Disposal of CCA-treated Wood:

An Evaluation of Existing and Alternative Management Options

(FINAL DRAFT)

November 18, 1999

Helena Solo-Gabriele, Principal Investigator
Vandin Calitu
Monika Kormienko
University of Miami, Coral Gables, FL

Timothy Townsend, Co-Principal Investigator
Brian Messick
University of Florida, Gainesville, FL

State University System of Florida
FLORIDA CENTER
FOR SOLID AND HAZARDOUS WASTE MANAGEMENT
2207 NW 13 Street, Suite D
Gainesville, FL  32609

Report #99-6
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABLE OF CONTENTS</td>
<td>i</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS AND ACRONYMANS</td>
<td>vii</td>
</tr>
<tr>
<td>UNITS OF MEASURE</td>
<td>viii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ix</td>
</tr>
<tr>
<td><strong>CHAPTER I</strong></td>
<td></td>
</tr>
<tr>
<td>I.1 Motivation</td>
<td>2</td>
</tr>
<tr>
<td>I.2 Objectives</td>
<td>2</td>
</tr>
<tr>
<td>I.3 Background</td>
<td>3</td>
</tr>
<tr>
<td><strong>CHAPTER II, LEACHING CHARACTERISTICS OF CCA-TREATED WOOD ASH</strong></td>
<td></td>
</tr>
<tr>
<td>II.1 Sample Preparation</td>
<td>10</td>
</tr>
<tr>
<td>II.2 Laboratory Methods</td>
<td>15</td>
</tr>
<tr>
<td>II.3 Laboratory Results</td>
<td>24</td>
</tr>
<tr>
<td><strong>CHAPTER III, SORTING TECHNOLOGIES FOR SEPARATING TREATED WOOD FROM UNTREATED WOOD</strong></td>
<td></td>
</tr>
<tr>
<td>III.1 Chemical Stain Tests</td>
<td>48</td>
</tr>
<tr>
<td>III.2 Tests Using XRF Technology</td>
<td>62</td>
</tr>
<tr>
<td><strong>CHAPTER IV</strong></td>
<td></td>
</tr>
<tr>
<td>IV.1 Regulatory Implications of Total Metals Concentrations in Treated Wood and Treated Wood Ash</td>
<td>84</td>
</tr>
<tr>
<td>IV.2 Regulatory Implications of TCLP and SPLP Results</td>
<td>86</td>
</tr>
<tr>
<td>IV.3 Practical Issues Associated with Solvent Extractions</td>
<td>88</td>
</tr>
<tr>
<td>IV.4 Evaluation of Sorting Technologies</td>
<td>89</td>
</tr>
<tr>
<td>IV.5 Recommendations</td>
<td>90</td>
</tr>
<tr>
<td>IV.6 Acknowledgments</td>
<td>92</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>93</td>
</tr>
<tr>
<td>APPENDIX A: Supplementary Tables for TCLP and SPLP Tests</td>
<td>A-1</td>
</tr>
<tr>
<td>APPENDIX B: Supplementary Tables for Solvent Extraction Study</td>
<td>B-1</td>
</tr>
<tr>
<td>APPENDIX C: Supplementary Information for Study with Chemical Stains</td>
<td>C-1</td>
</tr>
<tr>
<td>APPENDIX D: Supplementary Information for XRF Study</td>
<td>D-1</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure II.1  Samples Processed For Experimentation
Figure II.2  Schematic for Grate and Catch Pan Used to Incinerate Wood Samples.  (Dimensions are approximate.)
Figure II.3  Incinerator Temperatures (Primary Chamber) Versus Time
Figure II.4  Summary of Incineration Procedure
Figure II.5  Sample Analysis Conducted by Each University
Figure II.6  Flow Diagram of Sample Processing Procedure Used for Samples Processed by U.F.
Figure II.7  Schematic Diagram of Solvent Extraction Study
Figure II.7a  TCLP and SPLP Metal Concentrations for Small and Large Fraction of Ash
Figure II.8  TCLP and SPLP Results for Copper
Figure II.9  TCLP and SPLP Results for Chromium
Figure II.10  TCLP and SPLP Results for Arsenic
Figure II.11  % Copper Removal for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Figure II.12  % Removal of Copper for Nitric Acid Extraction
Figure II.13  Copper Leachate Concentration for Nitric Acid Extraction
Figure II.14  Leachate Copper Concentrations for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Figure II.15  % Chromium Removal for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Figure II.16  % Removal of Chromium for Nitric Acid Extraction
Figure II.17  Chromium Leachate Concentration for Nitric Acid Extraction
Figure II.18  Leachate Chromium Concentrations for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
LIST OF FIGURES (Continued)

Figure II.19  % Arsenic Removal for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, eithered Wood, and a Field Sample from C&D Facility #2
Figure II.20  % Removal of Arsenic for Nitric Acid Extraction
Figure II.21  Arsenic Leachate Concentration for Nitric Acid Extraction
Figure II.22  Leachate Arsenic Concentrations for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Figure III.1  Chemical Structure of Chrome Azurol S
Figure III.2  Chemical Structure of PAN Indicator
Figure III.3  Chemical Structure of Rubeanic Acid
Figure III.4  Stain Performance on Whole Pieces of Wood
Figure III.5  Performance of Stains on Shredded Wood Samples, (Unmixed)
Figure III.6  Cross-section of CCA-Treated Utility Pole
Figure III.7  Cross-section of CCA-Treated 2"x 4" lumber, 0.60 pcf
Figure III.8  Performance of Stains on Shredded Wood Samples, (Mixed)
Figure III.9  Performance of Stains on Field Samples Collected from C&D Recycling Facilities
Figure III.10  Emission of Characteristic X-ray
Figure III.11  ASOMA Model 400
Figure III.12  Sensor and Detector for ASOMA Model 400
Figure III.13  Counts of arsenic, chromium and copper for whole wood at a count time of 2 seconds.
Figure III.14  Counts of arsenic, chromium and copper for shredded wood at count time of 2 seconds.
Figure III.15  Determining the Detection Limit in the Mixtures of 0.25 pcf CCA-Treated Wood with Untreated Wood Before Extensive Instrument Calibration, Count Time 5 Seconds
LIST OF FIGURES  (Continued)

Figure III.16  Determining the Detection Limit in Mixtures of 0.25 pcf CCA-Treated Wood with Untreated Wood After Extensive Instrument Calibration, Count Time 5 Seconds

Figure III.17 Whole Wood at Different Retention Levels and Different Count Times (Counts as Arsenic)

Figure III.18 Shredded Wood at Different Retention Levels and Different Count Times (Counts as Arsenic)

Figure III.19 Distance Study on a Whole Wood Sample of 0.25 pcf CCA-Treated Wood Utilizing a Count Time of 5 Seconds.

Figure III.20 Distance Study on a Whole Piece of 0.25 pcf CCA-Treated Wood Utilizing a Count Time of 5 Seconds and with Shield Present

Figure A.1 Arsenic Concentration from TCLP and SPLP Tests for Each Size Fraction

Figure A.2 Chromium Concentration from TCLP and SPLP Tests for Each Size Fraction

Figure A.3 Copper Concentration from TCLP and SPLP Tests for Each Size Fraction

LIST OF TABLES

Table I.1 Metals Concentration (mg/kg) in CCA-Treated Wood and Other Wood Types as Provided in the Literature

Table I.2 Metals Analyzed in Determining Toxicity Characteristic (40 CFR 261.24)

Table I.3 Guidelines for Leachable Metals Concentrations

Table I.4 Risk-Based Standards for Total Metal Concentrations

Table II.1 Moisture Content

Table II.2 Summary of Solvent Extraction Procedures

Table II.3 Abbreviations Utilized to Describe Each Extraction

Table II.4 Initial Retention Level of Unburned Wood Samples

Table II.5 Results from EDX analysis

Table II.6 Computed Total Metals Concentrations in Each Sample
LIST OF TABLES (Continued)

| Table II.7 | Results from Neutron Activation Analysis |
| Table II.8 | Summary of TCLP and SPLP Results Conducted on CCA-Treated Wood Ash |
| Table III.1 | Types of Samples Utilized in the Chemical Stain Experiments |
| Table III.2 | Description of Field Samples from C&D Recycling Facilities |
| Table III.3 | Order Information for Companies that can Provide Reagents for Chemical Stains |
| Table III.4 | Samples Mailed to ASOMA Headquarters During First Experimental Effort |
| Table III.5 | A Summary of the Results of First Experimental Effort (Counts as As) |
| Table III.6 | Detection of CCA-treated Wood in Field Samples from C&D Recycling Facilities |
| Table III.7 | Results of the Detection Limit Study for Samples in the 0 - 10% CCA Range, Count Time of 3 seconds. |
| Table III.8 | Results of the Detection Limit Study for Samples in the 0 - 10% CCA Range, Count Time of 10 seconds. |
| Table IV.1 | Chromium, Copper, and Arsenic Concentrations in Treated Wood and Treated Wood Ash Used in This Study. Regulatory Levels Provided for Comparison. |
| Table IV.2 | Fraction of CCA-Treated Wood that Can be Mixed with Untreated Wood such that Mixture Equals Regulatory Limits or Guidelines. |
| Table IV.3 | Comparison of SPLP and TCLP Results to Regulatory Standards or Policy |
| Table A.1 | Results of Size Fractionation |
| Table A.2 | The Mass of Samples used in Leaching Procedures |
| Table A.3 | The Initial and Final pH of the Leaching Solutions (TCLP) |
| Table A.4 | The Final pH of the Leaching Solutions (SPLP) |
| Table A.5 | Results of the TCLP for Arsenic |
| Table A.6 | Results of the TCLP for Chromium |
| Table A.7 | Results of the TCLP for Copper |
| Table A.8 | Results of the SPLP for Arsenic |
| Table A.9 | Results of the SPLP for Chromium |
LIST OF TABLES (Continued)

Table A.10  Results of the SPLP for Copper
Table A.11  Quality Assurance Data for TCLP and SPLP Tests
Table B.1   Percent Copper Removal for Various Solvents
Table B.2   Copper Leachate Concentrations for Various Solvents
Table B.3   Percent Chromium Removal for Various Solvents
Table B.4   Chromium Leachate Concentrations for Various Solvents
Table B.5   Percent Arsenic Removal for Various Solvents
Table B.6   Arsenic Leachate Concentrations for Various Solvents
Table D.1   Counts for Various Samples for Different Count Times, All Samples Whole
Table D.2   Counts for Various Samples for Different Count Times, All Samples Shredded
Table D.3   Data Utilized for Estimating the Detection Limit of In Shredded Mixtures, Before Extensive Instrument Calibration
Table D.4   Data Utilized for Estimating the Detection Limit of In Shredded Mixtures, After Extensive Instrument Calibration, Count Time 25s
Table D.5   Additional Data Collected on Shredded Mixtures Using Arsenic as the Indicator Metal.
Table D.6   Distance Study on Whole Wood Samples, Count time 5 s
**LIST OF ABBREVIATIONS AND ACRONYMS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>Arsenic</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrophotometer</td>
</tr>
<tr>
<td>AsH₃</td>
<td>Arsine Gas</td>
</tr>
<tr>
<td>AWPA</td>
<td>American Wood Preservers Association</td>
</tr>
<tr>
<td>AWPI</td>
<td>American Wood Preservers’ Institute</td>
</tr>
<tr>
<td>CCA</td>
<td>Chromated Copper Arsenate</td>
</tr>
<tr>
<td>C&amp;D</td>
<td>Construction and Demolition</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>FPL</td>
<td>Florida Power and Light</td>
</tr>
<tr>
<td>GWGC</td>
<td>Groundwater Guidance Concentrations</td>
</tr>
<tr>
<td>DEP</td>
<td>Department of Environmental Protection</td>
</tr>
<tr>
<td>DW</td>
<td>Distilled Water</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Fluorescence</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>FAC</td>
<td>Florida Administrative Code</td>
</tr>
<tr>
<td>FLAA</td>
<td>Flame Atomic Absorption Spectrophotometer</td>
</tr>
<tr>
<td>GFAA</td>
<td>Graphite Furnace Atomic Absorption Spectrophotometer</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen Peroxide</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>HH</td>
<td>hydroxylamine hydrochloride</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Nitric Acid</td>
</tr>
<tr>
<td>MgCl₂ or MC</td>
<td>Magnesium Chloride</td>
</tr>
<tr>
<td>MIT</td>
<td>Massachusetts Institute of Technology</td>
</tr>
<tr>
<td>MSDS</td>
<td>Material Safety Data Sheet</td>
</tr>
<tr>
<td>MSW</td>
<td>Municipal Solid Waste</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>Pero</td>
<td>Hydrogen Peroxide</td>
</tr>
<tr>
<td>PCB</td>
<td>Polychlorinated Byphenyl</td>
</tr>
<tr>
<td>RCRA</td>
<td>Resource Conservation and Recovery Act</td>
</tr>
<tr>
<td>SCTL</td>
<td>Soil Clean-up Target Level</td>
</tr>
<tr>
<td>SHC</td>
<td>Sodium Hydroxide Plus Citric Acid</td>
</tr>
<tr>
<td>SPLP</td>
<td>Synthetic Precipitation Leaching Procedure</td>
</tr>
<tr>
<td>TCLP</td>
<td>Toxicity Characteristic Leaching Procedure</td>
</tr>
<tr>
<td>TRM</td>
<td>Total Recoverable Metals</td>
</tr>
<tr>
<td>UF</td>
<td>University of Florida</td>
</tr>
<tr>
<td>UM</td>
<td>University of Miami</td>
</tr>
</tbody>
</table>
UNITS OF MEASURE

\%
\mu g/L
ft^3
lb/ft^3
lbs.
mg/kg
mg/L
pcf

parts per hundred
micrograms per liter
cubic feet
pounds per cubic foot
pounds
milligrams per kilogram
milligrams per liter
pounds per cubic foot
ABSTRACT

A significant portion of CCA-treated wood waste produced in Florida is recycled and some is sold as boiler fuel. In the process, CCA-treated wood is inadvertently burned causing an accumulation of the CCA chemical within the resultant ash. The quality of this ash is questionable due to elevated metals concentrations and, given that the quantities of CCA-treated wood disposed are forecasted to increase, ash quality may degrade to the point where burning wood waste will not be economically nor environmentally acceptable for the future. The goal of this research was to improve the management of CCA-treated wood waste within the State of Florida so as to minimize its impact upon disposal. The current study focused on: characterizing the leachates from CCA-treated wood ash using various solvents and identifying methods for sorting CCA-treated wood from other wood types. The ash leaching studies focused on conducting TCLP and SPLP extractions and testing with other solvents for ash treatment purposes. TCLP and SPLP tests were conducted in accordance with EPA standard protocols. Ash treatment was investigated by subjecting CCA-treated wood ash to strong acids or weaker solvents and noting the amount of metals removed. The two sorting technologies investigated, chemical stains and x-ray fluorescence, are routinely used by the wood treatment sector. The focus of the current study was to determine whether these technologies are suitable for sorting CCA-treated wood waste from other wood types.

Results of this study indicate that all ash samples produced from 100% CCA-treated wood exceeded TCLP criteria and Florida Groundwater Guidance Concentrations for arsenic. TCLP limits were also exceeded for two of the three ash samples of C&D wood waste tested and for both of the laboratory produced mixtures containing 5% CCA-treated wood. Concentrated nitric acid, which was the most effective solvent tested, was capable of removing between 60% to 100% of the copper in CCA-treated wood ash, between 25 and 70% of the chromium, and 80 to 100% of the arsenic for samples characterized by low retention levels. These percent removals are based upon the true total metal concentration and not on the total recoverable metals concentrations as defined by EPA method 3050B. Higher percent removals would be reported if extractions were compared to the total recoverable metals. A particular finding of interest was the efficiency of distilled water and other weak solvents to extract measurable amounts of chromium, especially for ash samples containing low retention levels of CCA. Citric acid was particularly effective at removing arsenic (between 40 to 100%) for ash samples characterized by low retention levels.

The two sorting technologies evaluated through this study showed considerable promise for sorting CCA-treated wood from other wood types at C&D facilities. The chemical stains performed very well on laboratory mixtures of treated and untreated wood and for most of the field samples. X-ray fluorescence technology was found to readily detect the presence of treated wood in both whole and shredded samples. The minimum detection limit for wood mixtures lies between 3 and 5% treated wood which is near the level where the ash from such a mixture would fail TCLP criteria.

Results of this study suggest that the ash produced from C&D wood waste would likely fail TCLP criteria, especially if it contained more than 5% CCA-treated wood. The use of solvents for ash treatment purposes merits further study especially given that a relatively weak solvent, citric acid, was found to remove significant amounts of arsenic, the most problematic metal from a regulatory standpoint. Sorting wood waste prior to incineration also represents a plausible management alternative for CCA-treated wood waste. A pilot study conducted at C&D facilities is highly recommended to further explore the use of this technology in field situations. Assuming that the results of such pilot studies are positive, incentives should be provided to C&D facilities to sort CCA-treated wood.
This page left intentionally blank.
CHAPTER I

MOTIVATION, OBJECTIVES, AND BACKGROUND
I.1 MOTIVATION

Results of our first year study (Solo-Gabriele et al., 1998) indicate that quantities of CCA-treated wood waste will increase significantly in the near future and, in Florida, a significant fraction of this wood is burned for energy recovery. Our preliminary analysis of total disposal quantities indicated that approximately 1 million pounds of the chemical were disposed in Florida during 1996. We anticipate that by 2006 this figure will quadruple and by 2016 it will reach a value of 6.8 million pounds. Our preliminary results also indicated that the primary market for recycled wood waste is energy recovery and that approximately 6% of the recycled wood waste on average is CCA treated. If current disposal practices for CCA-treated wood are continued, it is anticipated that metals concentrations in wood ash will continue to increase. The degraded ash quality will greatly limit recycling opportunities and increase the cost for ash disposal.

In anticipation of the future trends, research is needed to address current and future disposal issues associated with discarded CCA-treated wood. Incineration of wood with energy recovery is a beneficial recycling alternative. However, the benefits of energy recovery may be compromised by elevated costs associated with ash disposal if significant quantities of CCA are burned. The approach in addressing this problem in the current study is two-fold. It is recognized that CCA-treated wood is difficult to visually distinguish from untreated wood especially after the wood has been weathered. First, there is a need to develop methods that can be used to sort treated wood from the remainder of the wood waste stream. Once CCA-treated wood is sorted out, other wood types can be burned without the added metals associated with CCA. Sorting technologies developed should be efficient enough such that the remaining wood stream would not “fail” certain regulatory requirements. There is also a need to ultimately dispose CCA-treated wood once CCA-treated wood is sorted-out from the remaining wood waste stream. Disposal via incineration is a viable alternative for volume reduction and energy recovery as long as the combustion process is carefully controlled, emissions are properly contained, and the ash is disposed in an environmentally sound manner. Furthermore, studies have shown that the ash from CCA-treated wood contains between 5 to 15% chromium, copper, and arsenic, by weight (Atkins and Fehrs, 1992; McGinnis, 1995; Fehrs, 1995). Given that the metals content in the ash is high, there may be opportunities for removing the metals in a concentrated form for recycling purposes. Research is needed to determine whether metals can be extracted from the wood ash. Such an extraction, if successful, may open new opportunities for treating wood ash and recycling the CCA chemical.

I.2 OBJECTIVES

The goal of this research is to improve the management of CCA-treated wood waste within the State of Florida. It was considered at the outset of this study that marked progress toward this goal would be provided by improved sorting practices at wood waste recycling facilities and through ash treatment and ash leaching studies. Such improvements are intended to maintain the economic viability of the wood treating industry while promoting recycling and environmental protection. The three objectives of this research are consistent with this goal and are summarized as follows.

