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Investigation of pyrolysis and electrokinetics as remediation techniques for the treatment of CCA-treated wood waste

By

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Investigation of pyrolysis and electrokinetics as remediation techniques for the treatment of CCA-treated wood waste

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Increasing volumes of Chromated Copper Arsenate (CCA) treated wood materials are being removed from service, either as a result of reaching the end of their service life or being replaced with non-treated wood materials. These materials, while not regulated as hazardous wastes, have the potential to leach toxic metals into the environment. Incineration and landfilling are not ideal disposal methods as incineration could result in the volatilization of carcinogenic arsenic and chromium, while landfilling requires the waste to be sorted and placed in appropriately lined landfills to prevent contaminant release. Viable disposal methods must be considered to manage the significant waste stream of CCA-treated wood.

This study investigates pyrolysis and electrokinetics (EK) as possible remediation techniques for the treatment of CCA-treated wood waste. A unique bench pyrolysis reactor was designed and optimized over three pyrolysis temperatures for retention of CCA metals within the char and bio-oil pyrolysis products. A batch pyrolysis system was constructed to produce large quantities of pyrolysis char for use in EK experiments. Mass balances were performed across both bench and batch pyrolysis systems, with

metal distribution trends ascertained. EK experiments were performed on the char generated during batch pyrolysis as well as CCA-treated wood waste to evaluate the efficiency of coupling the two technologies. These EK studies were performed using pH regulation at the cathode and applying constant current. Distribution of the CCA metals post-EK experiment was determined and removal efficiencies were calculated. The mobility of the CCA metals was evaluated during all phases of this investigation using Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), and Deionized Water Leaches to determine the likelihood of metal leaching under different environmental conditions.

DEDICATION

I would like to dedicate this dissertation to my husband, Joel, for his endless encouragement, support, and love, and to my daughter, Madeleine, for the boundless joy she brings to my life.

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CHAPTER I

INTRODUCTION

Wood is a commonly used building material that is susceptible to degradation when unprotected. Untreated wood is subject to attack by boring insects, fungal decay and micro-organisms, as well as weathering and mechanical stresses. Continual replacement and repair of damaged wood is costly; therefore, preservatives are applied to wood to prevent deterioration and prolong the service life of wood products. Many types of preservatives have been developed since the first patent for the chemical treatment of wood products was issued in 1832, with the three most recently utilized types being tar oils, organic solvents, and waterborne preservatives (Hunt and Garratt, 1967; Micklewright, 1998).

Chromated Copper Arsenate (CCA) is a waterborne preservative made from a combination of copper, chromium, and arsenic oxides, whose application protects against insect infestation and biological decay. Treatment with CCA can extend the useful life of a wood product by twenty to fifty years, when compared to untreated wood (Cooper, 2003). Given the potential to substantially increase service life, CCA was the most commonly used wood preservative in the U.S. for nearly 30 years, as seen in Figure 1.1 (Felton and De Groot, 1996; Gezer et al., 2006). Additionally, significant volumes of CCA-treated wood came to dominate the treated wood industry, as illustrated in Figure 1.2, and were utilized in a variety of construction applications (Solo-Gabriele and

Townsend, 1999). As these materials reach the end of their useful lives, this will necessitate the need for proper disposal of increasing volumes in coming years.

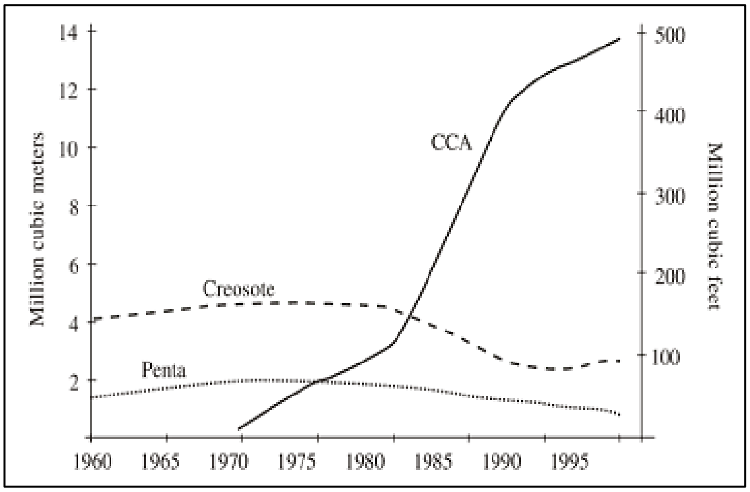


Figure 1.1 Annual Consumption of Treated Wood by Preservation Type, 1960-1996

Source: Felton and De Groot, 1996

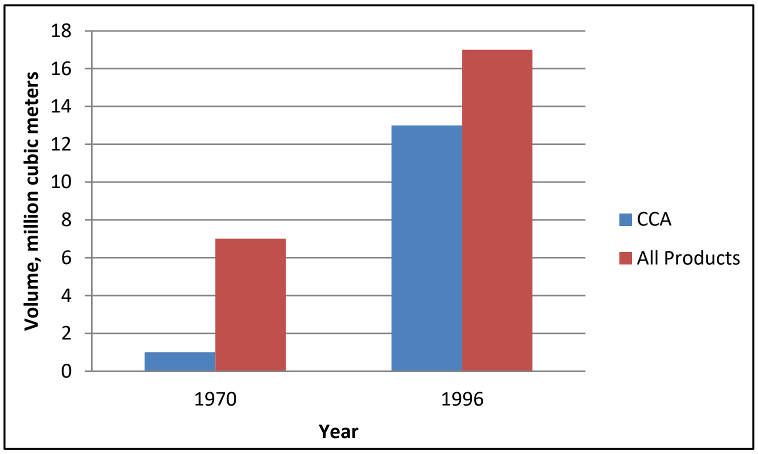


Figure 1.2 Volume of Treated Wood Products, 1970 and 1996

Source: Modified from Solo-Gabriele and Townsend, 1999

Although inorganic arsenic and hexavalent chromium are known carcinogens, and exposure to extremely high levels of copper can result in liver and kidney damage, CCA-treated wood waste is not classified by the Environmental Protection Agency (EPA) as a hazardous waste (U.S. Department of Health and Human Services, 2004, 2007, and 2012). The wood falls under specific regulations related to pesticides and wood treatment, and according to Title 40 Part 261.4b of the United States Code of Federal Regulations (45 FR 33119, 1980) is exempt from regulation as a hazardous waste. Reports from the EPA and the timber industry identify the primary disposal options for CCA-treated wood waste to include landfilling and incineration (Doyle and Malaiyandi, 1992; Cooper et al., 1993; Hinkley, 2003). While landfilling and incineration are not prohibited on a federal level, they present inherent environmental and sustainability concerns.

Landfilling, the most common disposal method, emphasizes containment of waste material via the use of different liners depending on the hazards of the waste (US EPA, 2017). As captured in Table 1.1, Subtitle D liners are utilized in solid waste landfills, while Subtitle C liners are utilized in hazardous waste landfills (US EPA, 2017). Although most modern landfills are lined to prevent interaction between the waste and surrounding environment, not all landfills are properly maintained. An additional concern arises when a waste has been delivered to an inappropriate landfill. Both of these scenarios can result in metals and other contaminants leaching from the waste, moving from the landfill, and contaminating the surrounding soil and groundwater. Exposure to high levels of arsenic and chromium in contaminated soil and groundwater through direct contact or ingestion ultimately increases risks of cancer as both arsenic and chromium are known carcinogens (U.S. Department of Health and Human Services, 2004, 2007, and 2012; Ohgami et al., 2015). Studies have indicated that as little as 2% of CCA-treated wood waste in a landfill can result in a landfill leachate concentration at least 50 times greater than the maximum toxicity concentration limits of 5 ppm for both chromium and arsenic (Hinkley, 2003; 55 FR 11798, 1990). In the absence of the existing exemption, CCA-treated wood waste would otherwise be classified as hazardous waste due to exceeding the 5 ppm concentration limits.

Table 1.1 Classes of Lined Landfills

Liner Type	**Landfill Type**	**Wastes Accepted**
Subtitle D	Municipal Solid Waste	Household
	Industrial Waste	Construction & Debris, Coal Combustion Residual
Subtitle C	Hazardous Waste	As defined in 40 CFR 261.3

Incineration of CCA-treated wood waste generates a metal-rich ash with concentrations up to 41,000 ppm chromium, 39,000 ppm copper, and 64,000 ppm arsenic (Doyle and Malaiyandi, 1992; Cooper et al., 1993; Hinkley, 2003). In many cases, as seen in Table 1.2, these concentrations are higher than the concentrations in the original treated wood waste (Solo-Gabriele and Townsend, 1999). This increased concentration is the result of complete CCA metals retention (i.e. metals are not destroyed by incineration) accompanied by significant mass reduction due to water loss and the breakdown of the wood structure. Use and disposal of the ash presents further problems due to the high mobility of the metals in the ash, and while the intention of incineration is the destruction of one waste stream, an additional waste stream is created (Solo-Gabriele and Townsend, 1999). Incineration of CCA-treated wood waste also produces arsenic oxides that sublime at approximately 540°C, which cannot be easily removed using existing air pollution control equipment. It is thought that the arsenic present in CCA-treated wood, in the form of arsenate (As^{+5}), is chemically reduced during incineration to the more hazardous arsenite (As^{+3}) (Helsen, 2000). Contact with or ingestion of the metals rich ash, contaminated soil or groundwater, or inhalation of the volatilized arsenic increases cancer risks.

Table 1.2 Comparison of CCA Metals Concentrations in Unburned CCA-Treated Wood and CCA-Treated Wood Ash

	Concentration (ppm)	
Metal	**Unburned Wood**	**Wood Ash**
Arsenic	1,200	33,000
Chromium	2,100	16,000
Copper	1,100	22,000

Source: Modified from Solo-Gabriele and Townsend, 1999

As more CCA-treated wood materials are taken out of service, either as a result of reaching the end of their service life or being replaced with non-treated wood materials, concerns surrounding the disposal options for CCA-treated wood waste will continue to grow. Some estimates indicate that over 16 million cubic meters of CCA-treated wood will be removed from service per year by 2020 (Humphrey, 2002; Cooper, 2003). Viable disposal methods must be investigated to manage the significant CCA-treated wood waste stream.

1.1 Wood Preservation

1.1.1 Wood Preservative Treatments

Multiple preservatives have been developed over the nearly 185 years since the first patent for the chemical treatment of wood products (Hunt and Garratt, 1967). The three main types of wood preservatives in recent history are tar oils, organic solvents, and waterborne preservatives (Hunt and Garratt, 1967; Micklewright, 1998). Characteristics of each preservative are provided in Table 1.3, and each type of preservative is described in more detail in the following sections. Preservative application methods are discussed in Section 1.1.2.

1.1.1.1 Tar Oils

Tar oils are most commonly known as "creosote" and are the product of high temperature distillation of coal tars, wood oils, solvents, petroleum oils, and light fuel oils. As such, creosote contains hundreds of organic compounds, most of which are grouped into one of the following categories: hydrocarbons, tar acids, and tar bases (Hunt and Garratt, 1967). Hydrocarbons, the largest fraction of organic compounds, provide significant protection from water damage and help prevent the leaching of water-soluble fractions of the preservative. This is achieved largely due to the hydrophobic nature of the hydrocarbon fraction and the formation of a thick layer on the exterior of the treated wood material. Tar acids and tar bases are typically toxic to many wood degradation agents, and are highly mobile within the wood matrix. This allows creosote preservative treatments to achieve high penetration within the wood product. Tar oil preservatives provide resistance to insect attack, biological deterioration, and moisture damage; however, products treated with creosote preservatives tend to emit strong odors, leach mobile portions of preservative solution over time, and render product surfaces un-paintable.

1.1.1.2 Organic Solvents

Organic solvents are preservatives that result from the mixing of different chemicals with petroleum oils to achieve improved preservative fixation within the wood matrix. Pentachlorophenol, one of the most recognizable organic solvent preservatives, was developed during the 1930's in the United States and is synthesized by chlorinating phenol. While organic solvent preservatives provide excellent resistance to moisture damage, they provide little resistance to insect attack. Additionally, they experience low fixation within the wood matrix and high volatility upon application to wood.

1.1.1.3 Waterborne Preservatives

Waterborne preservatives are formed from the mixture of inorganic ions with water. These preservatives readily and uniformly penetrate into the matrix of wood products, resulting in excellent resistance to insect attack and biological deterioration. Most waterborne preservatives are composed of two or more of the following elements: ammonium, arsenic, chromium, copper, mercury, and zinc. The most commonly used waterborne preservative for more than fifty years was Chromated Copper Arsenate (CCA), initially developed in the 1940's and produced using oxides of copper, chromium, and arsenic (Murphy, 2016). More detailed discussion on CCA-treated wood is provided in Section 1.2.2. In recent years, arsenic-free waterborne preservatives have been more widely available in response to concerns over arsenic exposure and usage restrictions. Examples of arsenic-free preservatives include Alkaline Copper Quarternary Compounds (ACQ) and Amine Copper Azole (ACA).

Table 1.3 Characteristics of Tar Oil, Organic Solvent, and Waterborne Preservatives

Preservative	**Penetration**	**Benefits**	**Challenges**
Tar Oil	High	Protection from moisture, insect attack, & biological deterioration	Emit strong odors; unpaintable surfaces; leach preservative over time
Organic Solvent	Low	Protection from moisture	Little resistance to insect attack; volatility after application
Waterborne	High	Resistance to insect attack & biological deterioration; paintable surface	Slight decrease in structural strength; may leach preservative over time

1.1.2 CCA-Treated Wood

The preservative CCA is generated through the combination of copper, chromium, and arsenic oxides. There are three different formulations of the preservative and each can be applied in different concentrations depending on the intended use of the wood. Chromium is utilized as a fixing agent in each formulation, improving the fixation of copper and arsenic compounds to the wood. Copper and arsenic oxides are the active fungicide and insecticide compounds, respectively, of CCA-treated wood. The different formulations, denoted as CCA Types A, B, and C, are provided in Table 1.4 (AWPA, 2000a). The most common formulation in the United States is Type C due to its lower leaching potential and demonstrated effectiveness, as compared to the other formulations (Groenier and Lebow, 2006).

Table 1.4 CCA Formulations

	Oxide %		
CCA Formulation	**CrO_3**	**CuO**	**As_2O_5**
Type A	65.5	18.1	16.4
Type B	35.5	19.6	45.1
Type C	47.5	18.5	34.0

Source: AWPA, 2000a

Fixation occurs when the chemical reactions between the copper, chromium, and arsenic oxides and the wood have reached completion (Cooper et al., 1993). These reactions are highly dependent on many factors including preservative formulation, processing and application techniques, variety of wood, as well as temperature, humidity, and airflow post-application (Lebow, 1996). Significant research has been performed to determine the effects of wood species on fixation, specifically in evaluating the fixation reactions of CCA with lignin, cellulose, and their model compounds (Dahlgren and Hartford, 1972; Arsenault, 1973; Smith and Williams, 1973; Kazi and Cooper, 2000; Kazi et al., 2000; Stevanovic-Janezic et al., 2000; Bull, 2001; Druz et al., 2001; Cooper et al., 2004; Nico et al., 2004; Radivojevic and Cooper, 2007; Radivojevic and Cooper, 2010; Murphy, 2016). While these investigations have been extensive, questions remain on the exact chemical mechanisms of fixation as some of the proposed chemical mechanisms are contradictory (Bull, 2001). Although consensus has not been reached on the specific mechanisms, a general fixation scheme is available. As illustrated in Table 1.5, the initial reaction includes the adsorption of Cr(VI) to wood, followed quickly by the reduction of free Cr(VI) to Cr(III) (Cooper et al., 1993). It is widely agreed that the fixation of all three CCA metals is facilitated by the reduction of Cr(VI) to Cr(III) (Radivojevic and Cooper, 2010; Murphy, 2016). Generation of Cr(III) is necessary for the co-precipitation of arsenic and creates favorable conditions for the cation-exchange fixation of copper (Dahlgren and Hartford, 1972; Smith and Williams, 1973).

Table 1.5 Scheme for CCA Fixation Reactions

Reactions	**Description**	**Products**
Initial (minutes)	Cu^{2+}, CrO_4^{2-} adsorption to wood	Cu^{2+}/wood Cr(VI)/wood
Main (hours/days)	Cr(VI) reduction	$CrAsO_4$ $Cu(OH)CuAsO_4$ $CuCrO_4$ $Cr_2(OH)_4CrO_4$ $Cr(OH)_3$ Cr(VI)/wood complexes Cr(III)/wood complexes Cr(II)/wood complexes

Source: Modified from Cooper et al., 1993

1.1.3 Wood Preservative Application Methods

1.1.3.1 Application Methods

There are two general wood preservative application methods: non-pressure and pressure processes. The desired retention level of preservative within the end product is the primary factor in determining the use of the two application methods. Non-pressure methods are typically utilized when little preservative protection is required, or when more thorough treatments are impractical (Lebow, 2010). Non-pressure processes can take the form of brush and spray, brief dipping, soaking, diffusion, and vacuum methods. Pressure processes are the most common preservative application methods and generally consist of immersing wood in a preservative in a high-pressure vessel and applying pressure to drive the preservative into the wood (AWPA, 2000b; Lebow, 2010). The overall process is illustrated in Figure 1.3. Wood is first placed into a steel cylinder, which is then closed, vacuum is applied, and the cylinder is filled with preservative while still under vacuum (Steps A-C). Pressure is applied, forcing preservative into the wood until the desired amount has been absorbed (Step D). The preservative is then pumped out, vacuum is pulled to remove any excess preservative from the surface of the wood, and the wood is finally removed from the cylinder (Steps E-F).

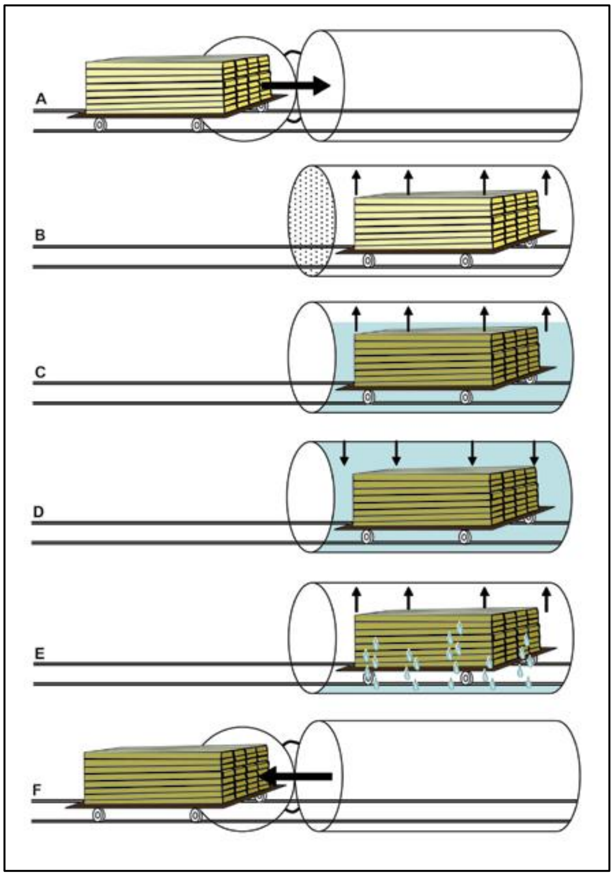


Figure 1.3 Steps in the Wood Preservative Pressure Treatment Process

Source: Lebow, 2010

1.1.3.2 Key Parameters

To achieve the desired preservative retention level multiple parameters must be considered, regardless of application method. These parameters include fluid penetration, treatment time, treatment pressure, and treatment temperature. The ability of wood to absorb preservatives through its pores is influenced by the surface tension of the preservative liquid, the diameter of the wood pore, and the angle of contact along the wood-liquid interface of the pore. The pore penetration rate, “R”, is given by Poiseuille’s equation:

$$R = \frac{P\, \pi\, r^4}{8\, v} = \frac{\pi\, d^3\; f\, \cos(\alpha)}{32\, v} \tag{1.1}$$

where: “P” = pressure developed by the capillary force

“r” = pore radius

“v” = coefficient of velocity of the preservative fluid

“d” = pore diameter

“f” = surface tension associated with the phase interface

“α” = contact angle.

Wood’s ability to absorb preservatives is directly related to the application time required to reach the desired preservative retention level. Products requiring higher retention levels will often necessitate longer treatment times (e.g. days vs. hours). Treatment pressures and temperatures are similarly dependent on the nature of the wood and preservative used, though these parameters are set according to American Wood Protection Association (AWPA) standards (Lebow, 2010).

1.2 CCA Waste Regulations

Historically, CCA-treated wood was used in multiple capacities including utility poles, decking, lumber for homes, railroad ties, and a variety of marine applications. Despite its widespread, successful use over several decades, CCA-treated wood began to fall out of favor by the 1980’s due to concerns about human contact with the CCA metals. Although the CCA treatment method provides excellent fixation when compared to other preservatives, the potential exists for the CCA metals to leach from the wood. Several studies have indicated that CCA metals can leach from treated wood products over the products' lifetimes (Townsend et al., 2003; Townsend et al., 2004, Townsend et al. 2005; Stook et al., 2005; Mercer and Frostick, 2012, 2014; Gress et al., 2014). It has been found that both copper and arsenic leach at higher rates when compared to the leaching rate of chromium and that the leaching rate of all CCA metals is increased when the treated wood product is in contact with water or installed below ground (Stook et al., 2005). Additionally, wet wood was found to contain 3-4 times more dislodgeable arsenic than dry wood (Gress et al., 2015).

The fact that all three CCA metals leach from treated wood products coupled with concerns over exposure to those metals has led to regulations governing CCA usage. Nearly twenty years ago, states began limiting its use in previously-common applications such as in residential decking, children's playground equipment, and utility poles. For example, in 1994 New Jersey prohibited the use of CCA-treated products in marine settings where shellfish were present, while in 2002 New York declared that new playgrounds must be constructed with non-CCA-treated wood. The same year (2002) the EPA announced a voluntary decision by the wood treatment industry to phase out CCA-treated wood products from the consumer market (Gezer et al., 2006). By 2004, the EPA restricted the use of CCA-treated wood to industrial and commercial applications, such as pilings and structures in marine facilities, foundations, bridge components, guardrails, and posts. This restricted use significantly impacted the CCA preservative industry as smaller quantities of CCA-treated wood products are being produced than in the past (Gezer et al., 2006).

Although smaller volumes of CCA-treated wood are currently being produced, it is expected that large volumes of CCA-treated wood will be removed from service as products installed decades ago reach the end of their serviceable life. When considering typical concentrations of CCA metals in the wood products historically in use, nearly 24 million tons of CCA metals will be available for disposal over the next several years. While the volume of CCA-treated wood waste slated for disposal is expected to decrease after 2020 due in large part to the current reduction in new CCA-treated products, an effective and efficient method for recovering and recycling CCA metals is needed.

1.3 CCA Waste Management Practices

Management of CCA-treated wood waste is crucial due to a variety of factors including efforts to minimize the amount of material going to landfills, particularly those landfills containing potentially hazardous components. Cooper (2003) proposed a hierarchy of handling/disposal alternatives, and each is reviewed in the following sections:

- Abatement, elimination, or reduction
- Reuse
- Refining for recycling
- Extraction of CCA metals
- Thermal destruction

1.3.1 Abatement, Elimination, or Reduction

The philosophy behind this handling option is that the amount of CCA-treated wood waste requiring disposal is minimized by simply treating less wood with CCA. Restricting CCA-treated wood to industrial usage will reduce the amount of CCA-treated wood waste requiring disposal, but over a long period of time. Utilizing alternative wood preservatives in the place of CCA in both consumer and industrial settings can also achieve a desired reduction. Even more simply, minimizing waste during construction and performing routine maintenance on in-service material can contribute to the overall reduction in CCA-treated wood waste (McQueen and Stevens, 1998; Cooper, 2003).

1.3.2 Reuse

Wood products that have not experienced physical or biological deterioration but have been removed from service have the potential to be reused in another capacity (Cooper, 2003). While separating the CCA-treated wood from other wood products in industrial settings may be difficult and in turn hinder the reuse process, the opportunity still exists. Residential CCA-treated wood may be easier to reuse on-site by individuals; however, discretion must be used to ensure the material is utilized in a safe manner. If spent residential CCA-treated wood is collected and utilized off-site there may be additional concerns regarding structural integrity due to damage caused by nails and dismantling of first-use structures (Cooper, 2003).

1.3.3 Refining for Recycling

Significant efforts have been made to investigate the use of CCA-treated wood waste in a variety of composite materials. Prior to use in composites, most CCA-treated wood products must be ground to smaller particle sizes than their initial use required. Issues surrounding the use of CCA-treated wood waste in composites include the loss of chain of ownership, the quality of spent wood product, as well as the potential use in interior applications (Konasewich et al., 2001; Cooper, 2003). Some of the more promising research has been conducted in utilizing CCA-treated wood waste in wood cement composites, thermoplastic polymers/wood composites, and exterior flakeboard products (Cooper, 2003). In most applications "out of service" CCA-treated wood provides protection in a similar manner to the wood's original use, while in other applications it provides other advantages such as lighter weight and higher strength to weight properties (Cooper, 2003). Ultimately, however, the risk of exposure to CCA metals and disposal concerns continue to limit refining as a viable long-term management practice.

1.3.4 Extraction of CCA Metals

Biological and chemical extraction techniques have all been investigated as methods to remove CCA metals from CCA-treated wood waste. Significant success has been achieved in extracting the different CCA components by using organisms that secrete mineral or organic acids (Cooper, 2003). Naturally occurring brown rot fungi has been identified as being capable of releasing arsenic and chromium while retaining copper (Stephan and Peek, 1992; Peek et al., 1993). Removal of the remaining copper can then be achieved by bacteria or ammonia extraction (Stephan et al., 1996). Biosorption, utilizing fungal, bacterial, and yeast has also proven successful at removing CCA metals (Dhillon et al., 2017). Dual remediation practices are frequently required to extract all three CCA components from treated wood waste, as solely using biological means is often insufficient for metals removal. For example, bacteria exposure alone released nearly 100% of copper, 98% of chromium, but only 48% of arsenic (Clausen 1997; Clausen and Smith, 1998; Clausen, 2000). Combining bacteria exposure and oxalic acid extractions improved the release of arsenic to 80% (Clausen, 2000).

The successful release of CCA metals using organic acids led to investigations into the use of synthetic acids and other extractants (Cooper, 2003). Many of the constraints of using biological extraction (temperature, pH, sterility, etc) are eliminated by using chemical extraction (Cooper, 2003). Relatively high removal efficiencies have been achieved by using a variety of extractants including: organic acids and ligands, sulfuric acid, hydrogen peroxide, bioxalate solution with a sodium hydroxide, and supercritical fluids modified with chelating agents (Velizarova et al., 2004; Clausen, 2000; Cooper, 1991; Hingston et al, 2001; Gezer, 2006; Kartal, 2003; Kazi and Cooper, 2006; Kakitani et al., 2006; El-Fatah et al., 2004; Takeshita et al., 2000; Stephan et al., 1993; Kamdem at al., 1998; Kazi and Cooper, 1999; Coudert et al., 2014). Although biological and chemical extraction have demonstrated high removal efficiencies for the CCA metals, the costs associated with the extraction techniques are high and thus limit their potential as CCA-treated wood waste management practices.

Electrokinetic (EK) remediation is an additional extraction technique capable of removing CCA metals from treated wood waste. The application of low voltage direct current to the treated wood waste mobilizes the metallic ions, facilitating the release of the metals from the wood. EK remediation has a number of advantages when compared to biological and chemical extraction techniques, including the limited use of solvents and temperature and pressure variations. Due to these advantages, EK remediation is discussed in detail in Section 1.4.

1.3.5 Thermal Destruction

The breakdown of CCA-treated wood waste via thermal methods has the potential to reduce the volume of waste material and recover energy (Cooper, 2003; Helsen and Van den Bulck, 2005). The relationship between incineration (or combustion), gasification, and pyrolysis, the three thermal destruction methods, is captured in Figure 1.4. All three methods convert the wood waste into more useful forms; however, incineration generates heat that must be used immediately, while gasification and pyrolysis create secondary energy carriers. Gasification generates a fuel gas with heating values between 5-20 MJ $^{m-3}$ and pyrolysis generates three products: solid char, bio-oil (i.e. pyrolysis liquid), and gas (Helsen and Van den Bulck, 2005).

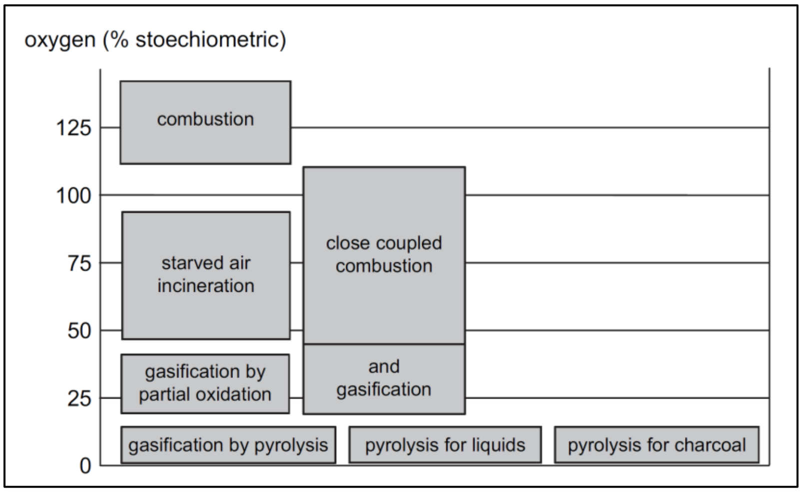


Figure 1.4 Relationship and Oxygen Requirements of Thermal Destruction Methods

Source: Helsen and Van den Bulck, 2005

Volatilization of arsenic is a primary concern when using any of the thermal destruction methods; however, this volatilization can be reduced through oxygen and temperature control making gasification and pyrolysis improved thermal destruction options (Cooper, 2003). In fact, arsenic may be completely converted to the more easily captured metallic arsenic during high temperature gasification (Lagoutte and Garnier, 2001; Helsen and Van den Bulck, 2005; Nzihou and Stanmore, 2013). Arsenic removal efficiencies of over 99.6% have been achieved utilizing hot filter technology on cooled gasification product gas (Kramb et al., 2016). Additionally, studies have indicated that pyrolysis at temperatures lower than 400°C with short reaction times (≤10 minutes) result in negligible losses of copper and chromium and approximately 10 percent arsenic (Helsen et al., 1999). Studies have also found that soils amended with metals-rich biochar experience reduced metal mobility when compared with non-pyrolysed wood (Mitchell, et al., 2017). The potential for reduction in waste material and improved recovery and recycling of CCA metals makes pyrolysis a potentially viable management practice. As such, pyrolysis is discussed in detail in Section 1.5.

1.4 Electrokinetic Remediation

Electrokinetic (EK) remediation is a technology capable of removing contaminants from a variety of porous media. It has the capacity to isolate and recover potentially valuable components while rendering a previously contaminated media clean. EK remediation has been demonstrated to be highly successful in removing contaminants from polluted soils and investigations into the removal of CCA metals from out of service wood have been promising. Results of one EK study produced removals of 93% copper, 95% chromium, and 99% arsenic (Cooper, 2003).

1.4.1 Electrokinetics Overview

Electrokinetic remediation has its origins as a remediation alternative for contaminated soils (Ribeiro et al., 2000; Sarahney et al., 2005; Pedersen et al., 2005; Ottosen et al., 2003). Electrokinetic processes involve creating an electric field by applying a direct current (DC) to electrodes inserted in contaminated media (Ribeiro et al., 2000; Sarahney et al., 2005; Pedersen et al., 2005; Ottosen et al., 2003). Application of a DC field across any media involves a number of phenomena including electroosmosis, electrophoresis, electromigration, diffusion, streaming potential, sedimentation potential, and water electrolysis. Detailed discussion of each is provided in the following sections.

1.4.2 Electroosmosis

Electroosmosis is the transport of pore fluids in media under the influence of an electric field. Multiple theories describing electroosmotic flow including the Hemholtz-Smoluchowski, Ion Hydration, Schmid, and Spiegler Friction Model theories [Gray and Mitchell, 1967; Mitchell, 1993]. The most widely accepted of these theories is the Hemholtz-Smoluchowski (H-S) Theory.

According to the H-S Theory, electroosmotic flow results from the transportation of positively charged ions from the anode to the cathode. During the transportation from anode to cathode, fluid surrounding the positively charged ions is moved as well. The end result is movement of fluid across the media due to the applied electric field. The bulk electroosmotic velocity (the rate at which the fluid moves) can be approximated by Equation 1.2 (Probstein and Hicks, 1993).

$$U_{EO} = \frac{\varepsilon \, \xi \, E}{\mu} \tag{1.2}$$

where: U_{EO} = Electroosmotic Velocity, $\left(cm^2/volt \cdot \sec\right)$

ε = Permittivity of the Solution, $\left(amp \cdot \sec / volt \cdot cm\right)$

ξ = Zeta Potential, $\left(volt\right)$

E = -[Gradient of Electric Potential], $\left(volt/cm\right)$

μ = Viscosity of the solution, $\left(gram/cm \cdot \sec\right)$

1.4.3 Electrophoresis

Electrophoresis is the movement of charged particles through a liquid phase under the influence of an electric field. The same forces are responsible for both electroosmotic and electrophoretic phenomenon; however, in electrophoresis the charged particle is induced to move toward an electrode with an opposite charge along with the pore fluid.

1.4.4 Electromigration

Electromigration occurs when positively and negatively charged ions migrate to the oppositely charged electrodes during the application of a DC electric field. The effective electron mobility estimates how quickly the ions will migrate to the oppositely charged electrode, and can be approximated by Equation 1.3.

$$U^* = \frac{D^* \, Z \, F}{R \, T} \tag{1.3}$$

where: U^* = Effective Ionic Mobility, $\left(cm^2/volt \cdot \sec\right)$

D^* = Effective Diffusion Coefficient, $\left(cm^2/\sec\right)$

Z = Ionic Valence, $\left(\pm e^-\right)$

F = Faradays Constant, $(coulombs)$

R = Universal Gas Constant, $(joule/Kelvin \cdot mole)$

T = Absolute Temperature, $(Kelvin)$

The effective diffusion coefficient is given by Equation 1.4.

$$D^{*} = D\,\tau\,\eta \tag{1.4}$$

where: D = Ionic Diffusion Coefficient at infinite dilution, $(cm^2/\sec)$

τ = Tortuosity of the medium

η = Porosity of the medium

1.4.5 Diffusion

Diffusion is the migration of ions from regions of higher concentrations to regions of lower concentration without the presence of an electric field. Fick's Law governs the diffusive molar flux of a chemical species due to a concentration gradient driving force and is provided in Equation 1.5.

$$J = -D^{*}\frac{d(c)}{dx} \tag{1.5}$$

where: J = Molar Flux, $(mole/cm^2 \cdot \sec)$

D^* = Effective Diffusion Coefficient, $(cm^2/\sec)$

c = Concentration at point x $(mole/cm^3)$

x = distance (cm)

1.4.6 Water Electrolysis

Water is transported toward electrodes when direct current is applied across a wet medium. Oxidation of water occurs at the interface of the anode, while reduction of water occurs at the interface of the cathode. Equations 1.6 and 1.7 capture the reactions at the anode and cathode, respectively.

$$2H_2O \rightarrow O_2\,(g) + 4H^+ + 4e^- \tag{1.6}$$

$$2H_2O + 2e^- \rightarrow H_2\,(g) + 2OH^- \tag{1.7}$$

1.5 Pyrolysis

Pyrolysis is the thermochemical conversion of biomass in the absence of oxygen to produce solid char, condensable liquids (bio-oil), and gases (Diebold and Bridgewater, 1997). It is also the initial reaction for combustion and gasification reactions (Maschio et al., 1992; Diebold and Bridgewater, 1997; Gronli and Melaaen, 2000; Bridgewater, 2004; Mohan et al., 2006; Zhang et al., 2006). Controlled pyrolysis (the thermal breakdown of biomass in the absence of oxygen) of CCA-treated wood waste has been identified as an improved alternative to incineration. It has been suggested that the low temperatures and lack of oxygen associated with pyrolysis provide distinct advantages over combustion as they lead to lower metal losses in comparison to incineration (Helsen et al., 1999). While high concentrations of the CCA metals are found in the char generated during pyrolysis, investigations indicate that the metals can be separated from the char matrix.

1.5.1 Pyrolysis Overview

Biomass pyrolysis has been utilized for centuries in a variety of capacities including the collection of embalming materials in ancient Egypt, the generation of charcoal during the early industrial period of the 1800's, as well as the distillation of tar chemicals and production of non-condensing gases for use in boilers in the early part of the 20th century (Maschio et al., 1992). The generally accepted reaction sequence for the pyrolysis of biomass is contained in Equations 1.8 through 1.10, below (Demirbas, 2004):

$$\text{Biomass} \rightarrow \text{Water} + \text{Unreactive residue} \quad (1.8)$$

$$\text{Unreacted residue} \rightarrow (\text{Volatile} + \text{Gases})_1 + (\text{Char})_1 \quad (1.9)$$

$$(\text{Char})_1 \rightarrow (\text{Volatile} + \text{Gases})_2 + (\text{Char})_2 \quad (1.10)$$

This reaction sequence is thought to occur partly due to the thermal degradation properties of the structural constituents of biomass: hemicellulous, cellulose, and lignin (Meier and Faix, 1999; Gronli and Melaaen, 2000; Demirbas, 2001; Demirbas and Arin, 2002; Zhang et al., 2006). Essentially, each component degrades at a specific rate which in turn influences the overall reaction mechanism, as well as the reaction products.

1.5.2 Pyrolysis Products

Each of the pyrolysis products has its own characteristics and potential valued use. Physical characteristics of char, one of the dominant pyrolysis products, are highly dependent on the characteristics of the original feedstock as well as the reactor conditions (Diebold and Bridgewater, 1997). Char has the potential to be used in furnaces and boilers due to its heating value and volatility (approximately 14,000 BTU/lb and 15 to 45 wt%, respectively) (Diebold and Bridgewater, 1997).

Non-condensable gases formed during pyrolysis of biomass are best characterized as a mixture of primary and secondary gases, each composed of carbon dioxide, carbon monoxide, hydrocarbons, and hydrogen (Diebold and Bridgewater, 1997). The significant difference between the primary and secondary gases is the percentage of each component gas (CO_2, CO, hydrocarbons, and H_2) (Diebold and Bridgewater, 1997). Although the heating value of the gases ranges between 280 – 510 BTU/SCF, the gases typically cannot be utilized on site to fuel the pyrolysis reactor, and they require reforming and shifting to be viable as a synthesis gas (Diebold and Bridgewater, 1997).

Pyrolysis liquid, or bio-oil, generated during the pyrolysis of biomass consists of a complex mixture of water and organic compounds that have been condensed following pyrolysis reactions (Diebold and Bridgewater, 1997; Bridgewater, 2004). This mixture contains molecular fragments of cellulose, hemicellulose, and lignin polymers, which can make identifying all individual components difficult (Diebold and Bridgewater, 1997; Bridgewater, 2004). Elemental analysis indicates that biomass-derived bio-oil is comprised of mostly carbon, oxygen, and hydrogen (Maschio at al., 1992; Siplia et al., 1998; Diebold and Bridgewater, 1997; Oasmaa and Czernik, 1999; Bridgewater, 2004; Demirbas and Arin, 2002; Demirbas, 2007). Potential bio-oil uses include being the primary combustion fuel source in furnace/boiler operations, diesel engines, and turbines. In one respect, the biomass derived fuel is considered CO_2 neutral, has a low sulfur content, and is a liquid so it can be easily stored and transported (Diebold and Bridgewater, 1997; Meier and Faix, 1999; Oasmaa and Czernik, 1999; Bridgewater, 2004; Czernik and Bridgewater, 2004). Unfortunately, bio-oil has relatively poor volatility, high viscosity, is capable of coking, and is highly corrosive, all of which limit the use of crude bio-oil (Oasmaa and Czernik, 1999; Bridgewater, 2004; Czernik and Bridgewater, 2004). Other potential uses are available that do not involve upgrading to transportation fuels but may require additional refining of the bio-oil: flavorings (e.g.

liquid smoke), fertilizers, wood preservatives, specialty chemicals, etc. (Diebold and Bridgewater, 1997; Bridgewater, 2004; Czernik and Bridgewater, 2004).

1.5.3 Types of Pyrolysis

Pyrolysis can be divided into types depending on the operating parameters of a given system. The parameters of interest are typically the temperature range, heating rate, residence time, and biomass particle size. Although there is variability in the exact operating conditions, there are at least three distinct types of pyrolysis: conventional, fast, and flash. Table 1.6 contains the accepted operating parameters for each type of pyrolysis.

Table 1.6 Operating Parameters for Pyrolysis Processes

	Pyrolysis Types		
	Conventional	**Fast**	**Flash**
Temperature (K)	550-950	850-1250	1050-1300
Heating Rate (K/s)	0.1-1	10-200	>1000
Particle Size (mm)	5-50	<1	<0.2
Residence Time (s)	450-550	0.5-10	<0.5

Source: Demirbas and Arin, 2002

Numerous studies have been performed to determine the precise effects of the different operating parameters on the pyrolysis of biomass. The overwhelming conclusion is that product distribution is directly linked to the type of pyrolysis, and that temperature and heating rate are the most significant variables (Maschio et al., 1992; Diebold and Bridgewater, 1997; Bridgewater, 2004; Zhang et al., 2006; Demirbas and Arin, 2002; Demirbas, 2007). For example, when char is the desired product, conventional pyrolysis should be used; however, if bio-oil is the desired product it is better to operate under fast pyrolysis conditions (Bridgewater, 2004; Demirbas and Arin, 2002; Demirbas, 2007).

1.5.4 Pyrolysis Reactors

A variety of reactor types are available for virtually all modes of biomass pyrolysis; however, it is imperative to have a reactor system capable of operating in such a manner as to generate the desired product. Six of the more applicable reactor designs for fast pyrolysis include fluidized bed, circulating fluidized bed, ablative, rotating cone, vortex, and vacuum reactors (Meier and Faix, 1999). Each is illustrated in Figure 1.4. One of the more important aspects of each reactor is that the systems are capable of separating out the individual reaction products. This is vital for industrial purposes as each product has the potential to be marketed for particular uses, as noted in Section 1.5.2. The most widely used reactor design is that of a fluidized bed reactor, followed closely by the circulating fluidized bed (Meier and Faix, 1999). These particular designs maximize the contact area between the heating element and the biomass particles to aid in rapid heat transfer. Similarly, the newer designed ablative reactor focuses on maximizing the potential for heat transfer through direct contact, and is successfully being used for fast pyrolysis applications (Meier and Faix, 1999). Rotating cone reactors operate similarly to fluidized bed reactors in that they utilize beds (typically sand) for even distribution of heat, but they also employ the use of the cone walls for direct heating through contact and do not require a carrier gas (Meier and Faix, 1999). Vortex reactors operate by heating through direct contact with the reactor wall, while vacuum reactors rely on molten salt and close contact to heat plates for successful pyrolysis (Meier and Faix, 1999).

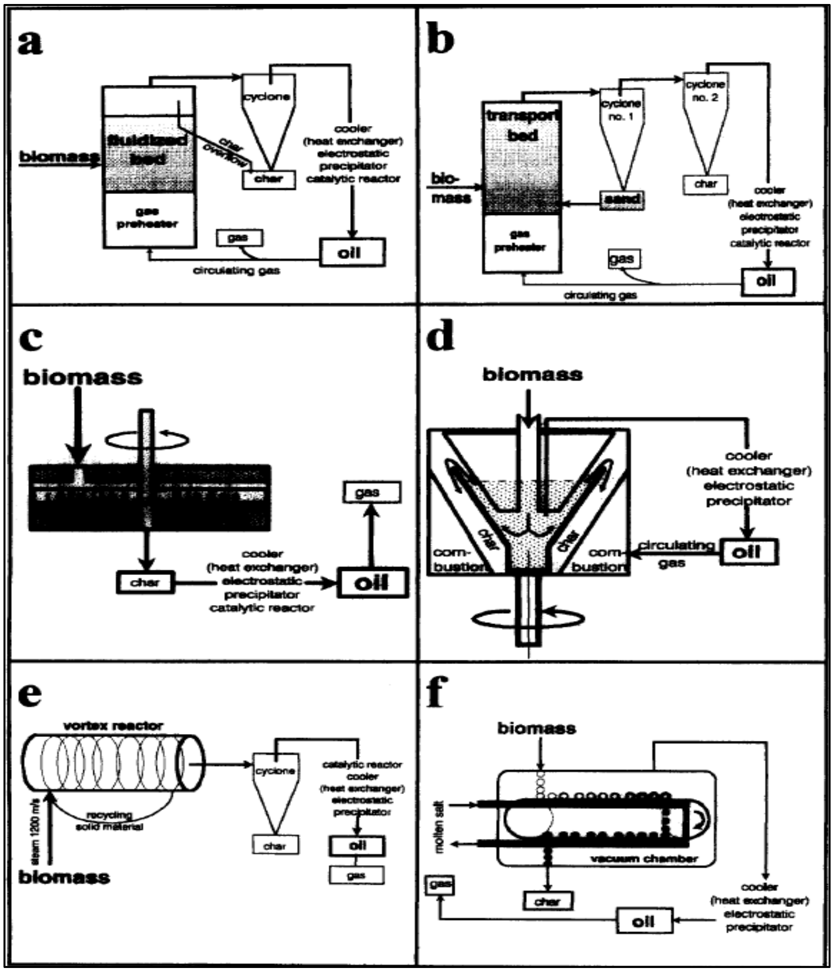


Figure 1.5 Schematic Illustrations of Pyrolysis Reactors

Note: a) Fluidized bed, b) Circulating fluidized bed, c) Ablative, d) Rotating cone, e) Vortex, f) Vacuum; Source: Meier and Faix, 1999

Pyrolysis offers the opportunity to generate three primary products (char, bio-oil, and non-condensable gases), each of which is potentially valuable. While many variables need to be considered during the pyrolysis of biomass, including the type of pyrolysis and the reactor used, these must be evaluated based on the production of the most desired product.

1.6 Research Objectives

Previous research, largely performed on newly treated wood, has indicated that neither pyrolysis nor electrokinetics are singularly viable disposal or treatment options for CCA-treated wood waste. For example, challenges remain with respect to high concentrations of CCA metals in pyrolysis char, as well as with the costs of using chemical pre-treatments and long operational periods. The primary objective of this study is to determine the feasibility of coupling pyrolysis and electrokinetic techniques to remediate "out of service" CCA-treated wood waste. Secondary objectives include:

- Optimizing a bench pyrolysis system for maximum bio-oil production and CCA metal retention;
- Evaluating the mobility of CCA metals in pyrolysis char;
- Determining the efficiencies of a lab-scale electrokinetic system for removal of CCA metals from pyrolysis char; and
- Evaluating the mobility of CCA metals in post-EK pyrolysis char.

CHAPTER II

LITERATURE REVIEW

The following sections contain technical reviews of the pyrolysis and electrokinetic studies performed on CCA-treated wood. Findings from these studies provide the background for this research.

2.1 Pyrolysis Studies

Multiple studies conducted over the past two decades investigated the pyrolysis of CCA-treated wood. A summary of operating conditions and results is provided in Table 2.2 at the end of Section 2.1. Key areas of study include mass reduction, metal distribution (mass balances) and metal behavior. Each area of study is discussed in the following sections.

2.1.1 Mass Reduction

As previously discussed, the large volume of CCA-treated wood waste generated by the removal of treated wood products from active service is a concern. If landfilled, disposal will require expansive amounts of landfill space. Research conducted by Van den Broeck, Helsen, and co-authors as well as Kakitani et al. investigated the mass reduction of CCA-treated wood through pyrolysis. Mass reductions ranging between 56% and 63% were reported by Helsen et al. (1997, 1998) and Van den Bulck (2001), while Kakitani et al. (2004) reported to achieve mass reductions between 50% and 77%.

The differences in percent mass reduction are due to variation in operating conditions, as varying pyrolysis temperatures and residence times impacts percent mass reduction. It was determined that the presence of CCA metals lowers the temperature at which pyrolysis begins, as well as the temperature at which the maximum rate of decomposition occurs (Hirata et al., 1993; Helsen and Van den Bulck, 2001; Fu et al., 2008). It was also concluded that the pyrolysis of CCA-treated wood led to the formation of more char than the pyrolysis of untreated wood (Hirata et al., 1993; Helsen and Van den Bulck, 2001). As expected, pyrolysis at higher temperatures produces higher yields of bio-oil as compared to yields of char (Hata et al., 2001; Fu et al., 2007).

2.1.2 Metal Distribution

Mass balances were performed on the char, bio-oil, and gases produced during pyrolysis of CCA-treated wood. Variation in metal distribution between the three pyrolysis products occurred; however, the majority of the metals remained in the char, followed by the bio-oil, and the remainder released as non-condensable gases. Despite lack of complete closure on the mass balances (due to sampling/analysis error) overall trends were identified:

1. Copper and chromium remained in the char in weight percentages of 94% to 100% and 18% to 97%, respectively over a wide range of operating conditions (Helsen and Van den Bulck, 1997, 2001; Helsen et al. 1997, 1998; Hirata et al., 1993; Fu et al., 2007). Extraction studies determined that chromium is more strongly bound in the char when compared to CCA-treated wood (Helsen et al., 1998; Helsen and Van den Bulck, 2001; Kakitani et al. 2004a).

2. Bio-oil concentrations of copper and chromium were low- approximately 4% and 0.05%, respectively (Helsen and Van den Bulck, 1997, 2001; Helsen et al. 1997, 1998).
3. Arsenic was determined to be the primary metal of concern as releases as high as 55% were recorded in the non-condensable gases. Additionally, arsenic retention in the char ranged from 36% to 94% and approximately 3% was retained in the bio-oil (Hata et al., 2001, 2004; Helsen and Van den Bulck, 1997, 2001; Helsen et al. 1997, 1998; Hirata et al., 1993; Fu et al., 2007; Kakitani et al., 2004b). In general, concentrations of arsenic in bio-oil increased at lower pyrolysis temperatures (350 °C) and longer pyrolysis times (60 minutes) (Hata et al., 2001).

2.1.3 Metal Behavior

Abundant arsenic release during the pyrolysis of CCA-treated wood has led to additional investigations targeted toward determining the chemical changes CCA-metals undergo during pyrolysis. Ottosen et al. (2005) reported that a redistribution of CCA within the wood will occur during pyrolysis because cellulose and hemicellulose are decomposed. This decomposition leads to the formation of reducing gases, such as carbon monoxide, which may then interact with present metal oxides resulting in highly reducing conditions (Helsen and Van den Bulck, 2005; Kercher and Nagle, 2001). Specific thermogravimetric (TG) studies with model compounds were performed by Helsen et al. (2004) and Kercher and Nagle (2001) to predict the thermal behavior of CCA-treated wood. Their primary conclusions (with respect to thermal behavior) of these studies are provided in Table 2.1.

Table 2.1 Conclusions From Thermogravimetric Studies with Model Compounds

Model Compound	**Conclusion**
As_2O_3	Volatilization occurs at 200 °C due to high vapor pressure
As_2O_5	No volatilization at $T<600$ °C; no influence of O_2; lower volatilization temperature in H_2
CuO	Thermal decomposition strongly dependent on O_2 content; Decomposition temperature = 775 °C in N_2, 1050 °C in air, 200 °C in H_2/N_2 mixture
Cr_2O_3	No significant reactions occur when heated in inert or air atmospheres
CuO + As_2O_5	Fraction of As volatilizes at $T<600$ °C, remainder forms mixed copper arsenates with Cu; strong atmosphere effects on thermal decomposition of copper arsenates, no decomposition in air at $T<900$ °C
Cr_2O_3 + As_2O_5	Free arsenic (V) oxide volatilizes, remainder forms chromium arsenate with Cr which then decomposes
As_2O_5 + Glucose	N_2 and N_2/O_2 atmospheres promote faster decomposition of As_2O_5 and glucose; 10% O_2 insufficient to reverse $As_2O_5 \rightarrow As_2O_3 + O_2$
As_2O_5 + Activated Carbon	Activated carbon promotes decomposition of As_2O_5 at $T>300$ °C
As_2O_5 + Wood	Products from pyrolysis promote volatilization of As_2O_5; rate of arsenic volatile loss increases with temperature
CuO + Wood	Reduction of copper (II) oxides at 305 °C

Source: Modified from Helsen and Van den Bulck, 2005

TG experiments performed on CCA-treated wood, not the model compounds, revealed additional information about the possible reactions that take place during pyrolysis of CCA-treated wood. These include the volatilization of unreacted As_2O_5 and the formation and decomposition of both $Cr_2As_4O_{12}$ and $CrAsO_4$, as they relate to arsenic release. Hata et al. (2003) contributed the percentage of arsenic released at 300 °C (20%) to the volatilization of unreacted As_2O_5, expressed by Kakitani et al. (2004a,b) as:

$$2As_2O_5 \leftrightarrow 2As_2O_3 + 2O_2 \tag{2.1}$$

$$2As_2O_3 \leftrightarrow As_4O_6 \tag{2.2}$$

$Cr_2As_4O_{12}$ is formed during the impregnation of the treated wood and decomposes only at temperatures higher than 700 °C by the following (Hata et al., 2003):

$$As_2O_5 + 2C \rightarrow As_2O_3 + 2CO \tag{2.3}$$

$$2CrO_3 + 2As_2O_3 \rightarrow Cr_2As_4O_{12} \tag{2.4}$$

$$Cr_2As_4O_{12} \rightarrow As_2O_5 \tag{2.5}$$

Other possible arsenic release reactions were presented by Helsen and Van den Bulck (2000; 2001) involving the reacted arsenic compound, $CrAsO_4$. The reactions appear to occur around 400-500 °C and utilize the gasification equilibrium reaction for As_2O_3 reported by Hirata et al. (1993):

$$4CrAsO_4 \cdot 6H_2O \leftrightarrow 24H_2O + 2CrO_3 + 2As_2O_5 \tag{2.6}$$

$$2As_2O_5 \leftrightarrow 2As_2O_3 + 2O_2 \tag{2.7}$$

$$2As_2O_3 \leftrightarrow As_4O_6 \tag{2.8}$$

While the exact mechanism responsible for arsenic release during pyrolysis of CCA-treated wood is not completely understood, many researchers have attempted to identify the compounds released as seen above. The accepted consensus of the scientific community is that the release of arsenic during pyrolysis is controlled by the reduction of pentavalent arsenic (As^{+5}) to trivalent arsenic (As^{+3}) (Helsen and Van den Bulck, 2000, 2001, 2005; Hata et al., 2003, 2004; Helsen et al., 2003a,b, 2004; Kakitani et al., 2004a; Cuypers and Helsen, 2011). According to Helsen and Van den Bulck (2001) this occurs at 327 °C (600 K), which falls directly in the range of conventional pyrolysis temperatures. Essentially, this means that even at the low temperatures recommended by Hirata et al. (1993), Kercher and Nagel (2001), Hata et al. (2001), and Helsen and Van den Bulck (2005) attaining arsenic release of “zero” is nearly impossible because of the reducing environment created by wood, char, and pyrolysis vapors (Kercher and Nagel, 2001; Helsen et al., 2004). Due to the release of toxic arsenic compounds during pyrolysis of CCA-treated wood substantial sampling and air pollution control devices are necessary. Helsen et al. (2003b) developed a four-part sampling train (a quartz cooling tube + external fan, a Na_2CO_3-glycerol impregnated cellulose ester membrane filter, an impinger containing HNO_3, and a second impinger containing NaOH) capable of achieving up to 97% arsenic capture. Additionally, Helsen (2005) performed an extensive literature review on the different devices that are available for capturing released arsenic.

