. First objective is to measure the rate of preservative depletion in order to assess the effective service life of the treated wood products. And the second objective is to amount and the rate of preservative lost when the wood is exposed to water. This assessment on the amount and rate of preservative leaching gives an indication on the potential contamination of soil, water and overall impact on the environment by the CCA components. There are various standards and methods of carrying out the laboratory based tests to determine the leaching characteristics of the waste materials.

Lysimeters are the leaching columns which are constructed and operated to perform experiments to simulate waste degradation and natural conditions. Figure 3.3 shows an example of a lysimeter with an integrated system to collect leachate. The lysimeter trials allow simulating some landfill conditions and hence, providing information and predictability of leaching of the CCA components after wood disposal [67]. The type of landfill can be very important because of differences in oxidation-reduction potential and chemistry resulting from biological reactions in the waste mass. Monofills, a type of landfill with only single waste type, containing a mix of new and weathered CCA treated wood in a simulated landfill (lysimeter) was examined by Jambeck [67]. Analysis of leachate showed low dissolved oxygen levels and reducing conditions which indicated towards microbial activity within the lysimeter. The concentration of CCA components was measured to be 42.2mg/l, 9.4mg/l and 2.4mg/l for arsenic, chromium and copper respectively. The cumulative amount of each metal leached from lysimeter was 3840mg, 859mg and 222mg of arsenic, chromium and copper respectively. The cumulative leached amounts can be calculated to 1.6%, 0.30% and 0.14% of arsenic, chromium and copper of the initial concentration of the leaching process. The wood material used for the trials was new CCA treated wood blocks and a 10 years old demolition CCA treated wooden blocks from a playground mixed in a ratio of 50/50.

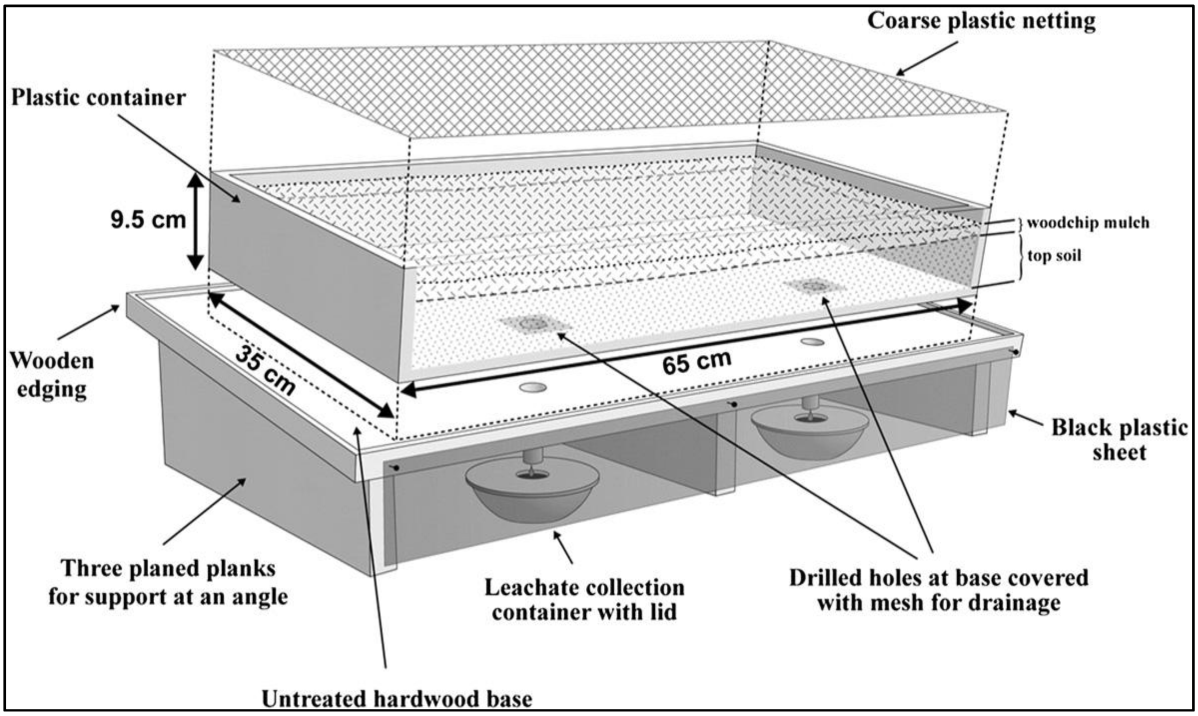


Figure 3.3Design of the Lysimeter with leachate collection system [68].

In another study, Mercer [68] used lysimeter trials with the weathered CCA wood mulch and soil for a period of 21 weeks. The trial was influenced by the rainfall leading to the waterlogged lysimeters and leachate overflow. This may have caused a higher leaching, but also a more diluted leachant than expected. Concentrations of arsenic, copper and chromium were at 1.89mg/l, 1.24mg/l and 1.26mg/l respectively. The concentrations detected in the leachate were exceeded by 42.6 times for arsenic and 4.6 times for chromium than the standards set for drinking water by the World Health Organisation (WHO).

3.5 Treatments and Destruction Techniques

Leaching of the preservative chemicals into the soil is a concern for landfill sites. There are potential technologies which are being explored in order to pre-treat or pre-process the CCA treated wood waste. These techniques can reduce the concentration of CCA components enabling the residue products to be utilised for the recycle purposes or disposed. This will reduce the impact and hazards associated with CCA on the environment in either way.

A Decision Tree (a type of flowchart) is designed to support ‘The Strategy Of Hazardous Waste Management’ in England by DEFRA [47]. The objective of the Strategy is to encourage recycling and recovery, and reducing reliance on landfill. Figure 3.4 shows a series of decisions recommended by the Strategy in order to help implement the waste hierarchy on the hazardous waste articles. It suggests that the waste should be treated by employing biological, physical, chemical or thermal method in order to recover the energy or value before considering the final option to landfill [47].

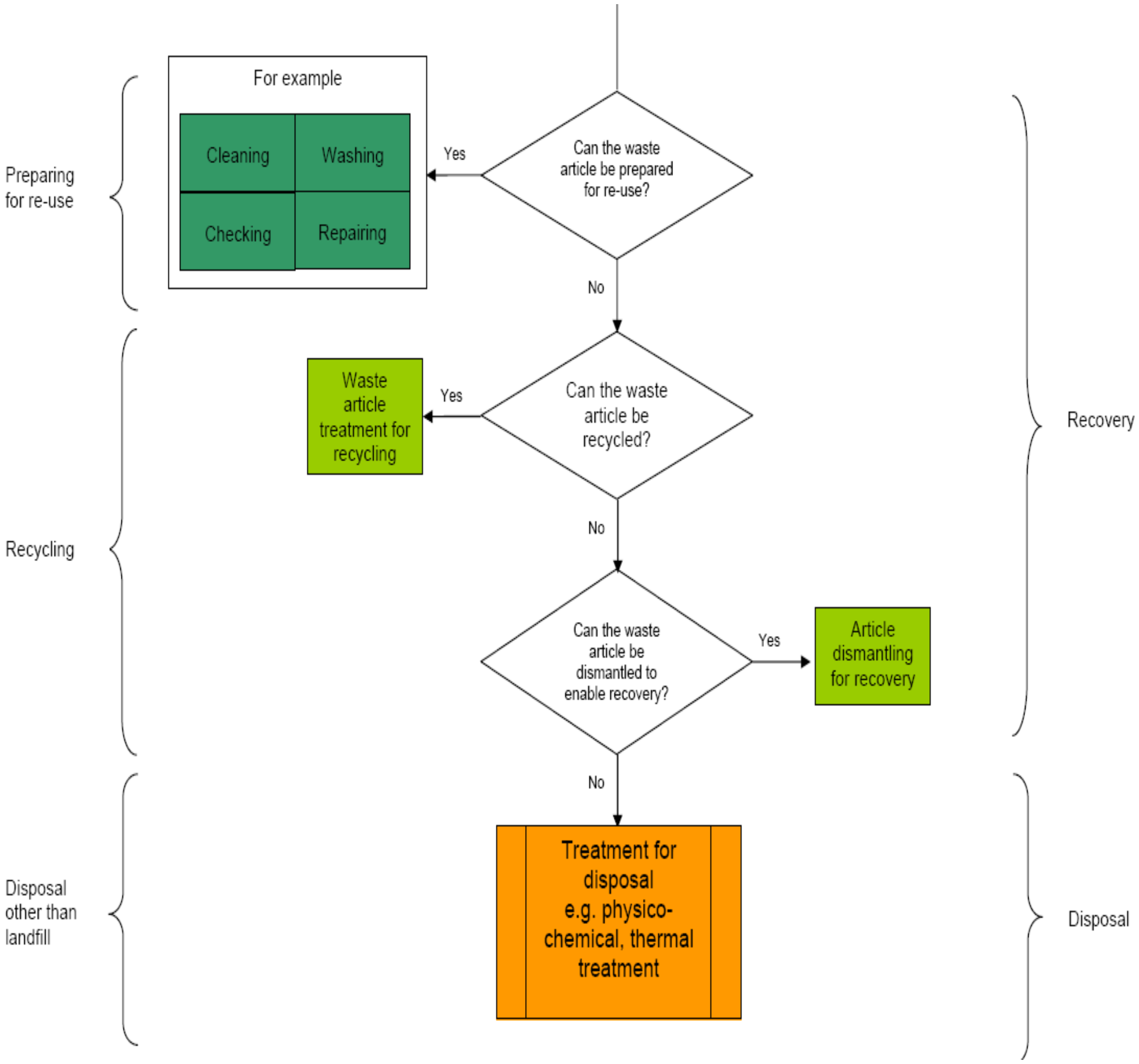


Figure 3.4Decision Tree for all hazardous waste articles [47]

3.5.1 Bioremediation

Bioremediation is a process of exploiting microorganisms to degrade or remove hazardous compounds of a waste from the environment. This process includes copper tolerant fungal strains and bacteria can be used for this process. The underlying principal is to convert the insoluble heavy metals in the waste wood to soluble form through acidification with organic acids. The soluble heavy metal complex can then be leached from the wood. Thus, both the remediated wood fibre and the metals can be reclaimed and recycled [9]. In bioremediation it is important to control the specific microorganism under specific environmental conditions such as moisture content, pH, temperature and control of nutrients in order to achieve the optimum removal and transformation of the contaminant.

Bacteria- Many strains of naturally occurring anaerobic and aerobic bacteria are able to extract metals. With no external energy source, bacteria and yeasts only need low levels of metal for cell function, where detoxification is probably their main reason for metal metabolism oxidise metals into water soluble forms [69].

The bacterial strains identified by Cole [51] were *Pseudomonas putida*, *Bacillus licheniformis*, or *Bacillus coagulans.* These bacteria showed a reduction up to 46% for copper, 9% for chromium, and 8% for arsenic by weight compared with the unexposed sawdust after a 3 week exposure time. This showed a potential and ability for bacteria to extract CCA. To achieve higher concentration the process of bacterial bioremediation of *Bacillus licheniformis* was combined with oxalic acid extraction, in a laboratory scale tests performed by Clausen [70]. The process removed up to 78% Cu, 100% Cr, and 97% As from 1 kg chipped CCA-treated wood and in a scaled up test parameters removed 65% Cu, 64% Cr, and 81% As from 11kg CCA wood chips in a 150 L reactor. The various factors that affected the efficiency of the scaled up study were wood size and thickness, recirculation of acid, bacterial growth medium and low regeneration time.

Fungi- There are some species of fungi which are able to remove heavy metals by producing large quantities of organic acids, particularly oxalic acid. A CCA-tolerant fungus was cultured under aerobic conditions in the dark at temperature between 27-32^{o}C and 70% of relative humidity. The fungal culture was incubated for 6 weeks. A total of 150 brown- and white-rot wood decay fungi were obtained from metal-treated wood. Most fungi grew toward non-treated wood with no growth toward CCA-treated wood. The 18 fungal isolates grew toward and/or on CCA-treated wood. Two strains of *Meruliporia incrassata* and *Antrodia* *radiculosa* were selected for capacity to degrade CCA wood; thereby reducing the volume of CCA treated wood waste by 20% of the original dry weight [71].

In another study, CCA treated wood samples were exposed to copper tolerant *(Antrodia vaillantii* and *Leucogyrophana pinastri)* and copper sensitive wood decay fungi *(Gloeophyllum trabeum* and *Poria monticola)*. Follows exposure to the fungi, specimens were leached and concentrations of copper and chromium leached were determined after a 12 week period. All wood decay fungi, copper tolerant as well as copper sensitive increased heavy metals leaching from the treated wood. The fastest colonization of impregnated wood was found at copper tolerant *A. vaillantii.* These fungi influenced the de-fixation process via oxalates formation. It was found that transformation of copper into copper oxalate by the fungi was essential but it was considered that other acids were also responsible for increased copper and chromium leaching [9].

Sierra-Alvarez [72] also used the copper tolerant brown rot fungi *Antrodia vaillantii* for the remediation of CCA treated wood. Fungal bioleaching resulted in high chromium and arsenic removal efficiencies at 84.9% and 66.0% respectively for a 49 day incubation period. The removal of copper was very poor and did not exceed 18.3%. Then after 56 days of fermentation the wood mass lost was 54.3%. After additional research, a chemical extraction process with citric acid (30mM, pH 3.10) was added before a 28 day solid-state fermentation period. The results for the two stage remediation process were 87% copper, 80% chromium and 100% arsenic removal.

Bioremediation of chromated copper arsenate (CCA)-treated wood was carried out by using three brown-rot fungi *Fomitopsis palustris*, *Coniophora puteana*, and *Laetiporus sulphureus*. The fungi were first cultivated in a fermentation broth to accumulate oxalic acid. Bioremediation of CCA-treated wood was then carried out by leaching of heavy metals with oxalic acid over a 10-day fermentation period. *F. palustris* removed the most of the CCA components with 100% arsenic, 87% chromium and 77% copper removal. The least amount removed was by *C. puteana* with arsenic only at 18%. These results suggest that *F. palustris* and *L. sulphureus* remediation processes can remove inorganic metal compounds via oxalic acid production by increasing the acidity of the substrate and increasing the solubility of the metals where *F. palustris* produced the maximum oxalic acid [73]. Another fungus which is known to release high amounts of oxalic acid is *Aspergillus niger*.

In another study by Kartal [74] with two-step remediation process with oxalic acid leaching and 10 day *A. niger* removed 97% of arsenic, 55% of chromium and 47% of copper form the CCA treated wood chips.

Bioremediation is a potential extraction and waste treatment method, but it is at an early stage and offers no practical industrial scale solution. In order to achieve high levels of extraction, the bioremediation process has to be used in conjunction with other processes such as chemical extraction due to the reason that most of the organisms lack the ability to tolerate preservatives present or metabolise the wood completely [56]. However, the costs associated with the nutrient culture medium are high and very long treatment or digestion times add up to the economic barrier. On the other hand degradation of the wood also makes the wood fibre damaged and lowers the quality for further use [12].

3.5.2 Electrodialytic Remediation (EDR)

Electrodialytic Remediation (EDR) was developed and patented at The Technical University of Denmark, where a pilot plant for the remediation of CCA treated wood has been designed and tested. Initially the method was developed for removing heavy metals from polluted soil. EDR uses a direct electric current as a cleaning agent and combines it with the use of ion exchange membranes to separate the electrolytes from the wood. The main principle used in EDR is that ions (including heavy metal ions) move in an electric field.

The laboratory cell consists of three compartments as shown in Figure 3.5 where an anode compartment (I), a cathode compartment (III) and a middle compartment (II) containing the wood chips. The catholyte is separated from the middle compartment by a cation exchange membrane, a membrane that only allows positive ions – cations to pass. The anolyte is separated from the middle compartment by an anion exchange membrane, a membrane that only allows negative ions –anions to pass [23].

When an electric potential is applied to the electrodes, the current in the cell will be carried by ions in the solutions in the compartments. Accordingly cationic (positive ions) species will migrate towards the cathode and anionic (negative ions) species will migrate towards the anode. This movement of ions in the electric field is called electromigration. The selectivity of ion exchange membranes placed as described above, prevents current carrying ions to pass from the electrode compartments into the middle compartment, but allows ions to be transported from the middle compartment into the electrode compartments. In this system the current is thus prevented from carrying highly mobile ions from one electrode compartment through the middle compartment into the other electrode compartment. Furthermore competition between such highly mobile ions from the electrode compartments and the ions in the middle compartment is avoided. In this manner the heavy metals ions migrate from middle compartment to the electrodes where they may be recovered by precipitation or electro-deposition [23].

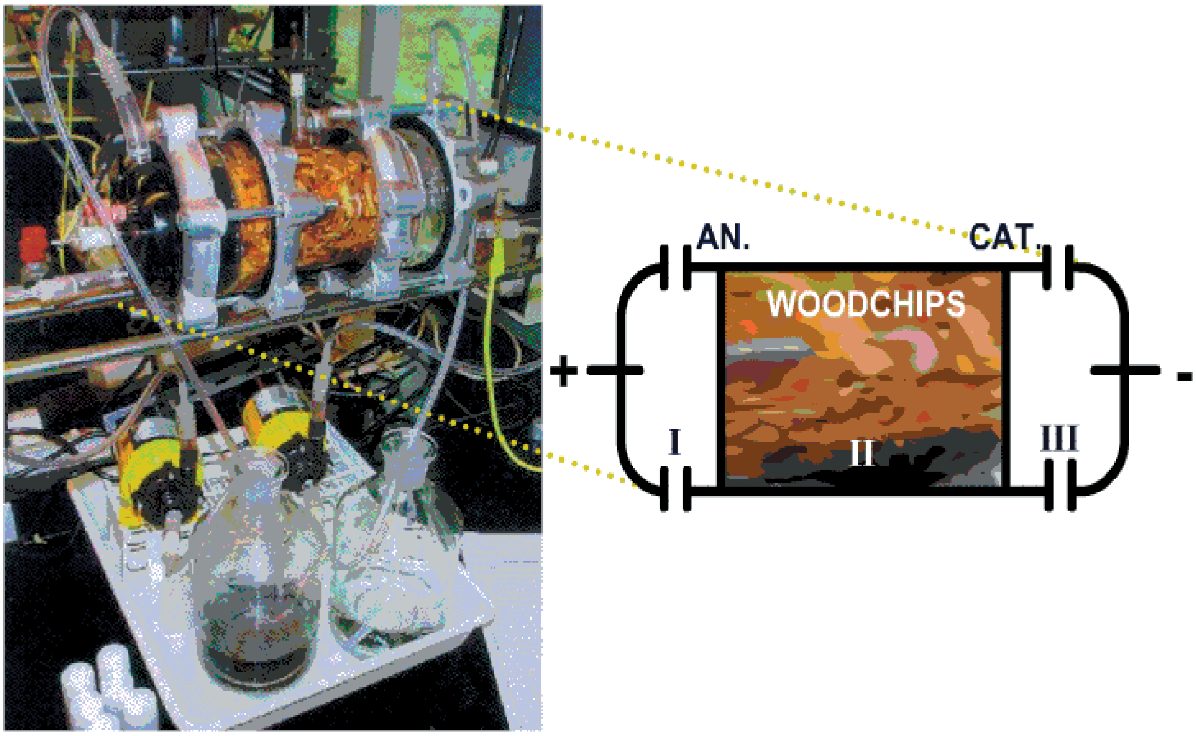


Figure 3.5 Electrodialytic Remediation (EDR) setup with different compartment I and III as anode and cathode compartments respectively. The wood chips placed in compartment II. AN and CAT are Anion and cation exchange membranes [10]

The CCA treated wood was soaked for 18 h in 0.5 M phosphoric acid, followed by 24 h of soaking in 5% oxalic acid before the remediation process. After soaking, the wood was placed in the pilot plant and covered with tap water and then the current was applied. In the electrode units and collecting units, 0.01 M $NaNO_3$ was circulated.

The highest removal rate was obtained where electrode distance was 60cm with one collecting unit used. 87% of copper, 81% of chromium and more than 95% of arsenic was removed after the EDR process [10]. This technology is, however, not yet economically feasible or developed at a commercial scale [56].

3.5.3 Chemical Extraction

There are a number of studies that have used the approach of chemical extraction to detoxify or extract CCA components from the treated wood. The important factors that govern the removal of CCA preservatives include diffusion of extracting agent into the wood, reaction of the chemical with the metals, wood particle size, pH, concentration of extracting chemical, temperature, extraction duration and mechanical agitation during the reaction. The chemical extraction processes involves reversal of the CCA fixation process by converting the CCA elements into water soluble form [17].

Acid Extraction- Kartal [75] examined the removal of CCA with Ethylenediaminetetracetic acid (EDTA) as a chelating agent using batch leaching experiments. Fresh CCA treated wood chips with 2 weeks of fixation period were exposed to 1% EDTA solution for 24 h. The treatment removed 60% copper, 13% chromium and 25% arsenic. EDTA solution also removed 93% copper, 36% chromium and 38% arsenic from smaller particles of CCA treated sawdust. High copper removal percentage was detected due to the strong complexing properties between EDTA and copper as EDTA forms strong complexes with metals and makes them soluble and easy to be removed from contaminated surfaces or soils.

In another study, Kartal [76], evaluated the effects of common chelating agents, EDTA, Nitrilotriacetic acid (NTA) and oxalic acid (OA) on the removal of metals oxides from freshly treated wood chips sawdust with CCA using a dual extraction process. The dual extraction was obtained by liquid to solid ratio (L:S 10:1) with EDTA/OA (1:1, v:v) solutions and NTA/OA (1:1, v:v) solutions. After a 24 h extraction period at $25^{o}C \underline{+} 2^{o}C$ 100 % Cu and more than 90 % Cr and As were removed from the sawdust and approximately 90 % Cu and 80-85 % Cr and As were removed from wood chips.

Moghaddam [77] investigated the effects of different factors on the leaching of CCA components of the treated wood. The tests were performed on unweathered CCA treated wood. The effects of three types of acids, namely sulphuric acid, nitric acid and acetic acid as leaching agent were investigated. Sulphuric acid was found to be the most effective of the three acids. Most of the leaching occurs in the first 5 days and the rate of leaching decreased significantly after 5 days. Increasing temperature increases the amount of leached metals, and arsenic is the least resistant to leaching when the temperature increases. Most of the leaching for all the metals occurred at pH 3. Copper was the least resistant and chromium was most resistant to leaching when the pH increases.

An optimised acid extraction - chemical leaching process for decontamination of CCA wood was designed by Janin [78]. In this study, various parameters such as choice of chemical reagent, reagent concentration, solid-to-liquid ratio, temperature, reaction time and wood particle size were optimised for the chemical leaching process of CCA components from treated wood. Sulphuric acid was found to the cheapest and most effective reagent. Optimum operation conditions were 75^oC with 0.2N H_2SO_4 and 150g of new CCA treated wood per litre with a total reaction time of 6h and wood particle size of less than 8mm. Under these conditions, three short leaching steps of 2h followed by a washing step of rinsing with 600ml of distilled water after each leach cycle was carried out. The final extraction percentage for the CCA components was found to be 99% arsenic and copper, and 91% of chromium. This technology was scaled up from a 200ml flask to an 80 L working volume stirred-tank reactor in a study by [3]. This procedure led to an average removal of 99.5% arsenic, 95.7% chromium and 99.6% copper from the wood chips.

Hydrogen Peroxide- In a separate study, Kazi [79] designed an extraction experiment to find suitable reaction conditions to maximize the extraction of CCA salts fixed on wood matrix using aqueous H_2O_2 (hydrogen peroxide) solution on CCA treated wood sawdust treated with CCA-Type C. The experiment was carried out with a liquid to solid ratio of 15:1 at 50^oC for 6 hours. The extraction of CCA ranged between 94-98% for all three CCA elements. It was also found that the solution containing extracted chromium (III) can be oxidized with dilute aqueous H_2O_2 at elevated temperature (>80^oC) and low pH. The mixture of rejuvenated/fresh

CCA-C solution (1:1) behaved similarly to that of fresh CCA-C solution in compatibility, fixation and leaching test.

Sodium Oxalate- A two-step extraction process was conducted on new CCA treated wood powder with a particle size under 20-mesh. The ratio of wood powder to solvent was fixed at 1 g to 100 ml. The extraction temperature was 75^{o}C. Extraction efficiency achieved after 3 h sodium oxalate treatment, following a 1 h pre-extraction process with oxalic acid was 100% for arsenic and chromium and 95.8% for copper. However, the same extraction process was ineffective for copper removal under alkaline conditions with pH at 11.2 [80].

Sodium Hypochlorite- Gezer [81], investigated the effects of time, temperature and sodium hypochlorite concentration on chromium oxidation and extraction of CCA components from the treated wood removed from service. Sodium hypochlorite was found to be effective to remove 95% of chromium, 99% of copper and 96% of arsenic with a 3 h treatment. The highest extraction conditions comprised of treatment for 1 h at room temperature followed by heating at 75^{o}C for 2 h. The extraction efficiencies included the effect of water washing due to filtration of solids. The extracted chromium was found to be in hexavalent state, oxidised from trivalent state during the extraction process. It was suggested by the authors that it could be recycled in a CCA treatment solution.

Wood Liquefaction- This is another method of removal of CCA metals from treated wood. During the liquefaction process, the lignocelluloses undergo decomposition and react with the liquefaction solvents such as phenol to produce materials with reactivity and flowability. The amount of phenol that reacts with the liquefied wood components (i.e., combined phenol) increases with an increase in liquefaction temperature, liquefaction time, catalyst content, or liquid ratio [82].

This technology was employed to remove CCA metals from the treated wood such that wood is liquefied using organic solvents, acid as the catalyst and additives such as ferrous salts with reactor temperature at 150^{o}C. The organic solvent used for liquefaction was polyethylene glycol 400/glycerine (2:1 w/w) and sulphuric acid was used as the catalyst. Ferrous salts and phosphoric acid were used as additives [83]. It was stated by Lin [83] that either of the additives improved the removal rate of CCA in an experiment performed on recycled CCA treated sawdust. Phosphoric acid was found to have improved the liquefaction rate, thereby reducing the unliquified residue to less than 1%, and removed 93.6% of copper, 100% of chromium and 99% arsenic. On the other hand, ferrous salt ($FeSo_4.7H_2O$) had a small effect on the liquefaction rate with 5.1% of unliquefied residue and removed 99.8% of copper, 99.3%of chromium and 98.9% of arsenic.

As discussed earlier in Section 2.3.3 post-treatment and chemical fixation of Chapter 2, the components of preserved wood with CCA are $CrAsO_4$ –lignin complexes, $CuCrO_4$ –lignin complexes, Cu^{2+} -lignin and Cu^{2+} -cellulose complexes and $Cr(OH)_3$ precipitates. According to Lin [83], the liquefaction process releases these water insoluble complexes from decomposed lignin and cellulose or still remain as complexes or chelates with decomposed lignin and cellulose in the form of organic matter or organic acids. Therefore, arsenic and chromium which are mostly present as $CrAsO_4$ or its chelates are insoluble in aqueous solvents and can be removed effectively by liquefaction followed by precipitation. However, Cu^{2+} has a tendency to form strong water soluble chelates with organic acids, which makes it difficult to extract. This was done by the addition of ferrous salts which has a stronger attraction with the chelate than copper ion and thereby breaking copper bonds and precipitates as an insoluble hydroxide [83].

3.5.4 Thermal Treatment

Wood waste can be disposed through a method of thermal breakdown. This will provide energy from waste as well as substantially reduce large volumes of waste. But waste management through the thermal treatment or disposal method is regulated across Europe. The European Waste Incineration Directive 2000/76/EC (WID) brings together and extends requirements under the 1989 Municipal Waste Incineration Directives (89/429/EEC and 89/369/EEC), and the Hazardous Waste Incineration Directive (94/67/EC) to bring incineration of waste legislation under a single Directive. In the UK the regulations applies to all incinerators and its implementation is largely being conducted via the Pollution Prevention and Control (PCC) regime [56]. The emission limits for discharges of waste water from cleaning of exhaust gases include, 0.15mg/l for arsenic and compounds, expressed as arsenic, and 0.5mg/l for both chromium and its compounds expressed as chromium, and copper and its compounds expressed as copper. For the same materials, emission limits to air are an average of 0.5mg/m^3 for a minimum sampling time of 30 minutes, and 1mg/m^3 for a maximum sampling time of eight hours [84].

Release of Arsenic: There are several hypothesis based on the release of arsenic during thermal decomposition and formation of various species.

- During the wood combustion, most of the volatilised arsenic was found to be in the condensed or particulate form and consisted of both arsenites and arsenates. It was reported that negligible amounts of arsine (AsH_3) was formed on the other hand volatile arsenic trioxide (As_2O_3) could not be trapped efficiently. Arsenic does not depend on the method of burning, but the on the duration of residual ash is exposed to high temperature [85].

- Hirata [86] stated that some amount of arsenic evolved in gaseous phase and increased with the increase in temperature and air supply whereas the other two CCA components – copper and chromium were retained in the ash in almost to the original concentrations. It was observed that arsenic compounds were first reduced to As_2O_3 with heating, after which they were gasified according to the equilibrium $2As_2O_3 \leftrightarrow As_4O_6$ and generally accepted to be As_4O_6 for temperatures up to 1073^{o}C. Therefore, it was concluded that burning of the CCA treated wood at low temperatures with reduced air supply will minimise the arsenic in gaseous toxicants.
- Cornfield [87] did not detect arsine or other metal compounds in volatile non-particulate forms rather it was suggested that the metals released were all present in particulate form.
- Helsen [88] concluded that the release of arsenic during the pyrolysis of CCA treated wood is controlled by the reduction of pentavalent to trivalent arsenic, which is accelerated by the presence of reducing compounds originating from the pyrolysing wood. It was also stated that once the arsenic trioxide is formed, it will be released at temperatures as low as 200^{o}C.

However, in a review study on thermochemical conversion processes by Helsen [12], they stated that energy from waste can be obtained from the following main processes: Incineration, Co-Incineration, Gasification and Pyrolysis (Slow and Flash).

Incineration: This method of thermal decomposition generates heat which has to be utilised or converted to electricity immediately, as there is no secondary fuel production. Incineration can be considered as one of the disposal methods for the CCA treated wood waste if the system is coupled with a recycling process. It was also stated that three requirements had to be satisfied by the incineration process: Arsenic emissions were to be avoided with an appropriate gas cleaning system and appropriate cooling trajectories for the flue gas; the arsenic captured (scrubber solution and filter dust) to be recycled in a safe manner; and ash treatment is required which should be environment friendly.

Co-Incineration: Co-incineration is a method with many advantages such as flexibility with regard to the waste usage and its dilution levels. If the waste streams are mixed the arsenic may be scavenged by the calcium present in the other waste streams. However, it is not advisable to mix CCA treated wood waste with other fuels because the legislation has issued a ban against mixing of all hazardous waste and CCA treated wood has been deemed as hazardous.

Gasification: Gasification has been characterised as higher energetic efficiencies and lower environmental impact compared to incineration. During high temperature (1100 to 1500^{o}C) gasification the arsenic may be totally converted to metallic arsenic, which is much easier to capture than arsenic trioxide because metallic arsenic that does not go through a liquid phase on cooling and has a higher sublimation temperature than arsenic trioxide. The advantages of gasification are that the various by-products formed can be utilised such as chromium and copper caught in the slag can be used as an abrasive. Pure metallic arsenic can be recycled and syngas (H_2 +CO, diluter with CO_2 +H_2O +N_2) can sold or used as fuel. A disadvantage of the process is that high temperature is required, but the heat can be recovered from the gas produced. This process is still at the pilot plant stage.

Slow Pyrolysis: Depending on temperature and heating rate, pyrolysis has three products: solid charcoal, pyrolysis oil and pyrolysis gas. During pyrolysis the metals compounds form agglomerates which could be easily recuperated. The amount of arsenic volatilised compared to incineration and gasification is much less, but arsenic losses were detected at as low temperature as 275°C. Lower temperatures mean slower decomposition rates of the wood and extremely long reaction times.

Flash Pyrolysis: The prime aim of this process is to achieve a maximum amount of pyrolysis oil possible. The advantage associated with the pyrolysis oil is that it can be stored, but a significant amount of arsenic makes it difficult to use, this ranges between 5 and 18%.

3.5.5 Other Processes and Methods:

There are other processes which have been employed to test the extraction and remediation of the CCA components from the treated wood.

Cement Kiln: Cement kiln are considered one of the route to utilise the CCA treated wood waste. There are considerable amounts of waste are burned in cement kilns in the UK at present, as it takes approximately 180 kg coal to produce one tonne of cement. Therefore cement kilns could be a potential to accommodate a greater proportion of treated waste wood generated [56].

In Canada however, there is a maximum permitted level of 0.1 kg/tonne clinker for chromium. For treated wood waste with average retentions of 3 – 4 kg/m^3 about 0.1 m^3 or 40 kg of CCA treated wood would be permitted per tonne of cement produced, which corresponds to 10 – 15% of the fuel required for the cement kiln [89]. Cooper [89] concluded that the Canadian industry could in theory accommodate approximately 1.45 million m^3 of CCA treated wood waste. Irle [56] used the same figures to determine the situation of the UK environment which showed the potential to accommodate an average of 1.08 – 1.2 million m^3 (432,000 – 480,000 tonnes) of CCA treated wood waste in cement kilns. But from 17th January 2005 the European Commission (EC) Chromium (VI) Directive restricts the level to

2 ppm of chromium in cement when wet, which may severely restrict the use of CCA treated wood waste as a fuel in cement kilns in Europe [56].

Electrokinetic: In an experiment carried out by Isosaari [11] at room temperature using 0.8 % of oxalic acid and 30 V (200 V/m) of direct current (DC). The best results were obtained by a three step process with pre-extraction, electrokinetic and post-extraction steps, yield removal of 67 % of copper, 64 % of chromium and 81% of arsenic. The process involved using the wood chips of recently treated utility pole with CCA-Type B preservative. Pre-extraction wood chips were mixed with 0.8% oxalic acid in solid:liquid ratio of 1:8(w/v) for 6h under stirring conditions. In electrokinetic treatment the wood chips in an acrylic bag were placed in the inner compartment of the electrokinetic cell separated with acrylic baffle plates and filled with ion exchange water up to the surface of wood chips. The duration of electrokinetic treatment was 7days with DC power supply. In post extraction, the wood chips were subjected to the same oxalic acid extraction as pre electrokinetic [11].

Multiple extraction level: This method is a combination of different waste treatment techniques in order to extract the CCA elements from the wood waste. The different technique are utilised in a series of treatment processes which include biological treatment, chemical extraction and heat treatment or other methods such as steam. Clausen [90] performed a combination of experiments in order to extract CCA from treated wood. The treated wood was subjected to three different process namely, steam explosion, oxalic acid extraction and bacterial fermentation. CCA treated wood used for the experiment was a 3 year old residential deck which was chipped. One of the combinations experimented by Clausen [90] was by sealing wood chips in a batch steam exploder and processed for 10 min at 205^{o}C and 2.4 GPa with instantaneous release of pressure. This step was followed by acid extraction by using oxalic acid (1 %, pH 2.0) for 24 h on a rotating platform. Wood samples were separated from the acid solution and then exposed to bacterial fermentation. *Bacillius licheniformis*, CC01 was used for a steady state bacterial growth with cultures incubated at 25°C on a rotating table at 200 rpm for 10 days. After the analysis of the final wood chips after the of CCA treated wood with oxalic acid as a precursor to bacterial fermentation with *B. licheniformis* CC01 removed 90% copper (CuO), 80 % chromium (CrO_3), and 100% arsenic (As_2O_5) from treated chips without steam explosion, such that steam explosion showed no enhancement of CCA removal.

Steam Explosion: Steam explosion produces a fibrous mass by saturating wood chips with steam at a given pressure followed by a rapid pressure release. Wood fibres are recoverable after post treatment, and the process can expose the carbohydrates in the wood for subsequent extraction methods [90]. Helsen [12] suggested that in practice steam explosion does not increase the extractability of chemical components if used as a pre-treatment prior to extraction. The release of organic acids during stream explosion can assist the release of 90% of CCA components, but it is generally considered to be less efficient than concentrated citric acid extraction [89].

These technologies and processes were subjected to an evaluation exercise by Irle [56]. This exercise was used to assess ‘Development Status’ of these technologies in order to determine the current position and potential for each technology to accommodate the treated wood waste. The assessment criteria for Development Status is based the availability of the process or is at laboratory scale or can the required equipment for the process can be purchased. Table 3.3 shows the score of Development Status awarded to the each technology where scale is from 1 to 5 where 1 signifies a poor performance such that the technology is at the basic research stage, 3 is where the process scale up is demonstrated on the treated wood waste and 5 is for the technologies which are commercially available with good performance.

According to Irle [56] incineration by thermal destruction has the best treatment method scoring development status as 5. This suggests that a number of technologies and processes are suitable or are able to accommodate the treated wood waste. However, most of the technologies are in development stage and results are mainly laboratory scale. Therefore the commercial effectiveness of the technologies is yet to be tested on a scaled up operation [56].

Table 3.3 Technology and treatment development status [56]

Treatment	Development Status
Reuse	**4.5**
Recycling	
Panels	4.0
Wood-plastic composites	3.0
Wood-cement composites	3.0
Mulch	1.0
Compost	1.0
Bedding	1.0
Pre-treatments	
Biological extraction	1.0
Chemical extraction	2.0
Steam explosion	2.0
Electrodialytic	3.0
Liquefaction	1.0
Thermal destruction	
Incineration	5.0
Cement Kiln	4.0
Pyrolysis	3.0
Gasification	3.0

After reviewing the environmental status of the CCA treated wood and the regulations associated with its disposal, it has become clear that the treated wood waste is required to undergo a waste management procedure. The CCA elements from the wood are either required to be extracted or the waste wood should be converted to a more accommodating form. This can be achieved by developing a technique or a process. There are different methods of treatment for this kind of waste as highlighted above.

Summary

Waste Framework Directive (WFD) established a legislative framework of handling the waste in the Europe. A waste hierarchy was defined which forms a backbone of the waste management. Waste prevention, recovery options and disposal options were highlighted in order to understand that how to cope with the waste generated. Statistical data on treated wood produced and wood waste generated across various parts of the world was discussed to determine the scope of the treated wood waste problem as a global issue. The waste hierarchy was implemented on CCA wood waste to understand the waste management options. Prevention methods for use of the CCA wood were introduced such as utilisation of arsenic-free preservatives. Reuse and recycling options of CCA treated wood waste were highlighted such as wood composites, particle boards and wood-plastics. Landfill option was then studied with UK legislation governing the landfill of hazardous waste including the introduction of Waste Acceptance Criteria (WAC). The leaching of CCA components with the potential to contaminate the soil and water were the major issues. A Decision Tree designed to support the strategy of hazardous waste management was introduced. In order to reduce the reliance on landfills making it the last disposal option, the waste treatments methods or processes were highlighted. Treatments methods such as chemical extraction, biological degradation, thermal destruction, electrodialytic remediation (EDR) and other processes like steam explosion, combination processes and electrokinetic were discussed with extraction or removal rate of CCA components. The chapter provided an understanding of the waste management and waste hierarchy. It provided knowledge of the technologies and waste treatment processes available to accommodate the CCA treated wood waste and remove the CCA components, thereby attempting to reduce its environmental impact and hazards.

Chapter 4. Materials and Experimental Methodology

4.1 Introduction

The sources of materials used in this research and the experimental procedures are described in this chapter. An overview of coke making and the function of a quenching tower in a coke ovens plant are introduced. The structure of a typical quenching tower is then described followed by the procedure of sampling wood from the tower during its demolition. The procedure of sample preparation for analytical purposes is then defined. The environment and emissions across steelworks site are highlighted. The various components in the vicinity of the quenching tower which could be responsible for potential changes in the wood properties during its service life are recognised, sampled and discussed.

The experimental methods and apparatus used in this research are outlined. Methods used for the characterisation of the CCA wood are described which include digestion procedures and analytical techniques. The procedures for different leaching tests are then discussed. A full extraction process for the removal of the treatments from the wood is outlined. The process of electrocoagulation for the precipitation of the CCA elements from the extracted leachate is then described.

4.2 Coke Ovens Plant

In the process of iron-making a skip car is used to charge an alternating layer of iron ore, coke and limestone to the top of a furnace which may be 30.5 m tall [91, 92].Coke and powdered coal are the main reducing agents and also act as a fuel [92]. In the lower portion of the blast furnace, a hot blast of air is injected at temperature of about 900-1100^{o}C. The air flows through the burden of raw materials in the furnace and gas exits the furnace top. This hot blast causes the coke (Carbon) to react with Fe_3O_4 and Fe_2O_3 in the furnace, releasing metallic iron in the liquid state and producing carbon monoxide (CO) and carbon dioxide (CO_2) gas. The iron sinks to the furnace hearth where the original impurities combine with the lime, forming a slag, which is a layer that floats on the top of the liquid iron. The residual gases leaving the furnace carries fine dust as it exits [91].

Thus coke is a primary ingredient for iron-making and is produced from coal by means of distillation in a coke ovens plant and has better physical and chemical characteristics than coal [92]. Carbonisation is a coal pyrolysis process at high temperature. During this process coal is indirectly heated at about 1000 – 1100^{o}C by flue gases at 1150 – 1350^{o}C in an oxygen free atmosphere for typically 18 hours [93]. This leads to the production of gases, liquids and a solid residue (char or coke).

A typical coking plant processes 2000 to 4000 tons of coal per day. The coking operation is carried out in a battery of between 10 to 100 individual ovens designed to provide relatively uniform production of finished product and to recover heat to minimise fuel consumption. Figure 4.1 shows a typical coke ovens plant located at Port Talbot, South Wales in the United Kingdom which consists of 2 batteries with 42 coke ovens in each. The blended crushed coal is fed to the ovens by a charging car mounted on the coke oven battery [91]. During the charging of the coal, there is a possibility of coal dust emissions [92].

The individual coke oven chambers are separated by heating walls which consist of heating flues with nozzles for fuel supply and air inlet boxes. The process of carbonisation starts immediately after charging of coal. The 8 – 10 % of the gases and moisture by weight are driven off from the initial charged coal. Depending on various factors such as oven width and heating conditions, grade of coke required and coal being processed, it takes around 14 – 24 hours [92].

Fully carbonised coke is pushed out of the oven into a container called a quenching car by the ram of the pusher machine as shown in the Figure 4.2. Coke starts to burn immediately after coming in contact with the atmospheric oxygen. The quenching car transports the hot coke to the quenching tower. The coke gets quenched directly with large volumes of water to bring down the temperature of coke to about 70^{o}C to prevent further loss by combustion [93].

Figure 4.1Coke ovens plant at Port Talbot steelworks

After the quenching, the coke is stored in a stock pile which is then transported to crushers and screens. The smaller fraction (< 20 mm) is usually set aside for a sinter process. The sinter process allows the smaller coke fraction to be fused with iron ore which is fed into the blast furnace. The larger fraction (20-70 mm) is used in the blast furnace directly as the energy source for iron-making [92].

Figure 4.2 Incandescent coke pushed from coke on a quenching car, ready to be taken to the quenching tower [94]

4.3 Quenching Tower

There are two methods of quenching the hot coke pushed from ovens namely, wet and dry quenching. The dry quenching process utilises cooled gas at 130°C blown into the bottom of the coke containing bunker. This gas is circulated through a particle separator and then through a steam generating waste heat boiler to cool down the gas to a required temperature [95]. However, wet quenching is utilised in the particular plant under examination. This process involves receiving the charge of hot coke from the coke ovens in the quenching car and then quenching with water. When the quenching car arrives at the quenching station, it is placed under the system of stationary sprays located in the quenching tower. The purpose of quenching is to rapidly cool the burning coke to stop further loss of material by combustion. Coke is required to have low moisture and hence sufficient heat is retained in the coke to dry the surface water by adjusting the amount of water from sprays and quenching duration [96]. Figure 4.3 show a particular quenching tower constructed in 2008 to replace an old tower.