Determine the leaching characteristics of CCA-treated wood ash using various solvents.
Examine two technologies for sorting CCA-treated wood prior to combustion.
Evaluate current and alternative management options for Florida.
The following three chapters address each of the objectives. The purpose of the leaching studies (Chapter II) was to conduct leaching tests (TCLP and SPLP) which are used for regulatory purposes and to identify a solvent that can be used to extract metals from CCA-treated wood ash. The two sorting technologies evaluated (Chapter III) are used routinely by the wood treatment sector. These methods include the use of chemical stains and x-ray fluorescence. The focus of the current study was to determine whether these technologies are suitable for sorting by the disposal sector. The focus of Chapter IV was to evaluate the results from Chapters II and III with respect to regulatory criteria and other practical issues.

I.3 BACKGROUND

The following sub-sections provide the background information necessary for this research project. The section begins by describing the general characteristics of CCA-treated wood (section I.3.a) including the concept of retention levels which will be repeatedly referenced in subsequent chapters. Section I.3.b summarizes the reported metals concentrations of treated wood and treated wood ash as well as leaching characteristics reported in the literature. This section provides the background information needed for Chapter II which presents the results of the leaching studies. The last section (section I.3.c) summarizes regulations and policies which impact waste management. These policies will be referenced when evaluating the results of this study in Chapter IV. Background information for Chapter III, which focuses on sorting technologies, is provided within Chapter III.

I.3.a Characteristics of CCA-Treated Wood

The most common wood preservative used in the U.S. is chromated copper arsenate (CCA). CCA represents roughly 75% of the treated wood market by wood product volume; among waterborne preservatives, CCA represents over 97% of the market. During 1997 40% of all treated poles and pilings and over 90% of treated lumber, timbers, posts, and plywood were treated with CCA. Approximately 144 million pounds of the chemical were utilized in the U.S. during 1997 to produce 450 million cubic feet of treated wood product (AWPI, 1997). The State of Florida produces between 6 and 15% of the U.S. production of CCA-treated wood products in any given year (Solo-Gabriele et al. 1998).

CCA is composed of the oxides of chromium, copper, and arsenic. The copper in the wood serves as the fungicide whereas the arsenic protects the wood against insects. The chromium fixes the copper and arsenic to the wood. The most common formulation for CCA is Type "C" which is composed of the following proportions of chemicals: 47.5% as CrO$_3$, 18.5% as CuO, and 34.0% as As$_2$O$_3$ (AWPA, 1998). The amount of CCA utilized to treat the wood or retention level depends upon the particular application for the wood product. Typical retention levels utilized by the industry are 0.25 pcf, 0.40 pcf, 0.60 pcf, 0.8 pcf, and 2.50 pcf. (Note: pcf = pounds per cubic foot). Low retention values (0.25 pcf) are permissible for plywood, lumber, and timbers if the wood is used for above ground applications. Higher retention values are required for load bearing wood components such as pilings, structural poles, and columns. The highest retention levels (0.8 and 2.5 pcf) are required for wood components which are used for foundations or saltwater applications.

CCA is a member of a class of wood preservatives called “waterborne preservatives.” All
Waterborne preservatives utilize water to carry the treatment chemical into the wood fiber. After chemical addition, most of the water is evaporated through kiln drying or natural processes leaving the CCA chemical behind within the wood. Waterborne preservatives differ from oilborne preservatives and creosote by providing wood with a surface that is easy to paint and by producing no odor or vapor. At low retention values it does not change the general appearance of the wood, maintaining the aesthetic quality of natural wood. CCA-treated wood is suitable for use indoors and is generally used for interior parts of a wood structure in contact with the floor. Drawbacks of the wood are a strong green color at high retention values. It should not be used in applications where it is in contact with food or drinking water.

I.3.b Prior Studies Investigating the Characteristics of Treated Wood and Treated Wood Ash

Solo-Gabriele *et al.* 1998 conducted a literature review on reported background metal’s concentrations in treated wood and treated wood ash (table I.1). The data clearly show that “other wood” which includes untreated wood and wood treated with other chemicals such as creosote and pentachlorophenol have significantly lower concentrations of arsenic, chromium, and copper than CCA-treated wood. This is the case if either unburned wood or ash samples are considered. Concentration differences are on the order of thousands for unburned wood and on the order of tens of thousands for wood ash. These data show that for every 100 pounds of CCA-treated wood ash, about 7 pounds on average and up to 10 pounds on the high end are composed of chromium, copper or arsenic. Please note that the data sources utilized to develop table I.1 did not provide information concerning the retention level for which the wood was originally treated and thus concentrations provided can possibly correspond to any particular retention level.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Unburned Other Wood (mg/kg)</th>
<th>CCA Treated (mg/kg)</th>
<th>Ash Other Wood (mg/kg)</th>
<th>CCA Treated (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mg/kg)</td>
<td>(mg/kg)</td>
<td>(mg/kg)</td>
<td>(mg/kg)</td>
</tr>
<tr>
<td>Arsenic</td>
<td>2.0 (0.26-7.2)</td>
<td>1200 (290-2050)</td>
<td>67 (7.5-79.7)</td>
<td>33,000 (8980 - 45000)</td>
</tr>
<tr>
<td>Chromium</td>
<td>7.0 (0.3-21)</td>
<td>2100 (1740-2360)</td>
<td>51 (13-143)</td>
<td>16,000 (1780-22500)</td>
</tr>
<tr>
<td>Copper</td>
<td>3.7 (1.1-3)</td>
<td>1100 (1040-1070)</td>
<td>120 (43.5 - 164)</td>
<td>22,000 (2720 - 31500)</td>
</tr>
</tbody>
</table>

Table I.1: Metals Concentration (mg/kg) in CCA-Treated Wood and Other Wood Types as Provided in the Literature. (Average Values and Ranges. Number of experimental values per data point range from 2 to 3 for CCA-treated wood and 5 to 48 for other wood types).

Leaching of unburned wood has been investigated by Warner and Solomon, 1990, who found that copper, chromium, and arsenic, were found in the leachate of both new and weathered CCA-treated jack pine with significantly higher levels of all metals occurring at lower more acidic pH levels.
The original preservative content of the wood was determined by x-ray fluorescence using an ASOMA Analyzer. Three sets of leaching solutions were prepared. One set was composed of citric acid and sodium hydroxide, another was composed of hydrochloric acid with borax, and the last set was composed of sulfuric acid. Results showed that up to 100% of the copper, chromium, and arsenic were found to have leached at a pH of 3.5, whereas a maximum of 9% of the metals leached at a pH of 8.5. Metal leaching was found to be higher in citric acid than in dilute sulfuric acid solutions. Cooper, 1991, also found that water buffered with sodium hydroxide and citric acid was capable of removing significant quantities of metals from CCA-treated wood. Initial metals analyses for wood was conducted using neutron activation analyses, a non-destructive analytical technique which provides a value for total metals. Samples were then subjected to two sets of leaching solutions. One set was prepared from mineral acids diluted to low concentrations and another set was prepared from sodium hydroxide/citric acid. Leaching tests were conducted over a period of 13 days. Results showed that the sodium hydroxide/citric acid buffer performed better than the mineral acid solutions. After thirteen days in contact with the wood sample, the sodium hydroxide/citric acid solution extracted up to 45% of the arsenic, 80% of the copper, and 11% of the chromium. The solutions with mineral acids extracted less than 5% of chromium, copper, and arsenic. The percent extracted was found to be a function of wood species used in the experiment. Red pine showed the highest leaching; no tests were conducted using Southern Yellow Pine. Smith and Shiau, 1998, evaluated the effects of citric acid and weak mineral acid solutions on the extraction of chromium, copper, and arsenic on CCA-treated sawdust and steam exploded CCA-treated wood fiber. Percent removals for this study were referenced to an extractable metals fraction. Extractable metals concentrations were determined through microwave digestion with concentrated nitric acid (Smith and Shiau 1993). The extractable fraction utilizing concentrated acids is likely lower than the total metals concentration and therefore percent removals reported through this study will generally over estimate the percent removals established through Warner and Solomon, 1990 and Cooper, 1991. Results from Smith and Shiau’s study indicate that 80% of the extractable copper and arsenic and 70% of the extractable chromium can be removed using citric acid. Diluted mineral acids did not perform as well, removing less than 30% of the extractable portion of each metal. In general, more metals were removed from the sawdust than from the steam exploded CCA-treated wood.

Leaching of CCA-treated wood ash has also been investigated by various researchers. Fehrs, 1996, reports that TCLP limits were exceeded for arsenic by a factor of 26 for ash produced from wood fuel containing 10.7% CCA-treated wood. (Note: TCLP will be defined and discussed in greater detail in the next section). One primary conclusion from this study was that TCLP limits for CCA-treated wood ash would be exceeded even if CCA represents a small fraction of the wood fuel. Gifford and Dare, 1998, found that chromium was the most mobile metal species during a TCLP extraction performed on the bottom ashes collected from wood combustion facilities that accept treated wood as part of their fuel stream. Leachate concentrations exceeded U.S. TCLP limits for chromium but did not exceed limits for arsenic. Copper concentrations were below the analytical detection limit of 0.01 mg/L. Results also showed that 60 to 70% of the extractable chromium and 8 to 10% of the extractable arsenic were removed during the TCLP leaching test. Extractable metals were determined from a digestion with concentrated sulfuric acid and hydrogen peroxide. Pohlandt, et al., 1993 conducted distilled water extractions (10 parts water to 1 part ash) on furnace, boiler, and fly ash produced from the combustion of 1 part CCA-treated wood with 3 parts untreated wood. The retention level for the treated wood and the wood species incinerated were not reported. The furnace ash produced the highest chromium concentrations (greater than 1,000 mg/L) and the fly ash produced the highest arsenic concentrations. The distilled water solvent utilized in this study was
I.3.c Background for Regulations and Policies Related to Waste Management

An evaluation of the appropriate management options for a solid waste involves a number of different testing protocols and comparison with several regulatory agency rules and policies. The first decision that must typically be made is whether a solid waste must be managed as a hazardous waste. Under U.S. federal regulations, a waste can be classified as hazardous if it is a listed waste or if it exhibits any of the four characteristics of ignitability, corrosivity, reactivity, and toxicity (40 CFR 261). Ash from the combustion of wood is not provided an exemption. Of the four characteristics, toxicity is the one that would likely be a potential issue with wood ash. In some cases, such as for unburned CCA-treated wood disposed by the end-user, wastes are exempted from a hazardous designation regardless of their characteristics and can therefore be managed in the same manner as domestic waste, such as disposal through an lined landfill.

Alternative management practices are desired, nonetheless, for many cases where disposal in a lined landfill is permitted. Alternative management practices include disposal in an unlined landfill or land application. Motivation for such alternatives to disposal in a lined landfill include economics and the potential for the waste to serve as beneficial reuse material (e.g. ash added to soil as an amendment). A separate set of evaluations must be made, beyond the determination of whether a waste is hazardous or not. This includes an evaluation of the potential leaching to groundwater, and the possible risk to humans through direct exposure.

If a solid waste is determined to be hazardous, then it must be managed according to a strict series of controls that include requirements for record keeping, storage, transportation, treatment and disposal. The management of a hazardous waste is typically at a much greater cost to the waste generator relative to a non-hazardous solid waste.

This subsection reviews the tests and regulatory pollutant limits as it relates to these management options, with specific regard to ash from the combustion of wood that contains CCA-treated wood.

Toxicity Characteristic Leaching Procedure, TCLP

The toxicity characteristic of a solid waste is determined through a toxicity characteristic leaching procedure (TCLP). In the TCLP test, contaminants from a solid waste are extracted using an acetic acid based leaching solution. The solution utilized is designed to simulate anaerobic conditions inside a municipal solid waste landfill. Limits are set based upon the concentration of contaminants in the leachate produced. If the concentration of any of these contaminants (metals or organic compounds) in the leachate is at or above these limits, then the waste is hazardous by the toxicity characteristic. In the case of CCA-containing wood ash, the organic priority pollutants are not typically a concern. Table I.2 presents a list of the eight Resource Conservation and Recovery Act (RCRA) metals that are evaluated in order to assess the toxicity of a waste. Only chromium, copper, and arsenic should be a concern for this ash; however it should be noted that copper analysis is not required when performing the TCLP test.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Regulatory Level (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>5.0</td>
</tr>
<tr>
<td>Barium</td>
<td>100.0</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1.0</td>
</tr>
<tr>
<td>Chromium</td>
<td>5.0</td>
</tr>
<tr>
<td>Lead</td>
<td>5.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.2</td>
</tr>
<tr>
<td>Selenium</td>
<td>1.0</td>
</tr>
<tr>
<td>Silver</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table I.2: Metals Analyzed in Determining Toxicity Characteristic (40 CFR 261.24)

Synthetic Precipitation Leaching Procedure, SPLP

While the TCLP test is primarily used to determine whether a solid waste is hazardous by the toxicity characteristic, it is also used at times to assess the potential risk to the environment from leaching at levels below the hazardous waste limits. For example, if a solid waste such as an ash is proposed to be added to the soil as an amendment, the TCLP may be used to examine the potential impact on groundwater. However, the TCLP has limitations for this application because it was designed to simulate the acidic environment encountered inside a municipal solid waste landfill. The SPLP has been proposed as a more appropriate method for determining the potential impact of a waste on the environment under scenarios such as previously indicated. It is the preferred choice by many regulators for determining impacts of waste on groundwater (including Florida). This test is performed in the same manner as the TCLP with the exception of the leaching solution, which simulates an acidic rainfall. The SPLP assay uses a leaching solution comprised of nitric and sulfuric acid.

The typical approach used to evaluate the impact of a waste in a non-landfilled environment due to leaching is to perform an SPLP, and to compare the concentration of pollutants of concern in the leachate to appropriate groundwater standards or limits. In Florida, this typically corresponds to the Florida Groundwater Guidance Concentrations (GWGC). Table I.3 presents the Florida GWGC for twelve metals. Note that the GWGC for As, Cr, and Cu correspond to the 0.05, 0.1, and 1 mg/L, respectively.

<table>
<thead>
<tr>
<th>Metal</th>
<th>FL Groundwater Guidance Concentrations (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>50</td>
</tr>
<tr>
<td>Barium</td>
<td>2,000</td>
</tr>
<tr>
<td>Cadmium</td>
<td>5</td>
</tr>
<tr>
<td>Chromium</td>
<td>100</td>
</tr>
<tr>
<td>Copper</td>
<td>1,000</td>
</tr>
<tr>
<td>Iron</td>
<td>300</td>
</tr>
<tr>
<td>Lead</td>
<td>15</td>
</tr>
<tr>
<td>Mercury</td>
<td>2</td>
</tr>
<tr>
<td>Nickel</td>
<td>100</td>
</tr>
<tr>
<td>Selenium</td>
<td>50</td>
</tr>
<tr>
<td>Silver</td>
<td>100</td>
</tr>
<tr>
<td>Zinc</td>
<td>5,000</td>
</tr>
</tbody>
</table>

Table I.3: Guidelines for Leachable Metals Concentration
A non-hazardous waste is still a solid waste and must be managed appropriately. It may be disposed in a lined landfill without additional testing. However, when the waste is accumulated, disposed on-site, land applied, or disposed in an unlined facility, it should be evaluated to assess the possible risk to human health through direct exposure. Direct exposure includes ingestion, dermal contact, and inhalation.

To assess the direct exposure risk of the CCA-containing wood ash, the total metal concentration is measured in mg/kg. The heavy metal concentrations in samples of the ash may be compared to risk-based exposure standards to determine what reuse or disposal options are appropriate. The Florida Department of Environmental Protection has developed Soil Cleanup Target Levels (SCTLs, formerly known as Soil Cleanup Goals). The SCTLs were designed for assessment of contaminated sites and were developed using a risk-assessment methodology. Table I.4 contains Florida SCTLs for heavy metals for both residential and industrial reuse settings. The direct exposure limits are not regulations, but are goals that may be used for several purposes, including determining limitations of land application of materials.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Residential SCTL (mg/kg)</th>
<th>Industrial SCTL (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.8</td>
<td>3.7</td>
</tr>
<tr>
<td>Barium</td>
<td>105</td>
<td>87,000</td>
</tr>
<tr>
<td>Cadmium</td>
<td>75</td>
<td>1300</td>
</tr>
<tr>
<td>Chromium</td>
<td>290</td>
<td>430</td>
</tr>
<tr>
<td>Copper</td>
<td>105</td>
<td>12,000</td>
</tr>
<tr>
<td>Iron</td>
<td>23,000</td>
<td>490,000</td>
</tr>
<tr>
<td>Lead</td>
<td>500</td>
<td>920</td>
</tr>
<tr>
<td>Mercury</td>
<td>3.7</td>
<td>28</td>
</tr>
<tr>
<td>Nickel</td>
<td>105</td>
<td>28,000</td>
</tr>
<tr>
<td>Selenium</td>
<td>390</td>
<td>10,000</td>
</tr>
<tr>
<td>Silver</td>
<td>390</td>
<td>9,100</td>
</tr>
<tr>
<td>Zinc</td>
<td>23,000</td>
<td>560,000</td>
</tr>
</tbody>
</table>

Table I.4: Risk-Based Standards for Total Metal Concentrations
CHAPTER II

LEACHING CHARACTERISTICS OF WOOD ASH
CHAPTER II,
LEACHING CHARACTERISTICS OF CCA-TREATED WOOD ASH

This chapter is separated into the following three sections: sample preparation (II.1), laboratory methods (II.2), and laboratory results (II.3). The sections on laboratory methods and results are further separated into: a) total metals analyses (sections II.2.a and II.3.a), b) the TCLP and SPLP determinations conducted at the University of Florida laboratories (sections II.2.b and II.3.b) and c) the solvent extraction study which was conducted at the University of Miami laboratories (sections II.2.c and II.3.c).

II.1 SAMPLE PREPARATION

Preparation of samples required collection, initial processing including shredding, followed by incineration.

II.1.a Sample Collection and Initial Processing

A total of ten batches of wood at 120 pounds each were processed for experimentation (figure II.1). Five of these 10 samples were control samples (batches 1 through 5), three were collected from C&D recycling facilities (batches 6 through 8), and the last two were laboratory prepared mixtures of CCA-treated wood with untreated wood designed to mimic C&D waste wood. The control samples were of known composition and included untreated southern yellow pine (batch 1), treated wood at 0.25, 0.60, and 2.50 pcf retention levels (batches 2, 3, & 4) and weathered wood of known age (batch 5). Batches 1 through 4 were purchased as 2"x 4" lumber (10 foot lengths) from a local retail outlet, Ace Hardware/Shell Lumber located in Miami, Florida. Upon purchase, the wood was immediately labeled and certification of the treatment level was provided by Ace Hardware. The weathered wood sample (batch 5) was obtained from a pole barn owned by Florida Power and Light (FPL) Company. The pole barn is located outdoors at the Distribution Environmental facility of FPL located in West Palm Beach, Florida. The weathered wood sample was collected during two trips. One trip was conducted on May 31, 1998 and the other was conducted on June 2, 1998. The process of collecting the sample involved selecting an aged CCA-treated utility pole from the pole barn. The pole chosen during the May 31st sampling trip was dated June 1980; the one chosen during the June 2nd sampling trip was dated October 1980. The age of the weathered wood sample utilized for this study was therefore 18 years. No obvious forms of deterioration were noted on either utility pole. Slices about 1 to 2 inches in thickness were cut using a chain saw from the top, center, and butt-end of the pole to obtain a representative sample of the entire pole. The slices were then placed in acid-washed pre-labeled containers and covered. Upon receipt in the laboratory, the slices were further reduced into wedges using a hammer and chisel.

The control samples (batches 1 through 5) were then shredded in the laboratory. Shredding was accomplished using a 55 horsepower industrial shredder which was wiped prior to shredding to remove observable debris. The untreated wood sample was shredded first followed by samples with increasing retention levels (i.e. untreated, 0.25 pcf, weathered wood, 0.6 pcf, and 2.50 pcf). This order was chosen to minimize carry-over of the CCA chemical from one sample to the next. The shredded wood was collected in pre-acid washed 30-gallon plastic containers. Sample containers and tops were labeled immediately.