2.1.4 Summary and Research Implications

Low-temperature pyrolysis was demonstrated to be a successful means of reducing the overall volume of material containing CCA metals, while retaining large percentages in of the metals in either the pyrolysis char or bio-oil. Few studies conducted to date were performed on aged CCA-treated wood; therefore, questions remain on the feasibility of low-temperture pyrolysis as a management practice for CCA-treated wood waste. Additionally, no information is available on the mobility of the metals that remain in the pyrolysis char. Given that leaching of the CCA metals into the surrounding environment is a primary concern, it is important to determine the effect pyrolysis has on the mobility of metals in char generated by the pyrolysis of CCA-treated wood waste.

Table 2.2 Summary of Pyrolysis Experimental Designs and Results

Researcher	Type of Reactor	Temperature Range	Gas Flow Rate	Loading Mass	Reaction Time	Char (wt %)	Bio-Oil (wt %)	Vapor (wt %)
a-c	Updraft fixed bed	250-450 °C	N_2: 5 N m^3/h N_2: 800 l/h	10 g 10 g	20-60 min	Cu: 64-100 Cr: 18-65 As: 36-78	n/a	n/a
a, c-g	Downdraft fixed bed	300-450 °C	N_2: 2 N m^3/h N_2: 5 N m^3/h N_2: 800 l/h	2 g 10 g 10 g	20-60 min	Cu: 94 Cr: 97 As: 85	Cu: 3.6 Cr: 0.05 As: 3.3	Cu: 2.3 Cr: 3 As: 7.3
h, i	Kugelrohr short-path distillation apparatus	275-350 °C	n/a	3 g	30-60 min	Cu: 88-90 Cr: 85-95 As: 75-82	n/a	n/a
j	Sinku Riko TGD-7000 thermal analyzer	505-1030 °C	He or Air: 150 mL/min	1 g	n/a	Cu: 99 Cr: 99 As: 58	n/a	Cu: 0.4 Cr: 0.15 As: 55
k-n	Pear shaped glass flask in an electric heater	300 °C 135-500 °C	N_2: 12.5 mL/s	25 g 1 g	0-60 min	As: 3-52	n/a	n/a
o	Glass Fluidized bed	300-500 °C	N_2: 2.25 l/min	1 g	80-3600 s	As: 60-94	As: 3-18	As: 0.3-3

a,b,c: Helsen and Van den Bulck, 1997, 2000, 2001
d: Van den Broeck et al., 1997
e,f,g: Helsen et al., 1997, 1998, 2003
h, i: Fu et al., 2007
j: Hirata et al., 1993
k, l: Kakitani et al., 2004a,b
m, n, o: Hata et al., 2001, 2003, 2004

2.2 Electrokinetic Studies

Electrokinetic remediation studies on CCA-treated wood have been performed for nearly two decades. As such, the studies have varied in size (e.g. laboratory vs. pilot plant) and in the specific parameters studied. Key areas of study have included the effects of particle size, extraction solutions, initial current, and electrode spacing on the behavior of metals and overall EK efficiency. Each area of study is discussed in the following sections.

2.2.1 Particle Size

Christensen and Broussard are the primary researchers investigating the effect of particle size (Christensen, 2006; Broussard, 2013). Christensen's study involved processing CCA-treated wood into three fractions (fine < 2 cm, medium < 4 cm, and large > 4 cm), then homogenizing the three fractions into one sample for EK treatment. Post-EK, the fractions were re-sorted and analyzed for chromium and copper content. Similarly, Broussard processed CCA-treated wood waste into three fractions [fines (sawdust), chips (> 9.5 mm), and plugs (1 in x 12 in)]; however, his study investigated each sample size individually.

Both Christensen and Broussard concluded that CCA metal removal efficiencies were highest for the smallest fractions investigated. Removal efficiencies were not reported by Christensen; however, Broussard reported that arsenic removal decreased steadily by 5% as the particle size increased, while the chromium removal percentage was higher than 5.6% for fines than for chips and plugs. Additionally, Broussard did not observe any effect on copper removal efficiency based on particle size.

2.2.2 Extraction Solutions

Two main types of chemical extraction solutions have been investigated (acids and bases) in varying capacities (as pre-treatment and as EK process solution) for their effects on removal efficiency and metal behavior. For ease of discussion, these studies are presented and organized according to author in the sections below.

2.2.2.1 Ribeiro et al.

Ribeiro et al's approach was to pre-soak CCA-treated wood sawdust with deionized water and oxalic acid solutions of varying strengths (2.5%, 5.0%, and 7.5% by weight oxalic acid) prior to loading the material into the EK system (Ribeiro et al., 2000). After operating at constant current of 0.2 mA/cm^2 for 30 days, the sawdust was removed and analyzed for CCA metal content. The primary results and conclusions of this study were:

1. Deionized water pre-treatment resulted in copper removal of over 90%; however, only 27% of arsenic and 0% chromium were removed. Copper migration was almost exclusively as a cation based on analysis of the catholyte and anolyte solutions.
2. Pre-treatment with oxalic acid improved overall removal efficiency for all three CCA metals. Decreasing order of efficiency is as follows: 2.5% acid pre-treatment > 5.0% acid pre-treatment > 7.5% acid pre-treatment > deionized water pre-treatment.
3. Improved removal efficiencies of 99% for arsenic, 95% for chromium, and 93% for copper were achieved. Both arsenic and chromium were primarily removed as anions, while copper again was removed as a cation.

4. A voltage drop across the EK system was observed that was inversely proportional to the solution strength of the oxalic acid pre-treatment. It was proposed that the oxalic acid pre-treatment increased the availability of free ions within the EK system, thus decreasing the overall resistance in the cell. This in turn contributed to the lower voltage drop observed at the higher pre-treatment levels.

2.2.2.2 Velizarova et al.

Velizarova et al. investigated the effect of different pre-treatment solutions on the EK removal efficiencies for chromium and copper (Velizarova et al., 2004). As in Ribeiro et al's study, CCA-treated wood chips were pre-treated prior to loading the EK cell. Pre-treatment solutions were: deionized water, 2.5% oxalic acid, 5.0% formic acid, a 2.5% oxalix acid and 5.0% formic acid mixture, 2.5% EDTA disodium salt, and 1.5% sodium chloride. Additionally, three experiments were performed with no current applied across the EK cell. These experiments utilized pre-treatment solutions of deionized water, 2.5% oxalic acid, and a 2.5% oxalic acid and 5.0% formic acid mixture. After operating at constant current of 0.2 mA/cm^2 for EK cells, and with no current for the dialytic cells, for 14 days, the sawdust was removed and analyzed for CCA metal content. The primary results and conclusions of this study are as follows:

1. Deionized water is the least effective at removing CCA metals under both EK and dialytic conditions. Copper was the most successfully removed under these conditions, achieving 71% removal and 20% removal under EK and dialytic conditions, respectively. Chromium removal percentages were lower at 1% and 8%.

2. Oxalic acid is most effective at removing both chromium and copper even in mixtures with formic acid. Removal efficiencies for chromium and copper were as follows:
    a. Chromium: 87% (oxalic acid), 90% (oxalic acid + formic acid)
    b. Copper: 81% (oxalic acid), 77% (oxalic acid +formic acid)
3. Formic acid is best at removal of copper, as removal efficiencies of 92% copper were achieved; however, this corresponded to only 44% removal for chromium.
4. EDTA was the least successful of the non-deionized water pre-treatment solutions. Only 81% copper and 11% chromium removal was achieved.
5. Pre-treatment solution strongly influences chromium and copper behavior, with respect to movement as anions or cations:
    a. Deionized water and sodium chloride: chromium is unaffected while copper has a strong tendency to migrate toward the cathode.
    b. Oxalic acid and formic acid: chromium and copper are both primarily transported toward the anode.
    c. EDTA: copper migrated largely toward the anode due to formation of complexes with EDTA, though chromium remained largely unaffected.
6. Voltage drops occurred across the EK cell, varying from cell to cell. Velizarova et al. hypothesized that these variations occurred due to the different amounts of available free ions based on the pre-treatment solution. For example, sodium chloride was proposed to have dissociated into ions

within the EK cell and the individual ions migrated toward the electrodes without forming complexes with other available free ions. This ultimately resulted in a high voltage drop across the EK cell.

2.2.2.3 Isosaari et al.

Isosaari et al. investigated the sequential application of chemical extractions with oxalic acid and EK on the overall CCA metal removal efficiencies (Isosaari et al., 2010). Baseline investigations were performed using only chemical extractions and EK experiments, followed by experiments using different sequences of chemical extraction and EK. For the baseline studies, chemical extraction utilized a 0.8% oxalic acid solution while the EK system operated under a 30 V potential difference for seven days. The different sequences investigated were: EK + EK, chemical extraction + EK, chemical extraction + EK + chemical extraction. Isosaari et al. discovered that the success of sequential application varied depending on the CCA metal. Results are as follows:

1. EK treatment alone removed 15% arsenic, chemical extraction + EK removed 75% arsenic, and chemical extraction + EK + chemical extraction removed 78% arsenic.
2. Chemical extraction was necessary to solubilize chromium as EK treatment alone was unsuccessful at removing chromium. Highest chromium removal of 68% was achieved using chemical extraction + EK.
3. Copper removal efficiency was highest with EK treatment alone. 91% copper removal was achieved using two EK treatments in series. Use of chemical extractants produces a reducing environment in the center of the EK cell, hindering copper migration.

4. The best overall sequence for removal of all three CCA metals was chemical extraction + EK + chemical extraction, as it achieved removal efficiencies of 81%, 64%, and 67% for arsenic, chromium, and copper, respectively.

2.2.2.4 Pedersen et al.

Pedersen et al. investigated both the effect of different pre-treatment solutions and electrode spacing on chromium and copper removal efficiencies. Electrode spacing effects will be discussed in Section 2.2.3. The use of 5% oxalic acid alone and a dual step treatment of 0.5 M phosphoric acid followed by 5% oxalic acid were investigated (Pedersen et al., 2005). Pedersen et al. found that the use of phosphoric acid increased chromium removal to 58% from 41% at oxalic acid treatment alone. A similar increase was found with copper as removal increased from 20% to 66%.

2.2.2.5 Sarahney et al.

Sarahney et al. approach was unique in that it evaluated the use of different chemical extraction solutions as the EK cell process solution, rather than as a pre-treatment (Sarahney et al., 2005). After investigating multiple combinations of oxalic acid, citric acid, EDTA, and ascorbic acid the researchers identified a mixture of oxalic acid and EDTA as the most promising at removing the CCA metals. The combination of 5% oxalic acid and 2.5% EDTA solution was later used as an EK process solution, as was distilled water as an experimental control. Results of these studies are provided below:

1. Distilled water as the EK process solution with no pre-treatment resulted in removal percentages of 32% arsenic, 8% chromium, and 29% copper. Arsenic migrated nearly exclusively toward the anode, while copper migrated

toward the cathode. Chromium migrated toward both electrodes, with slightly more present at the anode.

2. The 5% oxalic acid and 2.5% EDTA EK process solution with no pre-treatments resulted in removal percentages of 88% arsenic, 74% chromium, and 97% copper. Unlike in the control experiments, all three CCA metals migrated toward the anode. This change in behavior for copper was explained as being due to reactions between copper and EDTA.

2.2.2.6 Broussard

Broussard also investigated the effect of utilizing chemical pre-treatment in addition to studying the effect of particle size on removal efficiency (see Section 2.2.1). After determining extracting CCA-treated wood waste with a 16.7% by volume solution of NaOCl did not significantly damage the wood, Broussard investigated the efficiency of this pre-treatment for CCA metal removal (Broussard, 2013). In general, Broussard found that chemical pre-treatment had the largest effect on chromium removal efficiency, as it increased removal by 7% when compared to the removal efficiency without chemical pre-treatment. Increased removal efficiencies for arsenic and copper were lower at only 4% and 1%, respectively.

2.2.3 Initial Current

Velizarova et al. also investigated the effect of varying the initial current applied to EK cells on the EK removal efficiencies for chromium and copper (Velizarova et al., 2002). In these experiments, the initial current was varied at levels of 0 mA, 4 mA, 60 mA, and 120 mA for EK cells loaded with wood pre-treated with oxalic acid. The results of the investigation indicate that the higher the initial current, the faster the current achieves equilibrium across the EK cell. Velizarova et al. attribute this to a rapid depletion of available charged particles at the center of the EK cell. Increasing the initial applied current to 60 mA and 120 mA had little effect on removal efficiencies for all metals; however, the study indicated that copper was the most strongly influenced by the application of electric current. Copper removal efficiency improved from 48% to 82% when the initial applied current increased from 0 mA to 40mA.

2.2.4 Proximity to Electrodes/Electrode Spacing

Investigations into the proximity of the CCA-treated wood to the EK electrodes were performed by Virkutyte et al. In these investigations, wood samples were pre-treated with 2.5% oxalic acid prior to placement in the EK cells (Virkutyte et al., 2005). Three placement locations were evaluated: adjacent to the anode half-cell, in the middle of the center compartment, and adjacent to the cathode half-cell (Virkutyte et al., 2005). After operating for 14 days under constant current of 40 mA, the material was removed from the EK cell and analyzed for metal content. Results of the experiments are provided below:

1. When the treated wood sample was placed adjacent to the anode, copper behaved primarily as an anion and migrated toward the anode. Virkutyte et al., propose that this is likely due to the formation of negatively charged copper oxalate species generated during the pre-treatment with oxalic acid.
2. Placement near the center compartment resulted in copper behaving as both an anion and cation. The anionic behavior was explained as being due to the formation of copper oxalate species, and that once the free oxalic acid species

are spent, the predominant solubilized copper species are free copper cations that migrate toward the cathode.

3. When placed adjacent to the cathode, copper behaves almost exclusively as a cation, as would be expected due to the availability of free copper ions and the formation of copper hydroxides.
4. When placed near the anode or in the middle of the center compartment, chromium behaves as an anion and migrates toward the anode. Chromium also behaves as an anion when the treated wood is placed near the cathode; however, significant amounts of chromium do not migrate at all.

Pedersen et al. also investigated the impact of electrode spacing on removal efficiencies of CCA metals. Electrode spacing ranged from 60 cm to 150 cm and resulted in decreased removal efficiency for both chromium and copper. Decreases of 25% and 28% were observed for chromium and copper, respectively, while no impact was apparent on arsenic removal as it was 95% at both distances (Pedersen et al., 2005).

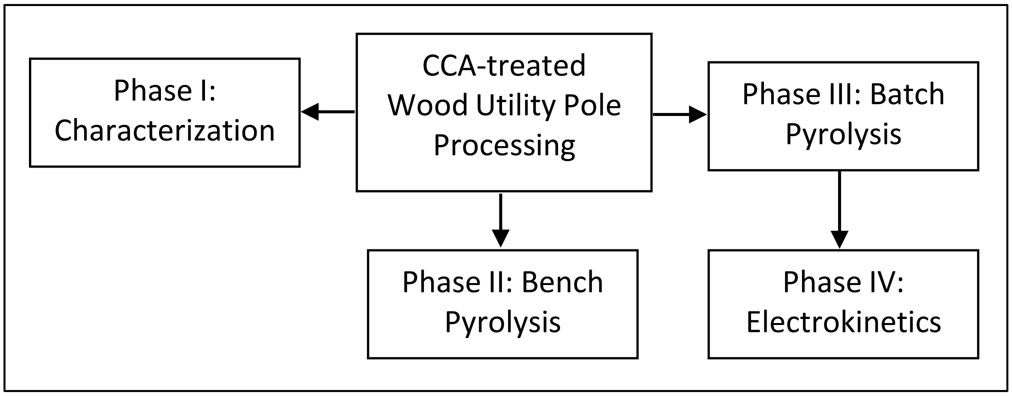
2.2.5 Summary and Research Implications

EK has been demonstrated to successfully remediate CCA-treated wood; however, most studies were performed on newly treated wood and thus questions remain on the applicability of EK to aged CCA-treated wood waste. Additionally, many of the EK investigations to date utilized chemical pre-treatment and/or operational solutions over relatively long periods of time. Investigations should be performed to evaluate EK efficiency without the use of chemical pre-treatments or operational solutions. Mobility of the CCA metals remaining in the solid material post-EK operation should also be evaluated, given the leaching concerns for all CCA-treated wood waste.

CHAPTER III

MATERIALS AND METHODS

The following sections contain details on the processing of CCA-treated wood waste for use in this study, as well as the four experimental phases performed to achieve the study objectives outlined in Section 1.6. A summary flowchart of this study is provided in Figure 3.1.



Electrokinetics as Remediation Techniques for the Treatment of CCA-treated Wood Waste

3.1 Materials Processing

An out-of-service cylindrical utility pole (treated with CCA) was donated for research to Mississippi State University by Starkville Electric Company in Starkville, Mississippi. The utility pole had approximate dimensions of 16 feet in length by 14 inches in diameter, and had been in service for nearly 15.5 years (December 1990-May 2005).

To facilitate the use of the utility pole throughout the study, a series of particle size reduction steps were performed. Each step is identified in Figure 3.2. First, the utility pole was cut into 4-foot length sections. Next, the sections were further divided, using a one-pound hammer and a spike wedge, into pieces smaller than 4 feet in length and 3 inches in diameter. These pieces were then chipped using a Yard Machine 6.5 horsepower chipper shredder. Next, the chipped wood was separated into two fractions by sieving through a 9.5 mm sieve. The larger diameter fraction of chipped wood was placed in 5-gallon buckets and stored at room temperature, while the smaller diameter fraction was ground into sawdust using a Thomas Scientific Model 5 Wiley Mill. Following the grinding procedure three Rubbermaid SnapTopper Shoe Box, 5.7 qt containers were filled with sawdust, while the remainder was placed in 5-gallon buckets. All sawdust was stored at room temperature. Figures 3.3, 3.4, and 3.5 illustrate the different particle sizes.

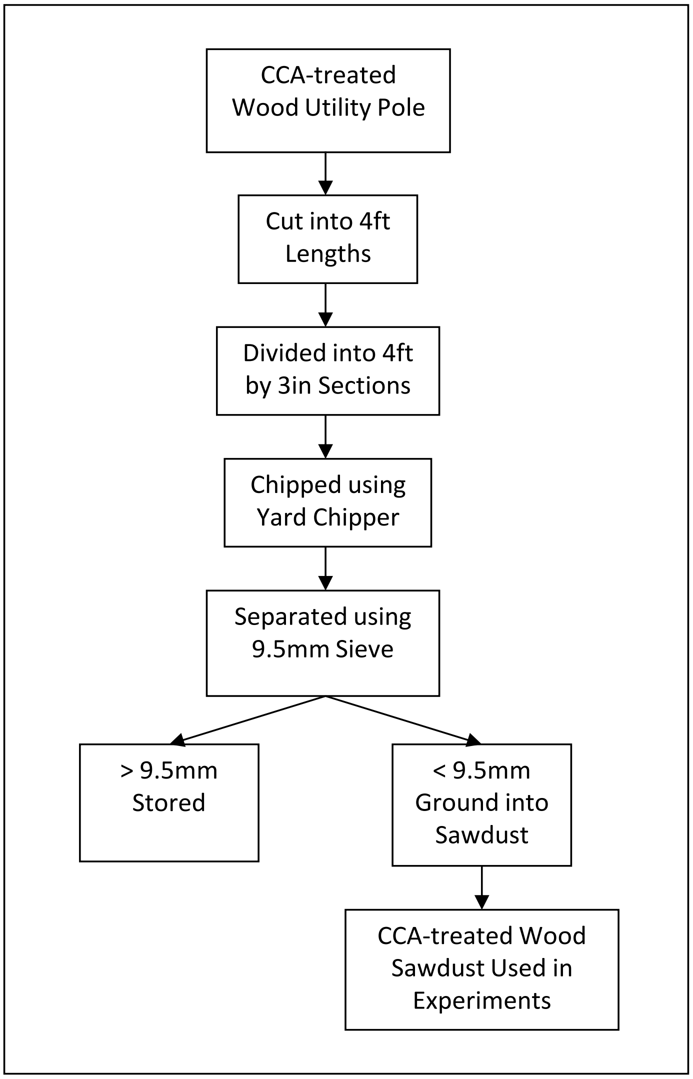


Figure 3.2 CCA-treated Wood Utility Pole Processing Steps for this Study

Figure 3.3	4 Foot Section of the CCA-treated Wood Utility Pole

Figure 3.4	Chipped Pieces of the CCA-treated Wood Utility Pole

Figure 3.5 CCA-Treated Wood Sawdust Used in All Experiments of this Study

3.2 Phase I: Characterization of CCA-Treated Wood Waste

Three characterization studies were performed to have a better understanding of the composition of the CCA-treated wood material, and to ensure that the properties were uniform throughout the wood samples generated during the processing sequence. The characterization studies consisted of determining the metal content, metal mobility, and moisture content of the CCA-treated wood waste and are described in the following sections. A summary of the characterization studies is captured in Figure 3.6 and the experimental matrix for Phase I is in Table 3.1.

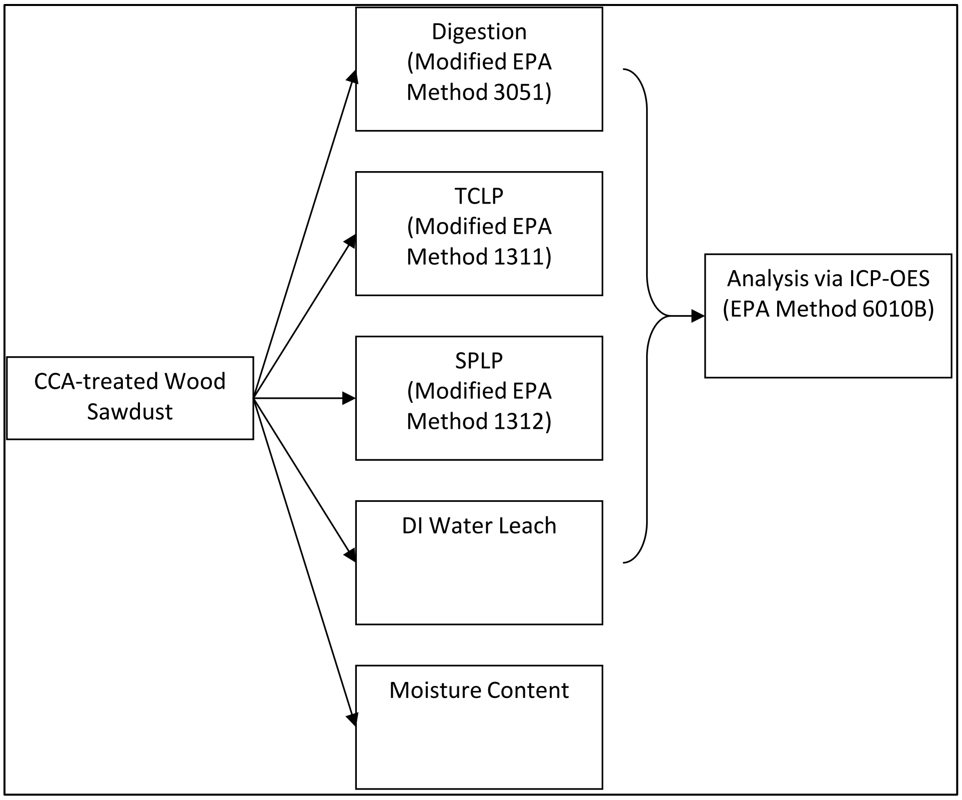


Figure 3.6 Flowchart of Phase I: Characterization of CCA-Treated Wood Waste

Table 3.1 Experimental Matrix of Characterization Studies on CCA-Treated Wood Waste

		Metal Mobility			Moisture Content
Sample ID	Digestion	TCLP	SPLP	DI Leach	
A-1	x	x	x	x	x
A-2	x	x	x	x	x
A-3	x	x	x	x	x
A-4	x	x	x	x	x
A-5	x	x	x	x	x
A-6	x	x	x	x	x
A-7					x
A-8					x
A-9					x
B-1	x	x	x	x	x
B-2	x	x	x	x	x
B-3	x	x	x	x	x
B-4	x	x	x	x	x
B-5	x	x	x	x	x
B-6	x	x	x	x	x
B-7					x
B-8					x
B-9					x
C-1	x	x	x	x	x
C-2	x	x	x	x	x
C-3	x	x	x	x	x
C-4	x	x	x	x	x
C-5	x	x	x	x	x
C-6	x	x	x	x	x
C-7					x
C-8					x
C-9					x

Note: “A”, “B”, and “C” represent the three containers used to store the CCA-treated wood sawdust; Numbers 1-9 indicate the number of replicates; “x” denotes experiment performed on the identified sample

3.2.1 CCA Metal Content

Sawdust samples were subjected to modified microwave assisted acid digestion (modified EPA Method 3051A) to determine the metal content of the CCA-treated wood. According to the altered method, 0.4000 ± 0.0010 grams of sawdust were weighed using a Mettler-Toledo Model AG204 analytical balance and transferred to a 60 mL CEM XP-1500 digestion vessel. Next, 8 mL of concentrated 15.8 M nitric acid and 3 mL of 30% hydrogen peroxide were added to the digestion vessel. Method blanks (i.e. nitric acid and hydrogen peroxide only, no sawdust) were performed after every 15 samples. The vessel was allowed to vent under a fume hood for 15-20 minutes since the addition of hydrogen peroxide results in a vigorous reaction between the contents of the vessel. Once there were no visible signs of continued reaction, the vessels were capped and loaded in a CEM MARSXpress turntable, which was then placed in a CEM MARS 5 Microwave. Figure 3.7 illustrates the capped digestion vessels and Figure 3.8 contains both the CEM MARSXpress turntable and the CEM MARS 5 Microwave. The CEM MARS 5 Microwave is supplied with a variety of pre-programmed EPA methods, so no additional input is required by the user. After loading the samples, EPA Method 3051 was selected from the main menu, and the digestion procedure was completed by the microwave according to the method specifications.

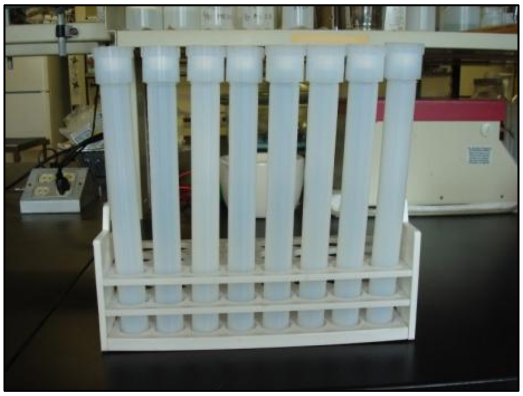


Figure 3.7 CEM XP-1500 Digestion Vessels

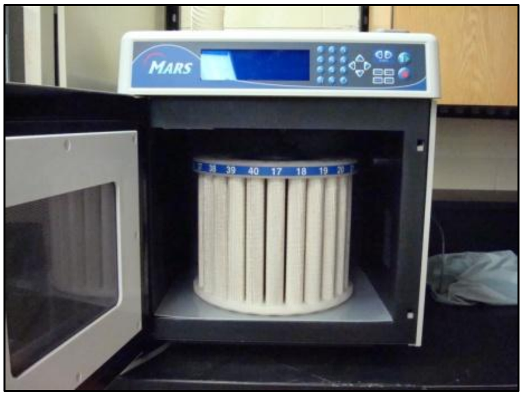


Figure 3.8 CEM MARSXpress Turntable and CEM MARS 5 Microwave

Once digestion of the samples was complete, the MARSXpress turntable was removed from the microwave, and the individual digestion vessels were removed from the turntable, uncapped, and allowed to vent under a fume hood for approximately 5 minutes. Each sample was then vacuum filtered using Millipore HA 0.45 μm filters, and the filtrate diluted to 100 mL with 2% nitric acid. Figure 3.9 illustrates the filtration apparatus set-up. The filtrate was then analyzed for CCA metals content using a Perkin Elmer Instruments Optima 4300DV Inductively Coupled Plasma Optical Emissions System (ICP-OES). Details on the ICP-OES analysis method are provided in Section 3.3 of this chapter.

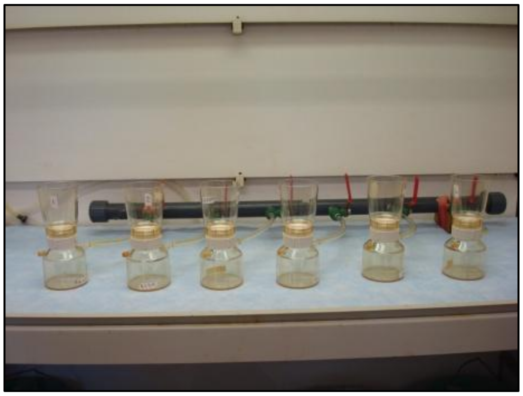


Figure 3.9 Vacuum Filtration Apparatus Set-up Utilized Throughout CCA-Treated Wood Study

3.2.2 CCA Metal Mobility

Although CCA-treated wood waste is exempt from EPA hazardous waste regulations, it is important to evaluate the mobility of CCA metals in wood waste products. As such, three leaching experiments were performed on the sawdust samples to evaluate the mobility of the CCA metals. The Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), and Deionized (DI) Water Leaches are described in Sections 3.2.2.1, 3.2.2.2, and 3.2.2.3.

3.2.2.1 TCLP

To simulate the behavior of CCA-treated wood waste materials in landfills, a modified Toxicity Characteristic Leaching Procedure (modified EPA Method 1311) was utilized throughout this study. Determination of the appropriate extraction fluid was conducted in direct accordance with EPA Method 1311. After determining the extraction fluid, 2.0000 ± 0.0010 grams of the solid samples were weighed using a Mettler-Toledo Model AG204 analytical balance and transferred to a 60 mL Nalgene high density polyethylene (HDPE) bottle. Next, 40 mL of TCLP extraction fluid were added to the bottle, after which the bottle was capped and tumbled end-over-end for a period of 18 ± 2 hours. The mass of solid to volume of extraction fluid was maintained at the 1:20 ratio required by EPA Method 1311. Method blanks (i.e. 40 mL extraction fluid, no sawdust) were performed after every 15 samples. Figures 3.10 and 3.11 illustrate the loading of samples into the tumbler. Once the tumbling period was complete, the contents of the bottles were vacuum filtered using Whatman Glass Fiber Filter (GF/F) 0.7 µm filters and the vacuum filtration set-up described in Section 3.2.1. The pH of the generated filtrate was then measured using an Oakton Model 310 pH meter with an Orion Model 9206B gel-epoxy probe according to EPA Method 9040C. The filtrate was subsequently analyzed for CCA metals content using the ICP-OES method described in Section 3.3.

Figure 3.10   Placing TCLP Samples in Tumbler for CCA-Treated Wood Waste Characterization Study

Figure 3.11 Placing TCLP Samples in Tumbler for CCA-Treated Wood Waste Characterization Study – Close View

3.2.2.2 SPLP

Simulation of the behavior of CCA-treated wood waste materials in-situ and exposed to rainfall was achieved utilizing a modified Synthetic Precipitation Leaching Procedure (modified EPA Method 1312). Determination of the appropriate extraction fluid was conducted in direct accordance with EPA Method 1312. Given that the CCA-treated wood utility pole originated east of the Mississippi River, extraction fluid #1 was selected. After determining the extraction fluid, 2.0000 ± 0.0010 grams of the sawdust samples were weighed using a Mettler-Toledo Model AG204 analytical balance and transferred to a 60 mL Nalgene high density polyethylene (HDPE) bottle. Next, 40 mL of SPLP extraction fluid were added to the bottle, after which the bottle was capped and tumbled end-over-end for a period of 18 ± 2 hours. Similar to the TCLP procedure, the ratio of mass of solid to volume of extraction fluid maintained the 1:20 ratio required by EPA Method 1312. Again, Method blanks (40 mL extraction fluid, no sawdust) were performed after every 15 samples. Once the tumbling period was complete, the contents of the bottles were vacuum filtered using Whatman Glass Fiber Filter (GF/F) 0.7 µm filters and the vacuum filtration set-up described in Section 3.2.1. The pH of the generated filtrate was then measured using an Oakton Model 310 pH meter with an Orion Model 9206B gel-epoxy probe according to EPA Method 9040C. The filtrate was subsequently analyzed for CCA metals content using the ICP-OES method described in Section 3.3.

3.2.2.3 DI Water Leach

A third leaching procedure was followed to evaluate the behavior of CCA metals in non-acidic conditions. Similar mass of solid to volume of extraction fluid ratios as those used in the TCLP and SPLP procedures were utilized for ease of comparison. 2.0000 ± 0.0010 grams of the sawdust samples were weighed using a Mettler-Toledo Model AG204 analytical balance and transferred to a 60 mL Nalgene high density polyethylene (HDPE) bottle. Next, 40 mL of deionized (DI) water were added to the bottle, after which the bottle was capped and tumbled end-over-end for a period of 18 ± 2 hours. Once again, Method blanks (40 mL extraction fluid, no sawdust) were performed after every 15 samples. After the tumbling period was complete, the contents of the bottles were vacuum filtered using Whatman Glass Fiber Filter (GF/F) 0.7 µm filters and the vacuum filtration set-up described in Section 3.2.1. The filtrate was subsequently analyzed for CCA metals content using the ICP-OES method described in Section 3.3.

3.2.3 Moisture Content

For this portion of the study, sawdust samples were used in evaluating the moisture content of the original CCA-treated wood sample. Moisture content was determined using a seven-step procedure provided in Table 3.2 in conjunction with Equation 3.1. Figures 3.12, 3.13, and 3.14 illustrate various steps of the moisture content procedure.

$$\%\ \text{Moisture} = \frac{(b-a)-(c-a)}{(c-a)} \times 100 \tag{3.1}$$

Table 3.2 Method for Determining Moisture Content

#	Action
1	Weigh sample tin (a)
2	Add wet wood sample of at least 0.5 g to tin and weigh the tin (b)
3	Place sample tin + wood sample in a forced air oven at 103°C for at least 3 hours
4	Remove sample tin + wood sample from the oven and place in dessicator for 15 minutes
5	Weigh sample tin + dry wood sample (c)
6	Repeat steps 3-5 until sample mass becomes constant
7	Calculate moisture content using Equation 3.1

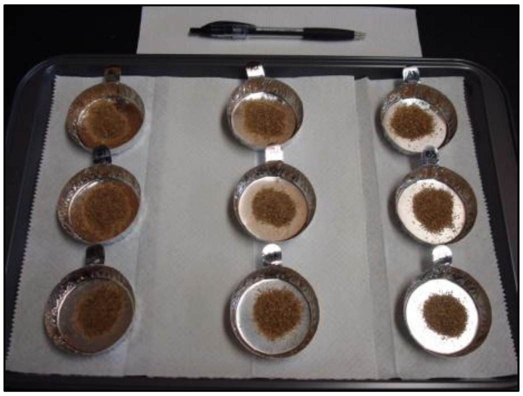


Figure 3.12 Sawdust Samples in Metal Sample Tins for Moisture Content Determination of CCA-Treated Wood Waste

Figure 3.13 Sawdust Samples in Forced Air Oven during Moisture Content Determination of CCA-Treated Wood Waste

Figure 3.14 Sawdust Samples in Dessicator during Moisture Content Determination of CCA-Treated Wood Waste

3.3 Analysis via ICP-OES

All filtrates generated throughout this study were analyzed for CCA metals content using a Perkin Elmer Instruments Optima 4300DV ICP-OES (see Figure 3.15) in accordance with EPA Method 6010D. Analytical quality control was achieved through a variety of means, as captured in Table 3.3. Details of all sample preparations are provided in Appendix A.

Table 3.3 Analytical Quality Control Objectives Utilized Throughout the CCA-Treated Wood Waste Investigations

Quality Control Sample Type	**Frequency of Use**	**Data Quality Objective**
Analytical Blank	1 per 9 samples	<MDL
Analytical Check Standard	1 per 9 samples	PE$^{(1)} < 25\%$
Analytical Internal Standard	Each sample	PE $< 25\%$
Analytical Duplicate Sample	1 per 9 samples	RPD$^{(2)} < 20$
Analytical Matrix Spike	1 per 9 samples	Recovery 75-125%
Analytical Matrix Spike Duplicate	1 per 9 samples	RPD $< 20\%$
Analytical Calibration (Target Compounds)	Daily or each new matrix	$r^{2(3)} \geq 0.995$

(1)PE – Percent error
(2)RPD – Relative percent difference
(3)r^2 – Coefficient of determination

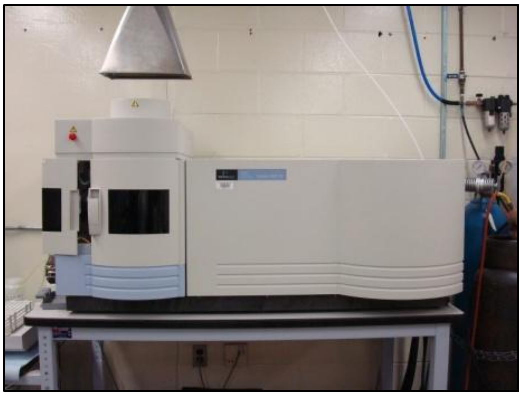


Figure 3.15 Perkin Elmer Instruments Optima 4300DV ICP-OES Utilized Throughout the CCA-Treated Wood Waste Investigations

3.4 Phase II: Bench Pyrolysis of CCA-Treated Wood Waste

Bench pyrolysis experiments were performed utilizing the CCA-treated wood sawdust generated by the processing steps documented in Section 3.1. The following sections describe the bench system, its operation, as well as the post-operation experiments and analysis.

3.4.1 System Set-up

A bench pyrolysis system was designed specifically for this study (see Figure 3.16 for the system schematic). The system was designed to consist of three primary units: the reactor, condensers, and gas sampling train.

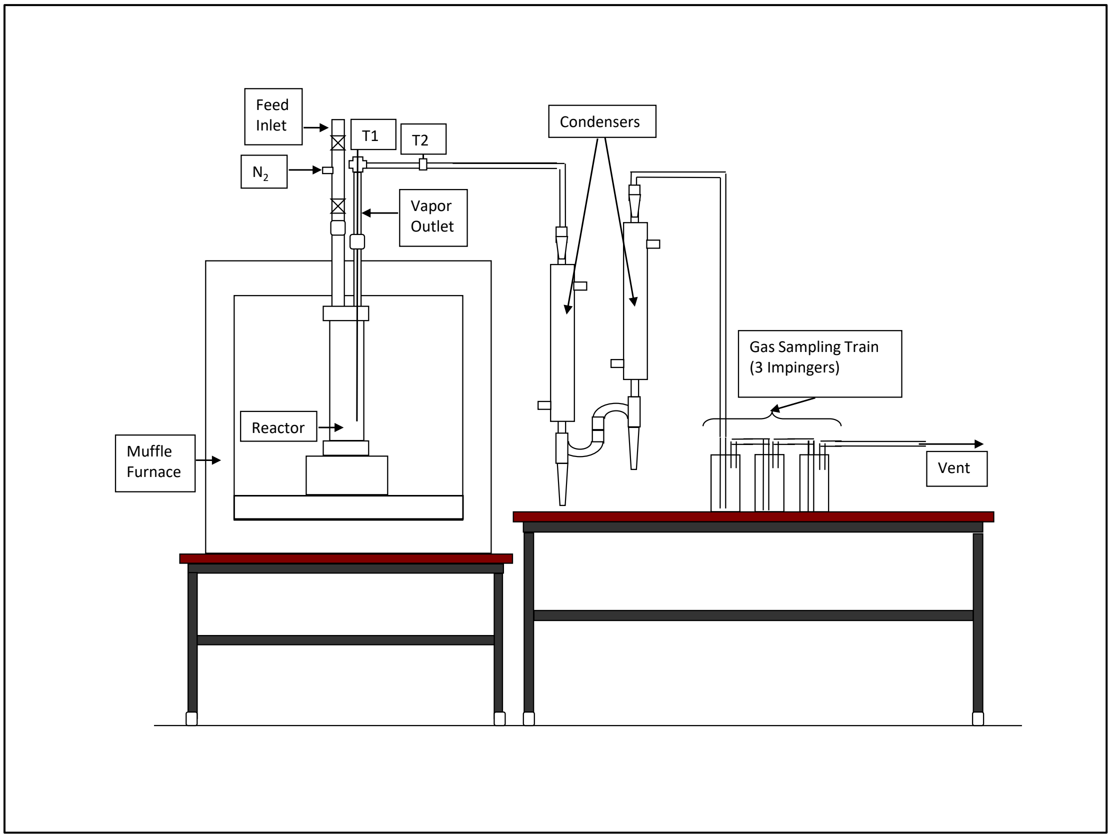


Figure 3.16 Bench Pyrolysis System of the CCA-Treated Wood Waste Study

Note: T1 and T2 are Type K thermocouples utilized to measure the system temperature within the reactor and at the outlet of the reactor, respectively.

3.4.1.1 Reactor

The reactor was made of 316 stainless steel pipe and was 2 inches in diameter and 8 inches long. Both the feed inlet and vapor outlet lines were constructed of 316 stainless steel pipe (3/4 inch diameter and 1/4 inch diameter, respectively) as were all fittings. The reactor was heated using a 1.26 cubic foot Fisher Isotemp Basic Muffle Furnace, and operated under nitrogen purge. The vapor outlet line was also heated and insulated to ensure no condensation occurred prior to the pyrolysis vapors entering the condensers. System temperature was measured in two locations (within the reactor and at the outlet of the reactor) using Type K thermocouples. Figures 3.17 and 3.18 are photographs of the reactor set-up.

Figure 3.17 Bench Pyrolysis Reactor of the CCA-Treated Wood Waste Study – Without Insulation

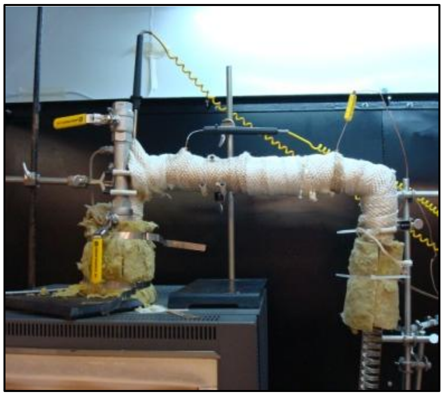


Figure 3.18 Bench Pyrolysis Reactor of the CCA-Treated Wood Waste Study – Feed Inlet, Insulated Reactor Outlet, & Thermocouples

3.4.1.2 Condensers

Two Graham full length condensers in series were used to cool pyrolysis vapors and collect bio-oil. Pyrolysis vapors enter one condenser where they were cooled and bio-oil was collected. The remaining vapors then entered the subsequent condenser where they were further cooled and additional bio-oil was collected. The cooling water used was the “house” cooling water which was passed through a series of copper coils submerged in an ice bath. Additional ice baths were utilized to further cool the bio-oil. The condenser arrangement can be seen in Figure 3.19.

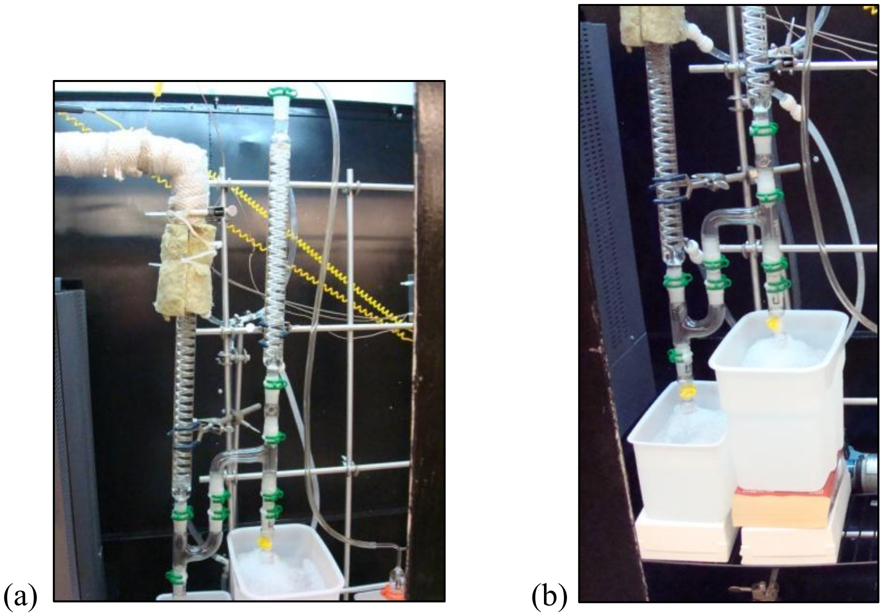


Figure 3.19 Bench Pyrolysis System Condensers of the CCA-Treated Wood Waste Study

(a) Wide view
(b) Close view with ice baths

3.4.1.3 Gas Sampling Train

Three impingers served as the gas sampling train for the bench pyrolysis system. This sampling train was utilized to collect the CCA metals present in the non-condensable pyrolysis vapors. The first impinger was a 125 mL capacity gas washing bottle with no frits. This impinger was utilized as an additional point for potential bio-oil collection, and as such, did not contain any solution and was submerged in an ice bath. The two remaining impingers were 125 mL capacity gas washing bottles with 25 mm fritted disks. The second impinger contained 70 mL of 1 M nitric acid while the third contained 70 mL of 0.1 M sodium hydroxide. Details of the sampling train can be seen in Figure 3.20.

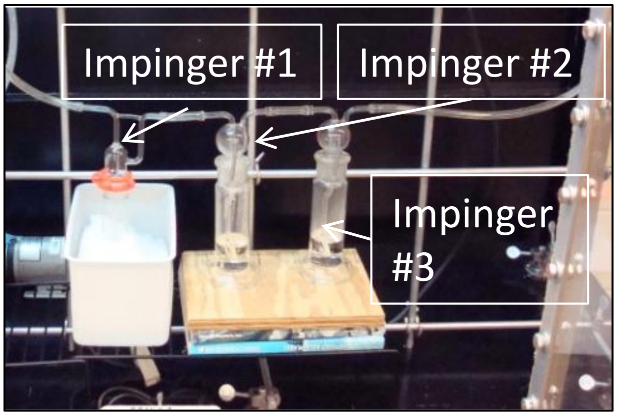


Figure 3.20 Bench Pyrolysis System Gas Sampling Train of the CCA-Treated Wood Waste Study

Note: Impinger #1 is empty, Impinger #2 contains HNO_3, & Impinger #3 contains NaOH

3.4.2 Bench Pyrolysis System Operation

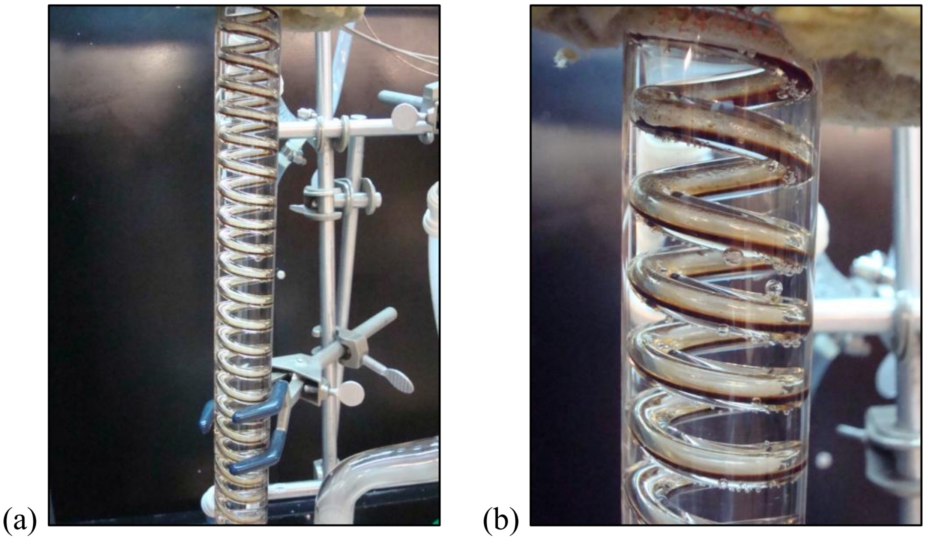
System operation began by heating the reactor to a desired set-point temperature (i.e. 350°C, 400°C, or 450°C) using the interface on the muffle furnace, and setting the heat tape on the reactor outlet to 43°C to ensure that the outlet line was sufficiently heated to prevent condensing of the pyrolysis vapors prior to the condensers. Triplicate runs were performed at each set-point temperature for a total of nine bench pyrolysis runs. It is important to note that appropriate safety measures were taken throughout system operation to minimize exposure to CCA dust and vapors, and to maintain general lab safety. These measures included posting signs indicating the work was being performed, wearing appropriate personal protective equipment (PPE) such as coveralls, respirator, and face shield, and performing the experimental runs in a dedicated laboratory hood. Once both thermocouples indicated the reactor and vapor outlet had reached the set-point, the system was purged with nitrogen gas at a flow rate of approximately 2 L/min for a minimum of 5 minutes, and again allowed to reach the desired set-point temperature. After the system warm-up was complete, a total of 30 g CCA-treated wood sawdust was loaded into the reactor through the double block valve inlet in rapid 10 g intervals. System temperature was monitored across the system as described in Section 3.4.1.2, and the produced pyrolysis vapor was visually observed. Observed residence time for the pyrolysis vapors was approximately 6 seconds. The reaction was determined to have reached completion when all downstream temperatures became constant and no pyrolysis vapor was observed.

At this point, the muffle furnace was turned off, the door to the furnace was opened to cool the reactor, and nitrogen gas flow was maintained. The system was considered "cooled" when the reactor reached 50°C. Once cooled, the vapor outlet line heat tape was turned off, nitrogen flow was ceased, and each unit of the pyrolysis system was disassembled. A summary of the system operating parameters is found in Table 3.4, and varying stages of bench pyrolysis operation are captured in Figure 3.21, 3.22, and Figure 3.23. Contents of the reactor, condensers, and impingers were collected for additional experiments and analysis as described in Section 3.4.3. Additionally, the condensers and impingers were each rinsed with 2% nitric acid, and this rinse was collected for analysis.

Table 3.4 Bench Pyrolysis System Operating Parameters of the CCA-Treated Wood Waste Study

Warm-up Time (average)	2.25 hours for 350°C set-point; 2.33 hours for 400°C set-point; 2.42 hours for 450°C set-point
Cool-down Time	3.5 hours (on average)
Loading Capability	10 grams of sawdust at a time
Nitrogen Gas Flow	≈ 2 L/min
Residence Time	≈ 6 seconds

Figure 3.21 Loading CCA-Treated Wood into the Bench Pyrolysis Reactor during Phase II of the CCA-Treated Wood Waste Study



(a)

(b)

Figure 3.22 Observed Pyrolysis Vapor and Bio-oil in a Condenser of the Bench Pyrolysis System during Phase II of the CCA-Treated Wood Waste Study

(a) Wide view
(b) Close view

Figure 3.23 Observed Pyrolysis Vapor in a Condenser Outlet of the Bench Pyrolysis System during Phase II of the CCA-Treated Wood Waste Study

3.4.3 Post-Operation Experiments and Analysis

Similar to the characterization studies performed in Phase I, several experiments were performed on the products of the bench pyrolysis runs performed during Phase II. A summary flowchart of the post-operation experiments and analysis is provided in Figure 3.24, and the experimental matrix for Phase II is in Table 3.5.