Fresh CCA treated wood was used in the construction on the replacement quenching tower. The new tower was taller than the old and consisted of a longer cooling column. Hence the tower utilised a greater quantity of treated wood. The quenching process utilises about 22 tons of water per quench cycle which lasts up to three minutes and there are up to 780 quench cycles per week [93]. The car with quenched coke moves to the coke wharf where the coke is discharged and stored for further use.

During the quenching process, the water that does not evaporate is collected in a water settlement pond. This water goes through a water treatment plant to be recycled and recirculated. To make up the evaporated water quantity, fresh top up water is regularly introduced [93].

Figure 4.3 New coke quenching tower constructed in Port Talbot steelworks in 2008 [97]

4.3.1 Wood Samples

Wood samples were collected from a typical wooden coke quenching tower which was located at the steelworks in question. The quenching tower was erected in 1977. All wooden parts of the tower including planks, staircases, fencing and support beams were produced using redwood (*Pinus Sylvestris*) and chemically treated with CCA preservative according to British Standard BS4072 [26] which was first published in 1966. The tower had come to the end of its service life in 2011and was demolished. As highlighted by the schematic shown in Figure 4.4, the tower consisted of three sections: top section, middle section and lower triangle.

The top section was the biggest part of the tower. It was used as a steam vent after a quench cycle. This part of the tower received the least amount of water splash and indirect wetting. The middle section of the tower was the water spray zone. This section consisted of water pipes and sprays. This section was subjected to direct wetting and exposed to high temperature. The lower triangle section was the water runoff zone. This section was of hood shape to accommodate a coke quenching car and received all the water which did not evaporate. The hot water running over the surface of the wood was collected and recycled by a water treatment plant.

Samples of untreated wood were also obtained from a local wood treatment plant. Elemental analysis of untreated wood provided the concentration levels of elements present naturally in the wood. Hence, these concentrations were used as a datum to determine any incremental changes to the wood properties.

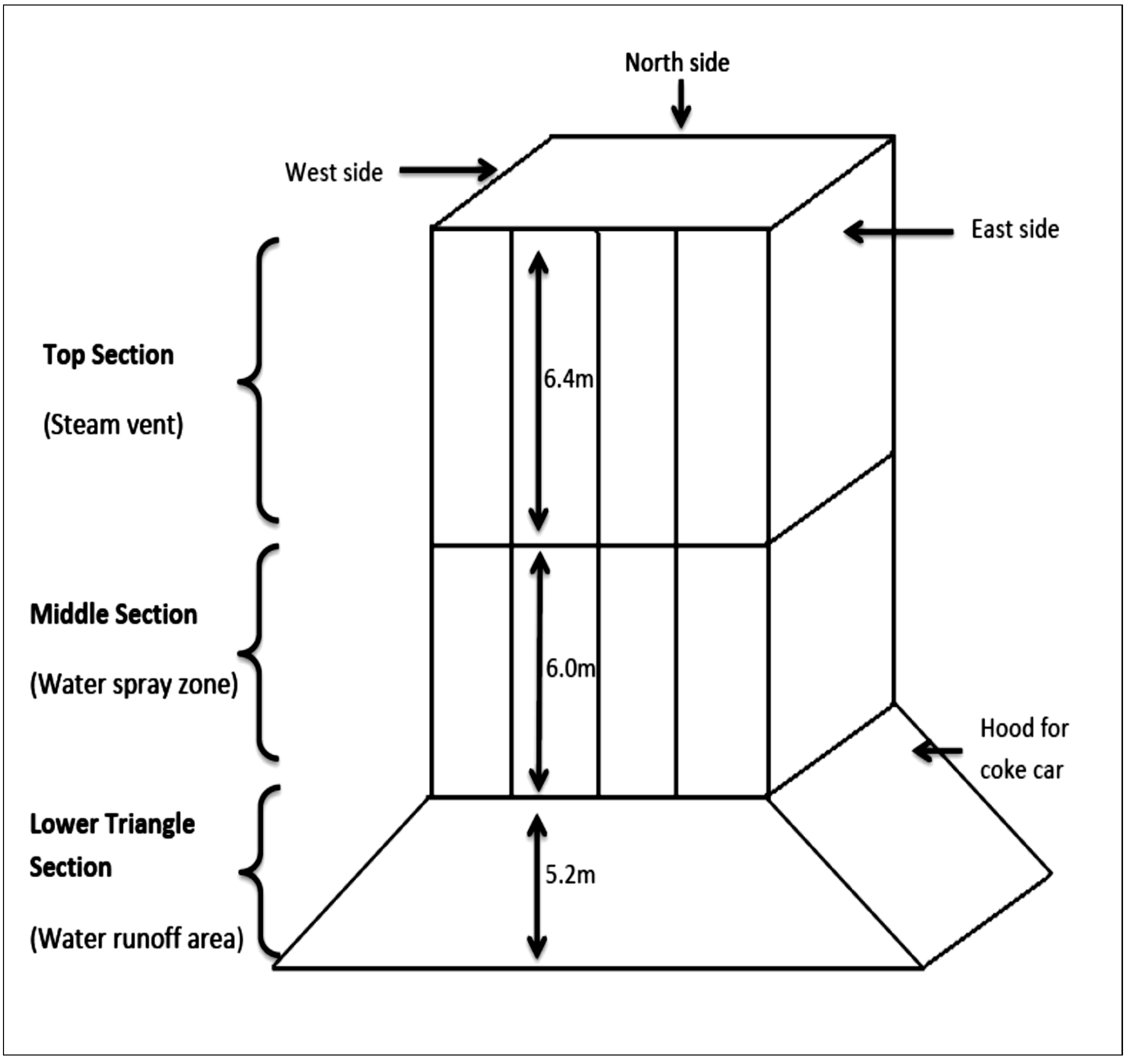


Figure 4.4 Schematic of demolished coke quenching tower illustrating different sections and sides of the structure

4.3.2 Sampling points

During the demolition of the quenching tower, various sampling points were recognised in order to obtain an array of samples to represent the characterisation and in service leaching behaviour and other properties exhibited by the CCA treated wood. Over the 33 years of service life, the quenching tower had undergone renovation and was fitted with fresh treated wood to a number of locations. Different parts of the tower were fitted with fresh CCA treated wood during the renovation were identified. Therefore, the wood samples collected from the tower were categorised as old and refurbished samples.

The tower was a big structure and hence it was possible for wood to possess variable chemical and physical characteristics depending on its location across different parts of the tower. As the tower consisted of three sections as highlighted earlier, different sampling points were recognised accordingly.

The lower triangle region was the bottom of the tower; and it was subject to the highest amount of water of all the sections. Hence, the possibility of leaching of CCA components during the service of this region was expected to be the highest due to the high quantity of hot water runoff after every quench cycle. There was also a probability of stagnant water in this region for short intervals of time during the coke quenching. Consequently, a low CCA concentration was expected in this wood.

Leaching of the CCA preservative from the wood at the top section of the tower was expected to be lowest and hence the CCA concentration would be potentially higher than the other sections. This could be due to less water runoff over the wood surface and negligible stagnant water. But, the presence of high amounts of steam could be responsible for changes in some characteristics.

In the middle section, the possibility of leaching of CCA components was thought to be higher when compared to the top section. But, there was also a moderate to high leaching probability due to water runoff because of the presence of water sprays and high temperature conditions. The overall CCA concentration was expected to be moderate and range between the CCA concentration in the wood from lower triangle and top section.

Due to the variations expected across the different parts of the tower, different sampling points across the structure were taken. In the schematic of the quenching tower shown in the figure 4.4 different samples were collected from all three sections and at different sides of the tower. Samples of both refurbished and old wood were taken in order to study the in-service leaching trend of CCA components from the wood of a typical coke quenching tower. Also, the wood obtained from different sections would identify the pattern in loss of CCA components over the service period of 33 years in an integrated steelworks site.

4.3.3 Sawdust

Wood samples were converted into sawdust in order to meet with the size requirements necessary for the experiment methodology used. Moreover, the conversion to sawdust provided exposure of higher wood surface area which would determine the best leachability characteristics. The conversion to sawdust also ensured the homogeneity of the samples considered for the analytical purposes.

All the wood samples obtained from the quenching tower demolition were first cut into small manageable sections. The sections were of 300mm length. Then smaller pieces were cut out of these sections. This made it easier to grind the sample into sawdust using a knife mill. Figure 4.5 shows the wood sequence during different stages of the sample preparation from planks to sawdust. Samples from untreated wood were prepared in the same way.

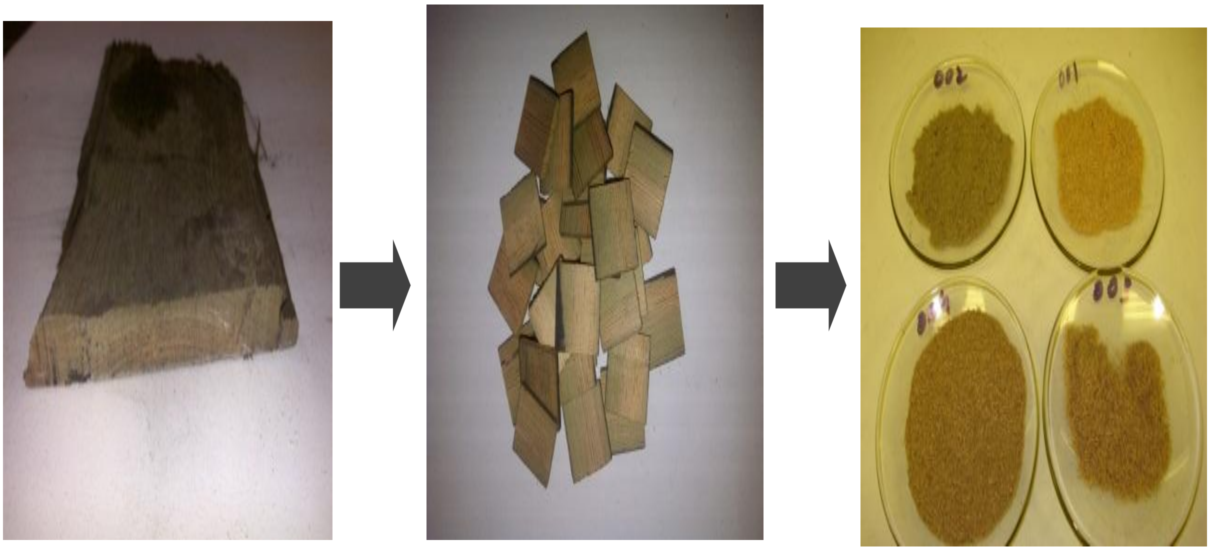


Figure 4.5 Sample preparation stages from wood section into chips then sawdust

Sawdust was dried in an oven at 105°C for about 16 hours as mentioned in the British Standard BSEN 14346 [98] to dry the sample overnight. After heating, the samples were weighed and heated further for one hour and weighed again until a constant mass of the sample was obtained. This ensured that the material was fully dry. Sawdust samples were then bagged in plastic lip seal pockets for air tight storage. This allowed testing of wood to be undertaken on a dry basis.

4.3.4 Growth Rings

Samples of wooden support beams from the quenching tower were obtained. These beams had a clear visible growth ring pattern. The elemental analysis of growth rings was performed to obtain vital information on the distribution of elements across the wooden beam. The support beam with visible growth rings was cross-sectioned to a thickness of 5mm and then the sample was oven dried at 105^{o}C as per the British Standard BSEN 14346 [98]. The elemental analysis of these growth rings was subjected to two types of assessments namely, Diagonal and Edge assessments.

Diagonal assessment was performed to determine the penetration of elements in the wood. Figure 4.6 shows outline marks used to cut the growth rings on the sample for diagonal assessment. A whole growth ring was cut out from edge to edge of the cross sectioned sample. The single growth ring was further cut in four pieces to approximately equal sizes of about 40mm and was labelled with R1D-series. All four pieces were subjected to elemental analysis for metal content.

Edge assessment was performed to obtain metal distribution along the surface of the wood. Figure 4.7 shows outline marks used to cut the growth rings perform from the sample and perform edge assessment. Growth rings of the cross-sectioned sample were carved out to a length of 40 mm from one edge of the wood and labelled with R-series. Every single growth ring was subjected to elemental analysis for metal content.

Figure 4.6 Diagonal assessment with single growth ring cut into four by cutting according to the indicated marks and labelled samples accordingly

Figure 4.7 Edge assessment with multiple growth rings cut according to the indicated marks and labelled samples accordingly

4.4 Integrated Steelworks and Its Environment

Steel production is a key sector for Europe's economy and accounts for 15 % of the world steel production [99]. The six largest steel producers in the EU are Germany, Italy, France, the United Kingdom, Spain and Belgium [92]. The integrated iron and steelmaking process is the main production route used in Europe and worldwide [100]. Figure 4.8 shows the aerial view of an integrated steelworks site located at Port Talbot, South Wales in the United Kingdom. The site view provides the spread of steelworks activities in the region. The figure shows various processes located across the site. It is a classic blast furnace/basic oxygen furnace steel making method with hot and cold rolling facilities taking place in large industrial complex which covers an area up to several square kilometres. Integrated steelworks are characterised by networks of interdependent material and energy flows between the various production units namely sinter plants, pelletisation plants, coke oven plants, blast furnaces and basic oxygen steel-making plants followed by casting plants and, hot and cold rolling mills [92].

Sammut [101] stated that steel plants are largely known for their emissions impact, especially for heavy metals emitted in the atmosphere. Dust is one of the main pollutants emitted from an integrated steelworks which consist of heavy metals covered in the particles. There are various processes across the site of an integrated steelworks which are recognised in Table 4.1. The Table shows the various processes and operations of iron/steel/coke making and rolling plants that are responsible for emissions to the atmosphere. The main components listed range primarily iron and other heavy metals, whereas the coke making process contributes organics and particulates as the main components of the emissions.

Figure 4.8Aerial view of the Port Talbot integrated steelworks with different various plant buildings labelled [102]

A study conducted by Dall'Osto [100] at Port Talbot, a town next to the integrated steelworks site, highlighted particles with high iron-content with elements such as potassium, sodium and nitrates with varying quantities of phosphate content. With the use of the directional analysis it was found that the main sources were within the steelworks: iron making, steel/coke making and rolling mills.

Another study by Hleis [99] conducted at an integrated steelworks located in Northern France determined that dust sources from the sinter plant, blast furnace, steelmaking and desulphurisation slag processing were found. Furthermore, iron, calcium, aluminium and magnesium were also the major elements found at each source.

Table 4.1 Emissions sources and its main components of various sectors and plants at a typical steelworks [100]

Sector / Plant	Plant / Operation	Components
Iron making		
Sinter Plant	Iron Ore Sintering	KCl, Fe, Pb, Zn, Mn
	Sinter Plant De-Dusting	Fe, Mn
Blast Furnace	Tapping	Fe, Mn
	Slag Processing	Ca, Al, Si, S
	Stove Heating	CO2, SO2, NOX
Raw materials	Unloading, stocking, blending wind entrainment	Fe, Ca, Mg, Mn
Steel making		
BOS Plant	Steelmaking	Fe, Zn, Pb, Mn
	Charging, Blowing, Tapping	Fe, Zn, Pb, Mn
Coke making		
Coke making	Battery Underfiring	CO2, SO2, NOX, soot (C)
	Charging	Organics, particulates
	Door and Top Leakages	Organics, particulates
	Pushing	Particulates
	Quenching	Particulates, soluble salts
Mills		
Rolling	Hot Mill	Fe, coolants
	Cold Mill	Lubricants, coolants

4.4.1 Kish Samples

Kish in general terms is defined as single crystals of flake graphite which precipitate from the super saturated solution of carbon in iron as the molten iron cools during tapping, pouring, teeming or any other operations during the production of iron and steel [103]. The steelworks environment consists of considerable amount of these airborne particles commonly called Kish. Hot metal from the blast furnace is brought to a BOS (Basic Oxygen Steelmaking) plant using transfer cars or torpedo ladles. This hot metal is subjected to a pre-treatment of desulphurisation in order to prepare it for the BOS process. Desulphurisation agents such as calcium carbide, caustic soda, soda ash, lime and magnesium impregnated materials are used for the removal of sulphur. The most commonly used agents, calcium carbide, magnesium and lime; provide the hot metal with final levels below 0.001 % of the initial sulphur content. A desulphurisation agent is blown through a lance into the hot metal with nitrogen as the carrier gas. The sulphur is bound in the slag, which floats to the top of the hot metal. The slag is then removed in the slag separation unit and if necessary, process agents are added, which may generate a second slag [92].

Slag scrapers are used to remove the slag formed on the top of the hot metal. This is skimmed from the surface of the liquid metal. Some iron is also removed during the process of skimming. It is this skimmed mixture which is called Kish. The quality of the kish generated and its chemical properties differ from plant to plant because of the variation in the grade of steel and the production practices. Kish upon full solidification forms lumps of rock and dust of different sizes which is usually disposed similar to the other slag streams produced at a steel plant [104]. The kish particles forms on or floats on the surface of the molten iron and is emitted from the hot surface in the form of fine particles. Kish particles are very light and therefore gets carried into the atmosphere by heat induced from the surface of the molten iron [103]. It was also known that light weight kish particles rises during the slag disposal.

It was indicated that there were high amount of heavy metals suspended in the atmosphere of an integrated steelwork site by various studies. Lumps of kish samples were collected from the slag processing site of the same steelworks that housed the demolished quenching tower. It was important to establish if the particulate matter in the air exposed to the wood of quenching tower was responsible for any changes in physical or chemical characteristics of the wood during its service life.

Lumps of kish were ground, in order to obtain a homogenous sample with fine particle size for analytical purposes. Each ground sample was dried in an oven according to the British Standard 14346 [98] at 105^{o}C for about 16 hours and then transferred into a lip seal plastic bag for air tight storage.

4.4.2 Coal and Coke Ash

Wood from the quenching tower in the vicinity of coke ovens was exposed to emissions produced by different coke making operations as previously stated in Table 4.1. It was important to understand that certain properties of coal and coke ash produced in order to determine if they had any effect on the wood or its properties.

Therefore, samples of coal were collected and coke ash was analysed for a period of one year by the steel company itself. The analysis was performed with the help of in plant sampling and testing procedures specific to the steelworks. These analyses provided trends or notable discrepancies which may arise with regard to the wood characterisation and its disposal methods.

4.4.3 Quenching Water

Water used in the quenching process was also analysed as this was repeatedly wetting the wood surface. The quenching tower had a dedicated water treatment plant. After every quenching cycle, excess water which did not evaporate was collected in a water settlement pond. The water was filtered and treated through a series of filtration and clarifying units. Analysis of water before and after the quench cycle was performed to observe if there was any difference in the water quality. Therefore, water was collected from the water treatment plant for the quenching tower. Water samples were bottled as water before quenching cycle from a bleed point located on the pipework of the spray nozzles. Also water samples were collected as water after quenching cycle from the return water pipeline to the water treatment plant. All the samples were collected for analysis purposes.

4.5 Characterisation Techniques

In order to characterise the waste it was important to determine certain properties exhibited by the wood. Various experimental methods and analytical techniques were employed to determine such physical and chemical properties of the samples collected. For the elemental analysis, Induced Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) was the primary technique used to determine the CCA content in a given sample. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to gather information on the mineral analysis and CCA distribution respectively.

4.5.1 Elemental Analysis

Elemental analysis was performed on various samples, which were first microwave digested in order to convert the solid matter into a liquefied state. De-ionised water was be added to the liquids to make up the final volume. The final volumes were analysed with the help of Induced Coupled Plasma (ICP) apparatus for the detection of elements and their concentration levels.

4.5.1.1 Wood Digestion

American Wood Protection Association (AWPA) Standard A7-04 [105] describes five procedures for the digestion of wood. These are;

a) Peroxide-Sulphuric Acid
b) Peroxide-Nitric Acid
c) Microwave Peroxide-Nitric Acid
d) Microwave Nitric Acid
e) Perchloric Acid

From the above methods of digestion ‘Microwave Peroxide-Nitric Acid’ was used to carry out all the wood digestions. The particular method was selected due to the following reasons;

- Peroxide-Sulphuric Acid method was given an obsolete status due to the lack of use.
- Peroxide-Nitric Acid was a trial and error procedure which added too many variables such as addition of hydrogen peroxide with no specific quantities. Heating temperatures and determination of the clarity of solution were also not specified by the standard which contributed to the uncertainty and homogeneity of the experiments.
- The procedure involved in Perchloric Acid digestion had a possibility of dangerous and violent explosions which increased the safety concerns and required extra precautions.
- The two microwave digestions methods were considered as best suited options. The presence of hydrogen peroxide acts as a strong oxidising agent that can form water soluble oxide salts and derivatives of many metals. Therefore the Peroxide-Nitric Acid digestion was selected over the only microwave Nitric Acid digestion method.

The digestion of wood was based on the wet ashing procedure according to American Wood Protection Association (AWPA) Standard A7-04 [105]. Approximately 0.50 g of dried sawdust was accurately weighed and added to a microwave digestion tube. 8ml of nitric acid was added to a 0.50 g dried wood sample followed by 3 ml of hydrogen peroxide in a microwave digestion tube. Hydrogen peroxide was added 1 ml at a time with about a couple of minutes between the three instalments so minimising the foaming caused by the immediate oxidation reaction. The digestion tube was placed into the digestion vessel with a firmly screwed cap. The vessel was placed into a carousel in a microwave oven and a pre-programmed digestion sequence was started. After digestion was completed, the contents of the vessel were removed and the volume was made up to 100ml with de-ionised water.

4.5.1.2 Kish Digestion

2 ml of hydrofluoric (HF) acid was added to 0.1 g of dried and ground kish sample in a digestion tube. This mixture was allowed to react overnight at ambient conditions. 6 ml of aqua regia was added to the contents of the tube. Aqua regia was prepared by mixing equal parts of hydrochloric and nitric acids. The digestion tube with a firmly screwed cap was placed in a microwave vessel and digested for 1.5 hours under a standard microwave digestion programme. After that 12 ml of 4 % boric acid (6 ml of boric acid per 1 ml of HF) was added to neutralise the remaining HF. The tube with the mixture was again microwave digested for 30 minutes to ensure complete digestion of the sample. After digestion the contents of the tube were decanted and the volume was made up to 100 ml with de-ionised water.

4.5.1.3 Induced Coupled Plasma (ICP) Analysis

All the digested samples were measured for elemental content using a Perkin-Elmer Optima 2100 DV, Induced Coupled Plasma (ICP) instrument. Following operating parameters of the instrument were utilised during this research:

- Power : 1500 watts
- Frequency : 40.68 MHz
- Nebuliser Flow : 0.60 L/min Argon
- Plasma Flow : 15 L/min Argon
- Auxiliary Flow : 0.2 L/min Argon
- Pump Rate : 2.0 mL/min

This instrument provided a multi-element analysis from a standard stock solution comprised of desired elements to be analysed. 28-multi-element standard stock solution by Primar-MS from Fisher Scientific was used. From the stock solution volume standards with varying concentrations of 0.1, 1, 10, 100 mg/l were prepared. These solutions were prepared by using 2 % nitric acid. Also 3-5 % (v/v) nitric acid was used to serve as a blank. The instrument was calibrated from the reading obtained from the stock solution which was then used to measure the elements in the volumes obtained by the digestion. The instrument was pre-flushed and rinsed with de-ionised water before and after every analytical run respectively.

4.5.1.4 Concentration Calculation

The concentration of the constituting elements expressed by the ICP results was in mg/l of the liquid sample. The final concentration of the amount of the elements present in the wood sample relative to the total mass was expressed in mg/kg of dry matter. This was calculated by using the following equation.

$$Concentration\ (mg/kg) = \left(\frac{ICP\ reading\ in \frac{mg}{L}\ X\ Volume\ used\ in\ ml}{Dry\ mass\ of\ the\ sample\ used\ in\ g}\right) \qquad \ldots\text{Equation (4.1)}$$

Where;

Concentration is the final value of elements found in mg/kg of the dry sample used initially;

ICP reading is the measurements with units expressed in mg/l by the analysers;

Final volume that made the solution expressed in ml;

The dry mass of the sample initially used in an experiment measured in grams.

4.5.1.5 Calibration, Detection Limits and Errors

A detection limit for the elements analysis by the ICP technique was calculated by analysing a blank specimen. 20 readings were obtained by the ICP analysis of the blank specimen. Then the detection limit was calculated as three times the value of standard deviation, such that the detection limits calculated for the CCA elements were;

- Chromium – 0.00131 mg/L
- Copper – 0.00246 mg/L

- Arsenic – 0.04419 mg/L

The experimental errors associated with the current investigation were recognised as systematic measurement errors, errors arising due to fluctuating experimental environment and conditions.

- Due to hydroscopic nature of the wood, a dry wood sample would immediately seek moisture from the air. This could lead to a variation in the wood mass measured. The sample was therefore, kept in dry conditions as long as possible in order to avoid any mass gain.
- Heat loss and differential heating of apparatus during high temperatures leaching processes. Pre-heating of the apparatus and the fume hood was used to minimise the heat loss.
- Vacuum filtration process induces a sample lost in the filter paper. Washing of the filter paper was one of the methods to reduce loss of sample. However, certain processes did not allow washing as a part of experimental procedure. Therefore the sample lost was considered as the 10 % experimental error.

4.5.2 X-Ray Diffraction (XRD)

Mineralogical analysis was performed by using X-Ray Diffraction (XRD) with a Philips PW 3830 X-Ray generator and a PW 1820/00 Diffractometer control. The specimen for the XRD was prepared by adding a levelled layer of the dry sawdust in the sample holder 2mm deep. The holder was gently tapped to uniformly spread and flatten the surface of the sawdust. A glass slide was used to secure the sawdust in the holder and prevent the movement of wood particles. The holder and slide assembly was carefully inserted in the XRD instrument. Figure 4.9 shows XRD instrument with sample holder where the holder and slide assembly were placed as well as the X-ray source and detector. Then the sample was exposed to the X-rays while rotating between 3^o to 70^o angles along the scanning arc as shown in Figure 4.9. The rate of rotation was set at 0.02^o for 0.5 second per step.

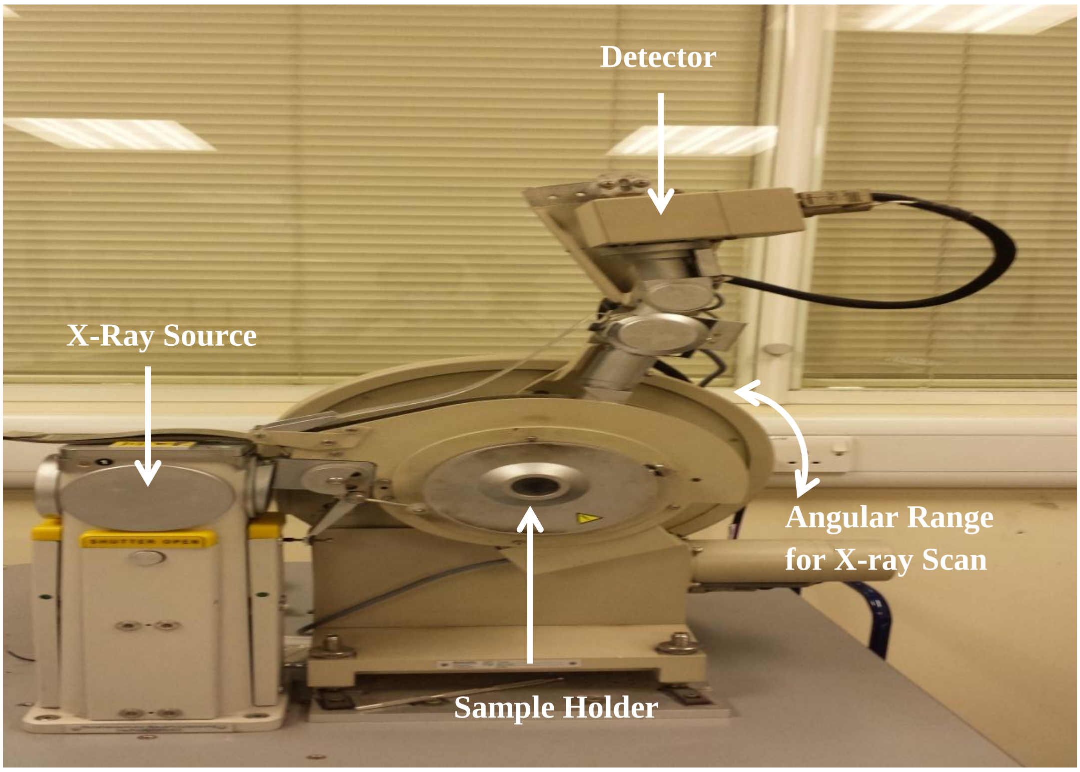


Figure 4.9 XRD instrument with detector range of 3o to 70o

4.5.3 Scanning Electron Microscope (SEM)

A wooden plank was cut in two along its length. Along the side of one of the pieces of the wooden plank a sample strip of 1mm thickness using a band saw was prepared. The strip was cut into 10 mm squares and was oven dried at 105^oC until moisture free. Analysis of the sample under high vacuum using SE1 (Secondary Electron) detector was not possible due to sample charging. For this reason the sample was imaged using a backscatter detector and variable pressure set-up. Analysis was performed using a Carl Zeiss EVO-40 Scanning Electron Microscope (SEM). Energy-dispersive X-ray (EDX) spectroscopy was done using Oxford Instruments detector and Inca analysis suite. All samples were analysed under uncoated conditions. Different images were taken of the treated edge, inside edge, sample with 90^o tilt as well as untreated samples.

4.6 Leaching Tests

Leaching tests were conducted to study the behaviour exhibited by the elements in the wood waste. These tests were to establish the understanding and assessment of the potential hazards posed to human and environment by the contamination of water and soil by CCA elements [66]. As even in small concentration of elements leached may be environmentally significant due to the toxicity of the CCA treatment [18].

4.6.1 Standard Leaching Procedure

Leaching tests were performed in accordance to the British Standard BS12457-2 with a solid to liquid ratio of 1:10 [106]. The sawdust sample was prepared for leaching as previously highlighted and dried at 105°C according to the British Standard BS14346 [98]. Leaching involved a 5 g dried sample in 50ml of de-ionised water and stirred by a magnetic stirrer (100-200 rpm) at room temperature (20 ± 5°C). These tests were completed in triplicate for one hour, one day, one week and one month.

After the leaching process, the wood and water mixture was allowed to settle for about 15 minutes. A vacuum filtration device was used with a 0.45 μm membrane filter paper to extract liquid leachate. No rinsing of filter paper or residue was performed. Solids obtained from the process were oven dried at 105°C and stored. The leachate was analysed using an ICP process to determining the concentration of elements present.

Further leaching tests were performed on the samples from the same batch of standard leaching. These tests were designed for a different sampling approach. These sampling methods helped to gain a deeper understanding of the leaching behaviour of CCA wood.

4.6.2 Continuous Sampling

This test monitored periodic changes in the leaching behaviour of elements in a continuous wood-water leaching system. A continuous sampling trial was carried out using a custom designed process with hourly sampling of the leachate in a continuous three hour leaching study. The initial leaching procedure was the same as of British Standard BS 12457-2 using a solid to liquid ratio of 1:10 [106]. Therefore, the experiment was started with the same procedure as mentioned for standard leaching but the duration of the experiment extended to three hours while the samples were taken at regular intervals. During the test, a 2 ml sample of leachate was taken every hour from the on-going leaching. Hence, at the end of three hour study, three leachate samples were available for the analysis. The final separation of solids and liquid was performed using the previously indicated filtration procedure. This leaching test was carried out in triplicate samples using the same type of wood samples used for standard leaching tests.

4.6.3 Interrupted Sampling

The interrupted sampling provided leaching data of a wood sample subjected to a number of leach cycles. This helped to simulate the operational conditions of the quenching tower where wood on the tower went through a repeated quench cycle and thereby introducing a wood-water leaching system. Similarly, during the interrupted sampling a same wood sample was subjected to a number of leaching cycles with fresh water. This method was another custom designed sampling procedure with repeated leaching cycles on the same wood sample. Again the leaching process was followed according to British Standard BS 12457-2 with solid to liquid ratio of 1:10 [106]. In this process four leaching cycles were carried out where each cycle was of one hour. A cycle can be described as an hour of leaching tests on the wood sample with leaching conditions as described by the British Standard BS 12457-2. The first cycle of the leaching process used the fresh sample wood sample and the following cycles were performed on the same sample. All the leaching cycles used a fresh batch of de-ionised water. After the first hour of leaching, solids and liquids were separated by vacuum filtration. After filtration, leachate was collected and solids were oven dried at 105^{o}C. The dried solids were subjected to the leaching process three more times. At the end of the fourth cycle, all four leachate samples were analysed for CCA elements using ICP. This test was conducted on wood samples in triplicate.

4.7 Sequential Leaching

The sequential leaching technique was used to identify the ability and efficiency of various chemical reagents and conditions for extracting the CCA elements from the treated wood waste. The basic leaching process was used according to the British Standard BS12457-2 [106]. The parameters of solid to liquid ratio, leaching duration were kept constant. For the extraction from leaching, different reagents with varying concentration solution were mixed with dried sawdust sample in liquid to solid ratio of 10:1. The leaching was performed at room temperature and 100^{o}C. De-ionised water was used throughout the experiments for making the volumes and preparation of the reagents. The pH of the mixture was recorded before the extraction began. All tests were carried out using 5 g of sawdust and reagents with 50 ml volume in 250 ml conical flasks on hot plates fitted with a magnetic stirrer. The stirring conditions were used to ensure a constant agitation of the mixture and a constant temperature was maintained for the whole duration of the tests. The conical flask was fitted with a Graham-type condenser for minimal loss of water due to high temperatures. Table 4.2 shows all the tests were leached for 1 hour duration with various temperature and different reagents and their concentrations under stirring conditions.

The sawdust and liquor obtained from the leaching step were allowed to cool for about 15 minutes and the pH of the mixture was recorded as post-extraction. A vacuum filtration device was used with a 0.45 μm membrane filter paper to extract liquids. The liquids were collected and labelled. The residue was rinsed with 100 ml of de-ionised water and the liquids were again collected using vacuum filtration. The liquids obtained from the rinsing process were also collected and labelled accordingly. Solids obtained from the process were oven dried at 105^{o}C and stored. The dried solids were prepared for ICP by microwave digestion and subjected for elemental analysis. The analysis was used to determine the concentration of elements extracted and compared with the initial concentration present in the sawdust.

Table 4.2 Sequential analysis with different reagents concentrations and experimental conditions

Reagent	Concentration (M)	Temperature (^{o}C)	Duration (Hrs)
Water	N/A	Room Temp.	1
	N/A	50	1
	N/A	75	1
	N/A	100	1
NaOH	1	Room Temp.	1
	1	50	1
	1	75	1
	1	100	1
	5	Room Temp.	1
	5	100	1
NH_4OH	1	Room Temp.	1
	1	100	1
	5	Room Temp.	1
	5	100	1
NH_4Cl	1	Room Temp.	1
	1	100	1
	5	Room Temp.	1
	5	100	1
H_2O_2	1	Room Temp.	1
	1	100	1
	5	Room Temp.	1
	5	100	1

4.8 CCA Extraction by Chemical Leaching

Following the sequential analysis, a range of chemical reagents were analysed against the effectiveness of the CCA elements removal from the wood. After studying the results, chemical reagents were selected and a full extraction process for the removal of CCA elements from the treated wood waste was designed. The process was a three step extraction procedure where the wood was subjected to three different chemical reagents. The three chemicals were selected because of the respective properties and leaching characteristics identified in during the sequential leaching. Sodium hydroxide (NaOH) was used because it provided good alkaline conditions for the wood structure to be weakened by causing lignin depolymerisation as well as has high arsenic removal percentages; the second reagent identified was ammonium chloride (NH_4Cl) which was used as copper has good affinity towards the ammonium groups and leads to better extractions results. Hydrogen peroxide (H_2O_2) was used for provided good oxidation conditions which were suitable for extracting higher amounts of chromium. It was a generalised trend that the extraction was highest at elevated temperature 100^{o}C with the selected chemicals. Extraction process was based on the principle of the leaching where a wood-solution system exists for a reaction time of 1 hour at elevated temperatures under stirring conditions. After the reaction the wood residue was separated from the solution with the help of filtration method. Then a washing step was introduced in order to rinse the wood residue of the chemical reagents by using 100 ml of deionised water. Washing step helped in cleaning of the wood residue such that there would be reduced interaction between the two chemical reagents. After the filtration of the washings, the washed residue was subject to oven drying in order to prepare the residue for the following extraction step. Optimisation of the extraction process was performed by analysing reagents in different order and at different concentration. The procedure for the most optimised process is described in Figure 4.10 which shows the flow diagram of the complete extraction process with the experimental conditions. The full process can be broken down in to three steps namely; Step 1 arsenic extraction process with 1 M of NaOH solution followed by Step 2 copper extraction process with 2 M NH_4Cl solution and then Step 3 chromium extraction process with 2 M of H_2O_2 solution. The procedure for all the process involved in the three step extraction can be described as;

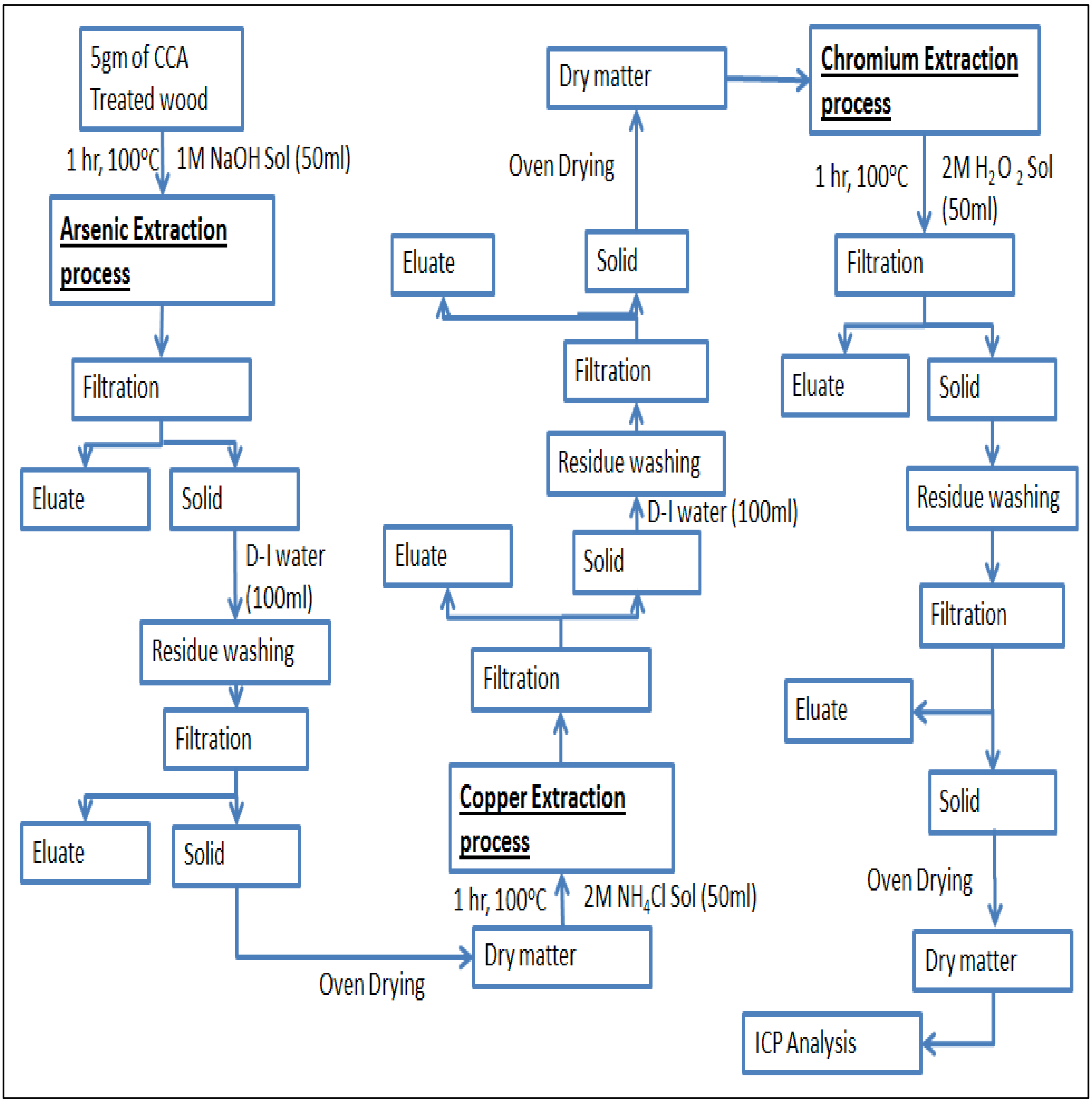


Figure 4.10 Flowchart for the complete chemical extraction process of CCA elements from treated wood waste of coke quenching tower

Step 1, Arsenic extraction process: In the first step 5 g of dried sawdust was mixed with 50 ml of sodium hydroxide (NaOH) solution at 1 M concentration. The pH of the mixture was measured before the extraction. Then the mixture in a 250ml conical flask was heated at 100°C for one hour under stirring conditions on a hot plate. The flask was attached to a Graham-type condenser. After heating, the mixture was allowed to cool down for 15 minutes and pH was measured as post extraction. A vacuum filtration apparatus with a 0.45 µm and

47mm diameter, Whatman cellulose nitrate membrane filter paper was used to filter the mixture. The leachate was collected, bottled and labelled accordingly. The solid residue obtained was washed with 100 ml of de-ionised water. The washings were again filtered with a fresh 0. 45 µm filter paper. The washed solids were weighed and then dried in an oven at 105°C.

Step 2, Copper extraction process: Dried solids obtained from step 1 were weighed which were then used as the sample for step 2. The solids were added to 50 ml of ammonium chloride (NH_4Cl) solution at 2 M concentration. After the pH was measured, the mixture was subjected to same experimental conditions as of step 1. After the extraction of one hour period, pH was again measured. Then the mixture was filtered and washed followed by collection and bottling of leachate. Washed solids were weighed and then dried in an oven at 105°C.

Step 3, Chromium extraction process: Dried solids obtained from step 2 were weighed before using in this step. The solids were added to 50 ml of hydrogen peroxide (H_2O_2) solution at 2M concentration. pH of the mixture was measured and then subjected to same experimental conditions as of step 1. After extraction for one hour, the mixture was filtered and washed followed by collection and bottling of leachate. Washed solids were weighed and then dried in an oven at 105°C.

Finally, the dried solids obtained after the three-step extraction process were weighed, to determine the final weight loss. The solids were microwave digested and elemental analysis was performed by ICP according to the procedure stated earlier.

4.9 CCA Precipitation by Electro – Coagulation

After the three-step extraction process the CCA elements were obtained in a solution. In order to develop a suitable method for removing the elements from the solution different methods were possible such as chemical displacement, evaporation and electrolysis.

Chemical displacement of CCA elements could be performed with the help of addition of chemicals to the solution to displace the heavy metal ions. However, due to the significantly difference in the reactivities of the three elements makes the process quite slow and a creates a possibility of secondary pollution due to the chemicals added [107]. This process involves multi-stage chemical reaction. Chromium is normally reduced by acid reduction with the help of chemicals such as sulphur dioxide, sodium sulphite or sodium bisulphate [107]. Whereas iron salts could be used for reduction of arsenic and copper where arsenate species are known to have a high affinity towards iron oxides [108, 109].