Batches 6, 7, and 8 were collected from wood waste piles from three C&D facilities distributed throughout Florida. Composite grab samples of chipped wood were collected in 35-gallon
plastic containers, with a minimum of 20 grabs from each pile. The facilities that were visited are termed for this paper as C&D 1, 2 and 3.

The last two batches were mixtures of untreated southern yellow pine (95% by weight) and CCA-treated wood at a 0.25 pcf retention level (5% by weight). These samples were designed to mimic the composition of typical C&D wood waste. The wood for these samples was purchased in 2"x 4" lengths from a retail store located in Gainesville, Florida. The samples were shredded into 1 inch pieces using a 5.5 horsepower shredder. All of the ash from these last two batches was provided to the University of Florida team for TCLP and SPLP analysis. Ash not utilized for TCLP and SPLP tests will be used for additional leaching tests.

**Figure II.1: Samples Processed For Experimentation**

| Batch 1 | Untreated Southern Yellow Pine. |
| Batch 2 | CCA-Treated Wood Type C. 0.25 pcf retention level. |
| Batch 3 | CCA-Treated Wood Type C. 0.60 pcf retention level. |
| Batch 4 | CCA-Treated Wood Type C. 2.50 pcf retention level. |
| Batch 5 | Weathered Wood. Utility pole treated with 0.6 pcf CCA Type C. |
| Batch 7 | Recycled Waste Wood from a C&D Recycling Facility, C&D 2. |
| Batch 9 | A mixture of CCA-Treated Wood (0.25 lb/ft³) and clean wood designed to mimic recycled C&D waste wood. |
| Batch 10 | Same as 9. |

**II.1.b Sample Incineration**

Samples were incinerated on July 7th and 8th 1998 using an industrial furnace (Al-Jon/United Inc.) which is owned and operated by Florida Power and Light (FPL), Distribution Environmental Facility located in West Palm Beach, Florida. The furnace is utilized by FPL to incinerate transformers containing polychlorinated biphenyls (PCBs). Prior to the burns a permit exemption was requested and granted by the Palm Beach Health Department, Air Pollution Control Division. The conditions of the permit exemption were monitored by the Health Department during the two day burn period.

The dimensions of the furnace were roughly 10 feet by 10 feet by 8 feet. The fuel utilized to initiate the burn was natural gas. Two grates and two catch pans were constructed by FPL to capture the ash. A schematic diagram of the grate and catch pan system is provided in figure II.2. Prior to the incineration process, the industrial furnace was broomed clean. The samples considered to contain the least amount of CCA were incinerated first followed by samples that contained progressively higher amounts of CCA. The order for sample incineration was as follows: batch 1, batch 6, batch 7, batch 8, batch 9, batch 10, batch 2, batch 5, batch 3, batch 4 (See Figure II.1 for a description of each batch). This order was chosen to minimize carry-over of the CCA chemical.

The incineration procedure involved cleaning the grate and catch pan with clean water and a wet-dry vacuum between samples. The water from the wet-dry vacuum was placed inside the FPL quencher. The bottom pan was towel dried and the grate was dried with compressed air. Tare weights were obtained for the bottom pan and grate at the beginning of the incineration process.

Sample application involved lining the grate with paper to avoid losing shredded wood pieces. A tare weight of the grate, bottom pan, and paper were recorded. Approximately one hundred
pounds of shredded wood sample were added to the grate. A sub-sample was then collected from the grate and placed in pre-labeled Zip-lock bags for moisture content analysis (Method 2540 B, Standard Methods 1995). The results of moisture content analysis are provided in table II.1. After sub-sample collection, the weight of the grate, catch pan, plus shredded wood sample was recorded. The grate, bottom pan, and sample were then placed in the furnace for approximately 1½ hours which was the time necessary to obtain a fine and powdery ash. During the 1½ hour period the burned wood chips were raked on two separate occasions to distribute the remaining unburned chips throughout the grate. The temperature of the primary chamber and after-burner were recorded once every 5 minutes. The after-burner temperature was always at or above 2200 °F. Ashing temperature curves for the primary chamber are provided in figure II.3. “Bumps” on these curves correspond to times when the sample was raked. Following the ashing process, the sample was removed from the incinerator and permitted to cool for 45 minutes. The grate and catch pan were reweighed to obtain an estimate for the % ash content of the wood. The ash was then removed from the catch pan using a clean dust pan and brush. Clean gloves, dust masks, and plastic aprons were worn by individuals collecting the ash. Ash samples were collected in pre-acid washed pre-weighed containers. Upon sample collection, containers were labeled and re-weighed. At least 500 g of sample were provided to the University of Florida research team and at least 200 g of sample were provided to the University of Miami team for subsequent analysis except for batches 9 and 10. The entire ash sample from batches 9 and 10 were provided to the University of Florida research team. Once samples were collected the grate and catch pan were cleaned and the process was repeated until all samples were ashed. A summary of this procedure is provided in figure II.4.
Figure II.3: Incinerator Temperatures (Primary Chamber) Versus Time

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>Sample I.D.</th>
<th>% Moisture Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Untreated Wood</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>CCA Treated Wood, 0.25 pcf</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>CCA Treated Wood, 0.60 pcf</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>CCA Treated Wood, 2.50 pcf</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>Weathered Wood</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>C&amp;D 1</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>C&amp;D 2</td>
<td>13</td>
</tr>
<tr>
<td>8</td>
<td>C&amp;D 3</td>
<td>12</td>
</tr>
<tr>
<td>9</td>
<td>Mixture 1</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>Mixture 2</td>
<td>12</td>
</tr>
</tbody>
</table>

Table II.1: Moisture Content
<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>The grate was placed inside the FPL quencher for cleaning. Pressurized water was applied to remove all debris. The grate was dried with compressed air.</td>
</tr>
<tr>
<td>2.</td>
<td>One corner of the bottom pan was elevated slightly by placing it on a piece of wood. The bottom pan was cleaned of residual ash by adding water and extracting the water and residual ash with a wet-dry vacuum. The water from the wet-dry vacuum was poured into the FPL quencher. The bottom pan was towel dried once all water and ash were removed.</td>
</tr>
<tr>
<td>3.</td>
<td>The grate and catch pan were placed on a weighing scale. The top of the grate was lined with paper. The weight of the grate and pan were recorded.</td>
</tr>
<tr>
<td>5.</td>
<td>100 pounds of wood sample were added to the pan. A wood sub-sample was placed in a plastic Zip-lock bag for moisture content analysis and labeled.</td>
</tr>
<tr>
<td>6.</td>
<td>The weight of the grate, bottom pan, and sample was recorded.</td>
</tr>
<tr>
<td>7.</td>
<td>The grate and bottom pan were placed in the furnace for approximately 1½ hours or until ash was fine and powdery. The maximum ashing temperature in primary chamber was approximately 1100 °F. The temperatures of the primary chamber and after-burner were recorded once every 5 minutes. During the 1½ hour period the ash was raked on two separate occasions.</td>
</tr>
<tr>
<td>8.</td>
<td>The pan was allowed to air cool for 45 minutes.</td>
</tr>
<tr>
<td>9.</td>
<td>Bottom pan with ash was reweighed.</td>
</tr>
<tr>
<td>10.</td>
<td>The ash was removed from the pan with a clean dust pan and brush. The ash sample was placed into pre-weighed pre-labeled sample containers. One set of sample containers with a minimum of 500 g of ash was provided to the University of Florida research team. The second set of containers with a minimum of 200 g ash was provided to the University of Miami. Containers were reweighed.</td>
</tr>
<tr>
<td>11.</td>
<td>The procedure was repeated for next sample. Note that batches for subsequent runs were prepared during waiting periods in steps 7 and 8.</td>
</tr>
</tbody>
</table>

Figure II.4: Summary of Incineration Procedure
II.2 LABORATORY METHODS

Laboratory analysis included measurements for the total amount of metal within each sample (section I.2.a) as well as measurements of the extractable fraction (sections I.2.b and I.2.c). Total metals concentrations in the samples were evaluated using neutron activation analysis. The results from neutron activation analysis were then checked against a computation method based upon measured retention values for the unburned wood samples and measurements of ash element ratios from energy dispersive x-ray fluorescence analysis (EDX). Total metals concentrations from neutron activation analysis were then compared to the extractable fractions.

Once samples were ashed, sub-samples from batches 1 through 10 were utilized by the University of Florida (UF) team for TCLP and SPLP tests and sub-samples from batches 1 through 8 were utilized by the University of Miami (UM) team for a solvent extraction study (figure II.5). Laboratory methods employed by each research team are provided in the following sections. Section I.2.b details the methods utilized at the University of Florida and section I.2.c corresponds to the work conducted at the University of Miami.

II.2.a Total Metals Analyses

Neutron activation analysis is based upon the bombardment of a sample with accelerated neutrons. After bombardment a sample will then emit a characteristic form of radiation that is dependent upon the amount and types of elements within a particular sample. Results from such analyses are considered to provide the absolute total metal concentration within a sample. Two sets of 1 gram samples were analyzed for total metals analyses. One set was provided on March 16, 1999 to Dr. William Vernetson, Director of the University of Florida’s Nuclear Reactor Facility located at the University of Florida campus in Gainesville, Florida. The second set was provided on September 1, 1999 to Dr. Michael Ames, Director of the Massachusetts Institute of Technology’s
Nuclear Reactor Facility located at the Massachusetts Institute of Technology campus in Cambridge, Massachusetts. Both sets were irradiated and counted during the month of October 1999.

The results from neutron activation analysis were then checked against a computation method. The computation method was considered to provide an order-of-magnitude estimate for the total metals concentrations. Calculations were based upon the following equation:

\[
C_a = \frac{C_u \cdot 10^6}{(AF) \cdot \rho_{\text{wood}}} \cdot (1 - F)
\]

equation 2.1

where:
- \( C_a \) = metal concentration in the ash (mg metal per kg ash)
- \( C_u \) = metal concentration in the unburned wood (pounds per cubic foot)
- \( AF \) = fraction of the original wood weight (dry wood basis) that becomes ash (pounds of ash per pound of wood)
- \( \rho_{\text{wood}} \) = density of wood (pounds per cubic foot)
- \( F \) = Fraction of metal that is volatilized during incineration (pounds of metal volatilized per pound of metal in unburned sample)

The density of southern yellow pine is approximately 32 pounds per cubic foot (AWPA, 1998). The weight of the chemical in the wood is significant and was added to the density of Southern Yellow Pine to estimate of “\( \rho_{\text{wood}} \)”. Values of “\( \rho_{\text{wood}} \)” used for the 0.25 pcf, 0.60 pcf, 2.50 pcf, and weathered wood sample were 32.34, 32.92, 35.42, and 32.89 pounds per cubic foot, respectively. The value of “\( C_u \)” was computed from measured values of CCA retention for the unburned samples. Retention measurements were coordinated through Bill Gay of Langdale Forest Products and Ken Cogan of Hickson Corp. Samples were first sent to Bill Gay. These samples along with the residual dust used for analysis were then provided to Ken Cogan for confirmatory analysis. Analyses conducted at Langdale Forest Products utilized an ASOMA X-ray Spectrometer Model 111. Samples were analyzed four times at Hickson Corp. Two set of analyses were conducted on an ASOMA X-ray Spectrometer Model 200. The last two sets of analyses were conducted on an ASOMA X-ray Spectrometer Model 200T. The value of “\( AF \)” used for computation purposes was 0.13. The value of “\( F \)” was assumed equal to zero for chromium and copper. This assumption is consistent with a 1100 °F (600 °C) incineration temperature and reported volatilization rates in laboratory-scale studies (McMahon et al. 1986; Hirata et al. 1993; Pasek 1994). The value of “\( F \)” for arsenic was determined from measured ratios of arsenic to copper or chromium. These ratios were obtained from EDX analyses. EDX analysis was conducted at the University of Miami Center for Advanced Microscopy. The instrument used was a Philips XL30 environmental scanning electron microscope with a field emission gun suitable for x-ray analysis. All samples were analyzed in quadruplicate under the supervision of Dr. Matthew Lynn.

EDX and retention level measurements were not suitable for untreated wood and for the three C&D samples, however, due to the sensitivity of the method and the relatively low metals concentrations. For the untreated wood, the initial metals concentrations were obtained from literature values (Atkins and Fehrs, 1992; Fehrs, 1995; McGinnis, 1995). It was then assumed that the amount of arsenic volatilized was equal to the average values observed for measured samples. The concentrations for samples collected from the C&D facilities were based upon the assumption that the metals in the leachate samples were from either treated (0.25 pcf) or untreated wood. The fraction of CCA-treated wood in each C&D sample as analyzed through the solvent extraction study (section II.2.c) was then computed from mass balance. The computation method used was similar
to that described by Tolaymat et al. 1999 and Solo-Gabriele et al. 1998. Samples were analyzed in triplicate.

II.2.b  Laboratory Methods, TCLP and SPLP, and Total Recoverable Metals Analyses

Laboratory methods for this phase of the study included pre-processing of the ash prior to analysis, followed by the extractions which included TCLP and SPLP, and total recoverable metals analyses.

Pre-Processing of Ash

Previous studies (Shieh 1998; Gifford and Dare 1998) have indicated that different ash particle sizes leach metals at different rates. Ash samples collected contained a mixture of fine, powdery, gray material that averaged less than 2 mm in diameter and larger black cinders that averaged in size from 5 to 10 mm in diameter. Given this variability, the samples for TCLP, SPLP, and total recoverable metals analyses were separated into different size fractions before analysis. The results for each size fraction for a given sample could be weighted and combined to report the concentration for that sample as a whole. Figure II.6 presents the schematic for the size separation procedure.

Two factors limited the available options for the separation process. First, the TCLP and SPLP tests dictate that samples be able to pass through a 0.125 inch sieve (equivalent passing particle size = 9.75 mm) after crushing. Additionally, the amount of each sample was limited so that there was not enough ash to separate the original sample into more than two size fractions. Visual observation of each of the samples was utilized to determine an appropriate size sieve to use for separation.

The first step in the size fractionation process was the utilization of a #4 sieve (equivalent passing particle size = 4.75 mm) to separate each original sample into a large (>4.75 mm) and small (<4.75 mm) fraction. From there the small fraction was thoroughly mixed and a sub-sample was taken for moisture content analysis. The large fraction was screened using a 0.125 inch (9.75 mm) sieve since the TCLP and SPLP tests require that the sample particle size be less than this value. The ash particles retained on the sieve were gently crushed to the point where they would just pass through the sieve. As with the small fraction, the large fraction was thoroughly mixed and a sub-sample was taken for moisture content analysis. Proper care was taken throughout this entire process to ensure that no contamination and minimal loss of sample occurred.

A summary of the size fractionation process is provided in table A.1 in appendix A. The mass of ash retained on the sieve (the large fraction) ranged from 2.7% (sample C&D 1) to 37.5% (5% CCA a). Please note that both size fractions were analyzed separately for all samples, with the exception of sample 4. Sample 4 was recombined for further experiments due to limited sample size.

The TCLP and SPLP tests recommend that at least 100g of sample be utilized for testing, whereas total metals analysis requires 1-2 g of material. While the majority of the testing followed these guidelines, smaller sample masses were selected on several occasions due to an insufficient quantity of ash. When smaller sample masses were used, the volume of the leaching fluid was adjusted accordingly to provide the recommended 20 to 1 liquid to solid ratio (by mass), as described by Gifford and Dare, 1998. A summary of the sample size used for each test is provided in table A.2 in appendix A. Please note that samples were analyzed in duplicate and are noted as run A and run B in table A.2.
Figure II.6: Flow Diagram of Sample Processing Procedure Used for Samples Processed by U.F.

TCLP

The first step in the TCLP process was the selection of the proper extraction fluid based upon the pH of the sample. If the pH of the sample was less than 5.0, then extraction fluid #1 (pH of 4.93) was selected. If the pH of the sample was greater than 5.0, then extraction fluid #2 (pH of 2.88) was chosen. By basing the selection on the characteristics of the waste itself, the procedure compensated for the buffering capacity of the waste. Following this step, each sample was thoroughly mixed and then a 100g portion of the sample was transferred to a 2L-polyethylene container using an acid-rinsed spoon. Then 2L of the appropriate extraction fluid were added to the container resulting in the 20:1 liquid/solid ratio that the method required. The container was then placed on a rotary extractor (Analytical Testing Corporation) for 18 (+/- 2) hours. After rotation, the sample was pressure filtered using an acid-rinsed glass fiber filter (Whatman 41). The pH of the leachate was measured. Concentrated nitric acid was then added as a preservative to lower the pH of the samples below 2. Samples were then stored at 4° C until analysis.

The next step in preparing the ash samples for analysis was to conduct a liquid acid digestion according to EPA SW-846 Methods 3010 and Method 7060 A (EPA 1994). Method 3010, which is for flame atomic absorption (AA) analysis, involves the digestion of 100 ml of aqueous sample on a hot plate with nitric acid and hydrochloric acid. The digestion procedure used for arsenic in the leachate was EPA method 7060A (EPA1994). This method involves the digestion of 100 ml of aqueous sample on a hot plate with hydrogen peroxide and nitric acid.

A Perkin Elmer atomic absorption spectrophotometer (Model 5100) equipped with a flame atomizer was used for the analysis of chromium and copper. Arsenic was also analyzed on the Perkin Elmer 5100 but sample atomization was accomplished with a graphite furnace (HGA 600). The results are determined in units of mg of metal (As, Cu, or Cr) per liter of leachate.
The SPLP test, EPA SW-846 Method 1312, is essentially the same as the TCLP test, with the exception that a different extraction fluid is used (EPA 1994). For locations east of the Mississippi River, extraction fluid #1 is used. This fluid is a combination of sulfuric and nitric acids that results in a pH of approximately 4.20. With the exception of the initial waste pH determination, each of the steps is exactly the same as the TCLP test. The results are determined in units of mg of metal (As, Cu, or Cr) per liter of leachate.

Total Recoverable Metals

The digestion procedure used for metals analysis of chromium and copper in the leachate was EPA method 3050 (EPA 1994). This method involved the digestions of 2 g of sample on a hot plate with nitric acid and hydrogen peroxide. The results were determined in units of mg of metal (As, Cu, or Cr) per kg of ash.

Quality Assurance\Quality Control

All analysis was performed in accordance with EPA SW-846 methodology as outlined in the University of Florida Environmental Engineering Sciences Solid and Hazardous Waste Research Program’s Comprehensive Quality Assurance Plan #960218. The results of the analysis on the appropriate blanks and matrix spikes are presented in table A.11 which is located in appendix A.

II.2.c Laboratory Methods, Solvent Extraction Study

The purpose of the solvent extraction study was to identify a solvent that could extract metals for ash treatment purposes. Solvents tested included: a) those found to remove metals from unburned wood, such as citric acid and a combination of sodium hydroxide (NaOH) and citric acid (Warner and Solomon 1990; Cooper 1991; Smith and Shiau 1997) and, b) those typically used in sequential extraction procedures for soils, such as distilled water (DW), magnesium chloride (MgCl₂), hydrogen peroxide (H₂O₂), hydroxylamine hydrochloride (HH), acetic acid, nitric acid (HNO₃), and hydrochloric acid (HCl) (Tessier 1970; Gatehouse 1977; Chao and Zhou 1983). Following each solvent extraction, a total recoverable metals (TRM) analysis was conducted using the U.S. Environmental Protection Agency (EPA) method 3050 B (EPA 1994). All results are provided in terms of mg of metal extracted versus kg of ash, as a percent of the total amount of metal present in the sample, or as mg/L within the leachates produced. After extraction, the leachates were analyzed for chromium and copper on an atomic absorption spectrophotometer. Arsenic was analyzed using a colorimetric method. More details of the laboratory procedures are provided below.