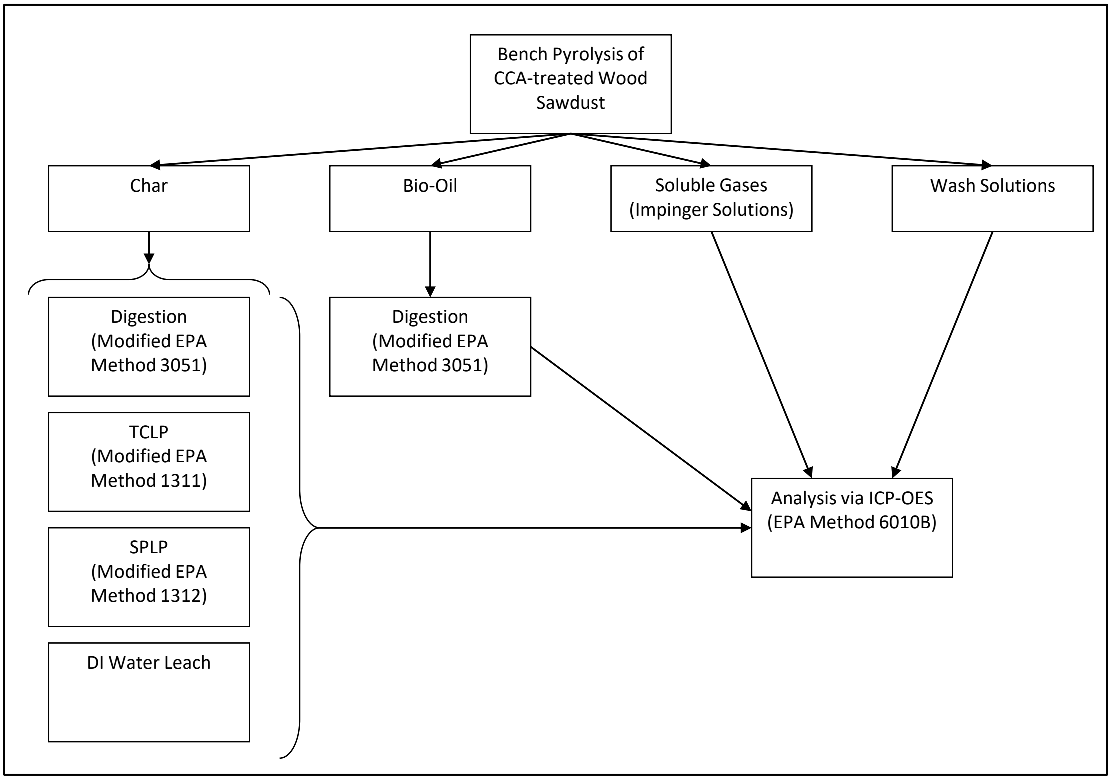


Figure 3.24 Flowchart of the Post-Operation Experiments and Analysis on Products of Bench Pyrolysis Runs for Phase II of the CCA-Treated Wood Waste Study

Table 3.5 Experimental Matrix for Phase II of the CCA-Treated Wood Waste Investigation

		Char Products				**Bio-Oil Products**
Pyrolysis Temperature	**Run ID**	**Digestion**	**TCLP**	**SPLP**	**DI Leach**	**Digestion**
350°C	A	x3	x3	x3	x3	x3
	B	x3	x3	x3	x3	x3
	C	x3	x3	x3	x3	x3
400°C	A	x3	x3	x3	x3	x3
	B	x3	x3	x3	x3	x3
	C	x3	x3	x3	x3	x3
450°C	A	x3	x3	x3	x3	x3
	B	x3	x3	x3	x3	x3
	C	x3	x3	x3	x3	x3

3.4.3.1 CCA Metal Content

To determine the metal distribution across each component and product of the bench pyrolysis system, the char and bio-oil products were subjected to the modified microwave assisted digestion procedure (modified EPA method 3051A) described in Section 3.2.1, with one further modification: 0.5000 ± 0.0010 grams of sample were used in the digestion procedure. Triplicate experiments were performed on each of the pyrolysis products, as indicated in Table 3.5, and Method blanks were performed after every 15 samples. The digestion filtrates, impinger solutions, and wash solutions collected from rinsing the system condensers and impingers were all analyzed for CCA metals content according to the ICP-OES method detailed in Section 3.3.

3.4.3.2 CCA Metal Mobility

The mobility of the CCA metals in the pyrolysis char was evaluated by performing the three leaching experiments (TCLP, SPLP, and DI Water Leaches) as described in Section 3.2.2, with one modification. The mass of solid to volume of extraction fluid ratio of 1:20 was maintained by using 0.5 g of sample and 10 mL of extraction fluid. Again, triplicate experiments were performed on each of the char samples, as indicated in Table 3.5, and Method blanks were performed after every 15 samples. The filtrates were all analyzed for CCA metals content in accordance with the ICP-OES method detailed in Section 3.3.

3.5 Phase III: Batch Pyrolysis of CCA-Treated Wood Waste

It was recognized that a significant mass of char would be needed for the planned electrokinetic (EK) experiments in Phase IV of this study; however, the bench pyrolysis system of Phase II was not capable of producing the necessary amount of char in a timely manner as each successful bench run took up to six hours to produce a small mass of char. A batch pyrolysis system was built and operated to quickly generate char for use in the EK experiments in Phase IV. The batch pyrolysis experiments were performed utilizing the CCA-treated wood sawdust generated by the processing steps documented in Section 3.1. The following sections describe the batch system, its operation, as well as the post-operation experiments and analysis.

3.5.1 System Set-Up

The batch system designed for this study consisted of three primary units: the reactor, condensers, and a gas scrubber. Figure 3.25 is a photograph of the complete batch system used to generate char for the EK experiments in Phase IV.

Figure 3.25 Batch Pyrolysis System Used to Generate Char for EK Experiments in the CCA-Treated Wood Waste Study

3.5.1.1 Reactor

The batch reactor was made of 316 stainless steel pipe and was 2 inches in diameter and 48 inches long. Both the CCA-treated wood inlet and char product outlets were constructed of 315 stainless steel pipe (2 inch diameter) and two brass 2 inch gate valves. A metal plunger was utilized to move the CCA-treated wood and pyrolysis char along the length of the reactor. The reactor was heated using a Thermo Scientific Lindberg Blue M Split Hinge, 3-Zone Tube Furnace, and operated under nitrogen purge. System temperature was measured within the reactor using a Type K thermocouple. Figures 3.26, 3.27, and 3.28 illustrate the reactor set-up.

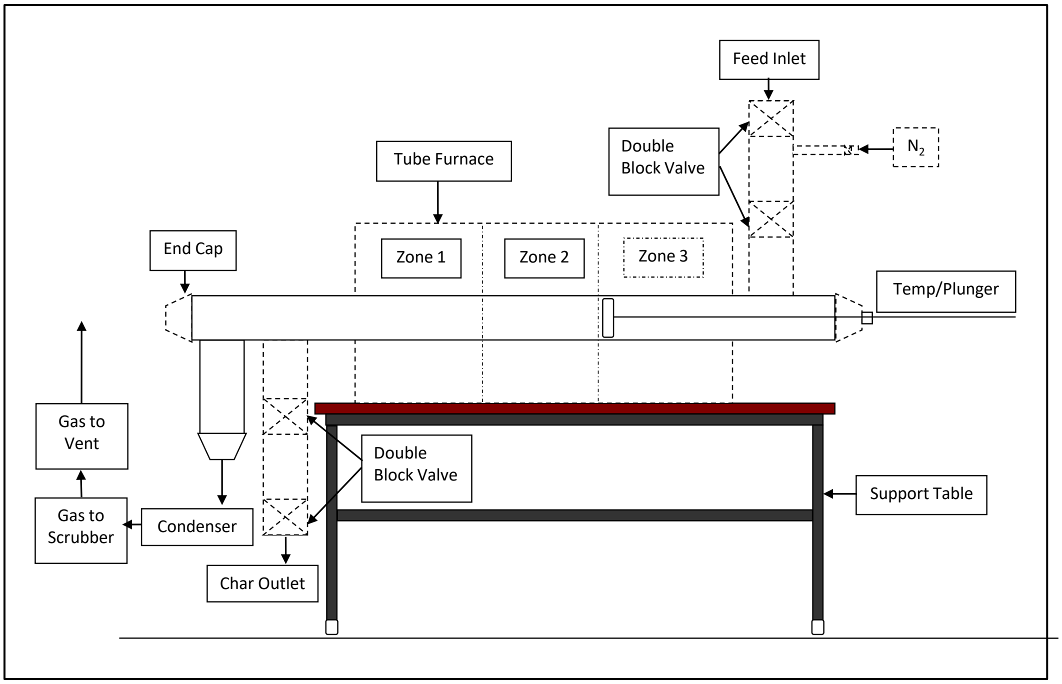


Figure 3.26 Schematic of Batch Pyrolysis System Used to Generate Char for EK Experiments in the CCA-Treated Wood Waste Study

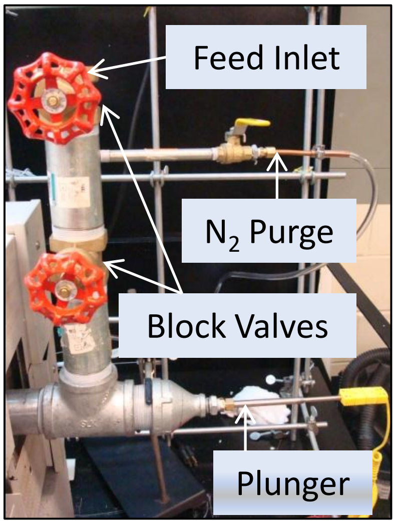


Figure 3.27 Batch Pyrolysis Reactor Inlet with Double Block Valve, Nitrogen Purge Gas, and Plunger/Thermocouple

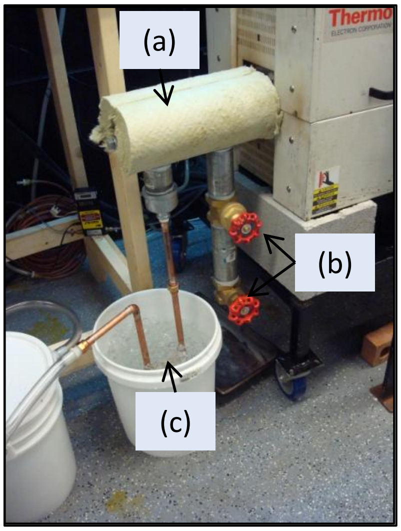


Figure 3.28 Outlet of Batch Pyrolysis Reactor Used to Generate Char for EK Experiments in the CCA-Treated Wood Waste Study

(a) Loosely insulated reactor outlet
(b) Block valves
(c) Condensers

3.5.1.2 Condensers

The batch condensers consisted of two 316 stainless steel reservoirs submerged in an ice bath and were used to collect bio-oil generated during each batch pyrolysis run. The vessels were two inches in diameter and 3 inches tall, and were connected to the reactor and each other by half-inch copper pipe. The condenser set-up can be seen in Figure 3.28 and Figure 3.29 is a full schematic.

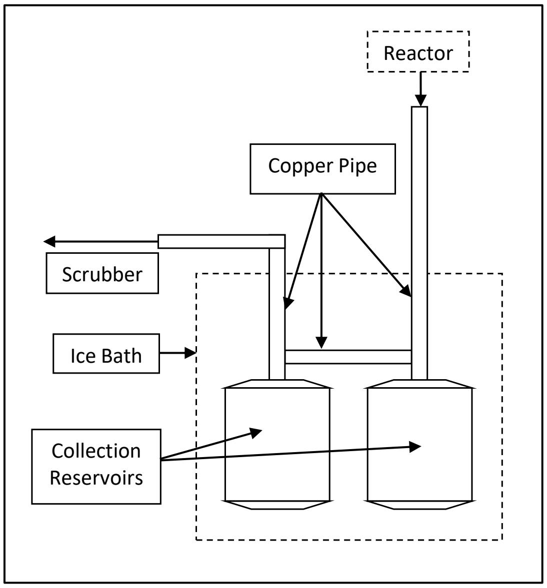


Figure 3.29 Schematic of the Condensers of the Batch Pyrolysis System Used to Generate Char for EK Experiments in the CCA-Treated Wood Waste Study

3.5.1.3 Gas Scrubber

The batch pyrolysis gas scrubber consisted of a 5-gallon plastic bucket with a perforated one inch diameter, 12 inch long PVC pipe on the interior of the bucket. The PVC pipe was submerged in 10 L of 0.1 M sodium hydroxide. The scrubber was connected to the condensers, and non-soluble gases were vented from the scrubber, via flexible 1 inch tubing. Figure 3.30 is a schematic of the gas scrubber and Figure 3.31 is a photograph of the scrubber in use.

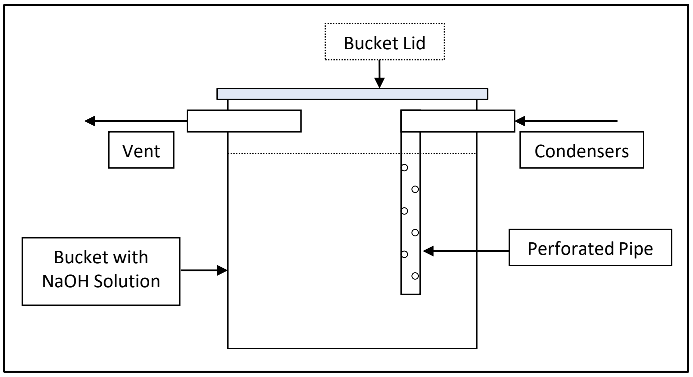


Figure 3.30 Schematic of the Gas Scrubber of the Batch Pyrolysis System Used to Generate Char for EK Experiments in the CCA-Treated Wood Waste Study

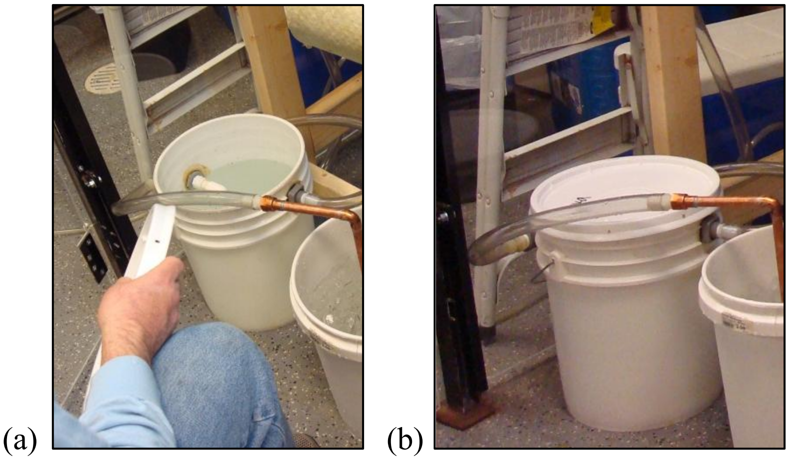


Figure 3.31 Gas Scrubber of the Batch Pyrolysis System Used to Generate Char for EK Experiments in the CCA-Treated Wood Waste Study

(a) Open scrubber, with visible scrubber solution
(b) Closed scrubber, as during system operation (i.e. gas tight)

3.5.2 Batch Pyrolysis System Operation

System operation began by turning the tube furnace on and setting the temperatures for each zone of the tube furnace according to the desired internal reactor set-point temperature (i.e. 350°C, 400°C, or 450°C). This was done using the interface on the tube furnace 3-zone controller. Table 3.6 summarizes the zone temperature settings based on each temperature set-point used in this study. The batch system was operated until 400 g of char was generated at each set-point temperature. Once the internal reactor thermocouple indicated that the reactor had reached the desired set-point, the system was purged with nitrogen gas at a flow rate of 1.5 L/min for a minimum of 5 minutes.

Table 3.6 Zone Temperature Settings for Each Set-Point Temperature Used During Batch Pyrolysis of the CCA-Treated Wood Waste Study

Set-Point Temperature	**Zone 1 Temperature**	**Zone 2 Temperature**	**Zone 3 Temperature**
350°C	350°C	350°C	225°C
400°C	400°C	400°C	275°C
450°C	450°C	450°C	300°C

After the system was fully warmed, a total of 60 g CCA-treated wood sawdust was loaded into the reactor through the double block valve inlet in two 30 g intervals. The bottom inlet valve was closed, then the top valve opened, and 30 g of CCA-treated wood was loaded into the reactor inlet. The top valve was then quickly closed, and the bottom valve opened to allow the wood to drop into the main body of the reactor. After loading the first 30 g batch into the reactor, the plunger was pushed to its full length a total of three times, to move the mass of wood deeper into the reactor. Only after the first batch was at its reaction location was the second 30 g batch loaded into the reactor. The plunger was pushed in to half its length a total of three times to properly move the second batch of wood into the reactor. The start time of the batch run was recorded once the second batch of sawdust was in place. System temperature was monitored via the thermocouple and controller readouts. The reaction duration was set to 25 minutes.

Once the 25 minutes had elapsed, a length extension was added to the plunger. This allowed the pyrolysis char to be moved to the reactor outlet by pushing the extended plunger through the length of the reactor at least three times. After this procedure, all char material was moved from the hot reactor to an area between the closed bottom valve and open top valve of the reactor outlet. The top valve was then closed and the char allowed to cool for 10 minutes. Once cooled, the char was collected in a metal container by opening the bottom valve and tapping the sides of the outlet with a rubber mallet. Contents of the condensers were collected after every five batch runs, while contents of the gas scrubber were collected once all experimental runs for a set-point temperature were completed. A summary of the system operating parameters is found in Table 3.7, and varying stages of batch reactor loading are illustrated in Figure 3.32 and Figure 3.33. The contents of the reactor, condensers, and gas scrubber were collected for additional experiments and analysis as described in Section 3.5.3.

Table 3.7 Batch Pyrolysis System Operating Parameters of the CCA-Treated Wood Waste Study

Warm-up Time (average)	30 minutes for 350°C set-point; 35 minutes for 400°C set-point; 42 minutes for 450°C set-point
Loading Capability	30 grams of sawdust each run
Nitrogen Purge Gas Flow Rate	1.5 L/min

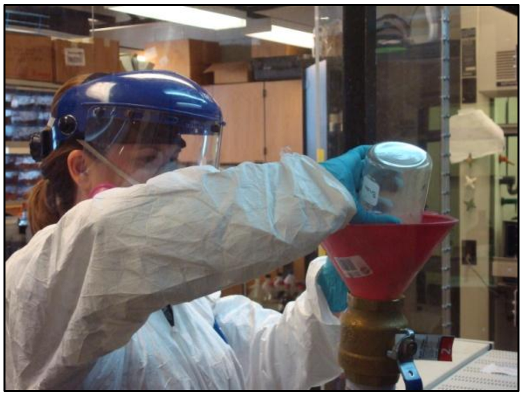


Figure 3.32 Loading CCA-Treated Wood into the Batch Pyrolysis Reactor during Phase III of the CCA-Treated Wood Waste Study

Figure 3.33 Pushing CCA-Treated Wood into the Batch Pyrolysis Reactor during Phase III of the CCA-Treated Wood Waste Study

3.5.3 Post-Operation Experiments and Analysis

The same post-operation experiments and analysis performed in Phase II were conducted on the products of the batch pyrolysis runs. No modifications were necessary to the mass determination procedure used in each post-operation experiment; therefore, all post-operation experiments were performed as described in Section 3.2. Triplicate experiments were performed on each of the pyrolysis products, and Method blanks were performed after every 15 samples for all digestions, TCLPs, SPLPs, and DI Water Leaches. A summary flowchart of these experiments and analysis is provided in Figure 3.34 and the experimental matrix for Phase III is in Table 3.8.

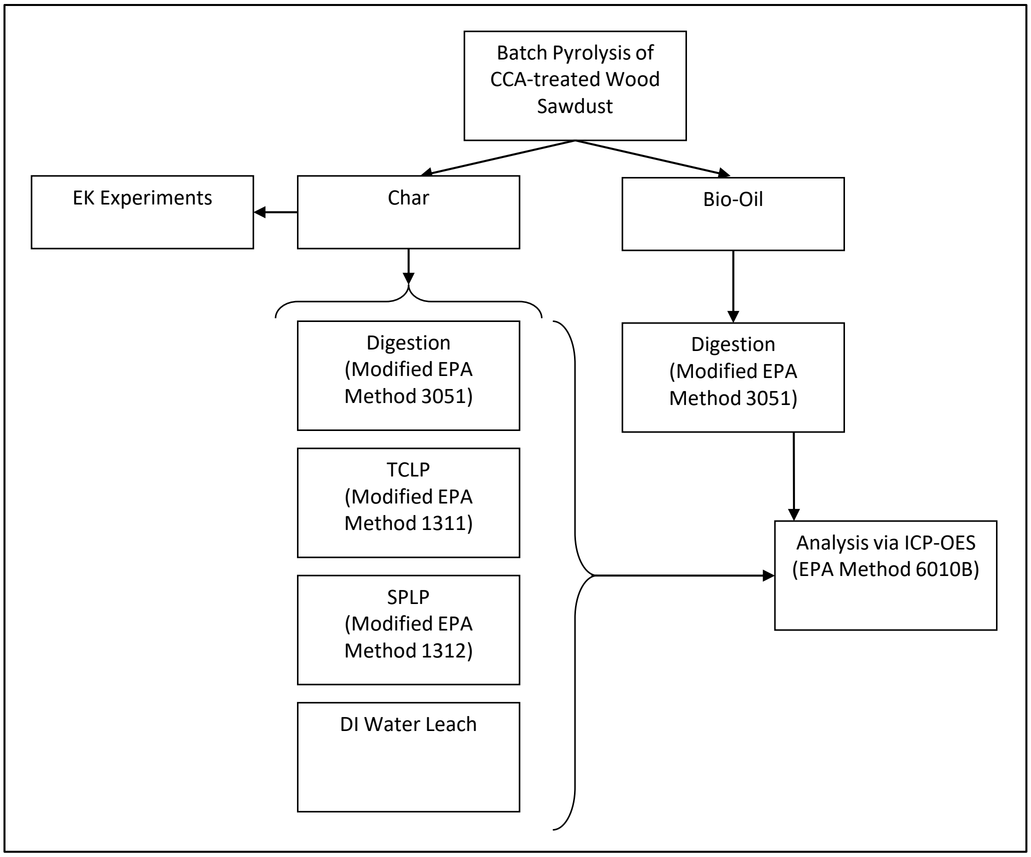


Figure 3.34 Flowchart of the Post-Operation Experiments and Analysis on Products of Batch Pyrolysis Runs for Phase III of the CCA-Treated Wood Waste Investigation

Table 3.8 Experimental Matrix for Phase III of the CCA-Treated Wood Waste Investigation

		Char Products				**Bio-Oil Products**
Pyrolysis Temperature	**Sample ID**	**Digestion**	**TCLP**	**SPLP**	**DI Leach**	**Digestion**
350°C	A	x	x	x	x	x
	B	x	x	x	x	x
	C	x	x	x	x	x
400°C	A	x	x	x	x	x
	B	x	x	x	x	x
	C	x	x	x	x	x
450°C	A	x	x	x	x	x
	B	x	x	x	x	x
	C	x	x	x	x	x

3.6 Phase IV: Electrokinetic Experiments on Pyrolysis Char and CCA-Treated Wood Waste

Electrokinetic (EK) experiments were performed utilizing the CCA-rich char generated during the batch pyrolysis experiments in Phase III. Additional control EK experiments were performed utilizing the CCA-treated wood sawdust generated by the processing steps documented in Section 3.1. The following sections describe the EK system, its operation, and the post-operation experiments and analysis.

3.6.1 System Set-up

The EK system used in these experiments consisted of three units: the EK cell, recirculation system, and operational support systems. The system schematic can be found in Figure 3.35.

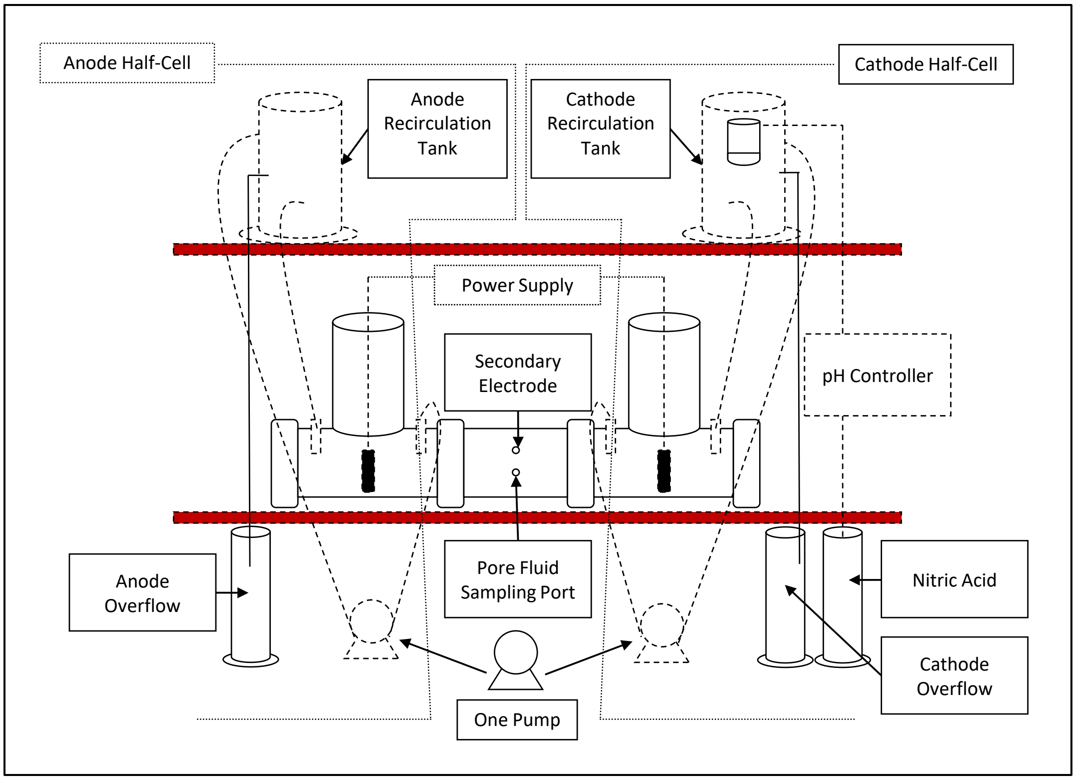


Figure 3.35 Schematic of the EK System of the CCA-Treated Wood Waste Study

Note: The center compartment is between the anode and cathode half-cells

3.6.1.1 EK Cell

Each EK cell consisted of three parts: anode half-cell, cathode half-cell, and a center compartment (see Figure 3.35). All EK cell parts were constructed using schedule 40 clear rigid PVC pipe and fittings. The half-cells were constructed using a combination of 3 inch ID pipe, 3 inch tees, and 3 inch gray PVC union and blind flanges with 3 inch Neoprene gaskets. Two holes were drilled on the top side of the half-cells on either side of the tees. These holes were the points where taps were placed to and from the recirculation tanks.

Unused carbon electrodes fabricated for a previous study were utilized throughout the EK experiments (Broussard, 2013). These electrodes had been fabricated by drilling a 0.040 inch hole into a 2 ¾ inch diameter by 3/8 inch thick resin impregnated carbon electrode disk. A mixture of silver epoxy and silver nitrate was poured into the drilled hole and a 12 inch length of 0.035 inch diameter tungsten wire, coated with heat shrinkable tubing, was inserted into the drilled hole. The electrodes were then baked in an oven at 85°C for 24 hours to cure the epoxy mixture and lock the tungsten wire in place. After removal from the oven and a period of cooling, the joint between the tungsten wire and carbon electrode was sealed with General Electric clear rubber silicon sealant. A close-view schematic of the half-cells, including the carbon electrodes, is in Figure 3.36.

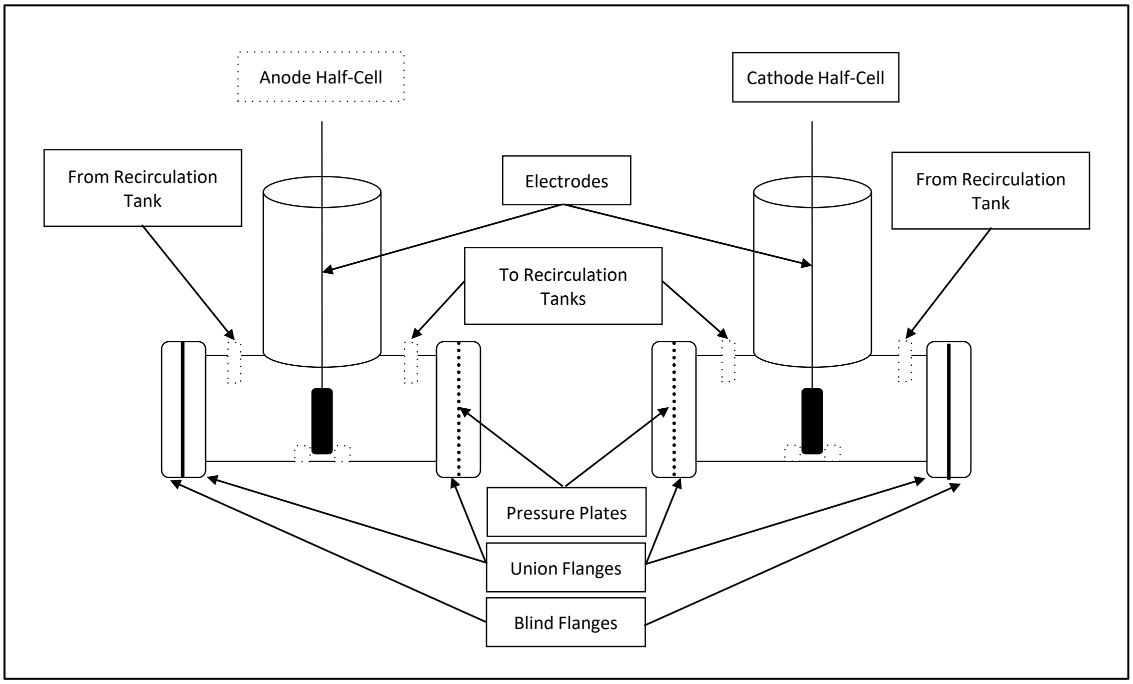


Figure 3.36 Close-view Schematic of the Half-Cells Used in the EK System of the CCA-Treated Wood Waste Study

Each center compartment was constructed with a 5 ½ inch length of 3 inch ID pipe and two 3 inch schedule 80 adjustable Vanstone flanges with 3 inch Neoprene gaskets. Sintered polyethylene plates (1/8 inch thick) were placed within the gaskets used with the Vanstone flanges to serve as "pressure plates" to hold the char and CCA-treated sawdust in place. Two holes were drilled into the midpoint of each center compartment for secondary electrodes and pore sampling ports. Figure 3.37 provides a close-view schematic of the center compartment.

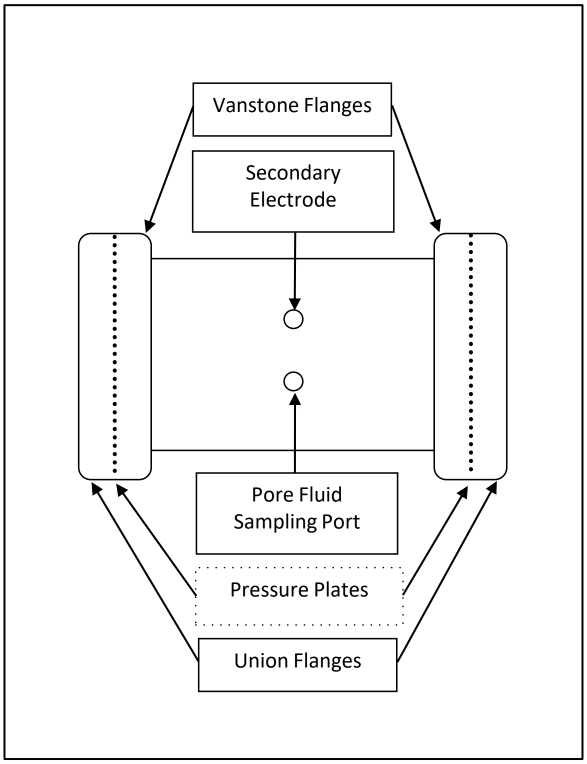


Figure 3.37 Close-view Schematic of the Center Compartments Used in the EK System of the CCA-Treated Wood Waste Study

Note: Samples are contained in the center compartments

Secondary electrodes were used to measure the voltage drop across the center compartment. These electrodes were constructed of a 0.035 inch tungsten clean and straight wire passed through a 1/8 inch Kynar® male straight adapter compression tube fitting, and sealed in place using General Electric clear rubber silicon sealant. The secondary electrodes were connected to a 5 circuit VAC 20 amp circuit block using 16 gauge copper wiring.

Pore fluid sampling units were used to collect fluid samples directly from the center compartment for the duration of the EK experiments. The sampling units were constructed of low pressure Teflon® tubing, two 1/4 inch-28 PEEK® thermoflare bolt fittings, two 1/4 inch-28 PEEK® unions, one 1/4 inch-28 PEEK® bolt, one 1/8 inch Kynar® male straight adapter compression tube fitting, and a threaded high pressure end line filter.

3.6.1.2 Recirculation System

The recirculation system was comprised of anode and cathode recirculation tanks and tank overflow containers, as well as a variable speed pump. The complete recirculation system can be seen in the EK System Schematic (Figure 3.34). Anode and cathode recirculation tanks consisted of a 6 inch ID by 12 in long plexiglass pipe glued to an 8 inch square plexiglass sheet. Each recirculation tank also had two holes which served as entry/exit points for fluid from/to the half-cells, as well as a third hole that connected to the half-cell overflow reservoirs. The cathode recirculation tank also contained a small pH control reservoir that was attached to the interior back of the tank. The reservoir served as the location of continuous cathode half-cell fluid pH sampling and control, and was constructed using a 3 ½ length of 2 inch ID clear PVC pipe and a 2 inch clear PVC pipe cap. Two holes were drilled into the small reservoir: one for fluid entry from the half-cell, the other to allow the fluid to exit into the main recirculation tank. Figure 3.38 provides a photo of two recirculation tanks, post-EK cell operation. EK cell fluid was pumped from the half-cells to and from the recirculation tanks using a Masterflex L/S variable speed pump (model 7553-80, 1-100 RPM, 115 VAC motor) with two Masterflex L/S Easy-Load pump heads.

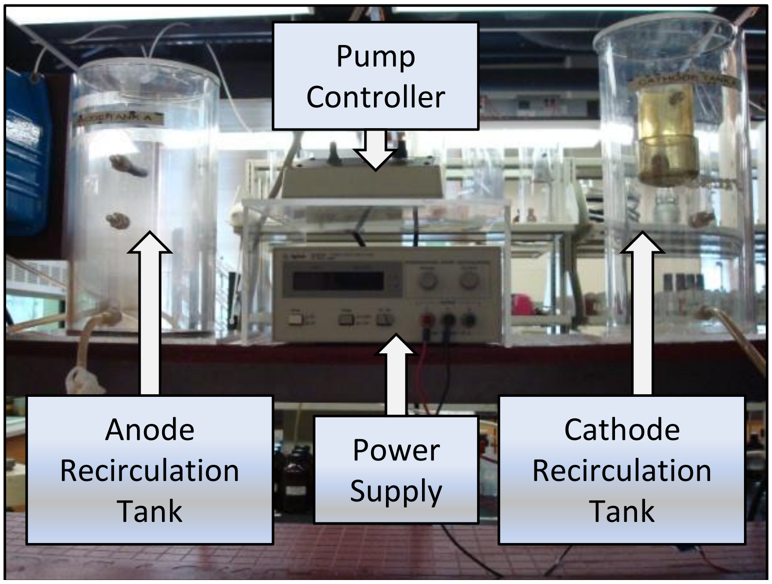


Figure 3.38 EK Recirculation Tanks, Post-Operation of the EK Cells during the CCA-Treated Wood Waste Study

3.6.1.3 Operational Support Units

Two support units were key to the operation of the EK cells: the power supply and pH control unit. Each center compartment had a direct current applied across its length by applying a potential difference across two electrodes via an Agilent power supply (model E3612A, 120 VAC). The power supply can be seen in Figure 3.38. Both electrodes were connected to the 5 circuit VAC 20 amp circuit block referenced in

Section 3.6.1.1, with the circuit block connected to the power supply, all connections via 16 gauge copper wire.

The pH control unit consisted of the small pH control reservoir described in Section 3.6.1.2, a pH control system with pH electrode, and 1 M nitric acid. Combined, these elements allowed for the cathode half-cell pH to be regulated throughout the experiment. A Barnart standing DLXB-pH/M Series metering pump with proportionating output along with a Sensorex pH probe (model 450C) served as the pH control system. Nitric acid was stored in a Nalgene 1000 mL polypropylene graduated cylinder and pumped into the cathode recirculation tank by the Barnart metering pump, as needed. The full arrangement can be seen in the EK System Schematic (Figure 3.35).

3.6.2 EK System Operation

Operation of the EK system began with the loading of the cell center compartments. Duplicate cells were created using char generated each batch pyrolysis temperature (350°C, 400°C, and 450°C) for a total of six char-filled EK cells. Two control cells were also created and contained CCA-treated wood sawdust generated during the material processing steps described in Section 3.1. EK cell center compartments were filled by first weighing out approximately 200 g of material into a 2 L Nalgene polypropylene beaker. Approximately 200 g of tap water was then slowly added to the char or sawdust, and slowly mixed. The addition of water minimized dust formation and facilitated expansion of the char/sawdust material to more easily fill the center compartments. Once thoroughly mixed, the material was ready to be loaded into the center compartments.

Loading of the center compartments began by capping the anode half-cell end of the compartment using a blind flange and Neoprene gasket with a pre-soaked, sintered polyethylene “pressure plate”. The wet char or sawdust was then carefully funneled into the center compartment until the material level was just below the secondary electrode and pore fluid sampling ports. Next, the material was lightly tapped with a 5 lb compression hammer to eliminate air pockets and ensure uniform filling. Both the secondary electrode and pore fluid sampling units were screwed into the center compartments at this time. After the electrodes and sampling units were in place, the remaining wet char/sawdust material was funneled into the center compartment until the compartment was completely full. Again, the material was gently tapped with a 5 lb compression hammer.

Once the center compartment was full, the cathode half-cell was attached utilizing another Neoprene gasket with a pre-soaked, sintered polyethylene “pressure plate”. The semi-assembled EK cell was then gently turned over to remove and replace the blind flange with the anode half-cell, keeping the Neoprene gasket and “pressure plate” in place. Table 3.9 summarizes the content of the loaded EK cell, while Figure 3.39, Figure 3.40 and Figure 3.41 capture various stages of the cell loading procedure.

Table 3.9 Mass Loaded into EK Cells for the CCA-Treated Wood Waste Study

Cell ID	Loaded Material	Material Mass	Total Loaded Wet Mass
Cell A	350°C Char	200.50 g	397.91 g
Cell B	350°C Char	200.16 g	411.89 g
Cell C	400°C Char	201.46 g	408.37 g
Cell D	400°C Char	202.15 g	410.22 g
Cell E	450°C Char	200.21 g	407.21 g
Cell F	450°C Char	202.52 g	410. 61 g
Cell G	CCA-rich Sawdust	209.59 g	414.92 g
Cell H	CCA-rich Sawdust	217.42 g	440.58 g

Note: Cells G and H are experimental controls

Figure 3.39 Assembling Center Compartments of EK Cells Used in the CCA-Treated Wood Waste Study

(a) Adding a pre-soaked pressure plate to a Neoprene gasket
(b) Attaching a blind flange to one end of a center compartment

(a)  (b) 

Figure 3.40 Mixing and Loading Material into the Center Compartments of EK Cells Used in the CCA-Treated Wood Waste Study

(a) Mixing CCA-treated wood sawdust with water
(b) Funneling pyrolysis char into the center compartment

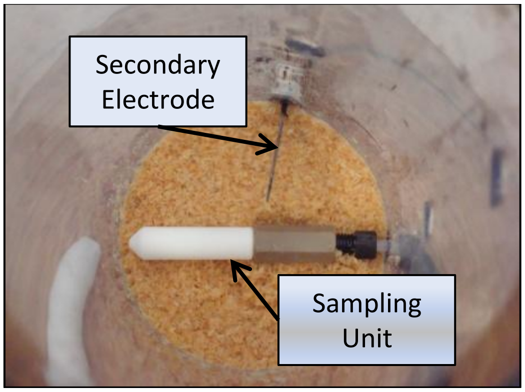


Figure 3.41 Secondary Electrode and Pore Fluid Sampling Unit in the Center Compartment of an EK Cell Used in the CCA-Treated Wood Waste Study

Once the EK cells were fully assembled they were placed on their support shelving, all fluid inputs and outputs were connected, and all electrical connections were made. Tap water was simultaneously added to the anode and cathode half-cells to maintain constant hydraulic head, and then to the recirculation tanks. Total volume of tap water added to each EK cell system is captured in Table 3.10. The Masterflex L/S variable speed pump was turned on for 12 hours to fully establish zero hydraulic head across the systems. At the end of the 12 hour period, power was turned on to the EK systems with the voltage drop set to the maximum possible electrical potential difference that could be achieved by the power supplies. The power supplies were then set to a constant current of 140 mA. At the same time, the pH controllers were turned on and set to maintain a cathode pH of 3.0.

Table 3.10 Volume of Tap Water Added to EK Cells at the Start of the EK Study

Cell ID	**Total Volume**
Cell A	8,470 mL
Cell B	7,970 mL
Cell C	8,450 mL
Cell D	8,740 mL
Cell E	8,640 mL
Cell F	8,260 mL
Cell G	8,370 mL
Cell H	8,430 mL

Liquid samples were collected every day from the recirculation tanks and every other day from the center compartment sampling port. The decreased sampling frequency was intended to minimally influence cell hydraulic transport. Figure 3.42 illustrates the collection of liquid samples. Additionally, daily measurements were recorded for the following: potential difference (V) across the cell, current (mA) across the cell, volume of fluid in the anode and cathode overflow reservoirs, volume of water added to the anode and cathode half-cells to maintain zero hydraulic head, and the volume of 1 M nitric acid consumed during pH control. The experimental matrix for the EK investigation is provided in Table 3.11.

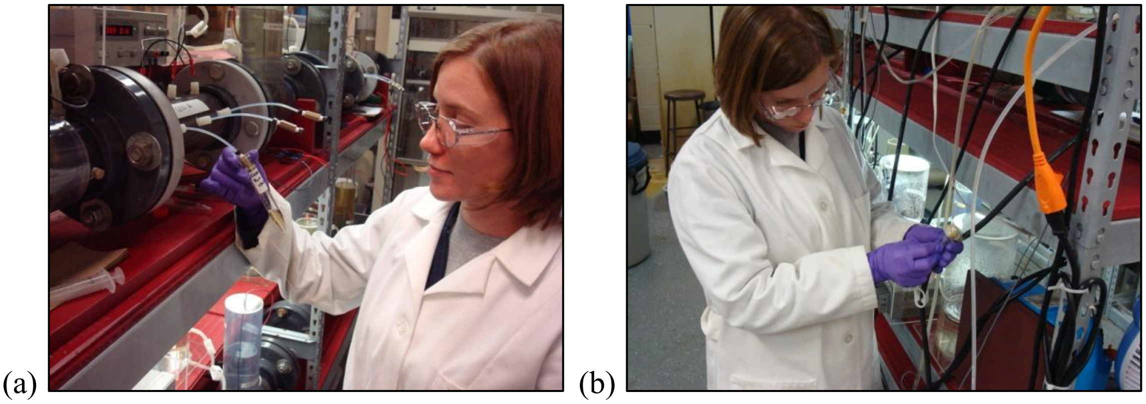


Figure 3.42 Collecting Daily EK Fluid Samples during the CCA-Treated Wood Waste Study

(a) Collecting 5 mL pore fluid sample from center compartment
(b) Collecting 10 mL sample from recirculation tank

Table 3.11 Experimental Matrix for Phase IV of the CCA-Treated Wood Waste Investigation

Pyrolysis Temperature	**Cell ID**	**pH**	**Current**	**Pore Sample Volume**	**Recirculation Tank Sample Volume**	**Duration**
350°C	A	3.0	149 mA	5 mL	10 mL	15 days
	B	3.0	149 mA	5 mL	10 mL	15 days
400°C	C	3.0	149 mA	5 mL	10 mL	15 days
	D	3.0	149 mA	5 mL	10 mL	15 days
450°C	E	3.0	149 mA	5 mL	10 mL	15 days
	F	3.0	149 mA	5 mL	10 mL	15 days
N/A (Control)	G	3.0	149 mA	5 mL	10 mL	15 days
	H	3.0	149 mA	5 mL	10 mL	15 days

Note: Cells A-F were loaded with pyrolysis char; Cells G and H were loaded with CCA-treated wood sawdust

After fifteen days, power to the cells was turned off and all electrical connections were disconnected. The pumps and pH controllers were also turned off, and the recirculation tanks and half-cells were isolated using pinch clamps. Fluids from the half-cells and recirculation tanks were drained and stored. Electrodes were rinsed with DI water to remove any deposits, and the solutions were collected and stored. The volume of all collected fluids was recorded. Once all fluids had been collected, the secondary electrodes were then removed from the center compartments and the holes were filled with plastic plugs. The anode and cathode half-cells were then detached and replaced with blind flanges. Center compartments were placed in a refrigerator freezer for approximately 12 hours to freeze the samples and facilitate their removal from the compartments. After the contents of the center compartments were solidified, the blind flange was removed from the cathode half-cell end of the compartment and the pressure plate was stored in a Ziploc® bag. The contents of the center compartments were then removed in four equally sized sections, as captured in Figure 3.43, and placed in Ziploc® 4 cup containers which were then stored in a standard refrigerator. Once the center compartment was empty of material, the blind flange was removed from the anode half-cell end of the compartment and the pressure plate was stored in a Ziploc® bag.

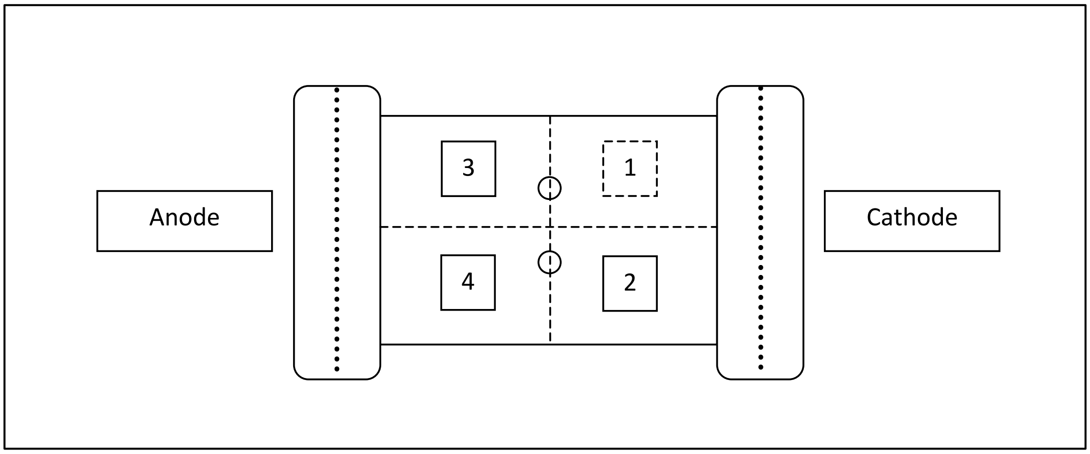


Figure 3.43 Sketch of the Center Compartment Sections of the EK Cells Used in the CCA-Treated Wood Waste Investigation

3.6.3 Post-Operation Experiments and Analysis

The same post-operation experiments and analysis performed in Phase II and Phase III, as well as moisture content determination, were also performed on the solid products of the EK experiments. Some modifications to the methodology described in Section 3.2 were necessary, and are described in the following sections. Two additional analyses and experiments were also performed: pH evaluation of the daily liquid samples and filtration of the post-EK fluids and subsequent digestion of the collected solid material. A summary flowchart of all post-operation experiments and analysis is provided in Figure 3.44, and the corresponding experimental matrix is in Table 3.12.

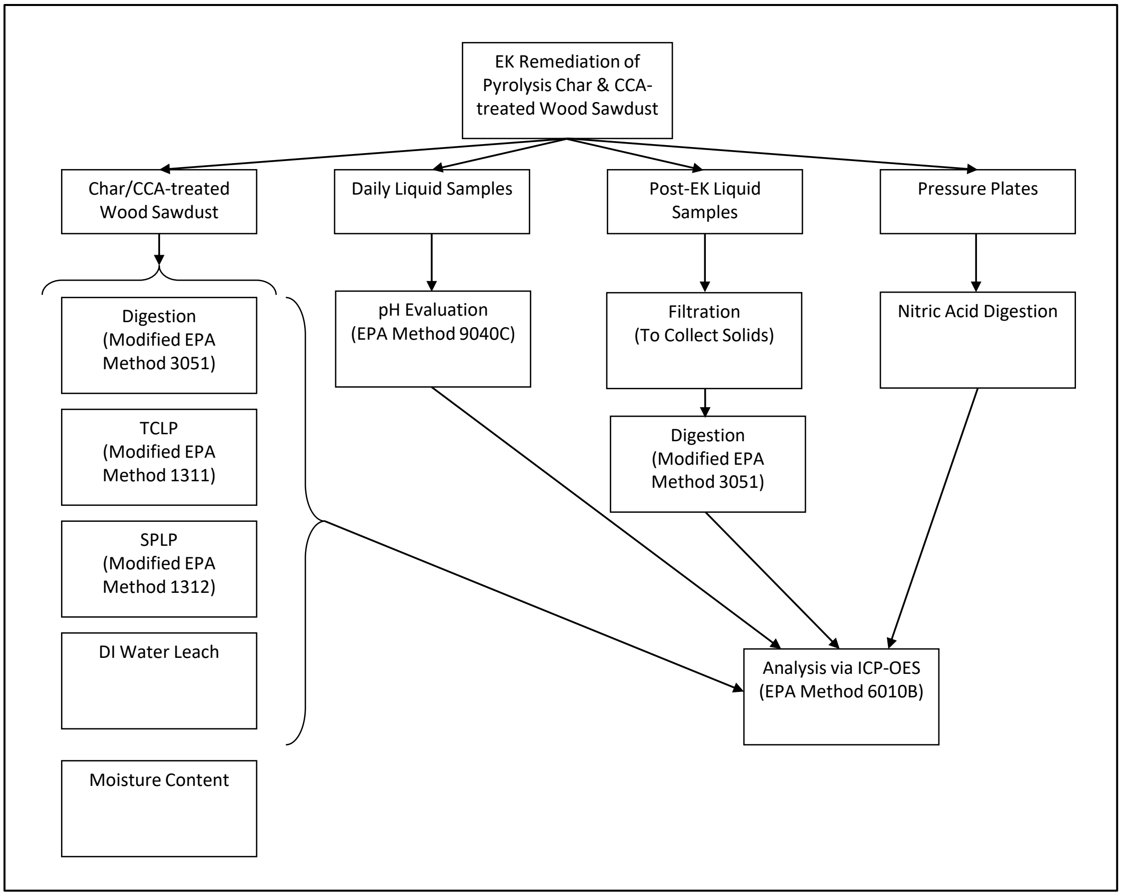


Figure 3.44 Flowchart of the Post-Operation Experiments and Analysis on Products of EK Runs for Phase IV of the CCA-Treated Wood Waste Investigation

Table 3.12 Post-Operation Experimental Matrix for Phase IV of the CCA-Treated Wood Waste Investigation

		Char					**Pressure Plates**	**Filters**
Cell ID	**Cell Section**	**Digestion**	**TCLP**	**SPLP**	**DI Leach**	**Moisture Content**	**HNO_3 Digestion**	**Digestion**
A	1	x3	x3	x3	x3	x3	*	%
	2	x3	x3	x3	x3	x3		
	3	x3	x3	x3	x3	x3	*	
	4	x3	x3	x3	x3	x3		
B	1	x3	x3	x3	x3	x3	*	%
	2	x3	x3	x3	x3	x3		
	3	x3	x3	x3	x3	x3	*	
	4	x3	x3	x3	x3	x3		
C	1	x3	x3	x3	x3	x3	*	%
	2	x3	x3	x3	x3	x3		
	3	x3	x3	x3	x3	x3	*	
	4	x3	x3	x3	x3	x3		
D	1	x3	x3	x3	x3	x3	*	%
	2	x3	x3	x3	x3	x3		
	3	x3	x3	x3	x3	x3	*	
	4	x3	x3	x3	x3	x3		
E	1	x3	x3	x3	x3	x3	*	%
	2	x3	x3	x3	x3	x3		
	3	x3	x3	x3	x3	x3	*	
	4	x3	x3	x3	x3	x3		
F	1	x3	x3	x3	x3	x3	*	%
	2	x3	x3	x3	x3	x3		
	3	x3	x3	x3	x3	x3	*	
	4	x3	x3	x3	x3	x3		
G	1	x3	x3	x3	x3	x3	*	%
	2	x3	x3	x3	x3	x3		
	3	x3	x3	x3	x3	x3	*	
	4	x3	x3	x3	x3	x3		
H	1	x3	x3	x3	x3	x3	*	%
	2	x3	x3	x3	x3	x3		
	3	x3	x3	x3	x3	x3	*	
	4	x3	x3	x3	x3	x3		

*: Two pressure plates were digested per EK cell for a total of 16 HNO_3 digestions;
%: The number of filter paper digestions was dependent upon the need to filter the half-cell liquid samples and varied by EK cell

3.6.3.1 pH of Daily Liquid Samples

The pH of all daily EK liquid samples was measured using an Oakton Model 310 pH meter with an Orion gel-epoxy probe (Model 9206B) according to EPA Method 9040C. The pH was measured within one day of the sample being collected. pH measurement was repeated at the completion of the EK experiments to verify initial measurements.