Evaporation of the de-ionised water will result in the heavy elements as the residue. However, the problem with this method is that the process will be very long and energy intensive. The quantity of energy required would be very expensive and makes this method very costly. As well as the heating possess problem due to the volatile nature of the heavy elements present especially arsenic which can produce free arsenic which volatises at much lower temperatures [49]. Therefore the evaporation method consisted of dangers associated with potential release of arsenic and high energy costs.

Electrocoagulation is a type of electrolysis in which a controlled electrical current is applied which causes the suspended particle to become charged causing them to bond together and form larger masses. This process is being used for an effective removal of suspended solids to a sub-micrometer level, to break emulsions, and oxidise and eradicate heavy metals from water [110]. In this method the in-situ generation of the coagulants takes place by electrolytic oxidation of the anode material such as iron or aluminium [111]. The coagulant differs depending on the anode material, as this in broken down by electrolytic oxidation to release metal ions (Me^+) into the solution. These ions along with the oxygen and hydrogen ions and gasses produced at the cathode due to the electrolysis of the deionised water react with each other or the heavy metal ions to form intermediate precipitates or pollutants.

The process of electrocoagulation was selected as the next step towards the disposal of CCA treated wood waste after chemical extraction. An electrocoagulation technique was employed for the removal of the CCA metals from the leachate obtained during the chemical extraction of the wood waste. The experiment involved a number of variables in treating the leachate such as current, electrodes, pH, duration and dilution/concentration. The procedure for the electrocoagulation was carried out in a series of different conditions to optimise the variables and obtain the best efficiency possible.

Preparation of Solution: CCA leachate solution obtained from NaOH extraction step was used for the initial experiments and determination of the optimum conditions for electrocoagulation. 3 ml of well shaken leachate was transferred into a 50 ml clean beaker with the help of a pipette. The same pipette was used to add 30 ml of de-ionised water to the 50 ml beaker. This washed any CCA solution remaining in the pipette. The volume obtained was of overall concentration of 1:10. The duplicates were prepared in the same way and from the same parent leachate to maintain the homogeneity of the experiments. Once all the optimisation experiments were completed, a bulk solution was prepared with a concentration ratio of 1:5. For all solutions, 33 ml of volume was prepared in a 50 ml beaker which was subjected to the electrocoagulation process.

Adjustment of pH: In order to adjust the pH of the solutions prepared, hydrochloric (HCl) acid was used. 1 M of hydrochloric acid was prepared from a 30 % stock solution by dilution with de-ionised water. The quantity of HCl was calculated as shown in the equation 4.2:

$$30\%\ Molar\ conc. = \frac{\%\ conc.\times 1000\times density}{atomic\ mass} = \frac{\frac{30}{100}\times 1000\times 1.18}{36.46} = \mathbf{9.7M} \qquad \ldots \text{Equation (4.1)}$$

Where HCl has;

Density = 1.18 g/ml

Atomic Mass = 36.46 g/mol

Therefore, To make 1 M of HCl solution from 9.7 M solution, 'x' ml of HCl solution is to be added per 1 ml of de-ionised water.

$$\therefore to\ make\ 1M \rightarrow (9.7)x = 1$$

$$\rightarrow x = \frac{1}{9.7} = 0.103\ {}^{ml\ HCl}/_{ml\ deionised\ water}$$

In order to make a 1 M solution of 250 ml volume, it should have 25.75 ml of HCl solution of 30 % stock.

$$\therefore \rightarrow for\ 250ml = 0.103\ \times 250 = 25.75ml \qquad \text{… Equation (4.2)}$$

After preparing the 1 M HCl solution it was added to CCA leachate solution in order to adjust the pH to the required value. Drop by drop 1 M HCl solution was added with the help of burette and was continuously monitored with a digital pH meter until the desired valued was achieved.

Therefore, 1 part of CCA leachate diluted with 10 parts of de-ionised water where 1 M hydrochloric (HCl) solution was used to adjust the pH of the sample was used for electrocoagulation. 33 ml of the diluted sample solution was carefully added to a beaker fixed with two cylindrical electrodes attached. Each electrode was 70 mm in length and 5 mm in diameter. Initially two different experiments were carried out one experiment consisted of set of mild steel electrodes (both anode and cathode made up of mild steel material to provide iron ions) and other experiment was performed with set of aluminium electrodes (both anode and cathode made of aluminium material to provide aluminium ions). This experiment was performed to determine the suitable set of electrodes to provide higher precipitation and removal rate of CCA. For each experiment, care was taken to ensure that the electrodes were fully dipped and not touching each other. Electrodes were connected to a radiometer potentiostat / galvanometer for a constant current supply. Figure 4.11 shows the power pack used, Farnell Instruments 'E' series bench power supplies model E30/1. One electrode functioned as a sacrificial anode and the other acted as cathode. All the experiments were carried out for duration of 15 minutes and at room temperature. The apparatus of the electrocoagulation was then placed in fume cupboard and before the current supply was switched on. The power pack used enabled to perform various experiments for different current supply from 0 to 1 A.

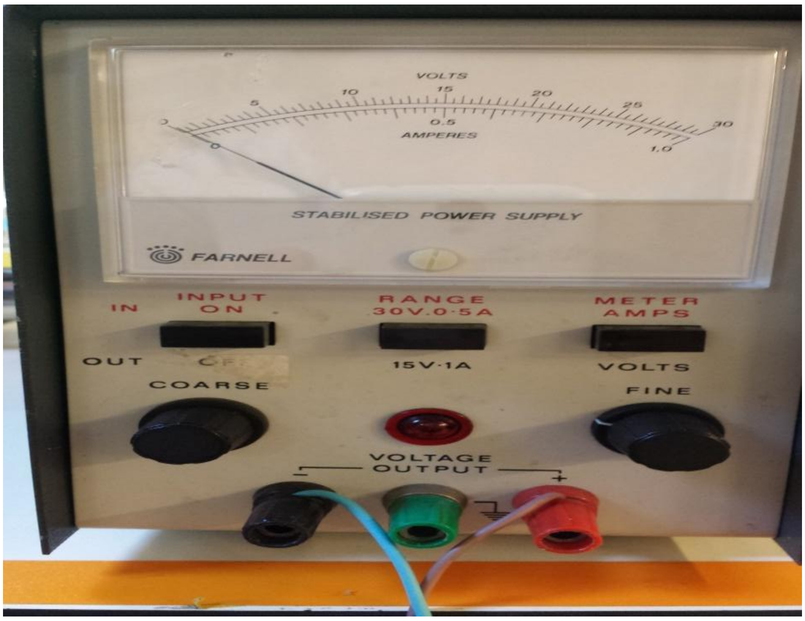


Figure 4.11Bench power supply unit for Electrocoagulation process

After the electrolysis, the sample was allowed to cool down for another 15 minutes. This led to the completion of the precipitation process. In order to separate the precipitated sludge and solution, a vacuum filtration method was used with a 0.45 µm and 47 mm diameter, whatman cellulose nitrate membrane filter paper. The solids obtained from filtration were stored after drying in oven at 105^{o}C. The solution obtained was bottled and taken to ICP for elemental analysis.

Summary

Samples of treated wood used in this research were obtained from a quenching tower which was demolished after a 33 year service in an integrated steelworks environment. This chapter provided basic information of a coke ovens plant, quenching tower and its structure. The knowledge of working of the quenching tower was also important. This provided an understanding of different temperatures, water and steam exposure and exposure duration to coal products which could influence the CCA preservative content in the wood. Samples were collected from different parts of the tower which may hold different concentrations of CCA. Samples for a growth ring analysis were also prepared from the wooden beam of the tower to determine the CCA distribution across the wood lattice.

Various components typical to an integrated steelworks environment were recognised which may be responsible to impart different characteristics or influence the wood properties if exposed during the service life of the quenching tower. Therefore, samples of kish, air borne particles, coal, coke and quenching water from the water treatment plant were also collected. All the samples were dried according to British Standards and kept in lip seal plastic bags for air tight storage. Therefore all the tests performed on samples were on a dry basis.

Procedures for experiments and apparatus used were described. Elemental analysis was carried out by using Inductively Coupled Plasma (ICP) after microwave digestion. Procedures for other analytical techniques included X-ray diffraction and Scanning Electron Microsopy (SEM) were described to study the mineralogical structure and element distribution respectively. Different tests were performed to understand the leaching behaviour exhibited by the elements in wood. A three step extraction method for the removal of CCA elements by the process of chemical leaching was described. The method of electrocoagulation was used to precipitate CCA elements from the eluate obtained by the chemical extraction.

Chapter 5. Characterisation of the CCA Treated Wood Waste

5.1 Introduction

The following chapter highlights the results and discussion on the characterisation phase of the CCA treated wood waste generated from the quenching tower. The sources of material used in the experimental study and the experimental methods as described in the chapter 4 were used to obtain the basic understanding of the components in the treated wood waste.

The characterisation began with the elemental analysis of the wood, obtained from different parts of the tower. The elemental composition of the untreated wood was used as the datum / control concentration. XRD and SEM tests were conducted to further characterise the treated wood properties and compared to the untreated wood.

The next stage of the characterisation included the leaching properties of the CCA components in the wood. Results from standard leaching tests with different leach durations are highlighted in this chapter. These results are discussed and compared to published research. Different types of sampling procedure were also carried out for the leaching tests. The leaching analyses were subjected to a mathematical model as well.

Iron contamination detected during elemental analysis was further investigated. The trend of iron contamination, the source of iron, distribution of iron across wood lattice, leaching properties were determined. The influence of the iron on the disposal of the CCA wood is also highlighted and discussed.

5.2 Characterisation Techniques

The first step in the characterisation of wood was to perform elemental analysis. The element content of the wood from different parts of the tower was analysed and compared. This provided valuable information on the status of the CCA content in the wood, any major changes occurred over the service life and amount of CCA lost from the wood in a typical quenching tower.

5.2.1 Elemental Analysis

The wood samples were tested for three primary elements copper, chromium and arsenic as well as three secondary elements iron, zinc and lead. A baseline of the elemental composition was established by testing a known untreated wood sample for the above mentioned six elements. The untreated wood sample was obtained from the local wood treatment plant where wood is treated for general domestic products, railway sleepers, and utility poles. The specific origin of the wood was unknown. However, the wood was a scots pine which was a species of pine native to Europe. The results for untreated wood are highlighted in Figure 5.1 which shows that there was no copper and lead found, whereas in a study Miranda [112] reported that 2.12 mg/kg of copper and 1.56 mg/kg of lead were detected in the pine wood analysed. A similar concentration were also reported by Harju [113] for copper and lead at 2.6 mg/kg and 2.1 mg/kg respectively. However, this difference in the concentration may be due to the differences between regional and environmental conditions where wood was grown.

Likewise, chromium and arsenic were present in traces, typically 2 mg/kg and 1 mg/kg respectively in the wood analysed in this study. When compared to the concentration reported by Miranda [112] of chromium and arsenic as 6.7 mg/kg and 4.53 mg/kg respectively which are again due to the regional differences.

The amounts of iron and zinc present were about 30 mg/kg and 10 mg/kg respectively in dry wood matter. However, as a whole these concentrations were considered to be at similar levels as elements present within the wood depending on its natural growing environment.

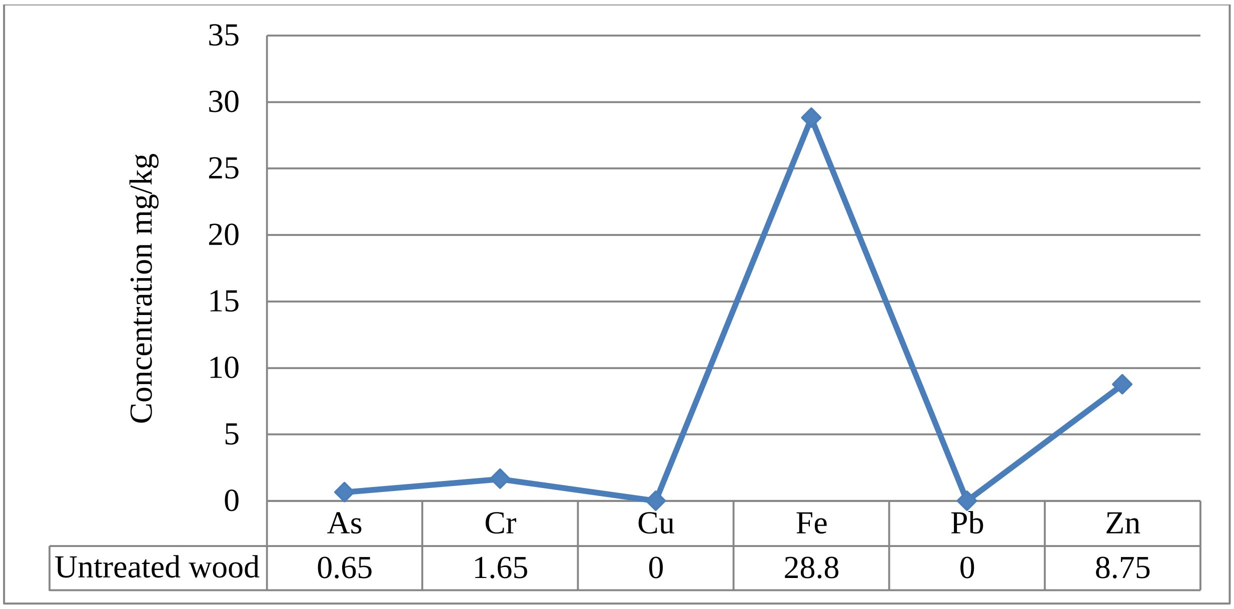


Figure 5.1 Elemental analysis of natural untreated and unused wood

As described in chapter 4, the wood samples were obtained from the three different sections of the quenching tower. Also the wood from each section consisted of samples of old and newer refurbished wood. These samples were prepared for analysis again according to the procedures highlighted in chapter 4 and analysed for elemental content by digesting the wood and then using the ICP technique.

5.2.1.1 Top Section

Figure 5.2 shows the concentration of the CCA metals in the dry wood samples taken from different sides of the top section. A low concentration of CCA elements was recorded in the old wood compared to the refurbished wood samples. The refurbished wood contained high concentration of these elements with an average of 9515 mg/kg, 9981 mg/kg and 4308 mg/kg of arsenic, chromium and copper respectively of dry matter, whereas an average concentration of arsenic, chromium and copper of 781 mg/kg, 2292 mg/kg and 328 mg/kg respectively were determined in the old wood from the top section. A generalised trend can be highlighted by observing the concentration gradient between old and refurbished wood. This trend was possibly as a result of quenching process which led to the leaching of the CCA elements over time from the wood. Therefore, the longer the wood had been in service the more CCA elements should have leached from it. This was attributed to the low water run off over the wood surface and minimum exposure. The top section was away from the splash zone and had a minimal exposure to the water. The exposure to the hot coke was also low, therefore, the effect of heat was also reduced. However, steam would have been responsible for majority of the leaching of elements. As reported by Clausen [90] that steam explosion is a potential method of removal of CCA elements from the treated wood. After analysing the concentrations of the CCA elements from the old wood, it was observed that chromium was most resistant to leaching followed by arsenic; copper was least resistant to leach from wood. This was in agreement with results obtained by Clausen [90] by exposing the treated wood to steam such that chromium was most resistant to leach and provided negligible extraction whereas copper and arsenic were about 80 % and 35 % respectively.

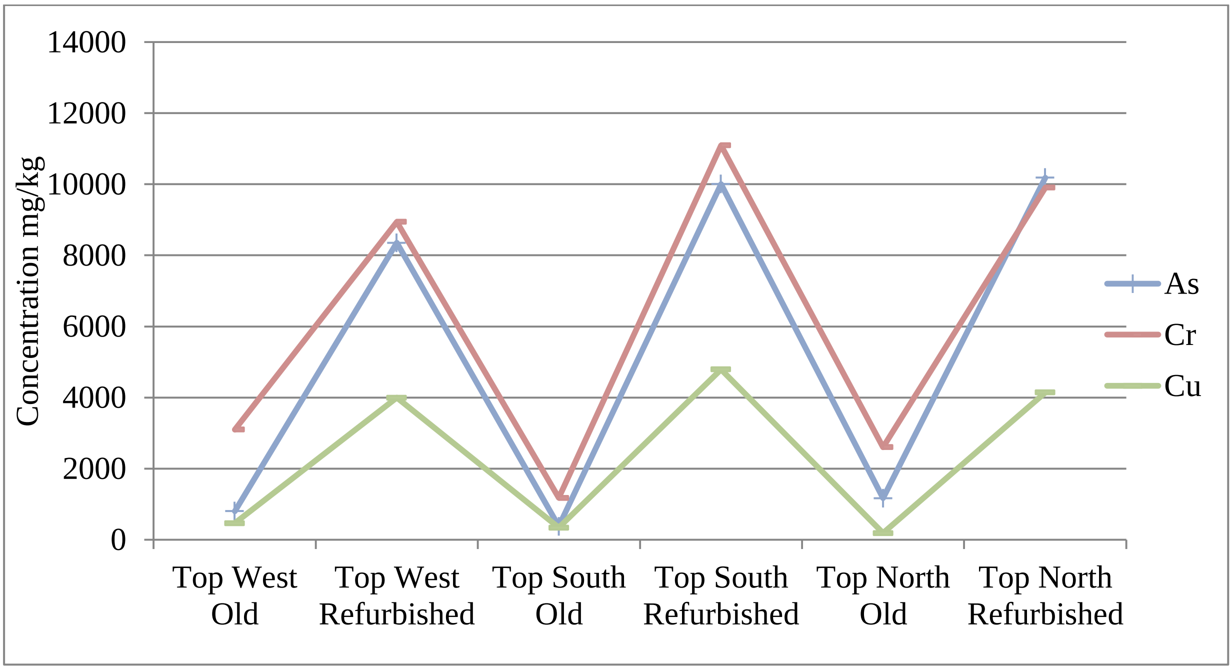


Figure 5.2 Elemental analysis of wood from top section of quenching tower

5.2.1.2 Middle Section

The metal concentrations in dry samples of refurbished and old wood from west side of the middle section are shown in Figure 5.3. Due to the degrading condition of the tower and ongoing demolition process only west side samples were salvaged which were in representable conditions. The analysis showed that old wood had a relatively low concentration of arsenic and copper, whereas, a substantial amount of chromium was observed. Though the chromium was expected to be at higher levels by showing a greater resistance towards leaching, the chromium concentration in the old wood was 9261 mg/kg as compared to only 3679 mg/kg of chromium in refurbished wood. This could be attributed to the probability of higher unfixed chromium in the refurbished wood at the time of preservation of the wood or a higher concentration of arsenic or lesser copper in the preservative solution during treatment. This change in concentration could have contributed to a lesser amount of Cr^{3+} in the wood which can slowly leach away [33] . However, the overall concentration of CCA elements in refurbished wood was comparable with the old wood. The direct water sprays and high temperature due to the close proximity to the burning coke could be responsible for the higher loss of CCA compared to the wood from the top section.

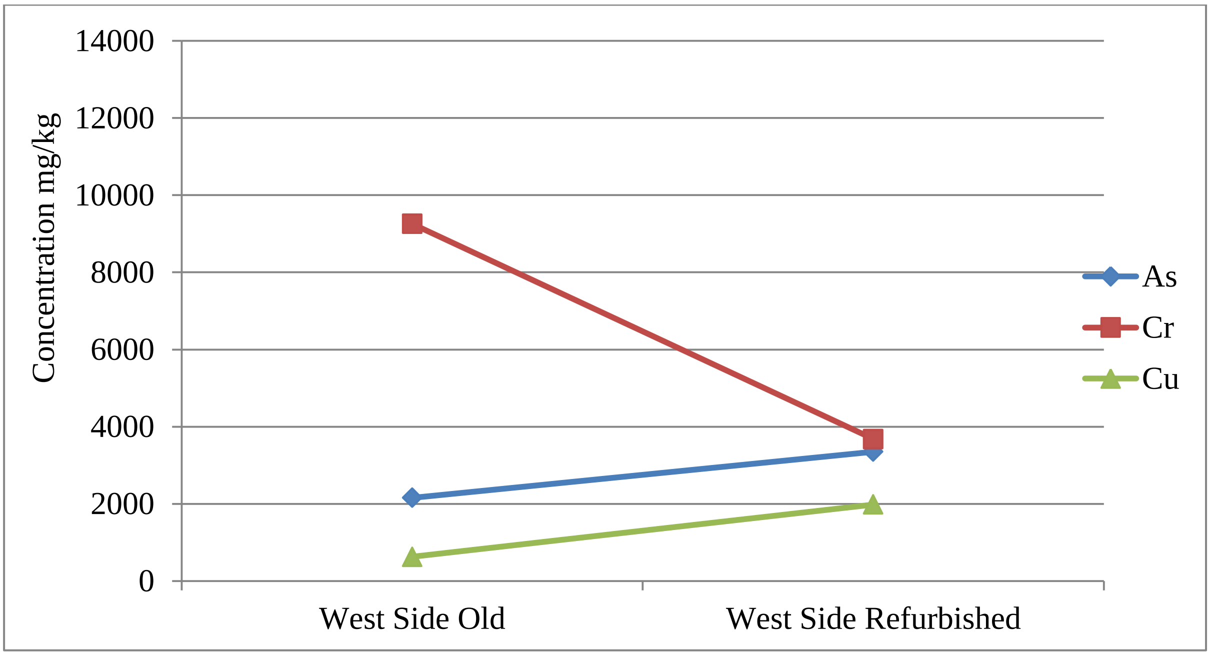


Figure 5.3 Elemental analysis of wood from middle section of quenching tower

5.2.1.3 Lower Triangle Section

The samples were taken from the bottom section of the tower identified as the lower triangle and lower stack as the sides of the tower from where wood was sampled. The lower triangle were the two opposite inclined sides of the lower region and the stacks were the vertical sides of the tower which are shown in the Figure 4.4 as a schematic of the demolished quenching tower in Chapter 4. In Figure 5.4, the concentration of CCA metals in dry wood from the lower triangle and lower stack regions are shown. The west side of the lower triangle contained 236 mg/kg, 1759 mg/kg and 409 mg/kg of arsenic, chromium and copper respectively. The east side of lower triangle area contained 138 mg/kg, 609 mg/kg and 91 mg/kg of arsenic, chromium and copper respectively. Refurbished wood from the lower stack contained 8769 mg/kg, 8646 mg/kg and 4856 mg/kg of arsenic, chromium and copper respectively of dry sample. CCA concentration in wood from the lower triangle was found to be the lowest of all the sections as the wood received heavy wash out during every quench cycle. This section received most of the water used in the quenching process. The water was at elevated temperatures which did not evaporate during quenching and probably was responsible for higher loss of CCA elements. Therefore this can be considered as the situation where a high liquid to solid ratio occurred during the in process leaching of CCA elements. As discussed by Jambeck [67] the liquid to solid ratio had a direct relationship with the leachability of the CCA such that each element released was a function of the liquid/solid ratio. The cumulative percentage of each element released increased with time. The instantaneous concentration of leached CCA elements varied and decreased with time due to the lower amount of CCA was available. The results also showed that chromium was the most resistant of the three CCA elements to leach such that the chromium content was mainly highest of the CCA left in the wood waste. CCA concentration was found to be the lowest in the wood waste arising from the bottom section of the tower but the concentrations were still comparable to the other sections and were also substantially higher than the concentration of such elements found in the natural untreated and unused wood.

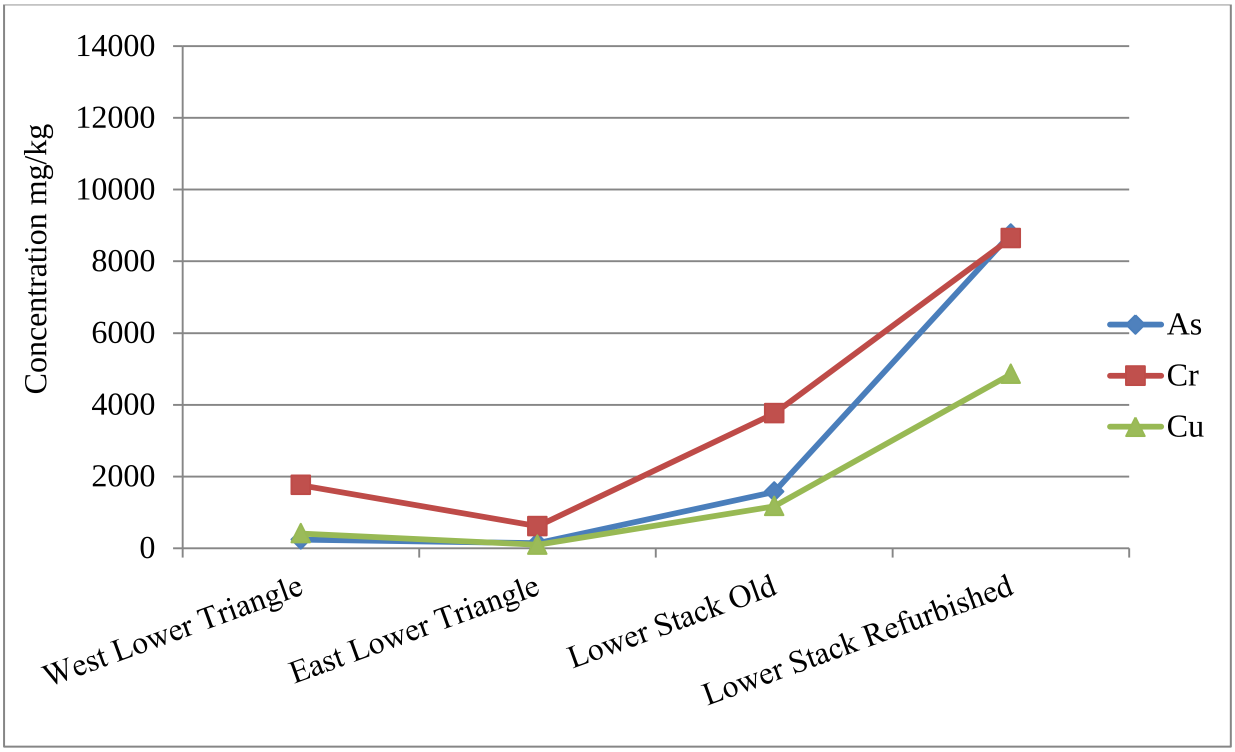


Figure 5.4 Elemental analysis of wood from Lower triangle section of quenching tower

It was expected that CCA elements would have leached out over a period of time, due to the repeated intense heat and water contact from the quenching cycles. Elemental analysis shows that after 33 years of service, the wood still contained considerable amount of elements. The waste wood generated from the quenching tower was deemed as hazardous, due to the presence of CCA elements [4-6]. The concentration of copper, chromium and arsenic varied widely due to the difference in age, service period and location of wood in the quenching tower. Over the period, a substantial amount of CCA had leached out from the old wood. The refurbished new wood which was installed ten years before demolition had retained a high elemental concentration.

According to Jambeck [67] CCA wood waste from a playground (approximately 10 years of service) was analysed by acid digestion. This wood waste contained 1960 mg/kg, 2550 mg/kg and 1340 mg/kg of arsenic, chromium and copper respectively. This suggests that the CCA final concentration in wood waste from steelworks after ten years of service was significantly high compared to the waste arising from domestic demolition wood waste. The difference between the end concentrations could be due to factors such as the wood species, initial preservative concentration and fixation of CCA within the wood. This advocates that the wood waste from the industrial applications consists of higher concentrations of CCA which are not readily leachable. Therefore, the improper disposal of this wood may lead to a low but constant leaching of CCA in the soil for a longer period of time.

Considering the initial concentration of CCA in the old wood to be similar to the concentration of the newly treated refurbished wood at the time of installation, old wood had experienced a significant leaching of the metals over a period of 33 years. It was observed that arsenic and copper were more prone to leaching than chromium. This was also in agreement with Hingston et al. [18] who showed that copper and arsenic tend to show losses at a greater degree than chromium. This was an anticipated trend of loss of the CCA elements i.e. CCA concentration reduced with the increase in the age of the treated wood [81].

5.2.2 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) analysis was undertaken to determine the presence of any crystalline structures of CCA in the wood. The detection of crystalline materials would provide more information on the chemical bonds and molecular structures of CCA elements present in the wood. This information could add to the value of characterisation and may facilitate the disposal method for the wood waste.

Samples of untreated and treated wood were analysed by XRD to distinguish between the crystalline structures of the two specimens. Figure 5.5 shows the XRD curves of untreated wood and treated wood sample used in the XRD analysis. There were only some and very tiny peaks on the treated sample compared to the untreated sample, but it was difficult to establish clearly if they were the phase peaks. Overall, there were no significant differences between the treated and untreated samples were found and hence phases could not be identified. This meant that the CCA elements possessed minimum crystalline properties which could be distinguished from untreated wood. Therefore, the results obtained from the XRD experiments for the two wood samples, namely treated wood from the quenching tower and untreated wood were similar. Due to the absence of any substantial information and data the XRD results were deemed to be a dead end in the research. This was found to be in agreement with the results from Nico [114] which stated that X-ray diffraction analysis of CCA-treated material showed no detectable crystalline phases other than that of the wood cellulose.

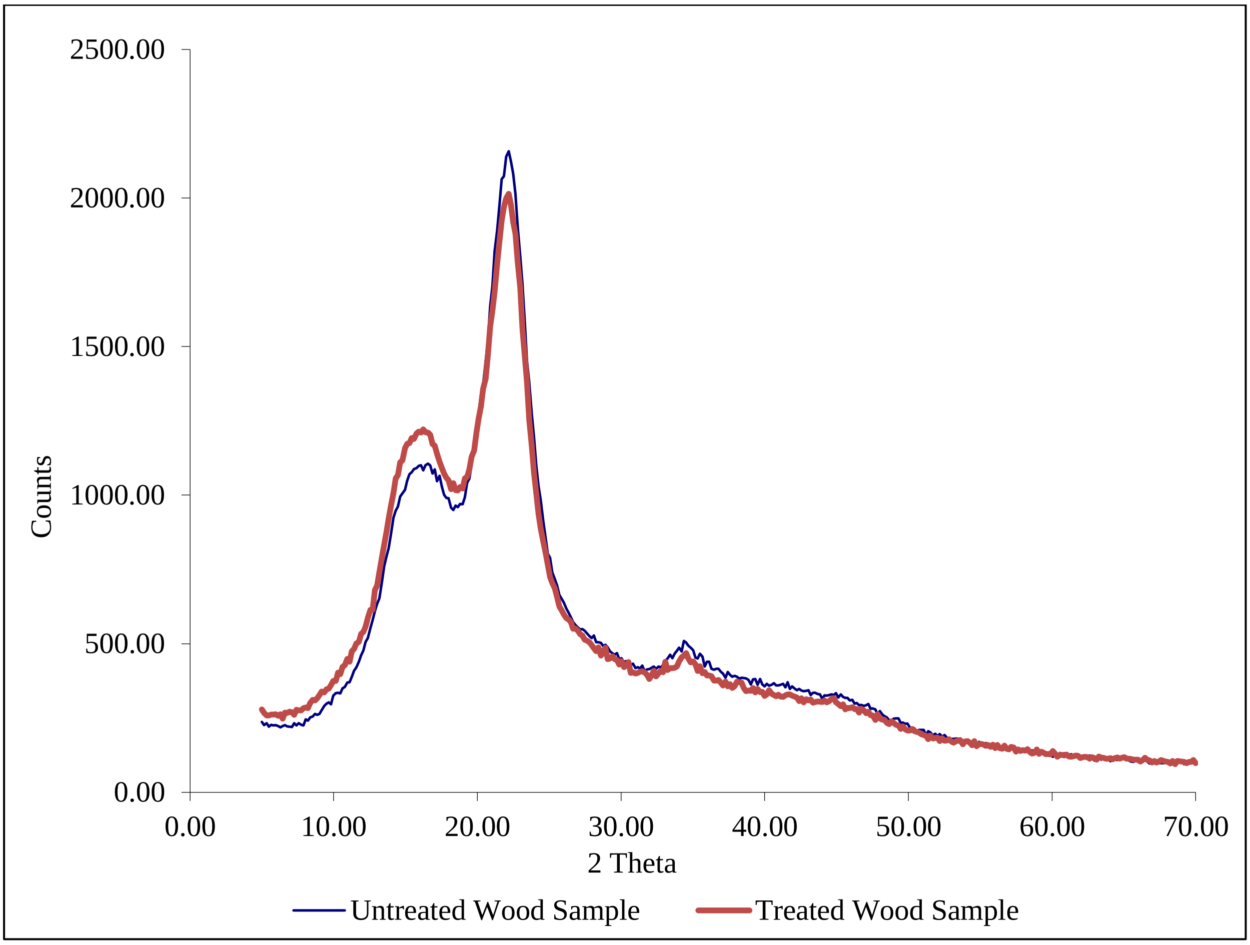


Figure 5.5 XRD curves of treated and untreated wood specimens

5.2.3 Scanning Electron Microscopy (SEM)

The wood samples were observed by SEM. Topographic images taken by electron microscope of the samples of the CCA treated wood were compared to the untreated wood sample. Figure 5.6 shows the image of the treated wood sample at 200 µm magnification. The image consists of white spots formed due to the charging phenomenon caused by a focused electron beam on the wood surface where elements are present while the sample is kept in a vacuum. The interaction of the electron beam with the sample produces various effects that were monitored with suitable detectors present in the SEM apparatus. The resulting signals which were secondary, and backscattered electrons along with characteristic X-rays, were collected in synchronization with the position of the beam to provide highly detailed spatial and compositional information [115]. Figure 5.7 shows the image of an untreated wood with no service history. The untreated wood sample was subjected to SEM at the same 200 µm magnification. This microscopic image did not show any white spots or distinguishing characteristic which could be caused by the electronic beams. This indicated that there was negligible concentration of elements such as CCA present on the sample surface which could have been charged and shown any colour changes. After comparing the two SEM images, it was visually confirmed that there was a presence of elements but these images did not provide any specific data about these elements.

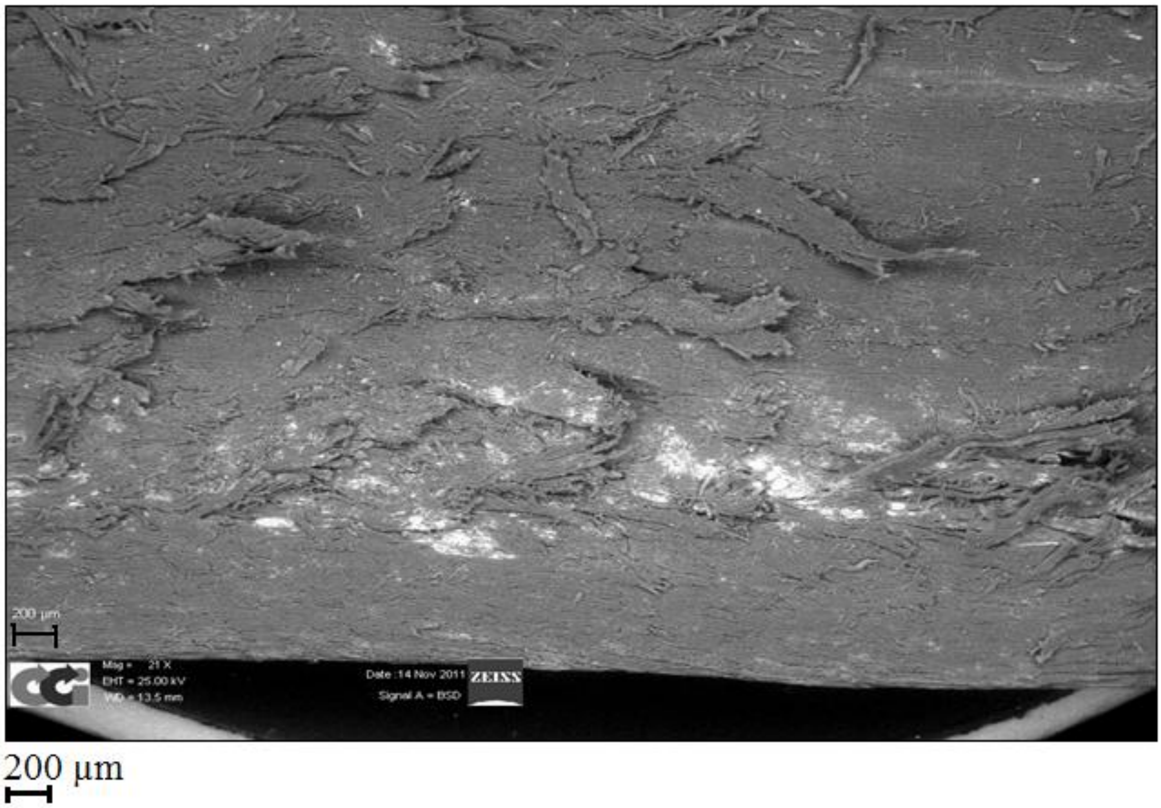


Figure 5.6 View of CCA treated wood under an electron microscope

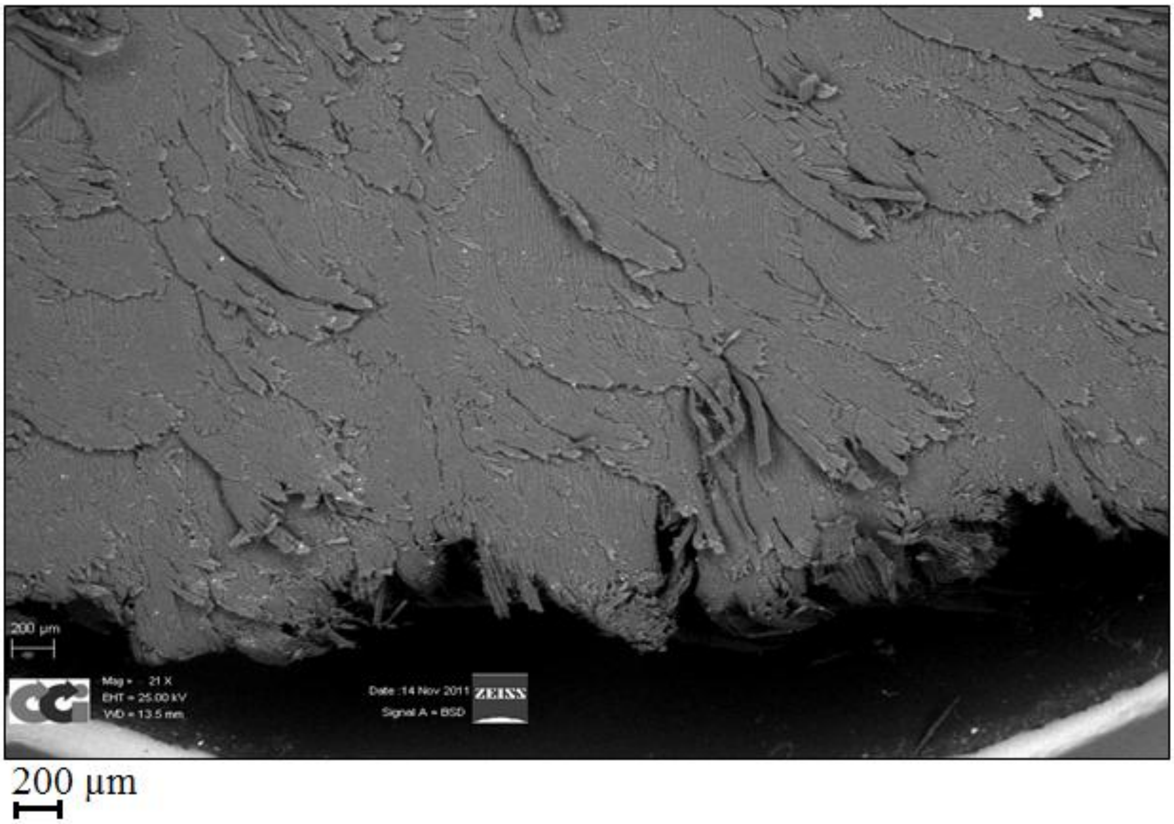


Figure 5.7 View of untreated and unused wood under an electron microscope

The SEM images shown in Figure 5.6 and Figure 5.7 were further magnified and subjected to analysis by using Energy Dispersive X-Ray (EDX) Spectroscopy in order to further investigate and obtain data on the elements on the wood surface. The EDX with point scan and line scan technology was employed to determine and understand the elemental distribution across the wood sample. Figure 5.8 and Figure 5.9 show the magnified images with different points which recognised as a spectrum for point scans on treated and untreated wood samples respectively. Table 5.1 provides the average readings obtained for the elements detected during the EDX point scans as illustrated in the respective images

Table 5.1 Element identified during the EDX point scan on the SEM images of treated and untreated wood specimens

Element	**Weight, %**				
	Treated wood sample				**Untreated wood sample**
	Spectrum 1	**Spectrum 2**	**Spectrum 3**	**Spectrum 4**	
Carbon, C	51.20	38.25	53.55	28.91	54.85
Oxygen, O	36.64	32.35	31.52	39.45	45.00
Silicon, Si	0.12	n/d*	0.07	0.08	0.05
Calcium, K	2.67	15.00	5.99	16.32	0.09
Chlorine, Cl	0.12	n/d*	0.13	n/d*	n/d*
Copper, Cu	1.03	1.63	0.85	0.72	n/d*
Chromium, Cr	3.26	1.41	1.84	0.62	n/d*
Arsenic, As	3.21	1.43	2.01	0.64	n/d*
Sulphur, S	1.76	9.93	4.04	13.26	n/d*
Total	100.00	100.00	100.00	100.00	100.00

* = n/d, not detected

Figure 5.8 and Figure 5.9. The weight percentage of the elements detected was calculated for each of the EDX point scans. The scans of untreated wood show ideal elemental content of carbon and oxygen to be 54.85 % and 45 % respectively whereas in treated wood the percentages dropped to as low as 28.91 %. An increase in the percentage of calcium and sulphur was recorded as well as CCA elements were also detected. The elemental content of wood detected during the EDX scan was corresponding to the analysis performed earlier with wood digestion and ICP such that no CCA element was detected in the untreated wood

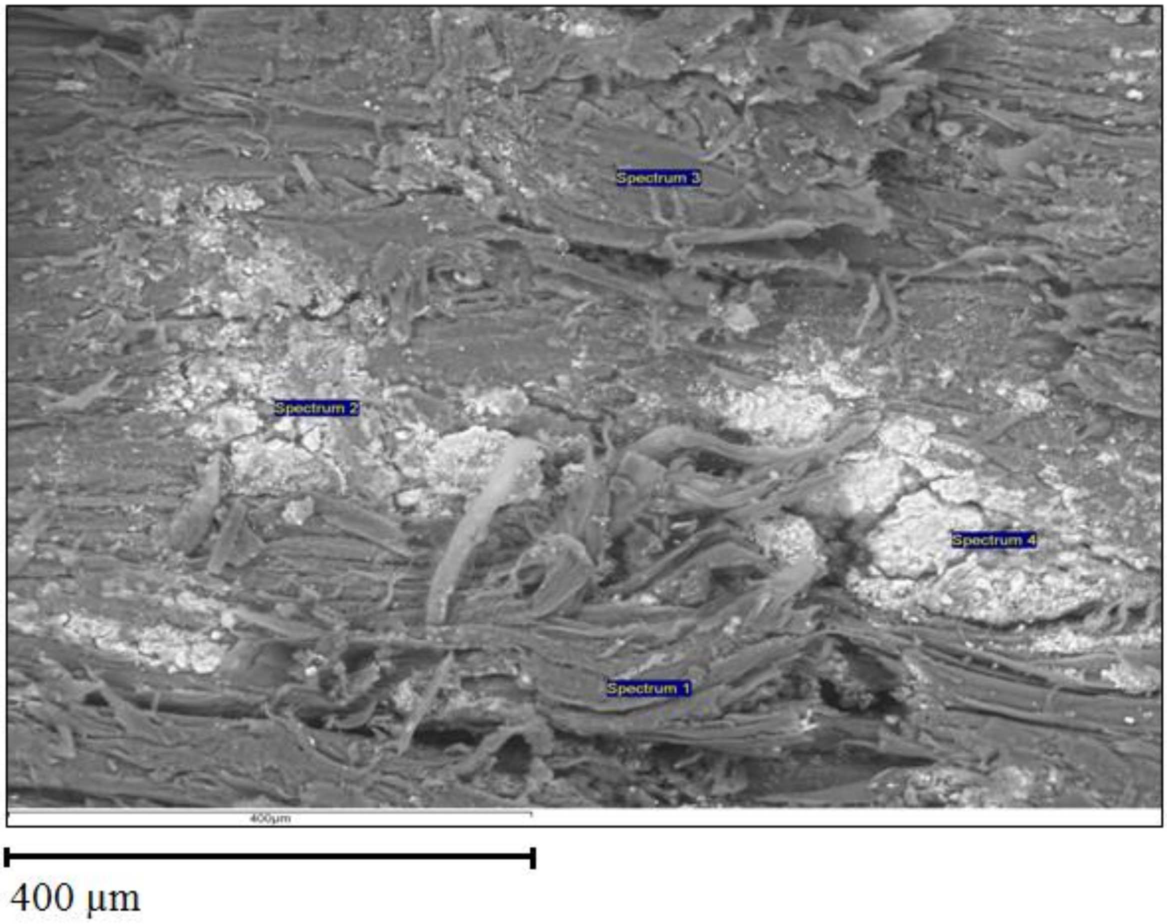


Figure 5.8 SEM image of treated wood with point scan locations identified for EDX analysis

The point scan on four different locations on a treated wood detected a well distributed CCA concentration across the wood surface. EDX point scans revealed that the white spots in the images of treated wood could be calcium deposits. Spectrum 1 and 3 in Figure 5.8 were points analysed away from the white spots and they consisted of calcium levels at 2.67 % and 5.99 % respectively. This compared to 15 % and 16.32 % for spectrum 2 and 4 respectively, the point scans of the heavy white spot region in the same image. The point scans also detected varying levels of CCA elements at the four different points in the treated wood, such that the chromium and arsenic detected by EDX scans at the respective points showed a direct relation between the two elements. Chromium and arsenic at 3.26 % and 3.21 % respectively were highest and in a similar range of weight percentage at spectrum 1. Moreover, chromium at 0.62 % and arsenic at 0.64 % were detected at spectrum 4 as the lowest values out of the four scans. This suggested that chromium and arsenic were present as a single compound which may be referred to $CrAsO_4$ [33]. On the other hand, copper was detected to be highest at 1.63 % in spectrum 2 scan and lowest at 0.72 % in spectrum 4. No direct relationship was established between the white spots and the presence of CCA elements on the wood surface.