Sample Preparation and Processing

All glassware and pipettes used in the analysis were pre-acid washed using 1 N HNO₃. Reagent blanks were prepared with each set of samples. For each sample, between 1 to 2 grams of ash were placed into a 125 ml Phillips beaker. Reagents for the solvent extraction study were added to the beaker for the specified period of time. The leachates were filtered through paper filter (Whatman No. 41, pore size > 20-25 μm, 10.5 cm diameter) and brought-up to a 100 ml volume. Leachate samples were diluted as required to provide concentrations within the limit of quantification for subsequent metals analyses. The residual ash was dried and reweighed. After drying, TRM analysis was conducted on the residual ash. The leachate from the TRM analysis was filtered as
described earlier and brought-up to a 100 ml volume. Samples were again diluted as required to provide concentrations within the limit of quantification.

**Solvent Extractions**

A total of 10 extractions were conducted (figure II.7). The first two extractions, distilled water and magnesium chloride, were designed to determine the water soluble and ion-exchangeable fractions of the metals in the ash samples, respectively. The next two solvents, hydrogen peroxide and hydroxylamine hydrochloride are strong oxidants and reductants, respectively. The remaining six extractions utilized either weak or strong acids to remove the metals from the ash. The last of these six extractions was a total recoverable metals test which employed a combination of concentrated acids and hydrogen peroxide to extract metals. Detailed procedures for each solvent extraction are provided in table II.2. A summary of the abbreviations utilized to describe each extraction is provided in table II.3. After each extraction, the solution was placed into 125 ml polyethylene bottles and labeled. Each set of samples was stored in catalogued Zip-lock plastic bags until analysis.

**Analysis for Copper, Chromium, and Arsenic**

Extractants were analyzed for copper and chromium using an atomic absorption spectrometer (AAS) fitted with a flame atomizer (Perkin Elmer Model 372). For each metal the procedure utilized was the same except for the analytical wavelength and different hollow cathode lamps. Calibration curves were developed from the following four standards prepared in 1% HNO$_3$: 0.1 mg/L, 1 mg/L, 10 mg/L, and 50 mg/L. Standards were run with every set of nine samples. A set included a reagent blank and extractants from ashed samples of untreated wood, treated wood at 0.25 pcf, 0.60 pcf, and 2.50 pcf retention levels, weathered wood, and three recycled wood waste samples from different C&D facilities. All sets including calibration standards were analyzed in triplicate. Data collection involved aspirating the sample through the AAS until the absorption reading on the display was steady. Between two successive samples distilled water was aspirated for cleaning purposes.

The silver diethyldithiocarbamate method (*Standard Methods*, 3500-C As) was utilized for arsenic analysis. The method involves reducing oxidized forms of arsenic using aqueous sodium borohydride to arsine gas (AsH$_3$). The arsine generated was swept by a stream of nitrogen gas from the reaction vessel through a scrubber into an absorber tube containing silver diethyldithiocarbamate and morpholine dissolved in chloroform. The presence of arsine in this solution causes the production of a red color, the intensity of which is proportional to the amount of arsine gas generated. The intensity of the color was measured at a wavelength of 520 nm using a spectrophotometer (Milton Roy Spectronic 20). Results were compared to calibration standards of 1 µg, 2.5 µg, 5 µg, and 10 µg as As.

After each sample run for Cu, Cr, and As, the absorption values were recorded in a tabular form in a lab notebook for further calculation using customized computer programs and Excel spreadsheets.
<table>
<thead>
<tr>
<th>Extraction Number</th>
<th>Name</th>
<th>Description</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Distilled Water (DW)</td>
<td>Add 10 ml distilled water, soak for 1 hour. Shake 20 min. on shaker. During the transfer of the supernatant solutions add 1 ml of conc. HNO₃ in the 100 ml volumetric flask.</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>Magnesium Chloride (MgCl₂)</td>
<td>Add 10 ml of 1 M MgCl₂ (pH 7.0), shake and wait 1 hr. Then add 10 ml of 1 M ammonium acetate.</td>
<td>b</td>
</tr>
<tr>
<td>3</td>
<td>Hydrogen Peroxide (H₂O₂)</td>
<td>Add 4 ml of 30% H₂O₂. Heat to 60°C until the initial reaction has ceased. Add some more H₂O₂ in 0.5 ml lots until the initial reaction has ceased. Takes 8-12 hours.</td>
<td>a</td>
</tr>
<tr>
<td>4</td>
<td>Hydroxylamine Hydrochloride (HH)</td>
<td>Add 10 ml of a 1 M hydroxylamine hydrochloride/1 M ammonium acetate solution. Shake 20 min. and decant through filter paper into 100 ml volumetric flasks. Repeat twice and bring flasks up to volume (100 ml) with de-ionized distilled water.</td>
<td>a</td>
</tr>
<tr>
<td>5</td>
<td>Acetic Acid</td>
<td>Soak ash in 60 ml concentrated glacial acetic acid. Shake for 30 min. and soak the sample for an additional 24 hours.</td>
<td>c</td>
</tr>
<tr>
<td>6</td>
<td>Citric Acid</td>
<td>Soak ash in 60 ml of 1 M citric acid. Shake for 30 min. and soak the sample for an additional 24 hours.</td>
<td>c</td>
</tr>
<tr>
<td>7</td>
<td>Nitric Acid (HNO₃)</td>
<td>Soak ash in 60 ml of concentrated nitric acid. Shake for 30 min. and soak the sample for an additional 24 hours.</td>
<td>c</td>
</tr>
<tr>
<td>8</td>
<td>Hydrochloric Acid (HCl)</td>
<td>Soak ash in 60 ml of concentrated hydrochloric acid. Shake for 30 min. and soak the sample for an additional 24 hours.</td>
<td>d</td>
</tr>
<tr>
<td>9</td>
<td>Sodium Hydroxide (NaOH) plus Citric Acid</td>
<td>Prepare a solution with 1 g NaOH and 1.50 g citric acid in 1 L of distilled water. Add 50 ml of the leaching solution to the ash. Shake for 10 min and leave overnight.</td>
<td>e</td>
</tr>
<tr>
<td>10</td>
<td>Total Recoverable Metals, EPA Method 3050B</td>
<td>Soak ash in 10 ml of 1:1 HNO₃ and heat to 95°C for 10 to 15 min. Allow sample to cool, add 5 ml of conc. HNO₃, and reflux for 30 min. Repeat previous step until no brown fumes are given off, heat sample to 95°C for 2 hrs and then cool sample. Add 3 ml of 30% H₂O₂ and heat for 2 hrs. then cool sample. Add 10 ml of conc. HCl and reflux for 15 min.</td>
<td>f</td>
</tr>
</tbody>
</table>

1 The description corresponds to the point after 1 to 2 grams of ash was transferred to a 125 ml Phillips beaker. At the end of the extraction all samples were filtered into a 100 ml volumetric flask and brought to volume with de-ionized distilled water.


Table II.2: Summary of Solvent Extraction Procedures
<table>
<thead>
<tr>
<th>Solvent Extract</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>DW</td>
</tr>
<tr>
<td>Magnesium Chloride</td>
<td>MC or MgCl₂</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>Pero or H₂O₂</td>
</tr>
<tr>
<td>Hydroxylamine Hydrochloride</td>
<td>HH</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>Acetic</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>Citric</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>Nitric or HNO₃</td>
</tr>
<tr>
<td>Hydrochloric Acid (HCl)</td>
<td>HCl</td>
</tr>
<tr>
<td>Sodium Hydroxide plus Citric Acid</td>
<td>SHC</td>
</tr>
<tr>
<td>Total Recoverable Metals</td>
<td>TRM</td>
</tr>
</tbody>
</table>

Table II.3: Abbreviations Utilized to Describe Each Extraction

Figure II.7: Schematic Diagram of Solvent Extraction Study
Quality Assurance\Quality Control

Analyses were conducted in accordance with the University of Miami’s Environmental Engineering Laboratory Comprehensive Quality Assurance Plan #980068, as approved by the Florida Department of Environmental Protection during April 1998.

Contamination of samples during processing was negligible as indicated by reagent blanks which were run with every experimental set. Reproducibility of the metal’s results for a given leachate were excellent within 5% as indicated by replicate analysis. More variability (+- 25%) was observed between different sub-samples which originated from the same batch. This variability was attributed primarily to sample heterogeneity within a given batch. Results from sample spike analysis indicate sample recoveries greater than 70%.
II.3 LABORATORY RESULTS

Results are presented for total metals analysis (section II.3.a), TCLP and SPLP tests (section II.3.b), and solvent extraction study (section II.3.c).

II.3.a Laboratory Results, Total Metals

Computation Method for Estimating Cr, Cu, and As in Ash Samples

The computation of metals concentrations for the 0.25 pcf, 0.60 pcf, 2.50 pcf, and weathered wood samples involved measurements of retention levels for unburned wood, "C_u," for all metals and "F" for arsenic (see section II.2.a). The measured values of "C_u" were consistent between Langdale Forest Products and Hickson Corporation. On average, the untreated, 0.25 pcf, 0.60 pcf, 2.50 pcf, and weathered wood samples were characterized by the following retention levels, respectively: 0.016 pcf, 0.34 pcf, 0.92 pcf, 3.42 pcf, and 0.89 pcf (table II.4). As observed from this data, the C_u values were higher, by 30 to 50%, than their rated value. These results emphasize the importance of measuring the retention values of samples prior to conducting solvent extraction studies.

The results from EDX analysis (table II.5) were used to compute "F" for arsenic. The method for computing "F" involved first checking the measured data with the theoretical value of Cr/Cu. Once the data were checked, the values of "F" for arsenic were computed. Results from EDX analysis indicate that the measured ratios of chromium to copper (1.48 on average) were within the range of theoretical values (1.38 to 1.93). The computation of the theoretical values assumes that no chromium or copper was volatilized during incineration and that the CCA is composed of CCA type C containing acceptable ranges of chromium and copper oxides as indicated by the 1998 AWPA Standards. The acceptable range for CrO_3 is from 44.5 to 50.5%, by weight, and the range for CuO is 17.0 to 21.0%. Given these ranges the theoretical ratio for Cr to Cu can vary from 1.38 to 1.93. The measured value of 1.48 is toward the lower end of this range. The recommended absolute composition of CCA type C as published by the AWPA is 47.5% for CrO_3, 18.5% for CuO, and 34.0% for As_2O_3. The chromium to copper ratio for this absolute composition is 1.67. Similarly, assuming that no arsenic volatilizes, the theoretical ratios of arsenic to copper and arsenic to chromium were computed as 1.50 and 0.90, respectively.

The difference between the theoretical value of As/Cu and As/Cr assuming no volatilization and the measured values were then used to compute the percent arsenic volatilized, "F," for each sample. The average percent volatilized was computed as 34%, 0%, 22%, and 18% for the 0.25 pcf, 0.60 pcf, 2.50 pcf, and weathered wood samples, respectively. The "F" value computed from As/Cu and As/Cr varied somewhat for the same samples. The most variability was observed for the 0.25 pcf sample for which the % As volatilized was computed as 40% from As/Cu and 28% from As/Cr.

The metals concentrations for the 0.25 pcf, 0.60 pcf, 2.50 pcf, and weathered wood samples were computed given the "C_u" and the "F" values determined above (table II.6). The metals concentrations are on the order of tens of thousands mg/kg for the 0.25 pcf, 0.60 pcf, and weathered wood samples and 100,000's mg/kg for the 2.50 pcf sample.

The metal concentrations of the untreated samples (table II.6), which were obtained from literature values, ranged from 25 mg/kg for arsenic to 175 mg/kg for chromium. The results of leaching tests indicate that the average fraction of CCA-treated wood in the C&D samples were 22%, 8.6%, and 8.7% respectively for facility 1, 2, and 3. These fractions were then utilized with the data in rows 2 and 3 in table II.6 to compute the total amount of copper, chromium, and arsenic in each...
sample. This computation indicates that the chromium concentrations for the C&D samples should range from 1,800 mg/kg to 4,500 mg/kg. Copper should be in the range of 1,100 mg/kg to 2,700 mg/kg and arsenic should be in the 1,000 to 2,600 mg/kg range. In a similar fashion as for the C&D samples, the values of the 5% CCA-treated wood mixtures (5% CCA at 0.25 pcf and 95% untreated wood) were used with the data in rows 2 and 3 in table II.6 to compute the total amount of copper, chromium, and arsenic in these samples. The 5% CCA ash samples should contain roughly 1,200 mg/kg, 680 mg/kg, and 600 mg/kg of chromium, copper, and arsenic, respectively.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Retention Level, pcf</th>
<th>Langdale Analysis</th>
<th>Hickson Analysis</th>
<th>Average of Langdale &amp; Hickson</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>#1</td>
<td>#2</td>
<td>#3</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.006</td>
<td>0.05</td>
<td>0.0</td>
<td>0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>0.352</td>
<td>0.32</td>
<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>0.933</td>
<td>0.89</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>3.229</td>
<td>3.42</td>
<td>3.77</td>
<td>3.49</td>
</tr>
<tr>
<td>Weathered</td>
<td>0.92</td>
<td>0.83</td>
<td>0.87</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Table II.4: Initial Retention Level of Unburned Wood Samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Cr/Cu Ave</th>
<th>Cr/Cu Std dev</th>
<th>As/Cu Ave</th>
<th>As/Cu Std dev</th>
<th>% As Vol.</th>
<th>As/Cr Ave</th>
<th>As/Cr Std dev</th>
<th>% As Vol.</th>
<th>Overall % As Volatilized</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 pcf</td>
<td>1.39</td>
<td>0.26</td>
<td>0.90</td>
<td>0.42</td>
<td>40</td>
<td>0.64</td>
<td>0.26</td>
<td>28</td>
<td>34</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>1.59</td>
<td>0.25</td>
<td>1.44</td>
<td>0.37</td>
<td>5</td>
<td>0.95</td>
<td>0.23</td>
<td>-5</td>
<td>0</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>1.44</td>
<td>0.06</td>
<td>1.08</td>
<td>0.09</td>
<td>28</td>
<td>0.75</td>
<td>0.05</td>
<td>17</td>
<td>22</td>
</tr>
<tr>
<td>Weathered</td>
<td>1.50</td>
<td>0.06</td>
<td>1.16</td>
<td>0.05</td>
<td>23</td>
<td>0.78</td>
<td>0.05</td>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td>Theoretical Value No Volatilization</td>
<td>1.67</td>
<td>-----</td>
<td>1.50</td>
<td>-----</td>
<td>-----</td>
<td>0.90</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
</tbody>
</table>

Table II.5: Results from EDX analysis
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Sample I.D. Abbreviation</th>
<th>Metals Concentration, mg metal per kg of ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Untreated Wood Ash</td>
<td>Untreated</td>
<td>175</td>
</tr>
<tr>
<td>Ash from Wood Treated at 0.25 pcf</td>
<td>0.25 pcf</td>
<td>19,800</td>
</tr>
<tr>
<td>Ash from Wood Treated at 0.60 pcf</td>
<td>0.60 pcf</td>
<td>53,000</td>
</tr>
<tr>
<td>Ash from Wood Treated at 2.50 pcf</td>
<td>2.50 pcf</td>
<td>183,500</td>
</tr>
<tr>
<td>Ash from Weathered Wood</td>
<td>Weathered</td>
<td>51,400</td>
</tr>
<tr>
<td>Ash from Recycled Wood Waste, C&amp;D Facility #1</td>
<td>C&amp;D 1</td>
<td>4,500</td>
</tr>
<tr>
<td>Ash from Recycled Wood Waste, C&amp;D Facility #2</td>
<td>C&amp;D 2</td>
<td>1,860</td>
</tr>
<tr>
<td>Ash from Recycled Wood Waste, C&amp;D Facility #3</td>
<td>C&amp;D 3</td>
<td>1,880</td>
</tr>
<tr>
<td>Ash from Laboratory Mixture of Untreated Wood (95%) and CCA-Treated Wood at 0.25 pcf (5%)</td>
<td>5% CCA a</td>
<td>1,160</td>
</tr>
<tr>
<td>Same as Above</td>
<td>5% CCA b</td>
<td>“</td>
</tr>
</tbody>
</table>

Table II.6: Computed Total Metals Concentrations in Each Sample

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>MIT Reactor (mg/kg)</th>
<th>UF Reactor (mg/kg)</th>
<th>Average (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
<td>Cu</td>
<td>As</td>
</tr>
<tr>
<td>Untreated Wood Ash</td>
<td>84</td>
<td>522</td>
<td>38</td>
</tr>
<tr>
<td>Ash from Wood Treated at 0.25 pcf</td>
<td>29,000</td>
<td>14,300</td>
<td>14,200</td>
</tr>
<tr>
<td>Ash from Wood Treated at 0.60 pcf</td>
<td>68,300</td>
<td>44,800</td>
<td>58,500</td>
</tr>
<tr>
<td>Ash from Wood Treated at 2.50 pcf</td>
<td>162,000</td>
<td>93,900</td>
<td>93,600</td>
</tr>
<tr>
<td>Ash from Weathered Wood</td>
<td>65,200</td>
<td>54,800</td>
<td>42,700</td>
</tr>
<tr>
<td>Ash from Recycled Wood Waste, C&amp;D Facility #1</td>
<td>1,100</td>
<td>1,400</td>
<td>730</td>
</tr>
<tr>
<td>Ash from Recycled Wood Waste, C&amp;D Facility #2</td>
<td>1,860</td>
<td>2,090</td>
<td>1,310</td>
</tr>
<tr>
<td>Ash from Recycled Wood Waste, C&amp;D Facility #3</td>
<td>3,530</td>
<td>1,900</td>
<td>2,250</td>
</tr>
</tbody>
</table>

Table II.7: Results from Neutron Activation Analysis
Neutron Activation Analysis

Results indicate that the computed metals concentrations (table II.6) were within the same order-of-magnitude as the values obtained from neutron activation analysis (table II.7). For the samples containing high metals concentrations (the 0.25 pcf, 0.60 pcf, 2.50 pcf, and weathered wood samples) the concentrations were within 10 to 20%. Neutron activation results between the MIT and UF reactors were also within the same order-of-magnitude. Differences in the results between each facility may be due to sample heterogeneity and differences in sample processing and analytical methods.

The average of: 1) the results from both reactor facilities (last three columns in table II.7) and 2) the computed values (last three columns in table II.6) were used to compute % metals removals by the various solvents.

II.3.b Laboratory Results, TCLP and SPLP

The results of the SPLP and TCLP experiments are presented in tabular form for each metal in the tables A.5 through A.10 in appendix A. Results (figures II.8 through II.10) show that arsenic followed the most predictable pattern. The leachable concentration for arsenic (figure II.10) was greatest in the CCA-treated wood samples with the greatest standard retention values (0.6, 2.5 pcf). The samples from the C&D recycling facilities and the premixed wood displayed measurable, but lower values. This trend was observed for both extractions. Copper (figure II.8) displayed a similar pattern, although the leachate concentrations were below detection limit (0.1 mg/l) for many of the samples, especially the SPLP samples. The chromium results (figure II.9) did not follow a predictable pattern and are similar to those presented later in the solvent extraction study. The greatest concentrations of leachable chromium were observed in the 0.25 pcf sample, while the 2.5 pcf sample had much smaller concentrations of chromium in the leachate. These results, although not as anticipated, were consistent with the results of the acetic acid extraction, an entirely independent analysis, conducted during the solvent extraction study (section II.3.c). The consistency between the two independent methods supports the validity of the results which indicate that chromium in the ash produced from samples containing lower CCA retention levels is apparently more mobile using an acetic acid solution. One hypothesis for this finding is that at higher retention levels, a greater proportion of the metals are bound in insoluble metal-metal solids, whereas at lower retention levels the likelihood of forming these acetic-acid insoluble metal-metal species is reduced, thereby resulting in the observed trend. This hypothesis is further discussed in section II.3.c.