3.6.3.2 Filtration of Post-EK Liquid Samples

Solid material was contained in the fluid collected from the EK half-cells, recirculation tanks, and electrode washes. It is important to note that the pressure plates prevented char from migrating to the EK half-cells; therefore the solid material in these sections of the EK cells was material that had precipitated out of solution over the course of the 15 day experimental run. See Figure 3.45 for examples of the observed foam, settled solid material, and deposits on the electrodes prior to EK cell disassembly. The fluid samples were all vacuum filtered using a Buchner funnel and filter flask with Whatman Grade 41 filter paper. After filtration the liquid samples were stored and the filter paper with collected material was allowed to air dry under a laboratory hood for 24 hours. Once dry, the filter paper was stored in Ziploc® bags awaiting modified microwave assisted digestion.

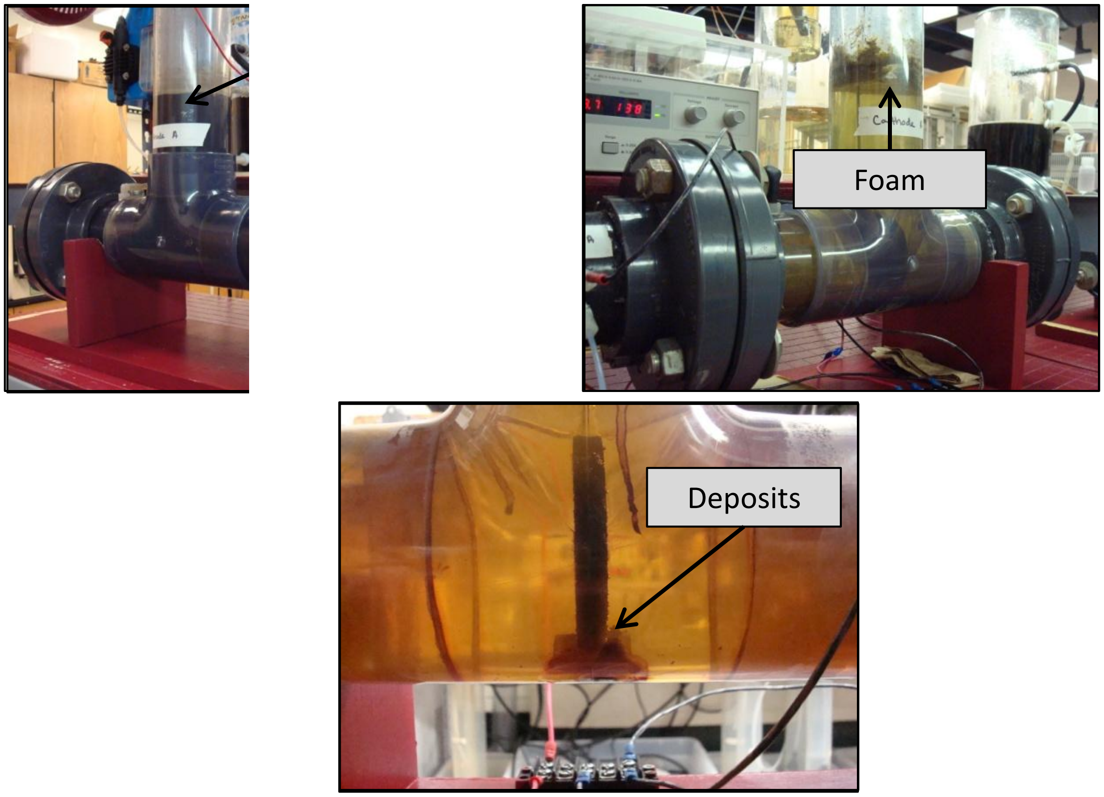


Figure 3.45 Solid Material in Different Parts of the EK Cell during the CCA-Treated Wood Waste Study

(a) Solids in anode half-cell and recirculation tank
(b) Foam in cathode half-cell
(c) Deposits beginning to collect on the on right side of electrode (photo taken from behind EK cell)

3.6.3.3 Moisture Content

Moisture content of the post-EK char/CCA-treated wood sawdust samples was determined utilizing the general procedure outlined in Section 3.2.3 (i.e. dry in oven, place in dessicator, check mass, repeat until mass is constant), with a several deviations due to the significant volumes of water that had been added to the EK cells. First, between 2.0-5.0 grams of sample were utilized for the initial sample weight. Second, the initial drying period was extended to 24 hours. Third, only the five heaviest initial samples went through the repeated drying/dessicator/mass check sequence until the sample mass was constant, while the others remained in the oven. Lastly, the repeat drying time was shortened to one hour. Only once the five samples reached constant mass, were the remaining samples weighed. Triplicate experiments were performed on each of the post-EK char/CCA-treated wood sawdust samples.

3.6.3.4 CCA Metal Content

Post-EK char/CCA-treated wood sawdust samples and the liquid sample filter papers underwent the modified microwave assisted digestion procedure detailed in Section 3.2.1. The only deviations from this described procedure involved increasing the mass utilized from 0.4000 ± 0.0010 grams to 1.0000 ± 0.0010 grams for the char/sawdust samples and to the total mass of the dried filter paper. Triplicate experiments were performed on each of the post-EK char/CCA-treated wood sawdust samples, but were not performed on the dried filter paper due to the varying quantity and mass of the filter paper. Method blanks were performed after every 15 samples for all digestions. The filtrates were all analyzed for CCA metals content in accordance with the ICP-OES method detailed in Section 3.3.

The daily liquid samples did not undergo any digestion procedures because there were no visible solids and they did not require any filtration. The samples were directly analyzed for CCA metals content in accordance with the ICP-OES method detailed in Section 3.3.

Each of the pressure plates underwent a bench-top nitric acid digestion. This digestion consisted of cutting each pressure plate into six pie-shaped pieces and placing them into 400 mL beakers. 200 mL of 20% nitric acid were then added to the beakers, and the beakers were placed on a stir plate. After the pressure plate pieces were digested for two hours, the contents of the beakers were vacuum filtered utilizing the set-up in Section 3.2.1. The undiluted filtrates were then analyzed for CCA metals content via the ICP-OES method described in Section 3.3.

3.6.3.5 CCA Metal Mobility

TCLP, SPLP, and DI Leaches were performed on all of the post-EK char/CCA-treated wood sawdust samples. No modifications were necessary to the sample mass used in each post-operation experiment; therefore, all post-operation experiments were performed as described in Section 3.2.2. Triplicate experiments were performed on each of the post-EK samples, and Method blanks were performed after every 15 samples.

CHAPTER IV

RESULTS AND DISCUSSION

As detailed in the previous chapter, numerous experiments were performed to determine the feasibility of coupling pyrolysis and electrokinetic techniques to remediate CCA-treated wood waste. The following sections detail results of these experiments including those related to the processing of CCA-treated wood waste for use in this study.

4.1 Phase I: Characterization of CCA-Treated Wood Waste

Three characterization studies were performed to gain a better understanding of the composition of the CCA-treated wood material, and to ensure that the properties were uniform for the wood samples generated during the processing sequence and utilized throughout this study. Results of these characterization studies determined the metal content, metal mobility, and moisture content of the CCA-treated wood waste and are presented in the following sections.

4.1.1 CCA Metal Content

Six sawdust samples from each of the three 5.7 qt storage containers underwent the modified microwave assisted acid digestion described in Section 3.2.1. The average concentration of each CCA metal present in the CCA-treated wood waste is provided in Figure 4.1. Metal content data for all replicates are provided in Appendix B. Average metal concentration values are in similar ratios to those of CCA Type B formulations, suggesting that the utility pole may have been originally treated using the Type B formulation. Additionally, there was little variation in results across all replicates for all three metals, as indicated by the error bars in Figure 4.1. The minor deviations across all replicates provided confidence that the prepared samples were well mixed and that concentration levels could be assumed to be constant for all CCA-treated wood sawdust samples used throughout this study.

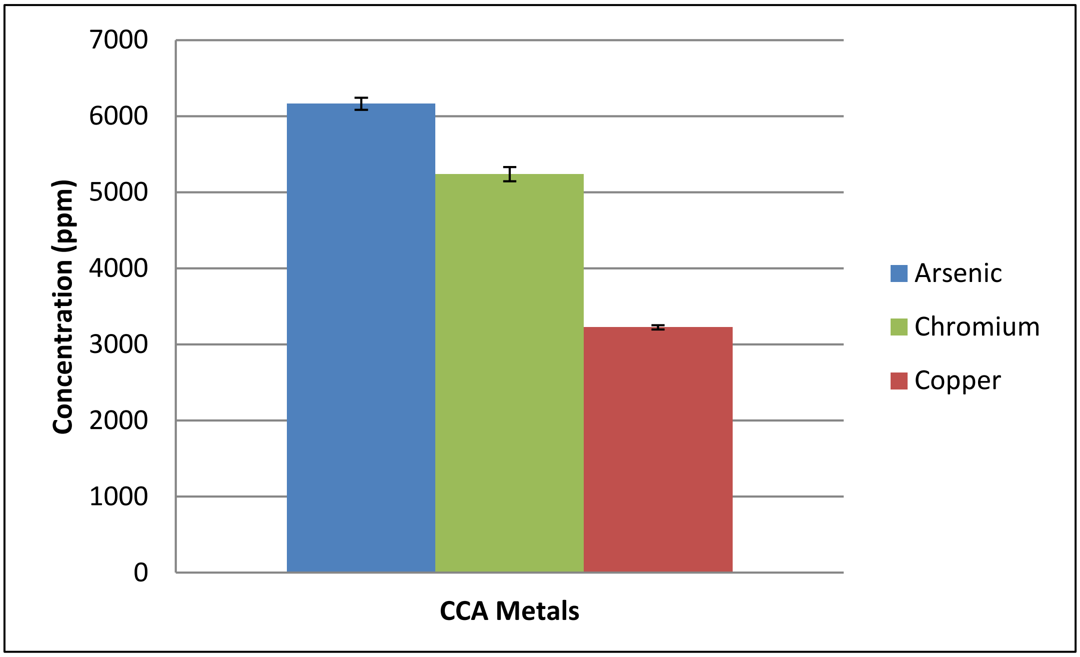


Figure 4.1 Average Concentration of CCA Metals in the CCA-Treated Wood Waste Used for this Study

Note: Error bars represent 95% confidence intervals

4.1.2 CCA Metal Mobility

The mobility of CCA metals in the processed sawdust was evaluated by performing three leaching experiments as described in Section 3.2.2.: the Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure

(SPLP), and Deionized (DI) Water Leaches. Six samples were utilized from each of the three 5.7 qt containers for each leaching experiment. Averaged results of the leaching experiments are presented here, with data for all replicates provided in Appendix B.

4.1.2.1 TCLP

The average concentration of each of the CCA metals in the TCLP leachate is provided in Figure 4.2. Arsenic and chromium exceed the TCLP threshold limit of 5.0 ppm; therefore, the utility pole would need to be disposed of in a regulated hazardous waste facility if CCA-treated wood was regulated as a hazardous material. Arsenic also exhibits the most mobility under TCLP conditions with a leachate concentration of 53.3 ppm, followed by copper and chromium at 32.7 ppm and 14.5 ppm, respectively. Chromium’s low mobility under TCLP conditions is expected due to its strong fixation with the wood matrix and formation of wood complexes, as discussed in Section 1.1.2. Similarly, as expected, arsenic and copper display higher mobility than chromium as these components are more likely to form precipitates on, or be physically adsorbed on wood constituents, and thus are more readily leached from CCA-treated wood.

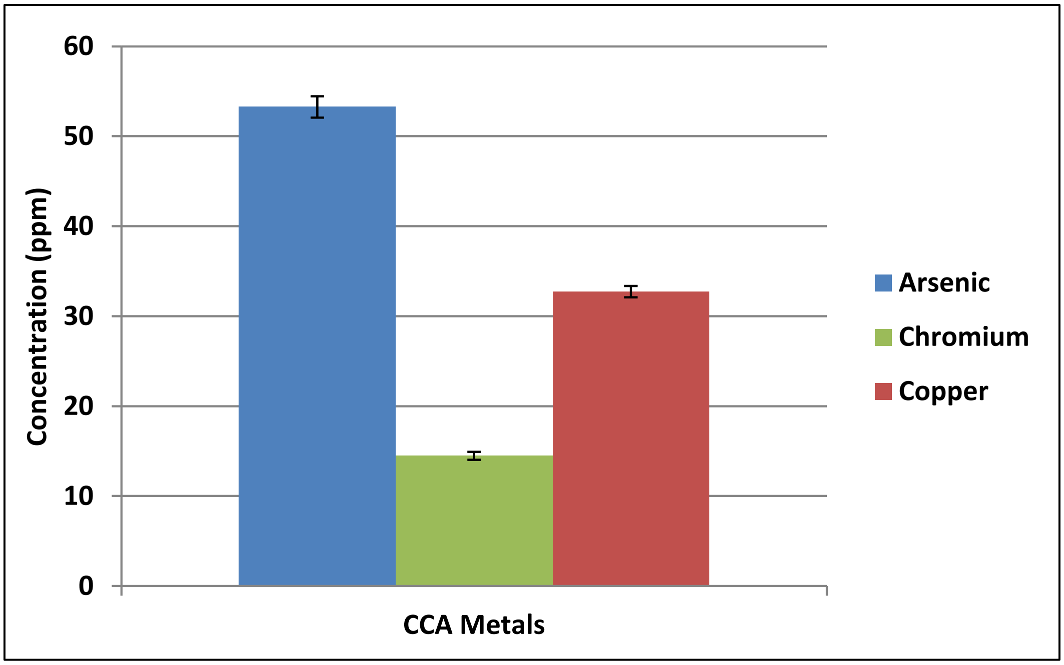


Figure 4.2 Average Concentration of CCA Metals in the TCLP Leachate of the CCA-Treated Wood Waste Used for this Study

Note: Error bars represent 95% confidence intervals

4.1.2.2 SPLP

Figure 4.3 captures the average concentration of each of the CCA metals in the SPLP leachate. Arsenic again exhibits the highest mobility under SPLP conditions of the three metals with a SPLP filtrate concentration of 45.7 ppm. Copper and chromium have SPLP leachate concentrations of 21.1 ppm and 12.6 ppm, respectively. All leachate concentrations are lower than those of the TCLP experiments indicating that simulated acid rain conditions of the SPLP have less of an impact on metal mobility than the relatively more alkaline simulated landfill conditions of the TCLP.

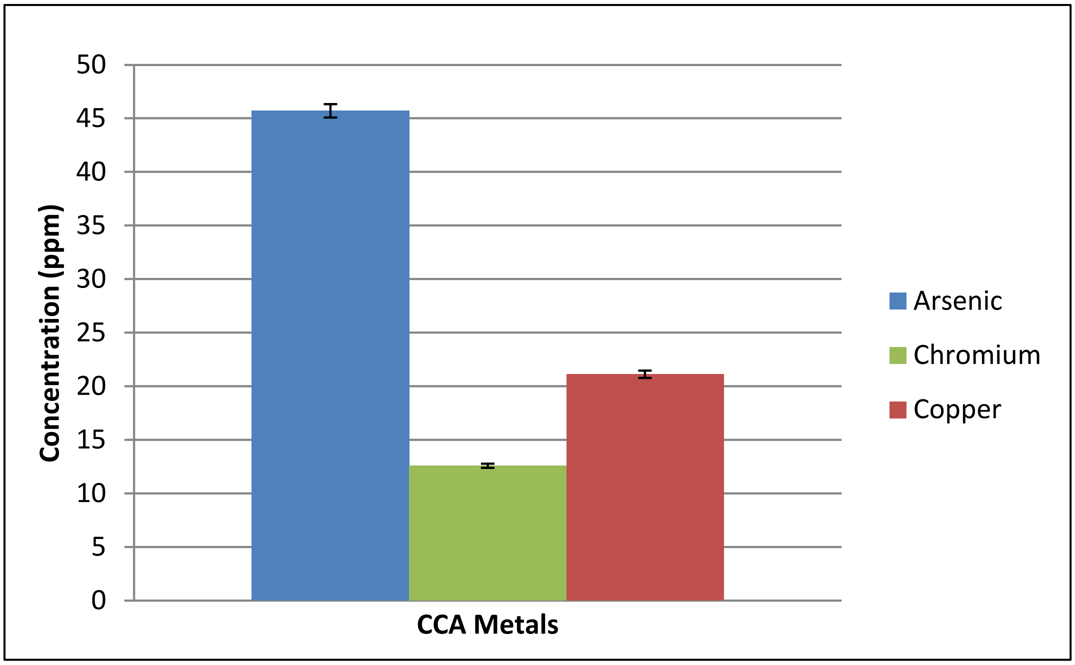


Figure 4.3 Average Concentration of CCA Metals in the SPLP Leachate of the CCA-Treated Wood Waste Used for this Study

Note: Error bars represent 95% confidence intervals

4.1.2.3 DI Water Leach

The average concentration of each of the CCA metals in the DI water leach leachate is provided in Figure 4.4. As with both the TCLP and SPLP results, arsenic exhibits the most mobility under DI water leach conditions [As (41.3 ppm) > Cu (19.7 ppm) > Cr (11.5 ppm)]. These results clearly indicate that all three metals are mobile even under the weak solvent conditions of the DI water leach. Results also illustrate the potential concern of metals leaching from installed CCA-treated wood materials into their surrounding environments.

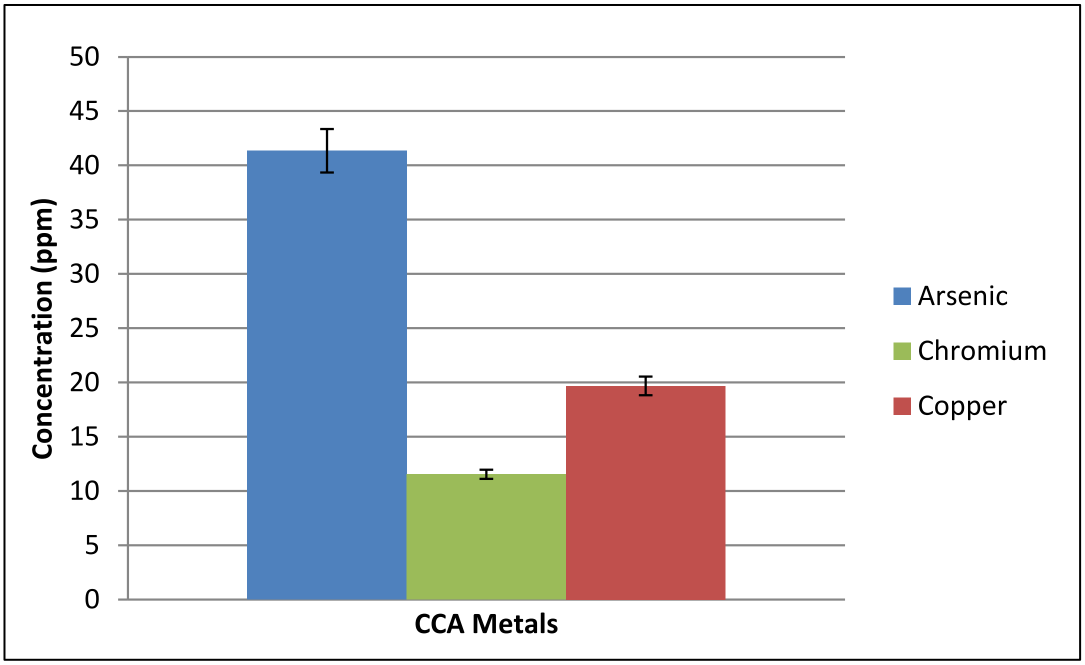


Figure 4.4 Average Concentration of CCA Metals in the DI Water Leachate of the CCA-Treated Wood Waste Used for this Study

Note: Error bars represent 95% confidence intervals

4.1.3 Moisture Content

Nine sawdust samples from each of the three 5.7 qt storage containers underwent the moisture content procedure described in Section 3.2.3. The sawdust used in all experiments contained 7.96% moisture, on average. Supporting moisture content data for all replicates are provided in Appendix B.

4.1.4 Summary of Characterization Study Findings

Results of the characterization studies indicate that the sawdust produced for use throughout the CCA-treated wood study were well homogenized, as there was very little variation in the data across replicates in each study. Concentrations of each CCA metal are in ratios similar to those of Type B formulations, and the overall moisture content of the wood waste was just under 8%. Metal mobility experiments (TCLP, SPLP, and DI water leaches) demonstrated that all three CCA metals were mobile under a variety of solvent conditions. Leachate values for all metals were highest for the TCLP experiments and second highest for the SPLP experiments (TCLP > SPLP > DI water leach), with arsenic being the most mobile under all experimental conditions (As > Cu > Cr). The prevalence of arsenic and copper in the leachates is likely due to the presence of free, unbound metals in the CCA-treated wood waste, while lower chromium levels suggest the chromium formed more complete complexes during treatment application.

4.2 Phase II: Bench Pyrolysis of CCA-Treated Wood Waste

A total of nine bench pyrolysis runs were performed utilizing the bench system described in Section 3.4.1. Triplicate runs were performed at each set-point temperature (i.e. 350°C, 400°C, or 450°C). Details on pyrolysis product generation, as well as the results of studies determining the metal content and metal mobility in the pyrolysis char are presented in the following sections.

4.2.1 Bench Pyrolysis Product Generation

The mass of char and volume of bio-oil produced were recorded after each pyrolysis run. Figure 4.5 and Figure 4.6 illustrate the average char mass and volume of bio-oil produced at each pyrolysis set-point temperature, while raw data are provided in Appendix C. As expected, the mass of char produced and the volume of bio-oil produced are inversely related. There is less destruction of the wood material at lower temperatures than at higher temperatures, with a large portion of the feed mass loss contributable to a drying effect due to the feed containing nearly 8% moisture. This phenomenon is observed in Figure 4.7 where the bio-oil produced at lower temperatures contains a larger water fraction than bio-oil produced at higher temperatures which contain a larger hydrocarbon fraction. The wood matrix is more thoroughly destroyed at higher temperatures, resulting in a lower char mass, more pyrolysis vapors, and an overall increase in volume of produced bio-oil. Again, the bio-oil produced at higher temperatures contains a larger hydrocarbon fraction, best illustrated in Figure 4.7.c.

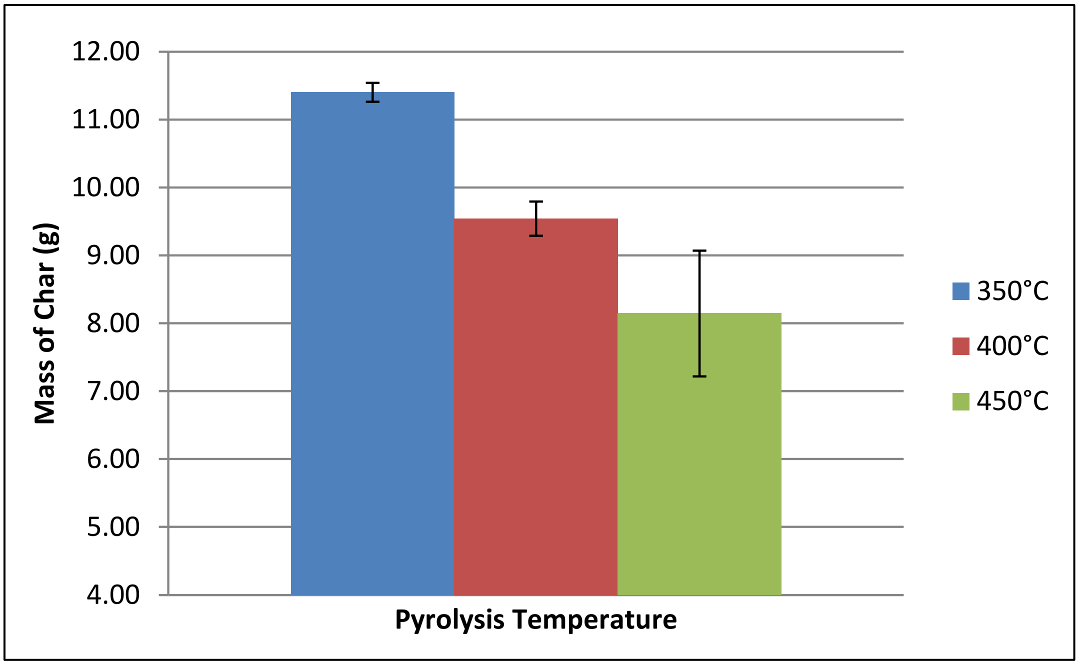


Figure 4.5 Average Mass of Char Produced During Bench Pyrolysis of CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

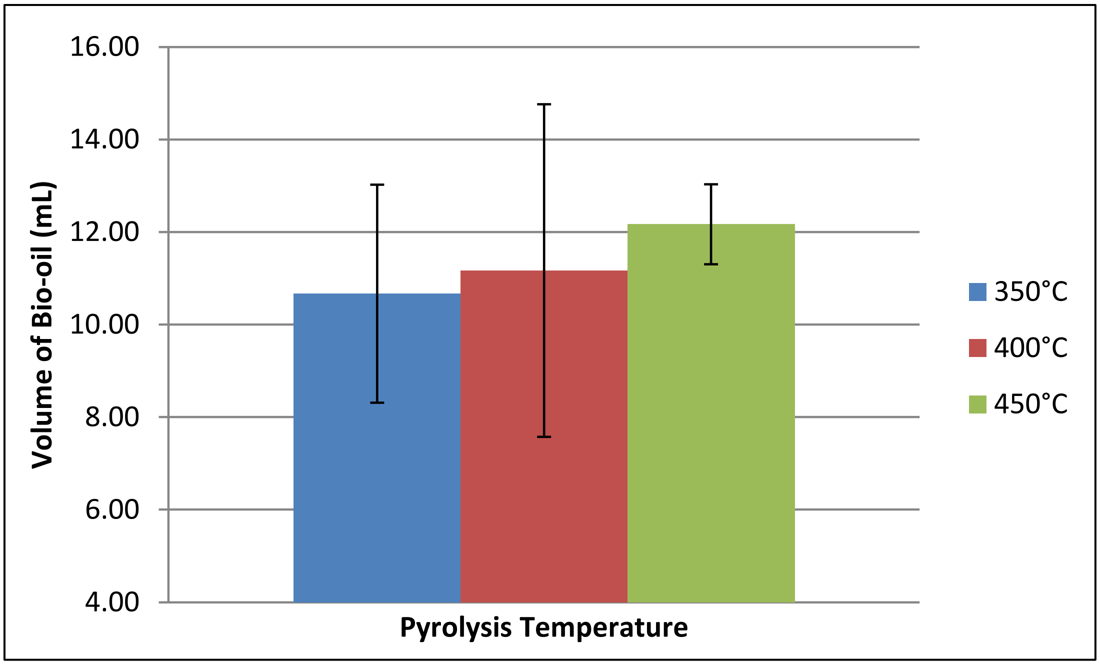


Figure 4.6 Average Volume of Bio-oil Produced During Bench Pyrolysis of CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

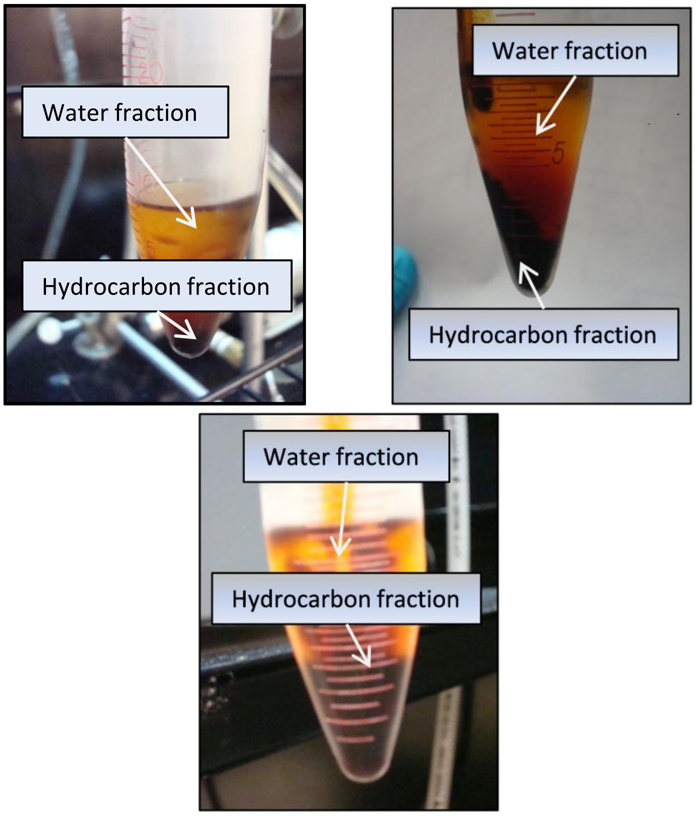


Figure 4.7 Photographs of the Bio-oil Fractions Produced During Bench Pyrolysis of CCA-Treated Wood Waste

(a) Bio-oil produced at 350°C
(b) Bio-oil produced at 400°C
(c) Bio-oil produced at 450°C

4.2.2 Bench Pyrolysis Post-Operation Experiments and Analysis

4.2.2.1 CCA Metal Distribution

Pyrolysis at all three set-point temperatures resulted in a char rich in metals (see Figure 4.8). The overall concentration of each metal in the char was more than double the concentration of the metals in the pyrolysis sawdust feed across all set-point temperatures, as illustrated in Figure 4.9. This result was expected, as the CCA metals are not destroyed or converted to other components during pyrolysis; rather, metals that do not volatilize will remain in the solid material while the wood components break down and are converted to other pyrolysis products. This ultimately results in a lower overall mass of solid material (char) that contains some of metals that were in the original sawdust feed; however, some of the CCA metals are volatized during pyrolysis, resulting in a lower concentration and mass of metals remaining in the char product.

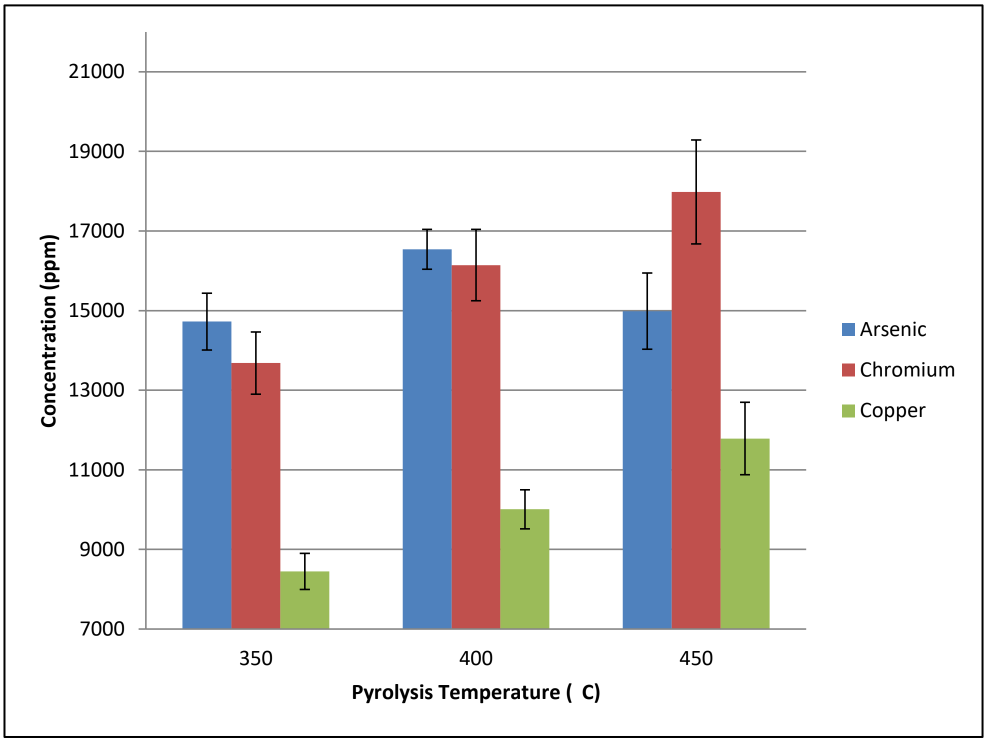


Figure 4.8 Average Concentration of CCA Metals in Char Produced During Bench Pyrolysis of CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

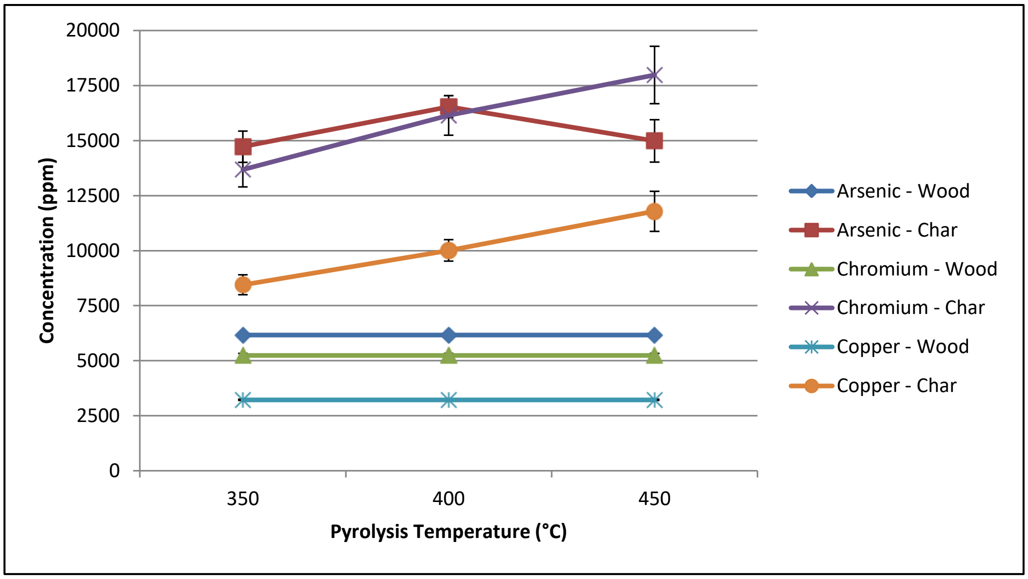


Figure 4.9 Comparison of the Average Concentration of CCA Metals in Bench Pyrolysis Char and CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

The average mass percentage of each metal retained in the char produced at each pyrolysis temperature was calculated using Equation 4.1, with results illustrated in Figure 4.10. The average mass percentage retained of each metal generally decreased as pyrolysis temperatures increased from 350°C to 450°C. For example, on average, arsenic was retained at 90.8% during pyrolysis at 350°C, while it was retained at only 66.0% during runs at 450°C. The only variation to this trend was with the mass percent retained for copper, though the deviation was less than 1%. As expected, these concentration and mass retention trends are due to the increased volatilization of each metal that occurs as pyrolysis temperatures increase. Raw data used in these calculations are in Appendix C.

$$\text{Metal Mass \% Retained} = \frac{\text{Mass of Metal in Char}}{\text{Mass of Metal in CCA−treatd Wood Feed}} \times 100 \qquad (4.1)$$

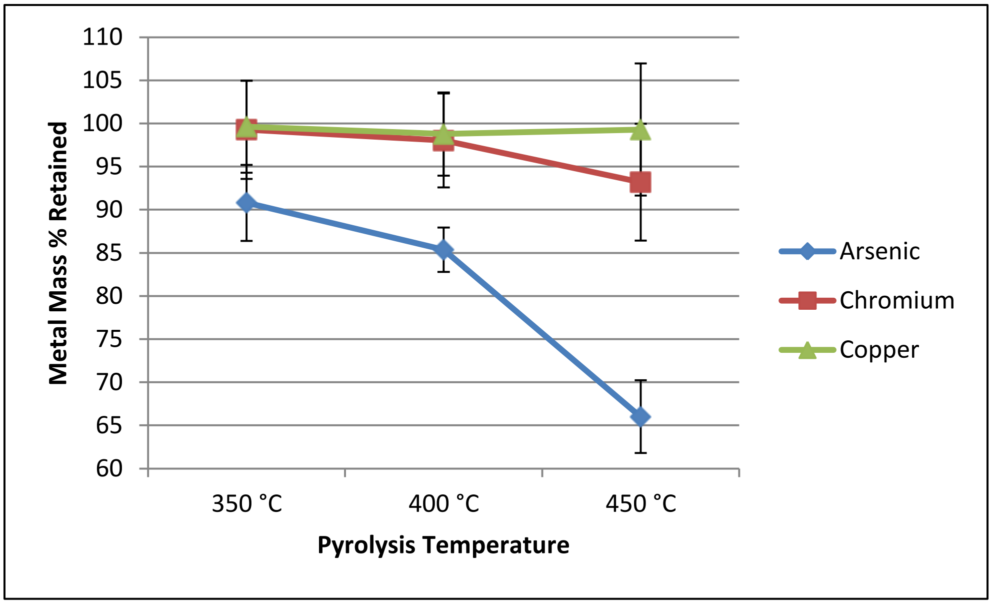


Figure 4.10 Average % CCA Metals Retained in Char Produced During Bench Pyrolysis of CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

A correlating trend is observed with the concentration of arsenic in the pyrolysis bio-oil: as the pyrolysis temperature increases, the concentration of the metal in the bio-oil also increases. Average metal concentrations in the bench pyrolysis bio-oil are in Figure 4.11, while raw data is available in Appendix C. Concentrations of copper remain approximately constant across all pyrolysis temperatures, while the concentration of chromium decreases by roughly 61% at 400°C to then increase by nearly 34% at 450°C, relative to the concentration at 350°C. Arsenic concentrations at 400°C and 450°C increase by approximately 42% and 63%, respectively, when compared to the concentration at 350°C. As expected, more metals are volatilized as the pyrolysis temperature increases, resulting in more of the CCA metals being distributed throughout the reaction products. The higher concentrations of arsenic compared to chromium and copper are also to be expected, as arsenic is known to volatilize at temperatures as low as

327°C, while chromium and copper volatilize at temperatures greater than 400°C. Thus, higher concentrations of chromium and copper will likely occur in bio-oils produced during pyrolysis at higher temperatures.

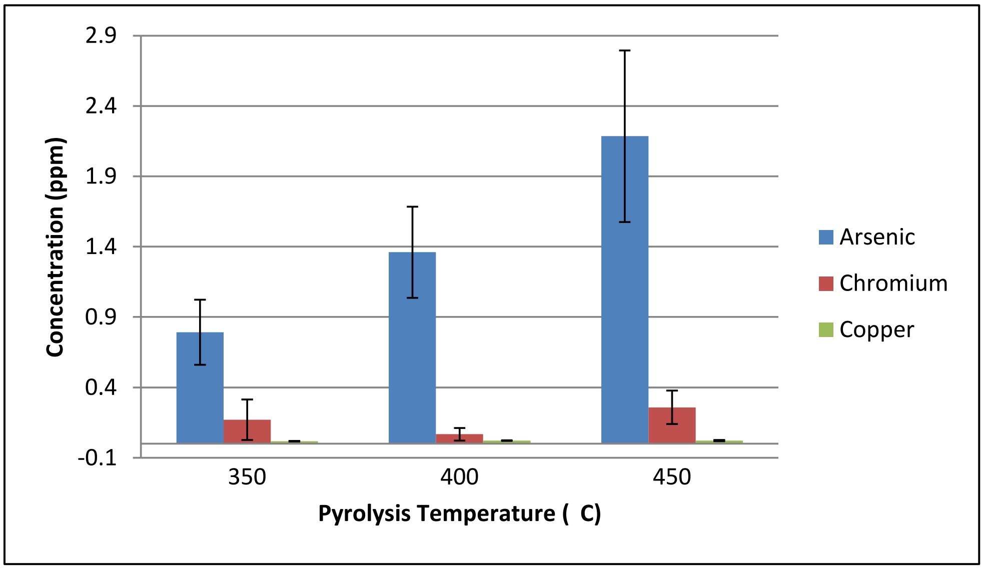


Figure 4.11 Average Concentration of CCA Metals in Bio-oil Produced During Bench Pyrolysis of CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

Mass balance calculations were performed for the three CCA metals for each bench pyrolysis set-point temperature. The mass of each metal was calculated across the product stream, and triplicate results were averaged. Table 4.1 contains these averaged values and the raw data used in these calculations is contained in Appendix C. Mass balance closure was determined by subtracting the total mass of each metal in the pyrolysis products from the mass of metals in the pyrolysis feed. This is indicated by the column labeled "Difference" in Table 4.1. The best overall balance closure occurred at the 350°C set-point, followed by 400°C and 450°C. Between 350°C and 450°C, arsenic losses increased by 73%, chromium losses increased by 90%, and copper losses increased by nearly 47%. As expected, there was more distribution of the CCA metals across the pyrolysis system as pyrolysis temperature increased, likely due to the increased volatilization of the metals at the higher experimental temperatures; however, the significant decrease in mass balance closure as the pyrolysis temperature increased was not expected. Although the system was relatively successful in capturing copper, it proved to be insufficient at capturing chromium and arsenic. This decreased efficiency was likely caused by a combination of factors:

1. Inappropriately sized impingers;
2. Impinger solutions incapable of adsorbing the CCA metals; and
3. Leaks in the pyrolysis system that were exacerbated at the higher operating temperatures.

Table 4.1 Mass Balances for Bench Pyrolysis Experiments

350°C									
	Feed	Char	Bio-oil	Impinger 1	Impinger 2	Impinger 3	Wash Soln	Total	Difference
As (mg)	184.9	167.9	0.0084	0.0010	0.0067	0	0.1465	168.0	16.84
Cr (mg)	157.1	156.0	0.0018	0.0245	0.0155	0.0113	0.0359	156.1	1.055
Cu (mg)	96.67	96.30	0.0002	0.0027	0.0009	0	0.0025	96.31	0.3610
400°C									
	Feed	Char	Bio-oil	Impinger 1	Impinger 2	Impinger 3	Wash Soln	Total	Difference
As (mg)	184.9	157.8	0.0152	0.0048	0.0207	0	0.4028	158.2	26.64
Cr (mg)	157.1	154.0	0.0007	0.0245	0.0154	0.01113	0.0295	154.1	3.021
Cu (mg)	96.67	95.48	0.0002	0.0025	0.0006	0	0.0024	95.48	1.183
450°C									
	Feed	Char	Bio-oil	Impinger 1	Impinger 2	Impinger 3	Wash Soln	Total	Difference
As (mg)	184.9	122.0	0.0266	0.0011	0.0050	0	0.3434	122.4	62.45
Cr (mg)	157.1	146.4	0.0031	0.0244	0.0154	0.0113	0.0367	146.5	10.61
Cu (mg)	96.67	95.99	0.0003	0.0027	0.0005	0	0.0025	95.99	0.6754

4.2.2.2 CCA Metal Mobility within Bench Pyrolysis Char

Averages of the TCLP, SPLP, and DI Water Leach leachate concentration values for bench pyrolysis char are contained in Figures 4.12 – 4.14, with raw data for each replicate provided in Appendix C. Figures 4.12 – 4.14 also provide comparisons to the average TCLP, SPLP, and DI Water leach leachate concentrations of the CCA-treated wood waste pyrolysis feed. Mobility of all three metals in the char decreased under all three leaching conditions for all pyrolysis temperatures compared to original wood levels; however, the char continued to exceed the arsenic TCLP limit of 5.0 ppm. Individual metals demonstrated similar trends to the sawdust feed across all leaching conditions and at all temperatures: both arsenic and copper mobility were higher than that of chromium. In fact, chromium did not leach under SPLP conditions. As seen in Figure 4.12, only under TCLP conditions does arsenic maintain higher mobility than copper for all temperatures. Under SPLP conditions (Figure 4.13), copper mobility is higher than arsenic for all temperatures except 450°C, while under DI Water Leach conditions (Figure 4.14), copper mobility is only higher than arsenic at 350°C.

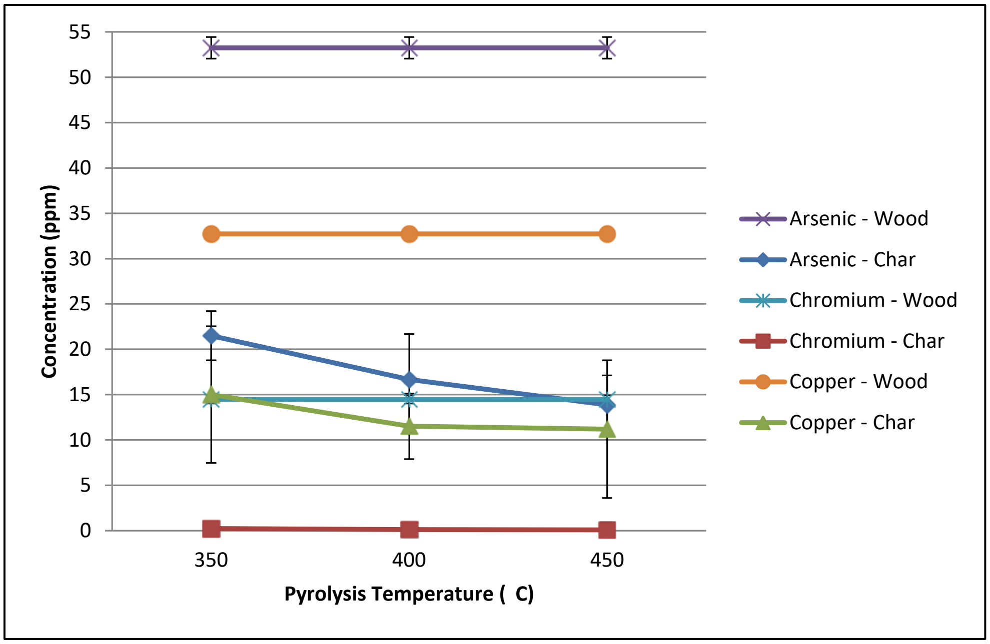


Figure 4.12 TCLP Averages of Bench Pyrolysis Char and CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

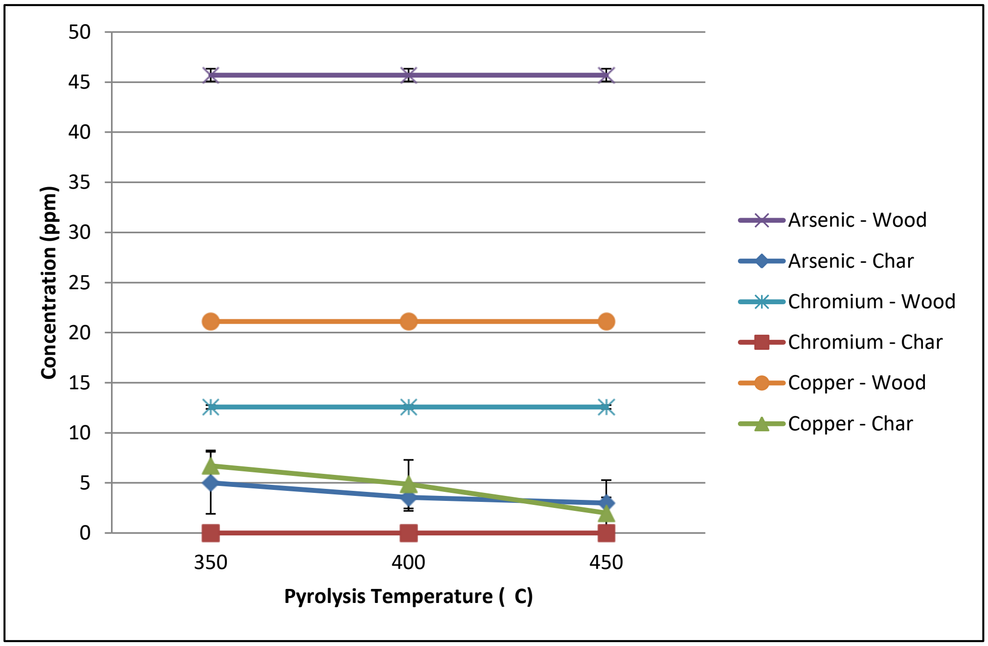


Figure 4.13 SPLP Averages of Bench Pyrolysis Char and CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

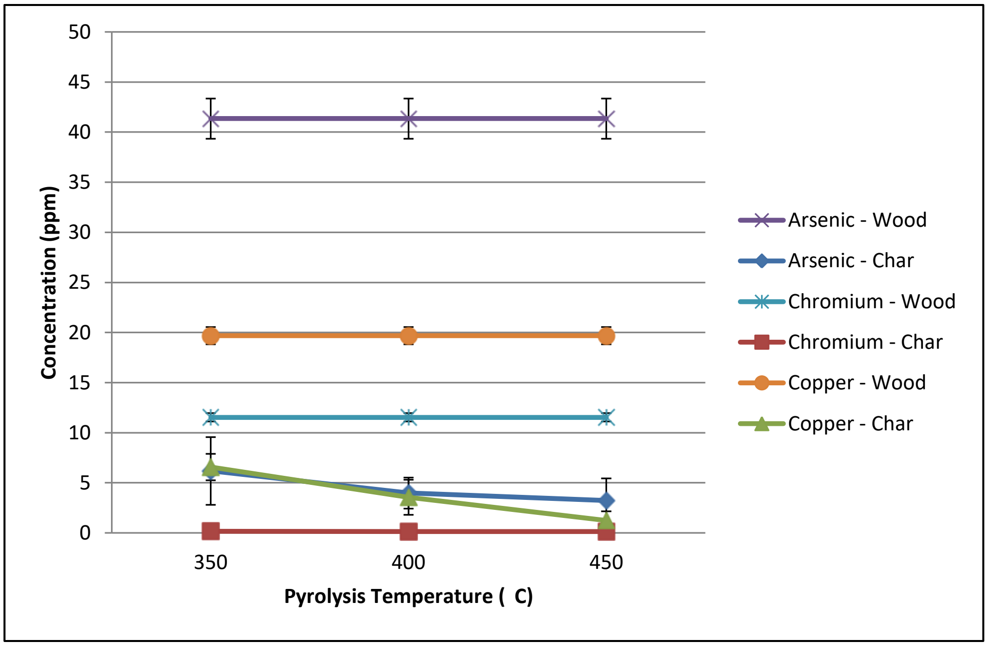


Figure 4.14 DI Water Leach Averages of Bench Pyrolysis Char and CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

Additionally, metal mobility for all three CCA metals also decreases as the pyrolysis temperature increases (i.e. Mobility @ 350°C > Mobility @ 400°C > Mobility @450°C). This is true under all leaching conditions. The most likely explanation for all of these trends is that the metals that remain in the pyrolysis char have formed stronger complexes with the char structure than they did in the original wood. This ultimately results in lower quantities of unbound metals and lower overall metal mobility.

4.2.3 Summary of Bench Pyrolysis Study Findings

Results of the bench pyrolysis study indicate that the optimal bench pyrolysis condition for bio-oil production and metal concentration is 450°C, while maximum metal retention in pyrolysis char occurred during pyrolysis at 350°C. Metal mobility experiments (TCLP, SPLP, and DI water leaches) demonstrated that pyrolysis decreases the mobility of all CCA metals when compared to the mobility of the metals in CCA-treated wood waste. As in the characterization studies, leachate values for all metals were highest for the TCLP experiments (TCLP > SPLP > DI water leach). Chromium is essentially immobile after pyrolysis, though arsenic continues to exceed the TCLP threshold of 5 ppm.

4.3 Phase III: Batch Pyrolysis of CCA-Treated Wood Waste

Approximately 30 runs were performed at each set-point temperature utilizing the batch system described in Section 3.5.1 to generate the mass of char needed for the EK experiments. The following sections describe the pyrolysis product generation and the results of metal content and metal mobility studies.

4.3.1 Product Generation

The primary objective of Phase III was to generate sufficient char for use in the EK experiments; therefore, only the mass of char produced was recorded after each pyrolysis run. As previously stated, roughly 30 runs were completed at each pyrolysis set-point temperature. There was considerable variability in the mass of char produced during each pyrolysis run, across all temperatures, as seen in the raw data provided in Appendix D. The large number of pyrolysis runs, the inconsistent mass of CCA-treated sawdust loaded into the reactor, and multiple system operators likely contributed to this variability.

Although the volume of bio-oil produced was not recorded after each run, the bio-oil was collected and stored for metal analysis. Figure 4.15 illustrates that on a qualitative basis more bio-oil was produced at higher pyrolysis temperatures than at lower pyrolysis temperatures. Visual inspection of the batch bio-oil indicated that the batch system produced bio-oil consisting primarily of a dark hydrocarbon fraction, with very little visible water.