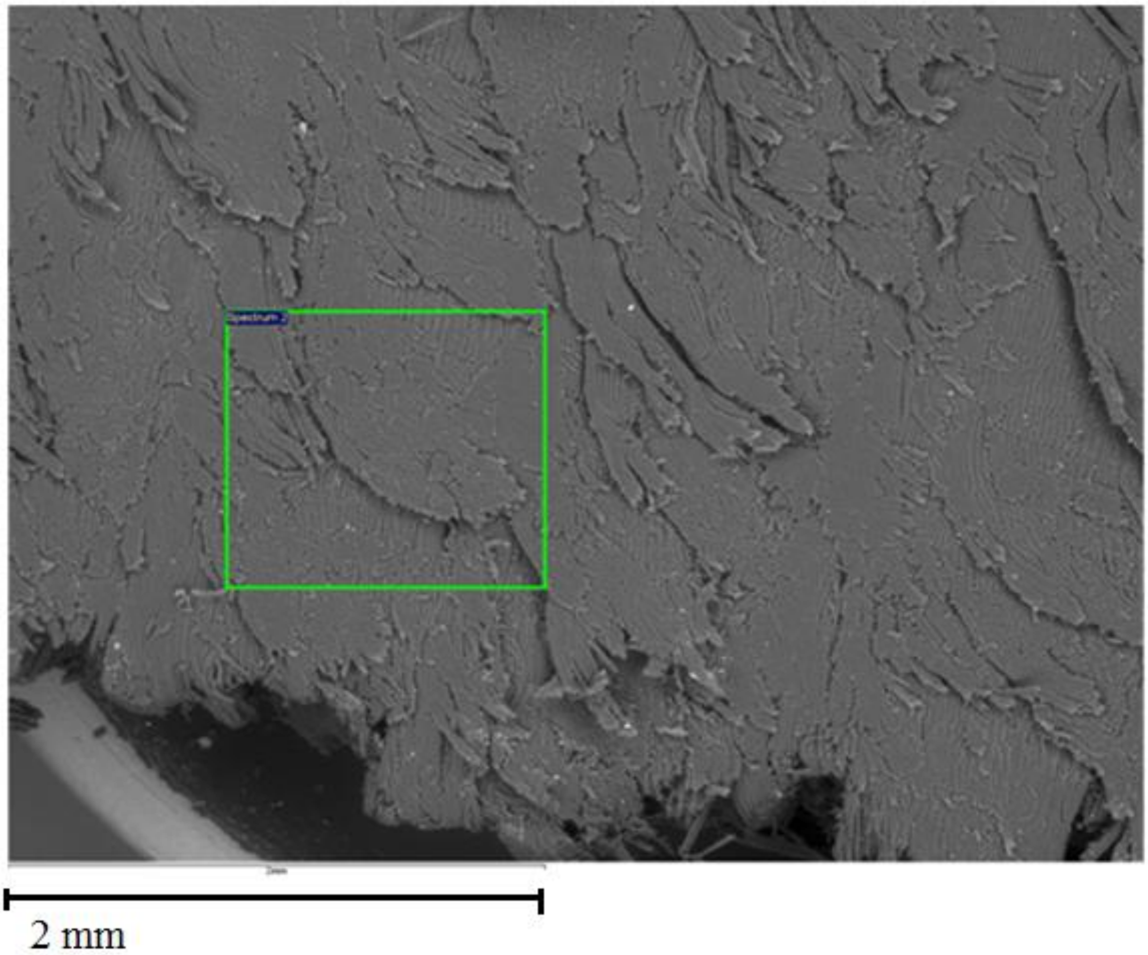


Figure 5.9 SEM image of untreated and unused wood with point scan location identified for EDX analysis

In order to determine the CCA distribution in the treated wood, EDX with line scan was performed. The line scans were obtained by analysing from edge to centre and centre to the edge of the sample. This provided information on how the concentrations of CCA vary with respect to the depth of the sample. Figure 5.10 shows the line scans recorded from front to the back such that the scan goes from the edge (0 mm) to the centre of the sample (3.2 mm). Figure 5.11 shows line scans recorded from back to front so 0 mm is at the centre and 2.5 mm at the edge. Copper detection was disabled in the line scan due to the interference caused by the copper tapes used to fasten the wood sample to the holder. However, the line scans showed that chromium and arsenic signatures provided a good reading on the distribution trends of the three CCA elements. A generalised pattern of steady decline in the signature of CCA concentration was detected when the scan moved from edge towards the centre of the sample. The line scans showed that CCA concentration at a given point on the edge was high which diminished with moving towards the centre or moving away from the edge. Calcium was also detected which followed a similar pattern of decreasing concentration with an increase in the distance from the edge. However, during the line scans high spikes of calcium were recorded at locations with white spots. This shows that the white spots were indeed calcium deposits which could have been accumulated as the result of the quenching process over the service period of the wood in the tower.

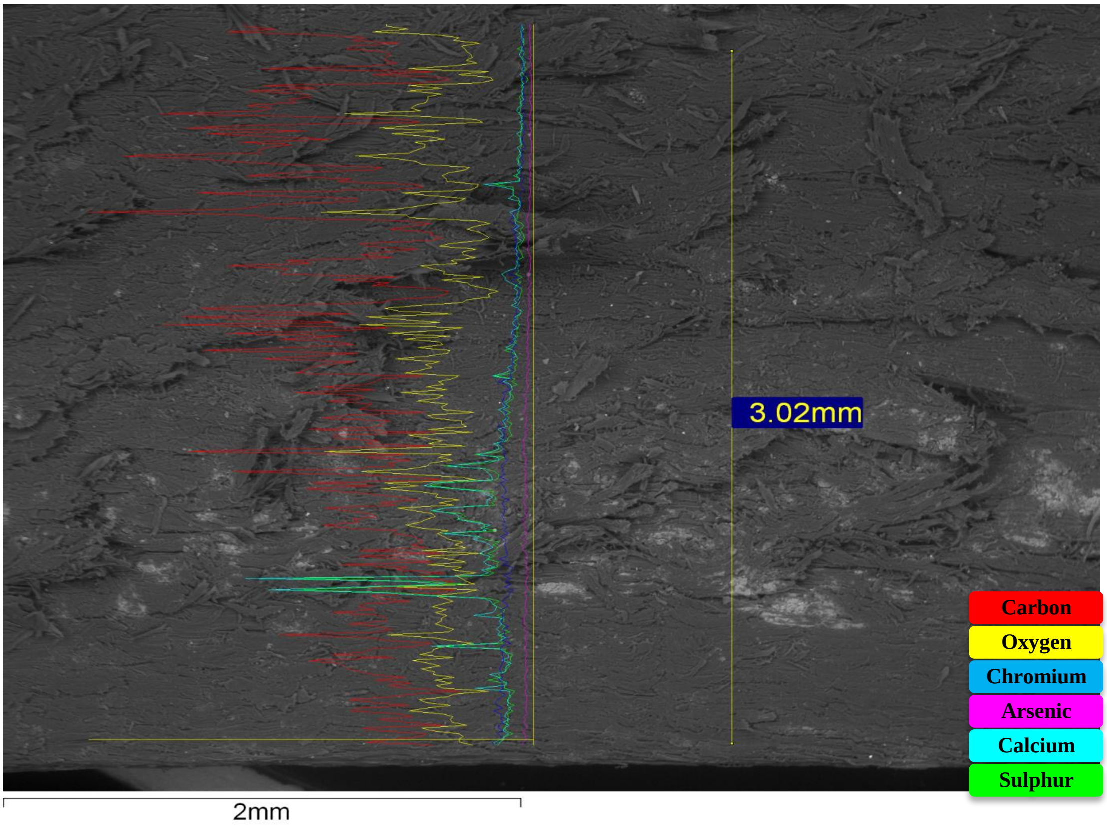


Figure 5.10 Elements detected by EDX line scan from edge to centre on SEM image of treated wood specimen

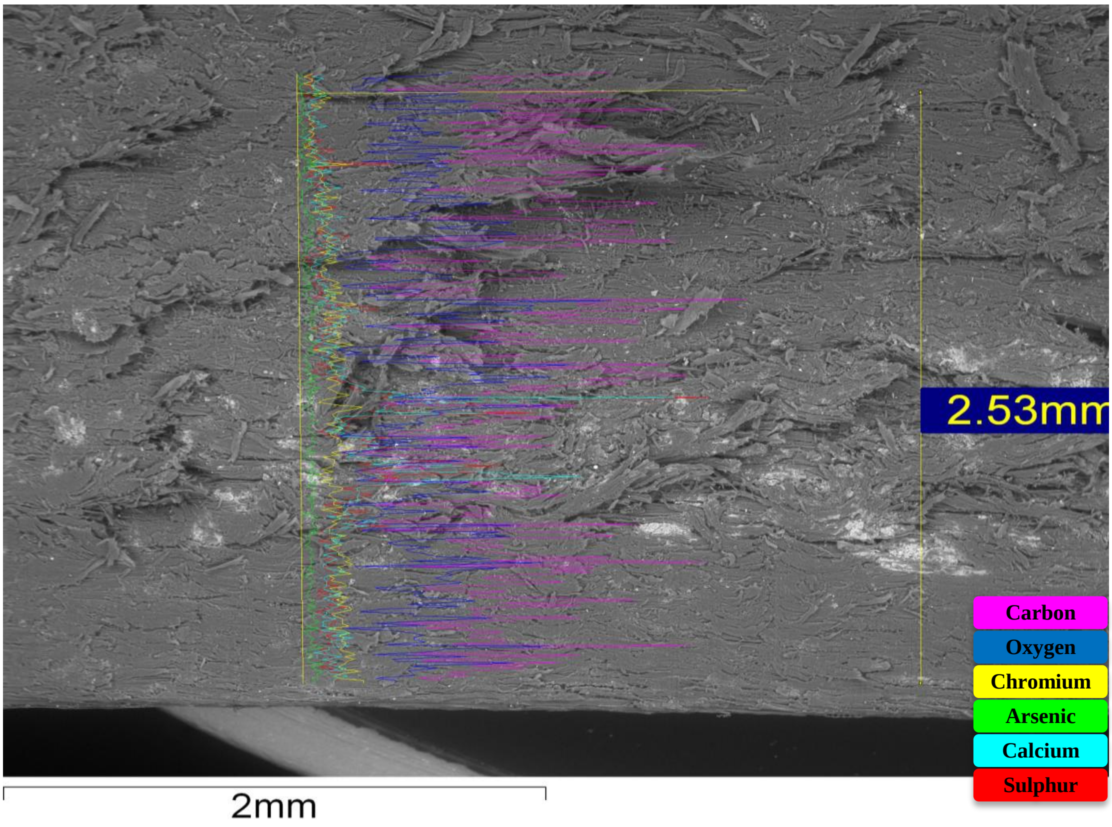


Figure 5.11 Elements detected by EDX line scan from centre to edge on SEM image of treated wood specimen

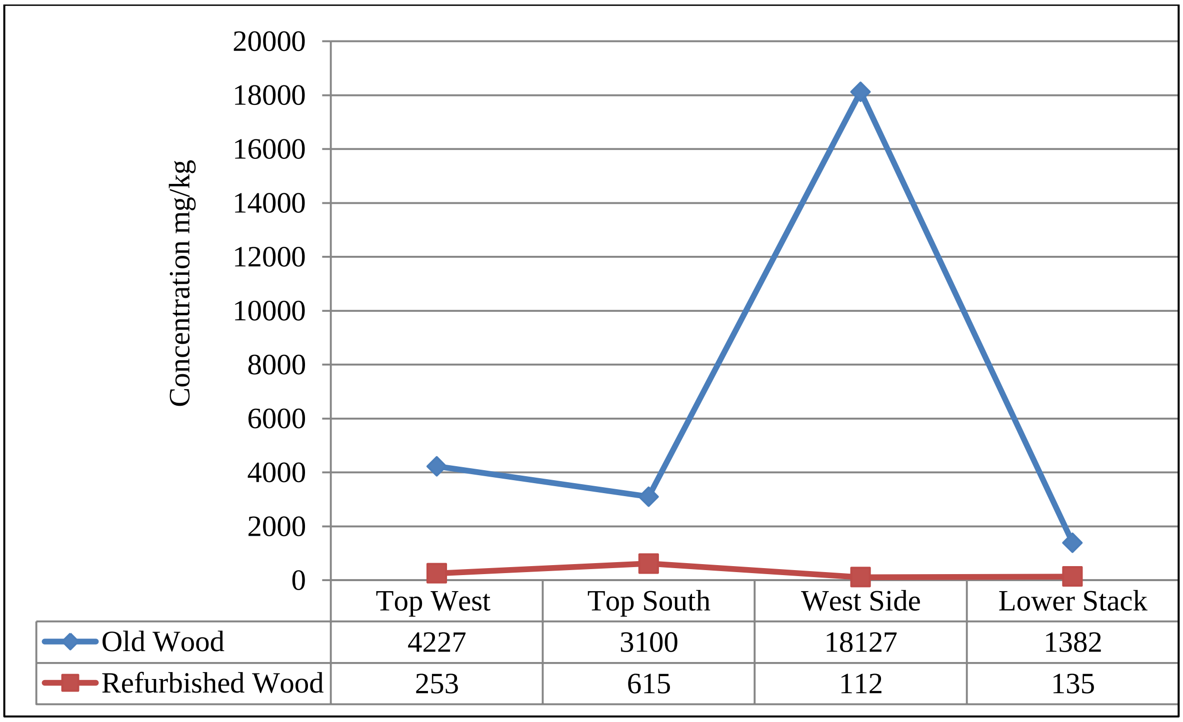
5.3 Iron Presence

The presence of iron in the CCA wood waste is a very important aspect due to the fact that iron oxides interact in different ways to influence the fate of the CCA elements after treated wood is disposed by landfill. Kumpiene [116] stated that using iron oxides as amendments can help to impart stabilisation in the copper, chromium and arsenic. Mobility of arsenic is reduced by the formation of amorphous iron (III) arsenate and/or insoluble secondary oxidation minerals at low pH and under oxidising conditions. Chromium is more stable at the natural oxidation state of Cr (III). Reduction of the Cr (VI) is accelerated by the presence of organic matter and divalent iron to trivalent chromium or is co-precipitated with Fe hydrous oxide which has low mobility and bioavailability. Stabilisation of copper is not very efficient as the mobility of copper increases with the decrease in pH.

On the other hand, the presence of organic matter with the iron and aluminium oxides in the soil also has effects on leaching and retention of CCA components in soil. Townsend [17] indicated that a specific complexation reaction between iron and aluminium oxides with humic acids leads to the decrease in their activity in soil solution. This increases the dissolution of arsenic compounds which are otherwise insoluble. Fulvic acid increases the solubility of arsenates and chromates by forming complexes with cations of any insoluble arsenate and chromate compounds. This is also supported by Kumpiene [116] stated that dissolved organic matter can compete with arsenic for the sorption sites by displacing arsenic in oxidation state of 3+ and 5+ from iron oxides.

This shows that the presence of iron plays a vital role in the chemistry of the CCA components and its release into the environment. Hence, it was important to understand the relation between wood waste and iron concentration, such that wood with higher service life had accumulated more iron. Characterisation of iron contamination in the wood waste from the quenching tower of an integrated steelworks was undertaken by determining the concentration of iron present, its distribution in the wood lattice and possible sources for this contamination.

The elemental analysis of the wood from the quenching tower showed varying levels of iron concentration. The pattern of the concentration of iron detected in the wood waste was very distinct and can be seen in Figure 5.12. The figure shows the concentrations of iron detected in the old wood from the quenching tower corresponding to the newer and refurbished wood of the similar part of the tower. The highest gain in the iron concentration at 18127 mg/kg was shown by the old wood from the west side of the middle section of the tower. The iron concentration in the refurbished wood was detected to be very low with a maximum of 615 mg/kg when compared to old wood. The pattern of concentration was such that iron concentration increased with the increase in the service life of the wood in the quenching tower. However, the iron concentration was extraordinarily high when compared to the results obtained from the elemental analysis of the untreated wood, which showed only about 30 mg/kg of iron.



	Top West	Top South	West Side	Lower Stack
Old Wood	4227	3100	18127	1382
Refurbished Wood	253	615	112	135

Figure 5.12 Iron concentration found in old and refurbished wood from different parts of the quenching tower

5.3.1 Iron distribution

After confirming the presence of the iron and its concentration, the distribution across the wood was investigated. The concentration of iron across the wood lattice was determined by growth rings analysis, a section taken from the wooden beam. The growth ring analysis was performed by diagonal assessment which provided information on the penetration of elements in the wood and edge assessment which provided information on the distribution pattern of the elements along the surface of the wood. The sample used for the analysis was a support beam from the quenching tower as the other samples were plank shaped and proved too tedious in order to carry out the representative growth ring analysis.

Figure 5.13 shows the diagonal assessment of the growth rings where a single ring was divided into four and then analysed with the help of ICP to detect the element concentration. Samples R1D1 and R1D4 were the edges of the ring which was directly exposed to the quenching process whereas the R1D2 and R1D3 were the central parts of the growth ring. R1D2 and R1D3 were the parts of core of the wood sample and therefore, not exposed directly to initial CCA preservative treatment or quenching process throughout the service life. The element concentration obtained from diagonal assessment provided that there was no consistent data on the CCA concentration when only one growth ring was analysed. The maximum concentration was detected for R1D1 where arsenic, chromium and copper were 4 mg/kg, 124 mg/kg and 25 mg/kg respectively. Assessment showed R1D1 and R1D4 had high iron concentration at about 270 mg/kg for growth ring pieces which were from the edge of the beam compared to central parts with samples R1D2 and R1D3 where the iron concentration was at about 10 mg/kg. Hence the majority of the iron detected in a wood sample was found on the outer most part of the wood rather than the internal structure.

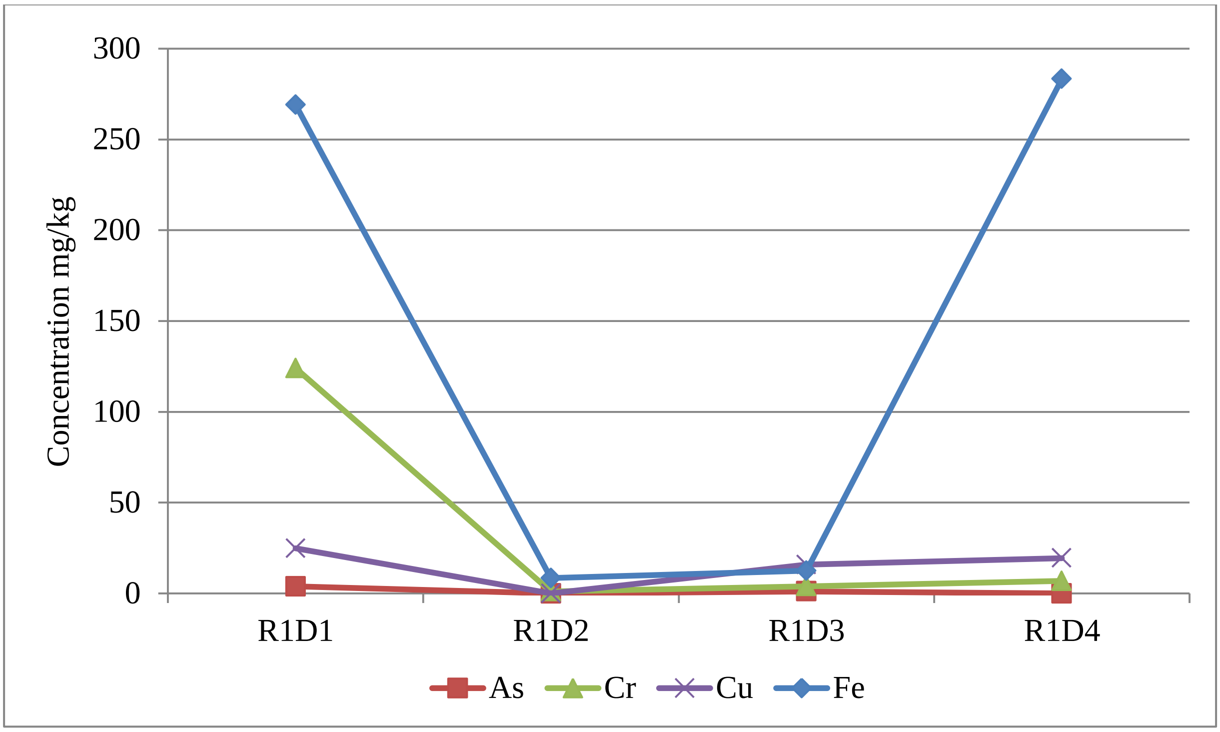


Figure 5.13 Diagonal assessment of growth rings to detect penetration of iron in wood

Figure 5.14 provide the data for the edge assessments of the growth rings of the support beam of the quenching tower. It was observed that the concentration of CCA was variable across the growth rings. The highest concentrations detected were 47 mg/kg, 38 mg/kg and 10 mg/kg for copper, chromium and arsenic respectively at random growth rings. For some of the growth rings no chromium and arsenic were recorded, whereas a minimum copper concentration of 2 mg/kg was noted. On the other hand, a substantial amount of iron was recorded with an average reading at about 485 mg/kg across the growth rings on the edge of the wood. The concentrations of iron obtained for the edges of the growth rings also correspond to the levels detected for the R1D1 and R1D4 from the diagonal assessment. This shows that most of the iron was detected on the edges of the growth ring, which means the surface of the wood contained the maximum level of iron.

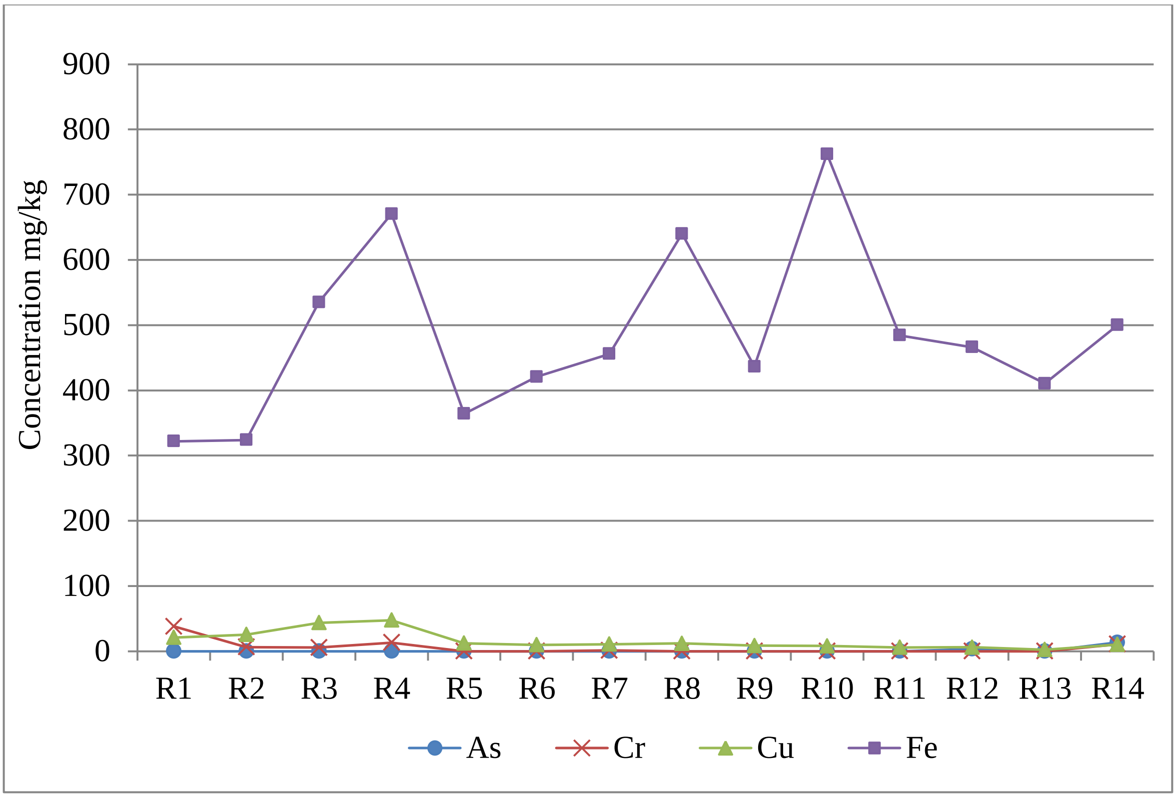


Figure 5.14 Edge assessment of growth rings to detect iron distribution across wood

Over the years, the outer surface of the wood of the quenching tower had accumulated a constant deposition of iron. The iron concentration present at natural levels in wood was detected to be about 30mg/kg. Considering the concentration levels detected in the edge and diagonal assessment, it was clear that the iron was deposited from an external source and was mainly present on the outer surface of the wood. The diagonal assessment showed that most of the iron did not penetrate deeper inside the wood lattice.

5.3.2 Iron source

In an integrated steelworks there are various ways in which wood may have been contaminated with iron. In order to complete the characterisation it was necessary to understand the sources of iron. Determining the source of iron would also provide the information if the iron contamination was limited to wastes arising in a steelworks environment and the processes involved or a general feature exhibited by CCA treated wood irrespective of its use.

5.3.2.1 Coal and coke ash

The analysis of coal and coke ash was provided by the steel company, as testing the amount coke ash generation and its constituents is a routine practice. The data gathered from the company archives is shown in Figure 5.15 which provides the percentage of the coke ash generated from coal used at coke ovens. It is this coke ash which ultimately comes in contact with the wood as it rises with the steam produced during the quenching process. An average of 11.4% of coke ash was generated from the coal injected in the coke ovens over an 11 month period. Figure 5.16 shows the composition of the coke ash during this period. Coke ash analyses were performed at the company labs as the routine monitoring system where the coke ash sampling and testing took place. Coke ash consisted of iron (III) oxide consists of about 8%, 50% of silicon oxide and 30% of aluminium oxide.

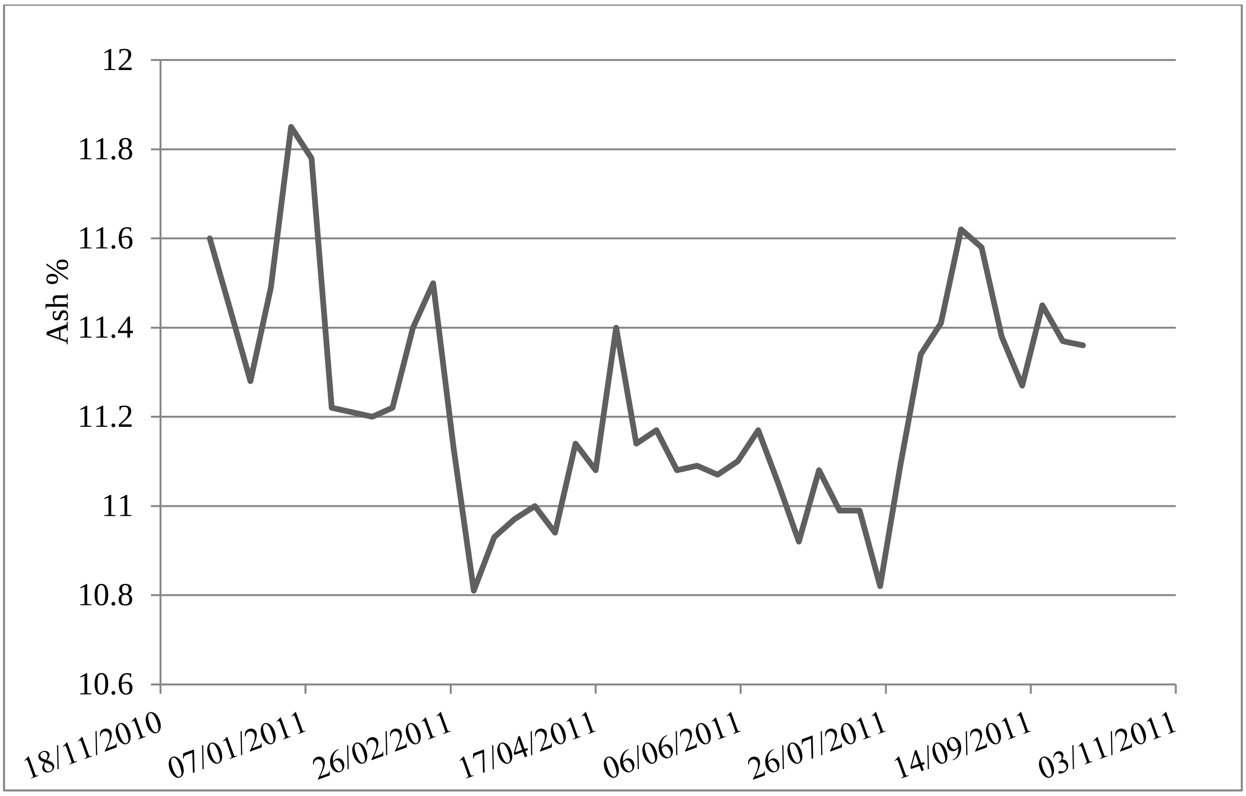


Figure 5.15 Percentage of coke ash generated from the coal processed at coke ovens

A typical coke plant processes 2000-4000 tons of coal per day. Therefore, an average of 3000 tons of coal will produce 342 tons of coke ash at the rate of 11.4 % conversion. According to the coke ash analysis, 342 tons will consist of 27.32 tons of iron (III) oxide (Fe_2O_3) at the rate of 8% content. Hence, the wood was exposed to about 19.09 tons of iron in a day which was present in the coke ash. Similarly, masses of silicon and aluminium present in coke ash in a day were calculated to be at 79.92 and 54.30 tons respectively.

This suggests that if the source of iron contamination was coke ash then the traces of aluminium and silicon should also be evident in the wood samples.

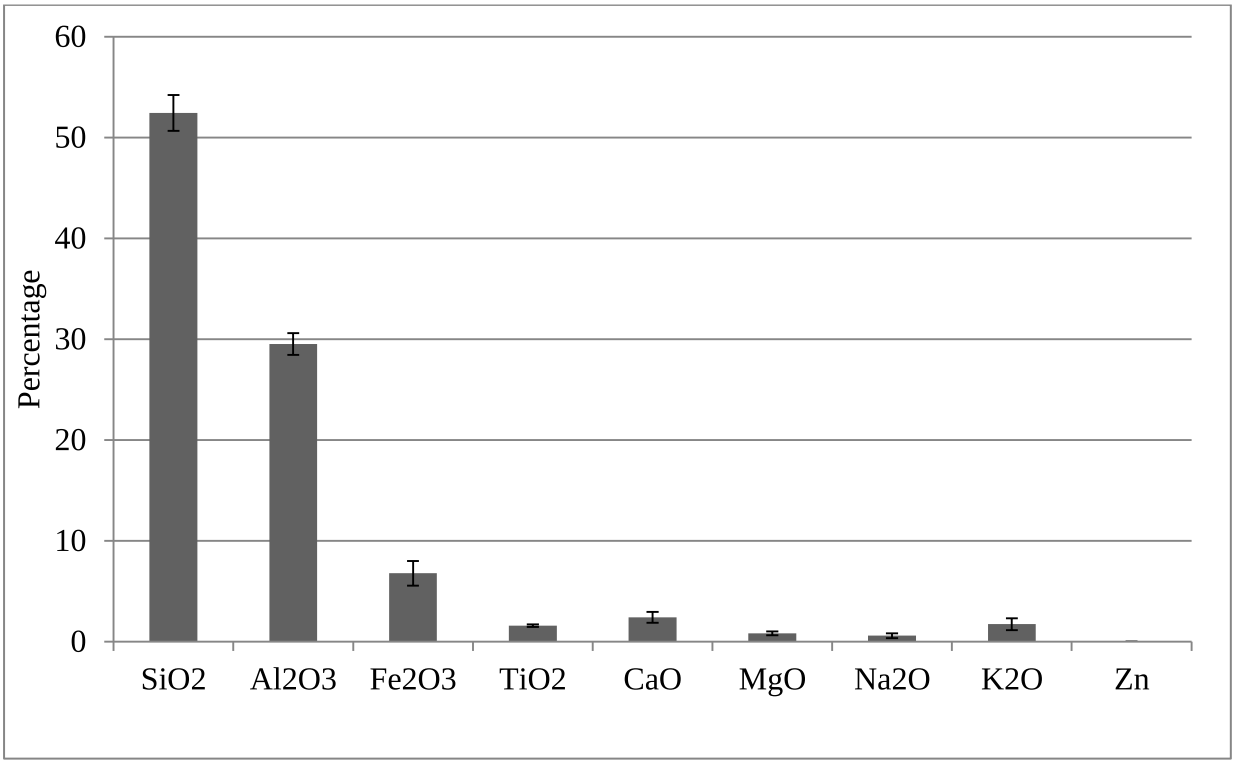


Figure 5.16 Average composition of Coke ash generated over a period of 1 year

5.3.2.2 Kish

Figure 5.17 shows the elemental analysis of the kish sample collected from the steel works. Kish consists of a very high iron concentration at 120.6 g/kg, silicon at 332.5 g/kg and aluminium at 96 g/kg of dry matter. Since kish is an airborne dust, it would be easily exposed to most of the wood surfaces. The concentration of aluminium and silicon were also found to be relatively high in kish. Thus, accumulation of kish on the wood surface may have contributed to the deposition of iron as well as aluminium and silicon.

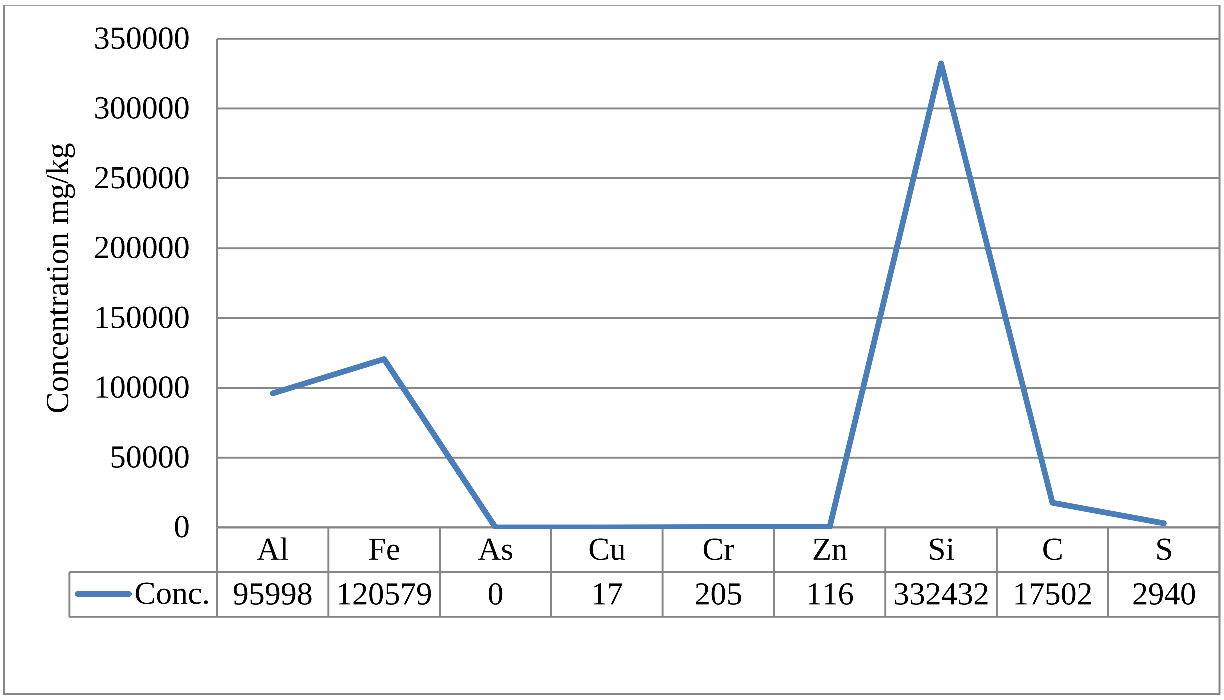
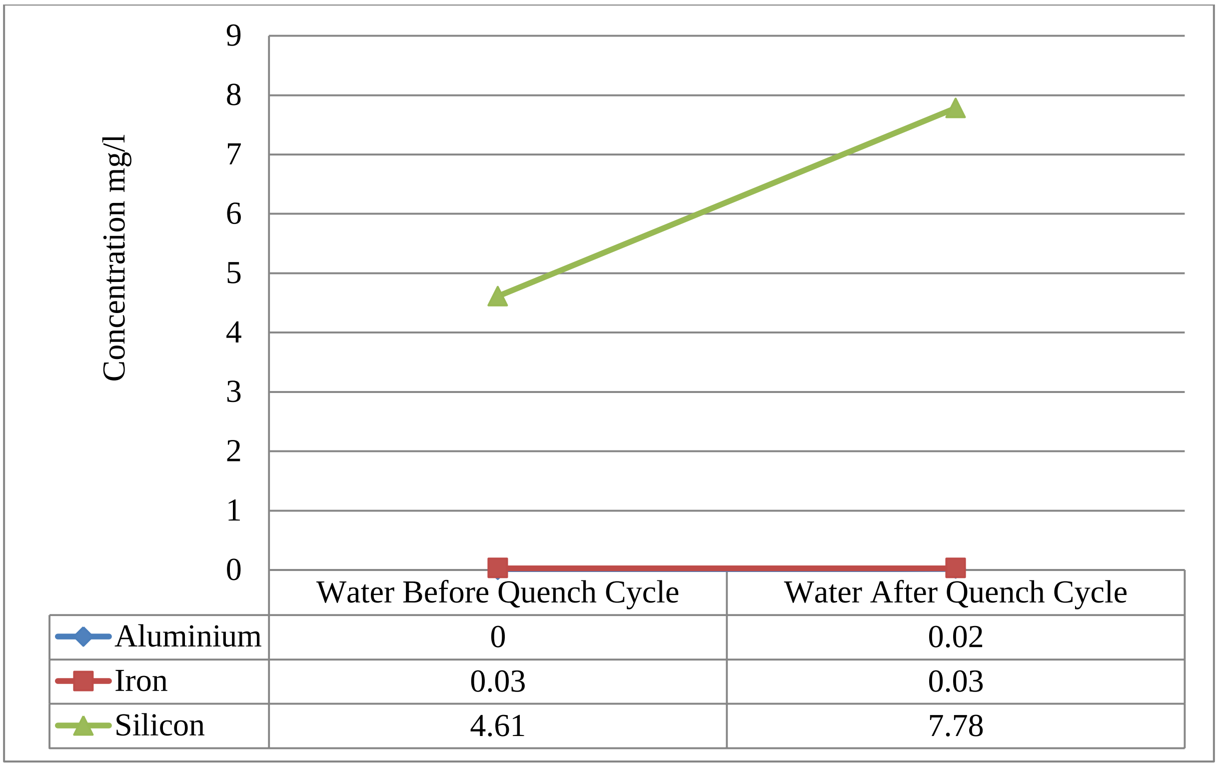


Figure 5.17 Elemental composition of Kish from an integrated steelworks

5.3.2.3 Quenching water

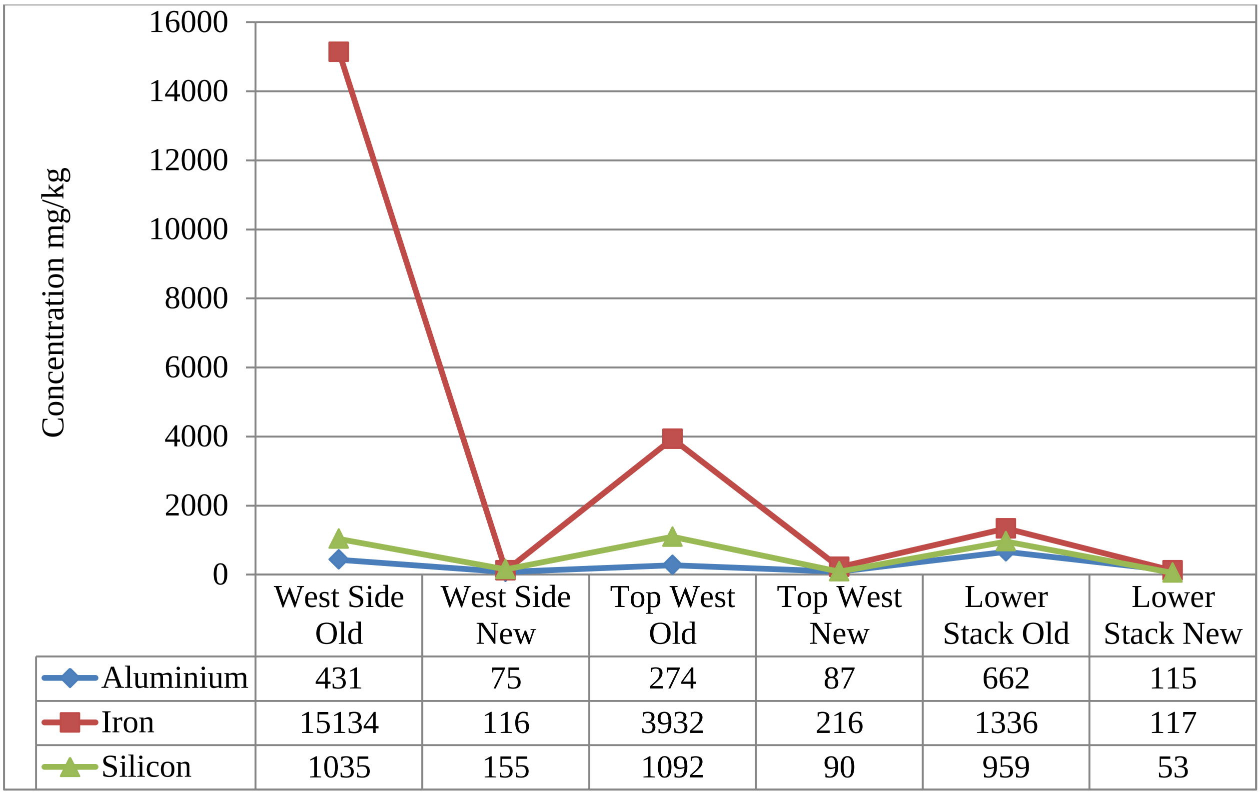
Quenching water sampled from the water treatment plant of the steelworks was analysed for the three elements, namely iron, aluminium and silicon. Figure 5.18 shows the concentration of these elements in the water before and after a quench cycle. There was a considerable amount of silicon detected in the water before a quench cycle and an elevated amount of silicon in the water after a quench cycle, whereas the iron concentration remains unchanged at 0.03 mg/l in water before and after quenching. However, the amount of aluminium recorded was very small at 0.02 mg/l in water after a quench cycle. Quenching water at the coke plant is processed through a closed water treatment system where the lost water in steam gets replenished by a fresh supply. This phenomenon suggests that the water before the quenching process was at the diluted stage as compared with after the process when the same concentration of iron was recorded. However, the lost water as steam meant the lower volume of water volume returned to the water treatment plant. This suggested that the water going in the quenching tower carried a higher levels of iron compared to the return. Therefore, the argument that quenching water is also a potential source of iron can be true, but the iron deposited by quenching water was probably at a much slower rate compared to the other sources discussed before.