Impact of Particle Size

The data in tables A.5 through A.10 in appendix “A” present the TCLP and SPLP leaching results for two different size fractions (with the exception of sample 4). The objective of the size fractionation employed in the methodology was not to characterize heavy metal concentration and leaching over a wide range of particle sizes, but rather to examine the characteristics of the larger “embers” and the very fine dust. The majority of the mass was associated with the fine ash, and thus this fraction would control the average properties of an ash sample. The results indicated that the particle size did have some impact (figure II.7a). In the case of arsenic which dominates the upper portion of figure II.7a, more arsenic was leached per unit mass from the finer ash relative to the larger ash particles as can be observed by the majority of the points falling significantly below the 1 to 1 line. For chromium, the same trend was observed. The opposite relationship was observed for a few of the copper data points where more copper was leached from the larger particles relative to the small
particles.

Comparison of TCLP and SPLP

The average leachate results for each size fraction were averaged for each sample based on the mass contribution of each fraction. These average results were then plotted for both TCLP and SPLP separately for each metal. A logarithmic scale was chosen for the presentation of results (figures II.8, II.9, and II.10) because of the wide range of sample concentrations.

The TCLP leachate concentrations were consistently greater than the SPLP leachate concentrations for both arsenic and copper. This was not the case, however, as the chromium concentrations in the SPLP leachate were often close to the TCLP, many times being slightly greater.

The Final pH of the Leaching Tests

An important measurement when conducting a standardized leaching test is the pH of the final solution. Although the pH of the TCLP fluid may be greater than the SPLP fluid (4.93 versus 4.20), the pH that occurs during the actual 18 hours of leaching may be different. There are more equivalents of acid in the TCLP fluid than the SPLP fluid. In a waste sample that is well buffered, the TCLP fluid will result in a lower average pH during the 18 hours of leaching relative to the SPLP. In a waste sample that has little or no buffering capacity, the average pH may be lower in the SPLP over the 18 hours. A measurement of the final pH thus provides some indication of the relative “aggressiveness” of the tests.

The initial and final pH of the TCLP leaching fluid are presented in table A.3 in appendix A. The final pH of the SPLP leaching fluid is presented in table A.4. The final pH from the TCLP ranged from 5.0 to 6.7. The final pH from the SPLP ranged from 4.7 to 12.3. The wide range of pH observed with the SPLP experiments likely results from the reasons indicated above. The lowest pH for both tests was observed with sample 4 (2.5 pcf CCA). In this case, the SPLP resulted in a lower pH than the TCLP. The alkalinity of this sample was apparently small. The remainder of the SPLP pH measurements was greater than the TCLP pH measurements. The samples with the highest SPLP pH values were the same as those samples that required the lower pH TCLP fluid. These samples included the C&D recycling facility samples that could possibly have a greater alkalinity as a result of some inorganic materials such as limestone being present. The other samples were mixes of CCA wood with clean wood, and thus the added buffering capacity may also have been a result of changing combustion conditions that occurred throughout the process. It is of interest to note that the final pH of the leaching fluid decreased with increasing retention value.
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Arsenic Conc. (mg/L)</th>
<th>Chromium Conc. (mg/L)</th>
<th>Copper Conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TCLP</td>
<td>SPLP</td>
<td>TCLP</td>
</tr>
<tr>
<td>Untreated</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>50.65</td>
<td>58.57</td>
<td>5.98</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>133.04</td>
<td>265.35</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>510.57</td>
<td>561.17</td>
<td>1.88</td>
</tr>
<tr>
<td>Weathered</td>
<td>199.4</td>
<td>161.5</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>3.46</td>
<td>0.79</td>
<td>24.1</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>0.21</td>
<td>0.29</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>6.74</td>
<td>0.54</td>
<td>2.72</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>5.16</td>
<td>1.09</td>
<td>0.16</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>8.39</td>
<td>2.42</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Regulatory Limit*</td>
<td>5.0</td>
<td>0.05</td>
<td>5.0</td>
</tr>
</tbody>
</table>

* TCLP Limits from 40CFR 261.24, Florida GWGC Criteria from FAC 62-777, GWGC Criteria listed under SPLP Column

Table II.8: Summary of TCLP and SPLP Results Conducted on CCA-Treated Wood Ash

---

**Figure II.7a:** TCLP and SPLP Metal Concentrations for Small and Large Fraction of Ash
Figure II.8: TCLP and SPLP Results for Copper
Figure II.9: TCLP and SPLP Results for Chromium
Figure II.10: TCLP and SPLP Results for Arsenic
II.3.c Laboratory Results, Solvent Extraction Study

A summary of the results in tabular format are provided in tables B.1 to B.6 in appendix “B.” A subset of the figures developed during the analysis of the data are provided within the following pages. Subsequent discussion of results are organized by metal. One section is included for each of the following metals: copper, chromium, and arsenic.

Copper

Less than 14% of the total copper was extracted with the following five solvents, distilled water, magnesium chloride, hydrogen peroxide, hydroxylamine hydrochloride, and citric acid with sodium hydroxide (figure II.11). Slightly better performance was obtained from the acetic and citric acids which extracted between 4 and 28% of the total copper. The best results were obtained from the total recoverable metals extraction and from hydrochloric and nitric acids. The highest percent extractions (between 76 and 100% in three cases) were obtained using nitric acid on the ash produced from the 0.60 pcf sample and ash samples from wood collected at C&D recycling facilities. It is interesting to note the nitric acid extraction and in some cases the hydrochloric acid extraction performed better than the TRM extraction. Recall that the TRM extraction is conducted with hydrogen peroxide and concentrated hydrochloric and nitric acids under heated conditions. The entire procedure takes roughly 4 to 6 hours, whereas the nitric and hydrochloric acid extractions require a 24 hour contact time with the ash. This increased contact time is one likely reason for the enhanced removal using either nitric or hydrochloric acid alone.

The percent removals using nitric acid for all samples (figure II.12) varied from 26 to 100%, with the lowest removals corresponding to the 2.50 pcf and C&D 1 samples. The greatest removals were associated with the remaining C&D samples and the 0.25 pcf and 0.60 pcf samples.

Although percent removals were generally small for the 2.50 pcf sample, the total mass of metal leached from this sample was the highest among those tested. This observation is evident in figure II.13 where the leachate concentration for the 2.50 pcf sample was over 900 mg/L as Cu, whereas the 0.60 pcf, weathered wood, and the 0.25 pcf sample contained leachate concentrations of 500 mg/L, 440 mg/L, and 150 mg/L, respectively. The leachate concentrations from the C&D samples were less than 30 mg/L and the concentration of the untreated wood sample was below detection. These results are consistent with the relative amount of CCA chemical in each sample, where the lowest concentration corresponds to the untreated wood sample; the next highest are the C&D samples; the remaining concentrations proceed from 0.25 pcf, weathered, 0.60 pcf, to 2.50 pcf.

A comparison of leachate concentrations for all solvents for selected samples is provided in figure II.14. Of interest is the fact that all four graphs in this figure possess the same general shape with the lowest leachate concentrations corresponding to distilled water, magnesium chloride, hydrogen peroxide, and hydroxylamine hydrochloride extractions and the highest leachate concentrations corresponding to the hydrochloric acid, nitric acid, and the total recoverable metals extractions.
Figure II.11: % Copper Removal for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Figure II.12: % Removal of Copper for Nitric Acid Extraction

Figure II.13: Copper Leachate Concentration for Nitric Acid Extraction
Figure II.14: Leachate Copper Concentrations for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Chromium

Chromium was more difficult to extract than copper. Please note that the maximum on the vertical axis in figure II.11 for copper is 80% whereas for figure II.15 for chromium is 25%. The percent removed varied with different samples. As indicated in figure II.15, the percent removal was generally less for the samples containing more CCA chemical. (The only exception to this trend were the results for the TRM extraction.) In other words, the smallest percent removals were obtained for the 2.50 pcf sample, followed by the 0.60 pcf and weathered wood samples, which were then followed by the 0.25 pcf sample. The greatest percent removals were obtained from the C&D2 and C&D3 samples. Solvents utilized on the C&D 2 sample, for example, extracted between 8 and 60% of the chromium. The reason for this trend is not entirely understood, especially since the leachate concentrations (e.g. figure II.17) do not indicate that the solvents are saturated. One possible hypothesis that can explain this trend is the formation of less soluble metal species in the combustion process. Pasek, 1994, reports the formation of copper chromite (CuCrO$_2$) and other metal - metal species in the residuals from CCA pyrolysis processes. It is quite possible for a larger proportion of the chromium to be bound in metal-metal species for samples containing higher retention levels of CCA. If such chromium-metal species are less soluble, then the percentage of chromium leached should decrease with increasing retention level as observed in the data presented. Another potential hypothesis may be associated with the wood ash content of each sample. Samples containing less CCA chemical produce more wood ash relative to the amount of chemical present. Wood ash is generally alkaline. If a higher proportion of wood ash is present in the sample then that sample would be characterized by a higher pH. If chromium extractions increase at higher pH levels then higher percent removals would be expected for samples of lower retention values as observed in the data.

Also of interest is the capability of distilled water to extract chromium. Up to 31% of the chromium was extracted by distilled water for the C&D 2 sample and up to 54% was extracted for the C&D 3 sample. A measurable amount of chromium (7.7%) was also removed from the 0.25 pcf sample using only distilled water. Other general findings from figure II.15 are that in general the greatest percent removals (5 to 65%) were obtained using hydrochloric acid, nitric acid, and the TRM extraction. The only exception to this finding were the citric acid and the SHC extractions on the C&D 2 sample which were capable of removing over 40% of the chromium for 2 of the 3 C&D samples.

Results of the nitric acid extraction for all the samples analyzed are provided in figure II.16. Again this figure emphasizes the observation from the earlier figure where the greatest % extractions were observed for samples with the lowest retention levels. In other words the % removal was greatest for the C&D samples (except for C&D 1) and least for 2.50 pcf sample which contained the highest retention level of CCA.

Although percent removals were generally the smallest for samples with the highest CCA retention levels, the total mass of chromium leached using the various solvents increased with increasing retention level as can be observed from the chromium leachate concentrations (mass per unit volume). For example, the nitric acid extraction (figure II.17) shows that the leachate concentrations were the lowest for the untreated wood sample and the C&D samples. The chromium leachate concentrations for the 0.25 pcf sample was 98 mg/L, for the weathered wood sample 160 mg/L, for the 0.60 pcf sample 180 mg/L, and for the 2.50 pcf sample 240 mg/L. Such a trend is as expected since a greater mass of chromium should be extracted from samples containing more CCA. The leachate concentrations for all the solvents on selected samples (figure II.18) exhibited the same general trend as for the % removal graphs showing the highest leachate concentrations for the hydrochloric acid, nitric acid, and the TRM extractions. For samples containing high retention levels (2.50 pcf and weathered wood) the weaker solvents, distilled water, magnesium chloride, hydrogen
peroxide, hydroxylamide hydrochloride removed immeasurable amounts of chromium, whereas for the samples containing lower retention levels (C&D 2 and 0.25 pcf) weaker solvents were capable of removing several milligrams of chromium per liter of solvent. This finding is consistent with the results from the TCLP tests described in section II.3.b which found that leachate concentrations were lower for ash produced from samples containing higher retention levels of CCA. Again the formation of acetic acid insoluble chromium-metal particles at higher retention levels, as described earlier, may explain this finding.
Figure II.15: % Chromium Removal for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Figure II.16: % Removal of Chromium for Nitric Acid Extraction

Figure II.17: Chromium Leachate Concentration for Nitric Acid Extraction
Figure II.18: Leachate Chromium Concentrations for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Among the metals analyzed, the highest percent removals were observed for arsenic. For the field samples (2 of the 3 C&D samples and the weathered wood sample), nitric acid and TRM were capable of removing between 90 and 100% of the arsenic. Also of interest is the ability of hydroxilamine hydrochloride and citric acid to extract greater than 40% of the arsenic for the 0.25 pcf sample. In most cases, citric acid performed better than concentrated hydrochloric acid. This finding is of significance given that citric acid is easier to handle than the mineral acids and may therefore be more economically feasible to use within an ash treatment system. In general as the retention levels increased the % arsenic removals decreased; two of the three C&D samples and the weathered wood control exhibited the highest percent removals. Such wood would be typically seen at recycling operations and therefore high % removals would be expected from ash produced from recycled C&D wood wastes.

The results from the concentrated nitric acid extraction (figure II.20) indicate that nitric acid was capable of removing greater than 80% of the arsenic for two of the three C&D samples, the weathered wood sample and the 0.25 pcf sample. Lower percent extractions were observed for the 0.60 and 2.50 pcf sample.

The total mass of arsenic removed is readily observed from figure II.21 for the nitric acid extraction. For this figure, the leachate arsenic concentrations generally increase with increasing retention levels. The lowest concentrations were observed for the untreated wood control and for the C&D samples. The 0.25 pcf, 0.60 pcf, and the 2.50 pcf followed in that sequence. The weathered wood sample was computed to have extracted an amount that was larger than the mass removed from the 2.50 pcf samples. This observation was consistently observed among several of the solvents utilized and may indicate that the weathering process may enhance the leachability of arsenic.

Leachate concentrations for all solvents tested on selected samples are illustrated in figure II.22. Again note the scale on the vertical axis. The minimum mass removals were observed for the C&D 2 which exhibited concentrations less than 40 mg/L and for the 0.25 pcf sample which exhibited removals less than 200 mg/L. It is also very interesting to note that the mass removals among the 2.5 pcf and weathered wood sample were very similar, even though the retention level for the weathered wood sample is less than the retention level of the 2.5 pcf sample. Again it is hypothesized that the weathering process may enhance the leachability of arsenic from wood ash.
Figure II.19: % Arsenic Removal for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
Figure II.20: % Removal of Arsenic for Nitric Acid Extraction

Figure II.21: Arsenic Leachate Concentration for Nitric Acid Extraction
Figure II.22: Leachate Arsenic Concentrations for Each Solvent for Wood Treated at 0.25 pcf and 2.5 pcf, Weathered Wood, and a Field Sample from C&D Facility #2
This page left intentionally blank.
CHAPTER III

SORTING TECHNOLOGIES FOR SEPARATING TREATED WOOD FROM UNTREATED WOOD
CHAPTER III,
SORTING TECHNOLOGIES FOR SEPARATING TREATED WOOD FROM UNTREATED WOOD

Two methods were evaluated during this phase of the study for sorting treated wood from untreated wood. These methods included a chemical stain test (section III.1) and x-ray fluorescence (XRF) (section III.2). Both of these techniques have been used successfully by the wood treatment industry to determine whether wood has been treated adequately. This study involved applying these existing technologies for use by the disposal sector. Potential applications of these technologies include sorting at C&D recycling facilities as well as screening fuel quality at combustion facilities.

III.1 CHEMICAL STAIN TESTS

The chemical stains discussed in this section were published as standards for determining penetration of CCA in treated wood by American Wood-Preservers’ Association (AWPA 1996). The purpose of this study was to determine whether these chemical stains could be applied to determine presence of CCA in treated wood (whole and shredded samples), as well as presence of CCA-treated wood in mixtures containing both treated and untreated wood. Even though the stains have several chemical names, here they will be referred to as Chrome Azurol S, PAN indicator, and rubeanic acid, respectively. The following sections provide: a description of wood samples analyzed (section III.1.a), background information for each chemical stain (III.1.b), results of experimentation (III.1.c), and discussion of results (III.1.d).

III.1.a Sample Description

Five control samples (columns in table III.1) along with 7 samples from C&D recycling facilities (table III.2) were utilized for this study. The control samples included untreated wood (southern yellow pine), a weathered utility pole originally treated at 0.60 pcf, and CCA-treated wood at 0.25 pcf, 0.60 pcf, and 2.50 pcf retention levels. The weathered utility pole was transported to the laboratory in about 1 to 2 inch thick slices. All of the remaining control samples were obtained as 2” x 4” lumbers. A portion of the original samples was maintained whole (unshredded) and another portion was shredded. In order to simulate field samples, an aliquot of the shredded treated wood sample was mixed in various proportions with untreated shredded wood. The control samples used for this set of experiments were the same as those used for the solvent extraction study. For more details concerning collection and processing of these samples please refer to section II.1.a.

The samples from the C&D recycling facilities were collected during the summer of 1997 by the University of Florida research team. Samples were collected in 35-gallon plastic containers. Composite grab samples were collected with a minimum of 20 grabs from each pile; and at some sites duplicate samples were collected. The samples utilized in this study were collected from 7 different facilities and are labeled by the letters “A” through “G” in this report. The amount of CCA present in each sample was determined by ashing a 700 gram sub-sample, digesting the ash, and analyzing the digestates for chromium and copper. Please refer to Tolaymat et al., 1999 or Solo-Gabriele et al. 1998 for more detail. Table III.2 provides the results of the analysis as well as a description of the C&D facilities visited and visual appearance of the samples.
<table>
<thead>
<tr>
<th>Type of Wood</th>
<th>Untreated</th>
<th>0.25 pcf</th>
<th>0.60 pcf</th>
<th>2.5 pcf</th>
<th>Weathered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Shredded</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>% Mixtures created with untreated wood</td>
<td>Not Applicable</td>
<td>1, 5, 10, 25, 50</td>
<td>1, 5, 10, 25, 50</td>
<td>1, 5, 10, 25, 50</td>
<td>1, 5, 10, 25, 50</td>
</tr>
</tbody>
</table>

Table III.1: Types of Samples Utilized in the Chemical Stain Experiments

<table>
<thead>
<tr>
<th>Location</th>
<th>Amount of CCA-Treated Wood (%)</th>
<th>Sample Description</th>
<th>Description of C&amp;D Facility</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3-4</td>
<td>Stringy wood with a lot of dirt and high moisture content</td>
<td>Processing facility of wood waste: separated C&amp;D, pallets</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>Relatively big pieces, and dry</td>
<td>Mixed C&amp;D waste recycling facility. Wood separated up front and in manual recovery system.</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>Relatively big pieces, and dry, a lot of other material, such as shredded plastic bags, etc.</td>
<td>Processing facility of wood waste: Separated C&amp;D, pallets.</td>
</tr>
<tr>
<td>D</td>
<td>&lt;8</td>
<td>Stringy type wood, with a lot of dirt and high moisture content</td>
<td>Mixed C&amp;D waste recycling facility. Wood separated up front and in mechanical separation system.</td>
</tr>
<tr>
<td>E</td>
<td>6-8</td>
<td>Relatively big pieces, dirt and a high moisture content</td>
<td>Mixed C&amp;D waste recycling facility. Wood separated up front and in manual recovery system.</td>
</tr>
<tr>
<td>F</td>
<td>8</td>
<td>Smaller pieces, high moisture content</td>
<td>Mixed C&amp;D waste recycling facility. Wood separated up front.</td>
</tr>
<tr>
<td>G</td>
<td>6</td>
<td>Relatively small pieces and dry</td>
<td>Mixed C&amp;D waste recycling facility. Wood separated up front and in manual recovery system.</td>
</tr>
</tbody>
</table>

Table III.2: Description of Field Samples from C&D Recycling Facilities
III.1.b Background Information for Each Chemical Stain

The following sections provide theoretical background for each chemical stain, the formula for preparing the chemical stains as published by the AWPA, 1996, and recommended modifications of the formulations for use at C&D recycling facilities. Purchasing information for each of the reagents needed in preparing the stains is provided at the end of this section. Safety information for proper handling of the chemicals is provided in Material Safety Data Sheets (MSDS) which are included in appendix C.

**Chrome Azurol S**

*Theory*

Chrome Azurol S comes from a parent family of sulfonephthalein compounds (Sandell and Onishi 1978). These compounds, also known as sulfonated dyes are used frequently because of their great solubility in water. The Chrome Azurol family includes Eriochrome Cyanine R, Eriochrome Azurol B and Chrome Azurol S. They are differentiated by having different functional groups.