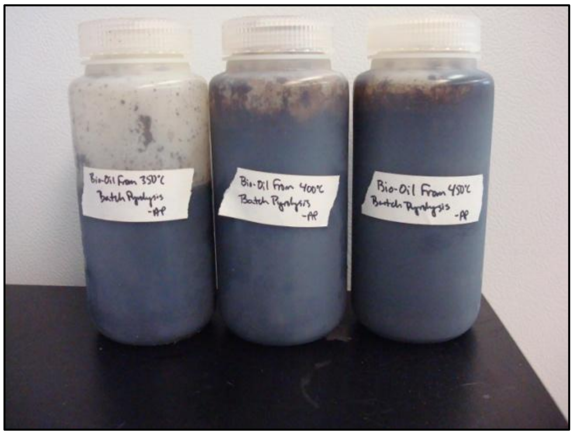


Figure 4.15 Photograph of the Bio-oil Produced During Batch Pyrolysis of CCA-Treated Wood Waste

Note: Left to right—Bio-oil produced at 350°C, Bio-oil produced at 400°C, Bio-oil produced at 450°C

4.3.2 Batch Pyrolysis Post- Operation Experiments and Analysis

4.3.2.1 CCA Metal Content of Batch Pyrolysis Char and Bio-oil

Char generated at all three set-point temperatures was again rich in CCA metals (see Figure 4.16). As seen in Figure 4.17, the concentration of arsenic and copper in the char was nearly double the concentration in the pyrolysis feed across all pyrolysis temperatures. A similar trend was seen at the 350°C pyrolysis temperature for chromium, but the concentrations were only 65% and 54% higher than that of the pyrolysis feed at 400°C and 450°C, respectively. The concentration of arsenic and chromium is lower in the batch char than in the bench char for all pyrolysis temperatures. Copper is the only outlier at 350°C where the batch concentration is higher than the bench concentration (7%); however, this is within the margin of error for the analysis and does not appear to be significant. Lower metal concentrations may be the result of increased volatilization of the CCA metals in the batch reactor versus the bench reactor. While the both systems utilized steel reactors heated by furnaces, the batch system's reactor was in direct contact with the tube furnace for its entire length. This direct contact likely provided more thorough and uniform heating than the reactor set-up of the bench pyrolysis system, allowing for a more complete pyrolysis reaction. This ultimately resulted in increased volatilization of CCA metals and lower metal retention in the batch pyrolysis char.

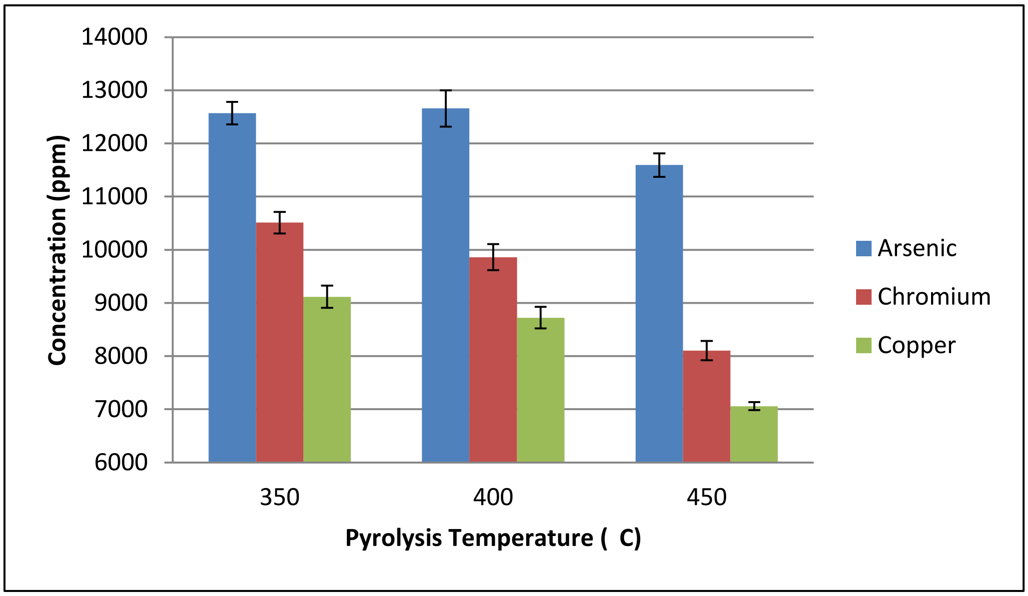


Figure 4.16 Average Concentration of CCA Metals in Char Produced During Batch Pyrolysis of CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

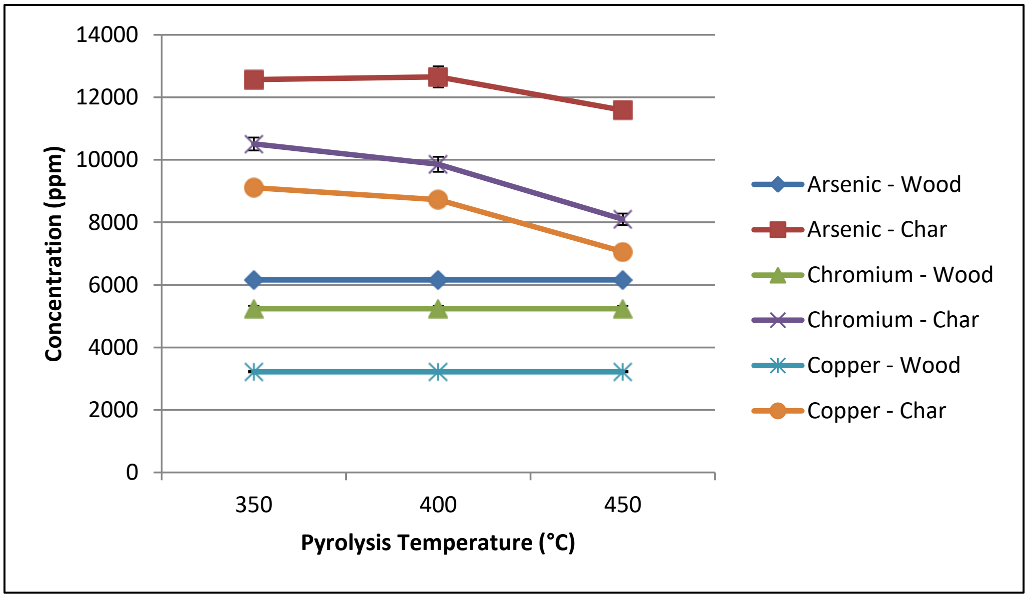


Figure 4.17 Comparison of the Average Concentration of CCA Metals in Batch Pyrolysis Char and CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

Similar to the bench pyrolysis results, the mass percentage of each metal retained in the char generally decreased from pyrolysis at 350°C to 450°C, as illustrated in Figure 4.18. Overall retention was lower for all three metals during the batch pyrolysis experiments than during the bench pyrolysis experiments. This is most noticeable for chromium and copper, where percent mass retained decreased to 51.5% and 73.0%, respectively.

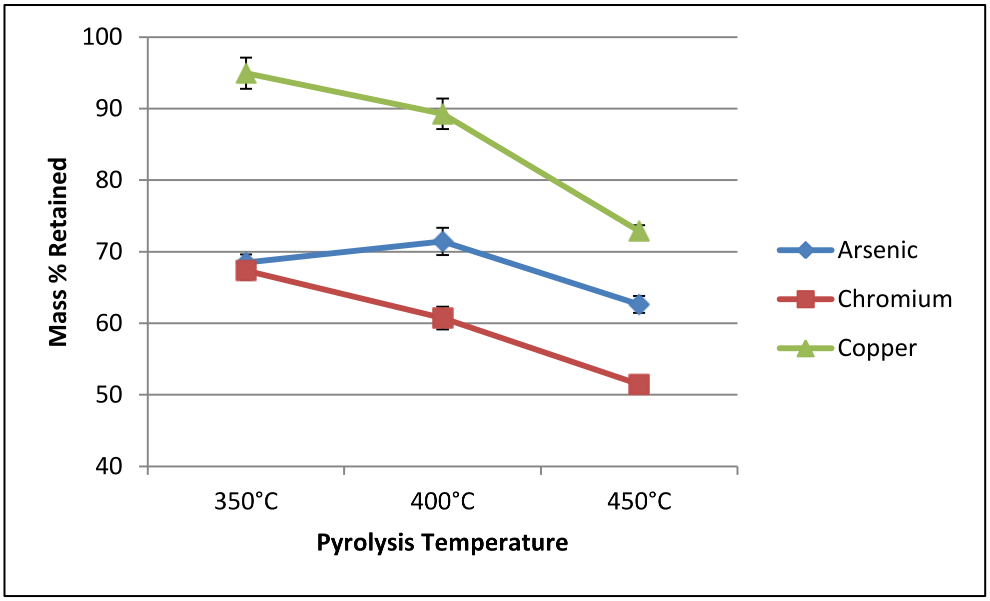


Figure 4.18 Average % CCA Metals Retained in Char Produced During Batch Pyrolysis of CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

Once again, as the pyrolysis temperature increases, the concentration of CCA metals increases in the pyrolysis bio-oil increases. This is true for all metals, across all pyrolysis temperatures. Average metal concentrations in the batch pyrolysis bio-oil are in Figure 4.19 and raw data are available in Appendix D. While the concentration increase for chromium is relatively minor (approximately 18% total) from 350°C to 450°C, the concentration increases for arsenic and copper are more significant. Arsenic and copper concentrations remained nearly constant from 350°C to 400°C, and would have been expected to remain constant at 450°C; however, both arsenic and copper saw increases of nearly 37% and 438%, respectively. Additionally, the concentration of all CCA metals is higher in the batch char than in the bench char for all pyrolysis temperatures. This is expected given the overall decrease in metal concentration in the batch char and is likely due to increased volatilization of the CCA metals during the batch pyrolysis experiments.

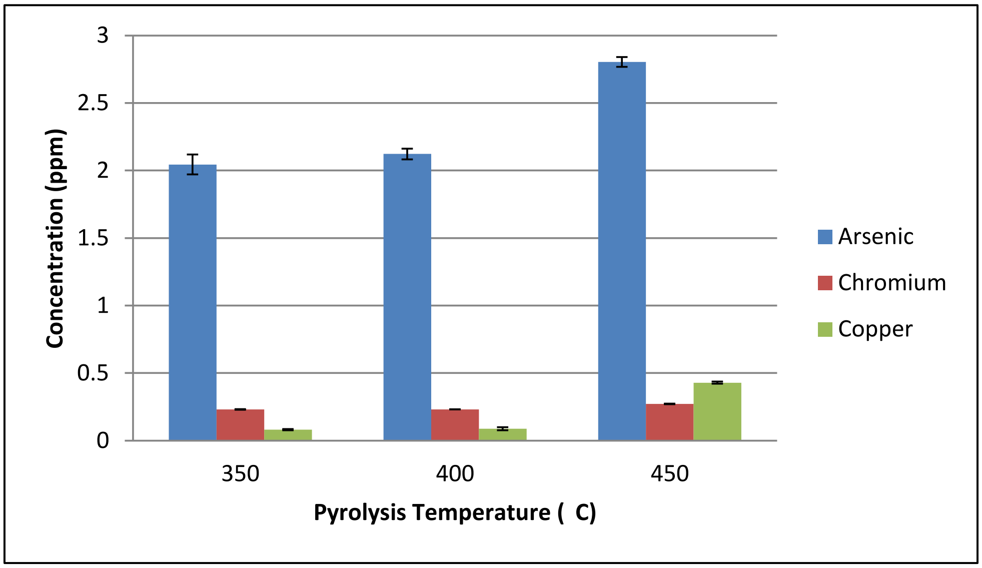


Figure 4.19 Average Concentration of CCA Metals in Bio-oil Produced During Batch Pyrolysis of CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

4.3.2.2 CCA Metal Mobility within Batch Pyrolysis Char

Averages of the TCLP, SPLP, and DI Water Leach leachate concentration values for batch pyrolysis char are contained in Figures 4.20 – 4.22, with raw data for each replicate provided in Appendix D. Figures 4.20 – 4.22 also provide comparisons to the average TCLP, SPLP, and DI Water leach leachate concentrations of the CCA-treated wood waste pyrolysis feed. Results of the batch mobility studies mirrored those of the bench mobility studies. Under all three leaching conditions across all pyrolysis temperatures, the mobility of the CCA metals in the char decreased compared to mobility levels of the sawdust feed; however, the arsenic TCLP concentration continued to exceed the TCLP limit of 5.0 ppm. As seen in Figures 4.20 – 4.22, arsenic and copper had similar leachate concentrations for all leaching tests, with arsenic mobility being just slightly higher than copper. Both arsenic and copper leachate concentrations were an order of magnitude higher than the concentrations for chromium across all leaching conditions. Additionally, as with the bench pyrolysis char, metal mobility decreases as the pyrolysis temperature increases for all leaching conditions and for all metals in the bench pyrolysis char. Again, this is likely explained by the metals remaining in the wood forming stronger complexes with the remaining wood structure than they did in the original CCA-treated wood waste.

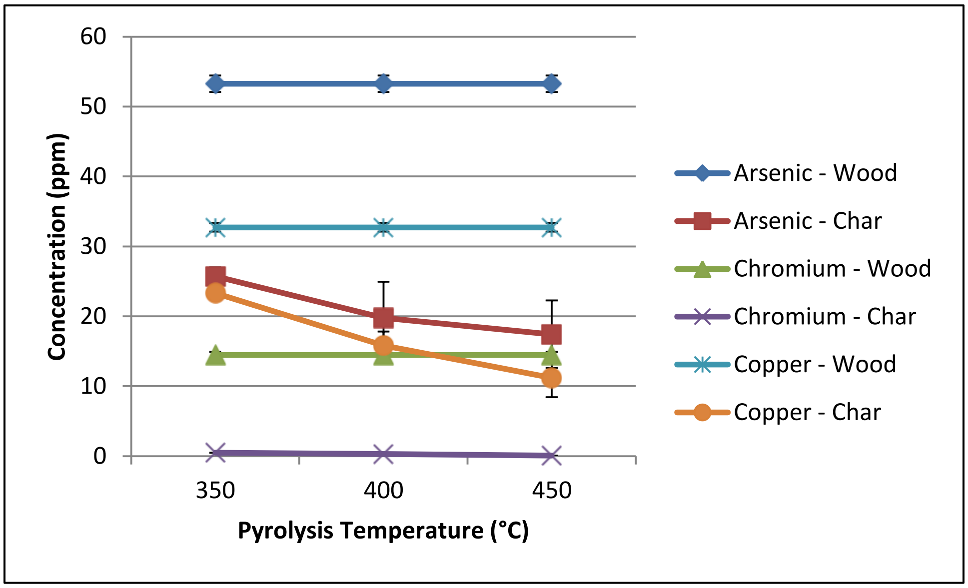


Figure 4.20 TCLP Averages of Bench Pyrolysis Char and CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

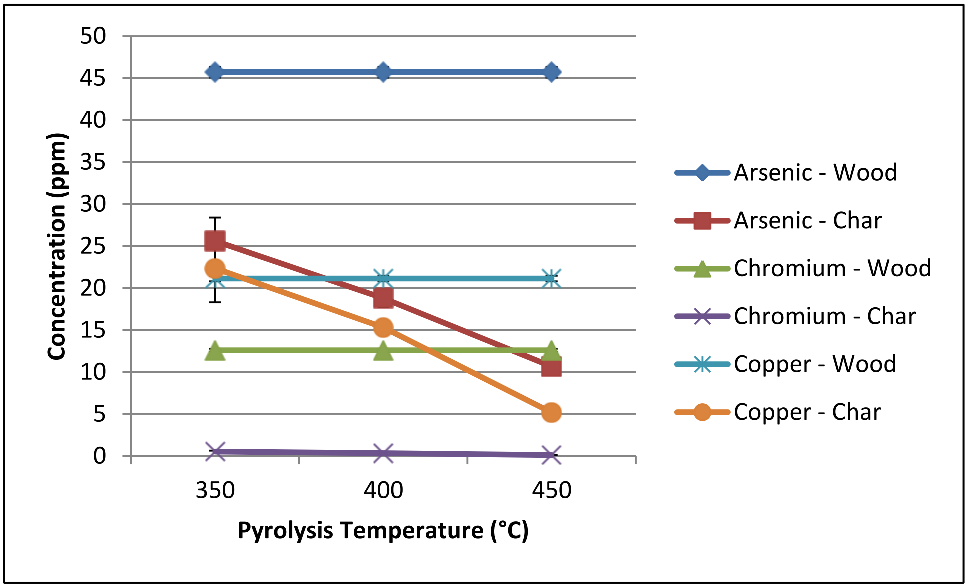


Figure 4.21 SPLP Averages of Bench Pyrolysis Char and CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

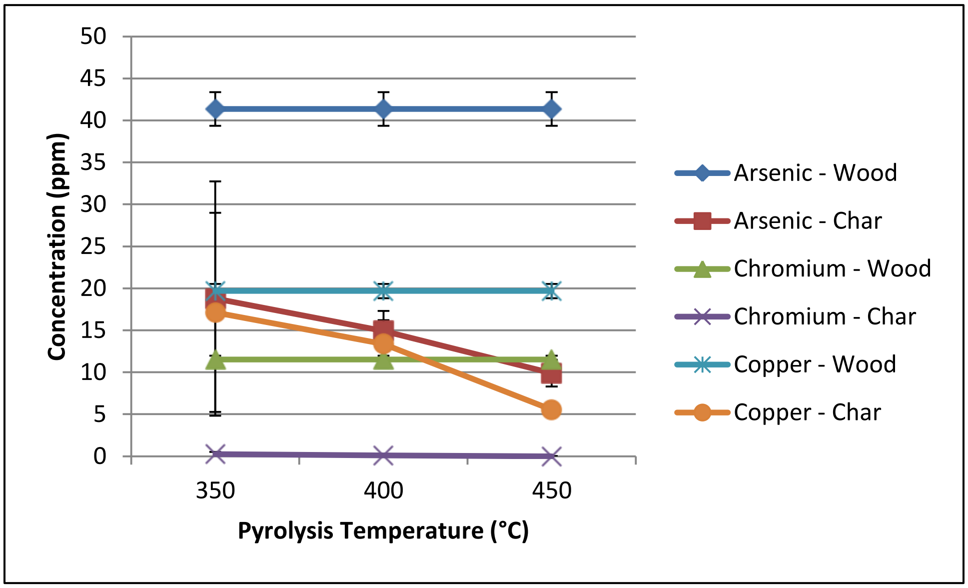


Figure 4.22 DI Water Leach Averages of Bench Pyrolysis Char and CCA-Treated Wood Waste

Note: Error bars represent 95% confidence intervals

4.3.3 Summary of Batch Pyrolysis Study Findings

Results of the batch pyrolysis study indicate similar trends to those of the bench pyrolysis study. Specifically, maximum metal concentration and retention in pyrolysis char occurred during pyrolysis at 350°C, and metal mobility decreased across all pyrolysis temperatures relative to the metal mobility displayed by the CCA-treated wood waste. The primary difference between the two pyrolysis studies was the overall decrease in metals retained in the pyrolysis char and increase in metals in the pyrolysis bio-oil during the batch study compared to the bench study. This difference is most likely due to improved heating of the pyrolysis reactor, resulting in increased volatilization of the CCA metals and ultimate distribution across the pyrolysis products.

4.4 Phase IV: Electrokinetic Experiments on Pyrolysis Char and CCA-Treated Wood Waste

The EK cells were operated for 15 days, during which multiple daily measurements recorded and samples were taken, as described in Section 3.7.2. After the 15 day operation period, the EK cells were disassembled as described in Section 3.6.2. Results of the post-operation experiments and analysis are presented in the following sections.

4.4.1 Daily Reading Results

Multiple measurements were recorded daily to monitor the operation of each EK cell. The measurements were also intended to identify any performance differences between cells, particularly across treatments. Analysis of these measurements is provided in the following sections and supplemental data is provided in Appendix E.

4.4.1.1 Power Usage

Power consumption was calculated for each cell using the recorded cell voltage and current measurements according to Equation 4.2.

$$\text{Power} = \text{Voltage x Current} \qquad (4.2)$$

Daily power consumption can be seen for each set of duplicate cells in Figures 4.23 – 4.26. For most cells, power consumption initially peaked by day two and was followed by a general decline over the remainder of the experimental period; however, Cell B experienced a steady increase in power consumption until it reached maximum consumption on day eleven before steadily declining. Additionally, Cell C and Cell D initially peaked at approximately 5.5 W and 7 W, respectively, on day two, and after declining for five days the power consumption increased to approximately 4 W and 7 W, respectively, for the remainder of the experimental period. While Cell H also initially peaked at day two at 18 W, power consumption remained near or above 14 W for five days before steadily declining to 3 W by day nine. This decline was followed by a sharp increase to 17 W on day ten, and another decline to 5 W by day 13.

Fluctuations in power consumption over the course of the operational period are not unexpected as power usage will adjust to changes in other system parameters. The primary cause of these fluctuations is changes in resistance across the center compartment of the EK cell. When resistance across the cell is high, power consumption is high, and when resistance across the cell is low, power consumption is reduced. Potential explanations for changes in resistance include:

1. The production of hydrogen ions at the anode during electrolysis of water ultimately results in an acidic front that moves across the center compartment

toward the cathode. As the front progresses, it lowers the overall pH of the compartment, facilitating desorption of CCA metals from the char and wood surface, increasing the available free ions. Movement of hydrogen ions and desorbed metal ions in the char and wood pore fluid results in a decrease in the overall resistance of the cell.

2. The production of hydroxyl ions at the cathode during electrolysis of water was continuously neutralized using HNO_3. As the nitrate ions (NO_3^-) migrate toward the anode they increase the free ions in the cell, again reducing the resistance of the cell.
3. A change in concentration of metals within the cell. This ultimately impacts the density of the metals within the cell, and density is directly proportional to resistance.
4. The breakdown of the structural matrices of the CCA-treated wood and char over the course of the EK experiments. This breakdown can increase the free ions in the cell, thus decreasing resistance of the cell; however, the breakdown can also impede the movement of ions across the cell, increasing the resistance for a period of time.

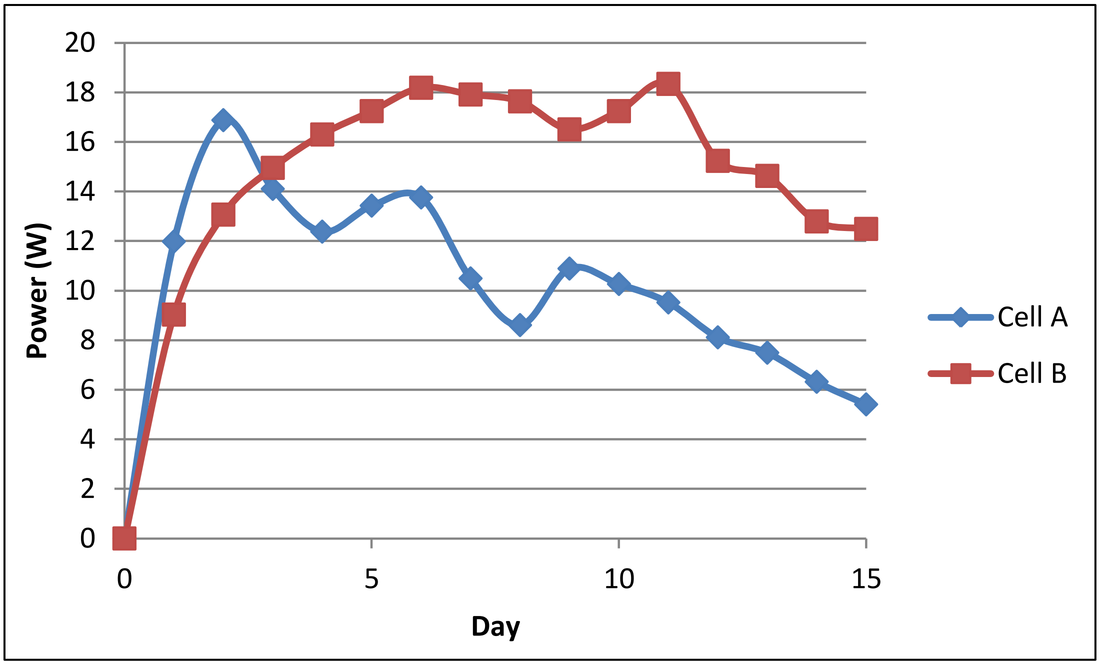


Figure 4.23 Daily Power Consumption: Cells A and B

Note: Cells A and B are duplicate EK cells for pyrolysis char generated at 350°C

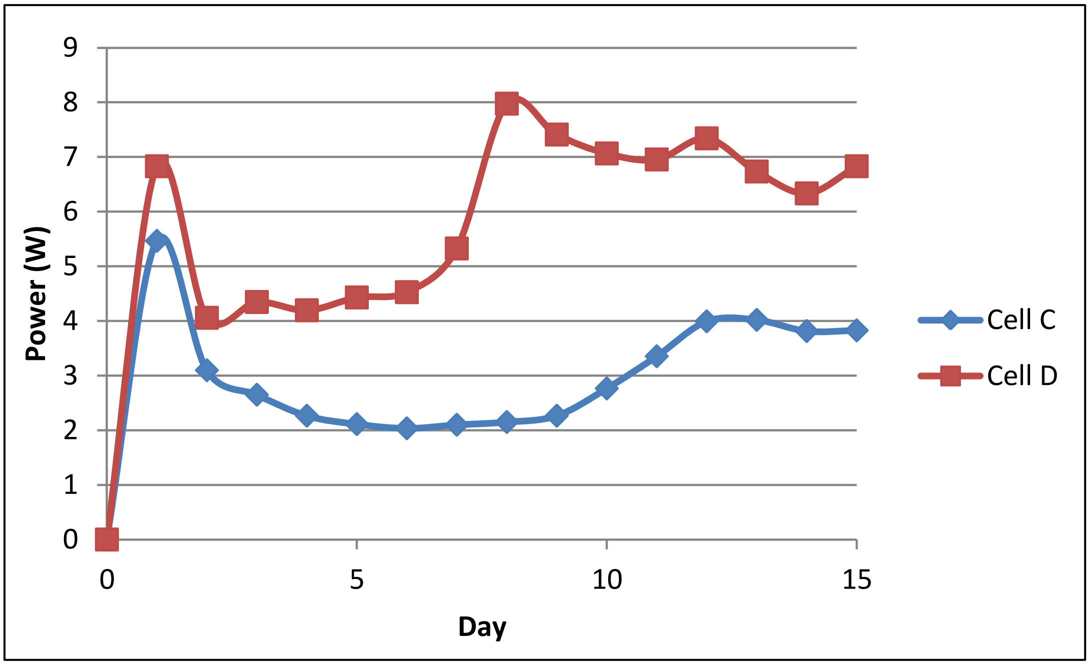


Figure 4.24 Daily Power Consumption: Cells C and D

Note: Cells C and D are duplicate EK cells for pyrolysis char generated at 400°C

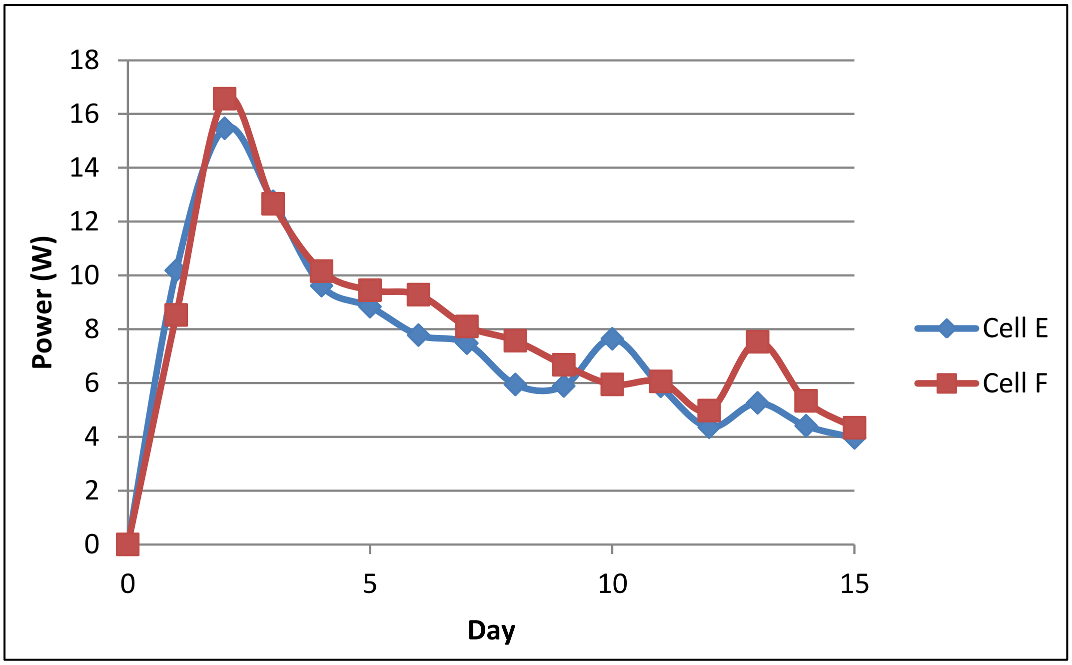


Figure 4.25 Daily Power Consumption: Cells E and F

Note: Cells E and F are duplicate EK cells for pyrolysis char generated at 450°C

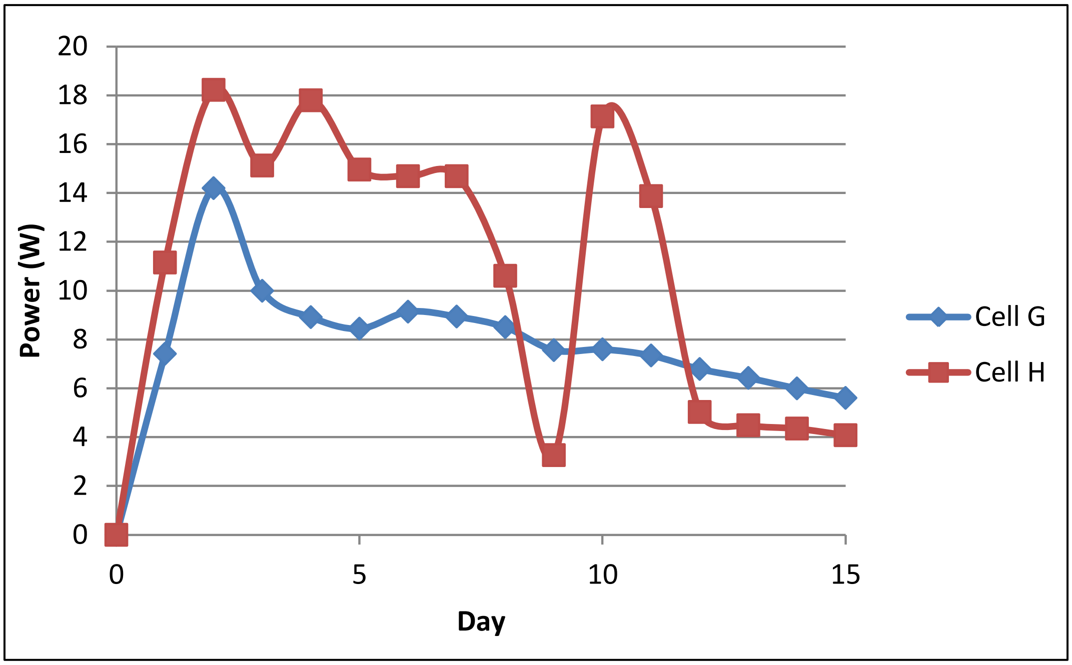


Figure 4.26 Daily Power Consumption: Cells G and H

Note: Cells G and H are duplicate EK cells for CCA-treated wood waste (Control)

Total average power consumption for all EK cells can be seen in Figure 4.27. Power consumption was greatest for cells of pyrolysis char generated at 350°C, followed by the control cells of CCA-treated wood waste, then cells of pyrolysis char generated at 450°C, and finally cells of pyrolysis char generated at 400°C. In general, EK cells loaded with material that had undergone little or no pyrolysis consumed more power. This may have been due to the large amount of highly mobile CCA metal ions available in the center compartment (see Section 4.2). Larger power consumption was necessary to overcome the initial resistance of the cell due to the slower migration caused by the high concentrations of CCA metals.

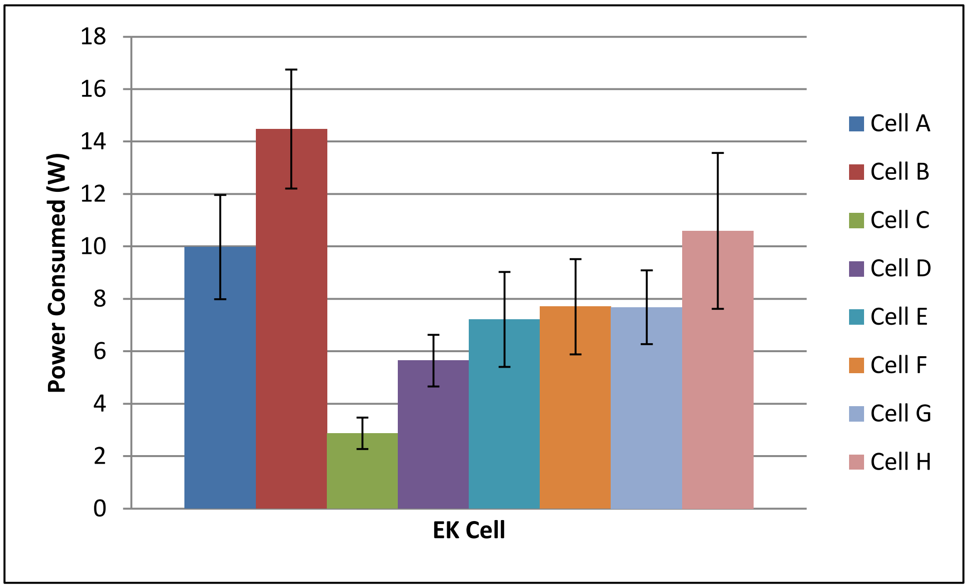


Figure 4.27 Average Power Consumption for all EK Cells

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

4.4.1.2 Daily Nitric Acid Consumption and Daily Sample pH

The pH of the cathode fluid was controlled at approximately 3 through the injection of nitric acid into the recirculation tank. pH regulation was key to minimizing the movement of reduced chemical species generated during hydrolysis reactions at the cathode from migrating toward the anode. pH regulation was also used to encourage electromigration of the CCA metals through the center compartment of the EK cell rather than electrolyzing water molecules at the electrodes. The total volume of nitric acid consumed by each cell is presented in Figure 4.28. On average, acid consumption increased as the pyrolysis temperature increased, and the cells loaded with CCA-treated wood waste averaged the lowest volume of acid consumption.

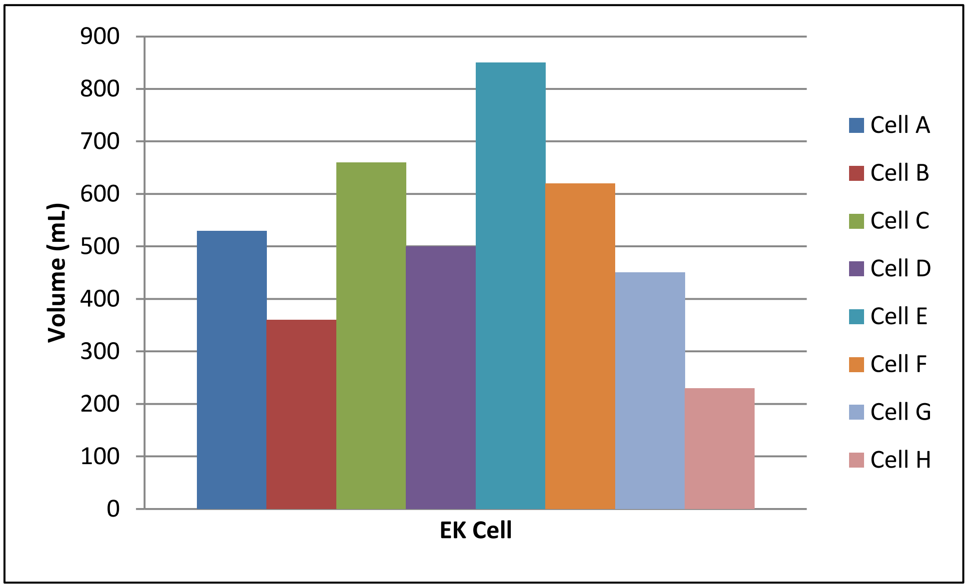


Figure 4.28 Total Volume of Nitric Acid Consumed in each EK Cell

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste

Acid consumption can be used as a metric to gauge performance of the EK cell. Generally speaking, if acid consumption is low, but removal efficiency of metals is high, the hydrolysis reactions have been minimized and the electromigration is the dominant phenomenon. When acid consumption is high and removal efficiency is low, it is a good indicator that hydrolysis is the dominant EK phenomenon. Removal efficiencies are discussed in Section 4.4.3.2.

The pH of the daily collected samples was measured and recorded for the duration of the EK experiments. These measurements are provided in Appendix E. Each EK cell generally exhibited the same pH behavior, as illustrated in the example plot for Cell A contained in Figure 4.29 (additional figures are provided in Appendix E). At the beginning of the experiments, the pH of all fluid samples is between 4 and 6. The anode and pore sampling fluids reach a pH near 2 by day two of operation and remain stable for the remainder of the experiment. The pH of the cathode fluid varies throughout the experiment; however, the pH generally trends downward between 3 and 4 over the course of the experiment. The only instance where this is not true is for Cell C and Cell D, which had significant volumes of acid added on the first day of operation due to equipment malfunction, dropping the pH to nearly 2 (see Appendix E). Approximately mid-way through the experimental run the pH began to increase to the desired pH of 3.

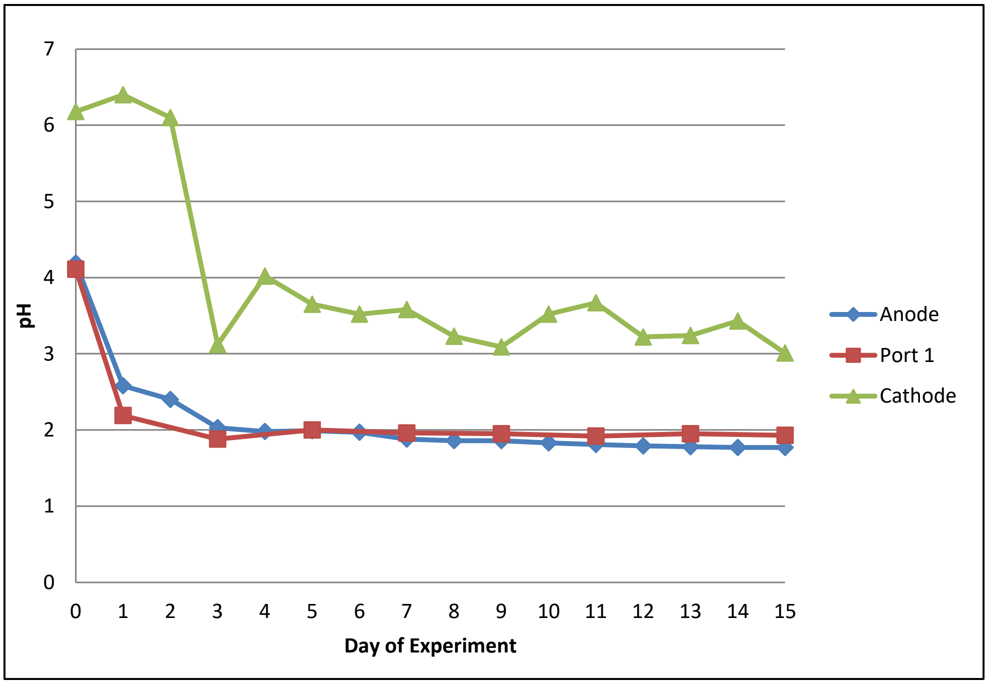


Figure 4.29 Daily pH measurements for EK Cell A

Note: Cell A is one replicate of the EK cell for pyrolysis char generated at 350°C

4.4.1.3 Hydraulic Head Maintenance

The hydraulic head across each cell was maintained by automatic removal of fluid from the anode and cathode recirculation tanks whenever the tanks reached a certain level, and addition of tap water to the recirculation tanks, as appropriate, to ensure the liquid levels were the same across the cell. The total volumes of fluid collected from and added to the recirculation tanks was are displayed in Figure 4.30, with the raw data found in Appendix E.

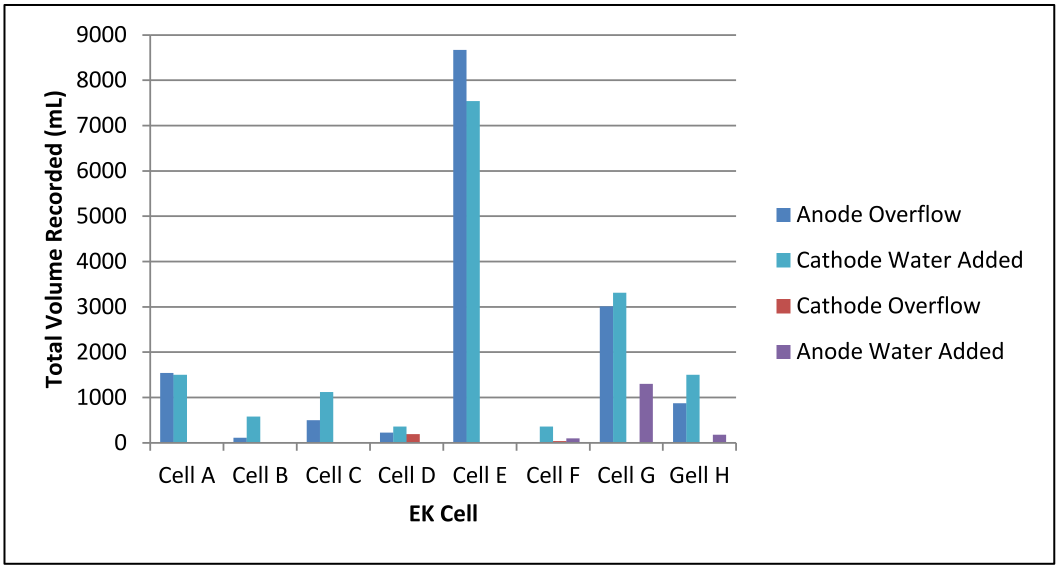


Figure 4.30 Total Volume of Overflow Liquid Collected from EK Half-Cells and Total Water Volume Added to EK Half-Cells

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste

No discernible trends are identified for the overflow volumes or the tap water added across cell types; however, it was observed that overflow volumes from the anode were significantly larger than volumes from the cathode. A correlating trend was observed in that the volume of tap water added to the cathode was much greater than the volume added to the anode. These trends indicate that there is a net flow of water away from the cathode half-cell toward the anode half-cell in all EK cells used in this study. This movement is likely due to water being transported toward the anode during the electromigration of anions. Given that the overflow volumes from the anode were much larger than those from the cathode, it is likely that anionic species (arsenic and chromium) are dominant in the EK cells.

4.4.2 Moisture Content of the Post-EK Pyrolysis Char and CCA-treated Wood Waste

Given the large volumes of water added to the EK system, it was critical to determine the moisture content of the material removed from the center compartments after EK treatment. This was to ensure moisture content was appropriately accounted for during all mass balance calculations (i.e. mass balances were performed on a dry basis, rather than on a wet basis). Moisture content was determined in accordance with the procedures outlined in Section 3.7.3.3 after the center compartments had been frozen post-operation. Figure 4.31 contains the average moisture content of the material in the center compartments of all eight EK cells, and raw data is provided in Appendix E. Moisture content was fairly consistent between replicates of each EK cell and ranged from 71% to 75% moisture. Consistent moisture content post-experiment indicates that the replicate EK cells performed similarly with respect to the different EK phenomena (electroosmosis, electromigration, and water electrolysis).

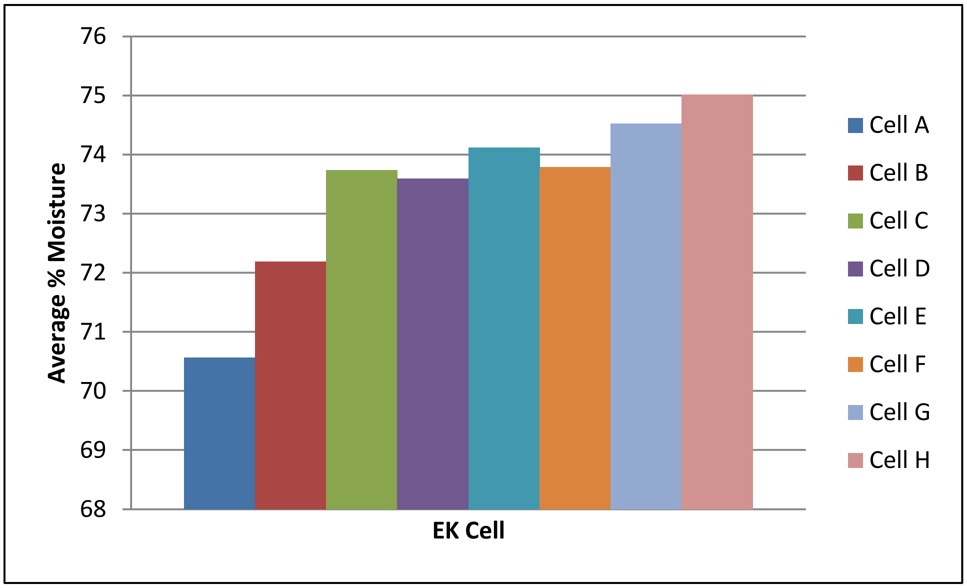


Figure 4.31 Average Moisture Content of the Post-EK Center Cell Material

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste

4.4.3 CCA Metal Content of Post-EK Samples

Metal content was determined for all post-EK samples (i.e. pyrolysis char, CCA-treated wood, filter paper, daily liquid samples, and pressure plates) in accordance with the procedures outlined in Section 3.7.3.4. These results were used to determine the distribution of the metals across the EK cells at the end of cell operation and to determine the metal removal efficiencies. Results are presented in the following sections.

4.4.3.1 CCA Metal Distribution Across EK Cells

4.4.3.1.1 CCA Metal Content in Post-EK Pyrolysis Char and CCA-treated Wood Waste

The average concentration of each metal in post-EK pyrolysis char and CCA-treated wood waste is presented in Figure 4.32 and raw data is provided in Appendix E. Two general trends are observed for all metals:

1. Metal concentrations in EK cells loaded with CCA-treated wood waste (Cells G and H) are significantly lower than those of the EK cells with CCA-treated wood waste (Cells A through F).
2. Concentration of the metals in the pyrolysis char post-EK increased as pyrolysis temperature increased (Cell A through Cell F).

Both of these trends are to be expected based on the results of the metal mobility studies documented in the previous sections. Mobility was highest for CCA-treated wood waste relative to the mobility of metals within batch pyrolysis char. Additionally, as discussed in Section 4.3.2.2, mobility of the CCA metals within the batch char decreased as pyrolysis temperature increased. Metals were more loosely bound in the CCA-treated wood waste and char generated at 350°C than the char generated at 400°C and 450°C, and thus were more likely to leach under EK conditions. Conversely, the more tightly bound CCA metals in the chars generated at the higher pyrolysis temperatures were less likely to leach under EK conditions. Figures 4.33 – 4.35 more clearly illustrate the average concentration trend results for each metal according to treatment type (i.e. char generated during pyrolysis at different temperatures).

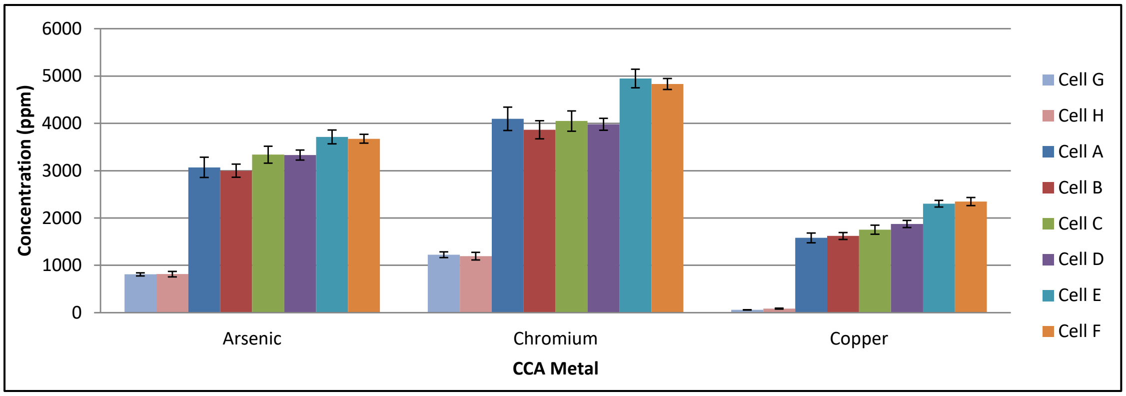


Figure 4.32 Average Concentration of CCA Metals in Post-EK Pyrolysis Char and CCA-treated Wood Waste

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

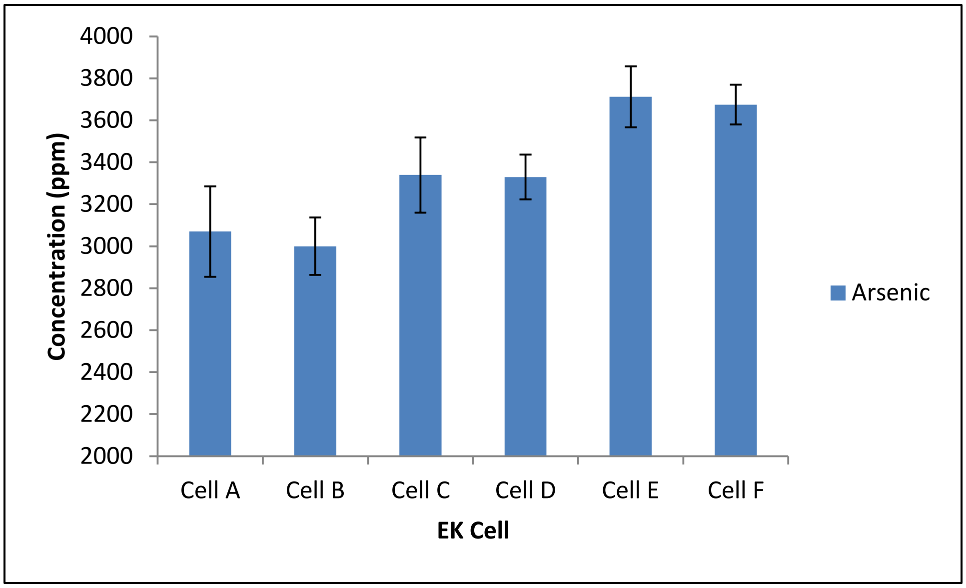


Figure 4.33 Average Arsenic Concentration in Each EK Cell Post-Operation

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

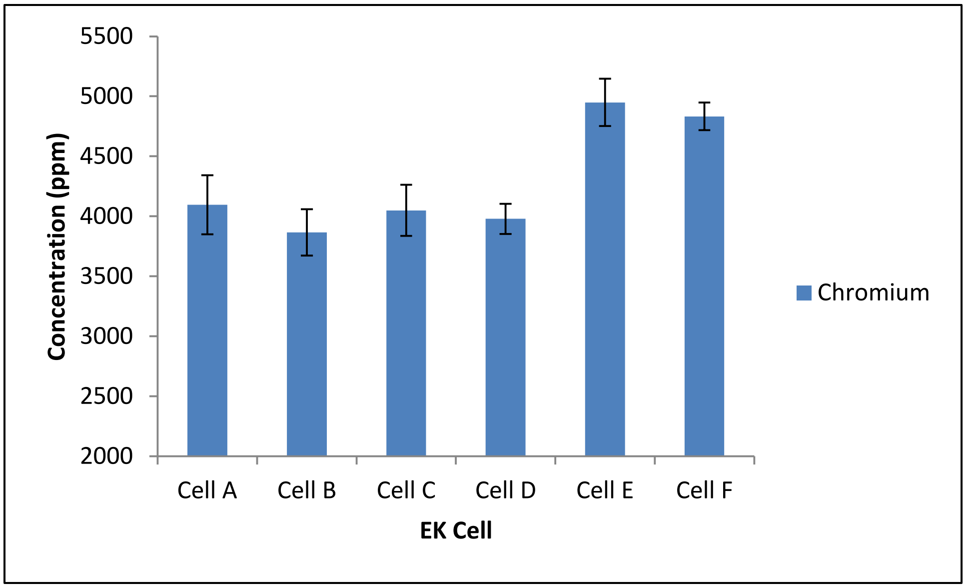


Figure 4.34 Average Chromium Concentration in Each EK Cell Post-Operation

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

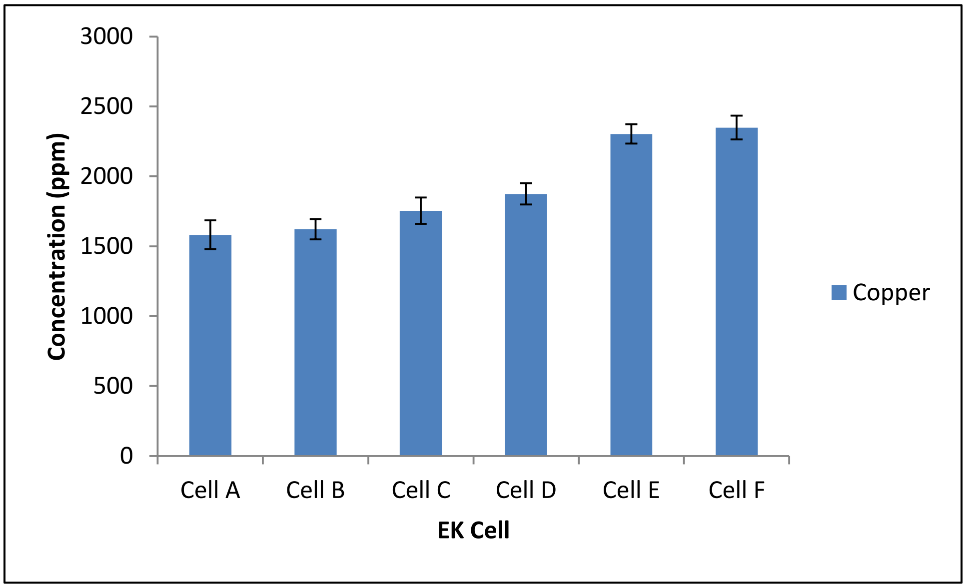


Figure 4.35 Average Copper Concentration in Each EK Cell Post-Operation

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

4.4.3.1.2 CCA Metal Content in Daily Liquid Samples

CCA metal concentrations within the liquid collected from the anode and cathode half-cells and recirculation tanks were determined by direct analysis via ICP-OES. Average concentrations within the half-cells and recirculation tanks are presented in Table 4.2 and Table 4.3. As these data illustrate, the CCA metals are removed from the masses loaded in the center compartments of the EK cells and transferred to the half-cells and recirculation tanks. Arsenic and chromium concentrations are highest in the anode sections of the EK cells, while copper concentrations are highest in the cathode sections of the cells. These phenomena are likely due to the generation of negatively charged arsenic and chromium ions and positively charged copper ions during the EK experiments. Additionally, while arsenic and chromium concentrations are nearly identical in both the half-cell and recirculation tanks of the anode and cathode sections of the cells, copper concentrations are higher in the half-cell section than in the recirculation tank. These results are expected given that copper precipitated onto the cathode half-cell electrodes, as illustrated in Figure 3.45 in Section 3.7.3.2.