	Water Before Quench Cycle	Water After Quench Cycle
◆ Aluminium	0	0.02
■ Iron	0.03	0.03
▲ Silicon	4.61	7.78

Figure 5.18 Aluminium, iron and silicon concentration in the quenching water used in the production of coke

While analysing for the possible sources of iron, it was found that there could also be the presence of aluminium and silicon in the wood samples. Figure 5.19 shows the concentration of elements in refurbished wood samples compared to old wood samples, where samples associated with high iron also contained elevated amounts of silicon and aluminium. The pattern of aluminium and silicon was similar to iron such that concentrations were higher in old wood compared to the newer refurbished parts.



	West Side Old	West Side New	Top West Old	Top West New	Lower Stack Old	Lower Stack New
Aluminium	431	75	274	87	662	115
Iron	15134	116	3932	216	1336	117
Silicon	1035	155	1092	90	959	53

Figure 5.19 Aluminium, Iron and silicon concentration in the old and new wood from different parts of the quenching tower

From the growth ring analysis it was confirmed that elements were deposited mainly on the surface of wood. The most likely sources of aluminium, iron and silicon were found in the kish and coke ash which slowly deposited on the wood of the tower over the period of 33 years. The quenching water played a vital role by washing out the elements during the every quench cycle. As shown in the Figure 5.18 that quenching water was taking away silicon at a steady rate of 7.78 mg for every litre of quenching water used in a cycle and aluminium at a much slower rate of 0.02 mg per litre of quench water per cycle. On the other hand, iron did not show any major sign of leaching during the quenching process. Therefore, iron was considered as the most resistant to washing away during the quenching process as compared to aluminium and silicon which were easily washed. Aluminium was washed at a moderate rate but was available in lesser quantities whereas silicon was abundantly available. This phenomenon led to the build-up of high iron concentration but kept the aluminium and silicon on stunted levels over the service period of 33 years of quenching tower.

5.4 Leaching Behaviour

The aim for these series of studies was to determine the leaching characteristics exhibited by the CCA elements in the particular wood waste stream originating from the steelworks. These characteristics established the potential environment concerns, as well as provided the basic knowledge required for the development of the disposal methods for the wood waste. The wood sample used for the leaching tests was 'West Side refurbished' as this sample contained a considerable amount of CCA elements while exposed to the quenching conditions. The CCA concentration obtained by elemental analysis in this dry wood before leaching was 3496 mg/kg, 3845 mg/kg and 1996 mg/kg of arsenic, chromium and copper respectively.

5.4.1 Standard Leaching

The leaching tests were carried out under the experimental conditions of room temperature and atmospheric pressure, solid to liquid ratio (S/L) of 1:10 and with constant stirring as detailed in Chapter 4. Results of standard leaching studies are shown in Figure 5.20, which includes the leaching concentrations for different time durations from 1 hour to 1 month while constantly maintaining all the other conditions. During these tests the pH was recorded to be in the range of 4 – 4.5. Concentrations of the CCA metals in the leachate increased with prolonged exposure of wood to water. Maximum concentrations of arsenic, chromium and copper were 306 mg/kg, 65 mg/kg and 22 mg/kg respectively in the leachate achieved after one week of leaching. It was observed that arsenic was the quickest to leach followed by copper, and chromium was slowest out of the three CCA elements. Thus, the leaching pattern was highlighted as As > Cu > Cr. For the 1 month period the concentration of all three CCA elements reduced compared to the 1 week and stabilised around 70 - 80 mg/kg in the leachate. Thus, equilibrium of metal concentration was established between the water and the wood leaching system for leaching system with duration of a month.

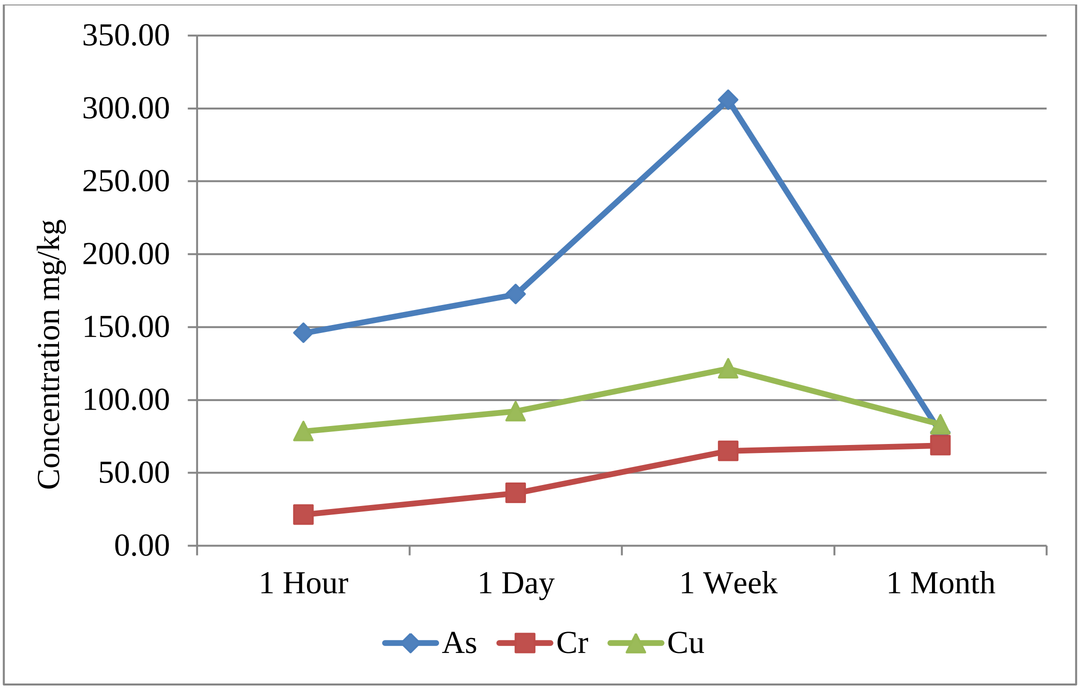


Figure 5.20 Standard leaching of CCA treated wood for different time duration with pH ranging between 4 – 4.5

This was in agreement with number of researchers. According to Jambeck [67] the same relationship was observed in the leaching of CCA elements from new treated wood as well as CCA demolition wood waste. Hingston [18] reported that leaching of individual metals were not proportional to the concentration in original formation. It was also stated that copper and arsenic were lost at a higher degree compared to chromium regardless of being present at lower concentrations. This can be noticed in the original concentration of CCA present in the wood to the leached. The final concentration of CCA elements in the old wood from the quenching tower resembles a similar leaching pattern. This shows that rate of leaching of arsenic and copper is much higher than chromium. Kartal [117] results showed an As > C r > Cu leaching pattern by using distilled water and tap water as leachant and As > Cu > Cr leaching patterns for sea water and humic acid as the leachant. On the other hand Townsend [66] observed Cu > As > Cr and As > Cu > Cr as leaching patterns for two types of leaching test performed. In leaching tests performed on CCA treated wood sawdust at similar pH level between 4 and 4.5, a similar pattern of As > Cu > Cr was detected. This showed that there could be differences due to many different factors such as leaching duration, type of leachate, liquid to solid ratio, pH levels and temperature, which could affect the leaching concentrations. However, overall arsenic seems to be the quickest to leach and the concentration between the copper and chromium depends on various factors even for the wood waste from this industrial application such as the quenching tower of the steelworks.

5.4.2 Continuous Versus Interrupted Process

Two types of sampling procedures for continuous and interrupted leaching were carried out. Sampling in the continuous leaching provided information about the on-going changes in the leaching of CCA elements during a three hour leaching cycle. On the other hand interrupted leaching simulated the repetition of 1 hour leaching cycles for three times to provide data on the changes in the concentration of CCA elements.

From the results of the continuous leaching study shown in Figure 5.21, the first hour has the highest rate of leaching such that arsenic was the quickest to leach at 118 mg/kg followed by copper at 91 mg/kg and then chromium at 24 mg/kg. After two hours of the leaching process, concentrations were stable. After three hours of continuous leaching, arsenic concentration had increased very slowly from 165 mg/kg to 169 mg/kg but the copper concentration showed a small drop from 114 mg/kg to 104 mg/kg in the leachate analysed. This drop in concentration was within the experimental error of 10% which could have arisen while carrying out the leaching test or during the sampling procedure. In the leachate from the continuous leaching process, chromium maintained its concentration around 33-34 mg/kg. The final concentrations in leachate for continuous leaching were in agreement with a standard one day leaching process where arsenic, copper and chromium were 172 mg/kg, 92 mg/kg and 36 mg/kg respectively. The continuous sampling revealed that most of the leaching of elements took place in the first hour, such that the leaching rate was the highest in the first hour and was reduced by 50% by the second hour. This was in agreement with

Jambeck [67] who stated that the cumulative percentage of the elements released increases over time but the concentration varies and eventually decreases with time. This was attributed to the fact that CCA concentrations were nearing to equilibrium and hence reducing the rate of leach with time.

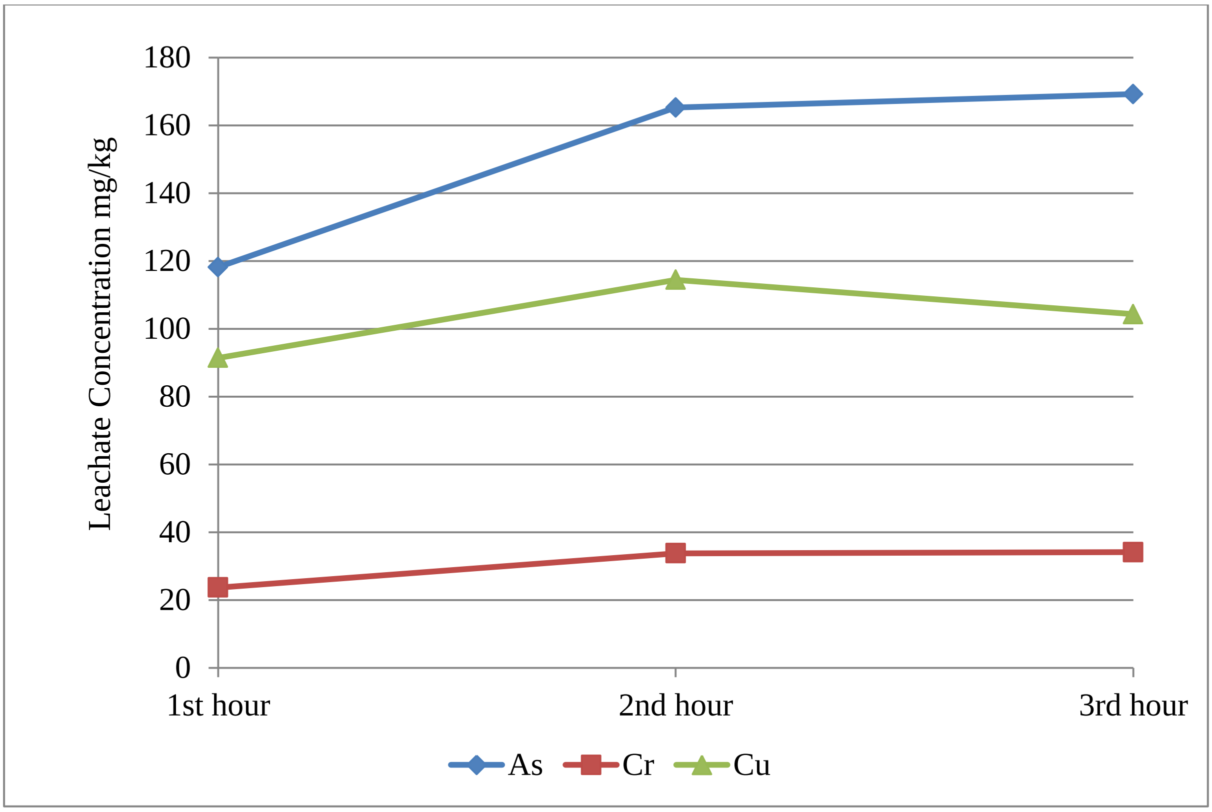


Figure 5.21Leaching concentrations for the continuous leaching for three hours

During the sampling of interrupted leaching every leach cycle had fresh de-ionised water on the same dried sample. Figure 5.22 shows the results for different leach cycles on the sample. A similar leaching pattern was noticed for the interrupted sampling tests, such that arsenic was the quickest to leach with the highest concentration followed by copper. Chromium was the most resistant element to leach. The average concentrations in the leachate were 96 mg/kg, 18 mg/kg and 61 mg/kg for arsenic, chromium and copper per cycle respectively. The interrupted sampling results helped in analysing the leaching behaviour of CCA wood. After the repeated leaching cycles on the same wood sample, the amount of CCA elements leached declined with the number of leach cycles. However, as the old batch of water was replaced with fresh de-ionised water for every cycle, a new equilibrium was required to be established which led to the higher loss of CCA after four leach cycles. This established the leaching pattern which was repeated in every cycle. However, the concentration of the CCA elements was reducing over every leach cycle.

Figure 5.22 also shows the cumulative amount of the CCA elements leached for the four consecutive leaching cycles with fresh water on the same wood sample. The pattern again clearly shows that the arsenic was the quickest to leach but also the total amount of arsenic leached at 385 mg/kg. on the other hand the chromium was the lowest at 69 mg/kg. The cumulative amount also provides the information that the amount of arsenic leached in four cycles (four hours of cumulative leach duration) was more than amount of arsenic leached or one week of leach duration.

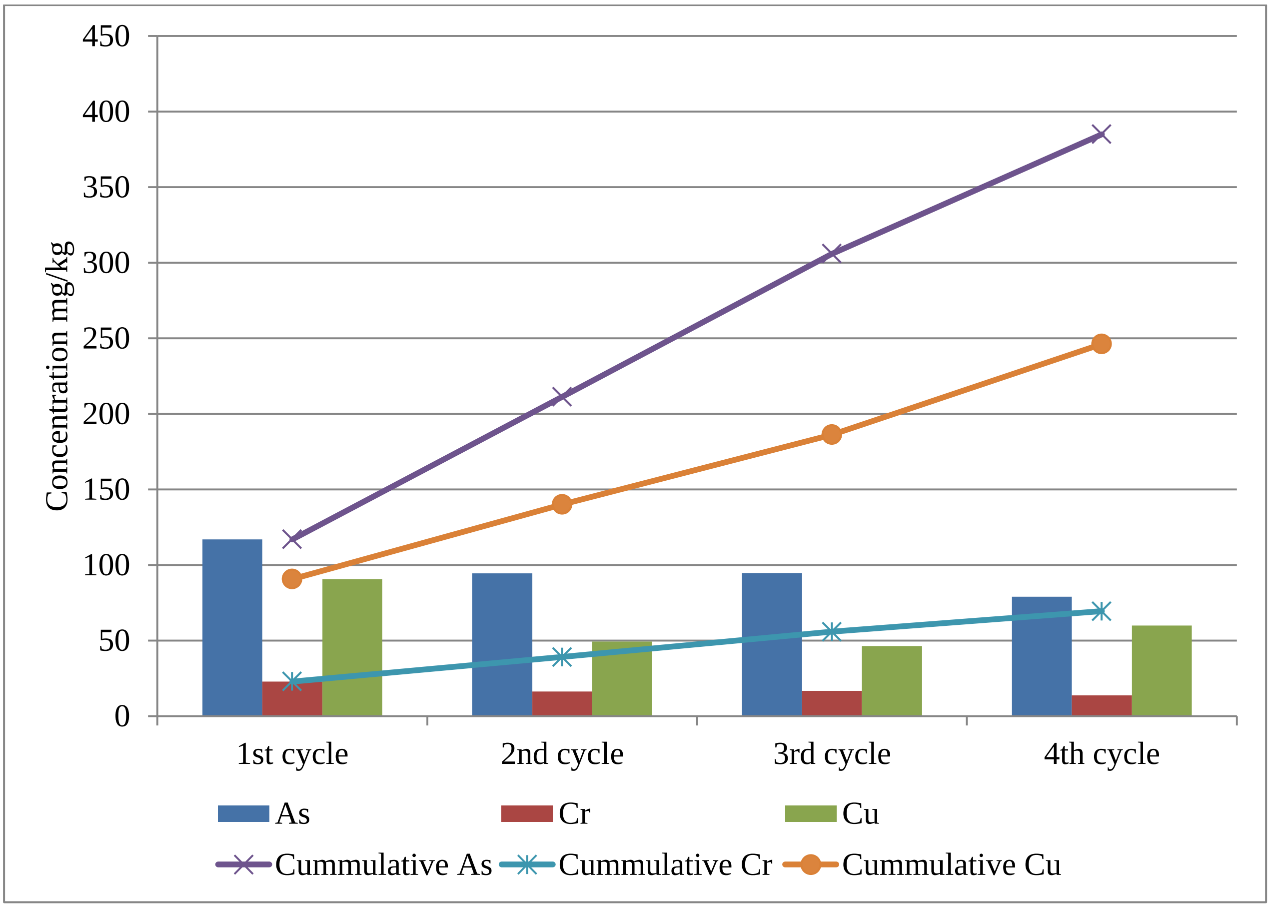


Figure 5.22 Leaching concentrations for the interrupted leaching procedure

The two different types of sampling for the continuous and interrupted leaching showed that there was a higher loss of CCA with short but repeating leach cycles rather than a continuous long leach cycle. The interrupted leaching mimicked the scenario of leaching at the quenching tower, where with every cycle wood was exposed to a fresh batch of water. This led to a higher gradient between the concentration of the elements and favoured a higher leaching process.

5.4.3 Prediction Method for CCA Leaching

After analysing the different leaching results, a pattern was recognised among the leached concentration of the three CCA metals. Therefore, a mathematical model was employed. Pearson's correlation coefficient, *r* was determined. The correlation provided information that a linear relationship can be established among the variables used [118]. This correlation was used to determine if a relationship could be established between the concentration of leaching metals. This was undertaken by using the following relationship:

$$r = \frac{n\sum x_1 y_1 - \sum x_1 \sum y_1}{\sqrt{[n\sum x_1^2 - (\sum x_1)^2]\,[n\sum y_1^2 - (\sum y_1)^2]}} \quad \text{… Equation (5.1)}$$

Where x_1 was the leaching concentration of arsenic and y_1 was the leaching concentration of chromium or copper and *n* was the number of leaching readings. After substituting the respective values in Equation (5.1) the correlation value obtained for arsenic-chromium was 0.998 and for arsenic-copper was 0.988. Hence, this strongly indicated that there was a high likelihood that a linear relationship exists between the amount of chromium and copper leaching to the amount of arsenic. Figure 5.23 and Figure 5.24 show relationships with leaching concentration of arsenic-copper and arsenic-chromium respectively, used to determine the concentration correlation. A line of best fit was plotted on the respective concentration correlation figures. The resulting lines provided a visual estimation of the relation which was deemed to be in agreement with Pearson's correlation coefficient, *r* calculated earlier.

Using the equation of a straight line:

$$y = ax + b \qquad \text{… Equation (5.2)}$$

Where

$$a = \frac{n\sum x_1 y_1 - \sum x_1 \sum y_1}{n\sum x_1^2 - (\sum x_1)^2} \qquad \text{… Equation (5.2a)}$$

And

$$b = \bar{y} - a\bar{x} \qquad \text{… Equation (5.2b)}$$

Such that the linear relationship between the leaching concentration of arsenic and chromium can be determined by substituting the respective values, hence:

[Cr] = 0.214 * [As] – 0.501 … Equation (5.3)

And the relationship between arsenic and copper was

[Cu] = 0.215 * [As] +55.86 … Equation (5.4)

Equation (5.3) and Equation (5.4) provide a mathematical relationship between the arsenic and chromium as well as arsenic and copper respectively. Using these equations, it should be possible to predict the other two CCA elements if the concentration of one of the elements is known, so that if a suspected CCA wood waste is analysed for the toxicity by detecting the arsenic content in the leachate then the concentration of chromium and copper leaching out in the leachant could be estimated. This would help to determine the concentration of all three elements in the wood waste and, thus simplify the testing procedures.

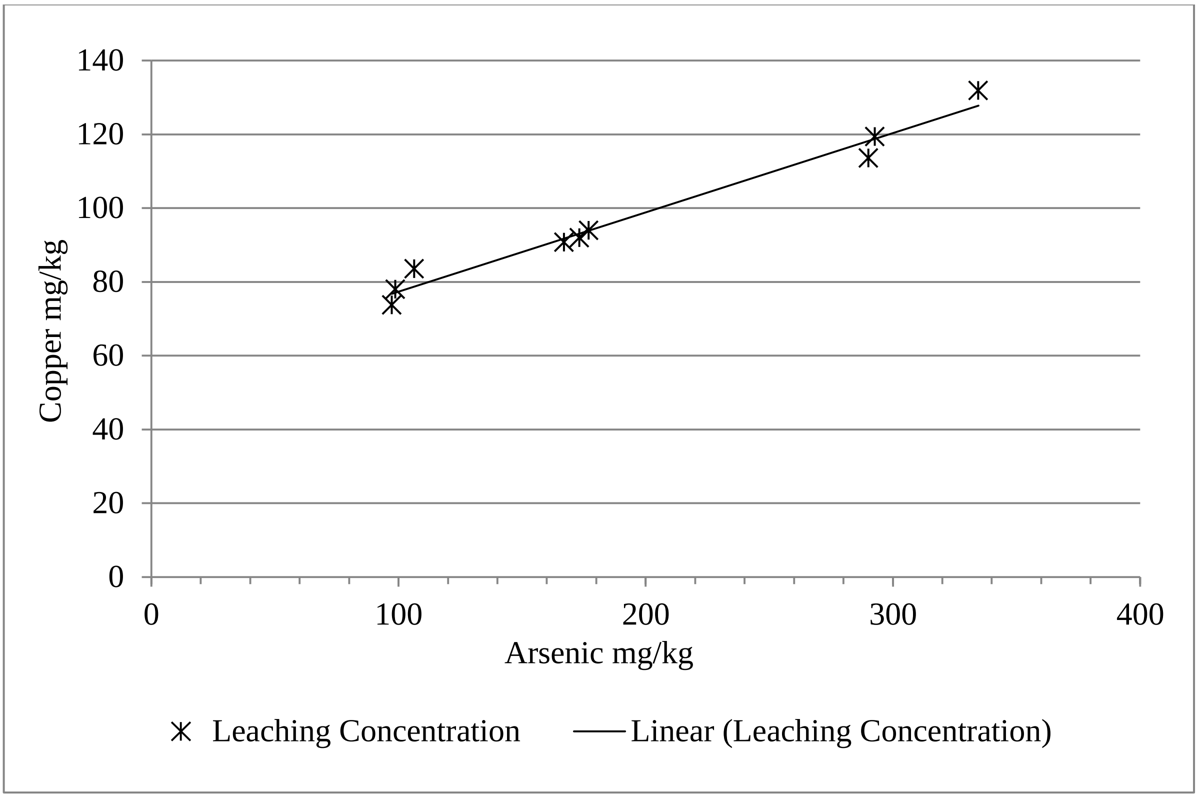


Figure 5.23 Leaching concentrations of chromium relative to corresponding leaching concentration of arsenic for various leaching durations.

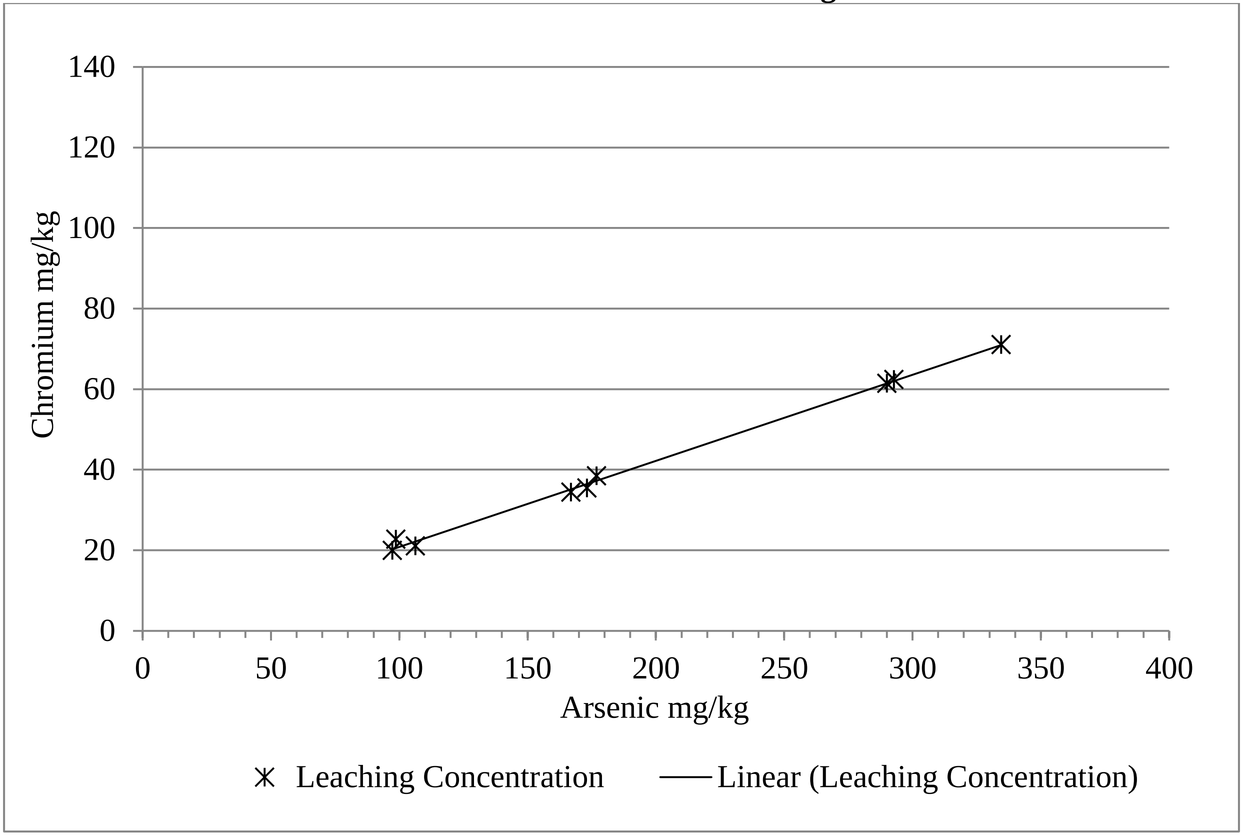


Figure 5.24 Leaching concentrations of chromium relative to corresponding leaching concentration of arsenic for various leaching durations.

These relationships hold true up to concentrations of CCA attained until the saturation point of the leaching system. It was observed that the saturation point was attained after around one week of continuous leaching. For a leaching process with duration longer than one week leaching period may result may have achieved saturated and equilibrium was attained. Then due to this equilibrium, a change in the leaching conditions occurs which disturbs the linear relationship between the leachability of the CCA elements. The conditions for the relation become invalid from that point onwards. Therefore, this prediction model can be used for the determination of the leaching behaviour of the CCA elements for a leaching process with one week of duration or to the saturation point of the solid/liquid ratio whichever is attained first.

As it can be seen in the Figure 5.22 for leaching process with interrupted sampling that mathematical relationship can be used to determine the value of the other two elements if the value of one of the CCA elements is known. This leaching system was only for one hour duration which meant that neither the equilibrium was achieved nor the 1 week duration conditions were attained. Therefore, the concentration of the three CCA elements hold true for the relationship in all four cycles.

5.4.4 Iron leaching

Certain tests were undertaken to gain knowledge about the leaching properties of the iron found in the wood from the quenching tower. The leaching tests were performed on the wood samples from the top section of the tower which consisted of both new and refurbished samples. Analysing the two types of samples would provide a comparison and behaviour exhibited by the iron in the presence of the CCA elements from the treated wood. Following the elemental analysis using ICP, initial concentrations in the old wood were 376 mg/kg of arsenic, 1177 mg/kg of chromium, 338 mg/kg of copper and 3100 mg/kg of iron. On the other hand, initial concentrations in new wood were 10005 mg/kg, 11094 mg/kg, 4790 mg/kg and 615 mg/kg for arsenic, chromium, copper and iron respectively. The leaching tests were carried out under same conditions as before according to the British Standard BS EN 14346 [98]. An additional leaching test was performed at higher temperature to determine any changes in the properties of iron leach ability. Figure 5.25 shows the leached concentrations of the respective elements from the old and new wood at room temperatures and 100°C with pH between 3.5 and 5.

The leachate obtained at room temperature, contained a very low amount of CCA from the old wood when compared to the leach results of new wood. On the other hand, 179 mg/kg of iron leached from the old wood compared to only 9 mg/kg of iron in the leachate from the new wood under similar leaching conditions at room temperature. Leaching performed at 100°C showed an increase in the concentrations of CCA and iron leached. A higher concentration of CCA leached out from the new wood and iron at 152 mg/kg from the same new wood sample. But a substantial amount of iron was detected in the leachate (878 mg/kg) from old wood. There was also an increase in leaching of arsenic and chromium at 50 mg/kg and 83 mg/kg respectively from the old wood sample at 100°C. However, a reduction in the concentration of copper was recorded at a mere 2 mg/kg.

It was noted that there was no particular leaching order for the three CCA elements. For the old wood at room temperature arsenic was most resistant, whereas in new wood at 100°C arsenic was most susceptible to leaching. Copper was most susceptible to leaching in both new and old wood at room temperature, but it was most resistant in old wood and moderate in new wood for leaching at 100°C. Chromium was the most resistant to leaching for new wood at both leaching temperatures, whereas for old wood chromium moderately leached out at room temperature but was most susceptible to leaching at 100°C.

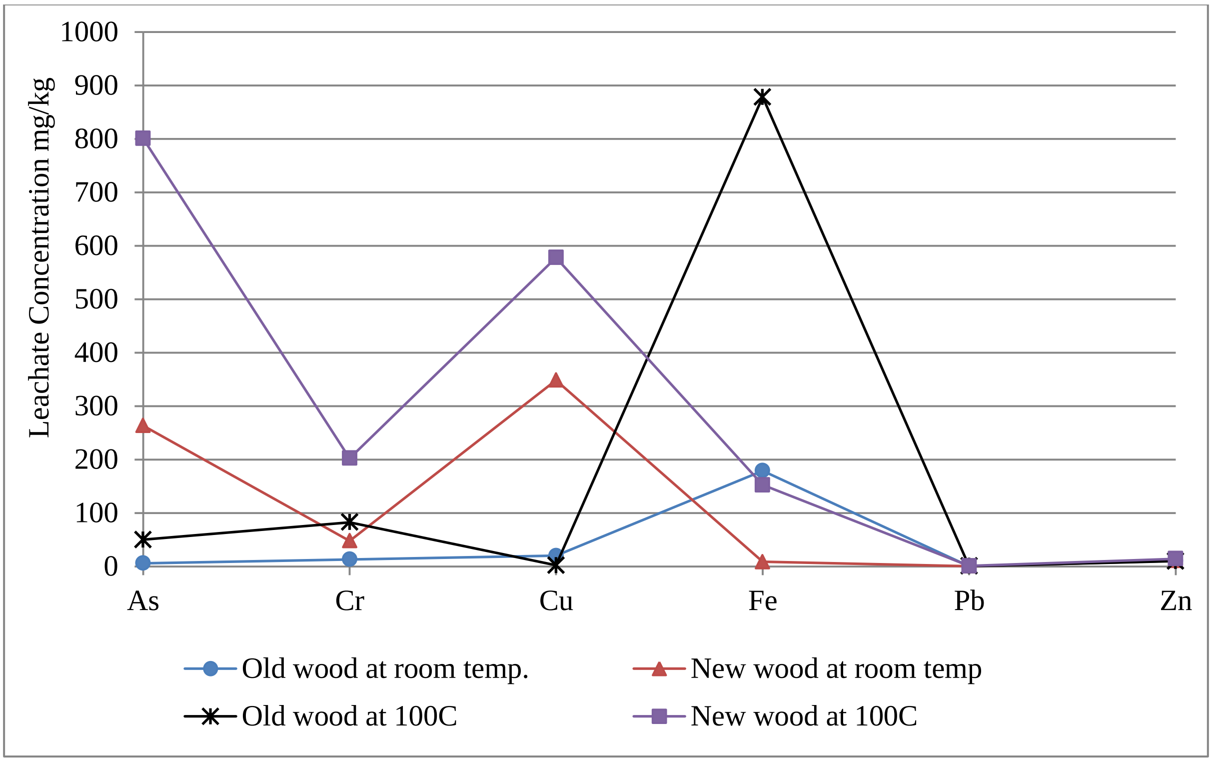


Figure 5.25 Leaching concentration of elements from the old and new wood waste at different temperature

There are number of factors which contributed towards the leaching pattern obtained. The initial concentration of CCA available for leaching in old wood was too low and the iron was too high, and vice versa in the new wood. Over 33 years of service, the rigorous quenching process had leached out most of the CCA from wood in the quenching tower, whereas iron was deposited on the surface of the wood from various recognised sources earlier in this chapter. The presence of this iron also played a vital role in the leaching process. Moghaddam [77] stated that the solubility of components increases with increase in temperature.

A number of studies have concluded that iron oxides reduce the mobility of CCA elements in soil by stabilising the arsenic, chromium and copper. Lidelöw [119] concluded in field trials that the concentration of CCA elements in the leachates and soil pore water was reduced by stabilisation using iron rich industrial by products. Iron oxides at low pH have a reverse effect on the leaching of cationic elements and thus help in the retention of arsenic and chromium

[116]. Copper concentration at 100^{o}C leaching was exceptionally low; this remains unexplained as the stability achieved by the iron for copper has so far provided mixed results [120]. It is supposed that this may be attributed to the lower initial concentration of CCA present in the old wood, especially copper.

Due to the hazardous nature of the wood waste generated from the quenching tower material, landfill was considered as the most common disposal option adhering to environmental regulations. Old wood could be mixed with the new wood waste at the time of disposal. The high concentration of iron deposit in the old wood could be deemed as a source of iron. Iron leached from the old wood would help in the stabilisation of the CCA elements leached from the new wood and could restrict the mobility of the elements in the soil. However, it would be difficult to make long term stability predictions, firstly because the proportion of the iron and CCA elements may not be sufficient to establish a permanent solution, and secondly the scale of studies performed on stabilisation and amendments were short term laboratory experiments.

Summary

A basic characterisation of the CCA treated wood waste was completed. The elemental analysis of old and refurbished, the two different types of wood samples from various parts of the tower, was performed. A general trend in the CCA concentration was that this reduced with the increase in the service life of the wood. The concentration also varied according to the location of the wood in the tower. Loss of CCA elements was the least at the top section due to the low water contact, whereas the lower triangle section faced a heavy loss of CCA elements due to the heavy wash out after every quench cycle. Overall reduced amount of CCA was expected due to the on-going in service leaching.

XRD and SEM tests were performed to further understand the properties of CCA across the wood lattice. XRD results were compared to the untreated wood and it was concluded that there was no change in the results obtained. This showed the absence of the crystalline structures due to the presence of CCA elements. The SEM results provided microscopic images of the wood. The images were compared with the images of untreated unused wood where the absence of heavy metals was clearly visible. The images were also used for an EDX scan to provide an elemental composition of the wood surface. The point scans were used to indicate the localised surface composition, whereas the line scan provided information on the distribution of the elements from edge towards the centre of the wood specimen.

The presence of iron was detected during the elemental analysis and a trend was identified regarding the iron contamination. Iron concentration increased with the increase in the service life of the wood from the quenching tower. The distribution of the iron was determined by analysing the wood growth rings. The diagonal and edge assessment of the growth rings showed that iron was mainly deposited on the surface of the wood. The sources of the iron were investigated by identifying and analysing the various components of a typical integrated steelworks. Kish, airborne particles, coal and coke ash, and quenching water before and after the cycles were tested.

The leaching behaviour of the CCA wood was studied. The standard leaching tests were performed for different leach durations. The results showed that equilibrium of leaching of the CCA elements was attained after a 1 week leaching period. A comparison between the interrupted and continuous leaching tests was also performed. This provided an additional understanding of the leaching behaviour. The leaching data were used in a mathematical model, which established a linear relationship between the arsenic and copper leach concentration as well as between arsenic and chromium leach concentration. This linearity was used to developed mathematical equations to predict the leaching concentration if the leaching concentration of any one of the three elements is known.

Leaching tests on the old and refurbished samples was also performed. These results regarding the leach ability of the iron were determined as iron has a potential to restrict the mobility of the CCA elements in soil. Hence, this property could be harnessed and employed for the disposal of the CCA treated wood waste.

Chapter 6. Waste Management of the CCA Treated Wood Waste

6.1 Introduction

The chemical extraction process of CCA elements from treated wood is described in this chapter. The technique for extraction was investigated and designed by performing sequential leaching analyses using various chemical reagents specific to their characteristic and reactions towards wood or complexes of CCA elements present in the wood structure. A three-step extraction process, 1 M sodium hydroxide (NaOH), 2 M ammonium chloride (NH_4Cl) and 2 M of hydrogen peroxide (H_2O_2) was developed. At the end of the extraction process, a solution was obtained which consisted of extracted CCA elements dissolved in leachate. These dissolved elements were precipitated with the help of an electrocoagulation process. The parameters of electrocoagulation were investigated to optimise the precipitation of CCA elements. A final electrocoagulation process was designed to provide the most efficient removal rate of CCA elements by precipitation from the solution obtained during three-step extraction.

6.2 Sequential Leaching

The aim of these tests was to evaluate the effectiveness of various chemical reagents to remove specific metals namely copper, chromium and arsenic from CCA treated wood. The tests were carried out by maintaining the conditions of standard leaching experiments while changing the reagent type, concentration and leaching temperature. The changes were made in order to determine the conditions which would provide higher extraction results. The wood samples used for the extraction were dry sawdust, due to the reason that small size distribution provides high surface area accessible by reagents for leaching. Also, in additional leaching tests conducted by Townsend [66] on four different sample sizes found that leachable metal concentrations inversely correlated with the sample size.

The ICP analysis technique was utilised to provide the initial concentrations of CCA in the wood sample prior to sequential analysis which was calculated to be 3468 mg/kg, 6804 mg/kg and 1996 mg/kg of arsenic, chromium and copper.

Sequential leaching started with the basic leaching procedure of testing the leachability of metals from wood with water at different temperatures for test duration of one hour. This provided the basic leachability trend of the three CCA elements from the material in question with respect to the leaching reagents employed under varying temperatures while maintaining general leaching conditions such as sample preparation, duration of test, solid to liquid ratio and filtration technique as detailed in Section 4.6 of Chapter 4.

6.2.1 Water Leaching

Leaching with de-ionised water provided the baseline leaching behaviour of the CCA and built on the knowledge and data acquired on leaching behaviour in Section 5.4 of Chapter 5. The leaching with water also provided the information regarding the pH conditions that would normally exist in the CCA treated wood solution. The change in pH and its effect of pH on leaching when temperature was increased was also observed. For the water leaching tests, the leachants used were de-ionised and saline water prepared with sodium chloride (NaCl) at different molar concentrations.

- ***Deionised water***

Figure 6.1 shows the results obtained during the water leaching of CCA treated sawdust sample at different temperatures. At room temperature, the leaching pattern was Cu > As > Cr such that chromium was most resistant to leach. As stated in the Section 5.4 of Chapter 5 arsenic was deemed as the most prone to leach, which was not the case in results shown in

Figure 6.1. The concentration of arsenic and copper in leachate obtained at room temperature leaching was 30 mg/kg and 62 mg/kg respectively, whereas chromium leached at 20 mg/kg as compared to results of standard leaching where arsenic, copper and chromium leached at 146 mg/kg, 78 mg/kg and 21 mg/kg respectively. The low concentration of arsenic leached in this test could be attributed to a high concentration of chromium initially present in the treated wood. As per the literature, during fixation arsenic reacts with chromium to form $CrAsO_4$ which forms lignin complexes in wood or inorganic precipitates on cellulose [33]. Therefore, an abundance of chromium could potentially be responsible to fix most of the arsenic in lignin and cellulose and thus this contributed towards increased resistance of arsenic against leaching.