Chrome Azurol S is also known as Mordant Blue 29, or Color Index 43825 (Fisher 1998). It can be used to determine the presence of copper, aluminum, beryllium, uranium and other metals (Sandell and Onishi 1978). The reaction with copper produces a blue color in the solution. It is a purely organic compound with molecular formula of $C_{23}H_{16}Cl_2O_9S$. It has the chemical structure shown in figure III.1 (Sandell and Onishi 1978).

![Figure III.1: Chemical Structure of Chrome Azurol S](image)

The complexes formed upon reaction with copper are not very well known, although it is thought that the $SO_3^2$ group substitutes with a metal. The color develops if the solution is slightly acidic or basic (Sandell and Onishi 1978).

*Formula Published in AWPA, 1996*

0.5 grams of Chrome Azurol S and 5.0 grams of sodium acetate are dissolved in 80 ml of distilled water and then diluted to 500 ml (AWPA 1996). Sodium acetate acts as a pH buffer in the
solution. The solution is then sprayed on wood and a deep blue color appears if the wood has been treated with CCA and a pinkish color if wood is untreated.

**Recommended Formula for Sorting at C&D Recycling Facilities**

The original formulation for the Chrome Azurol S stain required about a minute to soak into the treated wood and cause a color change. The reason for the slow reaction is because the stain is water based. To shorten the absorbance time of the Chrome Azurol S reagent, it was mixed with ethanol. The modified formulation is to dissolve 0.5 grams of Chrome Azurol S and 5.0 grams of sodium acetate in 500 ml of ethanol. The blue color appears almost instantaneously and dries much faster. Also untreated wood stains a slightly fainter shade of pink, making the distinction between treated and untreated wood easier.

**PAN Indicator**

**Theory**

PAN indicator comes from a family of heterocyclic azo reagents (Sandell and Onishi 1978). PAN stands for a chemical name of 1-(2-pyridylazo)-2-naphthol, an orange-red solid with a molecular formula $C_{15}H_{11}N_2O$ (Fisher 1998). It is used to determine presence of almost all metals (40 to 50 metals total) excluding alkali metals (beryllium, arsenic, geranium, selenium, and tellurium) (Sandell and Onishi 1978). PAN is insoluble in water and fairly soluble in alcohol solutions. It is important to mention that commercial products available are usually impure, therefore PAN Indicator comes in different percentage indicator grades. The following (figure III.2) is a chemical structure of PAN Indicator (Sandell and Onishi 1978).

![Figure III.2: Chemical Structure of PAN Indicator](image)

As an American Wood-Preservers’ Association standard, PAN Indicator is used for determining copper containing preservatives (AWPA 1996). It possible, however, that PAN is able to bond both with copper and chromium present in CCA-treated wood. To better understand the
undergoing reaction, it is important to mention the function of nitrogen atoms in the structure of PAN. PAN Indicator contains both pyridine and azo nitrogen atoms (Sandell and Onishi 1978). Pyridine is obtained by distillation of coal tar and is identified by a nitrogen-containing benzene ring (McMurry 1992). Azo compounds contain two benzene rings attached together by a double bond between two nitrogen atoms. Azo compounds are known for their reactivity as well as bright colors. PAN’s bright orange color comes from the azo nitrogen bond in the compound. During a reaction between a metal and PAN Indicator, the metal bonds to oxygen of the OH group by replacing the hydrogen atom, and to pyridine and azo nitrogen atoms (Sandell and Onishi 1978). Other, much more complicated reaction are also possible. The reaction with the metals in CCA-treated wood produces magenta to red color. The untreated pieces of wood turn orange in color.

*Formula Published in AWPA, 1996*

PAN indicator is added to methanol 0.05 % by weight to create a reagent that can be sprayed over wood (AWPA 1996). This method is able to detect copper in wood at about 0.01 pcf to 0.002 pcf. Even though PAN is a stable compound (Sandell and Onishi 1978), the solution in methanol becomes less sensitive as it ages and thus only fresh solutions can be used. Refrigeration can extend the useful life of the solution (AWPA 1996).

No modifications to the formulations were performed since the stain was quick to react and easy to use.

**Rubeanic Acid**

*Theory*

Rubeanic acid comes from a family of thiols, which are sulfur analogs of alcohols, with an SH group instead of OH (McMurry 1992). This compound has a molecular formula of $\text{C}_2\text{H}_4\text{N}_2\text{S}_2$. Rubeanic acid is thought to have various forms, and it has many names: dithiooxamide, dithioxamide, ethanedithioamide, hydronubeanic acid, rubean acid, rubeane acid, oxamide, oxaldiimidic acid, RVK, USAF ek-4394, USAF mk-6 and USAF B-43 (NIST 1998). The structure of the compound is shown in figure III.3.
Rubeanic acid reacts with copper to create an olive green color (Sandell and Onishi 1978). The actual bonds formed between copper and rubeanic acid are unknown but probably copper bonds to sulfur at each end of the ligand, replacing the hydrogen.

**Formula Published in AWPA, 1996**

The method requires two separate applications of the chemical to the wood: one with rubeanic acid solution and another with sodium acetate solution. A solution of rubeanic acid is made by dissolving 0.5 grams of rubeanic acid in 100 ml of ethanol. Sodium acetate solution is made by dissolving 5.0 grams of sodium acetate in distilled water (AWPA 1996). First wood is sprayed with rubeanic acid solution, then with the sodium acetate solution. Rubeanic acid is slightly acid and sodium acetate acts as a buffer (Sandell and Onishi 1978).

**Tests Performed on Modified Formulation**

The AWPA 1996 method requires application of two different solutions, which makes spraying more time consuming and inconvenient. A solution combining rubeanic acid and sodium acetate was prepared, but it resulted in a very dark stain (almost black) when sprayed on CCA-treated wood which would make the treated wood difficult to distinguish from very dirty pieces of weathered wood. Combining the reagents was not successful and therefore, application of the stain should follow the AWPA 1996 procedure.

**Purchase Information for Reagents Needed in Preparing Chemical Stains**

Table III.3 provides information concerning where to purchase the reagents needed to prepare the chemical stains. Please note that the provision of vendor names, contact information, and catalog numbers does not imply that the research team endorses the purchase of reagents from any particular vendor. The same chemicals can be purchased from other companies.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Supplier</th>
<th>Catalog Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrome Azurol S</td>
<td>Sigma Chemical</td>
<td>C1018 (10 grams)</td>
</tr>
<tr>
<td></td>
<td>P.O. Box 14508, St. Louis, MO 63178</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phone: 1-800-325-3010</td>
<td></td>
</tr>
<tr>
<td>Sodium Acetate Anhydrous</td>
<td>“</td>
<td>S5889 (100 g)</td>
</tr>
<tr>
<td>1-(2-pyridylazo)-2-naphthol, PAN</td>
<td>“</td>
<td>P9506 (5 g)</td>
</tr>
<tr>
<td>Dithio oxamide, rubeanic acid</td>
<td>Aldrich Chemical Company, Inc.</td>
<td>37,938-7 (5 g)</td>
</tr>
<tr>
<td></td>
<td>1001 West Saint Paul Ave., Milwaukee, WI 53233</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phone: 1-800-558-9160</td>
<td></td>
</tr>
<tr>
<td>Ethanol, undenatured</td>
<td>Spectrum Quality Products, Inc.</td>
<td>E1028</td>
</tr>
<tr>
<td></td>
<td>1442 South San Pedro St,, Gardena, CA 90248-9985</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phone: 1-800-772-8786</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>“</td>
<td>M1240</td>
</tr>
</tbody>
</table>

Table III.3: Order Information for Companies That Can Provide Reagents for Chemical Stains
III.1.c Results of Experimentation

Experiments were conducted on whole wood, shredded wood both mixed and unmixed, and on samples collected from C&D recycling facilities. A summary of the experimental results are provided below.

Whole Wood

Results of experimentation on whole wood are provided in figure III.4. The wood tested included untreated wood, and wood treated at 0.25 pcf, 0.60 pcf, and 2.5 pcf retention levels. During experimentation the cross-section of each wood piece was separated into 4 sections. One section remained unstained and the remaining three sections were stained with Chrome Azurol S, PAN indicator, and rubeanic acid, respectively. The Chrome Azurol S stained treated-wood a deep blue color. It was darkest for the 2.5 pcf sample and lightest for the 0.25 pcf sample. The deep blue color is contrasted with the red-brown color provided by the untreated wood making it easy to distinguish treated wood from untreated wood. PAN indicator stains the wood a deep red or magenta color. The magenta color is contrasted by an orange color for the untreated wood. Distinction between treated and untreated wood using the PAN indicator depends on one’s ability to distinguish orange from magenta. The rubeanic solution results in an immediate appearance of an olive green color which gets darker with increasing retention levels. The green color for treated wood is contrasted with no change in color for untreated wood.

Shredded Wood, Unmixed

Results for the shredded wood samples (unmixed) are provided in figure III.5. All samples were shredded in the laboratory. Rows in the figure correspond to different stains and columns correspond to different samples tested. The color of all of the unstained samples (row 1) were differing shades of beige to olive color. If samples are dirty (such as that observed at C&D recycling facilities) the color between treated wood and untreated wood would be even less distinguishable. The color of the unstained samples is contrasted by the color of the samples that were sprayed with the stains. Distinct color differences are observed between untreated and treated wood for all three stains tested. Also, note that within the weathered wood sample, and the 0.25 pcf and 0.60 pcf samples, portions of the samples did not stain. The reason for this observation is because the treatment chemical is designed to impregnate the outer layers of the wood leaving the inner core of the wood without chemicals. This is especially evident for the treated utility pole (figure III.6) which was characterized by a large diameter (18”). The dark outer ring (sapwood) contains the CCA chemical whereas the inner ring (heartwood) is untreated. A similar situation was observed for the cross-section of the 2” x 4” sample treated at 0.60 pcf (figure III.7). When these samples were shredded the heartwood is then exposed at the surface of the wood chip. Thus the unstained portions of the treated wood samples are chips of untreated wood which originated within the heartwood core of the treated wood.
Figure III.4: Stain Performance for Whole Pieces of Wood

Figure III.5: Stain Performance on Shredded Wood (Unmixed)
Figure III.6: Cross-section of CCA-Treated Utility Pole

Figure III.7: Cross-section of CCA-Treated 2”x 4” Lumber, 0.60 pcf
Shredded Wood, Mixed

The weathered wood control (originally 0.6 pcf) was mixed in various proportions with untreated wood. Each column in figure III.8 corresponds to a different mixture and includes 1% weathered wood (column 1), 5% weathered wood (column 2), 10% weathered wood (column 3), 25% weathered wood (column 4), and 50% weathered wood (column 5). Rows correspond to no stain, Chrome Azurol S, PAN indicator, and rubeanic acid. Results indicate that all three stains performed very well for the laboratory prepared mixtures since the treated-wood chips were easily distinguishable from untreated wood. The color difference is so distinct in these samples that one can “pick-out” the treated chips from the untreated portions, even for mixtures as low as 1% treated wood.

Field Samples From C&D Recycling Facilities

Stains were tested on 7 samples collected from C&D recycling facilities. The stains performed well for 5 of the 7 facilities. The 2 samples showing negative results contained a lot of dirt and fibrous or “string-like” woody material which did not stain properly. The samples providing positive results contained minimal dirt and characterized by distinct chips. The performance for samples showing positive results is illustrated in figure III.9. The sample utilized for this figure contained approximately 6% CCA-treated wood on average. The first sample was not stained whereas the remaining three were stained with rubeanic acid, PAN indicator, and Chrome Azurol S, respectively. Results show that all three stains performed well providing distinct color differences between treated and untreated wood. For each stain the treated wood chips can be readily “pick-out.”
This page left intentionally blank.
Figure III.8: Performance of Stains on Shredded Wood Samples, (Mixed)

Figure III.9: Performance of Stains on Field Samples Collected from C&D Recycling Facilities
III.1.d Discussion of Results

The stains performed quite well on most wood samples. One of the advantages of using chemical stains for sorting purposes is that these solutions are easy to make and the reagents used in the stains are purely organic compounds and contain no metals. So if the stained wood is ultimately burned, the stain will not add to the metal burden of the ash. The primary advantage of the chemical stains is that the presence of CCA in wood can be determined easily, with immediate, clearly visible results. In terms of capital investments, it is also quite cost effective compared to x-ray fluorescence described later.

The chemical stains have some disadvantages associated with them. The problem with absorbency of Chrome Azurol S in wood was solved by mixing it in ethanol. AWPA recommends that the stain be used on freshly treated wood because of the possibility of interference reactions. In the samples tested very little or no interference was observed. It is also noted that PAN indicator can react with many metals also increasing the possibility for interference reactions. There was some evidence of interferences when the stain was tested on samples collected from C&D recycling facilities. Another potential disadvantage of PAN indicator is that it should be refrigerated to prolong its life and sensitivity, which could create a problem for on-site applications at some facilities. Rubeanic acid stains wood a very dark green at high retention levels and application of this stain may be difficult if treated wood is to be distinguished from highly soiled chips of untreated wood. Rubeanic acid also requires the application of two solutions, which makes spraying more time consuming and inconvenient. A solution combining rubeanic acid and sodium acetate was made, but it resulted in an even darker color and is not recommended. The one advantage of rubeanic acid is that it is very specific to copper and subject to less interference reactions (AWPA 1996). However, the color produced and the inconvenience associated with using two solutions do not outweigh this advantage. Overall the recommendation is to use either the modified formulation for the Chrome Azurol S or PAN Indicator stains for whole and shredded wood, because of a very distinct blue or magenta color, unlikely to be found in weathered wood. For mixtures, both PAN and the modified formulation of Chrome Azurol S performed very well and were easy to use.

Another disadvantage of the stains is that their use is labor intensive and may be too time consuming for sorting very large quantities of wood waste. The primary application of the stains is for “spot-checking” fuel quality at both wood recycling and burning facilities. The stains can also be used to sort small quantities of wood waste. A focus of future research is to evaluate the performance of the stains through field pilot studies. The purpose of such a study is to evaluate the amount of additional labor involved in use of the stains and to document the improvements in wood-waste quality.
X-ray fluorescence (XRF) is the technique utilized by many wood treating plants to test the retention value of treated wood (Eldridge and Pray, 1989) and the analytical method has been standardized by the AWPA (AWPA 1998). During a visit to the Koppers wood treating plant in Gainesville during June of 1997, the performance of XRF equipment was illustrated to the research team. Although this technique is considerably easier and faster than traditional wet-chemical methods, the XRF method employed by Koppers required considerable pre-processing which included coring a sample, grinding, and compacting the sample into a cup. Once the sample was placed in a cup, a metals value was provided by the instrument within about a minute. The researchers consider that for field applications within the disposal sector, pre-processing must be kept to a minimum and analysis times must be further reduced. The primary objectives of the current XRF study were to determine the extent to which sample pre-processing could be minimized with existing XRF equipment and to determine if existing equipment is amenable to the development of on-line systems. Potential applications of the technology included the use of existing equipment to screen wood waste for the presence of CCA-treated wood. If pre-processing could be minimized it was considered that screening could occur with existing XRF equipment on relatively small samples at C&D recycling facilities and at wood cogeneration plants. Furthermore, with the development of an on-line system there is a potential for screening large quantities of wood mixtures and for sorting large quantities of whole wood.

The XRF equipment manufacturer chosen for collaboration in this investigation was ASOMA Instruments. ASOMA Instruments was the first company to successfully develop a field-portable computer-controlled XRF analyzer and the first company to develop an analyzer tailored toward analysis by the wood treatment industry. Up until 1997 ASOMA had 100% of the CCA-treated wood related business. ASOMA’s expertise in XRF combined with its interest in working with the research team were the determining factors in choosing it for this research project. It is important to note that there are other reputable companies that produce bench-top XRF analyzers. These other companies include Oxford Instruments located in the United Kingdom and Outokumpu Electronics located in Finland.

This chapter is organized into the following sections: III.2.a Theoretical Background, III.2.b Experiments Conducted, and III.2.c Experimental Results, and III.2.d Discussion.

### III.2.a Theoretical Background

An atom consists of a nucleus and orbiting electrons. Respective electron orbits have their corresponding energies; orbits of the same energies are grouped in shells. A given electron will occupy the lowest energy shell available. When the incident x-ray, from XRF spectrometer hits the atom, the innermost electron (the one with lowest energy) absorbs it (Williams 1987). This ejects that electron creating a vacancy in the shell. Next an electron from a higher energy shell falls to the created vacancy, and in the process excess x-ray energy is emitted that is equal to the difference of energy between those shells. An XRF analyzer registers the emitted energy and compares it to the known energies of a given element. Following is a diagram showing the process (figure III.10).
Elements can be identified using either energy-dispersive x-ray fluorescence or wavelength-dispersive x-ray fluorescence, given that energy is related to the wavelength emitted (Dejmkova 1990). The relationship between wavelength and energy is represented by the following equation (Williams 1987).

\[ E(keV) = \frac{hc}{\lambda(nm)e} = \frac{1.239}{\lambda(nm)} \]  

(equation III.1)

where,
- \( h \) = Plank’s constant
- \( c \) = speed of light
- \( e \) = electron charge
- \( E \) = photon energy
- \( \lambda \) = wavelength

The spectrum for Energy Dispersive X-ray Fluorescence (EDX) falls between 0.5 keV and 150 keV (kilo-electron volts), but is usually analyzed between 1 and 40 keV (ASOMA Instruments, personal communication, 1998). Elements are distinguished from one another by the wavelength or energy level of the x-ray emitted. The concentration of a particular element is determined from the frequency or intensity of the emitted x-ray which is usually compared with calibration standards (Williams 1987).

Concentration of an element using ASOMA equipment is given in terms of “counts” per unit time. Each count corresponds to the fluorescence of an atom with its characteristic x-ray.
III.2.b Experiments conducted

Experiments were conducted on ASOMA equipment during three separate efforts. These efforts were coordinated through Julie Kyler, ASOMA’s product specialist. The first effort (experimental set #1) was run independently by ASOMA. The second effort (experimental set #2) involved a trip by the research team to the headquarters of ASOMA located in Austin, Texas where experiments were conducted over a two day period. The third effort (experimental set #3) was conducted independently by ASOMA as follow-up to the second experimental effort. A description of the equipment utilized along with each experimental effort are provided in the following sections.

ASOMA Equipment Utilized

Some of the models of interest that ASOMA offers include Model 200, Model 200T and Model 400. Model 200 is used mostly for heavier elements, whereas 200T analyzes lower energy x-rays emitted by an element. Both of these models are used to analyze relatively small samples (few grams at a time).

The Model 400 (figure III.11) is useful for samples of all varieties and sizes, and it combines qualities of both Models 200 and 200T. The Model 400 unlike other models includes a hand-held probe, which is attached to the main analyzer with cable connecting the head. Lengths of the cable can be as long as 100 feet. The remote probe (head) weights about 10 pounds and its dimensions are 8 x 8 x 4 inches. It includes a sensor approximately 1 inch in diameter or about the size of a quarter (figure III.12). The typical life span of the instrument is about 10-12 years. The source of x-rays within the instrument is from a radioactive source of curium (Cm\textsuperscript{244}). The detector (figure III.12) is a hollow metal cylinder fitted with a very thin wire along its radial axis (Williams 1987). It contains neon or argon gas at a pressure of 2 atmospheres. Emitted photons are able to ionize gas and create a pulse read by the instrument. X-rays enter the detector through a very thin window of approximately 100 \mu m thick made of beryllium (Williams 1987). The beryllium window protects the detector and it prevents the gas from leaking out. Beryllium is the chosen material for this window because it is a low absorber of x-rays. The detector should be replaced every five years. The XRF analyzer also contains a filter, which helps distinguish between two atoms which fluorescence at similar energy levels. The Model 400 also comes with software developed by ASOMA to feed data obtained from the analyzer to a personal computer, where it can be read and manipulated for statistical analysis.