Table 4.2 Average CCA Metal Concentrations in Each EK Half-Cell Post-Operation

350°C Anode Half-Cell			**350°C Cathode Half-Cell**	
Metal	Concentration		Metal	Concentration
Arsenic	57.70 ppm		Arsenic	1.43 ppm
Chromium	2.40 ppm		Chromium	0.26 ppm
Copper	6.47 ppm		Copper	18.25 ppm
400°C Anode Half-Cell			**400°C Cathode Half-Cell**	
Metal	Concentration		Metal	Concentration
Arsenic	31.42 ppm		Arsenic	4.62 ppm
Chromium	0.65 ppm		Chromium	0.30 ppm
Copper	7.70 ppm		Copper	17.54 ppm
450°C Anode Half-Cell			**450°C Cathode Half-Cell**	
Metal	Concentration		Metal	Concentration
Arsenic	14.75 ppm		Arsenic	0.19 ppm
Chromium	0.19 ppm		Chromium	0.05 ppm
Copper	5.06 ppm		Copper	12.65 ppm
Wood Anode Half-Cell			**Wood Cathode Half-Cell**	
Metal	Concentration		Metal	Concentration
Arsenic	53.0311 ppm		Arsenic	1.19 ppm
Chromium	16.29 ppm		Chromium	1.44 ppm
Copper	7.13 ppm		Copper	21.48 ppm

Table 4.3 Average CCA Metal Concentrations in Each EK Recirculation Tank Post-Operation

350°C Anode Recirc. Tank			**350°C Cathode Recirc. Tank**	
Metal	Concentration		Metal	Concentration
Arsenic	56.29 ppm		Arsenic	1.58 ppm
Chromium	2.34 ppm		Chromium	0.29 ppm
Copper	6.32 ppm		Copper	9.03 ppm
400°C Anode Recirc. Tank			**400°C Cathode Recirc. Tank**	
Metal	Concentration		Metal	Concentration
Arsenic	30.95 ppm		Arsenic	4.63 ppm
Chromium	0.64 ppm		Chromium	0.30 ppm
Copper	7.58 ppm		Copper	13.50 ppm
450°C Anode Recirc. Tank			**450°C Cathode Recirc. Tank**	
Metal	Concentration		Metal	Concentration
Arsenic	14.60 ppm		Arsenic	0.19 ppm
Chromium	0.19 ppm		Chromium	0.05 ppm
Copper	5.01 ppm		Copper	9.04 ppm
Wood Anode Recirc. Tank			**Wood Cathode Recirc. Tank**	
Metal	Concentration		Metal	Concentration
Arsenic	51.89 ppm		Arsenic	0.99 ppm
Chromium	15.94 ppm		Chromium	1.20 ppm
Copper	6.98 ppm		Copper	7.81 ppm

4.4.3.1.3 CCA Metal Content in Anode and Cathode Half-Cell Filtered Solids

As described in Section 3.7.3.2, solid material that was contained in the fluid collected from the EK half-cells, recirculation tanks, and electrode washes was filtered out of the fluids. After filtration, the solids then were digested to determine the concentration of CCA metals in these solids. There was wide variability in the number of samples collected from each section of the EK cells; therefore, for ease of comparison, the individual concentration results for a given section were combined into an average anode and cathode value for each cell. For example, two filters were necessary to completely collect the solids contained in the recirculation tank for Cell A. Both digestion samples were analyzed via ICP-OES, and these results were averaged. Figures

4.36 and 4.37 capture the results. Within the anode section, higher concentrations of all three metals were found in the filtered solids from the 400°C and 450°C than the other EK cells. The reverse was true for the cathode sections for solids from the 400°C cells. The prevalence of metals in the system fluids generated by EK of pyrolysis char generated at higher temperatures may be due to the increased destruction of the wood matrix that occurs at these higher temperatures. It is possible that the char material was simply more friable and small particles may have escaped the bounds of the center compartment. One distinct trend is apparent: chromium concentrations were highest in the anode section while copper concentrations were highest in the cathode section. This is to be expected due to the ion speciation that occurred during the EK experiments.

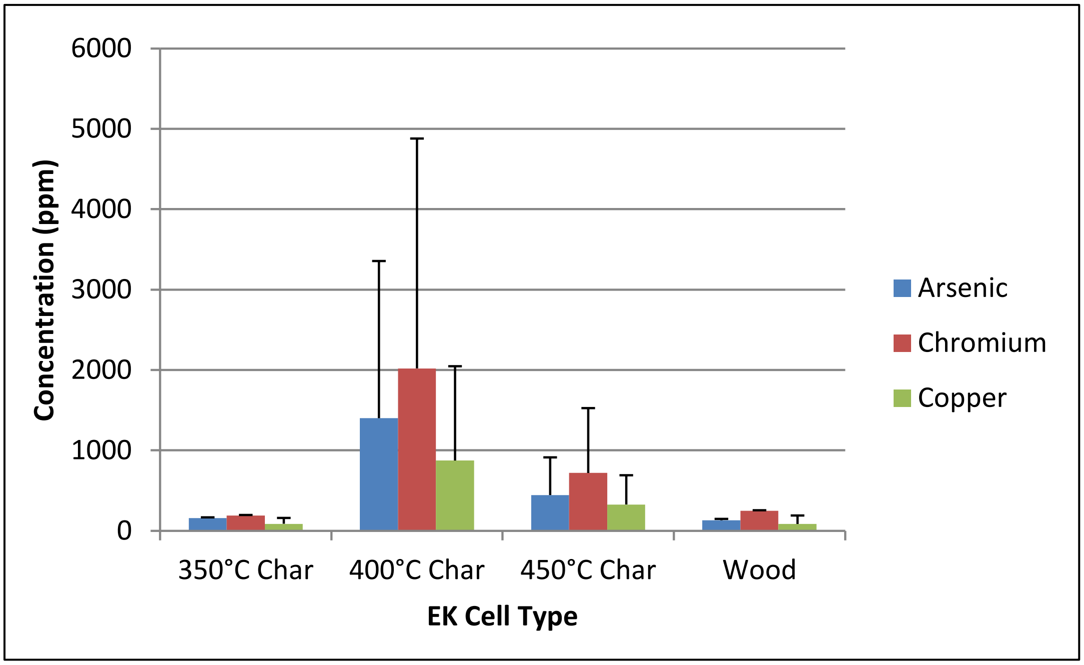


Figure 4.36 Average CCA Metal Content in Anode Half-Cell Filtered Solids

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

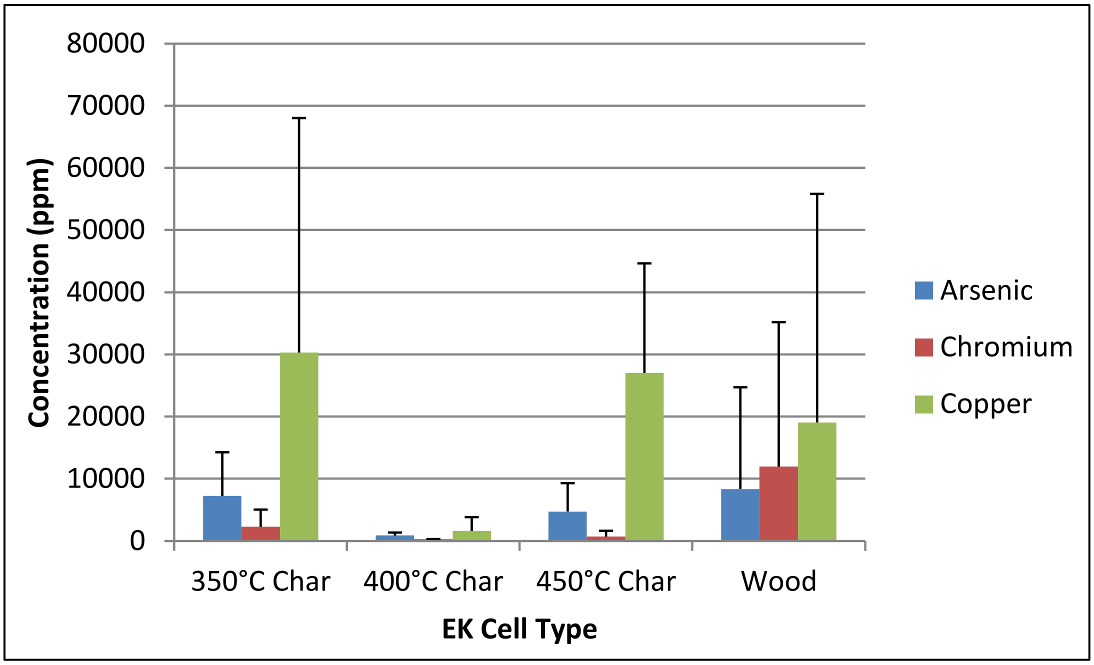


Figure 4.37 Average CCA Metal Content in Cathode Half-Cell Filtered Solids

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

4.4.3.1.4 CCA Metal Content in EK Cell Pressure Plates

Nitric acid digestions assisted in determining the CCA metal concentrations within the anode and cathode pressure plates for each EK cell. Figure 4.38 illustrates the average concentration of each CCA metal in the anode and cathode pressure plates. Two general trends were identified:

1. Concentrations of arsenic and copper were significantly higher than the concentration of chromium for both the anode and cathode pressure plates for all char cells. This is likely due to the overall higher mobility of arsenic and copper as established in the mobility studies of the previous sections. Increased mobility results in increased movement of the CCA metals and the

likelihood that some metals would remain in the pressure plates at the end of the EK experiments.

2. Metal concentration increased in both pressure plates for all metals as the pyrolysis temperature increased. This trend is to be expected given that the center compartments of EK cells loaded with char generated at 450°C contained higher concentrations of the metals at the start of the experiments than those cells loaded with char generated at 350°C or the CCA-treated wood waste (i.e. $[\text{Metals}]_{450°C} > [\text{Metals}]_{400°C} > [\text{Metals}]_{350°C} > [\text{Metals}]_{\text{Wood}}$).

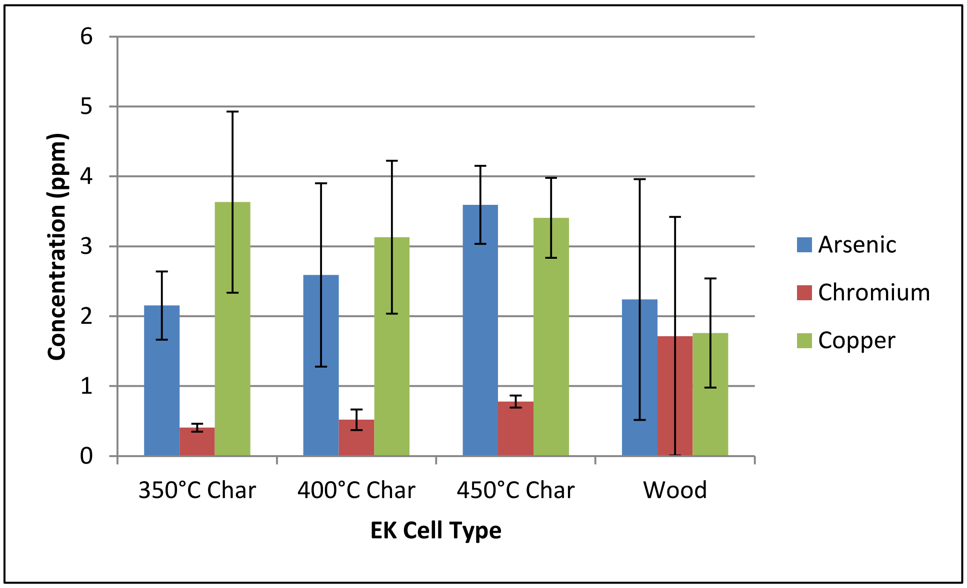


Figure 4.38 Average CCA Metal Content in Anode Pressure Plates

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

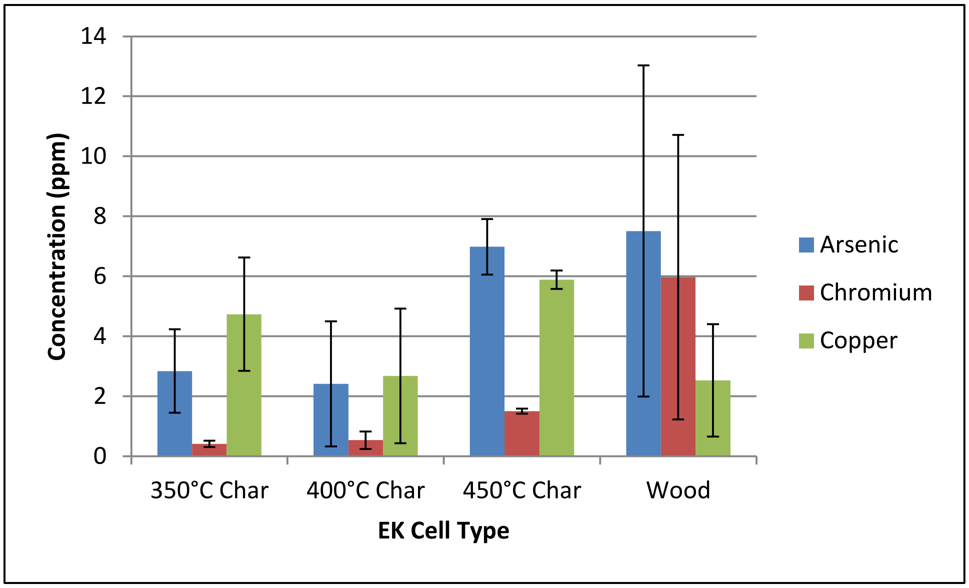


Figure 4.39 Average CCA Metal Content in Cathode Pressure Plates

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste; Error bars represent 95% confidence intervals

4.4.3.2 CCA Metal Removal

Mass removal percentages of each CCA metal were calculated after each EK treatment (i.e. pyrolysis char and CCA-treated wood waste). The overall mass removal percentages were calculated using Equation 4.3 and based on the concentrations of each metal as determined in Section 4.1 (Pre-Experiment), Section 4.3 (Pre-EK) and Section 4.4 (Post-EK). Results are provided in the following sections.

$$Mass\ \%\ Removed\ = \frac{Post{-}EK\ Metal\ Mass}{Pre{-}Experiment\ or\ Pre{-}EK\ Metal\ Mass} \times 100 \qquad (4.3)$$

4.4.3.2.1 Overall CCA Metal Removal

Overall mass removal percentages were calculated based on the pre-experiment and post-EK mass of each CCA metal within the center compartment of each EK cell. Masses from duplicate cells (e.g. Cell A and Cell B) were averaged and are illustrated in

Figure 4.40. Coupling pyrolysis and EK resulted in the highest overall removal percentages for arsenic and chromium, while EK of CCA-treated wood waste had the highest removal percentage for copper. Volatilization and distribution of arsenic and chromium across other pyrolysis products rather than remaining in the char largely contributed to the overall removal of these metals from the solid waste material. Conversely, as discussed in Section 4.X, the mass percent copper retained in the pyrolysis char was significantly greater than arsenic and chromium, suggesting that pyrolysis has less of an impact on the overall removal of copper from the solid waste material.

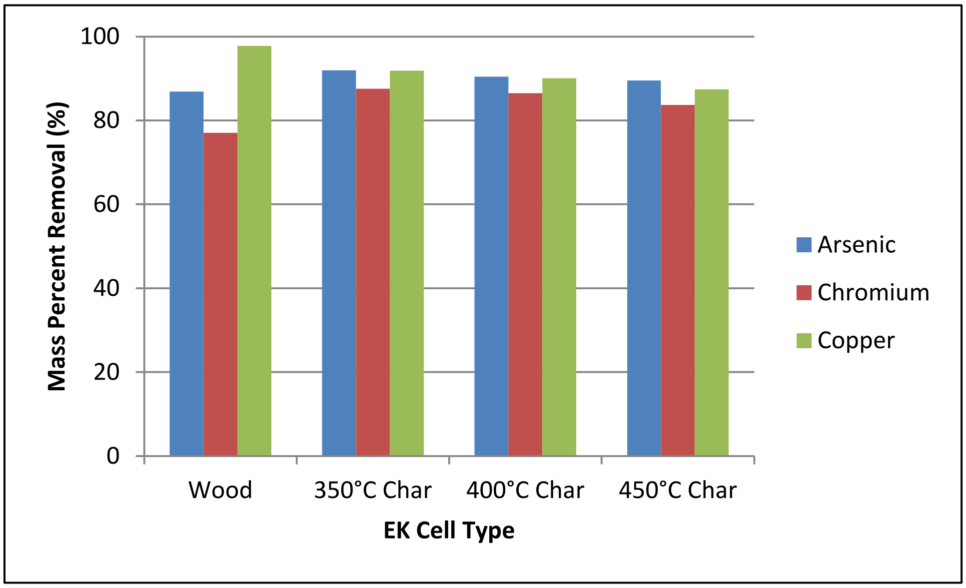


Figure 4.40 Overall Mass Percent CCA Metal Removed in this Study

Additionally, EK efficiency decreased as pyrolysis temperature increased for all metals. As discussed in Section 4.4.3.1.1, this was likely due to each of the CCA metals being more mobile in the CCA-treated wood waste and chars generated at lower pyrolysis temperatures than the higher pyrolysis chars. Increased metal mobility indicates a general propensity toward leaching, resulting in higher EK efficiencies for pyrolysis char generated at 350°C and raw CCA-treated wood waste. Specific analysis for each metal is provided in the following sections.

4.4.3.2.2 Arsenic Removal by EK

As illustrated in Figure 4.41, the percent arsenic removed from the CCA-treated wood waste and pyrolysis char decreased as pyrolysis temperature increased. In comparison to removal of the CCA-treated wood waste, utilizing pyrolysis resulted in a decrease in arsenic removal efficiency by 11%, 14%, and 19% for pyrolysis temperatures of 350°C, 400°C, and 450°C, respectively. Arsenic was identified as the most mobile CCA metal in the characterization studies of Section 4.1. As previously discussed, the high mobility of the arsenic, likely due to the precipitation of arsenic on the wood matrix during the preservative treatment application process, indicated potential for successful EK treatment. Figure 4.41 illustrates that arsenic removal was efficient across all EK cells and that in this capacity the cells performed as expected.

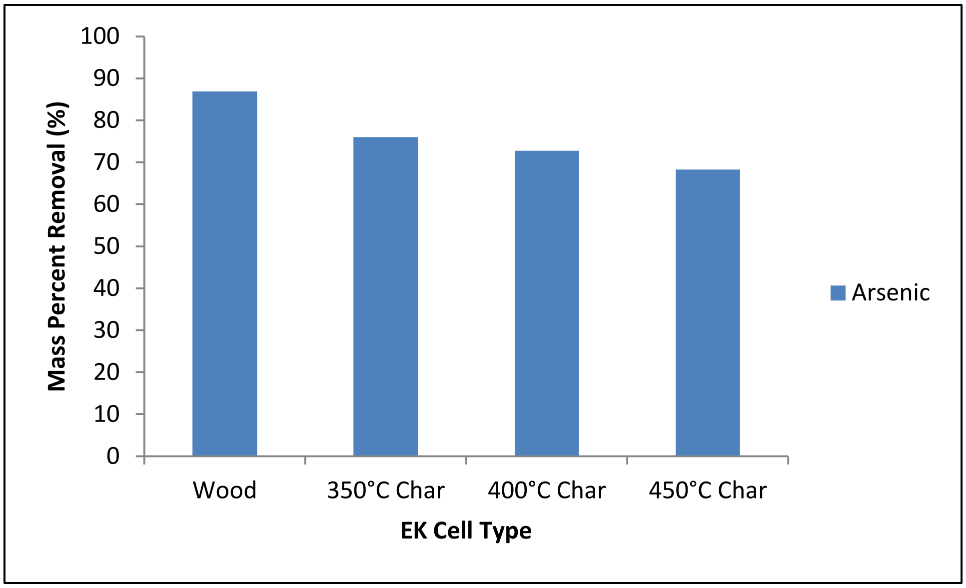


Figure 4.41 Average Mass Percent of Arsenic Removed for Each EK Cell Used in this Study

4.4.3.2.3 Chromium Removal by EK

The percent chromium removed from the CCA-treated wood waste and pyrolysis char decreased as pyrolysis temperature increased, as seen in Figure 4.42. Chromium removal efficiency decreased by 15%, 23%, and 37% for pyrolysis temperatures of 350°C, 400°C, and 450°C, respectively, when compared to the removal efficiency for CCA-treated wood waste. Chromium was identified as the least mobile CCA metal in the characterization studies of Section 4.1, likely reducing its potential for successful removal via EK treatment. The marked decrease in removal efficiency for pyrolysis char generated at 450°C may be due to the formation of chromium-char agglomerates which are larger particles that are less responsive to the electrical current used in the EK experiments. Larger quantities of these agglomerates may form at the higher pyrolysis temperatures, resulting in the trend of declining removal efficiency for chromium.

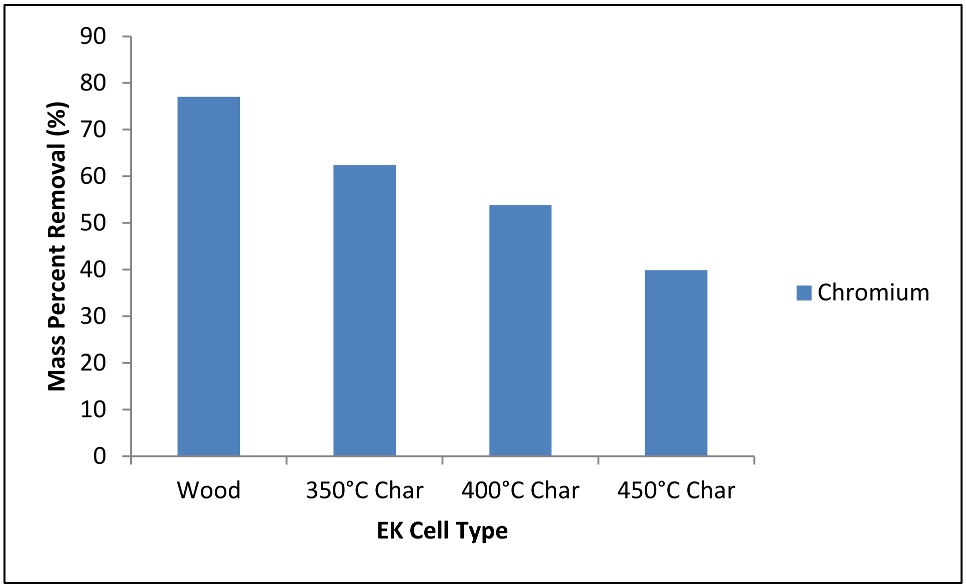


Figure 4.42 Average Mass Percent of Chromium Removed for Each EK Cell Used in this Study

4.4.3.2.4 Copper Removal by EK

As with arsenic and chromium, the percent arsenic removed from the CCA-treated wood waste and pyrolysis char decreased as pyrolysis temperature increased. This trend can be seen in Figure 4.43. Utilizing pyrolysis resulted in a decrease in copper removal efficiency by 15%, 21%, and 30% for pyrolysis temperatures of 350°C, 400°C, and 450°C, respectively, when compared to the removal efficiency of CCA-treated wood waste. Copper was the second most mobile CCA metal in the characterization studies of Section 4.1, indicating that copper could be successfully removed from the wood and char via EK. Again, this high mobility was likely due to the simple adsorption of copper on the wood and char matrices. Given that the percent copper removed at 450°C observed the largest decrease, it is possible that the copper contained in high temperature pyrolysis chars have formed additional complexes with the wood and char matrices, resulting in a lower amount of free copper ions conducive to removal via EK treatment.

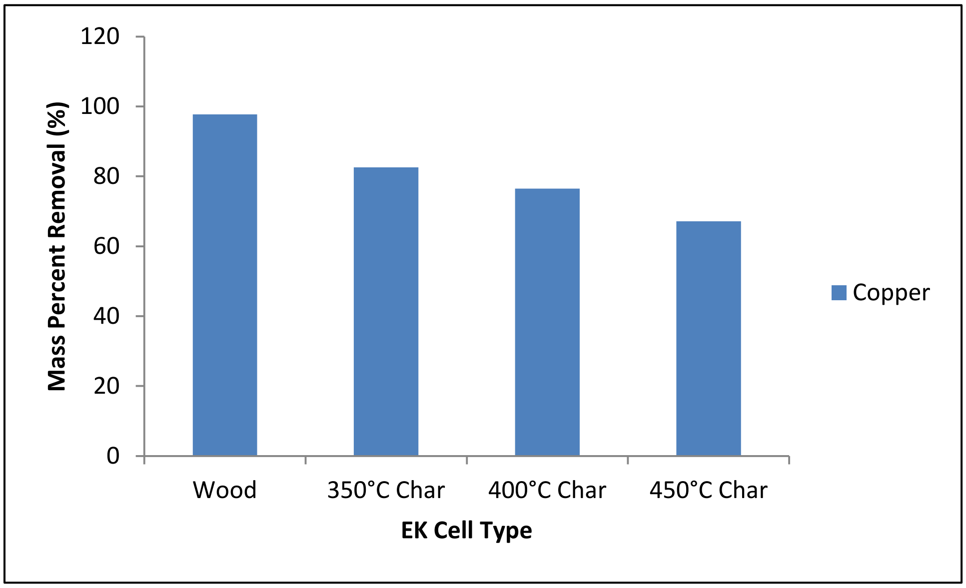


Figure 4.43 Average Mass Percent of Copper Removed for Each EK Cell Used in this Study

4.4.3.2.5 Sectional CCA Metal Removal

Contents of the center compartment of each cell were divided into four sections as described in Section 3.6.2. The mass removal percentages for each section were calculated and examined for trends (see Figures 4.44 through 4.46). Removal of arsenic and chromium were slightly higher in sections 1 and 2 (i.e. sections closest to the anode) than in sections 3 and 4. This is best explained by the ionization occurring during the EK experiments where arsenic and chromium both primarily for anions which migrated toward the anode half-cell. This indicates that higher masses of these two metals remained in the sections closest to the anode electrode. A reversed trend is identified for copper as removal is slightly higher in sections 3 and 4 (i.e. sections closest to the cathode) than in sections 1 and 2. Again, this is likely due to the ionization occurring during the EK experiments where copper cations are formed and migrate toward the cathode half-cell. While these trends have been identified, it should be noted that overall removal percentages across each section were within 5% for all metals, indicating that metal removal was largely consistent across the length of the cell due to the close spacing of the electrodes.

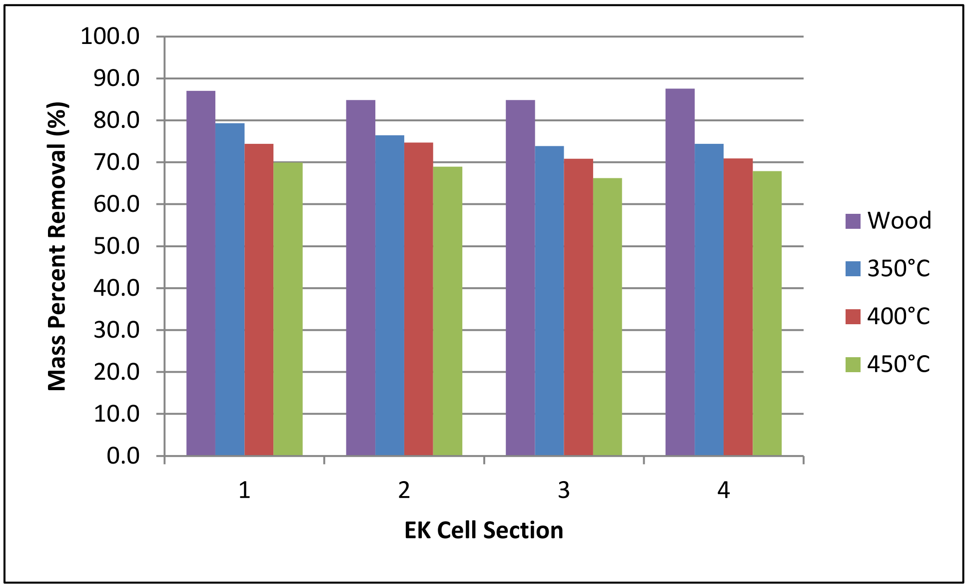


Figure 4.44 Average Mass Percent of Arsenic Removed by Section for Each EK Cell Used in this Study

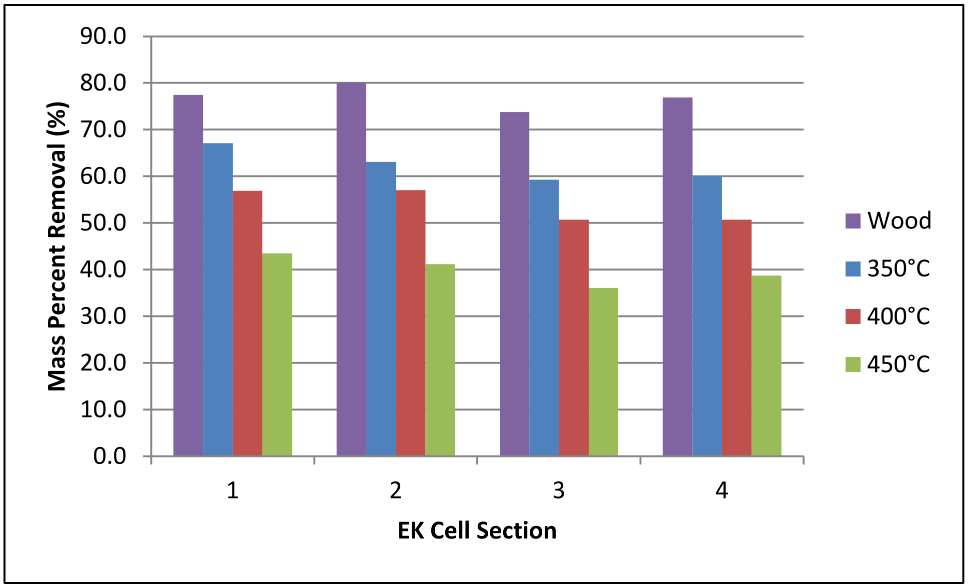


Figure 4.45 Average Mass Percent of Chromium Removed by Section for Each EK Cell Used in this Study

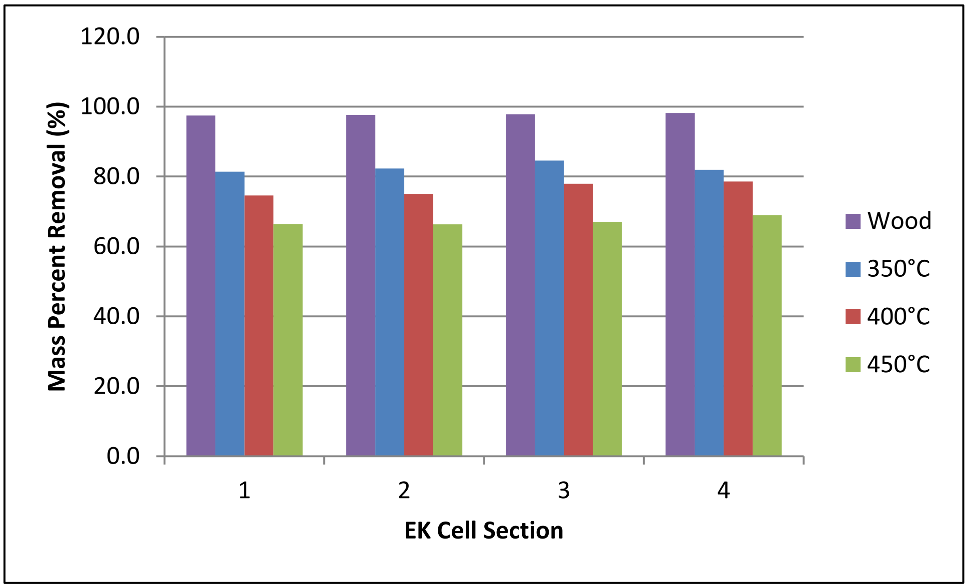


Figure 4.46 Average Mass Percent of Copper Removed by Section for Each EK Cell Used in this Study

4.4.4 CCA Metal Mobility of Post-EK Samples

Mobility of the CCA metals within the post-EK pyrolysis char and CCA-treated wood was evaluated via the three mobility tests outlined in Section 3.7.3.5.5. Figures 4.47 though 4.49 contain the average post-EK concentrations of CCA metals within the leachate from TCLP, SPLP, and DI Water Leaches.

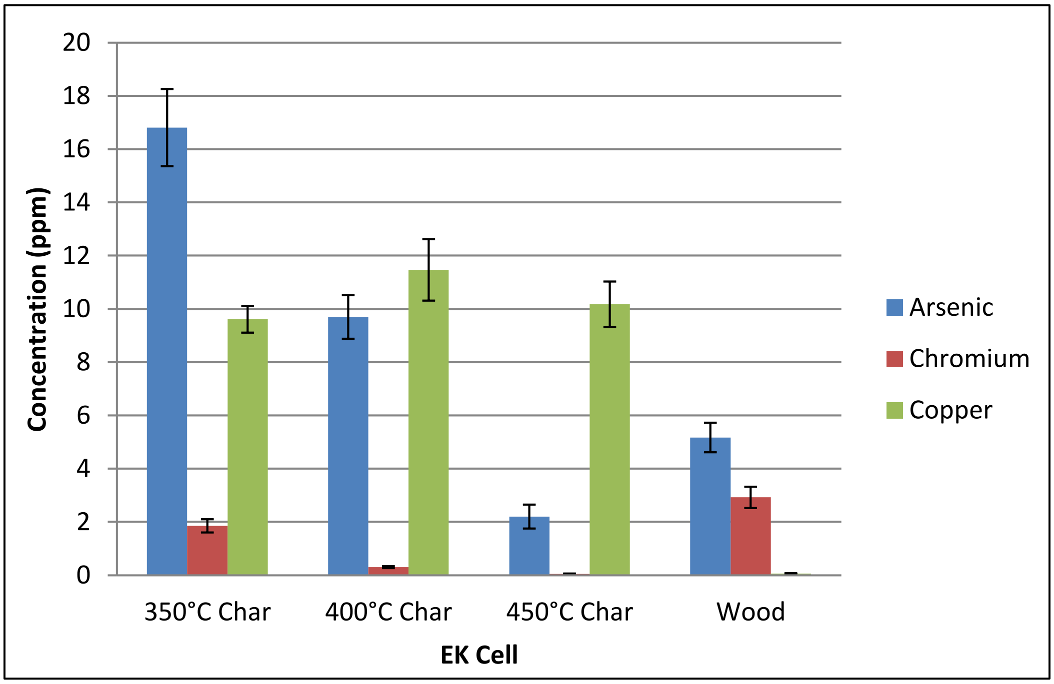


Figure 4.47 Average Post-EK TCLP Metal Concentrations of the Pyrolysis Char and CCA-treated Wood Waste

Note: Error bars represent 95% confidence intervals

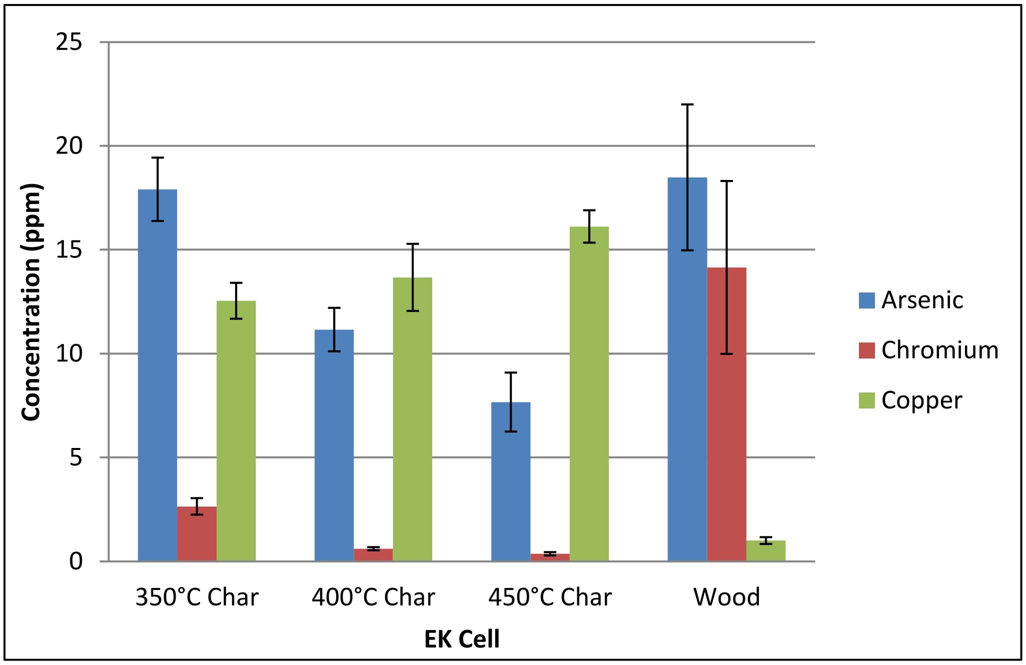


Figure 4.48 Average Post-EK SPLP Metal Concentrations of the Pyrolysis Char and CCA-treated Wood Waste

Note: Error bars represent 95% confidence intervals

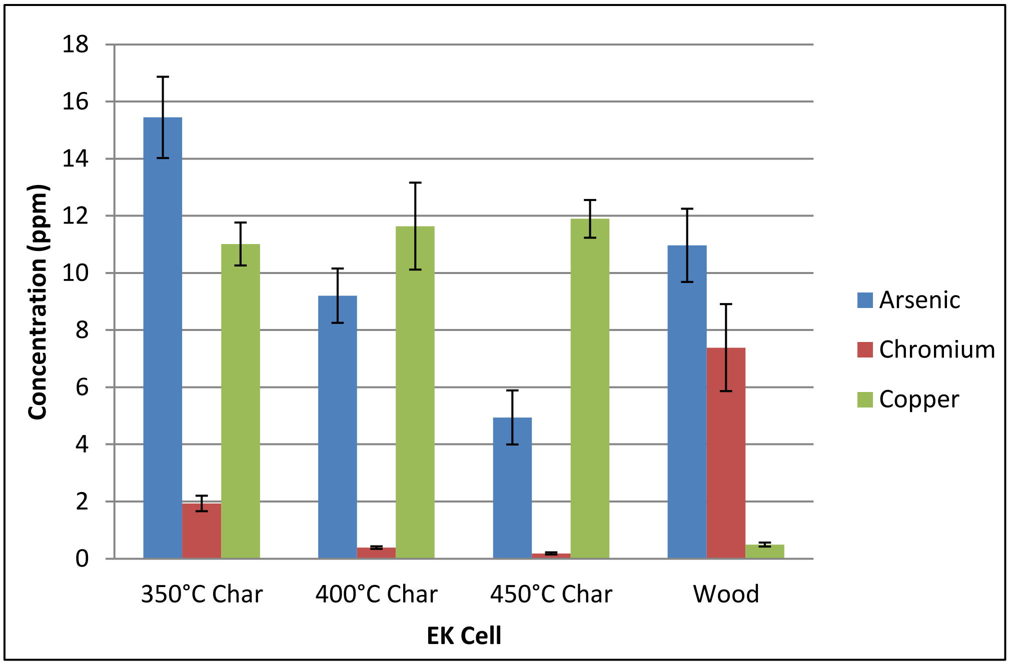


Figure 4.49 Average Post-EK DI Water Leach Metal Concentrations of the Pyrolysis Char and CCA-treated Wood Waste

Note: Error bars represent 95% confidence intervals

Mobility within the post-EK CCA-treated wood samples was lower than the pre-EK mobility for all metals under all leaching conditions; however, arsenic in the post-EK sawdust continues to exceed the TCLP limit of 5.0 ppm. Additionally, all three CCA metals continue to leach under relatively weak conditions (DI Water Leaches). This could be indicative of free metals remaining on the CCA-treated wood surface at the conclusion of the EK experiments (15 days), as these metals would be readily available and prone to leaching under all three leaching conditions investigated during this study.

Generally, mobility decreases with increasing pyrolysis temperature across all leaching conditions for arsenic and chromium. In fact, arsenic does not exceed the TCLP limit at 450°C. Under TCLP conditions, mobility of arsenic and chromium increases as pyrolysis temperature increases when compared to pre-EK mobility levels. This trend is only true for chromium at 450°C as leachate concentrations increase by 1.38 ppm and 0.021 ppm at 350°C and 400°C, respectively. The same mobility trend occurs for arsenic under SPLP conditions. Chromium leachate concentration increases as pyrolysis temperature increases compared to pre-EK mobility. Concentration increases of 2.02 ppm, 0.268 ppm, and 0.291 ppm are observed at pyrolysis temperatures of 350°C, 400°C, and 450°C, respectively. Copper concentration generally decreases as pyrolysis temperature increases relative to pre-EK values except at 450°C where the concentration increases by 10.9 ppm. The same trends are observed for each metal under DI water leach conditions as those observed under SPLP conditions.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Pyrolysis and electrokinetic techniques were investigated as remediation methods for "out of service" CCA-treated wood waste. Additionally, a bench pyrolysis system was optimized for maximum bio-oil production and CCA metal retention, and the impact of pyrolysis on the mobility of CCA metals in pyrolysis char was evaluated. Finally, the efficiencies of a lab-scale electrokinetic system for removal of CCA metals from pyrolysis char were determined. Conclusions and recommendations for future work are detailed in the following sections.

5.1 Conclusions

The following conclusions can be drawn based on the results of this study:

- Low-temperature pyrolysis is successful at reducing the overall mass percentage of CCA-containing waste material.
    - Highest overall mass percent reduction in CCA-containing waste was achieved at a pyrolysis temperature of 450°C. This anticipated result was due to more complete destruction of the wood matrix at higher pyrolysis temperatures.
    - As expected, maximum bio-oil production occurred at the 450°C pyrolysis temperature. Average bench system bio-oil production was as follows:

450°C (12.2 mL) > 400°C (11.2 mL) > 350°C (10.7 mL)

- CCA metal distribution across the three pyrolysis products (char, bio-oil, and non-condensable gases) is highly dependent on pyrolysis temperature, as expected.
    - Maximum mass percent metal retention within char was achieved at the 350°C pyrolysis temperature for all metals. An overall trend of decreased metal retention with increase in pyrolysis temperature was identified. This was observed for both bench and batch pyrolysis systems, and is best explained by increased volatilization of the CCA metals as pyrolysis temperature increases.
    - Similarly, maximum metal concentration for all metals within the bio-oil was achieved at the 450°C pyrolysis temperature. A trend of increased metal concentration with increase in pyrolysis temperature was observed, again due to the increased volatilization of CCA metals at higher pyrolysis temperatures. This also held true for both bench and batch pyrolysis systems.
    - Improved direct heating of the CCA-treated wood in the batch pyrolysis reactor yielded decreased metal content in the char and increased metal content in the bio-oil. This was to be expected given that the loaded CCA-treated wood material was more thoroughly and directly heated due to the use of a tube furnace, and ultimately resulted in increased volatilization of the CCA metals. This phenomenon demonstrates the effect of pyrolysis reactor

  design on the overall pyrolysis process as discussed in Section 1.5.4.
  - Release of non-condensable gases increased as pyrolysis temperature increased. As expected based on literature, arsenic was the primary metal of concern with releases of more than 62% at 450°C. Given that arsenic volatilizes at roughly 327°C, it is unsurprising to observe lower levels of release at 350°C than at the higher pyrolysis temperatures.
- Pyrolysis reduces the overall CCA metal mobility in comparison to CCA-treated wood waste.
  - Metal mobility within the bench and batch pyrolysis char was reduced across all leaching studies (TCLP, SPLP, and DI water leaches) compared with CCA-treated wood; however, arsenic exceeded the TCLP limit of 5.0 ppm for all temperatures. Reduced mobility is likely due to stronger complexes formed between the CCA metals and the char matrix than in the original waste wood. Decreased mobility indicates that the potential for leaching of each metal has been reduced based on utilizing pyrolysis techniques; however, the decrease is not sufficient for the pyrolysis char to be considered a non-hazardous waste per the TCLP.
  - As pyrolysis temperature increased, metal mobility decreased within the char for all metals across all leaching studies. This generally indicates that the remaining metals are more tightly fixed

    to the charred wood matrix at higher temperatures. The formation of metal-char complexes decreases the propensity for successful remediation via EK.

- CCA metal fixation and speciation impact overall EK efficiency.
    - Power consumption was highest for EK cells containing material that had undergone little (pyrolysis at 350°C) or no pyrolysis (CCA-treated wood waste). The higher power consumption may have been necessary to overcome the resistance within the cell due to higher concentrations of unbound CCA metals in these two materials.
    - Electromigration is the dominant EK phenomenon in cells loaded with CCA-treated wood waste and pyrolysis char generated at 350°C, based on low acid consumption and higher metal removal efficiencies. Higher acid consumption, used to regulate the pH at the cathode, indicates that hydrolysis reactions are more dominant in cells loaded with pyrolysis char generated at 400°C and 450°C.
    - A net flow of water away from the cathode half-cell toward the anode-half cell across all experimental conditions indicates that anionic species are dominant in the EK cells.
    - Higher concentrations of arsenic and chromium in the anode half-cell indicate that arsenic and chromium are likely present as anions (e.g. $Cr_2O_7^{2-}$ and AsO_4^{3-}), while higher concentrations of copper in the cathode half-cell indicate copper is present as cations (Cu^{2+}).

- EK is moderately successful at removing CCA metals from pyrolysis char.
    - EK mass percent removal efficiencies decreased as pyrolysis temperature increased for all metals. Again, this is likely due to the formation of strong metal-char bonds formed at the higher pyrolysis temperatures. This decreased efficiency is expected based on the results of mobility studies on the pyrolysis char, which indicated that CCA metals in char produced at higher pyrolysis temperatures were less likely to have a proclivity toward successful removal via EK techniques.
    - Utilizing pyrolysis resulted in a decrease in removal efficiency for all metals in comparison to the removal percentages achieved for each EK of CCA-treated wood waste. Average removal percentages for each metal were as follows:

      As: CCA Wood (87%) > 350°C (76%) > 400°C (73%) > 450°C (68%)
      Cr: CCA Wood (77%) > 350°C (62%) > 400°C (54%) > 450°C (40%)
      Cu: CCA Wood (98%) > 350°C (83%) > 400°C (77%) > 450°C (67%)
- Coupling pyrolysis and EK techniques successfully removes CCA metals from treated wood waste. Maximum overall mass removal percentages of approximately 92% arsenic, 88% chromium, and 92% copper were achieved after coupling the techniques.
    - The combined techniques were most effective at removing arsenic, followed by copper and chromium. Average effectiveness at removing each CCA metal was as follows:

        As (91%) > Cu (90%) > Cr (86%)

    - Coupling pyrolysis and EK improved the overall removal efficiency over EK of CCA-rich sawdust for arsenic and chromium. The distribution of arsenic and chromium in pyrolysis bio-oil and non-condensable gases results in lower concentrations of the metals in the pre-EK char. This ultimately results in an overall lower concentration of metals in the solid waste material.
    - Copper removal was most efficient for EK treatment alone with 98% mass removed. Highly mobile, unbound copper in the CCA-treated wood waste was more readily removed than the bound copper in the pyrolysis char.
- Coupling pyrolysis and EK techniques reduced the overall mobility of all CCA metals across all temperatures compared to CCA-treated wood waste levels. While the decrease was significant, only post-EK char generated at 450°C did not exceed the TCLP limit for arsenic. This ultimately indicates that pyrolysis char that has undergone EK is less likely to leach CCA metals than the original CCA-treated wood waste.

5.2 Recommendations for Future Work

The following are recommendations for future work:

- The scale of the pyrolysis system should be increased to generate more material for subsequent testing and analysis. Additionally, the system should utilize automated controls and temperature monitoring as these should ensure better repeatability and an increase in pyrolysis system efficiency.

- SEM analysis should be performed on the pyrolysis char in order to identify and quantify the complexes and agglomerates that formed between the CCA metals and char matrix. This analysis could provide better insight into metals' speciation and better inform the approach taken for further removal of the metals.
- Investigations into the characterization and stability of bio-oil produced from pyrolysis of CCA-treated wood waste should be perfomed. These studies would include determining the pH, viscosity, and water content under various conditions, and the results could be used to evaluate potential uses for the produced bio-oil.
- The fungicidal value of bio-oil produced from pyrolysis of CCA-treated wood waste should be determined in order to evaluate the potential for the bio-oil to be utilized as a wood preservative.
- A life-cycle analysis should be performed for the coupled pyrolysis and EK systems. These results could then be compared to existing disposal options and the two stand-alone techniques, to better identify which management and treatment approach is most effective.