The leaching pattern obtained for tests carried out at 100^{o}C was changed to As > Cu > Cr. The final leaching concentration of arsenic, chromium and copper at 100^{o}C were recorded as 164 mg/kg, 87 mg/kg and 137 mg/kg respectively in the leachate analysed. The increase in temperature led to the increase in concentration of CCA elements leached from the wood as high temperatures speed up metal solubilisation from wood and increase the extraction yield [78]. Leached concentration of all three elements was seen rising where arsenic release increased exponentially. The increase in leached chromium concentration may have aided the leaching of arsenic, arsenic being the least resistant to the leaching with the change in temperature. This was in agreement with research by Moghaddam [77]

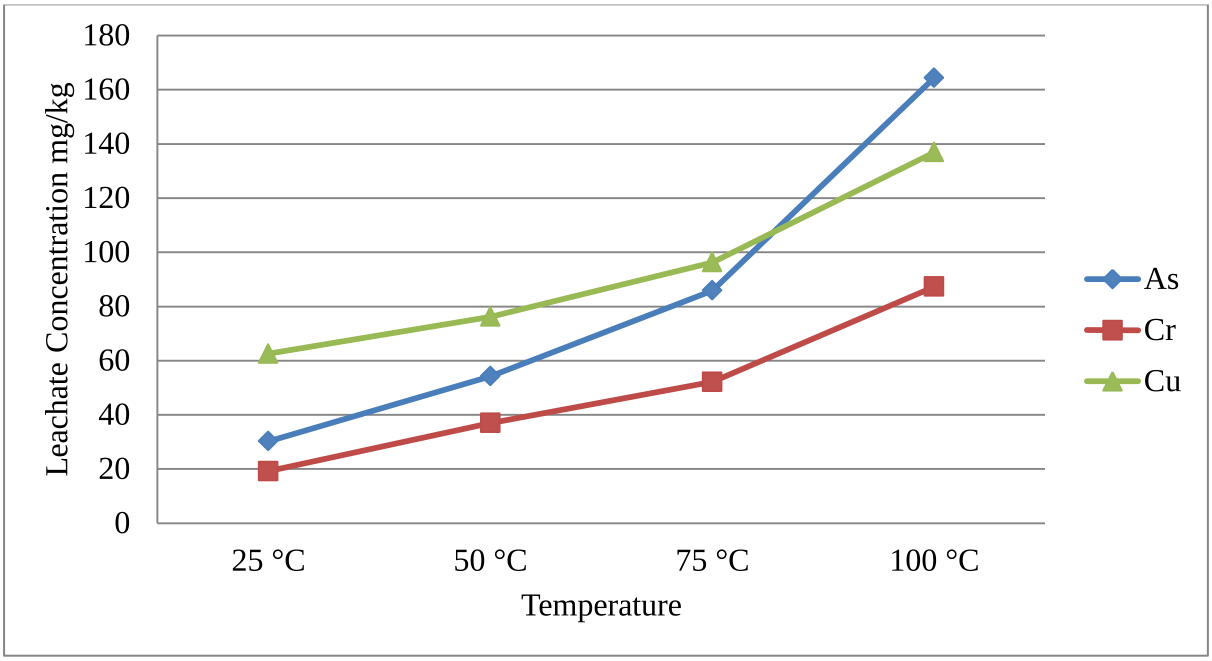


Figure 6.1 Leaching of CCA elements with de-ionised water at different temperatures

- ***Saline Water***

The saline water with different concentration was prepared by adding sodium chloride (NaCl) to de-ionised water. Figure 6.2 shows the results of CCA concentrations obtained from leaching at room temperature and 100^{o}C by using 1 M NaCl solution as leachate. Copper leached slightly more than arsenic whereas the chromium was very resistant to leach under saline conditions. At room temperature the concentration of chromium was 16 mg/kg, whereas under the same conditions arsenic and copper concentrations in the leachate were 86 mg/kg and 163 mg/kg respectively. For 100^{o}C leaching, arsenic and copper concentration increased to 828 mg/kg and 896 mg/kg respectively, compared to relatively low chromium concentration with 164 mg/kg of the leachate analysed.

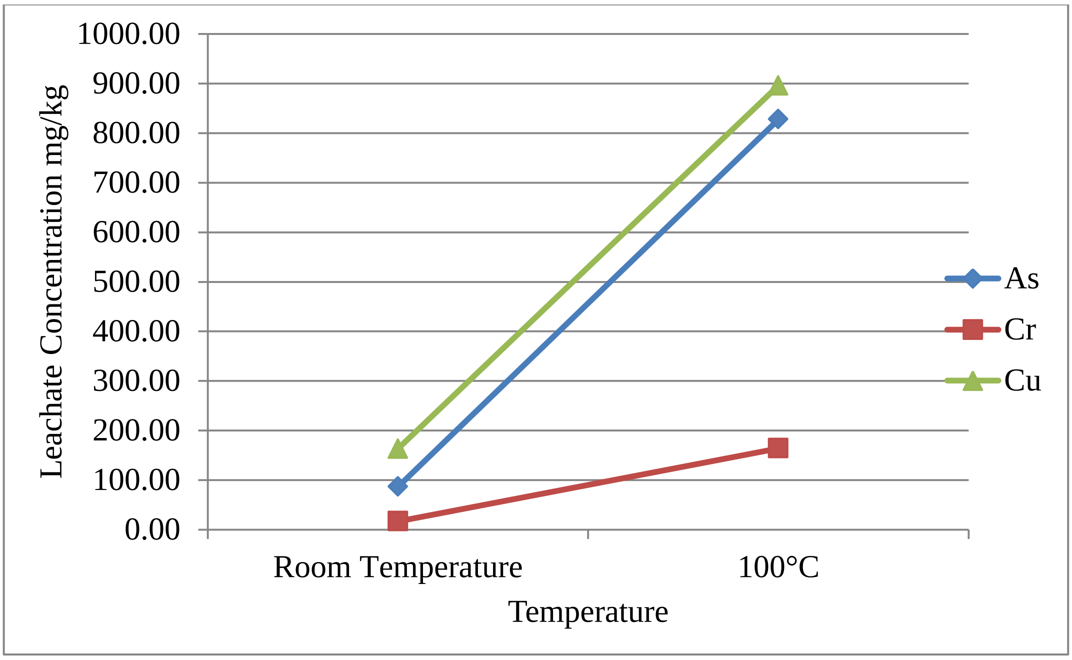


Figure 6.2 Leaching of CCA elements with saline water (1M NaCl) at different temperatures

The leaching tests on the CCA treated wood were repeated with a higher concentration of NaCl at 5 M. Figure 6.3 shows the results obtained for leaching by using 5 M NaCl at room temperature and 100°C. The leaching test performed at the room temperature with highly saline water provided CCA concentrations in leachate at 31 mg/kg for arsenic whereas, chromium and copper were below 10 mg/kg. But with the increase in the temperature to 100°C the concentrations in leachate changed dramatically, with copper at 1607 mg/kg and arsenic 667 mg/kg, whereas chromium was only at 113 mg/kg.

From the analysis of leaching solutions, Lebow [121] concluded that seawater had mixed results on leaching of the CCA elements, such that the steady-state release of copper was much greater in seawater than de-ionised water, which was in agreement with the experiments performed in this study. Copper was the most easily leachable element out of the three with the concentrations analysed at much higher levels compared to the de-ionised water leaching results [121]. In a review, Hingston [18] stated that, at low salinities, NaCl has a coagulating effect on the crystallite Cu fixation complexes increasing surface area and decreasing solubility, whereas at higher salinities the formation of complexes between chloride and copper may occur which would explain the higher copper removal rate. This mechanism is enhanced at a higher temperature by releasing more ionic chlorides thereby increasing the removal rates especially of copper. This is in agreement with the results such that concentration of copper was highest among the three elements for leaching with saline water at high temperature.

A 10-week leaching trial conducted by Brown [122] obtained a leaching hierarchy of Cu > Cr > As which supports the fact that the copper was the most leachable element. On the other hand, the leachability of arsenic was not found to be in agreement. Such that a study by Kartal [117] revealed a different leaching hierarchy of As > Cu > Cr. The arsenic losses were higher than copper and chromium, this may be due to the initial concentration of the arsenic being higher compared to the concentration of chromium [117]. As the preservative composition was a contributing factor to the fixation reactions of chemicals with wood this could affect the amount of the components released from the treated wood [123].

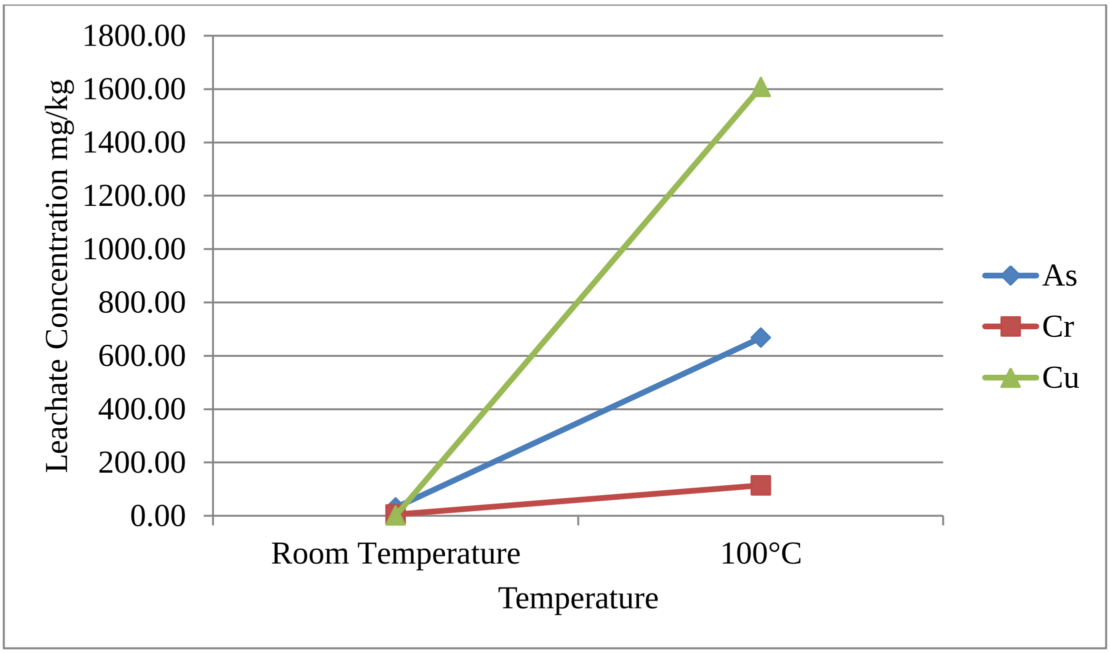


Figure 6.3 Leaching of CCA elements with saline water (5M NaCl) at different temperatures

6.2.2 Sodium Hydroxide Leaching

In an extensive study carried out by Pizzi [33] on the chemistry and kinetic behaviour of the CCA wood preservatives, it was observed that a series of fixation reactions take place between CCA elements and the wood components such as lignin and cellulose. The formation of various complexes such as $CrAsO_4$ with lignin and Cu^{2+} precipitation with lignin and cellulose and other CrO_4^{2-} complexes with lignin are adsorbed or simply precipitated on wood carbohydrates or lignin which are unable to leach [18]. In order to break these bonds, alkaline conditions were employed. It is known that sodium hydroxide (NaOH) solution is used to dissolve lignin and part of hemicelluloses in the pulp and paper industry [124]. When a wood structure is treated with NaOH, it induces a decrease in microfibril crystallinity which causes contraction of the microfibril along the longitudinal axis, ultimately leading to a contraction of the wood along its longitudinal axis [125]. Therefore, NaOH treatment would allow contraction and anisotropic dimensional changes for cells of wood, thereby aiding to weaken the bond between CCA preservatives and wood lattice.

Figure 6.4 shows the results of leaching tests which were performed by using 1 M NaOH solution at room temperature and at 100^{o}C. The analysis of leachant showed that concentration of arsenic leached at 260 mg/kg and 1261 mg/kg from a dry sample at room temperature and 100^{o}C respectively. At room temperature the copper leached slightly more than chromium with respective concentrations of 154 mg/kg and 92 mg/kg. However, the leaching concentration of copper and chromium changed at 100^{o}C with copper at 240mg/kg and chromium at 389 mg/kg for the leachate analysed. Arsenic was the easiest to leach out of the three CCA metals for different temperature under alkaline conditions.

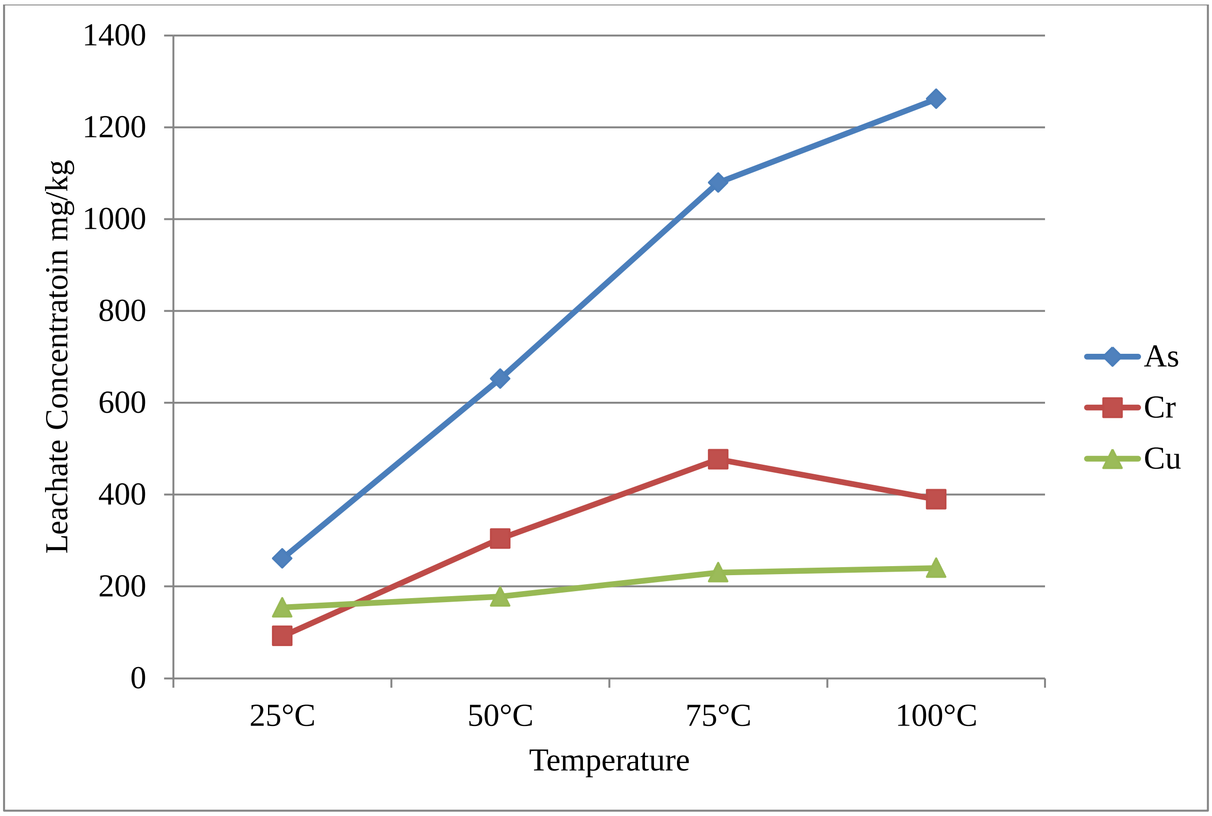


Figure 6.4 Leaching of CCA elements with sodium hydroxide (1M NaOH) solution at different temperatures

The concentration of the NaOH in the alkaline solution was increased to 5 M from 1 M in order to further determine the effect of stronger alkaline conditions on CCA treated wood. Figure 6.5 shows the amount of the CCA elements leached for treated wood by using 5 M NaOH solution as leachant at different temperatures. It was recorded that 122 mg/kg of copper leached at room temperature but dropped to 86 mg/kg for the leaching at 100^{o}C. On the other hand chromium leached at 495 mg/kg at room temperature and increased to 1355 mg/kg for the leaching performed at 100^{o}C. The concentration of arsenic leached was 1804 mg/kg at room temperature and for 100^{o}C was 4786 mg/kg when leachate was analysed. However, due to the exposure to the very high amount of NaOH, excessive lignin depolymerisation took place. These conditions dissolved the aromatic rings of lignin structure as a low molecular compounds[80]. This phenomenon led to a dark, high viscosity leachate. Therefore, the leachate had to be filtered and diluted in order to analyse by ICP. The additional steps required for the analysis of dark leachate induced experimental error which showed a 123% arsenic concentration leached from treated wood for 5M NaOH at 100^{o}C. Similarly, the reduction in concentration of copper in leachate could be attributed to the same. However, these leaching results were deemed to be indicative that a high arsenic release took place under alkaline conditions.

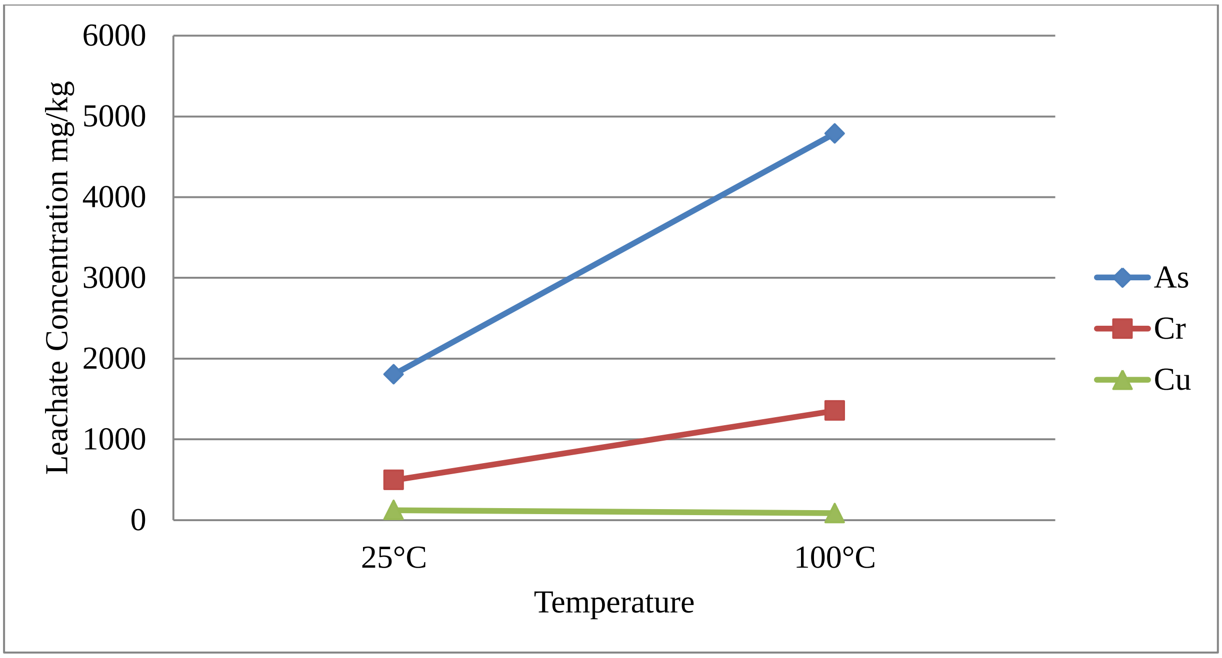


Figure 6.5 Leaching of CCA elements with sodium hydroxide (5M NaOH) solution at different temperatures

6.2.3 Hydrogen Peroxide Leaching

Hydrogen peroxide (H_2O_2) is a strong oxidising agent and an important bleaching agent which is widely used in the production of virgin and secondary recycled wood pulps [126]. The property of H_2O_2 is being selective towards lignin which maximises the delignification of wood fibres. This was used as the basis of the research by López [127] to determine the optimal operational conditions of H_2O_2 in bleaching of wood pulp. The similar principle of bleaching of pulp and delignification caused by H_2O_2 was employed to understand the leaching of CCA from the treated wood.

Figure 6.6 provides the results of leaching tests performed with 1 M H_2O_2 solution at different temperatures. At room temperature the concentration of CCA elements detected in the leachate was low with 131 mg/kg, 167 mg/kg and 49 mg/kg of copper, chromium and arsenic respectively. However, the concentration of the three CCA elements in the leachate increased to 537 mg/kg, 4681 mg/kg and 2766 mg/kg for copper, chromium and arsenic respectively at 100^{o}C. Overall, H_2O_2 provided good extraction results for chromium and arsenic at 1 M concentration.

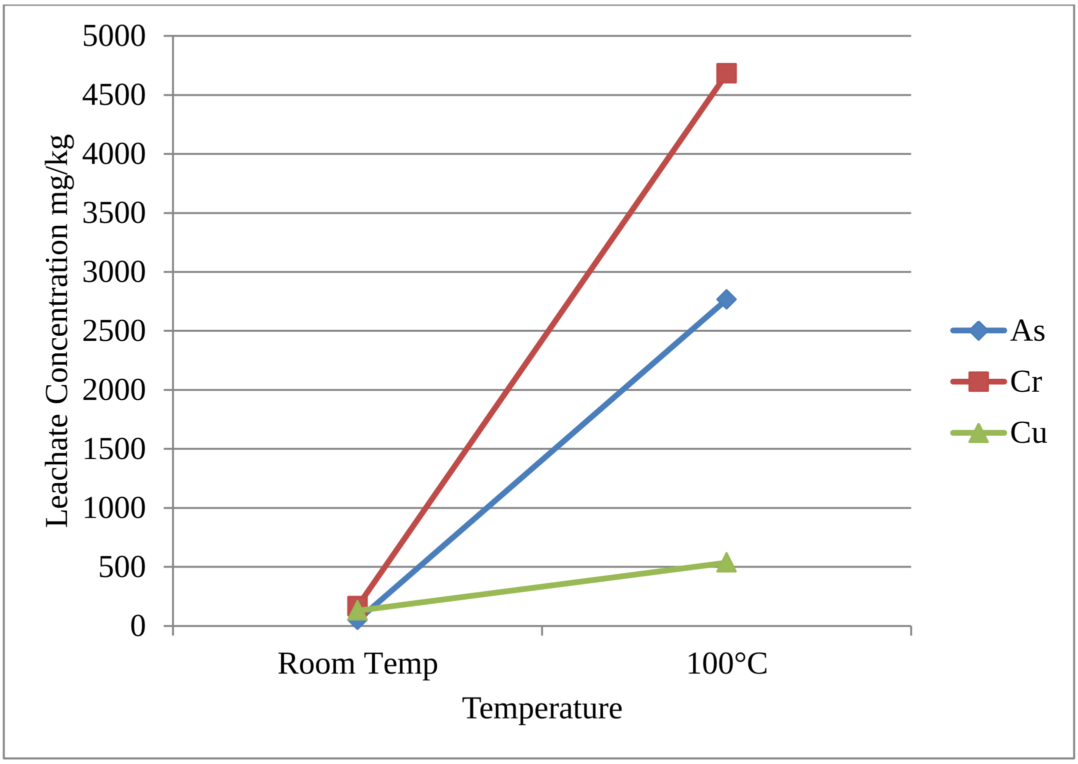


Figure 6.6 Leaching of CCA elements with hydrogen peroxide (1M H_2O_2) solution at different temperatures

The concentration of H_2O_2 was increased from 1 M to 5 M while the other parameters of testing were kept constant. Figure 6.7 shows the results obtained after increasing the concentration of H_2O_2 in the leaching experiments. A similar trend in the extraction levels of the three CCA elements was observed, such that concentration of elements leached from wood was very low at room temperature, but after changing the temperature to 100^{o}C, an increase in the concentrations of all three elements was observed. The concentration of the chromium detected in the leachate was very high at 5797 mg/kg, and significant concentrations of copper and arsenic at 1831 mg/kg and 3125 mg/kg respectively were recorded at 100^{o}C.

In an extraction process carried out by Janin [78] extraction yields for arsenic, chromium and copper were found to be 71.2%, 57.7 % and 82.7% respectively at 25^{o}C for 0.1-10% H_2O_2 concentration. In another study by Kazi [128] average extraction efficiencies for a 6 hour period were 98% for arsenic, 95% for chromium and 94% for copper at 50^{o}C for 10% H_2O_2 concentration. Janin [78] agreed that H_2O_2 has a high metal-extraction ability but further study was abandoned due to the cost associated.

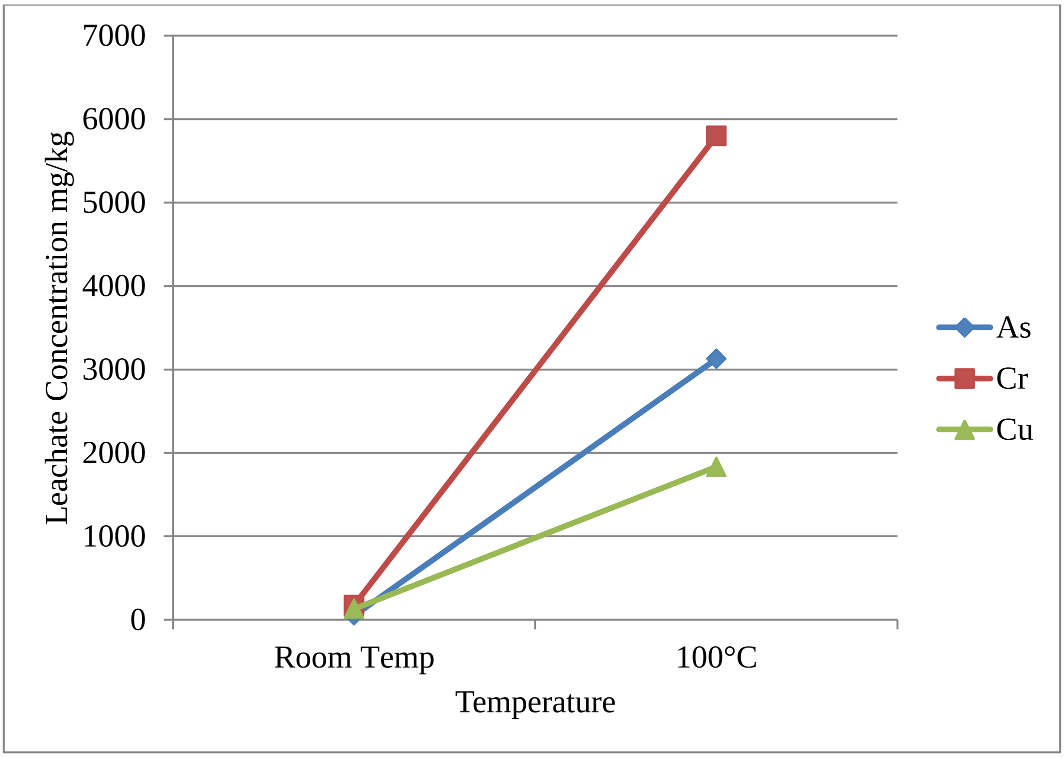


Figure 6.7 Leaching of CCA elements with hydrogen peroxide (5M H_2O_2) solution at different temperatures

6.2.4 Ammonium Hydroxide Leaching

In number of hydrometallurgical routes for the processing of lean grade ores and reserves one of the most preferred methods is the ammonia leaching system. In these systems, desired elements such as nickel, copper, cobalt etc. are extracted into leachates as their complexes which are then processed for their separation and recovery [129]. The addition of ammonium hydroxide (NH_4OH) was used for the leaching primarily to understand the leaching behaviour of copper.

Figure 6.8 shows the leaching results obtained by using 1 M NH_4OH solution on CCA treated wood for one-hour duration at different temperatures. Leaching results at room temperature showed that copper was most prone to leach at 375 mg/kg, whereas arsenic and chromium leached at 7 mg/kg and 23 mg/kg respectively in the leachate analysed. The leaching tests performed at 100^{o}C with 1 M NH_4OH showed an increase in the concentration of copper leached to 705 mg/kg, whereas very small increases in concentrations of arsenic and chromium were detected to be below 10 mg/kg.

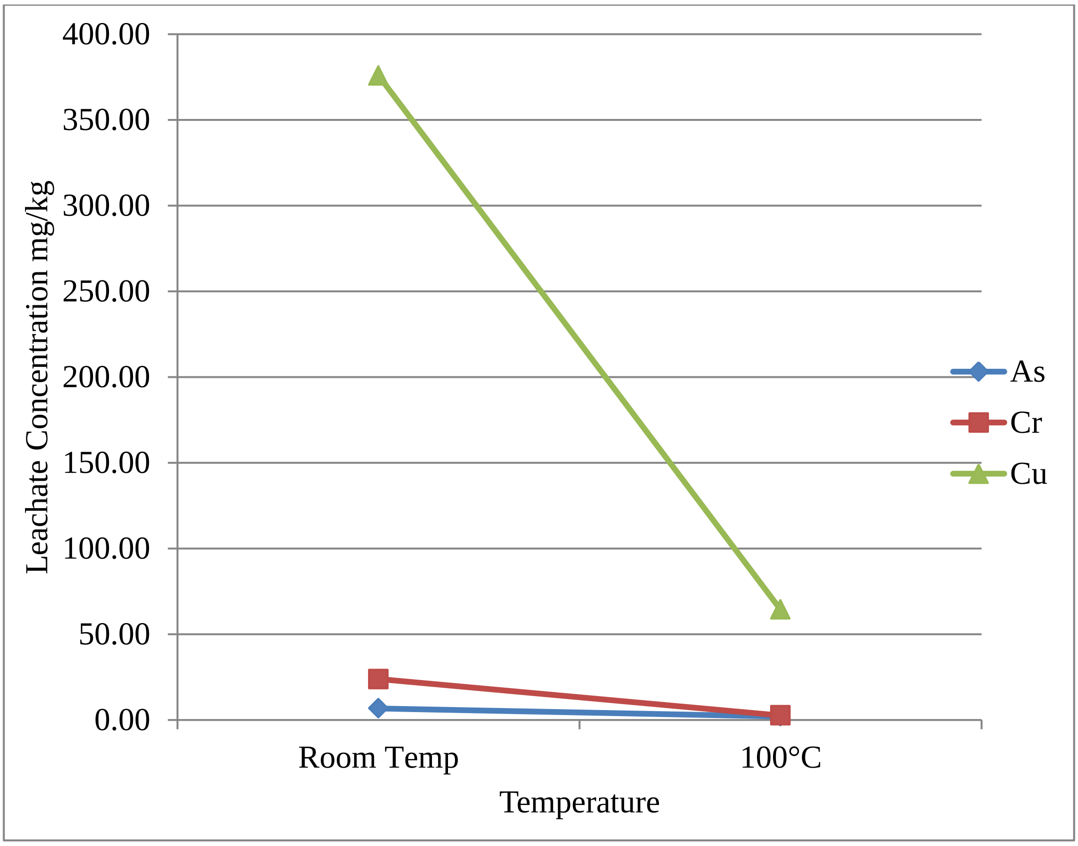


Figure 6.8 Leaching of CCA elements with ammonium hydroxide (1M NH_4OH) solution at different temperatures

The concentration of the NH_4OH was increased further to 5 M in order to test the leaching limits of the reagent. Figure 6.9 shows the results obtained from the one-hour leaching tests performed on CCA treated wood by using 5 M NH_4OH at different temperature. Analysis of the leachate obtained showed that the concentration of arsenic leached was below 10 mg/kg and concentration of chromium was also low at 38 mg/kg on the other hand concentration of copper leached at room temperature was 990 mg/kg. For the leaching tests performed at 100^oC with 5 M NH_4OH concentration total copper leached dropped to 485 mg/kg when compared to the room temperature leaching. Arsenic and chromium concentrations were detected to be below 50 mg/kg for one hour leaching at 100^oC.

After the leachate analysis from NH_4OH leaching, a drop in concentration of copper was recorded from room temperature to 100^oC while vice versa was expected. NH_4OH 29.4% (w/w) solution has a boiling point of 27.2^oC, which meant heating the leaching system at 100^oC, this leads to NH_3 escapes from the system causing a deficiency of leachant as NH_4OH [130]. $NH_3(aq)$ solution which was necessary to dissolve copper by making it water soluble through complexation reactions was lost due to heating [131]. Hence, the loss of the ammonia at high temperature leaching processes was the reason for a reduction in the concentration of CCA leached especially copper.

In a study by Kakitani [80] in a two-step extraction with oxalic and ammonia water achieved arsenic, chromium and copper at 93%, 100% and 74% respectively for 4 hours duration at 15^oC. In the research, oxalic acid was used followed by ammonia water which provided high arsenic and chromium extraction compared to this research, whereas the probable cause of low copper extraction was due to the ineffectiveness of the solvent to remove copper oxalate from the treated wood [80].

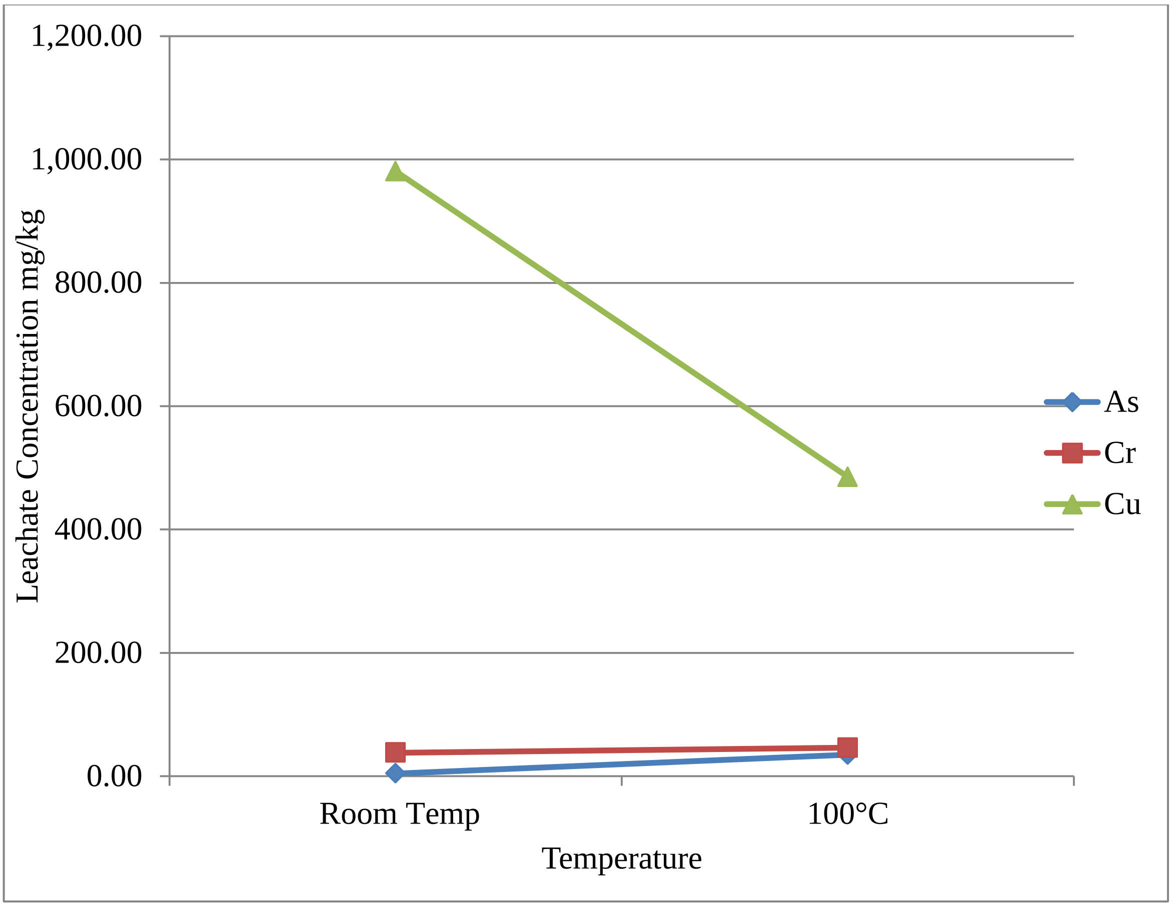


Figure 6.9 Leaching of CCA elements with ammonium hydroxide (5M NH_4OH) solution at different temperatures

6.2.5 Ammonium Chloride Leaching

An aqueous solution of ammonium chloride (NH_4Cl) with 5 % (w/v) has a pH range of 4.6 to 6.0. Ammonium chloride (NH_4Cl) dissociates into an ammonium ion (NH_4^+) and chloride ion (Cl^-) [132]. The acid dissociation constant (pK_a) of ammonium ion is 9.24 and this provided an acid conditions to form stable copper soluble complexes. Therefore, NH_4Cl solution was employed to overcome the loss of the ammonia due to heating seen during ammonium hydroxide leaching.

Results for the leaching experiments with 1 M NH_4Cl solution performed for one-hour duration at room temperatures and 100^oC are shown in Figure 6.10. For the leaching tests at room temperature, the concentration of copper was detected to be the highest of the three CCA elements at 190 mg/kg, followed by arsenic and chromium at 30 mg/kg and 25 mg/kg respectively. On the other hand the leaching tests at 100^{o}C showed a sharp increase in the concentration of leached copper at 1180 mg/kg, whereas minor increases in the concentrations of the arsenic and chromium were recorded at 160 mg/kg and 80 mg/kg respectively.

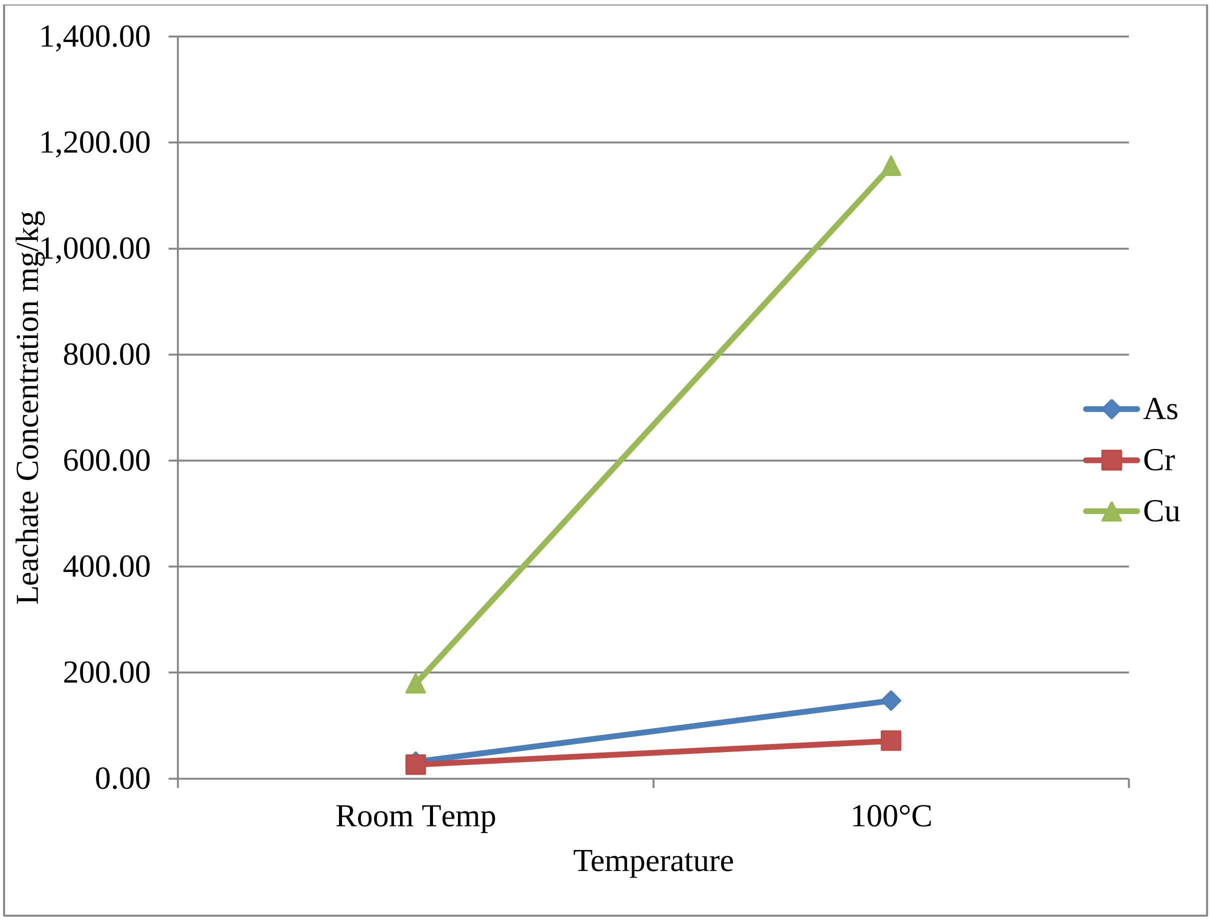


Figure 6.10 Leaching of CCA elements with ammonium chloride (1M NH_4Cl) solution at different temperatures

Figure 6.11 shows results of the leaching tests performed with 5 M NH4Cl solution as leachant with one-hour duration at room temperature and 100^{o}C. The concentration of the copper at 1820 mg/kg was highest at 100^{o}C compared to the 610 mg/kg leached at room temperature with 5 M NH4Cl. Concentrations of arsenic and chromium in leachate obtained were very low at room temperature but increased slightly to 300 mg/kg and 180 mg/kg respectively when leached at 100^{o}C. High copper concentration in the leachate was again attributed to the high affinity of the ammines towards the copper. Also the leaching of copper was enhanced by the presence of the chloride ions, as the similar increase in the copper leaching was recorded for the saline water leaching test.

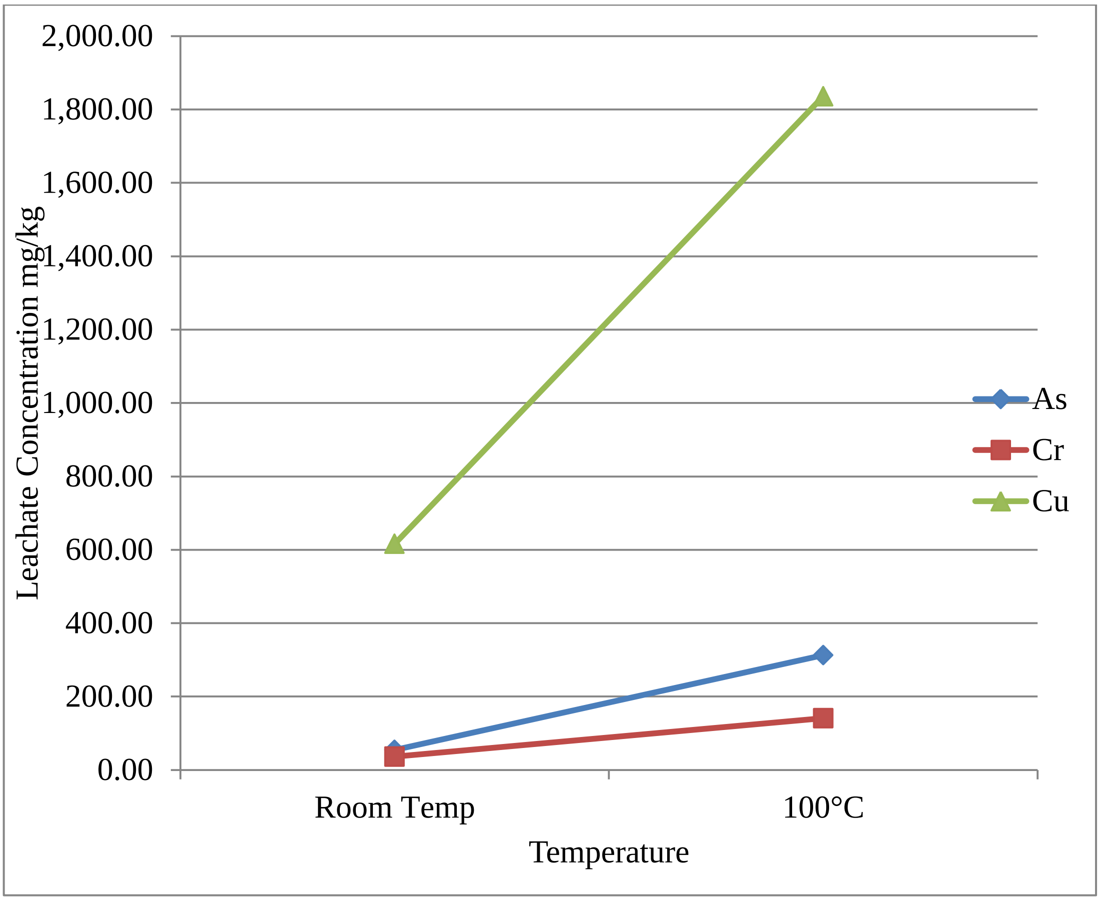


Figure 6.11 Leaching of CCA elements with ammonium chloride (5M NH_4Cl) solution at different temperatures

6.3 Effect of pH

During the whole sequential leaching, pH had greatly influenced the leaching of CCA elements from the treated wood. Different pH levels were recorded and its effects were observed with respective leachant used. For leaching tests with de-ionised water a higher pH around 5.3 – 5.5 was obtained compared to pH 4 – 4.5 from standard leaching. However, with the increase in the temperature from room temperature (25^{o}C) to 100^{o}C the pH changed from 5.3 to 4.6 respectively. According to Dahlgren [30], the fixation process leads to a fluctuation in the pH because of the absorption of chromic acid in the wood. Therefore, the increase in pH may be attributed to higher chromium content. Chromium concentration in the wood sample used for standard leaching was 3845 mg/kg, whereas the concentration of chromium in the sample used for sequential leaching was 6804 mg/kg. For the leaching with saline water, no major change in the pH values was recorded, irrespective of the concentration of NaCl or the temperature at which leaching tests were conducted. The overall pH observed for all saline leaching tests ranged between 3.3 – 3.9.