No special training is necessary for operation of the Model 400. It is quite simple and user friendly. The keypad contains an ‘analyze’ key, ‘count time’, ‘sample ID’ and other helpful keys. In order to begin analysis a second analyze key located on the head must be depressed. This separate key is included for safety purposes to assure that the instrument is not turned on accidentally which can result in an exposure to x-rays if the head is not positioned properly. Printout of results, either from analyzer itself of from a PC, is easy to read and understand.
Figure III.11: ASOMA Model 400

Figure III.12: Sensor and Detector for ASOMA Model 400
Experimental Set #1

The purpose of this set of experiments was to determine whether the Model 400 could be used to detect the presence of CCA in whole and shredded samples. Shredded wood samples analyzed included mixtures of treated and untreated wood and the results from these samples were also used to obtain an estimate of the detection limit for such mixtures. The detection limit is defined as the largest value among: “2.5 times the blank value” or “3 times the standard deviation of the blank value.” In preparation for this effort the samples listed in table III.4 were mailed to ASOMA headquarters. The particular field sample chosen, containing approximately 6% CCA-treated wood, is considered to be representative of average conditions at C&D recycling facilities. Sample preparation and collection is described in section II.1. ASOMA was provided a full description of all samples except for two which were used for quality control purposes. All samples were placed in plastic Zip-lock bags. Shredded wood samples were analyzed by placing the remote probe on the outside of the bag and the whole pieces of wood were removed from the plastic bag prior to analysis. The Model 400 was programmed for a count time (time during which the instrument measures x-ray emissions) of 100 seconds. The remote probe was stationary throughout the count time. Experimental results were provided to the research team on August 17, 1998. A copy of the full report provided by ASOMA is included in appendix D. The results are discussed in section III.2.c.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Information Provided to ASOMA</th>
<th>Whole “W” or Shredded “S”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Southern Yellow Pine</td>
<td>Same as sample description</td>
<td>W</td>
</tr>
<tr>
<td>CCA-treated wood at 0.25 pcf</td>
<td>Control</td>
<td>W</td>
</tr>
<tr>
<td>CCA-treated wood, weathered</td>
<td>Same as sample description</td>
<td>W</td>
</tr>
<tr>
<td>CCA treated wood at 2.50 pcf</td>
<td>“</td>
<td>W</td>
</tr>
<tr>
<td>Untreated Southern Yellow Pine</td>
<td>Same as sample description</td>
<td>S</td>
</tr>
<tr>
<td>Mixture of Wood Chips, 99% Untreated, 1% treated at 0.25 pcf</td>
<td>“</td>
<td>S</td>
</tr>
<tr>
<td>Mixture of Wood Chips, 90% Untreated, 10% treated at 0.25 pcf</td>
<td>“</td>
<td>S</td>
</tr>
<tr>
<td>Mixture of Wood Chips, 50% Untreated, 50% treated at 0.25 pcf</td>
<td>“</td>
<td>S</td>
</tr>
<tr>
<td>Wood chips, 100% treated at 0.25 pcf</td>
<td>Control</td>
<td>S</td>
</tr>
<tr>
<td>Wood chips, 100% weathered wood</td>
<td>Same as sample description</td>
<td>S</td>
</tr>
<tr>
<td>Wood chips, 100% treated at 2.5 pcf</td>
<td>“</td>
<td>S</td>
</tr>
<tr>
<td>Wood chips from C&amp;D recycling facility, approximately 6% CCA-treated</td>
<td>Wood chips from C&amp;D recycling facility</td>
<td>S</td>
</tr>
</tbody>
</table>

Table III.4: Samples Mailed to ASOMA Headquarters During First Experimental Effort
Experimental set #2

The goal of experimental set #2 was to establish operating parameters for stationary and on-line systems. Both stationary and on-line systems can be used for screening and for sorting purposes. It was established early during experimentation, however, that sorting would be most effective if performed on whole wood. The specific objectives of the analyses were as follows:

1) Identify the best target metal for analysis.
2) Determine the detection limit for mixtures of treated and untreated wood, after implementing improvements to the method.
3) Determine the shortest analysis time.
4) Determine the maximum spacing between the sensor and wood, both with and without a shield.

The analysis for the best target metal was based upon the assumption that the only source of chromium, copper, and arsenic in the sample was from CCA. Therefore, the “best” metal will be the one providing the greatest sensitivity or, in other words, the largest difference in counts between untreated wood and treated wood. Further work also focused on improving the detection limit of shredded wood mixtures. Improvements implemented during experimental set #2 were careful re-calibration of the equipment using a more exhaustive set of standards, and movement of the probe during analysis to obtain a more representative reading of the sample. The minimum analysis time was also evaluated during this experiment since it has a direct impact on the through-put (board feet per unit time) for an on-line sorting system. The shorter the time the greater the amount of wood that can be processed for a given piece of equipment. One of the challenges of sorting whole pieces of wood using an on-line system is sample introduction to the detector. The farther the distance between the detector and the wood waste the simpler the conveyer system which exposes the wood to the sensor. It is also important to note that the detector contains a delicate beryllium window which costs a few hundred dollars if damaged. Given that wood waste is composed of all different shapes and sizes and may contain nails, shielding will be a necessary component of an on-line system and was therefore also evaluated during experimentation.

Experiments were conducted over a two day period (October 14 and 15, 1998) at ASOMA headquarters located in Austin, Texas. Two members of the research team, Dr. Helena Solo-Gabriele and Monika Kormienko, conducted the experiments along with the assistance received from ASOMA representatives. The same samples prepared for experimental set #1 were used for this set of experiments along with the addition of 7 wood waste samples from C&D recycling facilities and the following wood mixtures: 2%, 3%, 4%, 5%, 10%, 15%, and 20% CCA-treated wood chips (0.25 pcf) by weight. The 7 wood waste samples collected from C&D facilities were the same as those used for the chemical stain study. Please refer to table III.2 for a more detailed description of these samples.

The analysis method involved setting the instrument to read counts as chromium, copper, and arsenic. Count time was set (time needed to analyze specimen effectively) and the head was placed on a sample for analysis. In case of shredded wood, the head was moved slowly across it, giving a more composite analysis of the specimen. The probe was placed directly on the surface of the whole wood sample and placed outside a plastic Zip-lock bag during the analysis of shredded samples.
Experiment #3

The purpose of experimental set #3 was to re-run the detection limit study for laboratory prepared mixtures of CCA-treated wood and untreated wood. This experiment was conducted by representatives of ASOMA Instruments. Two different calibration curves were developed based on arsenic counts: one for 0 to 10% CCA-treated wood mixtures and another for 10 to 100% mixtures. Results were provided to the research team on October 21, 1998. A copy of this report is provided in appendix D.

III.2.c Experimental Results

Experimental Set #1

Results are available for counts based on arsenic, chromium, and copper. The same general conclusions can be drawn for each target metal. A summary of the arsenic data are provided in table III.5 on the following page. Please see appendix D for details concerning all analyses including chromium and copper results.

For whole wood (samples 1 to 4 in table III.5), results indicate that the Model 400 was capable of detecting CCA in all treated-wood samples. For example, untreated wood received an arsenic count of 69. Assuming that the detection limit of the method is 2.5 times the “blank” (i.e. untreated wood), then a positive detection for CCA would occur for arsenic counts greater than 173. All whole wood that contained CCA had readings significantly higher than 173 (table III.5). The smallest value (1242) occurred for wood treated at the lowest retention level, 0.25 pcf, whereas the largest value (2650) occurred for wood treated at the highest retention level, 2.50 pcf. If one linearly interpolates the results from the tests conducted on 0.25 pcf and 2.5 pcf retention levels, a 0.60 pcf retention level would correspond to 1461 counts. The counts for the weathered wood sample, which was originally treated at 0.60 pcf, is slightly lower by about 3% with 1414 counts of arsenic. This difference may be due to the loss of the CCA chemical during the weathered pole’s service life, variability in the measurement technique, and/or variability in the original treating process. Regardless of this difference, the results appear fairly linear indicating that arsenic counts are proportional to the amount of CCA present in whole wood.

For shredded wood chips (samples 5 -11), the arsenic count for untreated wood was 67, which was very close to the value obtained for whole untreated wood. The slightly lower reading for the shredded wood sample may be due to the presence of the plastic bag outside the shredded wood sample, random error of analytical instrument, the more jagged surface associated with the shredded wood sample, or slight differences in the untreated samples. Again, assuming that the detection limit is roughly 2.5 times the blank value, the detection limit for CCA in shredded wood chips is therefore 168 counts as arsenic. All samples which were prepared of 100% CCA-treated wood were above the detection limit. An arsenic count of 536 was obtained for a sample containing wood treated at 0.25 pcf, 1022 was obtained for the weathered wood sample, and 2399 was obtained for the sample containing wood treated at 2.50 pcf. All counts are lower than the values obtained for whole wood. The most pronounced difference is observed for the 0.25 pcf sample where for whole wood the arsenic count (1242) was almost 2½ times larger than for shredded wood (536). The reason for the decrease in arsenic counts is due to the shredding process which results in the exposure of untreated portions of treated wood. Figure III.6 in the previous section, which illustrates a cross-section of a CCA-treated utility pole, emphasizes the fact that the CCA chemical does not penetrate to the heartwood core of the pole. The presence of the CCA chemical is apparent in the darker outer ring (sapwood). The untreated portion is given by the lighter heartwood portion. The same
phenomenon was observed for treated 2" x 4" lumbers (figure III.7). Thus once the wood is chipped, the heartwood portions of the wood are exposed to the surface. Keeping in mind that the area analyzed by the Model 400 is about the size of a quarter, the reading would be sensitive to the precise location that was utilized by the equipment for analysis. If the sensor is placed on a chip produced from the central portion of the pole or lumber, then a lower value would be measured. If the sensor is placed on a chip produced from outer portion, then readings should be similar to that observed for whole wood. It is also noted that some of the linearity is lost as a result of the shredding process. Although arsenic counts increase with increasing retention level, the amount of increase is not directly proportional to the retention level.

Results from the wood mixtures consisting of CCA-treated wood chips at 0.25 pcf retention level and untreated wood chips, indicate that a mixture of 50% treated wood is detectable with an arsenic count of 303 whereas samples consisting of 10% or less were not. The value for the 50% mixture (303) is slightly higher (by about 13%) than ½ of the 100% mixture (268 = 536/2) which again indicates that the shredding and mixing process affects the linearity of the system. Interpolating between the 100% and 50% treated wood sample, the detection limit for this experimental set is estimated at a 20% mixture of CCA-treated wood. In other words, this preliminary experiment indicates that the ASOMA Model 400 is capable of establishing the presence of CCA-treated wood in a mixture of 20% CCA-treated wood (0.25 pcf) and 80% untreated. A twenty percent detection limit is considered high for wood screening purposes and subsequent experimentation during efforts #2 and #3 focused on improving the detection limit.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Description</th>
<th>Whole “W” or Shredded “S”</th>
<th>Counts as As</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>1</td>
<td>Untreated Southern Yellow Pine</td>
<td>W</td>
<td>69</td>
</tr>
<tr>
<td>2</td>
<td>CCA-treated wood at 0.25 pcf</td>
<td>W</td>
<td>1242</td>
</tr>
<tr>
<td>3</td>
<td>CCA-treated wood, weathered, wood originally treated at 0.60 pcf</td>
<td>W</td>
<td>1414</td>
</tr>
<tr>
<td>4</td>
<td>CCA treated wood at 2.50 pcf</td>
<td>W</td>
<td>2650</td>
</tr>
<tr>
<td>5</td>
<td>Untreated Southern Yellow Pine</td>
<td>S</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>Mixture of Wood Chips, 99% Untreated, 1% treated at 0.25 pcf</td>
<td>S</td>
<td>67</td>
</tr>
<tr>
<td>7</td>
<td>Mixture of Wood Chips, 90% Untreated, 10% treated at 0.25 pcf</td>
<td>S</td>
<td>68</td>
</tr>
<tr>
<td>8</td>
<td>Mixture of Wood Chips, 50% Untreated, 50% treated at 0.25 pcf</td>
<td>S</td>
<td>303</td>
</tr>
<tr>
<td>9</td>
<td>Wood chips, 100% treated at 0.25 pcf</td>
<td>S</td>
<td>536</td>
</tr>
<tr>
<td>10</td>
<td>Wood chips, 100% weathered wood, wood originally treated at 0.60 pcf</td>
<td>S</td>
<td>1022</td>
</tr>
<tr>
<td>11</td>
<td>Wood chips, 100% treated at 2.50 pcf</td>
<td>S</td>
<td>2399</td>
</tr>
<tr>
<td>12</td>
<td>Wood chips from C&amp;D recycling facility, approximately 6% CCA-treated</td>
<td>S</td>
<td>61</td>
</tr>
</tbody>
</table>

Table III.5: A Summary of the Results of First Experimental Effort (Counts as As)
Experimental Set #2

The following sections summarize the results for the experiments aimed at establishing: a) the best target metal for analysis, b) the detection limit for mixtures of treated and untreated wood, d) the shortest analysis time, and e) the maximum spacing between the sensor and the wood sample, both with and without a shield.

The Best Target Metal for Analysis

Figure III.13 and III.14 clearly show that the greatest sensitivity of analysis is provided by arsenic for whole wood and for wood chips, respectively. Copper appears to be the next most sensitive metal followed by chromium. The reason for this observation is due to the increase in an atom’s fluorescent yield with increasing atomic number (Jenkins 1988). A fluorescent yield is the ratio of counts of radiation emitted per ionized atom. Thus chromium with atomic number of 24 has the lowest fluorescent yield, followed by copper, atomic number 29, and arsenic, atomic number 33.
Figure III.14: Counts of arsenic, chromium and copper for shredded wood at count time of 2 seconds.
Detection Limit for Mixtures of Treated and Untreated Wood

Three sets of experiments were performed to determine the detection limit of wood mixtures. One set of studies was conducted with limited calibration utilizing only ASOMA provided standards; the second set was conducted on an extensive set of prepared standards containing 1%, 2%, 3%, 4%, 5%, 10%, 15%, 20%, and 50% mixtures of treated wood. Both calibration sets were conducted on laboratory prepared mixtures of CCA-treated wood and untreated wood. The last set of experiments was conducted on wood waste samples collected from C&D recycling facilities. During all experiments the probe was moved along the sample to obtain a more representative reading.

Results from the experiments conducted with limited calibration (Figure III.15) indicate that detection limit (approximately 170 counts of arsenic) is on the order of a 20 to 25% mixture of treated wood. The detection limit was reduced further for experiments conducted after the more extensive calibration (figure III.16). Other than two outliers at 3 and 4% CCA mixtures, a good fit is achieved with the 1:1 line. The interpretation of these results is that more extensive calibration of the instrument lowers the detection limit to at least 5% and possibly even 3%. However, it is recommended that the experiment be repeated in an effort to determine the cause of the outliers.

![Graph showing detection limit for mixtures of treated and untreated wood](image-url)
For the 7 field samples from construction and demolition facilities, CCA-treated wood was detected in 6 of them (table III.6). The one sample that received a non-detect contained the lowest concentration (3-4%) of CCA-treated wood. Samples with slightly higher values of treated wood, 5% and 6%, received positive-detection readings again confirming that the detection limit for the Model 400, after extensive calibration, is on the order of 5%.

<table>
<thead>
<tr>
<th>Location</th>
<th>% CCA Treated Wood in the Field Sample</th>
<th>Percent of the Metal as analyzed in the Model 400</th>
<th>Detected (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3-4</td>
<td>As 0  Cu 4  Cr 8</td>
<td>No</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>7 10 14</td>
<td>Yes</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>10 15 17</td>
<td>Yes</td>
</tr>
<tr>
<td>D</td>
<td>&lt;8</td>
<td>3 9 12</td>
<td>Yes</td>
</tr>
<tr>
<td>E</td>
<td>6-8</td>
<td>5 9 14</td>
<td>Yes</td>
</tr>
<tr>
<td>F</td>
<td>8</td>
<td>6 9 15</td>
<td>Yes</td>
</tr>
<tr>
<td>G</td>
<td>6</td>
<td>5 10 19</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table III.6: Detection of CCA-treated Wood in Field Samples from C&D Recycling Facilities
Shortest Analysis Time

Shredded as well as whole samples of wood at different retention levels (0.25 pcf, 0.60 pcf, and 2.50 pcf) were run using different count times. Whole wood was analyzed at count times of 1, 2, 3, 5, 10 and 50 seconds, whereas shredded wood was analyzed for chromium, copper and arsenic simultaneously at count times of 2, 3, and 10 seconds. Figure III.17 and figure III.18 show that the longer the count time, the higher the count readings for arsenic for both whole wood and shredded wood chips. However, it is also clear that a count time of 2 seconds is able to determine presence and concentration of CCA. Similar results were obtained for chromium and copper.
Figure III.18: Shredded Wood at Different Retention Levels and Different Count Times (Counts as Arsenic)
**Maximum Spacing Between the Sensor and the Wood Sample**

The purpose of this part of the experiment was to determine the maximum permissible separation distance between the probe and sample. The samples utilized were a whole wood samples of 0.25 pcf CCA-treated wood and untreated wood. A retention level of 0.25 pcf was chosen because it was the lowest concentration available. Figure III.19 shows that the distance between sample and the sensor impacts the number of counts of arsenic read by the XRF analyzer; the larger the distance the lower the readings. It is still possible, however, to determine presence and concentration of CCA in a given sample of wood, at a distance of about 1 inch. Following this experiment, a plastic shield of ~ 2-3 mm thickness was placed on the sensor, and a similar distance study was performed. Results (figure III.20) indicate that the plastic shield reduces the sensitivity of the instrument. Nevertheless, the presence of treated wood can be detected at a distance of 1 inch from the sensor even with the plastic shield.

![Graph showing arsenic counts vs. distance away from head](image)

**Figure III.19: Distance Study on a Whole Wood Sample of 0.25 pcf CCA-Treated Wood Utilizing a Count Time of 5 Seconds.**
Figure III.20 Distance Study on a Whole Wood Sample of 0.25 pcf CCA-Treated Wood Utilizing a Count Time of 5 Seconds and with Shield Present
Experimental Set #3

The results of experimental set #3 indicate that the detection limit of the XRF equipment for a 3 second count time on arsenic is on the order of 2 to 3% (table III.7) and for a 10 second count time is on the order of 1 to 2% (table III.8). For a 3 second count time, the untreated wood sample resulted in a mean reading of 0.3% CCA with a standard deviation of 0.73. For this experiment, the detection limit is given by the standard deviation of the blank value given the relatively large variation observed. The detection limit is thus calculated as 3 times the standard deviation which in this case would be 2.1%. For a 10 second count time, the mean value for untreated wood was 0.5% and the standard deviation was 0.31. Three times the standard deviation resulted in a value of 0.93%, whereas a value of 2.5 times the blank resulted in a CCA value of 1.1%, thereby indicating that the detection limit is on the order of 1% for a 10 second count time. However, one disturbing feature of the results is that the data for the 3% and 5% mixtures for both count times were almost indistinguishable from one another, which raises skepticism concerning such a low detection limit.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Measured % CCA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>100% untreated wood</td>
<td>0.3</td>
</tr>
<tr>
<td>3% CCA-treated wood at 0.25 pcf + 97% untreated wood</td>
<td>1.33</td>
</tr>
<tr>
<td>5% CCA-treated wood at 0.25 pcf + 95% untreated wood</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Table III.7: Results of the Detection Limit Study for Samples in the 0 - 10% CCA Range, Count Time of 3 seconds.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Measured % CCA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>100% untreated wood</td>
<td>0.5</td>
</tr>
<tr>
<td>3% CCA-treated wood at 0.25 pcf + 97% untreated wood</td>
<td>2.53</td>
</tr>
<tr>
<td>5% CCA-treated wood at 0.25 pcf + 95% untreated wood</td>
<td>2.91</td>
</tr>
</tbody>
</table>

Table III.8: Results of the Detection Limit Study for Samples in the 0 - 10% CCA Range, Count Time of 10 seconds.
III.2.d Discussion of XRF Results

Overall Results

Arsenic proved to be the best indicator for presence of CCA in wood, because of the higher number of counts provided by this element. Copper and chromium could be used to double-check for the presence of CCA. The detection limit of XRF technology, is on the order of 3 to 5% at best, assuming that extensive calibration is conducted on the equipment. There is some evidence to suggest that the detection limit can be lowered to potentially 1 or 2% with extended count times. It was determined that a 2 second count time was the shortest time for the determination of presence and concentration of CCA in an unmixed wood sample. A 1 second count time is not an option for Model 400, because it takes approximately 1 second for the instrument’s “shutter” to open and release x-rays. In an on-line system, x-rays would be continuous, which implies that the minimum count time could be 1 second or even a fraction of a second, thereby increasing the speed at which wood could be processed at a C&D recycling facility. For a count time of 2 seconds and a minimum board length of 2 feet, the processing speed is about 3,600 ft/hr; this increases to 14,400 ft/hr for a count time of 0.5 seconds. The distance study was very significant from a point of view of an on-line system. There is a possibility that the head could be placed an inch or more away from the wood and still effectively detect the presence of arsenic. A plastic shield used in the experiment was meant to mimic a possible shield placed on the detector in order to protect it. The instrument is capable of registering the presence of arsenic up to a one-inch distance with a shield. It is thought that segregation of wood would be most effective before it is shredded and mixed because of more effective detection as well as difficulties in sorting small wood chips.