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APPENDIX A

STANDARDS AND SAMPLE PREPARATION FOR ICP-OES ANALYSIS

Table A.1 Creating 10 ppm Standards from 1000 ppm Stock Standards

10 ppm Y (Internal Standard)
1 mL 1000 ppm Y
20 mL Concentrated Nitric Acid
Fill to line of 100 mL volumetric flask with DI Water
10 ppm Cu, Cr Standard
1 mL 1000 ppm Cu
1 mL 1000 ppm Cr
20 mL Concentrated Nitric Acid
Fill to line of 100 mL volumetric flask with DI Water
10 ppm As Standard
1 mL 1000 ppm As
20 mL Concentrated Nitric Acid
Fill to line of 100 mL volumetric flask with DI Water
10 ppm Cu, Cr, As Spike Standard
1 mL 1000 ppm Cu
1 mL 1000 ppm Cr
1 mL 1000 ppm As
20 mL Concentrated Nitric Acid
Fill to line of 100 mL volumetric flask with DI Water

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Table A.2 Creating Digestion Calibration Standards

0.1 ppm Cu, Cr Standard		**0.1 ppm As Standard**
0.1 mL 10 ppm Cu, Cr		0.1 mL 10 ppm As
1.0 mL 10 ppm Y		1.0 mL 10 ppm Y
8.9 mL 20% Nitric Acid		8.9 mL 20% Nitric Acid
1.0 ppm Cu, Cr Standard		**1.0 ppm Cu, Cr Standard**
1.0 mL 10 ppm Cu, Cr		1.0 mL 10 ppm Cu, Cr
1.0 mL 10 ppm Y		1.0 mL 10 ppm Y
8.0 mL 20% Nitric Acid		8.0 mL 20% Nitric Acid
10 ppm Cu, Cr Standard		**10 ppm Cu, Cr Standard**
0.1 mL 1000 ppm Cu		0.1 mL 1000 ppm As
0.1 mL 1000 ppm Cr		1.0 ml 10 ppm Y
1.0 ml 10 ppm Y		8.9 mL 20% Nitric Acid
8.8 mL 20% Nitric Acid		

Note: Standards are made in 10 mL ICP vials

Table A.3 Creating TCLP Calibration Standards

0.1 ppm Cu, Cr Standard		**0.1 ppm As Standard**
0.1 mL 10 ppm Cu, Cr		0.1 mL 10 ppm As
1.0 mL 10 ppm Y		1.0 mL 10 ppm Y
2.0 mL TCLP Fluid		2.0 mL TCLP Fluid
6.9 mL 20% Nitric Acid		6.9 mL 20% Nitric Acid
1.0 ppm Cu, Cr Standard		**1.0 ppm Cu, Cr Standard**
1.0 mL 10 ppm Cu, Cr		1.0 mL 10 ppm Cu, Cr
1.0 mL 10 ppm Y		1.0 mL 10 ppm Y
2.0 mL TCLP Fluid		2.0 mL TCLP Fluid
6.0 mL 20% Nitric Acid		6.0 mL 20% Nitric Acid
10 ppm Cu, Cr Standard		**10 ppm Cu, Cr Standard**
0.1 mL 1000 ppm Cu		0.1 mL 1000 ppm As
0.1 mL 1000 ppm Cr		1.0 ml 10 ppm Y
1.0 ml 10 ppm Y		2.0 mL TCLP Fluid
2.0 mL TCLP Fluid		6.9 mL 20% Nitric Acid
6.8 mL 20% Nitric Acid		

Note: Standards are made in 10 mL ICP vials

Table A.4 Creating SPLP Calibration Standards

0.1 ppm Cu, Cr Standard		**0.1 ppm As Standard**
0.1 mL 10 ppm Cu, Cr		0.1 mL 10 ppm As
1.0 mL 10 ppm Y		1.0 mL 10 ppm Y
2.0 mL SPLP Fluid		2.0 mL SPLP Fluid
6.9 mL 20% Nitric Acid		6.9 mL 20% Nitric Acid
1.0 ppm Cu, Cr Standard		**1.0 ppm Cu, Cr Standard**
1.0 mL 10 ppm Cu, Cr		1.0 mL 10 ppm Cu, Cr
1.0 mL 10 ppm Y		1.0 mL 10 ppm Y
2.0 mL SPLP Fluid		2.0 mL SPLP Fluid
6.0 mL 20% Nitric Acid		6.0 mL 20% Nitric Acid
10 ppm Cu, Cr Standard		**10 ppm Cu, Cr Standard**
0.1 mL 1000 ppm Cu		0.1 mL 1000 ppm As
0.1 mL 1000 ppm Cr		1.0 ml 10 ppm Y
1.0 ml 10 ppm Y		2.0 mL SPLP Fluid
2.0 mL SPLP Fluid		6.9 mL 20% Nitric Acid
6.8 mL 20% Nitric Acid		

Note: Standards are made in 10 mL ICP vials

Table A.5 Creating DI Water Leach Calibration Standards

0.1 ppm Cu, Cr Standard		**0.1 ppm As Standard**
0.1 mL 10 ppm Cu, Cr		0.1 mL 10 ppm As
1.0 mL 10 ppm Y		1.0 mL 10 ppm Y
2.0 mL DI Water		2.0 mL DI Water
6.9 mL 20% Nitric Acid		6.9 mL 20% Nitric Acid
1.0 ppm Cu, Cr Standard		**1.0 ppm Cu, Cr Standard**
1.0 mL 10 ppm Cu, Cr		1.0 mL 10 ppm Cu, Cr
1.0 mL 10 ppm Y		1.0 mL 10 ppm Y
2.0 mL DI Water		2.0 mL DI Water
6.0 mL 20% Nitric Acid		6.0 mL 20% Nitric Acid
10 ppm Cu, Cr Standard		**10 ppm Cu, Cr Standard**
0.1 mL 1000 ppm Cu		0.1 mL 1000 ppm As
0.1 mL 1000 ppm Cr		1.0 ml 10 ppm Y
1.0 ml 10 ppm Y		2.0 mL DI Water
2.0 mL DI Water		6.9 mL 20% Nitric Acid
6.8 mL 20% Nitric Acid		

Note: Standards are made in 10 mL ICP vials

Table A.6 Digestion Sample Preparation

Samples/Duplicates		**Blanks**
2 mL Sample		50 mL 20% Nitric Acid
1 mL 10 ppm Y		
7 mL 20% Nitric Acid		
Spikes		**1 ppm Checks**
2 mL Sample		5 mL 10 ppm Y
1 mL 10 ppm Y		5 mL 10 ppm Cu, Cr, As Spike
1 mL 10 ppm Cu, Cr, As Spike		40 mL 20% Nitric Acid
6 mL 20% Nitric Acid		

Note: Samples, duplicates, and spikes are prepared in 10 mL ICP vials; Blanks and 1 ppm checks are prepared in 50 mL plastic vials

Table A.7 TCLP Sample Preparation

Samples/Duplicates		**Blanks**
2 mL Sample		10 mL TCLP Fluid
1 mL 10 ppm Y		50 mL 20% Nitric Acid
7 mL 20% Nitric Acid		
Spikes		**1 ppm Checks**
2 mL Sample		10 mL TCLP Fluid
1 mL 10 ppm Y		5 mL 10 ppm Y
1 mL 10 ppm Cu, Cr, As Spike		5 mL 10 ppm Cu, Cr, As Spike
6 mL 20% Nitric Acid		30 mL 20% Nitric Acid

Note: Samples, duplicates, and spikes are prepared in 10 mL ICP vials; Blanks and 1 ppm checks are prepared in 50 mL plastic vials

Table A.8 SPLP Sample Preparation

Samples/Duplicates		**Blanks**
2 mL Sample		10 mL SPLP Fluid
1 mL 10 ppm Y		50 mL 20% Nitric Acid
7 mL 20% Nitric Acid		
Spikes		**1 ppm Checks**
2 mL Sample		10 mL SPLP Fluid
1 mL 10 ppm Y		5 mL 10 ppm Y
1 mL 10 ppm Cu, Cr, As Spike		5 mL 10 ppm Cu, Cr, As Spike
6 mL 20% Nitric Acid		30 mL 20% Nitric Acid

Note: Samples, duplicates, and spikes are prepared in 10 mL ICP vials; Blanks and 1 ppm checks are prepared in 50 mL plastic vials

Table A.9 DI Water Leach Sample Preparation

Samples/Duplicates		Blanks
2 mL Sample		10 mL DI Water
1 mL 10 ppm Y		50 mL 20% Nitric Acid
7 mL 20% Nitric Acid		
Spikes		**1 ppm Checks**
2 mL Sample		10 mL DI Water
1 mL 10 ppm Y		5 mL 10 ppm Y
1 mL 10 ppm Cu, Cr, As Spike		5 mL 10 ppm Cu, Cr, As Spike
6 mL 20% Nitric Acid		30 mL 20% Nitric Acid

Note: Samples, duplicates, and spikes are prepared in 10 mL ICP vials; Blanks and 1 ppm checks are prepared in 50 mL plastic vials

Table A.10 Daily EK Liquid Sample Preparation

Samples/Duplicates		Blanks
2 mL Sample		50 mL 20% Nitric Acid
1 mL 10 ppm Y		
7 mL 20% Nitric Acid		
Spikes		**1 ppm Checks**
2 mL Sample		5 mL 10 ppm Y
1 mL 10 ppm Y		5 mL 10 ppm Cu, Cr, As Spike
1 mL 10 ppm Cu, Cr, As Spike		40 mL 20% Nitric Acid
6 mL 20% Nitric Acid		

Note: Samples, duplicates, and spikes are prepared in 10 mL ICP vials; Blanks and 1 ppm checks are prepared in 50 mL plastic vials

APPENDIX B

EXPERIMENTAL RESULTS FOR PHASE I: CHARACTERIZATION OF CCA-TREATED WOOD WASTE

Table B.1 Digestion Results for CCA-treated Wood Sawdust

Sample ID	**As Concentration**	**Cu Concentration**	**Cr Concentration**
CCA A-1	5,963.3 ppm	3,216.5 ppm	4,915.3 ppm
CCA A-2	6,038.9 ppm	3,229.1 ppm	5,007.5 ppm
CCA A-3	6,006.7 ppm	3,164.2 ppm	4,895.0 ppm
CCA A-4	5,910.8 ppm	3,234.1 ppm	5,384.1 ppm
CCA A-5	5,959.1 ppm	3,193.5 ppm	5,372.9 ppm
CCA A-6	6,079.7 ppm	3,258.4 ppm	5,492.4 ppm
CCA B-1	5,919.9 ppm	3,153.8 ppm	4,865.7 ppm
CCA B-2	6,128.3 ppm	3,245.9 ppm	4,997.2 ppm
CCA B-3	6,068.4 ppm	3,219.6 ppm	4,984.2 ppm
CCA B-4	5,943.6 ppm	3,207.7 ppm	5,377.7 ppm
CCA B-5	6,229.3 ppm	3,332.1 ppm	5,586.0 ppm
CCA B-6	6,112.1 ppm	3,253.8 ppm	5,474.7 ppm
CCA C-1	6,309.5 ppm	3,265.6 ppm	5,038.6 ppm
CCA C-2	5,871.6 ppm	3,197.4 ppm	4,908.4 ppm
CCA C-3	6,052.9 ppm	3,141.4 ppm	4,815.3 ppm
CCA C-4	6,068.7 ppm	3,248.3 ppm	5,434.0 ppm
CCA C-5	5,806.4 ppm	3,144.5 ppm	5,258.8 ppm
CCA C-6	5,862.5 ppm	3,136.4 ppm	5,225.7 ppm
Average	6,162.1 ppm	3,222.2 ppm	5,237.3 ppm
Std Dev	174.6 ppm	61.8 ppm	203.1 ppm

Note: "A", "B", and "C" are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

Table B.2 TCLP Results for CCA-treated Wood Sawdust

Sample ID	As Concentration	Cu Concentration	Cr Concentration
CCA A-1	51.4 ppm	32.1 ppm	13.8 ppm
CCA A-2	51.3 ppm	31.7 ppm	13.6 ppm
CCA A-3	50.9 ppm	31.4 ppm	13.5 ppm
CCA A-4	52.8 ppm	32.2 ppm	14.6 ppm
CCA A-5	51.6 ppm	32.5 ppm	14.8 ppm
CCA A-6	52.6 ppm	32.0 ppm	14.4 ppm
CCA B-1	51.5 ppm	30.9 ppm	13.4 ppm
CCA B-2	52.1 ppm	31.3 ppm	13.5 ppm
CCA B-3	52.0 ppm	32.0 ppm	13.8 ppm
CCA B-4	53.7 ppm	33.2 ppm	15.0 ppm
CCA B-5	53.7 ppm	33.0 ppm	14.7 ppm
CCA B-6	55.1 ppm	34.4 ppm	15.3 ppm
CCA C-1	52.5 ppm	32.6 ppm	14.2 ppm
CCA C-2	52.5 ppm	32.7 ppm	14.2 ppm
CCA C-3	50.6 ppm	31.9 ppm	13.6 ppm
CCA C-4	58.2 ppm	34.9 ppm	16.0 ppm
CCA C-5	55.9 ppm	33.8 ppm	15.4 ppm
CCA C-6	60.1 ppm	36.2 ppm	16.9 ppm
Average	53.3 ppm	32.7 ppm	14.5 ppm
Std Dev	2.57 ppm	1.36 ppm	0.958 ppm

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

Table B.3 SPLP Results for CCA-treated Wood Sawdust

Sample ID	As Concentration	Cu Concentration	Cr Concentration
CCA A-1	44.9 ppm	21.2 ppm	12.1 ppm
CCA A-2	44.9 ppm	21.5 ppm	12.2 ppm
CCA A-3	46.0 ppm	21.5 ppm	12.4 ppm
CCA A-4	44.3 ppm	20.0 ppm	12.3 ppm
CCA A-5	49.1 ppm	22.3 ppm	13.7 ppm
CCA A-6	45.0 ppm	20.3 ppm	12.6 ppm
CCA B-1	45.8 ppm	21.3 ppm	12.4 ppm
CCA B-2	45.5 ppm	21.3 ppm	12.3 ppm
CCA B-3	46.1 ppm	21.6 ppm	12.5 ppm
CCA B-4	48.9 ppm	22.1 ppm	13.4 ppm
CCA B-5	46.2 ppm	20.9 ppm	12.9 ppm
CCA B-6	44.0 ppm	19.8 ppm	12.2 ppm
CCA C-1	46.1 ppm	22.1 ppm	12.8 ppm
CCA C-2	45.6 ppm	21.7 ppm	12.5 ppm
CCA C-3	45.4 ppm	21.4 ppm	12.3 ppm
CCA C-4	45.7 ppm	20.4 ppm	12.6 ppm
CCA C-5	44.7 ppm	20.2 ppm	12.4 ppm
CCA C-6	44.6 ppm	20.5 ppm	12.6 ppm
Average	55.7 ppm	21.1 ppm	12.6 ppm
Std Dev	1.36 ppm	0.742 ppm	0.421 ppm

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

Table B.4 DI Water Leach Results for CCA-treated Wood Sawdust

Sample ID	As Concentration	Cu Concentration	Cr Concentration
CCA A-1	44.7 ppm	20.9 ppm	12.0 ppm
CCA A-2	44.0 ppm	20.8 ppm	11.9 ppm
CCA A-3	44.6 ppm	20.6 ppm	11.7 ppm
CCA A-4	38.5 ppm	18.5 ppm	11.1 ppm
CCA A-5	38.4 ppm	18.5 ppm	11.1 ppm
CCA A-6	37.4 ppm	17.8 ppm	10.7 ppm
CCA B-1	44.5 ppm	21.0 ppm	12.1 ppm
CCA B-2	43.5 ppm	20.7 ppm	11.8 ppm
CCA B-3	49.9 ppm	23.3 ppm	13.6 ppm
CCA B-4	35.2 ppm	16.8 ppm	10.1 ppm
CCA B-5	37.5 ppm	18.0 ppm	10.8 ppm
CCA B-6	38.6 ppm	18.5 ppm	11.2 ppm
CCA C-1	47.3 ppm	22.2 ppm	12.8 ppm
CCA C-2	46.6 ppm	22.4 ppm	12.9 ppm
CCA C-3	40.7 ppm	19.7 ppm	11.2 ppm
CCA C-4	36.0 ppm	17.5 ppm	10.5 ppm
CCA C-5	39.2 ppm	18.5 ppm	11.2 ppm
CCA C-6	37.8 ppm	18.3 ppm	10.9 ppm
Average	41.3 ppm	19.7 ppm	11.5 ppm
Std Dev	4.34 ppm	1.86 ppm	0.912 ppm

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

Table B.5 Moisture Content Results for CCA-treated Wood Waste

Sample ID	Moisture Content
CCA A-1	7.94%
CCA A-2	8.56%
CCA A-3	7.90%
CCA A-4	8.04%
CCA A-5	7.87%
CCA A-6	8.50%
CCA A-7	8.14%
CCA A-8	8.08%
CCA A-9	8.12%
CCA B-1	7.88%
CCA B-2	7.96%
CCA B-3	8.03%
CCA B-4	7.45%
CCA B-5	8.45%
CCA B-6	7.98%
CCA B-7	7.86%
CCA B-8	7.84%
CCA B-9	7.67%
CCA C-1	8.03%
CCA C-2	7.72%
CCA C-3	7.67%
CCA C-4	7.57%
CCA C-5	7.45%
CCA C-6	7.75%
CCA C-7	8.11%
CCA C-8	8.16%
CCA C-9	8.23%

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

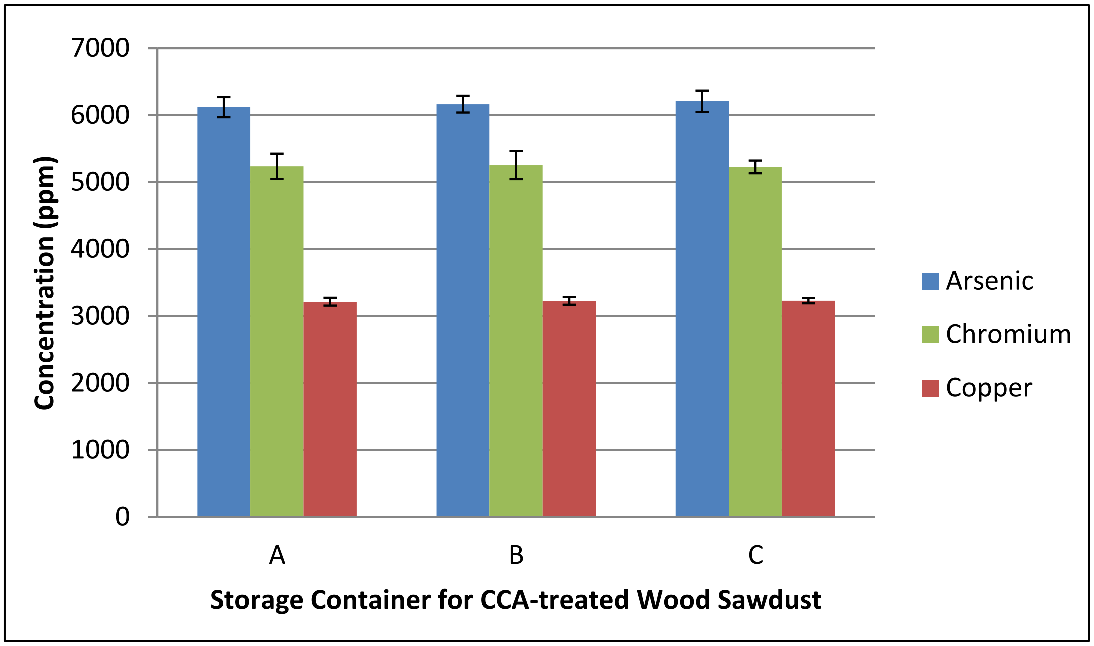

Figure B.1 Average Digestion Results for CCA-treated Wood Sawdust by Storage Container

Note: Error bars represent 95% confidence intervals

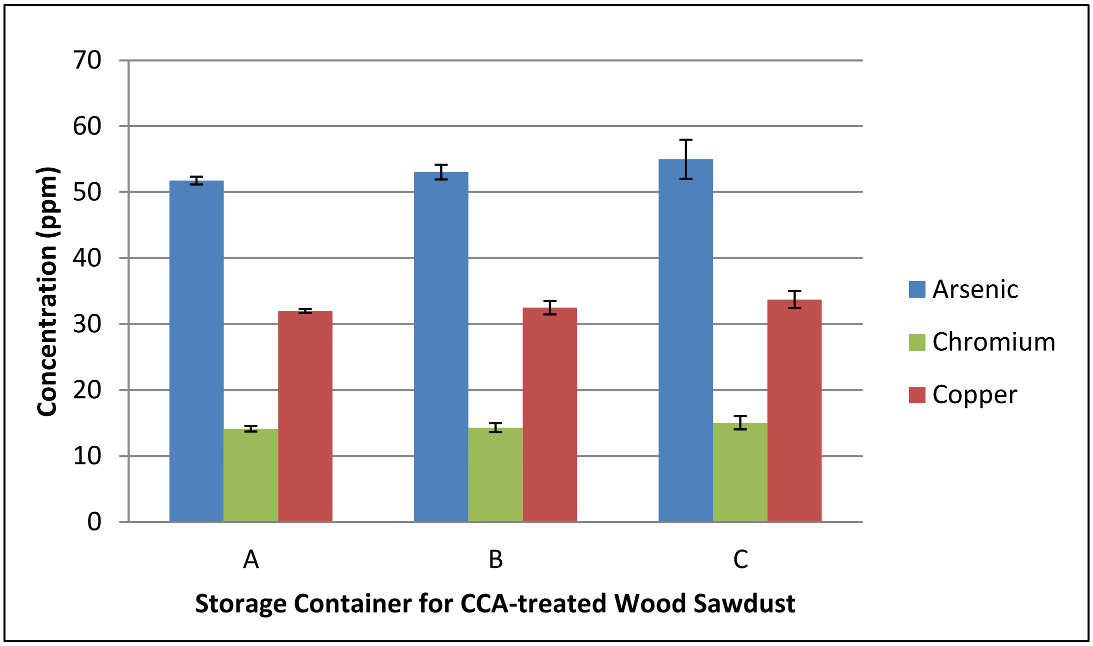

Figure B.2 Average TCLP Results for CCA-treated Wood Sawdust by Storage Container

Note: Error bars represent 95% confidence intervals

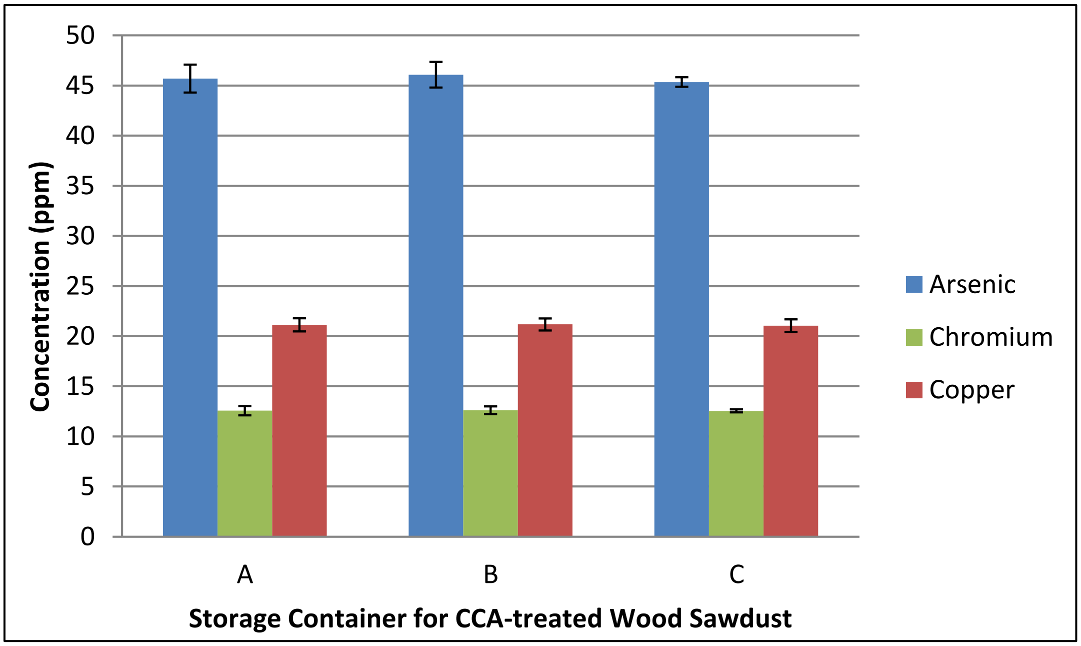

Figure B.3 Average SPLP Results for CCA-treated Wood Sawdust by Storage Container

Note: Error bars represent 95% confidence intervals

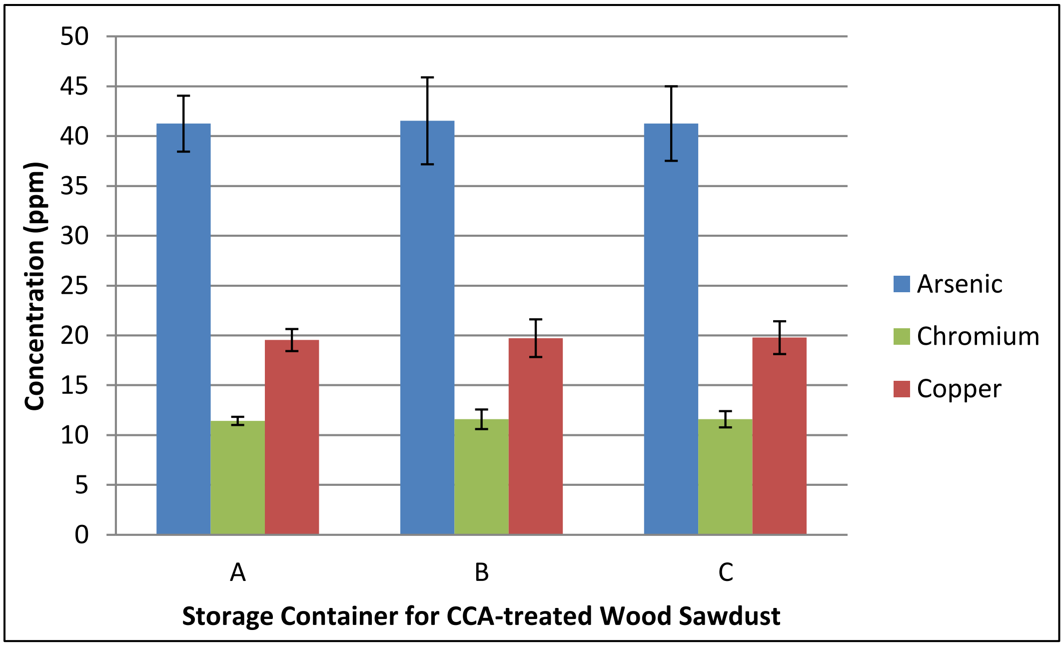

Figure B.4 Average DI Water Leach Results for CCA-treated Wood Sawdust by Storage Container

Note: Error bars represent 95% confidence intervals

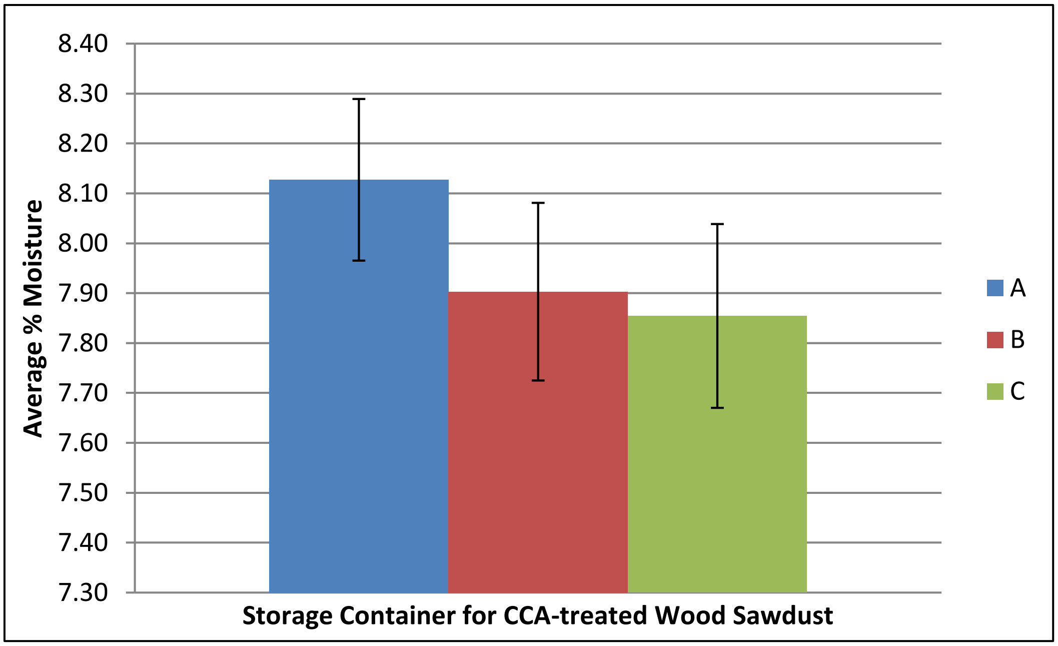

Figure B.5 Average Moisture Content Results for CCA-treated Wood Sawdust by Storage Container

Note: Error bars represent 95% confidence intervals

APPENDIX C

EXPERIMENTAL RESULTS FOR PHASE II: BENCH PYROLYSIS OF CCA-TREATED WOOD WASTE

Table C.1 Char and Bio-oil Production Totals from the Bench Pyrolysis of CCA-treated Wood Waste

Pyrolysis Set-point Temperature	**Char**	**Bio-oil**
350°C-A	11.31 g	9 mL
350°C-B	11.35 g	10 mL
350°C-C	11.54 g	13 mL
400°C-A	9.58 g	7.5 mL
400°C-B	9.74 g	13 mL
400°C-C	9.30 g	13 mL
450°C-A	9.00 g	12 mL
450°C-B	7.37 g	11.5 mL
450°C-C	8.06 g	13 mL

Table C.2 Digestion Results for Bench Pyrolysis Char

Sample ID	**As Concentration (ppm)**	**Cr Concentration (ppm)**	**Cu Concentration (ppm)**
350-A-1	12114.5	10908.1	6805.8
350-A-2	14401.1	13325.6	8184.1
350-A-3	14452.2	13182.1	8087.2
350-B-1	15025.6	13802.0	8759.5
350-B-2	14970.6	14044.3	8636.7
350-B-3	14698.0	13707.9	8778.9
350-C-1	15469.9	14546.5	8809.0
350-C-2	15706.1	14820.6	8961.9
350-C-3	15679.8	14799.7	9003.0
Average	14724.2	13681.9	8447.3
Std Dev	1094.0	1199.5	692.9
400-A-1	15973.1	14853.7	9370.9
400-A-2	15439.0	14408.3	9227.2
400-A-3	15922.1	15017.2	9308.6
400-B-1	16231.6	15692.7	9671.5
400-B-2	16640.1	16055.6	9917.5
400-B-3	16674.9	16125.0	9921.8
400-C-1	16613.1	16723.8	10285.2
400-C-2	17828.5	18192.6	11138.0
400-C-3	17522.8	18228.4	11232.8
Average	16538.4	16144.1	10008.2
Std Dev	764.0	1371.0	749.0
450-A-1	16407.3	17371.1	10653.6
450-A-2	15123.1	15174.8	9387.9
450-A-3	15977.8	16163.4	9982.2
450-B-1	13298.4	18111.1	12553.1
450-B-2	13224.5	17440.5	12779.7
450-B-3	12789.7	16544.9	12695.8
450-C-1	16039.1	19911.2	12317.8
450-C-2	16358.1	21265.3	13235.8
450-C-3	15651.2	19840.7	12477.3
Average	14985.5	17980.3	11787.0
Std Dev	1467.6	1996.6	1394.3

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

Table C.3 Digestion Results for Bench Pyrolysis Bio-oil

Sample ID	**As Concentration (ppm)**	**Cr Concentration (ppm)**	**Cu Concentration (ppm)**
350-A-1	1.2132	0.0271	0.0166
350-A-2	1.1970	0.0257	0.0181
350-A-3	1.2765	0.0269	0.0196
350-B-1	0.5327	0.0249	0.0141
350-B-2	0.4245	0.0232	0.0156
350-B-3	0.3454	0.0220	0.0173
350-C-1	0.6853	0.4580	0.0227
350-C-2	0.7477	0.5091	0.0200
350-C-3	0.6997	0.4238	0.0244
Average	0.7913	0.1712	0.0187
Std Dev	0.3535	0.2204	0.0033
400-A-1	1.9707	0.0182	0.0230
400-A-2	2.1573	0.0293	0.0240
400-A-3	1.8174	0.0201	0.0172
400-B-1	0.9450	0.0197	0.0230
400-B-2	1.3263	0.0349	0.0222
400-B-3	1.0592	0.0200	0.0211
400-C-1	1.1187	0.1459	0.0220
400-C-2	0.7788	0.1074	0.0174
400-C-3	1.0685	0.2060	0.0270
Average	1.3602	0.0668	0.0219
Std Dev	0.4953	0.0695	0.0031
450-A-1	3.5673	0.0229	0.0171
450-A-2	3.3437	0.0207	0.0182
450-A-3	3.2601	0.0213	0.0201
450-B-1	1.5442	0.3989	0.0264
450-B-2	1.5306	0.4140	0.0360
450-B-3	1.3139	0.3367	0.0212
450-C-1	2.0994	0.4482	0.0194
450-C-2	1.6289	0.3580	0.0286
450-C-3	1.3814	0.3038	0.0154
Average	2.1855	0.2583	0.0225
Std Dev	0.9333	0.1824	0.0033

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

Table C.4 TCLP Results for Bench Pyrolysis Char

Sample ID	As Concentration (ppm)	Cr Concentration (ppm)	Cu Concentration (ppm)
350-A-1	19.8	0.25	18.1
350-A-2	19.4	0.24	19.4
350-A-3	17.9	0.24	18.5
350-B-1	29.6	0.22	13.0
350-B-2	20.2	0.21	14.9
350-B-3	20.2	0.21	12.0
350-C-1	27.8	0.15	12.4
350-C-2	19.6	0.20	13.5
350-C-3	19.0	0.22	13.2
Average	21.5	0.22	15.0
Std Dev	4.2	0.03	11.5
400-A-1	12.3	0.17	11.7
400-A-2	12.3	0.17	10.8
400-A-3	11.9	0.17	13.3
400-B-1	14.4	0.13	13.6
400-B-2	13.7	0.13	12.5
400-B-3	6.2	0.05	11.3
400-C-1	24.9	0.07	10.8
400-C-2	27.0	0.09	9.9
400-C-3	27.2	0.08	9.7
Average	16.7	0.12	11.5
Std Dev	7.7	0.05	5.53
450-A-1	8.9	0.15	15.3
450-A-2	8.4	0.12	14.5
450-A-3	9.7	0.10	13.7
450-B-1	13.4	0.06	9.2
450-B-2	11.5	0.05	8.2
450-B-3	12.4	0.06	8.4
450-C-1	20.3	0.03	13.1
450-C-2	20.4	0.02	9.7
450-C-3	19.7	0.03	8.7
Average	13.9	0.07	11.2
Std Dev	5.0	0.05	11.6

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

Table C.5 SPLP Results for Bench Pyrolysis Char

Sample ID	As Concentration (ppm)	Cr Concentration (ppm)	Cu Concentration (ppm)
350-A-1	0.55	0.00	5.87
350-A-2	1.22	0.00	10.40
350-A-3	1.16	0.00	9.41
350-B-1	1.81	0.00	4.35
350-B-2	4.34	0.00	9.37
350-B-3	2.48	0.00	5.67
350-C-1	11.34	0.00	5.34
350-C-2	10.79	0.00	4.82
350-C-3	11.42	0.00	5.18
Average	5.01	0.00	6.71
Std Dev	4.75	0.00	2.32
400-A-1	0.85	0.00	0.32
400-A-2	1.05	0.00	0.93
400-A-3	0.98	0.00	0.49
400-B-1	4.96	0.00	9.07
400-B-2	5.02	0.00	7.63
400-B-3	6.46	0.00	10.05
400-C-1	4.35	0.00	5.33
400-C-2	4.56	0.00	5.95
400-C-3	3.73	0.00	4.13
Average	3.55	0.00	4.88
Std Dev	2.07	0.00	3.70
450-A-1	0.34	0.00	5.39
450-A-2	0.26	0.00	3.25
450-A-3	0.50	0.00	6.41
450-B-1	1.09	0.00	0.41
450-B-2	1.09	0.00	0.79
450-B-3	0.90	0.00	0.73
450-C-1	7.20	0.00	0.44
450-C-2	7.91	0.00	0.19
450-C-3	7.70	0.00	0.22
Average	3.00	0.00	1.98
Std Dev	3.47	0.00	2.42

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

Table C.6 DI Water Leach Results for Bench Pyrolysis Char

Sample ID	**As Concentration (ppm)**	**Cr Concentration (ppm)**	**Cu Concentration (ppm)**
350-A-1	1.02	0.14	7.55
350-A-2	1.46	0.14	6.17
350-A-3	1.42	0.14	8.48
350-B-1	3.44	0.15	6.28
350-B-2	7.29	0.19	9.95
350-B-3	3.61	0.20	5.90
350-C-1	11.31	0.17	3.76
350-C-2	14.72	0.18	7.29
350-C-3	11.45	0.17	3.81
Average	6.19	0.16	6.58
Std Dev	5.17	0.020	2.02
400-A-1	1.08	0.14	0.67
400-A-2	1.20	0.13	0.21
400-A-3	1.27	0.14	0.19
400-B-1	6.11	0.14	6.33
400-B-2	6.29	0.14	6.34
400-B-3	7.32	0.14	6.91
400-C-1	4.68	0.13	4.18
400-C-2	3.94	0.13	3.45
400-C-3	3.88	0.13	3.73
Average	3.97	0.14	3.56
Std Dev	2.37	0.002	2.69
450-A-1	0.62	0.14	2.60
450-A-2	0.79	0.14	2.94
450-A-3	0.69	0.14	3.58
450-B-1	1.26	0.14	0.56
450-B-2	1.22	0.14	0.57
450-B-3	1.44	0.14	0.41
450-C-1	7.74	0.14	0.21
450-C-2	7.53	0.14	0.19
450-C-3	7.87	0.13	0.18
Average	3.24	0.14	1.25
Std Dev	3.37	0.001	1.37

Note: “A”, “B”, and “C” are the identifiers for each of the three containers used to store the CCA-treated wood sawdust used throughout this study

APPENDIX D

EXPERIMENTAL RESULTS FOR PHASE III: BATCH PYROLYSIS OF CCA-TREATED WOOD WASTE

Table D.1 Char Production Total from the Batch Pyrolysis of CCA-treated Wood Waste

Pyrolysis Set-point Temperature	**350°C**	**400°C**	**450°C**
Mass of Char Collected	11.99 g	12.54 g	12.96 g
	14.77 g	10.12 g	12.26 g
	12.31 g	9.17 g	10.25 g
	12.24 g	9.35 g	15.28 g
	16.99 g	5.79 g	22.05 g
	8.95 g	15.08 g	13.54 g
	12.25 g	15.14 g	10.15 g
	14.1 g	15.62 g	6.94 g
	14.15 g	15.03 g	10.22 g
	10.88 g	14.79 g	14.49 g
	19.13 g	11.87 g	6.3 g
	14.59 g	10.26 g	7.08 g
	15.36 g	13.2 g	2.94 g
	8.76 g	11.16 g	7.44 g
	12.23 g	11.88 g	10.42 g
	12.85 g	10.94 g	10.07 g
	14.42 g	11.9 g	10.64 g
	13.73 g	15.79 g	13.61 g
	13.55 g	12.05 g	14.77 g
	10.13 g	12.51 g	16.44 g
	10.12 g	13.47 g	9.4 g
	7.68 g	16.94 g	16.59 g
	13.26 g	12.79 g	20.51 g
	13.62 g	37.76 g	20.04 g
	18.53 g	7.42 g	12.16 g
	16.62 g	7.71 g	34.1 g
	14.21 g	13.59 g	11.53 g
	14.92 g	10.32 g	17.24 g
	15.35 g	12.38 g	13.33 g
		9.83 g	21.14 g
		7.49 g	

Table D.2 Digestion Results for Batch Pyrolysis Char

Sample ID	**As Concentration (ppm)**	**Cr Concentration (ppm)**	**Cu Concentration (ppm)**
350-A	12609.3	10528.1	9114.9
350-B	12365.5	10320.6	8929.9
350-C	12733.5	10679.5	9299.5
Average	12569.4	10509.4	9114.8
Std Dev	187.2	180.2	184.8
400-A	12398.2	8962.3	8127.2
400-B	12929.7	9331.8	8436.4
400-C	12909.9	9339.0	8431.0
Average	12657.7	9860.2	8723.2
Std Dev	301.3	215.5	177.0
450-A	11374.2	7915.2	6981.3
450-B	11741.6	8199.2	7110.1
450-C	11660.8	8189.0	7082.4
Average	11592.2	8101.1	7057.9
Std Dev	193.1	161.1	67.8

Note: “A”, “B”, and “C” are the identifiers for each replicate performed in this study

Table D.3 Digestion Results for Batch Pyrolysis Bio-oil

Sample ID	**As Concentration (ppm)**	**Cr Concentration (ppm)**	**Cu Concentration (ppm)**
350-A	1.97	0.23	0.08
350-B	2.08	0.23	0.08
350-C	2.09	0.23	0.08
Average	2.04	0.23	0.08
Std Dev	0.06	0	0
400-A	2.23	0.23	0.10
400-B	2.16	0.23	0.10
400-C	2.21	0.23	0.08
Average	2.12	0.23	0.09
Std Dev	0.04	0	0.01
450-A	2.82	0.27	0.43
450-B	2.77	0.27	0.42
450-C	2.82	0.27	0.44
Average	2.80	0.27	0.43
Std Dev	0.03	0	0.01

Note: “A”, “B”, and “C” are the identifiers for each replicate performed in this study

Table D.4 TCLP Results for Batch Pyrolysis Char

Sample ID	**As Concentration (ppm)**	**Cr Concentration (ppm)**	**Cu Concentration (ppm)**
350-A	24.43	0.44	23.19
350-B	26.42	0.49	23.40
350-C	26.32	0.49	23.32
Average	25.72	0.47	23.30
Std Dev	1.12	0.02	0.11
400-A	19.09	0.25	15.84
400-B	20.77	0.31	15.73
400-C	19.42	0.28	15.82
Average	19.76	0.09	15.80
Std Dev	4.59	0.03	1.79
450-A	16.72	0.07	11.32
450-B	13.53	0.08	13.62
450-C	21.98	0.07	8.69
Average	17.41	0.07	11.21
Std Dev	4.27	0	2.47

Note: “A”, “B”, and “C” are the identifiers for each replicate performed in this study

Table D.5 SPLP Results for Batch Pyrolysis Char

Sample ID	**As Concentration (ppm)**	**Cr Concentration (ppm)**	**Cu Concentration (ppm)**
350-A	23.83	0.44	19.12
350-B	28.41	0.61	26.22
350-C	24.57	0.53	21.68
Average	25.60	0.53	22.34
Std Dev	2.46	0.08	3.60
400-A	18.77	0.34	15.33
400-B	18.80	0.32	15.30
400-C	18.74	0.33	15.29
Average	18.77	0.33	15.31
Std Dev	0.92	0.01	0.01
450-A	10.96	0.09	5.20
450-B	11.03	0.10	5.05
450-C	9.98	0.08	5.26
Average	10.66	0.09	5.17
Std Dev	0.59	0.01	0.11

Note: “A”, “B”, and “C” are the identifiers for each replicate performed in this study

Table D.6 DI Water Leach Results for Batch Pyrolysis Char

Sample ID	**As Concentration (ppm)**	**Cr Concentration (ppm)**	**Cu Concentration (ppm)**
350-A	24.34	0.25	24.32
350-B	27.36	0.23	21.98
350-C	4.64	0.22	5.09
Average	18.78	0.23	17.13
Std Dev	12.34	0.26	10.49
400-A	14.96	0.08	13.77
400-B	14.92	0.10	13.38
400-C	14.93	0.08	12.98
Average	14.94	0.09	13.38
Std Dev	0.02	0.01	2.51
450-A	8.45	0	6.10
450-B	9.97	0	5.12
450-C	11.25	0	5.36
Average	9.89	0	5.53
Std Dev	1.40	0	0.51

Note: “A”, “B”, and “C” are the identifiers for each replicate performed in this study

APPENDIX E

EXPERIMENTAL RESULTS FOR PHASE IV: ELECTROKINETIC EXPERIMENTS ON PYROLYSIS CHAR AND CCA-TREATED WOOD WASTE

Table E.1 Daily Power Measurements: Cell A

Cell A			
Day	**Cell Current (mA)**	**Cell Voltage (V)**	**Port 1 Voltage (V)**
1	89	134.6	36.2
2	138	122.3	25.8
3	138	102.2	21.9
4	138	89.7	17.9
5	138	97.3	15.9
6	138	99.7	14.3
7	78	134.5	8.3
8	64	134.5	6.9
9	138	78.9	12.2
10	138	74.4	11.6
11	138	69	11.3
12	138	58.8	10
13	138	54.3	9.6
14	138	45.8	9.5
15	138	39.2	8.9

Note: Cell A is one of two EK cells containing pyrolysis char generated at 350°C

Table E.2 Daily Power Measurements: Cell B

Cell B			
Date	Cell Current (mA)	Cell Voltage (V)	Port 1 Voltage (V)
1	67	134.8	54.4
2	97	134.7	32.9
3	111	134.7	29
4	121	134.7	26.3
5	128	134.7	24.6
6	135	134.7	22.7
7	138	129.8	21
8	138	127.8	17
9	138	119.6	15.2
10	128	134.7	14.3
11	138	132.9	15.1
12	138	110.4	13.8
13	138	106	11.7
14	138	92.7	10.8
15	138	90.5	10.1

Note: Cell B is one of two EK cells containing pyrolysis char generated at 350°C

Table E.3 Daily Power Measurements: Cell C

Cell C			
Date	Cell Current (mA)	Cell Voltage (V)	Port 1 Voltage (V)
1	128	42.7	35
2	128	24.2	17.6
3	128	20.7	13.7
4	128	17.7	10.6
5	128	16.5	8.7
6	128	15.9	7.8
7	128	16.4	7.6
8	128	16.8	7.2
9	128	17.7	6.8
10	128	21.6	6.4
11	128	26.2	6.2
12	128	31.2	5.8
13	128	31.4	5.6
14	128	29.8	5.4
15	128	29.9	5.2

Note: Cell C is one of two EK cells containing pyrolysis char generated at 400°C

Table E.4 Daily Power Measurements: Cell D

Cell D			
Date	Cell Current (mA)	Cell Voltage (V)	Port 1 Voltage (V)
1	138	49.5	39.3
2	138	29.4	20.3
3	138	31.5	19.5
4	138	30.4	19.3
5	138	32.1	19
6	138	32.8	16.3
7	138	38.6	15.7
8	138	57.8	21.3
9	138	53.7	19.5
10	138	51.2	15.4
11	138	50.4	14.6
12	138	53.2	17.4
13	138	48.8	15.4
14	138	45.9	11.2
15	138	49.5	14.8

Note: Cell D is one of two EK cells containing pyrolysis char generated at 400°C

Table E.5 Daily Power Measurements: Cell E

Cell E			
Date	Cell Current (mA)	Cell Voltage (V)	Port 1 Voltage (V)
1	75	135.8	46.5
2	114	135.7	34.8
3	137	93.1	23.9
4	137	70.2	18.4
5	137	64.5	15.5
6	137	56.8	13.5
7	137	54.6	13.3
8	137	43.4	11.4
9	137	43	10.4
10	137	55.8	11.1
11	137	42.9	11.4
12	137	31.8	9
13	137	38.4	10.1
14	137	32.2	8.6
15	137	28.9	8.4

Note: Cell E is one of two EK cells containing pyrolysis char generated at 450°C

Table E.6 Daily Power Measurements: Cell F

Cell F			
Date	Cell Current (mA)	Cell Voltage (V)	Port 1 Voltage (V)
1	63	135.4	44.6
2	139	119.2	28.9
3	139	91.1	21.5
4	139	73.1	17.7
5	139	68	19.8
6	139	66.8	19.1
7	139	58.3	18.6
8	139	54.5	16.3
9	140	47.7	15.7
10	139	42.8	13.6
11	139	43.6	14.8
12	139	35.8	12.1
13	139	54.2	13
14	139	38.4	14
15	139	31.2	11.6

Note: Cell F is one of two EK cells containing pyrolysis char generated at 450°C

Table E.7 Daily Power Measurements: Cell G

Cell G			
Date	Cell Current (mA)	Cell Voltage (V)	Port 1 Voltage (V)
1	55	134.8	40.4
2	124	114.5	31.9
3	124	80.6	21.9
4	124	71.9	17.3
5	124	68.1	15
6	124	73.7	16.7
7	124	72.1	14.5
8	124	68.6	12.7
9	124	61	11.1
10	126	60.3	11.6
11	126	58.3	10.6
12	126	53.9	9.3
13	126	51	8.6
14	126	47.6	8.1
15	126	44.5	7.6

Note: Cell G is one of two EK cells containing CCA-treated wood waste

Table E.8 Daily Power Measurements: Cell H

Cell H			
Date	Cell Current (mA)	Cell Voltage (V)	Port 1 Voltage (V)
1	136	82	39.5
2	136	134	24.6
3	110.4	137	23.6
4	129.9	137	26.6
5	136	110	27.4
6	136	108	29.6
7	136	108	25.4
8	136	78	19.5
9	136	24	14.8
10	136	126	28
11	136	102	20.3
12	136	37	20.3
13	136	33	19.9
14	136	32	22.4
15	136	30	17.3

Note: Cell G is one of two EK cells containing CCA-treated wood waste

Table E.9 Daily pH Measurements: Cell A

Day	Sample ID	pH	Day	Sample ID	pH	Day	Sample ID	pH
0	Anode	4.19	0	Cathode	6.18	0	Port 1	4.11
1	Anode	2.58	1	Cathode	6.4	1	Port 1	2.19
2	Anode	2.4	2	Cathode	6.1	3	Port 1	1.88
3	Anode	2.03	3	Cathode	3.12	5	Port 1	2
4	Anode	1.98	4	Cathode	4.02	7	Port 1	1.96
5	Anode	1.99	5	Cathode	3.65	9	Port 1	1.95
6	Anode	1.97	6	Cathode	3.52	11	Port 1	1.92
7	Anode	1.88	7	Cathode	3.58	13	Port 1	1.95
8	Anode	1.86	8	Cathode	3.23	15	Port 1	1.93
9	Anode	1.86	9	Cathode	3.09			
10	Anode	1.83	10	Cathode	3.52			
11	Anode	1.81	11	Cathode	3.67			
12	Anode	1.79	12	Cathode	3.22			
13	Anode	1.78	13	Cathode	3.24			
14	Anode	1.77	14	Cathode	3.43			
15	Anode	1.77	15	Cathode	3.01			

Note: Cell A is one of two EK cells containing pyrolysis char generated at 350°C

Table E.10 Daily pH Measurements: Cell B

Day	Sample ID	pH	Day	Sample ID	pH	Day	Sample ID	pH
0	Anode	4.72	0	Cathode	5.27	0	Port 1	4.2
1	Anode	2.71	1	Cathode	5.1	1	Port 1	2.5
2	Anode	2.36	2	Cathode	3.94	3	Port 1	2.18
3	Anode	2.18	3	Cathode	4.12	5	Port 1	2.24
4	Anode	2.07	4	Cathode	3.53	7	Port 1	2.11
5	Anode	2.09	5	Cathode	3.48	9	Port 1	2.09
6	Anode	2.06	6	Cathode	3.06	11	Port 1	2.19
7	Anode	1.95	7	Cathode	3.02	13	Port 1	1.99
8	Anode	1.92	8	Cathode	3.82	15	Port 1	1.86
9	Anode	1.88	9	Cathode	3.59			
10	Anode	1.86	10	Cathode	3.34			
11	Anode	1.84	11	Cathode	3.04			
12	Anode	1.82	12	Cathode	2.87			
13	Anode	1.8	13	Cathode	2.93			
14	Anode	1.76	14	Cathode	3.45			
15	Anode	1.73	15	Cathode	3.32			

Note: Cell B is one of two EK cells containing pyrolysis char generated at 350°C

Table E.11 Daily pH Measurements: Cell C

Day	**Sample ID**	**pH**	**Day**	**Sample ID**	**pH**	**Day**	**Sample ID**	**pH**
0	Anode	4.79	0	Cathode	4.38	0	Port 1	4.49
1	Anode	2.43	1	Cathode	1.57	1	Port 1	1.99
2	Anode	2.09	2	Cathode	1.55	3	Port 1	1.8
3	Anode	1.94	3	Cathode	1.6	5	Port 1	1.74
4	Anode	1.86	4	Cathode	1.63	7	Port 1	1.8
5	Anode	1.81	5	Cathode	1.68	9	Port 1	1.75
6	Anode	1.9	6	Cathode	1.85	11	Port 1	1.74
7	Anode	1.82	7	Cathode	1.86	13	Port 1	1.73
8	Anode	1.8	8	Cathode	1.91	15	Port 1	1.71
9	Anode	1.79	9	Cathode	1.99			
10	Anode	1.76	10	Cathode	2.18			
11	Anode	1.75	11	Cathode	2.5			
12	Anode	1.74	12	Cathode	3.65			
13	Anode	1.71	13	Cathode	4.3			
14	Anode	1.68	14	Cathode	3.75			
15	Anode	1.71	15	Cathode	3.55			

Note: Cell C is one of two EK cells containing pyrolysis char generated at 400°C

Table E.12 Daily pH Measurements: Cell D

Day	**Sample ID**	**pH**	**Day**	**Sample ID**	**pH**	**Day**	**Sample ID**	**pH**
0	Anode	5.06	0	Cathode	6.34	0	Port 1	4.38
1	Anode	2.48	1	Cathode	1.74	1	Port 1	1.89
2	Anode	2.14	2	Cathode	1.78	3	Port 1	1.77
3	Anode	2	3	Cathode	1.79	5	Port 1	1.77
4	Anode	1.91	4	Cathode	1.89	7	Port 1	1.85
5	Anode	1.88	5	Cathode	2.01	9	Port 1	1.83
6	Anode	1.89	6	Cathode	2.18	11	Port 1	1.81
7	Anode	1.87	7	Cathode	2.42	13	Port 1	1.78
8	Anode	1.83	8	Cathode	3.14	15	Port 1	1.8
9	Anode	1.82	9	Cathode	3.24			
10	Anode	1.8	10	Cathode	3.51			
11	Anode	1.8	11	Cathode	3.92			
12	Anode	1.79	12	Cathode	3.31			
13	Anode	1.77	13	Cathode	3.51			
14	Anode	1.7	14	Cathode	3.13			
15	Anode	1.72	15	Cathode	3.83			

Note: Cell D is one of two EK cells containing pyrolysis char generated at 400°C

Table E.13 Daily pH Measurements: Cell E

Day	Sample ID	pH	Day	Sample ID	pH	Day	Sample ID	pH
0	Anode	5.91	0	Cathode	5.94	0	Port 1	4.66
1	Anode	2.82	1	Cathode	6.31	1	Port 1	2.61
2	Anode	2.37	2	Cathode	5.64	3	Port 1	2.16
3	Anode	2.18	3	Cathode	4.08	5	Port 1	1.93
4	Anode	1.98	4	Cathode	3.41	7	Port 1	2.05
5	Anode	1.85	5	Cathode	3.24	9	Port 1	1.99
6	Anode	1.7	6	Cathode	3.48	11	Port 1	2.02
7	Anode	1.92	7	Cathode	3.73	13	Port 1	2.15
8	Anode	1.9	8	Cathode	3.86	15	Port 1	2.05
9	Anode	1.89	9	Cathode	3.53			
10	Anode	1.87	10	Cathode	3.54			
11	Anode	1.87	11	Cathode	3.88			
12	Anode	1.86	12	Cathode	4.52			
13	Anode	1.83	13	Cathode	4.33			
14	Anode	1.82	14	Cathode	3.77			
15	Anode	1.84	15	Cathode	3.82			

Note: Cell E is one of two EK cells containing pyrolysis char generated at 450°C

Table E.14 Daily pH Measurements: Cell F

Day	Sample ID	pH	Day	Sample ID	pH	Day	Sample ID	pH
0	Anode	5.47	0	Cathode	5.51	0	Port 1	4.72
1	Anode	2.75	1	Cathode	6.63	1	Port 1	2.72
2	Anode	2.36	2	Cathode	6.83	3	Port 1	1.99
3	Anode	2.17	3	Cathode	5.87	5	Port 1	1.97
4	Anode	2.09	4	Cathode	4.39	7	Port 1	1.92
5	Anode	2.01	5	Cathode	4.31	9	Port 1	1.9
6	Anode	1.97	6	Cathode	5.08	11	Port 1	1.84
7	Anode	1.89	7	Cathode	5.23	13	Port 1	1.8
8	Anode	1.84	8	Cathode	4.7	15	Port 1	1.82
9	Anode	1.83	9	Cathode	4.72			
10	Anode	1.82	10	Cathode	3.98			
11	Anode	1.8	11	Cathode	4.15			
12	Anode	1.8	12	Cathode	4.95			
13	Anode	1.75	13	Cathode	4.33			
14	Anode	1.71	14	Cathode	3.92			
15	Anode	1.74	15	Cathode	3.45			