During NaOH leaching at room temperature with 1 M concentration as well as 5 M concentration the pH recorded was 13.3, but a drop in the pH observed for both concentrations when leaching was performed at 100^{o}C, such that pH values for 1 M and 5 M NaOH were 11.6 and 12.3 respectively. The high pH value played a vital role such that it provided favourable conditions for arsenic to form water soluble compounds with sodium ions present in alkaline medium. Also the alkaline medium liberated arsenic which was mainly attached to the lignin during the lignin depolymerisation.

The pH was recorded at around 4 for concentrations of H_2O_2 at 1 M and 5 M when leaching experiments were conducted at room temperature. However, when the leaching was performed at 100^{o}C for different concentrations of H_2O_2 solution, the pH ranged between 2.5 to 3. The change of pH value from alkaline medium to acidic medium helped in the oxidation of the chromium present in the wood which did not form water soluble complexes during the NaOH leaching. The strong oxidising conditions also formed complexes of copper as well as some arsenic which were readily water soluble.

The pH for the leaching at room temperature was recorded at 10.7 and 11.7 for 1 M and 5 M NH_4OH respectively with no significant change was observed between the start and the end of the experiments. On the other hand pH was about 10.5 and 11.7 for 1 M and 5 M concentration of NH_4OH respectively at the start of leaching which changed to pH 8 after 1 hour of leaching at 100^{o}C. This drop in the pH over the experiment duration was caused by the heating which lead to the release of NH_3 gas.

No significant change was recorded in pH from the before and after of the 1 hour leaching with NH_4Cl. The pH was 4.5 and 3.8 for the leaching with 1 M and 5 M NH_4Cl respectively. In the weak acidic medium and high affinity of copper towards the ammines provided suitable conditions for the copper to form complexes which were water soluble.

In a study by Townsend [66], the impact of pH on leaching of CCA elements was examined from pH 1 to pH 13. It was concluded that leached concentrations of all three elements were highest at low pH (four or less) and high pH (greater than 11). The leaching was lowest at neutral conditions. Copper and chromium were found to exhibit a decreased leachability at the highest pH 12.7. This trend can be identified during the sequential leaching of NaOH performed in this study, when the pH was high (pH greater than 11), there was low concentration of copper and chromium leached whereas arsenic was seen to leach at higher concentrations.

Moghaddam [77] stated that the pH affects the inorganic and organic adsorption of copper which determines the copper mobility whereas the mobility of arsenic is function of its oxidation state with arsenite exhibiting greater mobility than arsenate. Another study performed on the leaching of the CCA elements from the treated wood by Jambeck [67] agreed copper exists as a cation in solution (Cu^{2+}) which tends to form compounds with anions present in the solution. This gives copper low to moderate mobility. On the other hand arsenic is an oxyanion and does not behave like a typical metal. Arsenic leachability correlated with pH and indicated that reducing conditions did not affect its leachability when compared to chromium and copper [67].

6.4 CCA Extraction by Chemical Leaching

Following the sequential leaching, it was identified that different reagents at different concentrations were responsible for the removal of particular elements of the CCA from the treated wood. Sodium hydroxide was deemed as mainly responsible for the breaking of the wood lattice and freeing of CCA elements from the lignin and cellulose complexes. Sodium hydroxide also served the purpose of extraction of arsenic from treated wood. Hydrogen peroxide enhanced breakage of the wood fibres and released CCA elements from treated wood and was mainly responsible for the extraction of chromium. Ammonium hydroxide was accountable for the removal of copper, but it showed a drop in extraction levels due to heating at higher temperature. However, ammonium chloride served the same purpose and showed promising results for copper extraction from the treated wood.

The key reagents were identified for their respective roles in breaking, releasing and extracting the CCA elements from the treated wood. A full extraction process designed for the removal of the CCA elements was employed. In this full extraction process, a sample of wood was subjected to a three-step leaching process with the three recognized reagents namely, sodium hydroxide ($NaOH$), ammonium chloride (NH_4Cl) and hydrogen peroxide (H_2O_2).

6.4.1 Optimisation of Three-Step Extraction Process

To obtain a complete extraction process, it was necessary to define certain parameters. These include the sequence in which a wood sample was required to be exposed to reagents as well as the concentration of reagents to be used for respective leaching steps.

- ***Order Determination*:**

A wood sample was exposed to a three-step extraction process with a one hour leaching cycle per step at 100^{o}C. The recognised reagents were used as leachant at respective extraction steps. The concentration of these chemical solution used was kept constant at 1 M as this was adjusted at a later stage. Firstly, the order of reagents to be used in the three-step extraction process was determined. The priority and extractability of each leachant was required to be examined and understood. Regarding the first-step of the extraction process, NaOH solution was used which initiated the process of breaking down of wood fibres and released CCA elements from lignin and cellulose complexes. However, to determine the next leachant in sequence following NaOH extraction, two tests were performed such that

a) 1 M H_2O_2 used as second-step with 1 M NH_4Cl as third step of extraction,

b) 1 M NH_4Cl used as second-step with 1 M H_2O_2 as third step of extraction.

The wood sample exposed leachant at every step for one hour at 100°C was vacuum filtered and the residue was rinsed with 100 ml of de-ionised water. The rinsed wood sample was oven dried and was exposed to the next leachant of the three step extraction process. After the third step of full extraction process, the oven dried wood residue was analysed for the remaining CCA content. The results so obtained were calculated and compared to the original CCA content of the wood in order to calculate the extraction percentage. The Figure 6.12 shows the results obtained for the two full extraction tests with different leachant sequence.

In the process (a) after the final extraction step of wood with NH_4Cl, the wood residue was dried and analysed for the CCA content by using ICP technique. The results as described in the Figure 6.12 show that 52 % of arsenic, 40 % of chromium and 78 % of copper was removed, whereas analysis performed on the wood residue from the process (b) show that 94 % of arsenic, 64 % of chromium and 77 % of copper was extracted.

H_2O_2 at the third step was observed to be more effective to extract CCA from wood rather to be used at the second step of extraction process. Comparing the processes a) and b), copper extraction levels were not greatly affected by re-ordering the leachant used. The percentage of chromium extracted was increased to more than half of the initial concentration. Arsenic was observed to have the highest change in the extraction percentage of the three elements. The order of the chemicals used as leachant played a vital role in extraction of CCA elements, especially arsenic.

Changes in pH values were also recorded such that for the process (a) starting pH was around 13 with NaOH extraction step, this pH value dropped to 8.6 pre-extraction of H_2O_2 step and post-extraction pH value further fell to 7.5, which was not affected by adding NH_4Cl, so that, the final step of pre-extraction pH was 7 and pH of post-three step extraction was 5.8.

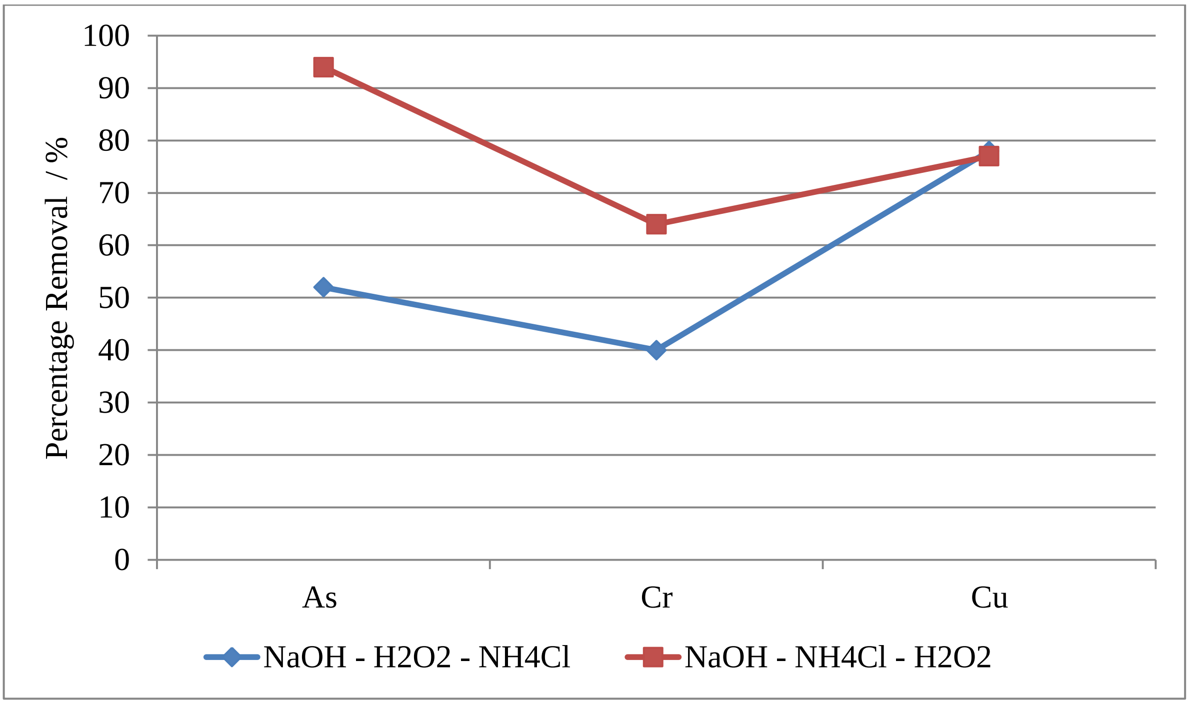


Figure 6.12 Three-step chemical extractions of CCA elements with different leachant sequence for order determination

In process (b) starting pH value was same as process (a) first step around 13. This was due to the same experimental conditions and leachant used as NaOH in this stage. The value of pH dropped to 7.9 at pre-extraction when NH_4Cl was added and post-extraction the value recorded for pH was 6.4. Drop in the pH continued with the addition of the H_2O_2 leading to more oxidising conditions such that the pre-extraction pH was 4.5 and post-extraction pH was 3.3.

It was observed that pH had a great influence on the extraction percentage of the processes. The process (b) provided the reduction conditions at the beginning of the experiment, gradually bringing the oxidising conditions towards the end. In the process (a) H_2O_2 was added at the second step but the oxidising condition of H_2O_2 was neutralised by the reducing action of NaOH which was induced by the first step of NaOH extraction. These weak oxidising conditions nullified the effect of H_2O_2, and hence dropped the extraction percentage. On the other hand in process (b) the gradual reduction in pH or gradual change towards the oxidising conditions from reducing conditions of NaOH exposed the wood to a wider array of pH resulting in better extraction percentages.

Therefore, process (b) was selected as the order determined for three-step extraction process. The reagents to be used as leachant were in sequence of NaOH, NH_4Cl and H_2O_2.

- ***Concentration Determination***

After confirming the order of the leaching reagents to be used, the next step in optimising the extraction process was to determine the concentration of the chemicals. The use of the NaOH at 1 M concentration was deemed as strong enough due the reason that leachate obtained from the experiment was a dark viscous leachate depicting a heavy decomposition of wood. The use of 1 M NaOH provided an average reduction of 1gm in weight of wood sample. Moreover, as stated by Kakitani [80], there are two conditions required for the extraction of the CCA elements which are namely a stronger extractant than the affinity between lignin and chromium as chromium is a bonding agent between CCA elements and wood, and the formation of a soluble complex. The use of NaOH at 1 M was deemed enough to satisfy first condition of dissociating the bonds between lignin and chromium. However, the concentration of the other two extractant was required to be adjusted to improve the extraction percentages of CCA elements from wood by forming the required soluble complexes. Therefore the concentration of the NaOH was kept constant at 1 M whereas the concentration of the following reagents was changed. In order to achieve optimum extraction levels, three experiments were carried out with the following concentration levels:

i. NaOH 1 M, NH_4Cl 1 M, and H_2O_2 2 M

ii. NaOH 1 M, NH_4Cl 2 M, and H_2O_2 2 M

iii. NaOH 1 M, NH_4Cl 2 M, and H_2O_2 1 M

Figure 6.13 shows the extraction percentages of the CCA obtained for three-step extraction process with different leachant concentration. After a full three-step extraction, process (i) was analysed and was able to extract 95 %, 89 % and 90 % of arsenic, chromium and copper respectively by analysing the wood residue obtained. The extraction level of copper was further increased by increasing the concentration of NH_4Cl to 2 M while keeping concentration of H_2O_2 the same at 2 M. In process (ii) the extraction percentages obtained from the wood residue were 98 %, 89 % and 96 % for arsenic, chromium and copper respectively. The process (iii) showed a steep decline in the extraction level, 95 % of arsenic, 64 % of chromium and 73 % of copper extraction. This was due to the reduction in the concentration of the H_2O_2 from 2 M to 1 M which was not able to induce the required level of oxidative conditions from the water soluble complexes of the CCA elements.

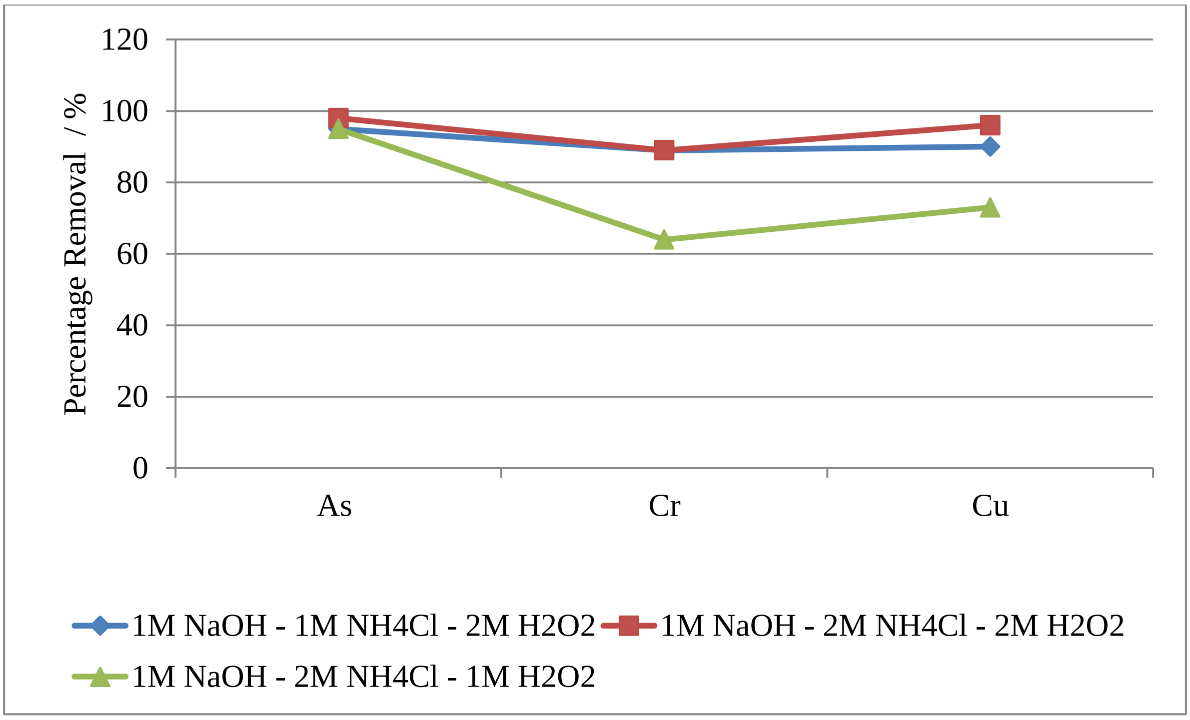


Figure 6.13 Three-step extraction percentages of the CCA obtained with different leachant concentration

From these results it can be seen that process (ii) achieved the best extraction levels of CCA elements. Process (i) did not consist of enough NH_4^+ ions to extract the copper from wood by converting it into water soluble complexes. Hence, in process (ii) the increase in the NH_4Cl concentration led to a higher extraction result.

All three processes had a very similar pH. At the start of the experiments, pH was detected at 13.5, and reduced with each extraction step to a final value of pH 1.8 for process (i) and (ii) but process (iii) reduced to a final pH 2.2. Low extraction of process (iii) could be attributed to the lower concentration of H_2O_2 such that most of the chemical would be consumed to neutralise the reducing conditions of the previous extraction steps. This mechanism reduced the availability of the ions to react with CCA to form water soluble complexes. This is comparable to the extraction results obtained in the process (b) performed during the order determination section.

6.5 CCA Precipitation by Electrocoagulation

With the help of chemical extraction method, CCA elements were transferred in a water soluble stage. Three distinct leachates were obtained for three respective extraction steps employed in the previous section. These leachates exhibited specific properties to the parent leachant and held different concentrations of CCA elements extracted from wood. In order to complete the disposal of the CCA treated wood, it was necessary to precipitate these elements to a solid form from the leachate. The method of electrocoagulation was employed in order to achieve this.

6.5.1 Optimising the process

The process of electrocoagulation was employed to precipitate the CCA elements, but the process was required to be optimised for various parameters which were responsible for the precipitation process through electrocoagulation. These parameters were determined through a series of experiments performed.

- ***Electrodes***

During an electrocoagulation process, the type of electrode material can greatly influence the removal rate of the CCA elements from the leachate. Electrodes of different materials release different ions into the solution such as in the studies carried out by Kılıç [111] and Heidmann [107] using aluminium and iron electrodes respectively. In another study by Daniel [133] effects of iron electrodes over aluminium electrodes in electrocoagulation for removal of arsenic from industrial effluent.

In the electrocoagulation process, leachate obtained from first extraction step (NaOH 1 M) was used with the electrode rods. However, the electrodes with higher precipitation or extraction were required to be chosen from two types of material mild steel or aluminium. Rods of mild steel and aluminium were prepared with 6 mm diameter. Two experiments were performed with each set of electrodes i.e. mild steel electrodes and aluminium electrodes. But due to the unknown volatility of the solution and other parameters were which were also not known, electric current was set to a moderate to low value of 0.6 A and duration was set to 15 minutes. Also the concentration of the solution was reduced to 1:10 ratio by diluting the leachate with de-ionised water as discussed in chapter 4.

After the process of electrocoagulation, the solution was filtered using a vacuum filtration technique. The filtered solution was analysed by using ICP for arsenic, chromium and copper concentration. Figure 6.14 shows the different percentages obtained for the removal of CCA from the leachate by using mild steel and aluminium electrodes. The results showed that 22 % of arsenic and 33 % of both chromium and copper were removed by using mild steel as electrode compared to aluminium which removed 6% of arsenic, 5 % of chromium and 7 %

of copper. Therefore it was considered that the mild steel electrodes were more promising in the removal of the CCA elements from the leachate. These results were in agreement with Daniel [133], who obtained the better removal rate for the iron electrodes as compared to aluminium.

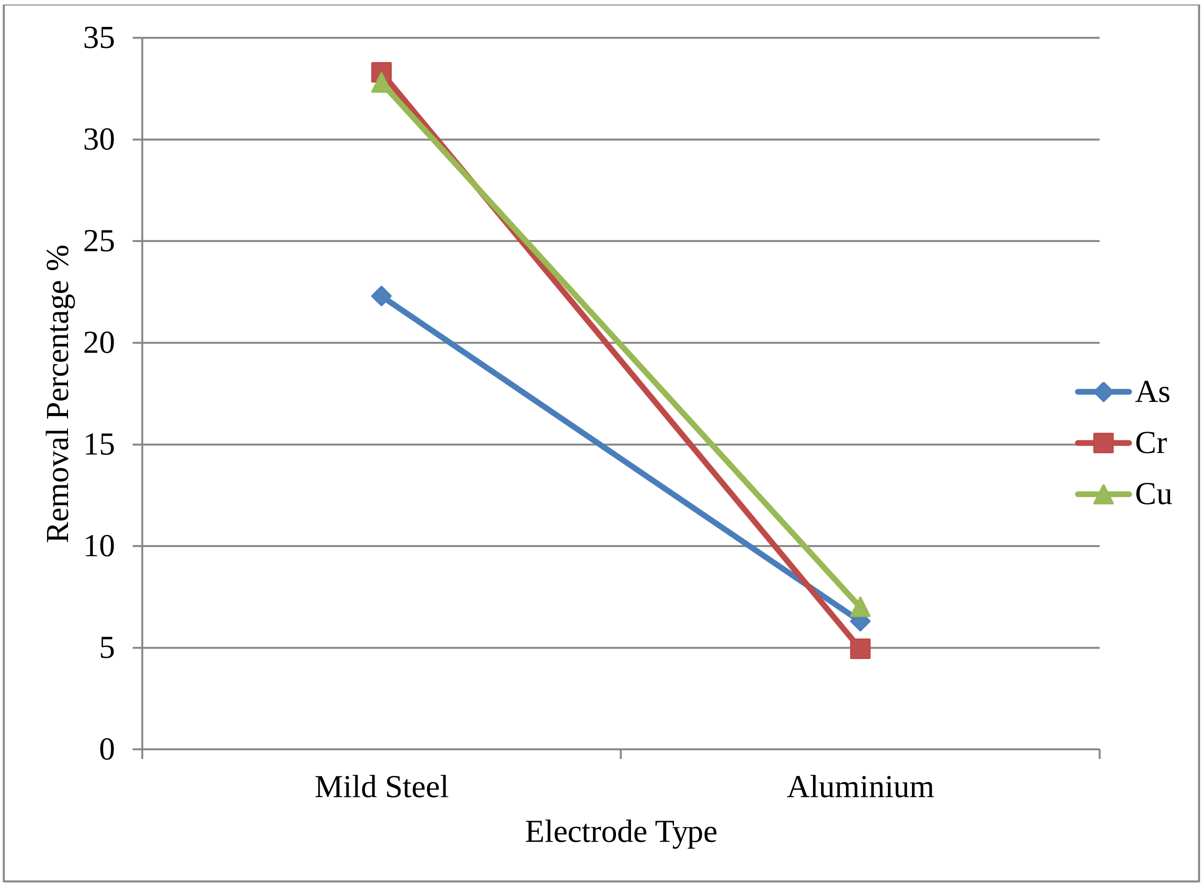


Figure 6.14 Removal of CCA elements from leachate with different types of electrodes

The main reason for the improved rate of removal with mild steel is due to the release of Fe^{2+}, which forms ferric oxide at the anode. This ferric oxide soon bonds with water to form Hydrous Ferric Oxide (HFO). The strong affinity of arsenic towards HFO increases the degree of coagulation [108]. HFO was also believed to be responsible for removal of the copper, due to the reason that HFO was significantly more reactive than the much more stable hydrous aluminium oxides, therefore CCA elements are more likely to be oxidised to the surface of HFO. The removal of chromium was assisted by the mechanism of reduction of Cr^{6+} to Cr^{3+} which was precipitated by the coagulant $Fe(OH)_3$ [134]. Such that Fe^{3+} ions are mainly soluble in strongly acidic conditions whereas it remained insoluble in water due to the pH of the solution was recorded to be 12.9 The removal results were in agreement with Zongo [134] and Heidmann [107] who both found iron to be a more effective electrode for removing chromium.

On the other hand aluminium ions as Al^{3+} remains water soluble at the pH of 12.9 which suggests that even if aluminium formed any omplexes with the CCA if would remain as water soluble compound and hence negligibly small precipitation was observed.

- ***Current***

In order to determine the optimal current for the electrocoagulation process in removing the heavy metals from leachate, the current was varied from 0.2 A to 1 A, with 0.2 A intervals. Heidmann [107] tested electrocoagulation for the removal of chromium and found the process was most effective at currents under 0.1 A, whereas when Daniel [133] concluded that effective current for removal of arsenic was at 0.8 A.

The solution diluted with de-ionised water at 1:10 was made from the leachate from NaOH extraction process for continuity. In the experiment, mild steel electrodes were used for duration of 15 minutes. After that the solution was vacuum filtered and analysed by using ICP for the CCA elements. The percentages for removal of CCA elements to determine the optimum current are shown in Figure 6.15. The removal rate of the heavy metals was expected to increase as the current increased according to Faraday’s law of electrolysis [135]. Faraday's law states that increasing the current density leads to a higher coagulant dosage per time unit. The electrocoagulation process should therefore accelerate this [107].

The removal rate of the CCA elements was negligibly small when electrocoagulation was performed at currents of 0.2 A and even 0.4 A. This could be attributed to inefficient energy available for the ions to cause a reaction. The critical energy requirement was attained at 0.6

A allowing copper to achieve a sudden increase in precipitation and hence removal. The ICP analysis of the filtered solution after electrocoagulation showed the precipitation and removal of copper increased with the increase in current. The increased current created enough energy for the ions to react and displace the copper. The removal rate after 0.6 A continued to increase with the increase in current, but the rate of removal was not directly proportional to the increase in current. However, the trend of increasing copper removal was expected. It was due to the reason that higher current caused more ions to be released into the solution from the electrodes as per Faradays' law. Therefore, it increased the possibility of reaction taking place and hence, enhanced extraction rate.

On the other hand ICP analysis showed that that the chromium removal was highest at 0.8 A and removal percentage dropped at 1 A. Heidmann [107] reported that low currents were most effective for the removal of chromium. High chromium removal percentage was achieved at lower current values from 0.5 A to 0.8 A and it was observed that chromium removal dropped when the current approached 1 A. This chromium removal trend was in agreement with the current results obtained. This was because as more current was applied, the more Fe^{2+} and OH^- ions were released resulting in Cr^{6+} to be reduced and precipitated. However, it was stated by Heidmann [107] that when a critical value of effective Fe^{2+} dissolution was exceeded, then the oxygen evolution results in a decrease in iron dissolution and increased simultaneously the oxidation of Fe^{2+} to Fe^{3+}. Therefore, no or lesser Fe^{2+} ions were available for the Cr^{6+} reduction.

It was determined that arsenic removal was most efficient with a current of 0.8 A, when wastewater was treated with electrocoagulation for 10 minutes [133]. Another research Ribeiro [136] on CCA wood chips found most efficient arsenic removal at 0.4 A by using an electrodialytic process for 25 minutes.

The Figure 6.15 also shows that negligibly small arsenic was removed during the electrocoagulation process when the current was 0.2 A. This could be assumed to be due to the similar reasons that not enough energy was available for the reactions to occur. The removal rate showed an increased at 0.4 A and 0.6 A due to the increase in current which created more Fe^{2+} ions and hence more HFO to precipitate arsenic. When the current reached 0.8 A the removal rate of arsenic decreased. This could be due to the similar principle explained earlier regarding the drop in chromium removal levels. The slowdown in oxidation of Fe^{2+} to Fe^{3+}, could be the prime factor responsible for the limiting step in arsenic removal [108]. The drop in the removal percentage could also be due to the higher consumption or preference of Fe^{2+} ions towards copper and chromium complexes which are also at the most efficient and active stage when current is at 0.8 A, as the removal rate showed an increase when current reached 1 A. This could be explained if the Fe^{2+} ions were made available after a slowdown in the reaction with copper and chromium. Thus the removal of arsenic seemed to have picked up again.

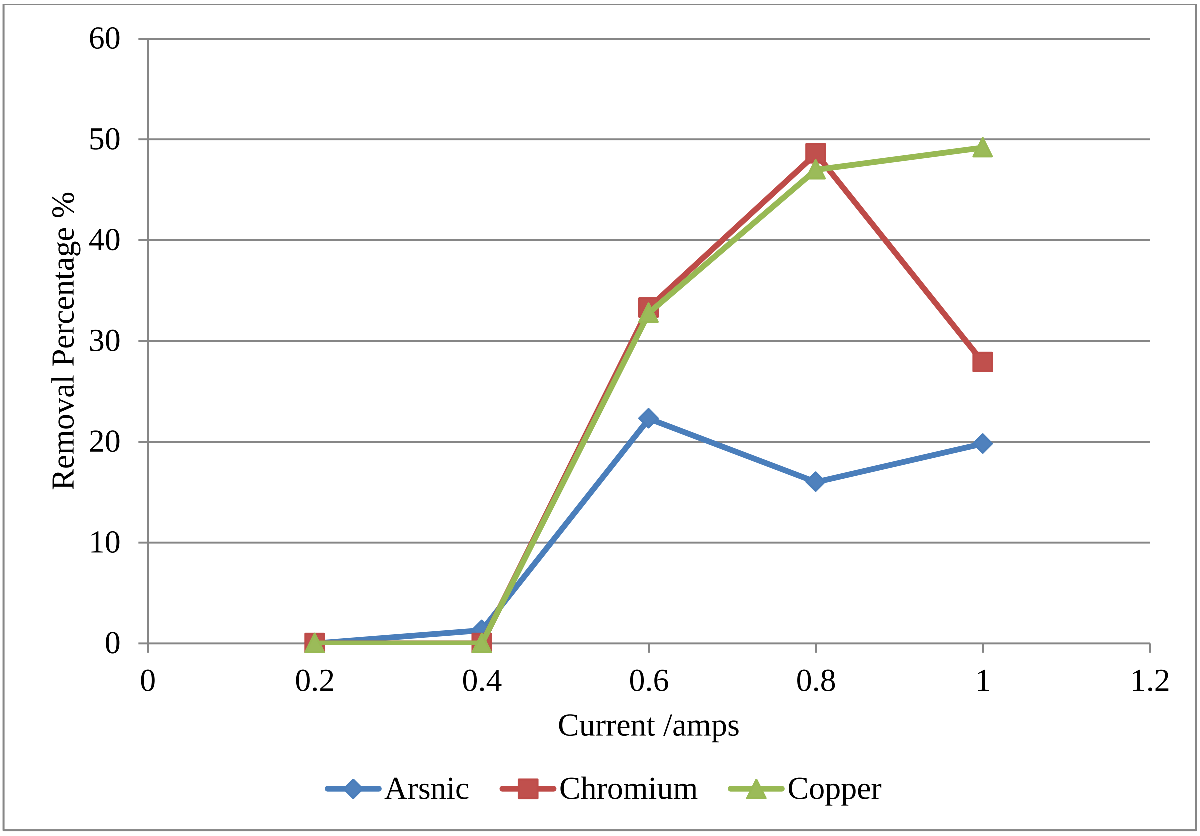


Figure 6.15 Removal of CCA elements from leachate for different current settings

Regarding the electrocoagulation, the current at 0.8 A was considered to be the optimum. This was because two out of the three metals were achieving the most efficient removal rate. However, once the Fe^{2+} ions would be available the extraction with arsenic would pick up even at current 0.8 A.

- ***pH***

The pH range tested for electrocoagulation experiments was between 4 and 13. The electrocoagulation experiments were carried out on the leachate from the NaOH extraction step. The experiment was performed with current at 0.8 A which was previously tested to be the most optimum value for the removal of CCA elements for 15 minutes using mild steel electrodes. The starting pH of leachate was around 13, which was reduced with the help of 1 M HCl solution. Using a digital pH meter, a continuous monitoring was carried out while changing the pH to a desired value. The results for CCA removal from the leachate at different pH levels as shown in Figure 6.16

The results show that the removal rate at pH 13 is significantly lower for all the metals, as the solution used was of alkaline nature this meant very low availability of concentration of H^+ ions. This also meant that there are no extra hydrogen bonds for the acid-ion-exchange reactions at the acid adsorption points on the wood cell walls [11]. On the other hand for the low pH, use of HCl led to the drop in the pH and hence introduced a higher concentration of H^+ ions. At low pH the percentage removed in all CCA elements dramatically increased to 99 %. Considering the high removal rate at the low pH, pH 4 was deemed to the optimum value for the CCA removal. Therefore, the adjustment of pH was required by the help of 1 M HCl solution.

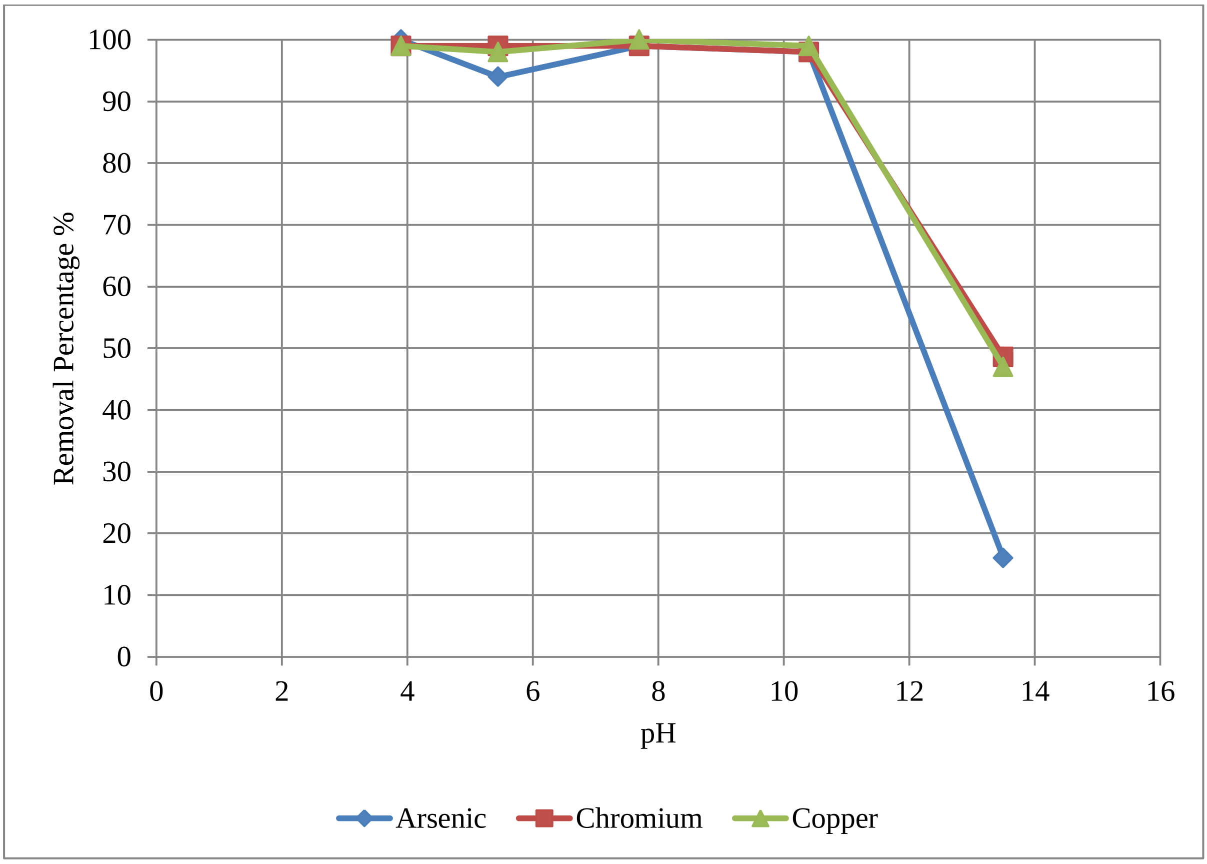


Figure 6.16 CCA removal from leachate at different pH

- ***Type of Solution***

Different parameters were analysed by using leachate from the NaOH extraction step. But it was also necessary to test other leachates obtained during the three step-extraction process of CCA from treated wood namely leachate from NH_4Cl and H_2O_2. The optimal conditions from previous experiments were used. Leachates were diluted to 1:10 ratio to make-up a volume of 33 ml; electric current was set at 0.8 A and the pH was adjusted to 4. For all the experiments, mild steel electrodes were used for duration of 15 minutes. Figure 6.17 shows the percentage of CCA elements removed from the solutions for above described parameters.

The initial pH recorded for NH_4Cl solution was 5.6, which was adjusted by adding 1 M HCl solution. After the electrocoagulation process, the solution was vacuum filtered and then analysed by ICP for the remaining CCA elements. The removal rates for NH_4Cl were very similar to the removal percentages obtained for the NaOH solution. Regarding electrocoagulation of H_2O_2 solution which had a pH of 3.2, no adjustment in pH was made prior to the experiment. The filtered solution of H_2O_2 was also analysed by ICP and the removal rate of CCA elements from solution was determined. The percentage of arsenic removed was similar to other solutions which remained at 98 %. On the other hand, the removal percentages of copper and chromium were observed to have dropped to 93 % and 42 % respectively.

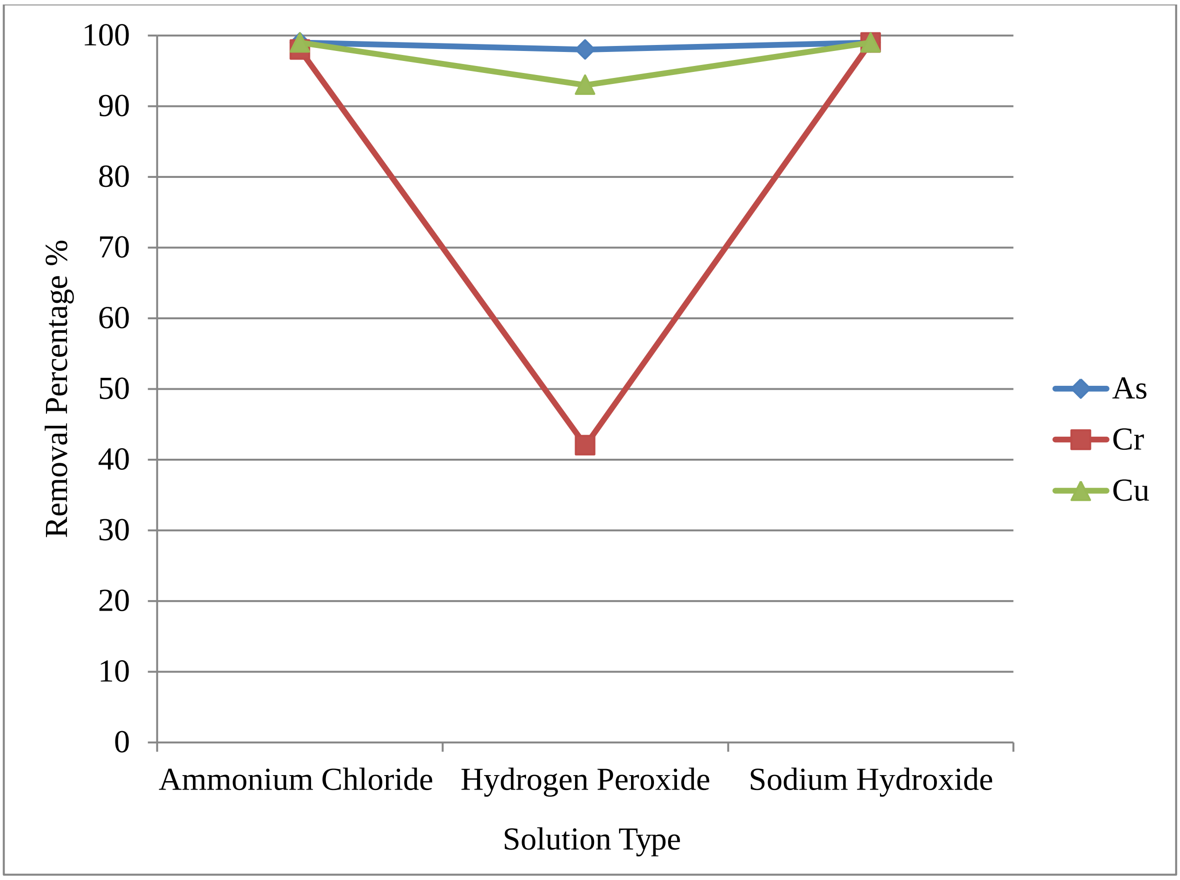


Figure 6.17 Removal of CCA elements from different solutions of leachates

The drop in the removal percentages for H_2O_2 solution may be attributed to the species of the CCA elements formed during the extraction process from the treated wood with H_2O_2. These may consist of uncharged species of CCA which would just prevent the electro-migration of elements [11], but the energy required to dissociate these species was not enough in the case of the H_2O_2 solution. On the other hand it could be understood that, unlike NaOH and NH_4Cl leachate, there was no Na^+ or NH_4^+ ions to enhance the ionic strength of the solution as Fe ions may be unreactive towards the species present or lack the energy required.

- ***Concentration and Mixing of Solutions***

In order to finalise the optimisation of the process, the concentration of the samples used in experiments was increased. The leachate obtained from the NaOH extraction step was used, and the dilution factor was changed from 1:10 to 1:5 ratio with de-ionised water whilst all the other parameters were kept at the optimum conditions obtained from the previous experiments. 1 M HCl solution was used to adjust the pH to 4 before electrocoagulation.

The previous experiments showed that during electrocoagulation of solution of H_2O_2 leachate had the lowest removal percentages of CCA elements. Therefore, two tests were performed to detect the most compatible option by mixing leachate of H_2O_2 with leachate of NaOH in one test and in the other mixing leachate of H_2O_2 with leachate of NH_4Cl.

The leachate of H_2O_2 was mixed with leachate of NaOH in equal parts and then diluted with deionised water according to the ratio of 1:5. The initial pH of the obtained solution was 13 which was adjusted to pH 4 with the aid of 1 M HCl solution. The removal percentage of CCA elements from the solution mix of NaOH and H_2O_2 leachate such that 99 % of all three elements were removed.

This showed that improved removal rate was due to the presence of Na^+ ions in the solution, which remained in the solution after the NaOH extraction stage. These ions must have aided in the coagulation of CCA elements and enhanced the removal rate from the H_2O_2 solution as well. These ions were not present in the H_2O_2 solution where reduced removal percentages were observed. This phenomenon strengthens the argument of Na^+ being a key factor in electrocoagulation.

When the solution mix of H_2O_2 and NH_4Cl leachate was tested under the same conditions, similar removal rates were obtained, a 99 % CCA elements removed from the solution mix. There was no pH adjustment made by adding HCl solution as the pH of the solution mix was already at 3.2. However, in this solution the presence of NH_4^+ ions in the solutions which remained from the extraction stage enhanced the complex formation of CCA elements and their precipitation. This, the presence of these ions aided in the coagulation process of the CCA elements.

All the solutions obtained were allowed to cool after the electrocoagulation before being filtered, as the ongoing precipitation process was observed. As the solution cooled down more precipitate was formed completing the electrocoagulation process.

Both mixtures, first using the NaOH and using the NH_4Cl, achieved a high level of removal percentage with similar values for arsenic, chromium and copper. However, the NH_4Cl was considered a preferable solution due to the fact that it mitigated the need to add acid for pH adjustment, before electrocoagulation.

By reducing the dilution factor, mixing of leachate reduced the quantity to be precipitated through electrocoagulation. Also this solved the issue of lower removal percentage for the leachate of H_2O_2 extraction as well as reducing the time required in electrocoagulation for two leachates as opposed to three. However, another experiment was performed to determine the limit of the process; a cocktail of the three solutions was prepared and was diluted with de-ionised water by a factor of 1:10, the pH was adjusted to 3.8 with the help of 1 M of HCl solution while other parameters were kept as previously determined. The electrocoagulation of the cocktail of the extracted solutions achieved removal percentages to 99 % for all three CCA elements. The concentration of the elements was determined by ICP analysis in the filtered solution from post-electrocoagulation treatment of the cocktail. Following the results of the other two experiments, this was predicted due to the Na^+ and NH_4^+ ions aiding the coagulation.