Note: Cell F is one of two EK cells containing pyrolysis char generated at 450°C

Table E.15 Daily pH Measurements: Cell G

Day	**Sample ID**	**pH**	**Day**	**Sample ID**	**pH**	**Day**	**Sample ID**	**pH**
0	Anode	4.6	0	Cathode	6.1	0	Port 1	5.12
1	Anode	3.81	1	Cathode	6.89	1	Port 1	3.53
2	Anode	2.6	2	Cathode	4.91	3	Port 1	2.02
3	Anode	2.28	3	Cathode	4.55	5	Port 1	2
4	Anode	2.15	4	Cathode	4.28	7	Port 1	2
5	Anode	2.09	5	Cathode	3.37	9	Port 1	1.93
6	Anode	2.06	6	Cathode	3.38	11	Port 1	1.9
7	Anode	1.99	7	Cathode	4.14	13	Port 1	1.85
8	Anode	1.97	8	Cathode	3.36	15	Port 1	1.83
9	Anode	1.91	9	Cathode	3.99			
10	Anode	1.89	10	Cathode	3.44			
11	Anode	1.89	11	Cathode	4.29			
12	Anode	1.85	12	Cathode	4			
13	Anode	1.84	13	Cathode	4.04			
14	Anode	1.82	14	Cathode	4.76			
15	Anode	1.82	15	Cathode	4.02			

Note: Cell G is one of two EK cells containing CCA-treated wood waste

Table E.16 Daily pH Measurements: Cell H

Day	**Sample ID**	**pH**	**Day**	**Sample ID**	**pH**	**Day**	**Sample ID**	**pH**
0	Anode	6.08	0	Cathode	5.91	0	Port 1	4.56
1	Anode	2.77	1	Cathode	3.06	1	Port 1	3.13
2	Anode	2.35	2	Cathode	6.2	3	Port 1	2.08
3	Anode	2.13	3	Cathode	4.15	5	Port 1	2.07
4	Anode	2.03	4	Cathode	3.41	7	Port 1	2.31
5	Anode	2.01	5	Cathode	3.25	9	Port 1	2.08
6	Anode	1.97	6	Cathode	3.95	11	Port 1	1.95
7	Anode	1.98	7	Cathode	3.77	13	Port 1	1.97
8	Anode	1.97	8	Cathode	3.78	15	Port 1	1.95
9	Anode	1.95	9	Cathode	3.84			
10	Anode	1.91	10	Cathode	3.45			
11	Anode	1.92	11	Cathode	3.86			
12	Anode	1.89	12	Cathode	3.91			
13	Anode	1.89	13	Cathode	3.74			
14	Anode	1.9	14	Cathode	3.53			
15	Anode	1.9	15	Cathode	3.35			

Note: Cell H is one of two EK cells containing CCA-treated wood waste

Table E.17 Liquid Volumes Collected from Cell Sections Post-EK Operation

	Anode Recirc. Tank	Anode Half-Cell	Cathode Recirc. Tank	Cathode Half-Cell
Cell A	1510 mL	2190 mL	1280 mL	2370 mL
Cell B	1490 mL	2180 mL	1260 mL	2370 mL
Cell C	1460 mL	2830 mL	1490 mL	2040 mL
Cell D	1520 mL	2230 mL	1300 mL	2400 mL
Cell E	1250 mL	1870 mL	1090 mL	2030 mL
Cell F	1520 mL	2210 mL	1290 mL	2400 mL
Cell G	1460 mL	2840 mL	1480 mL	2850 mL
Cell H	1610 mL	2330 mL	1370 mL	2530 mL

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste

Table E.18 Total Volume of Overflow Fluid Recorded During Operation

Overflow		
	Anode	Cathode
Cell A	1,540 mL	0 mL
Cell B	110 mL	0 mL
Cell C	500 mL	0 mL
Cell D	225 mL	190 mL
Cell E	8,670 mL	0 mL
Cell F	0 mL	40 mL
Cell G	3,010 mL	0 mL
Cell H	870 mL	0 mL

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste

Table E.19 Total Volume of Tap Water Added to EK Cells During Operation

Water Added		
	Anode	Cathode
Cell A	0	1,500
Cell B	0	580
Cell C	0	1,120
Cell D	0	360
Cell E	0	7,537
Cell F	100	360
Cell G	1,300	3,310
Cell H	180	1,500

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste

Table E.20 Post-EK Moisture Content of Pyrolysis Char and CCA-treated Wood

Sample ID	**Moisture Content (%)**	**Sample ID**	**Moisture Content (%)**
A1A	72.73	E1A	74.66
A1B	72.79	E1B	74.35
A1C	72.52	E1C	74.91
A2A	71.63	E2A	74.74
A2B	72.76	E2B	75.08
A2C	70.19	E2C	74.67
A3A	67.68	E3A	72.51
A3B	67.73	E3B	73.71
A3C	67.94	E3C	73.31
A4A	70.32	E4A	73.66
A4B	70.81	E4B	73.75
A4C	69.68	E4C	74.04
B1A	75.93	F1A	75.83
B1B	75.15	F1B	75.17
B1C	75.00	F1C	75.74
B2A	72.81	F2A	74.31
B2B	73.00	F2B	74.39
B2C	72.65	F2C	74.43
B3A	71.56	F3A	71.51
B3B	72.21	F3B	71.93
B3C	72.07	F3C	70.27
B4A	68.62	F4A	73.30
B4B	68.74	F4B	74.43
B4C	68.56	F4C	74.18
C1A	72.36	G1A	76.99
C1B	72.22	G1B	77.02
C1C	72.40	G1C	77.63
C2A	71.12	G2A	78.61
C2B	71.45	G2B	77.60
C2C	70.98	G2C	76.94
C3A	75.30	G3A	70.39
C3B	75.98	G3B	70.48
C3C	75.78	G3C	70.72
C4A	75.65	G4A	72.89
C4B	75.48	G4B	72.40
C4C	76.18	G4C	72.65
D1A	74.46	H1A	76.76
D1B	74.93	H1B	78.17
D1C	74.44	H1C	76.08
D2A	75.11	H2A	78.80
D2B	75.31	H2B	78.54
D2C	74.93	H2C	78.14
D3A	72.52	H3A	70.17
D3B	73.26	H3B	70.14
D3C	72.39	H3C	69.89
D4A	73.01	H4A	74.84
D4B	72.13	H4B	74.28
D4C	70.63	H4C	74.33

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste

Table E.21 CCA Metal Content in Cell A Post-EK

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
A1A	2435.5	3365.5	1304.9
A1B	2820.8	3915.3	1500.8
A1C	2470.2	3383.5	1297.6
A2A	2922.5	3939.2	1560.3
A2B	2989.8	4005.4	1581.0
A2C	3021.6	4037.9	1614.1
A3A	3591.2	4663.3	1850.2
A3B	3477.6	4571.8	1794.0
A3C	3580.0	4723.2	1858.0
A4A	3192.7	4260.7	1571.3
A4B	3196.3	4168.1	1535.9
A4C	3139.6	4097.7	1506.0
Average	3069.8	4094.3	1581.2
Std Dev	380.0	435.3	182.6

Note: Cell A is one of two EK cells containing pyrolysis char generated at 350°C

Table E.22 CCA Metal Content in Cell B Post-EK

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
B1A	2747.5	3537.7	1495.7
B1B	2675.4	3402.7	1506.0
B1C	2561.3	3258.8	1391.6
B2A	2973.6	3769.6	1626.9
B2B	2963.7	3802.9	1892.2
B2C	3003.0	3854.5	1649.5
B3A	3049.4	3937.3	1573.9
B3B	3108.2	3998.9	1607.7
B3C	3043.8	3957.9	1587.4
B4A	3233.2	4190.6	1675.5
B4B	3376.8	4359.1	1729.9
B4C	3262.6	4308.5	1717.4
Average	2999.9	3864.9	1621.1
Std Dev	242.2	341.1	129.2

Note: Cell B is one of two EK cells containing pyrolysis char generated at 350°C

Table E.23 CCA Metal Content in Cell C Post-EK

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
C1A	3560.4	4342.9	1899.3
C1B	3577.7	4373.3	1891.6
C1C	3642.2	4365.3	1903.7
C2A	3551.4	4342.1	1890.7
C2B	3714.6	4428.1	1909.4
C2C	3679.7	4490.8	1929.4
C3A	3059.7	3734.1	1619.2
C3B	2892.9	3493.5	1520.2
C3C	3361.8	4022.2	1751.5
C4A	2957.2	3583.0	1540.4
C4B	3031.2	3710.4	1603.4
C4C	3045.3	3705.1	1587.5
Average	3339.5	4049.2	1753.9
Std Dev	316.9	378.4	166.5

Note: Cell C is one of two EK cells containing pyrolysis char generated at 400°C

Table E.24 CCA Metal Content in Cell D Post-EK

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
D1A	3059.1	3664.3	1740.0
D1B	3170.7	3765.8	1795.1
D1C	3224.2	3809.9	1788.7
D2A	3230.5	3885.7	1774.1
D2B	3179.8	3820.0	1739.6
D2C	3090.6	3707.3	1690.1
D3A	3584.3	4260.1	2066.5
D3B	3527.2	4233.5	2040.0
D3C	3507.8	4150.1	1998.3
D4A	3508.5	4200.8	1984.1
D4B	3393.6	4082.8	1923.2
D4C	3477.7	4157.4	1951.9
Average	3329.5	3978.2	1874.3
Std Dev	188.9	222.7	132.8

Note: Cell D is one of two EK cells containing pyrolysis char generated at 400°C

Table E.25 CCA Metal Content in Cell E Post-EK

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
E1A	3400.2	4554.5	2167.8
E1B	3416.6	4539.5	2186.9
E1C	3390.0	4417.3	2097.2
E2A	3398.6	4542.8	2146.4
E2B	3683.9	4972.2	2331.1
E2C	3616.5	4861.7	2284.7
E3A	3999.3	5332.1	2442.7
E3B	3888.5	5249.2	2419.3
E3C	3927.0	5240.0	2423.0
E4A	3920.5	5255.7	2393.2
E4B	4039.1	5272.5	2388.4
E4C	3862.3	5142.3	2358.0
Average	3711.9	4948.3	2303.2
Std Dev	257.5	348.6	122.7

Note: Cell E is one of two EK cells containing pyrolysis char generated at 450°C

Table E.26 CCA Metal Content in Cell F Post-EK

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
F1A	3592.6	4679.5	2337.4
F1B	3588.5	4677.4	2334.1
F1C	3598.3	4695.0	2320.9
F2A	3648.0	4787.2	2397.4
F2B	3671.5	4810.0	2413.6
F2C	3644.9	4725.6	2380.4
F3A	4059.1	5329.5	2615.7
F3B	3886.7	5097.8	2508.3
F3C	3794.4	4947.2	2446.6
F4A	3484.2	4673.2	2102.3
F4B	3652.2	4861.8	2178.9
F4C	3472.8	4698.2	2143.2
Average	3674.4	4831.9	2348.2
Std Dev	166.8	203.4	149.8

Note: Cell F is one of two EK cells containing pyrolysis char generated at 450°C

Table E.27 CCA Metal Content in Cell G Post-EK

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
G1A	791.7	1179.8	62.6
G1B	797.9	1189.3	62.4
G1C	808.6	1188.0	62.7
G2A	732.6	1066.6	57.8
G2B	738.3	1086.1	59.3
G2C	758.2	1116.7	57.4
G3A	897.4	1356.4	59.6
G3B	907.1	1370.4	59.5
G3C	901.7	1366.7	61.4
G4A	780.3	1234.5	55.0
G4B	796.3	1275.0	53.1
G4C	790.3	1245.8	53.4
Average	808.4	1223.0	58.7
Std Dev	61.2	105.4	3.4

Note: Cell G is one of two EK cells containing CCA-treated wood waste

Table E.28 CCA Metal Content in Cell H Post-EK

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
H1A	804.0	1189.0	104.3
H1B	800.5	1161.1	101.9
H1C	810.7	1221.9	106.7
H2A	728.0	1000.7	96.8
H2B	729.4	1001.8	97.6
H2C	722.8	1022.9	98.4
H3A	962.4	1394.3	83.5
H3B	984.6	1395.6	85.4
H3C	983.2	1398.8	85.0
H4A	749.2	1162.0	61.6
H4B	741.7	1166.9	61.7
H4C	755.2	1203.3	62.8
Average	814.3	1193.2	87.1
Std Dev	102.6	144.6	16.9

Note: Cell H is one of two EK cells containing CCA-treated wood waste

Table E.29 CCA Metal Content in EK Cell Pressure Plates

	EK Cell	Arsenic Concentration (ppm)	Chromium Concentration (ppm)	Copper Concentration (ppm)
Anode	Cell A	1.90	0.43	2.97
	Cell B	2.40	0.38	4.29
	Average	1.15	0.40	3.63
	Std Dev	0.35	0.04	0.93
	Cell C	1.92	0.44	2.57
	Cell D	3.26	0.59	3.69
	Average	2.59	0.52	3.13
	Std Dev	0.95	0.11	0.79
	Cell E	3.31	0.73	3.11
	Cell F	3.88	0.82	3.70
	Average	3.59	0.78	3.41
	Std Dev	0.40	0.06	0.41
	Cell G	3.12	2.59	2.16
	Cell H	1.36	0.84	1.36
	Average	2.24	1.71	1.76
	Std Dev	1.24	1.23	0.56
Cathode	Cell A	2.13	0.35	3.77
	Cell B	3.55	0.46	5.70
	Average	2.84	0.41	4.73
	Std Dev	1.00	0.08	1.37
	Cell C	3.47	0.68	3.82
	Cell D	1.34	0.38	1.53
	Average	2.41	0.53	2.67
	Std Dev	1.51	0.21	1.63
	Cell E	6.51	1.46	5.72
	Cell F	7.45	1.54	6.03
	Average	6.98	1.50	5.88
	Std Dev	0.67	0.06	0.22
	Cell G	13.14	10.81	3.49
	Cell H	1.87	1.13	1.57
	Average	7.51	5.97	2.53
	Std Dev	7.97	6.84	1.36

Note: Cells A & B, C& D, and E & F are duplicate EK cells for pyrolysis char generated at 350°C, 400°C, and 450°C, respectively; Cells G & H are duplicate EK cells for CCA-treated wood waste

Table E.30 TCLP Results for Post-EK Pyrolysis Char: Cell A

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
A1A	15.0	1.9	10.1
A1B	13.8	1.7	9.5
A1C	14.6	1.8	9.7
A2A	14.2	1.5	10.4
A2B	16.0	1.7	11.8
A2C	17.0	1.8	12.2
A3A	18.9	2.2	10.2
A3B	18.7	2.2	10.7
A3C	20.8	2.4	11.5
A4A	19.2	2.4	8.8
A4B	19.9	2.5	8.9
A4C	19.4	2.4	8.5
Average	17.3	2.0	10.2
Std Dev	2.4	0.3	1.2

Note: Cell A is one of two EK cells containing pyrolysis char generated at 350°C

Table E.31 TCLP Results for Post-EK Pyrolysis Char: Cell B

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
B1A	10.4	0.8	7.6
B1B	12.3	0.9	9.0
B1C	11.6	0.9	8.5
B2A	12.7	1.0	8.2
B2B	12.5	1.0	8.2
B2C	15.5	1.2	10.1
B3A	18.5	2.3	8.6
B3B	19.2	2.3	9.2
B3C	15.9	1.9	7.9
B4A	23.1	2.7	10.7
B4B	22.4	2.6	10.4
B4C	21.7	2.5	9.6
Average	16.3	1.7	9.0
Std Dev	4.4	0.7	1.0

Note: Cell B is one of two EK cells containing pyrolysis char generated at 350°C

Table E.32 TCLP Results for Post-EK Pyrolysis Char: Cell C

Sample ID	Arsenic Concentration (ppm)	Chromium Concentration (ppm)	Copper Concentration (ppm)
C1A	7.4	0.3	8.1
C1B	7.1	0.3	7.9
C1C	7.4	0.3	8.3
C2A	10.5	0.4	13.2
C2B	9.7	0.4	12.3
C2C	10.3	0.4	12.9
C3A	11.9	0.4	14.6
C3B	13.2	0.4	16.3
C3C	13.6	0.4	16.2
C4A	11.2	0.3	15.7
C4B	12.0	0.4	16.5
C4C	10.6	0.3	14.9
Average	10.4	0.4	13.1
Std Dev	2.2	0.1	3.3

Note: Cell C is one of two EK cells containing pyrolysis char generated at 400°C

Table E.33 TCLP Results for Post-EK Pyrolysis Char: Cell D

Sample ID	Arsenic Concentration (ppm)	Chromium Concentration (ppm)	Copper Concentration (ppm)
D1A	9.5	0.2	9.6
D1B	8.5	0.2	9.0
D1C	10.2	0.2	11.5
D2A	11.5	0.4	11.3
D2B	11.2	0.4	10.9
D2C	10.7	0.4	10.5
D3A	7.2	0.2	9.8
D3B	6.1	0.1	8.3
D3C	7.3	0.2	9.8
D4A	8.4	0.2	9.0
D4B	8.8	0.2	9.9
D4C	8.4	0.2	8.7
Average	9.0	0.2	9.9
Std Dev	1.7	0.1	1.0

Note: Cell D is one of two EK cells containing pyrolysis char generated at 400°C

Table E.34 TCLP Results for Post-EK Pyrolysis Char: Cell E

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
E1A	1.6	0.1	12.9
E1B	1.4	0.1	11.6
E1C	1.1	0.0	9.1
E2A	2.9	0.0	11.6
E2B	2.9	0.0	11.5
E2C	2.6	0.0	10.4
E3A	2.6	0.0	9.2
E3B	2.7	0.1	10.0
E3C	2.2	0.0	8.0
E4A	2.6	0.1	10.0
E4B	2.9	0.1	11.4
E4C	2.9	0.1	11.8
Average	2.4	0.0	10.6
Std Dev	0.6	0.0	1.4

Note: Cell E is one of two EK cells containing pyrolysis char generated at 450°C

Table E.35 TCLP Results for Post-EK Pyrolysis Char: Cell F

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
F1A	0.5	0.0	9.2
F1B	0.6	0.0	9.3
F1C	0.5	0.0	9.6
F2A	2.9	0.1	13.3
F2B	3.1	0.1	11.4
F2C	3.1	0.1	13.7
F3A	1.0	0.1	13.6
F3B	0.7	0.0	8.7
F3C	0.6	0.0	7.6
F4A	3.7	0.1	6.3
F4B	4.0	0.1	7.3
F4C	3.7	0.1	6.8
Average	2.0	0.0	9.7
Std Dev	1.5	0.0	2.7

Note: Cell F is one of two EK cells containing pyrolysis char generated at 450°C

Table E.36 TCLP Results for Post-EK CCA-treated Wood Waste: Cell G

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
G1A	3.4	1.8	0.0
G1B	3.7	2.0	0.0
G1C	4.1	2.2	0.0
G2A	6.6	3.7	0.1
G2B	5.4	3.1	0.1
G2C	6.0	3.4	0.1
G3A	6.1	3.6	0.0
G3B	6.6	3.9	0.0
G3C	6.4	3.8	0.0
G4A	7.6	4.7	0.0
G4B	7.7	4.8	0.0
G4C	7.2	4.5	0.0
Average	5.9	1.8	0.0
Std Dev	1.5	2.0	0.0

Note: Cell G is one of two EK cells containing CCA-treated wood waste

Table E.37 TCLP Results for Post-EK CCA-treated Wood Waste: Cell H

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
H1A	3.0	1.2	0.1
H1B	3.1	1.3	0.1
H1C	3.4	1.4	0.1
H2A	5.1	2.8	0.2
H2B	4.9	2.7	0.1
H2C	5.0	2.8	0.2
H3A	4.4	2.5	0.0
H3B	4.3	2.4	0.0
H3C	4.5	2.5	0.0
H4A	5.5	3.1	0.0
H4B	5.4	3.1	0.0
H4C	4.6	2.7	0.0
Average	4.4	2.4	0.1
Std Dev	0.8	0.7	0.1

Note: Cell H is one of two EK cells containing CCA-treated wood waste

Table E.38 SPLP Results for Post-EK Pyrolysis Char: Cell A

Sample ID	Arsenic Concentration (ppm)	Chromium Concentration (ppm)	Copper Concentration (ppm)
A1A	16.3	2.7	13.0
A1B	15.8	2.7	12.6
A1C	16.4	2.8	13.0
A2A	15.2	2.1	13.0
A2B	15.1	2.1	13.0
A2C	15.4	2.2	13.1
A3A	21.9	3.4	15.9
A3B	23.4	3.6	16.8
A3C	25.1	3.9	18.0
A4A	21.5	3.6	12.8
A4B	21.6	3.6	12.9
A4C	22.1	3.7	13.1
Average	19.1	3.0	13.9
Std Dev	3.7	0.7	1.8

Note: Cell A is one of two EK cells containing pyrolysis char generated at 350°C

Table E.39 SPLP Results for Post-EK Pyrolysis Char: Cell B

Sample ID	Arsenic Concentration (ppm)	Chromium Concentration (ppm)	Copper Concentration (ppm)
B1A	12.7	1.0	10.5
B1B	12.6	1.0	10.3
B1C	12.1	1.0	10.0
B2A	14.8	1.4	10.4
B2B	14.2	1.4	10.0
B2C	15.3	1.5	10.6
B3A	17.7	3.0	10.5
B3B	18.3	3.1	10.7
B3C	17.7	3.0	10.3
B4A	21.8	3.6	13.6
B4B	22.6	3.8	14.2
B4C	20.1	3.3	12.5
Average	16.7	2.3	11.1
Std Dev	3.6	1.1	1.5

Note: Cell B is one of two EK cells containing pyrolysis char generated at 350°C

Table E.40 SPLP Results for Post-EK Pyrolysis Char: Cell C

Sample ID	Arsenic Concentration (ppm)	Chromium Concentration (ppm)	Copper Concentration (ppm)
C1A	6.4	0.4	7.7
C1B	6.7	0.4	8.0
C1C	6.4	0.4	7.4
C2A	11.0	0.7	13.8
C2B	11.3	0.8	14.1
C2C	11.2	0.8	14.1
C3A	16.3	0.9	21.8
C3B	15.5	0.9	21.3
C3C	14.7	0.8	19.7
C4A	13.1	0.7	18.3
C4B	12.8	0.7	18.0
C4C	12.6	0.7	17.5
Average	11.5	0.7	15.1
Std Dev	3.4	0.2	5.2

Note: Cell C is one of two EK cells containing pyrolysis char generated at 400°C

Table E.41 SPLP Results for Post-EK Pyrolysis Char: Cell D

Sample ID	Arsenic Concentration (ppm)	Chromium Concentration (ppm)	Copper Concentration (ppm)
D1A	11.2	0.5	13.2
D1B	11.3	0.5	13.1
D1C	12.0	0.5	14.1
D2A	13.2	0.8	14.4
D2B	11.5	0.7	12.3
D2C	12.8	0.7	13.7
D3A	8.8	0.3	10.4
D3B	9.0	0.3	10.5
D3C	8.8	0.3	10.2
D4A	10.3	0.6	11.4
D4B	10.6	0.6	11.8
D4C	10.1	0.5	11.0
Average	10.8	0.5	12.2
Std Dev	1.5	0.2	1.5

Note: Cell D is one of two EK cells containing pyrolysis char generated at 400°C

Table E.42 SPLP Results for Post-EK Pyrolysis Char: Cell E

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
E1A	5.6	0.2	13.2
E1B	6.0	0.3	14.5
E1C	5.5	0.2	13.1
E2A	7.8	0.3	16.2
E2B	8.3	0.3	17.1
E2C	8.2	0.3	17.2
E3A	9.7	0.4	18.1
E3B	9.1	0.4	16.4
E3C	9.2	0.4	16.4
E4A	9.9	0.4	18.3
E4B	9.6	0.4	17.5
E4C	9.9	0.4	18.0
Average	8.2	0.3	16.3
Std Dev	1.7	0.1	1.8

Note: Cell E is one of two EK cells containing pyrolysis char generated at 450°C

Table E.43 SPLP Results for Post-EK Pyrolysis Char: Cell F

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
F1A	1.7	0.2	12.6
F1B	1.8	0.2	12.5
F1C	1.7	0.2	12.6
F2A	7.9	0.3	18.1
F2B	7.7	0.3	17.5
F2C	7.8	0.3	17.8
F3A	4.9	0.3	16.9
F3B	4.7	0.3	16.3
F3C	4.6	0.3	15.4
F4A	14.3	0.9	17.2
F4B	13.6	0.8	16.3
F4C	14.4	0.9	17.5
Average	7.1	0.4	15.9
Std Dev	4.8	0.3	2.1

Note: Cell F is one of two EK cells containing pyrolysis char generated at 450°C

Table E.44 SPLP Results for Post-EK CCA-treated Wood Waste: Cell G

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
G1A	10.1	7.4	0.7
G1B	10.0	7.3	0.7
G1C	9.8	7.1	0.7
G2A	16.5	14.0	1.1
G2B	16.5	14.1	1.1
G2C	17.2	14.7	1.1
G3A	25.5	23.1	1.4
G3B	23.7	20.8	1.2
G3C	22.7	19.7	1.2
G4A	38.9	38.0	1.8
G4B	36.8	35.6	1.7
G4C	37.2	35.9	1.7
Average	22.1	19.8	1.2
Std Dev	10.7	11.3	0.4

Note: Cell G is one of two EK cells containing CCA-treated wood waste

Table E.45 SPLP Results for Post-EK CCA-treated Wood Waste: Cell H

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
H1A	11.3	2.9	0.4
H1B	11.2	2.9	0.4
H1C	11.2	2.8	0.4
H2A	12.5	6.6	1.0
H2B	13.5	7.1	1.0
H2C	13.0	6.7	1.0
H3A	13.7	7.7	0.6
H3B	13.4	7.4	0.6
H3C	13.8	7.9	0.6
H4A	21.8	16.6	1.2
H4B	21.5	16.5	1.2
H4C	21.8	16.6	1.2
Average	14.9	8.5	0.8
Std Dev	4.2	5.2	0.3

Note: Cell H is one of two EK cells containing CCA-treated wood waste

Table E.46 DI Water Leach Results for Post-EK Pyrolysis Char: Cell A

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
A1A	12.3	1.8	10.3
A1B	12.7	1.8	10.8
A1C	6.1	0.9	5.2
A2A	11.3	1.4	10.4
A2B	13.0	1.6	11.8
A2C	13.5	1.6	12.4
A3A	17.9	2.5	13.1
A3B	20.3	2.8	14.9
A3C	16.7	2.3	12.1
A4A	15.3	2.3	8.7
A4B	16.6	2.5	9.6
A4C	22.1	3.3	12.9
Average	14.8	2.1	11.0
Std Dev	4.3	0.7	2.5

Note: Cell A is one of two EK cells containing pyrolysis char generated at 350°C

Table E.47 DI Water Leach Results for Post-EK Pyrolysis Char: Cell B

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
B1A	12.6	1.0	10.3
B1B	13.2	1.0	10.9
B1C	13.0	1.0	10.7
B2A	14.8	1.3	11.0
B2B	14.2	1.2	10.6
B2C	14.9	1.3	11.1
B3A	17.5	2.4	10.3
B3B	17.3	2.4	10.0
B3C	17.2	2.4	10.0
B4A	19.9	2.6	12.7
B4B	17.5	2.2	11.5
B4C	20.7	2.6	13.3
Average	16.1	1.8	11.0
Std Dev	2.7	0.7	1.0

Note: Cell B is one of two EK cells containing pyrolysis char generated at 350°C

Table E.48 DI Water Leach Results for Post-EK Pyrolysis Char: Cell C

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
C1A	6.2	0.3	7.5
C1B	6.3	0.3	7.5
C1C	6.4	0.3	7.1
C2A	10.0	0.5	13.1
C2B	10.1	0.5	13.2
C2C	9.5	0.5	12.3
C3A	13.5	0.5	18.9
C3B	15.3	0.6	21.2
C3C	13.1	0.5	18.5
C4A	11.8	0.5	17.3
C4B	7.8	0.3	11.3
C4C	8.0	0.3	11.5
Average	9.8	0.4	13.3
Std Dev	3.1	0.1	4.8

Note: Cell C is one of two EK cells containing pyrolysis char generated at 400°C

Table E.49 DI Water Leach Results for Post-EK Pyrolysis Char: Cell D

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
D1A	9.6	0.3	11.6
D1B	9.6	0.3	11.6
D1C	8.4	0.3	10.1
D2A	9.4	0.4	10.3
D2B	10.1	0.5	11.0
D2C	10.2	0.5	11.2
D3A	6.3	0.2	7.7
D3B	8.2	0.3	10.1
D3C	6.7	0.2	8.3
D4A	8.8	0.3	9.9
D4B	7.8	0.3	9.1
D4C	8.0	0.3	9.3
Average	8.6	0.3	10.0
Std Dev	1.3	0.1	1.2

Note: Cell D is one of two EK cells containing pyrolysis char generated at 400°C

Table E.50 DI Water Leach Results for Post-EK Pyrolysis Char: Cell E

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
E1A	3.8	0.2	12.2
E1B	3.9	0.2	11.7
E1C	3.6	0.1	11.6
E2A	5.2	0.1	12.6
E2B	5.4	0.1	13.3
E2C	4.7	0.1	11.4
E3A	5.8	0.2	12.2
E3B	6.0	0.2	12.3
E3C	5.8	0.2	12.2
E4A	6.4	0.2	13.2
E4B	6.2	0.2	12.8
E4C	5.1	0.2	10.5
Average	5.2	0.2	12.2
Std Dev	1.0	0.0	0.8

Note: Cell E is one of two EK cells containing pyrolysis char generated at 450°C

Table E.51 DI Water Leach Results for Post-EK Pyrolysis Char: Cell F

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
F1A	1.3	0.1	9.2
F1B	1.3	0.1	9.3
F1C	1.4	0.1	9.8
F2A	5.2	0.1	12.7
F2B	5.8	0.2	14.4
F2C	5.7	0.2	14.1
F3A	3.4	0.2	13.2
F3B	2.1	0.1	8.2
F3C	2.4	0.1	9.5
F4A	9.7	0.4	13.5
F4B	9.4	0.4	13.0
F4C	9.1	0.4	12.6
Average	4.7	0.2	11.6
Std Dev	3.3	0.1	2.2

Note: Cell F is one of two EK cells containing pyrolysis char generated at 450°C

Table E.52 DI Water Leach Results for Post-EK CCA-treated Wood Waste: Cell G

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
G1A	8.0	5.3	0.5
G1B	7.3	4.9	0.4
G1C	7.3	4.8	0.4
G2A	11.5	9.4	0.7
G2B	10.7	8.9	0.7
G2C	10.9	8.8	0.7
G3A	13.1	10.9	0.6
G3B	14.0	11.7	0.6
G3C	13.2	11.0	0.6
G4A	15.2	12.7	0.6
G4B	18.1	15.3	0.7
G4C	17.7	15.0	0.7
Average	12.2	9.9	0.6
Std Dev	3.7	3.6	0.1

Note: Cell G is one of two EK cells containing CCA-treated wood waste

Table E.53 DI Water Leach Results for Post-EK CCA-treated Wood Waste: Cell H

Sample ID	**Arsenic Concentration (ppm)**	**Chromium Concentration (ppm)**	**Copper Concentration (ppm)**
H1A	6.2	2.2	0.2
H1B	7.1	2.5	0.2
H1C	6.4	2.3	0.2
H2A	9.8	4.9	0.6
H2B	10.8	5.5	0.6
H2C	10.5	5.3	0.6
H3A	9.7	4.6	0.2
H3B	9.9	4.7	0.3
H3C	9.9	4.6	0.2
H4A	12.4	7.6	0.5
H4B	11.4	6.8	0.5
H4C	12.3	7.5	0.5
Average	9.7	4.9	0.4
Std Dev	2.1	1.9	0.2

Note: Cell H is one of two EK cells containing CCA-treated wood waste

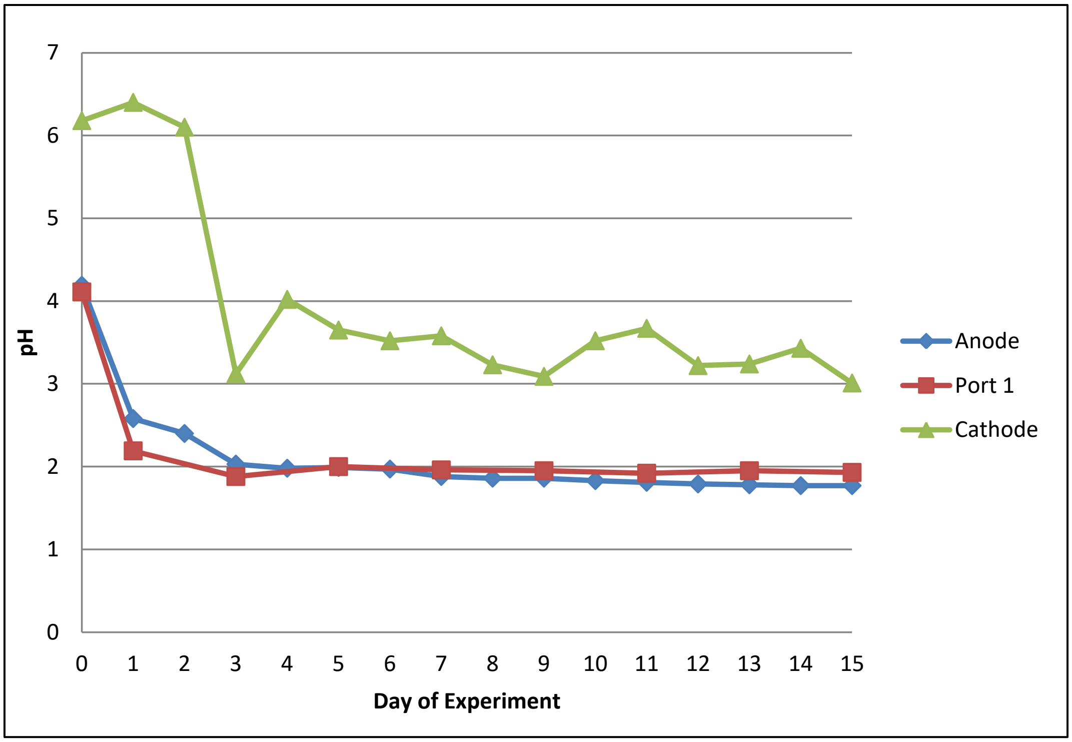

Figure E.1 Daily pH Measurements: Cell A

Note: Cell A is one of two EK cells containing pyrolysis char generated at 350°C

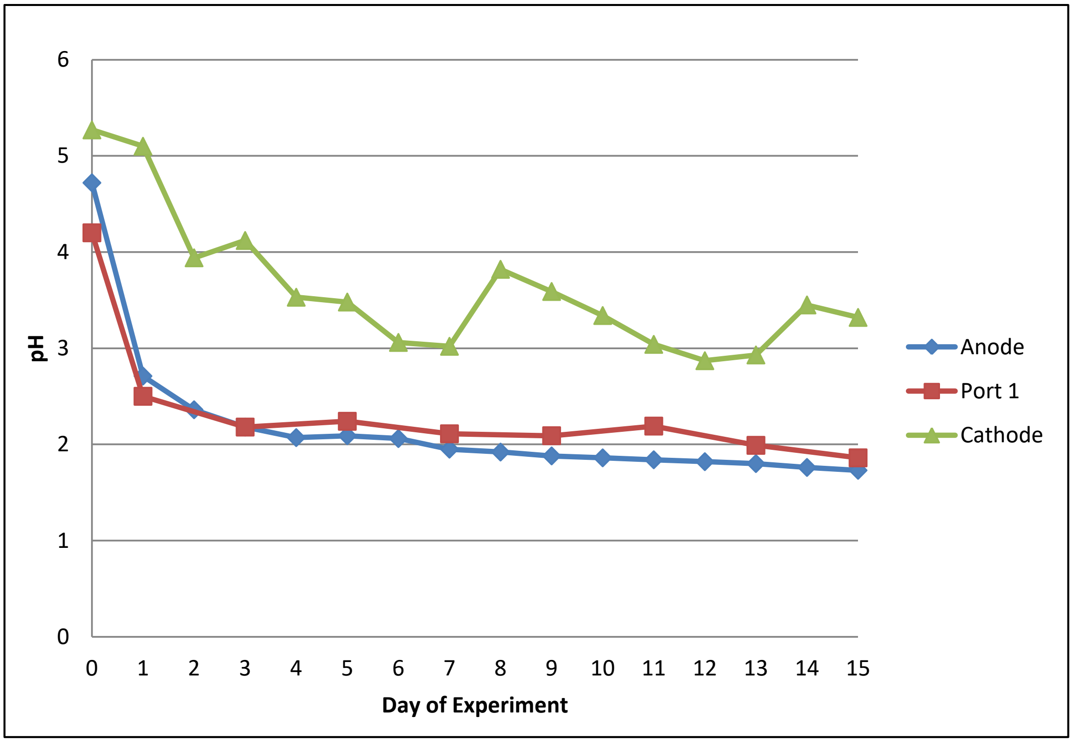

Figure E.2 Daily pH Measurements: Cell B

Note: Cell B is one of two EK cells containing pyrolysis char generated at 350°C

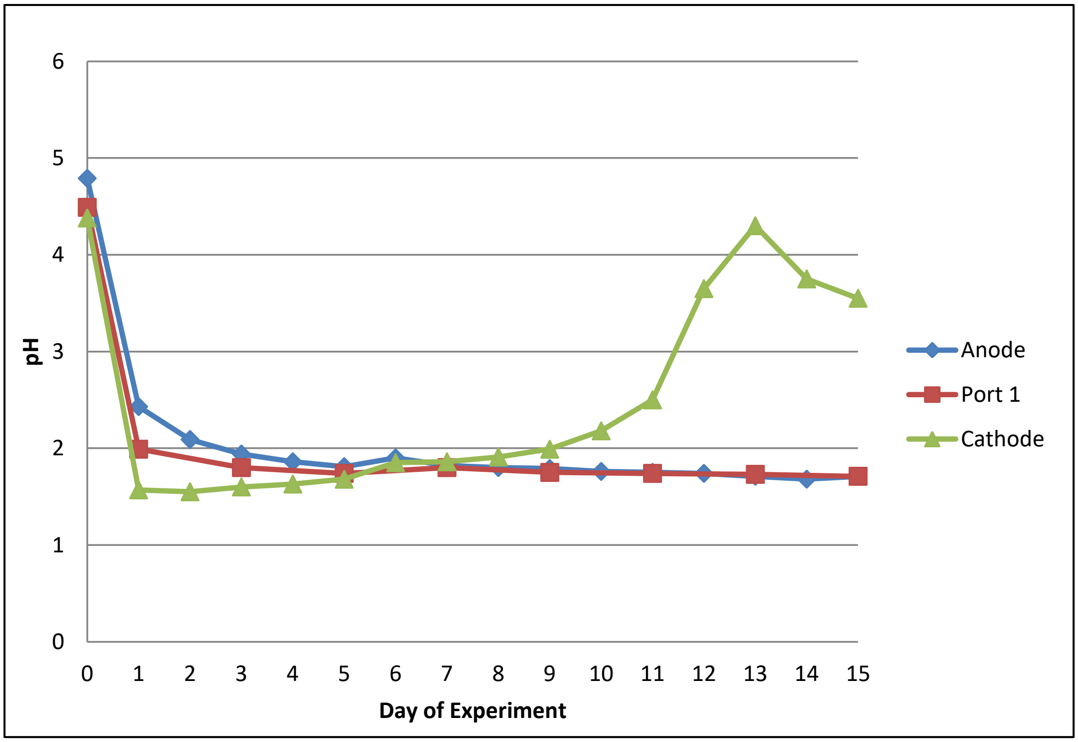

Figure E.3 Daily pH Measurements: Cell C

Note: Cell C is one of two EK cells containing pyrolysis char generated at 400°C

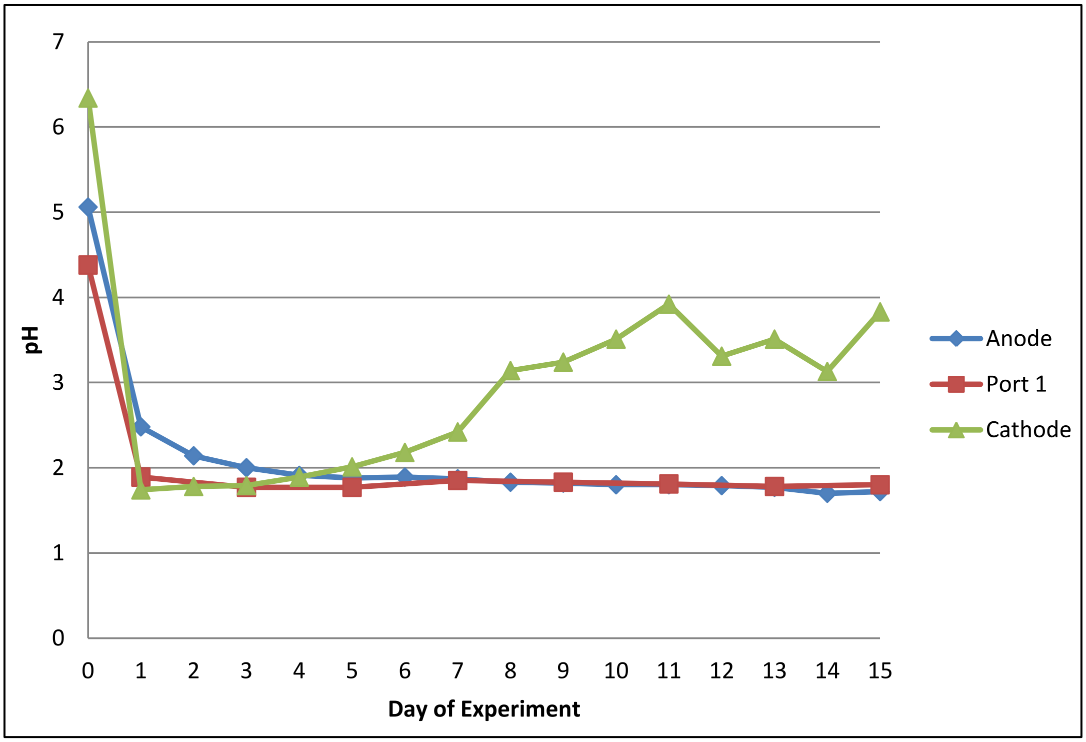

Figure E.4 Daily pH Measurements: Cell D

Note: Cell D is one of two EK cells containing pyrolysis char generated at 400°C

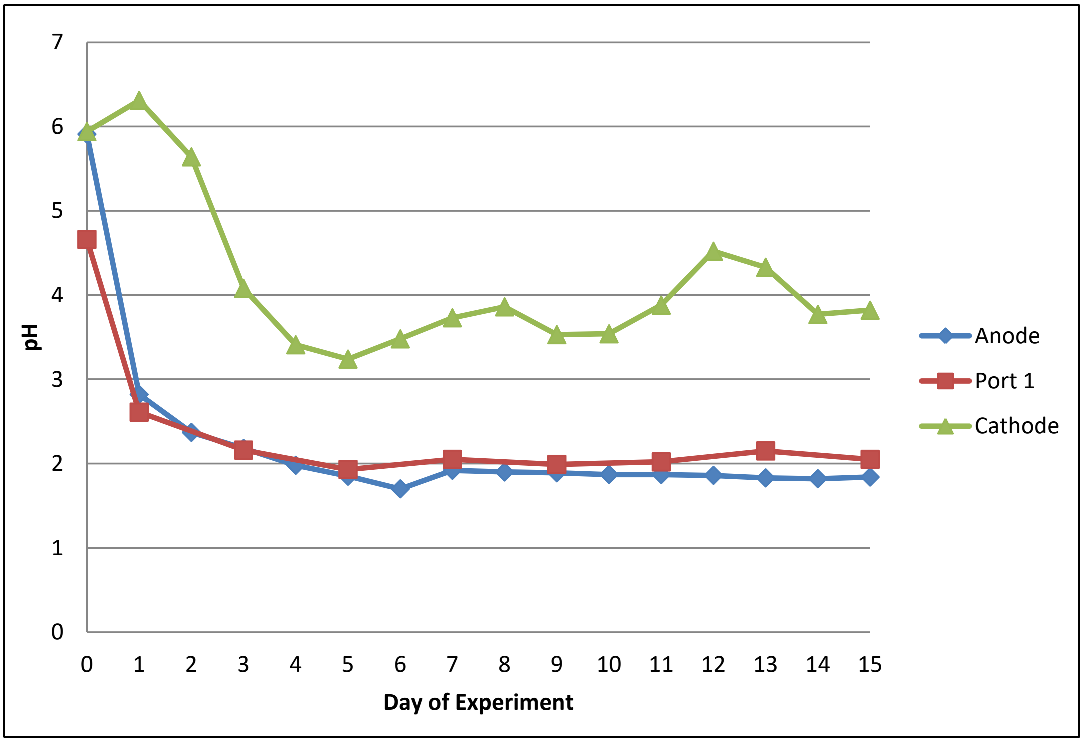

Figure E.5 Daily pH Measurements: Cell E

Note: Cell E is one of two EK cells containing pyrolysis char generated at 450°C

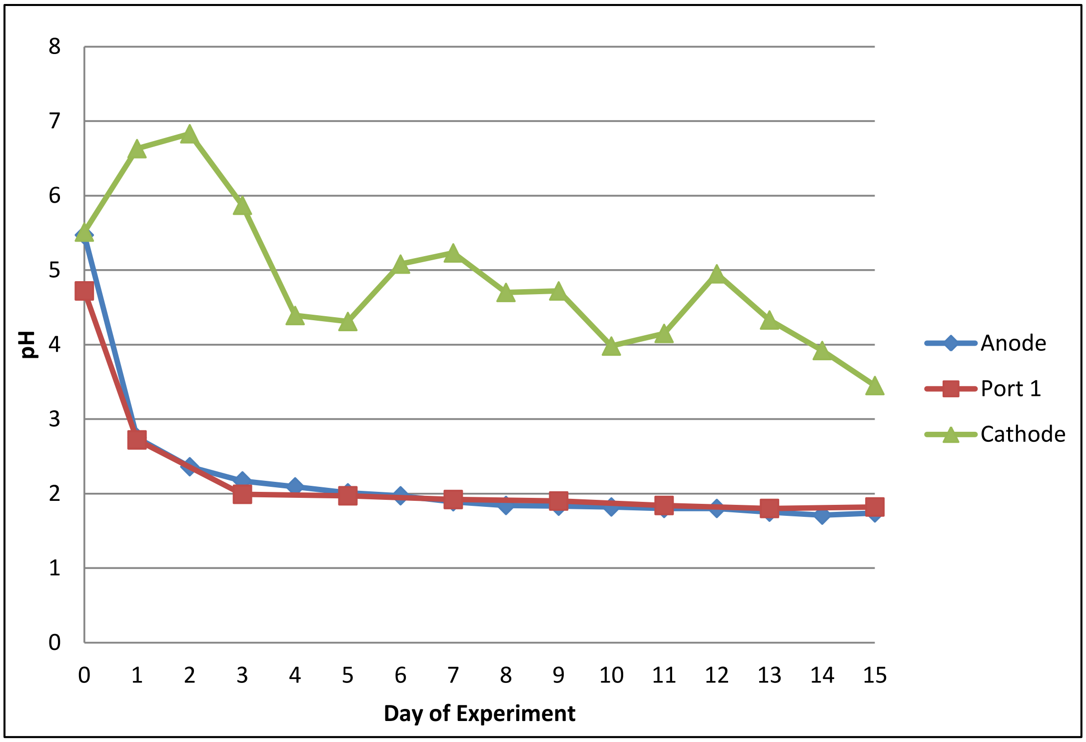

Figure E.6 Daily pH Measurements: Cell F

Note: Cell F is one of two EK cells containing pyrolysis char generated at 450°C

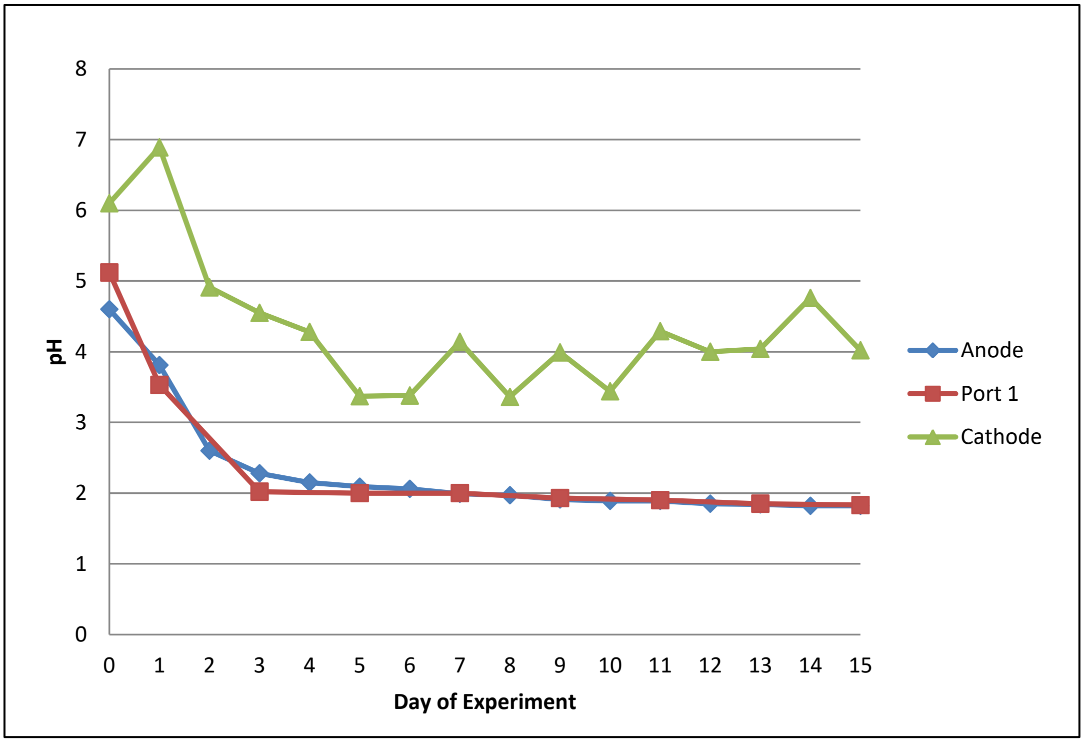

Figure E.7 Daily pH Measurements: Cell G

Note: Cell G is one of two EK cells containing CCA-treated wood waste

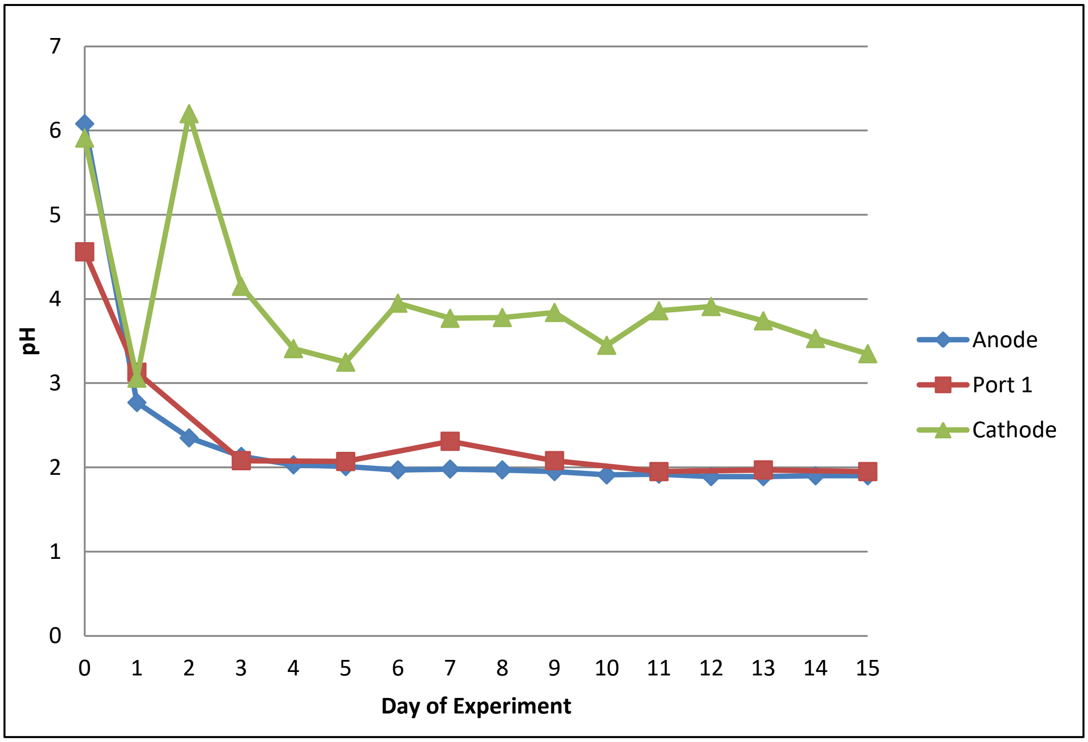

Figure E.8 Daily pH Measurements: Cell H

Note: Cell H is one of two EK cells containing CCA-treated wood waste