Through a sequence of controlled experiments, a process was developed with optimum parameters which were capable of removing substantial amount of CCA elements from the treated wood.

The added advantage of this discovery was that mixing the solutions together would make the process much easier and significantly quicker. The whole extraction and electrocoagulation process can be developed to scale up to a full pilot plant and even to a commercial level.

Summary

A three-step extraction process was designed by performing a sequential analysis with different chemical reagents as leachant. Sequential analysis consisted of carrying out leaching tests with varying concentration of chemicals at room temperature and at 100^{o}C. Water and saline leaching tests were performed to obtain a basic leaching pattern at elevated temperature. Other tests included leaching solutions with different concentrations of sodium chloride (NaCl), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl). From the results NaOH provided good alkaline conditions for the wood structure to be weakened by lignin depolymerisation. NaOH dissolved the lignin which in turn released CCA elements from the complexes. Furthermore, it was found that NaOH extracted a high concentration of arsenic by forming water soluble complexes with arsenic. NH_4Cl was found to have good extraction results for the copper due to the high affinity of ammonium group to form complexes with copper. H_2O_2 provided good oxidation conditions which were suitable in oxidising chromium and other CCA elements to form complexes which are readily soluble in water. Hence, the three chemical reagents were selected to develop a three-step extraction process owing to their specific characteristic and reaction towards the CCA elements in treated wood.

The three-step process was optimised by analysing the best concentration and order of treatment of a CCA wood sample with different chemical reagents. A process was developed using 1M sodium hydroxide (NaOH), 2 M ammonium chloride (NH_4Cl) and 2 M of hydrogen peroxide (H_2O_2). The best results achieved by the process were 98 %, 89 % and 96 % for arsenic, chromium and copper respectively. From every step of the extraction process respective leachate were obtained with dissolved CCA elements. Therefore it was necessary to precipitate the CCA elements for final disposal.

The electrocoagulation process was employed for the precipitation of the dissolved CCA elements from the leachate obtained. Various parameters such as duration, current, pH, electrodes and concentration were analysed to optimise the electrocoagulation process. A full experiment with electrocoagulation was performed with mild steel electrodes, at 0.8 A, for 15 minutes, solution to de-ionised water was 1:5. This provided about 99 % of CCA elements to be removed from the solution by precipitation, followed by filtration.

Chapter 7. Conclusions and Recommendations

7.1 Introduction

The aim of this study was to perform a basic characterisation of CCA treated wood waste generated from a coke quenching tower from an integrated steelworks. Following the characterisation, the study went on to develop a waste treatment method to separate or extract CCA elements from the wood. This chapter provides the conclusions of this thesis. It draws upon the implications of the study and it also highlights the key findings and integrates the issues raised in the discussion. The chapter also provides the direction areas for future research and further work.

7.2 General Overview

There are two aspects associated with waste management, economic factors and environmental compliance. Economics play a vital role in the dealing with the waste and different costs associated with it. There are costs associated with waste handling, value lost, treatment and disposal costs. However, the cost factor is mainly governed by the environmental legislation and laws associated with the waste. The CCA treated wood waste is a typical example where, due to the changing legislation and regulations, use of such wood is restricted to industrial applications only. Moreover, the waste generated from treated wood is deemed as hazardous which makes the disposal of the wood and its treatment of primary concern. The strict regulations are a result of the severe health hazards associated with the chemicals used in the CCA wood treatment. Also the improper disposal of CCA treated wood may introduce copper, chromium and arsenic in the food chain posing a dangerous threat and increasing the exposure level. However, the regulations do not place any requirement for the removal of the CCA treated wood currently in-service. This means over the coming years, CCA treated wood would may regularly be seen in the waste stream.

These two aspects of environmental compliance and economic factors are strongly influencing the drive for a more efficient waste treatment method in order to dispose of CCA treated wood waste safely and in accordance with the regulations. Separating the CCA elements from the wood would provide residue wood for recycling and the recovered CCA elements could be reused for various other applications. The recycled wood is widely used in the world for different recycled products as particleboard, cardboard, paper or biomass.

7.3 Conclusions

In order to develop a treatment technique, it was important to characterise the wood waste and obtain a basic understanding about it. The CCA wood waste samples were obtained from demolition of a 33 year old quenching tower at an integrated steelworks site. Therefore, the first phase of the study involved performing a basic characterisation. From this work, the following conclusion were made;

- The wood had lost substantial amount of CCA over the years of service where low CCA concentration was recorded in the old wood when compared to the refurbished wood. Old wood contained a considerable amount of CCA concentration relative to untreated wood analysed. This showed that all wood samples were required to be considered for the waste treatment.
- Different sections of the quenching tower lost CCA elements at different rates over time. This was attributed to the working of the tower and variation in exposure to heat, water and steam. Chromium was observed as being the most resistant to leach away from wood.

- No crystalline structures of CCA elements were detected when the XRD results of untreated and CCA treated wood were compared. XRD analysis only picked up the structure of wood.
- White spots on the wood surface were detected in the topographic images obtained during SEM analysis. EDX point and line scans performed showed CCA distribution across the wood surface such that a higher concentration of CCA elements was present on the edges than the core of the wood. EDX also confirmed the white spots as calcium deposits which could have accumulated over time due to the quenching process of the tower.

Leaching characteristics exhibited by CCA treated wood were studied. This study established the potential environmental concern and also provided a basic knowledge for the development of the waste treatment and disposal technique.

- Standard leaching tests performed for different durations revealed a leaching pattern of As > Cu > Cr, such that arsenic and copper leached more than chromium. The results of this pattern were visible in final concentrations as loss of arsenic and copper caused by the leaching during its service life was higher than chromium.
- After a one week leaching period, leachant tends to be saturated with CCA elements and equilibrium was attained. Continuous sampling showed that leaching was highest during the first hour. Rates of leaching drastically slowed down after 1st hour in a three hour process, whereas interrupted sampling showed higher loss of CCA in three leach cycles for same period of time.
- A specific correlation was established between the arsenic-chromium and arsenic-copper leaching concentrations. This correlation indicated a very likely linear relationship between leaching of CCA elements and an equation to predict the concentrations of elements was established.

After elemental analysis CCA wood waste was found to be contaminated with iron. The concentration of CCA was found to be reducing whereas iron concentration in the wood was increasing with increase in the service life of the tower wood. The iron contamination was characterised and studied to understand the disposal options.

- Growth ring analysis showed that iron was mainly present on the surface of the wood and did not penetrate deep inside.
- Coal, coke ash, kish and quenching water were analysed for iron as possible sources of iron. Kish was airborne and was easily exposed to most of the wood surfaces with very high iron content. Kish deposited most of the iron, aluminium and silicon followed by the coke ash which comes in the immediate contact with the wood during the quenching process.
- Quenching water analysis showed the silicon and aluminium are prone to easy leaching compared to iron. But still elevated silicon and aluminium concentrations corresponded to the high iron containing wood samples.
- Leaching tests performed on old and new wood showed iron plays a vital part in the leaching of the CCA. Due to the stabilisation effect of the iron, a very low leaching of metals took place in old wood when compared to the leaching concentrations from the new wood. This suggested that the presence of iron in the waste could be used as an advantage for the disposal of the wood waste, such that the mixture of old and new wood could be disposed in landfill.

The second phase of this study was to develop a technique to extract CCA elements from wood and improve the disposal method of CCA wood waste. The following conclusions were made from this work;

- Different chemical reagents were investigated as leachant at room temperature and 100^{o}C. De-ionised and saline water provided a basic leaching pattern at elevated temperatures. NaOH was used to depolymerise lignin in wood with a high arsenic removal rate and H_2O_2 was used to enhance the polymerisation and removed the CCA elements through oxidisation especially chromium. NH_4Cl and NH_4OH were used because of the strong affinity of amines towards copper.
- A chemical extraction process was designed on principle of leaching by using NaOH, NH_4Cl and H_2O_2. The process was optimised by determining the order and concentration of the chemical reagents to be used.
- An hour of extraction, each with NaOH, NH_4Cl and H_2O_2 at concentration 1M, 2M and 2M respectively. A rinsing procedure after every extraction step was also introduced. Three –step process provided the extraction up to 98 %, 89 % and 96 % of arsenic, chromium and copper respectively. Extraction process resulted in wood residue with reduced CCA content and leachates from three respective extraction steps with varying CCA concentration.
- CCA elements were precipitated from the leachates of chemical extraction by using electrocoagulation process. A series of experiments were performed to optimise the type of electrodes, value of current, pH and concentration of solutions to be used.
- With the optimised parameters the electrocoagulation was performed for duration of 15 minutes to precipitate the CCA elements and yield clear water solution.
- Electrocoagulation achieved 99 % removal rate of CCA elements from the leachates.

The end products from the waste treatment technique were wood residue from the extraction process, CCA precipitates and water from electrocoagulation.

7.4 Recommendations

The recommendations that can be derived from this study are as follows;

- Further research should be built up on the changes to properties of waste due to the presence of iron and its full disposal route according to the environment regulations.
- Leaching behaviour of the CCA elements from treated wood should be studied in presence / absence of iron salts.
- A comparative analysis of various leaching results on CCA treated wood from other research by using mathematical relationship on leaching developed in this study should be performed.
- Further research should be undertaken to convert the three-step extraction into one full step process while keeping the concentration of the reagents required to a minimum and achieving same or better extraction results.
- Further study should be carried out to investigate the uses of the wood residue from the extraction process in various industries such as recycle paper, cardboard, particle board or as biomass.
- After the encouraging results from the electrocoagulation process, further work should be undertaken on a scaled up the process.
- A life cycle assessment to be performed on CCA treated wood from quenching tower while using the three step extraction and electrocoagulation as disposal methods.
- Characterisation of the precipitates obtained from electrocoagulation and its end of cycle assessment.

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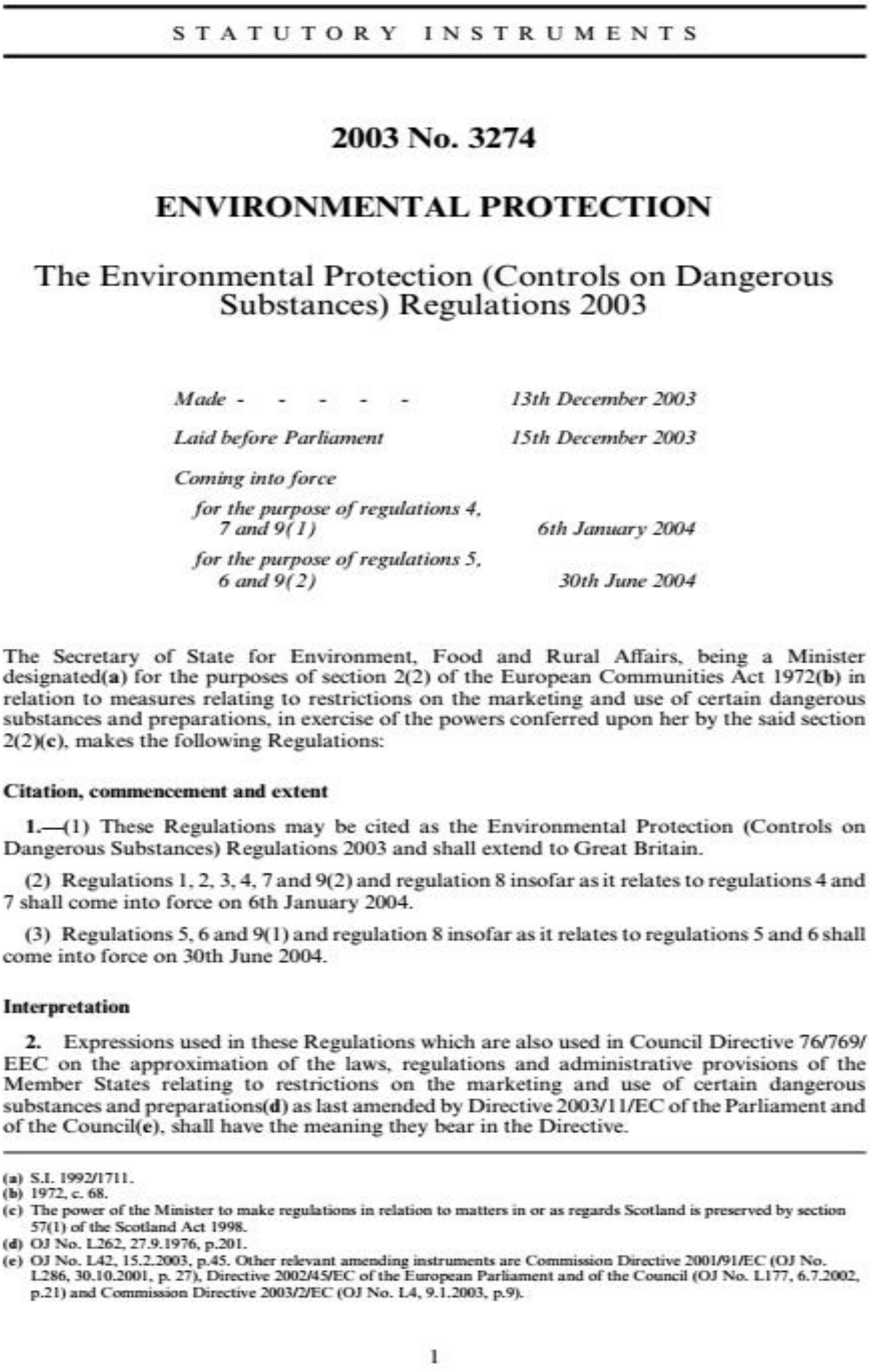
Appendices

Appendix A



STATUTORY INSTRUMENTS

2003 No. 3274

ENVIRONMENTAL PROTECTION

The Environmental Protection (Controls on Dangerous Substances) Regulations 2003

Made - - - - -	*13th December 2003*
Laid before Parliament	*15th December 2003*
Coming into force	
for the purpose of regulations 4, 7 and 9(1)	*6th January 2004*
for the purpose of regulations 5, 6 and 9(2)	*30th June 2004*

The Secretary of State for Environment, Food and Rural Affairs, being a Minister designated[**a**] for the purposes of section 2(2) of the European Communities Act 1972[**b**] in relation to measures relating to restrictions on the marketing and use of certain dangerous substances and preparations, in exercise of the powers conferred upon her by the said section 2(2)[**c**], makes the following Regulations:

Citation, commencement and extent

1.—(1) These Regulations may be cited as the Environmental Protection (Controls on Dangerous Substances) Regulations 2003 and shall extend to Great Britain.

(2) Regulations 1, 2, 3, 4, 7 and 9(2) and regulation 8 insofar as it relates to regulations 4 and 7 shall come into force on 6th January 2004.

(3) Regulations 5, 6 and 9(1) and regulation 8 insofar as it relates to regulations 5 and 6 shall come into force on 30th June 2004.

Interpretation

2. Expressions used in these Regulations which are also used in Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations[**d**] as last amended by Directive 2003/11/EC of the Parliament and of the Council[**e**], shall have the meaning they bear in the Directive.

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[a] S.I. 1992/1711.

[b] 1972, c. 68.

[c] The power of the Minister to make regulations in relation to matters in or as regards Scotland is preserved by section 57(1) of the Scotland Act 1998.

[d] OJ No. L262, 27.9.1976, p.201.

[e] OJ No. L42, 15.2.2003, p.45. Other relevant amending instruments are Commission Directive 2001/91/EC (OJ No. L286, 30.10.2001, p. 27), Directive 2002/45/EC of the European Parliament and of the Council (OJ No. L177, 6.7.2002, p.21) and Commission Directive 2003/2/EC (OJ No. L4, 9.1.2003, p.9).

1

Scope

3. These Regulations do not apply to—

(a) the placing on the market or use of dangerous substances or preparations for research and development or analysis purposes;

(b) the carriage of dangerous substances or preparations by rail, road, inland waterway, sea or air;

(c) dangerous substances or preparations exported to a country which is not a Member State of the European Community nor Norway, Iceland or Liechtenstein;

(d) dangerous substances or preparations in transit and subject to customs inspection, provided that they undergo no processing.

Prohibition on the placing on the market of short chain chlorinated paraffins

4. No person shall place short chain chlorinated paraffins (alkanes, C_{10}-C_{13}, chloro) on the market for use as substances, or as constituents of other substances or preparations in concentrations higher than 1%, either in metalworking or for fat liquoring of leather.

Restrictions on the marketing and use of arsenic compounds

5.—(1) Subject to regulation 6, arsenic compounds may not be used as substances or constituents of preparations intended for use—

(a) to prevent the fouling by micro-organisms, plants or animals of—

  (i) the hulls of boats,

  (ii) cages, floats, nets and any other appliances or equipment used for fish or shellfish farming,

  (iii) any totally or partly submerged appliances or equipment;

(b) in the preservation of wood;

(c) in the treatment of industrial waters, irrespective of their use.

(2) Subject to regulation 6, wood treated with a substance or preparation containing an arsenic compound for the purpose of preserving the wood may not be placed on the market.

Permitted marketing and use of arsenic compounds and treated wood

6.—(1) Solutions of inorganic compounds of the copper, chromium, arsenic (CCA) type C may be used as substances or preparations in the preservation of wood in industrial installations if vacuum or pressure is used to impregnate the wood with the solution.

(2) Subject to the conditions in paragraph (3), wood treated with CCA solutions in industrial installations in accordance with paragraph (1) may be placed on the market but not before fixation of the preservative is completed.

(3) The conditions referred to in paragraph (2) are that—

(a) the wood is placed on the market for professional and industrial use;

(b) in the use for which the wood is placed on the market, the structural integrity of the wood is required for human or livestock safety;

(c) in the use for which the wood is placed on the market, skin contact by the general public during its service life is unlikely; and

(d) the wood is placed on the market for any of the following uses—

  (i) as structural timber in public and agricultural buildings, office buildings, and industrial premises;

  (ii) in bridges and bridgework;

  (iii) as constructional timber in freshwater areas and brackish waters eg jetties and bridges;

  (iv) as noise barriers;

  (v) in avalanche control;

  (vi) in highway safety fencing and barriers;

  (vii) as debarked round conifer livestock fence posts;

  (viii) in earth retaining structures;

  (ix) as electric power transmission and telecommunications poles; or

(x) as underground railway sleepers.

(4) Subject to paragraph (5), wood treated in accordance with paragraph (1) may not be used—

(a) in residential or domestic constructions, whatever the purpose;

(b) in any application where there is a risk of repeated skin contact;

(c) in marine waters;

(d) for agricultural purposes, save that such wood may be used for livestock fence posts or for the structural uses set out in paragraph (3)(d), provided that the structural integrity of the wood is required for human or livestock safety and skin contact by the general public during its service life is unlikely; or

(e) in any application where the treated wood may come into contact with intermediate or finished products intended for human or animal consumption.

(5) Paragraph (4) does not apply to wood in place before 30 June 2004.

(6) Without prejudice to the application of other rules and regulations on the classification, packaging and labelling of dangerous substances and preparations, all treated wood placed on the market pursuant to this regulation shall be individually labelled using the following words—

> "For professional and industrial installation and use only, contains arsenic".

(7) In addition, all wood placed on the market in packs shall bear a label stating—

> "Wear gloves when handling this wood. Wear a dust mask and eye protection when cutting or otherwise crafting this wood. Waste from this wood shall be treated as hazardous by an authorised undertaking".

Prohibition on the use of hexachloroethane in the manufacturing and processing of non-ferrous metals

7. No person shall use hexachloroethane in the manufacturing or processing of non-ferrous metals.

Offences and penalties

8.—(1) Any person who contravenes regulation 4, 5, 6 or 7, or causes or permits another person to contravene those regulations, shall be guilty of an offence.

(2) Any person guilty of an offence under paragraph (1) shall be liable—

(a) on summary conviction, to a fine not exceeding the statutory maximum;

(b) on conviction on indictment, to a fine.

(3) Where an offence under paragraph (1) committed by a body corporate is proved—

(a) to have been committed with the consent or connivance of an officer, or

(b) to be attributable to any neglect on his part,

the officer as well as the body corporate shall be guilty of that offence and liable to be proceeded against and punished accordingly.

(4) In paragraph (3) "officer", in relation to a body corporate, means a director, manager, secretary or other similar officer of the body, or a person purporting to act in any such capacity.

(5) If the affairs of a body corporate are managed by its members, paragraph (3) shall apply in relation to the acts or defaults of a member in connection with his functions of management as if he were a director of the body corporate.

(6) Where an offence under paragraph (1) arising from a contravention of regulation 4, 5, 6 or 7 is committed by a partnership in Scotland and is proved—

(a) to have been committed with the consent or connivance of a partner, or

(b) to be attributable to any neglect on his part,

the partner as well as the partnership shall be guilty of that offence and liable to be proceeded against and punished accordingly.

(7) In paragraph (6) "partner" includes a person purporting to act as a partner.

Amendment and revocation of Regulations

9.—(1) In regulation 5 of the Environmental Protection (Controls on Injurious Substances) Regulations 1992(**a**) the word "arsenic" wherever it appears is deleted.

(2) The Environmental Protection (Controls on Hexachloroethane) Regulations 2003(**b**) are hereby revoked.

Alun Michael
Minister of State
13th December 2003 Department for Environment, Food and Rural Affairs

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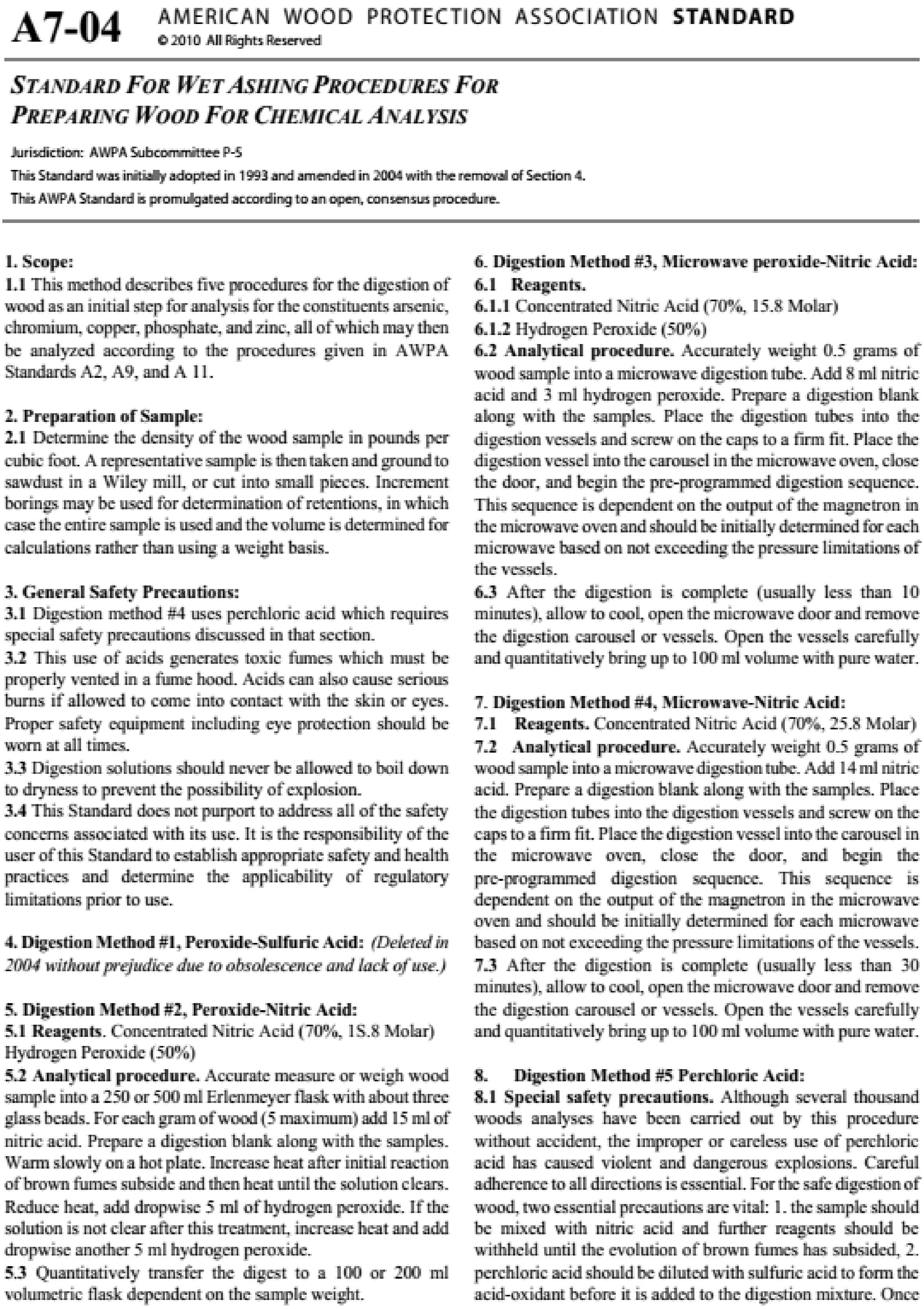
(**a**) S.I. 1992/31.
(**b**) S.I. 2003/602.

Appendix B Wood Digestion Procedure for Chemical Analysis



A7-04 AMERICAN WOOD PROTECTION ASSOCIATION **STANDARD**

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STANDARD FOR WET ASHING PROCEDURES FOR PREPARING WOOD FOR CHEMICAL ANALYSIS

Jurisdiction: AWPA Subcommittee P-5

This Standard was initially adopted in 1993 and amended in 2004 with the removal of Section 4.

This AWPA Standard is promulgated according to an open, consensus procedure.

1. Scope:

1.1 This method describes five procedures for the digestion of wood as an initial step for analysis for the constituents arsenic, chromium, copper, phosphate, and zinc, all of which may then be analyzed according to the procedures given in AWPA Standards A2, A9, and A 11.

2. Preparation of Sample:

2.1 Determine the density of the wood sample in pounds per cubic foot. A representative sample is then taken and ground to sawdust in a Wiley mill, or cut into small pieces. Increment borings may be used for determination of retentions, in which case the entire sample is used and the volume is determined for calculations rather than using a weight basis.

3. General Safety Precautions:

3.1 Digestion method #4 uses perchloric acid which requires special safety precautions discussed in that section.

3.2 This use of acids generates toxic fumes which must be properly vented in a fume hood. Acids can also cause serious burns if allowed to come into contact with the skin or eyes. Proper safety equipment including eye protection should be worn at all times.

3.3 Digestion solutions should never be allowed to boil down to dryness to prevent the possibility of explosion.

3.4 This Standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

4. Digestion Method #1, Peroxide-Sulfuric Acid: *(Deleted in 2004 without prejudice due to obsolescence and lack of use.)*

5. Digestion Method #2, Peroxide-Nitric Acid:

5.1 Reagents. Concentrated Nitric Acid (70%, 1S.8 Molar) Hydrogen Peroxide (50%)

5.2 Analytical procedure. Accurate measure or weigh wood sample into a 250 or 500 ml Erlenmeyer flask with about three glass beads. For each gram of wood (5 maximum) add 15 ml of nitric acid. Prepare a digestion blank along with the samples. Warm slowly on a hot plate. Increase heat after initial reaction of brown fumes subside and then heat until the solution clears. Reduce heat, add dropwise 5 ml of hydrogen peroxide. If the solution is not clear after this treatment, increase heat and add dropwise another 5 ml hydrogen peroxide.

5.3 Quantitatively transfer the digest to a 100 or 200 ml volumetric flask dependent on the sample weight.

6. Digestion Method #3, Microwave peroxide-Nitric Acid:

6.1 Reagents.

6.1.1 Concentrated Nitric Acid (70%, 15.8 Molar)

6.1.2 Hydrogen Peroxide (50%)

6.2 Analytical procedure. Accurately weight 0.5 grams of wood sample into a microwave digestion tube. Add 8 ml nitric acid and 3 ml hydrogen peroxide. Prepare a digestion blank along with the samples. Place the digestion tubes into the digestion vessels and screw on the caps to a firm fit. Place the digestion vessel into the carousel in the microwave oven, close the door, and begin the pre-programmed digestion sequence. This sequence is dependent on the output of the magnetron in the microwave oven and should be initially determined for each microwave based on not exceeding the pressure limitations of the vessels.

6.3 After the digestion is complete (usually less than 10 minutes), allow to cool, open the microwave door and remove the digestion carousel or vessels. Open the vessels carefully and quantitatively bring up to 100 ml volume with pure water.

7. Digestion Method #4, Microwave-Nitric Acid:

7.1 Reagents. Concentrated Nitric Acid (70%, 25.8 Molar)

7.2 Analytical procedure. Accurately weight 0.5 grams of wood sample into a microwave digestion tube. Add 14 ml nitric acid. Prepare a digestion blank along with the samples. Place the digestion tubes into the digestion vessels and screw on the caps to a firm fit. Place the digestion vessel into the carousel in the microwave oven, close the door, and begin the pre-programmed digestion sequence. This sequence is dependent on the output of the magnetron in the microwave oven and should be initially determined for each microwave based on not exceeding the pressure limitations of the vessels.

7.3 After the digestion is complete (usually less than 30 minutes), allow to cool, open the microwave door and remove the digestion carousel or vessels. Open the vessels carefully and quantitatively bring up to 100 ml volume with pure water.

8. Digestion Method #5 Perchloric Acid:

8.1 Special safety precautions. Although several thousand woods analyses have been carried out by this procedure without accident, the improper or careless use of perchloric acid has caused violent and dangerous explosions. Careful adherence to all directions is essential. For the safe digestion of wood, two essential precautions are vital: 1. the sample should be mixed with nitric acid and further reagents should be withheld until the evolution of brown fumes has subsided, 2. perchloric acid should be diluted with sulfuric acid to form the acid-oxidant before it is added to the digestion mixture. Once the digestion has started, addition of wood, or contact with other organic matter, should be avoided. If such contact should inadvertently occur, floor the digestion flask with large amounts of cold water immediately.

8.1.1 The following general rules apply to the use of perchloric acid: Virtually all known explosions may be attributed to contact of raw organic matter or other easily oxidized material with concentrated perchloric acid, or by taking perchloric acid to dryness, forming the anhydrous acid. Organic matter should be pretreated with nitric acid, and perchloric acid should be used in conjunction with nitric and sulfuric acids. Do not let a digestion boil dry.

8.1.2 Special exhausting equipment must be used. Special fame hoods, equipped with washing facilities, and constructed entirely of inorganic materials should be used.

8.1.3 Use of protective equipment (goggles, shields) should be mandatory. Avoid use of large amounts of acid. Explosions involving one or two grains of acid have caused serious damage and personal injury. Do not store more than one, one-pound bottle in the laboratory. Keep this on a stone bench or a glass or ceramic tray, not in contact with wood or plastic. Do not increase the amounts in the procedure.

8.1.4 Clean up all spills with large volumes of water. Do not use sawdust, rags, or other organic material to mop up perchloric acid.

8.2 Reagents. Nitric Acid (concentrated 15.8 Molar)
Sulfuric Acid (concentrated 17.8 Molar)
Perchloric Acid (70%)

8.2.1 Acid oxidant: Add 185 volumes of perchloric acid to 100 volumes of distilled water and then add slowly with mixing 270 volumes of concentrated sulfuric acid.

8.3 Procedure. This method is applicable for use with up to 5-gram wood samples, as boring or ground wood. Dry the samples in an oven for approximately 2 1/2 hours or to constant weight at 125°C. Weigh samples accurately and place them in a 500 ml Erlenmeyer flask with 3 to 5 glass beads. Add 30 ml of nitric acid. Digest slowly on low heat (approximately 100°C).

8.3.1 In about 20 minutes, the evolution of brown fumes will cease and the wood will be completely dissolved. If this is not the case, add 10 ml additional nitric acid and digest further. Experience may dictate the use of more than 30 ml in the original digestion, but use of excess nitric acid should be avoided. Add 10 ml of acid oxidant dropwise using a pipet or syringe to the flask. In about 40 minutes, dense white fumes will be observed and the solution will be green in color. If the solution turns black, cool, add 10 ml of nitric acid and heat slowly until the solution turns green. If chromium is not present, the digestion is now complete. If chromium is present (See note), continue to heat until the solution becomes orange. Remove immediately from the heater. The digestion is now complete, and the solution may be analyzed for the various components after cooling to room temperature and following normal dilution procedures. **Note:** Chromium: Care must be taken not to heat too strongly at any time. If this occurs, green insoluble chromic sulfates may form which cannot readily be redissolved. On the final digestion, heating should be stopped as soon as the solution becomes a clear orange color. The solution should then be chilled immediately and diluted as above for analysis by standard procedure.

8.3.2 Arsenic, Copper, Zinc, and Phosphate: Dilute the digestion, using a volumetric flask and suitable aliquots if feasible. Do not use undiluted solutions for arsenic or copper determinations, or permit the solutions to boil to too low a volume. Explosions have occurred as a result.

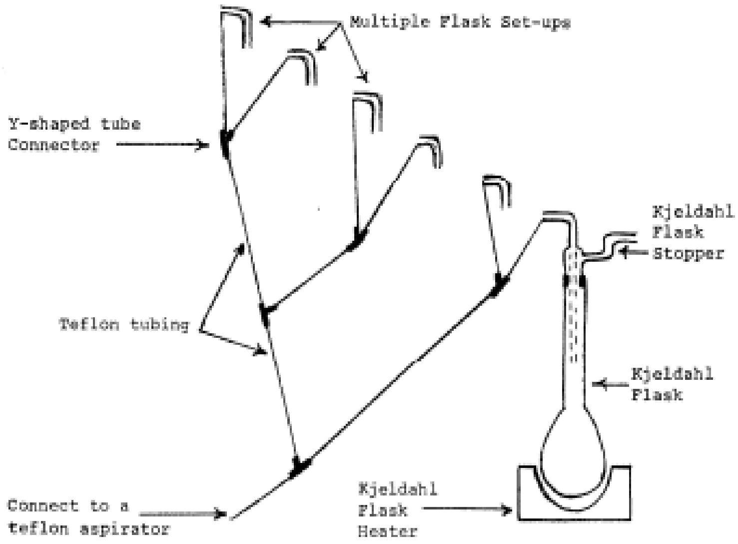
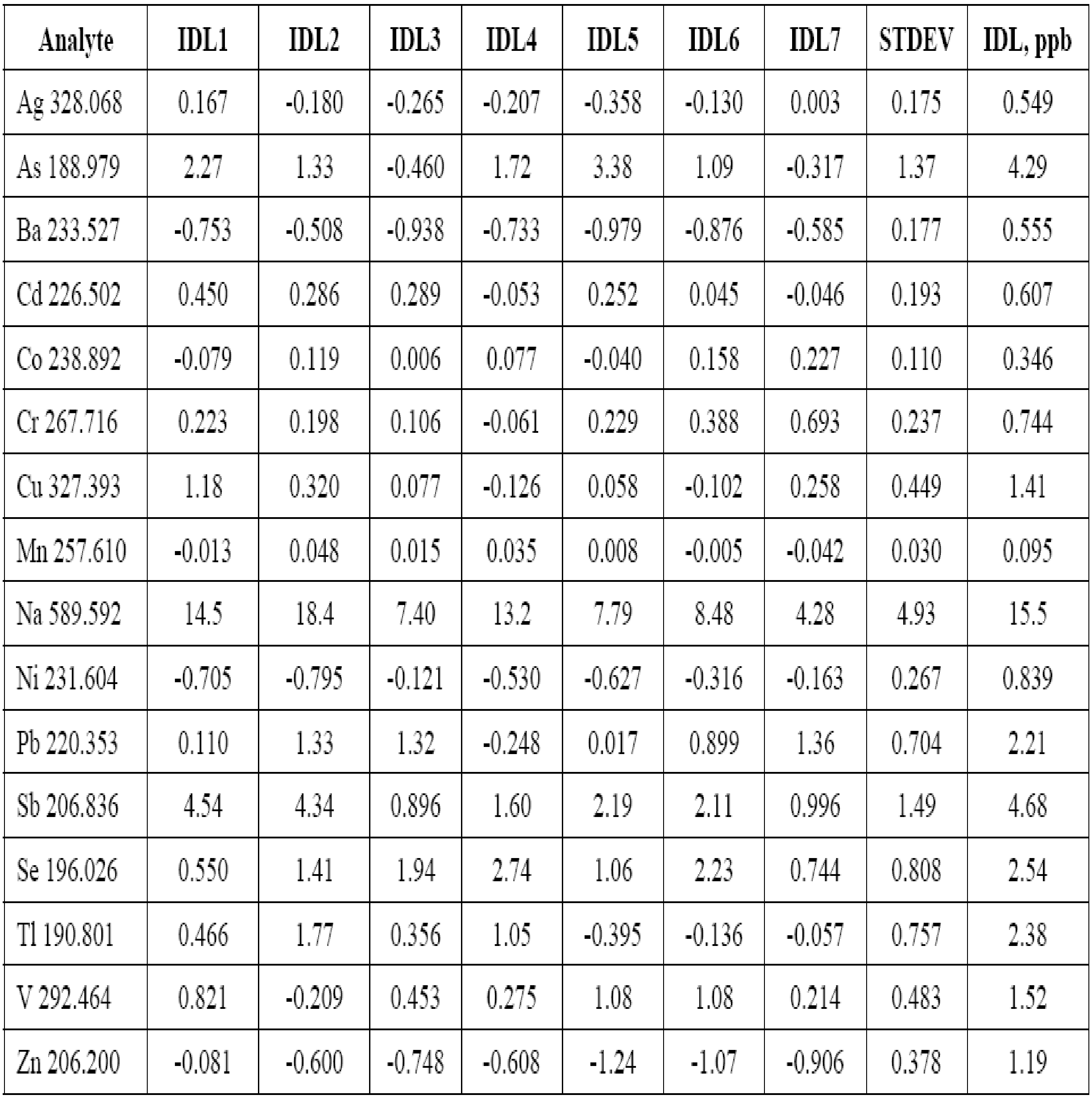


Figure 1. – Schematic Sketch of Set-up of Digestion Apparatus

Appendix C Detection limits of ICP Optical Emission

Following are the detection limits for the elemental analysis of by the ICP technique.

The table shows the detection limits of different elements which were provided by the manufacturer of the ICP instrument.



Analyte	IDL1	IDL2	IDL3	IDL4	IDL5	IDL6	IDL7	STDEV	IDL, ppb
Ag 328.068	0.167	-0.180	-0.265	-0.207	-0.358	-0.130	0.003	0.175	0.549
As 188.979	2.27	1.33	-0.460	1.72	3.38	1.09	-0.317	1.37	4.29
Ba 233.527	-0.753	-0.508	-0.938	-0.733	-0.979	-0.876	-0.585	0.177	0.555
Cd 226.502	0.450	0.286	0.289	-0.053	0.252	0.045	-0.046	0.193	0.607
Co 238.892	-0.079	0.119	0.006	0.077	-0.040	0.158	0.227	0.110	0.346
Cr 267.716	0.223	0.198	0.106	-0.061	0.229	0.388	0.693	0.237	0.744
Cu 327.393	1.18	0.320	0.077	-0.126	0.058	-0.102	0.258	0.449	1.41
Mn 257.610	-0.013	0.048	0.015	0.035	0.008	-0.005	-0.042	0.030	0.095
Na 589.592	14.5	18.4	7.40	13.2	7.79	8.48	4.28	4.93	15.5
Ni 231.604	-0.705	-0.795	-0.121	-0.530	-0.627	-0.316	-0.163	0.267	0.839
Pb 220.353	0.110	1.33	1.32	-0.248	0.017	0.899	1.36	0.704	2.21
Sb 206.836	4.54	4.34	0.896	1.60	2.19	2.11	0.996	1.49	4.68
Se 196.026	0.550	1.41	1.94	2.74	1.06	2.23	0.744	0.808	2.54
Tl 190.801	0.466	1.77	0.356	1.05	-0.395	-0.136	-0.057	0.757	2.38
V 292.464	0.821	-0.209	0.453	0.275	1.08	1.08	0.214	0.483	1.52
Zn 206.200	-0.081	-0.600	-0.748	-0.608	-1.24	-1.07	-0.906	0.378	1.19

The table shows detection limits of the elements tested on the instrument by analysing 20 correct readings in table to four significant figures during the research.

As 193.696	Cu 327.393	Cr 267.716	Ba 233.527	Cd 228.802	Mo 202.031	Ni 231.604	Pb 220.353	Sb 206.836	Zn 206.200	Se 196.026	Cd 214.440	Sb 217.582
0.009	0.0009691	0.00026161	0.000559	0.000783	0.004027	0.00235	0.011712	0.019498	0.001164	0.007907	0.000473	0.00749
0.007	0.0072936	0.0001819	0.000124	0.000622	0.005896	0.001918	0.005054	0.006509	0.001643	0.006823	7.87E-05	0.000898
0.014	8.43E-05	0.00061034	0.000486	6.76E-05	0.003268	0.000295	0.002674	0.010575	0.000842	0.014233	0.000121	0.008426
0.012	0.0004065	0.00025149	0.000249	0.000139	0.001473	0.00026	0.004953	0.010596	0.001039	0.013202	0.000329	0.010501
0.002	0.0001655	0.00037859	0.000321	0.000367	0.003196	0.000997	0.008702	0.00573	0.001519	0.027539	3.82E-05	0.007073
0.002	0.000854	0.00021946	0.000542	0.00034	0.001651	0.000247	0.002818	0.010399	0.001036	0.002838	0.000261	0.001066
0.014	0.000175	0.00091551	0.000184	0.000546	0.001647	0.001328	0.005188	0.010374	0.002667	0.012335	0.000314	0.006359
0.019	0.0003555	0.00068879	0.000362	0.000558	0.001887	0.000642	0.003431	0.007973	0.001637	0.016144	0.000454	0.004286
0.021	0.0006354	0.00071132	0.000479	0.000611	0.00273	0.00135	0.001829	0.010987	0.001849	0.021745	0.000735	0.011749
0.008	0.000646	0.00028273	1.92E-05	0.000719	0.000745	0.000937	0.008488	0.015713	0.000859	0.008012	0.001561	0.011501
0.023	0.0006734	0.00042768	0.000205	0.000378	0.004877	0.001942	0.010623	0.001142	0.001277	0.016707	0.000639	0.008432
0.013	0.0005503	0.00040456	0.000334	0.000153	0.001041	0.000788	0.003213	0.009256	0.001731	0.00347	0.00091	0.004688
0.012	0.0003377	0.00025986	0.000109	0.000351	0.00181	0.000446	0.002249	0.009715	0.000463	0.013325	0.000445	0.008642
0.018	0.0005284	0.00081621	0.000265	0.000175	0.002214	0.000963	0.00316	0.009452	0.001002	0.027939	0.00081	0.008513
0.023	0.0004996	0.00038652	0.000704	0.000468	0.002072	0.000636	0.010368	0.010065	0.000398	0.013724	0.000427	0.012385
0.008	0.0003315	0.00030424	0.000879	0.000397	0.003549	0.000491	0.000776	0.003432	0.002231	0.005145	0.000603	0.004979
0.003	0.0003538	0.0004856	0.000154	0.000556	0.002785	0.00152	0.001952	0.005205	0.001486	0.025879	0.000417	0.007453
0.021	0.0007033	0.00075009	0.000266	0.000378	0.002284	0.000791	0.005893	0.003981	0.000847	0.018082	0.000351	0.006552
0.029	0.0006007	0.00025159	0.000341	0.00038	0.004322	0.001514	0.002511	0.005452	0.002068	0.022778	7.69E-05	0.007374
0.034	0.0002334	0.00013661	0.000177	0.000193	0.001696	0.002407	0.004307	0.006714	0.001854	0.007552	0.000193	0.016575
0.04419	**0.00246**	**0.00131**	**0.00101**	**0.00123**	**0.00798**	**0.00327**	**0.01499**	**0.02592**	**0.00414**	**0.04281**	**0.00139**	**0.02324**