Advantages

The XRF technique is well suited for applications within the wood waste disposal sector. Analysis of wood waste samples is easy and fast. Once an on-line system is in place, there is no sample preparation, and data acquisition gives results in seconds. The XRF method does not alter, contaminate, or damage the wood analyzed. In the AWPA standard method wood has to be ground, mixed, compacted, and mounted in the sample holder before analysis by x-ray spectroscopy (AWPA 1996). The operation of the Model 400 is much simpler eliminating sample processing. The method is also low maintenance, with no reagents and very few consumables, and easy cleaning. XRF is also very precise, meaning that no repetitive calibration is necessary, since every calibration lasts 6 months to 2 years. The long life span of 10 years is also an advantage. After that period the instrument can be traded-in to ASOMA toward the purchase of a new instrument. The Model 400 does not generate any waste. It is small and easy to transport.

Disadvantages

Costs depend on the type of system and arrangements with the company. ASOMA can provide the Model 400 detector alone at a base price of $20,000-$25,000. In this case a C&D facility would have to develop their own on-line sampling system that would work for them. ASOMA can also develop an on-line system specifically tailored to a given facility at a cost of about $100,000. The detector containing argon or neon gas has a life span of about five years. The replacement cost can vary between $1,800-$2,400. Smaller disadvantages include a beryllium window which is present in the head of the model, and which can cost up to $100 if damaged, and can cause serious harm to the instrument if not present. A shield could be placed to protect this window.

Because the Model 400 as well as all XRF models carry a radioactive source (Curium 244 in case of Model 400) a user needs to have a license to operate such equipment. ASOMA is able to
extend its license to a user only if the instrument is set in one place at all times. Otherwise, a facility would need to get independent licensure from the State of Florida. This could present a problem if a facility would choose to use the instrument for portable purposes. It is also important to note that other XRF analyzers (e.g. those produced by Oxford Instruments) contain an x-ray tube rather than a radioactive source which produces the needed x-rays for analysis. It may be easier to license instruments containing an x-ray tube.
CHAPTER IV
EVALUATION OF MANAGEMENT OPTIONS
IV.1 REGULATORY IMPLICATIONS OF TOTAL METALS
CONCENTRATIONS IN TREATED WOOD
AND TREATED WOOD ASH

How much metal is in CCA-treated wood and wood ash?

Results (table IV.1) indicate that chromium, copper, and arsenic concentrations in CCA-
treated wood exceed values in untreated wood by several thousand mg/kg for retention levels of 0.25
pcf and 0.60 pcf and by tens-of-thousands of mg/kg for a retention level 2.50 pcf. After incineration,
the concentration differences between untreated and treated wood are more pronounced. For
untreated-wood ash, the sum of the chromium, copper, and arsenic concentration is less than a few
hundred mg/kg. For treated wood with retention levels of 0.25 pcf and 0.60 pcf, metals represent
about 4% and 13% of the ash weight, respectively. In other words, for every 100 pounds of ash,
many pounds (4 or 13 pounds respectively for 0.25 pcf and 0.60 pcf) would be in the form of metals.
At a 2.50 pcf retention level, metals account for about 39% of the ash weight.

Should CCA-treated wood and wood ash be land applied?

Comparisons with regulatory limits indicate that unburned CCA-treated wood (no mixing with
untreated wood), even at the lowest retention level, will not meet federal or state regulatory limits
due to excessive arsenic concentrations (table IV.1). If untreated wood were inadvertently mixed
with treated wood1, CCA-treated wood at a 0.25 pcf retention level could represent up to 2% of the
mixture and still meet the federal pollution limit for arsenic of 41 mg/kg (table IV.2). At retention
levels of 0.6 pcf and 2.50 pcf only 0.9% and 0.2% of the mixture could be composed of treated
wood. In order to meet the State industrial standard, treated wood at 0.25 pcf could represent a
maximum of 0.09% of the mixture. No treated wood could be mixed with untreated wood and meet
the State residential standard, especially given that it is questionable whether even untreated wood
could meet the residential standard for arsenic. Wood waste processed for land application purposes
(e.g. mulch) should be therefore essentially free of CCA if it is to be used in Florida.

The ash from CCA-treated wood far exceeds all regulatory limits. In this case, untreated
wood just qualifies within federal regulatory criteria for land application of sewage sludge and thus
even minute quantities (0.11% estimated) of CCA-treated wood treated at 0.25 pcf would likely
cause an ash to exceed Federal regulatory criteria. The ash from untreated wood exceeds State
regulatory levels by a considerable margin and it is questionable whether even 100% untreated wood
ash could be land applied within Florida. Land application of wood ash containing minute quantities
of CCA should be prohibited in Florida.

Is there room for relaxing land application standards?

It is important to note that Florida regulations are open to interpretation concerning how
metals concentrations are defined. If total recoverable metals (TRM) are used for regulatory
purposes instead of the true total metals concentration, then some of the above conclusions may be
relaxed given that only a fraction of the total metals are “recoverable” using the accepted protocols.
Our results indicate that TRM represents roughly 25 to 60% of the total for copper, 10 to 30% of
the total for chromium, and 40 to 100% of the total for arsenic.

---

1The research team does not promote mixing of treated and untreated wood. The
following computations are provided for discussion purposes only.
Due to the significant differences between TRM and total values, we have chosen here a conservative approach comparing regulatory limits to total values. Such an approach is further justified given that the long-term leaching characteristics of wood ash have not yet been documented.

<table>
<thead>
<tr>
<th>Wood Type</th>
<th>Metals Concentration, mg metal per kg of wood or ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Unburned Wood(^a)</td>
<td></td>
</tr>
<tr>
<td>Untreated Wood</td>
<td>7.0</td>
</tr>
<tr>
<td>CCA-Treated Wood at 0.25 pcf</td>
<td>2,060</td>
</tr>
<tr>
<td>CCA-Treated Wood at 0.60 pcf</td>
<td>4,940</td>
</tr>
<tr>
<td>CCA-Treated Wood at 2.50 pcf</td>
<td>20,600</td>
</tr>
<tr>
<td>Ash(^b)</td>
<td></td>
</tr>
<tr>
<td>Non-CCA-Treated Wood</td>
<td>141</td>
</tr>
<tr>
<td>CCA-Treated Wood at 0.25 pcf</td>
<td>20,600</td>
</tr>
<tr>
<td>CCA-Treated Wood at 0.60 pcf</td>
<td>51,100</td>
</tr>
<tr>
<td>CCA-Treated Wood at 2.50 pcf</td>
<td>174,000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Regulatory Limits</th>
<th>Federal(^c)</th>
<th>Florida(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ceiling (mg/kg)</td>
<td>Industrial (mg/kg)</td>
</tr>
<tr>
<td></td>
<td>Not Applicable</td>
<td>Not Applicable</td>
</tr>
<tr>
<td></td>
<td>4300</td>
<td>430</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>3.7</td>
</tr>
</tbody>
</table>

\(^a\) Computed values assuming that retention rating equals amount of chemical in wood.
\(^b\) Measured values
\(^c\) Federal Register 40 CFR Part 503.13, Standards for the Use or Disposal of Sewage Sludge, Subpart B, Land Application
\(^d\) Florida Department of Environmental Protection, Proposed Chapter 62-777, F.A.C. Contaminant Target Clean-up Levels

Table IV.1: Chromium, Copper, and Arsenic Concentrations in Treated Wood and Treated Wood Ash Samples Used in This Study. Regulatory Levels Provided for Comparison.

<table>
<thead>
<tr>
<th>Type of Mixture</th>
<th>Federal Limit, Pollution Level</th>
<th>State Guideline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unburned</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25 pcf</td>
<td>2 %</td>
</tr>
<tr>
<td></td>
<td>0.60 pcf</td>
<td>0.9%</td>
</tr>
<tr>
<td></td>
<td>2.50 pcf</td>
<td>0.2%</td>
</tr>
<tr>
<td></td>
<td>Ash</td>
<td>&lt; 0.11%</td>
</tr>
</tbody>
</table>

\(^a\) Mixture of treated wood ash with untreated wood ash

Table IV.2: Fraction of CCA-Treated Wood that Can be Mixed with Untreated Wood such that Mixture Equals Regulatory Limits or Guidelines.
IV.2 REGULATORY IMPLICATIONS OF TCLP AND SPLP RESULTS

Table IV.3 summarizes the results of leaching tests with respect to when a sample exceeded a particular TCLP limit or groundwater guidance concentration. Sample leachate concentrations from the SPLP tests were also compared to Florida GWGCs. A “Y” in this table indicates that the standard was exceeded; an “N” indicates that leachate concentrations were below the recommended levels.

Should CCA-treated wood ash be land applied: the SPLP perspective?

It is likely that land application of ash containing even minute quantities of CCA will not be permitted. The ash produced from the 2.50 pcf sample exceeded GWGC limits for all metals including copper. For chromium, all samples except untreated wood and one other exceeded GWGC limits. All samples, except untreated wood, exceeded the GWGC for arsenic. Only untreated wood ash passed the GWGC for all metals. Whether or not 100% untreated wood can be land applied will depend upon the interpretation of the SCTL’s as described in the previous section.

Should CCA-treated wood ash be disposed in a lined MSW landfill: the TCLP perspective?

TCLP limits were also exceeded for arsenic for all ash samples, except untreated wood and 2 of the 3 C&D samples. For arsenic, the degree to which the limits were exceeded were strongly dependent upon the retention level of the original wood sample. For the lowest retention level, 0.25 pcf, the TCLP limit for arsenic was exceeded by a factor of 10. Values were exceeded by a factor of 30 to 100 for samples containing higher retention values (0.60 pcf, 2.50 pcf, and weathered wood samples). For chromium, the 0.25 pcf sample and one of the C&D samples exceeded TCLP limits. Of interest is that although arsenic appears to be the most problematic metal from a regulatory standpoint, the C&D 1 sample failed TCLP criteria for chromium but not for arsenic. Therefore, 2 of the 3 C&D samples tested failed TCLP criteria. One failed for arsenic and the other failed for chromium.

Recall that if a sample exceeds TCLP limits it is usually considered a hazardous waste and therefore cannot be disposed in a lined municipal solid waste landfill. Costs for disposing hazardous wastes far exceed the costs for disposing a regular solid waste and therefore efforts should focus on limiting the amount of CCA-treated wood burned in wood waste cogeneration facilities. Results indicate that there is a significant likelihood that ash produced from C&D wood waste would fail TCLP criteria, especially if the wood waste contains more than 5% CCA treated wood by weight. It is difficult to assign one number for the “%CCA” that can be burned with untreated wood waste before being considered a hazardous waste. Variability was observed in the data, presumably due to differences in wood waste and combustion characteristics. However, clearly the data show that the number for the %CCA should be below 5%.
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Sample Exceeds TCLP Limit?</th>
<th>Sample Exceeds Florida GWGC TCLP Leachate</th>
<th>Sample Exceeds Florida GWGC SPLP Leachate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>Cr</td>
<td>As</td>
</tr>
<tr>
<td>Untreated</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Weathered</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
</tbody>
</table>

Table IV.3: Comparison of SPLP and TCLP Results to Regulatory Standards or Policy
IV.3 PRACTICAL ISSUES ASSOCIATED WITH SOLVENT EXTRactions

Summary of Results

Maximum metals removals (from the total) were 60 to 100% for copper, 25 to 70% for chromium, and 80 to 100% for arsenic for samples characterized by low retention levels. These maximum removals were observed for the nitric acid or TRM extractions. The maximum leachate concentrations were observed for the 2.50 pcf sample which produced over 900 mg/L of copper, 600 mg/L of chromium, and 750 mg/L of arsenic. Another finding of interest is the efficiency of distilled water and other weak solvents to extract measurable amounts of chromium, especially for samples containing low retention levels of CCA. For the C&D 3 sample, for example, distilled water was capable of extracting 54% of the total chromium, hydrogen peroxide removed 49%, while a weak solution of citric acid with sodium hydroxide removed 57%. Also of significance is the ability of citric acid to extract most of the arsenic from the samples characterized by low retention levels. 41% of the arsenic was removed for the 0.25 pcf sample, 54% for the weathered wood sample, and between 90 to 100% was removed for two of the three C&D samples. Chromium removals using citric acid were not quite as effective. Chromium removals of 40 to 57% were observed for two of the three C&D samples.

Implications

It is important to note that CCA manufacturers purchase raw chromium, copper, and arsenic from various sources. After some processing they then mix the metals in given proportions to provide a marketable CCA chemical. The CCA manufacturers prefer receiving the chemicals individually to ease with the mixing process. Thus they prefer receiving the copper separate from the chromium which is also separate from the arsenic (Pasek, personal communication). CCA manufacturers also emphasize the importance of producing relatively pure solutions of chromium, copper, and arsenic with minimal contamination from silica, lead, and other metals which can be problematic especially when the metals are derived from processed wood waste. Even if the CCA manufacturers could utilize the solvent extracts, the metals must be oxidized to their appropriate valence (e.g. chromium as Cr$^{+6}$, and arsenic as As$^{+5}$, and Copper as Cu$^{+2}$) which would further escalate recycling costs. Given the criteria imposed by the CCA manufacturers it is not clear whether solvent extraction technologies for recycling the CCA chemical could be cost effective.

Nevertheless results indicate that weak solvents can be used for removing chromium from CCA-treated wood ash and that citric acid can be used to remove arsenic. It is highly recommended that the efficiency of the weak solvents, especially citric acid, be investigated further given that their use would be more cost effective than use of mineral acids. Other extraction methods not investigated through this study also merit consideration. These include extractions with surfactants, organic-based chemicals, and use of ultrasonic methods for enhance desorption of the metals from the remaining ash. Once the best solvent is identified, efforts should focus on developing further processing methods for the extract such that it can be ultimately re-cycled into the CCA manufacturing process.
IV.4 EVALUATION OF SORTING TECHNOLOGIES

Chemical Stains

The chemical stains performed very well on whole lumbers and on laboratory mixtures of shredded wood. The stains also worked well for 5 of the 7 field samples of recycled wood waste. The two samples that did not show adequate results contained a considerable amount of soil and very fibrous or string-like material. One of the advantages of using chemical stains for sorting purposes is that these solutions are easy to make and the reagents used in the stains are purely organic compounds and contain no metals. So if the stained wood is ultimately burned, the stain will not add to the metal burden of the ash. Another important advantage for the chemical stains is that they require minimal investment in capital costs; their use at C&D recycling facilities, however, will likely be labor intensive. Potential uses of the chemical stains identified through the current study include sorting relatively small quantities of wood waste and “spot-checking” fuel quality at both wood recycling and burning facilities. Field pilot studies are needed to determine whether stains can be used to sort large quantities of CCA-treated wood in an economical fashion.

X-ray Fluorescence

X-ray fluorescence technology was found to easily detect the presence of treated wood in both whole and shredded samples. The minimum detection limit for wood mixtures lies between 3 and 5% treated wood (0.25 pcf). This detection limit is of significance since results of the TCLP experiments indicate that a hazardous designation can occur for mixtures containing more than 5% CCA treated wood by weight. X-ray fluorescence can thus be used for screening fuel quality if regulations for burning of wood waste are set below levels considered to produce a hazardous ash (i.e. less than 5% CCA-treated wood). Various operation parameters were also defined through this study for x-ray fluorescence technology. Sample pre-processing was greatly simplified and results indicate that this technology is well suited for on-line automated sorting. Such a system, however, will require considerable capital investment by a C&D facility which can be partially off-set by the labor costs associated with using chemical stains.
IV.5 RECOMMENDATIONS

Results indicate that wood mixtures containing more than 5% CCA treated wood will exceed TCLP limits and Florida’s GWGC concentrations. Last’s year’s study characterizing C&D wood waste indicated that recycled wood from C&D recycling facilities located throughout Florida is composed of 6% CCA-treated wood on average. At the current time, most wood burning facilities that accept recycled wood waste also accept wood from additional sources thereby diluting the fraction of CCA-treated wood to approximately 2 to 3%. Given that the quantities of CCA-treated wood disposed are forecasted to increase significantly, it is likely that current disposal practices will not be economically nor environmentally desirable in the future due to the production of a hazardous ash.

Results of the solvent extraction study showed that arsenic was readily removed by citric acid for samples containing low retention levels. Given the high percent removals, solvent extraction methods merit further evaluation for potentially removing CCA from the ash so that the ash can be classified as a non-hazardous waste. An ideal scenario would be use of the solvent extract, containing the CCA chemical, within the CCA manufacturing process. Such a recycling option will require further research in purifying the solvent extract and converting the metals in the extract to the proper valence needed for wood treatment purposes. Other research options include evaluating other solvents, such as organic solvents and surfactants, for removing CCA from the ash. There is also a potential for processing the ash in a dry form, without extraction into a liquid, to convert the metals in the ash to their proper valence.

Results of the solvent extraction study can also be utilized to assess the fate of metals within CCA-treated wood ash once released into the environment. Data indicate that chromium is especially mobile for weak solvents and for samples containing relatively low retention levels. These results greatly limit recycling opportunities for wood ash containing CCA due to the potential for metals leaching and thus wood ash containing minute quantities of CCA should not be land applied. Furthermore, the hazardous nature of an ash produced from a mixture containing more than 5% CCA-treated wood should be questioned. It is likely that such ash (> 5% CCA) will require disposal through a hazardous waste facility.

In the absence of a good ash treatment method, removal of CCA-treated wood from the remaining wood stream prior to incineration is the only viable alternative which will minimize the amount of metals within wood ash. The two methods investigated through this study, chemical stains and x-ray fluorescence technology, performed extremely well at distinguishing between CCA-treated wood and other wood types during laboratory testing. The chemical stain method requires a relatively small capital investment for its use. A pilot study at C&D recycling facilities is highly recommended to further explore the use of this technology in field situations. Such tests should include experiments with and without the stains to document improvements in separating treated from untreated wood. Assuming that results are positive, a workshop should be developed that trains C&D recyclers on the proper use of the stains. X-ray fluorescence would require considerable capital investment, on the order of several tens of thousands of dollars; however, the technology is well suited for on-line automated operation. The research team does recognize that sample introduction to the x-ray detector represents a challenge. Research should be promoted to develop an x-ray fluorescence demonstration unit that can be tested in the field at C&D recycling facilities. After the performance of both sorting technologies is proven in pilot field tests, incentives should be provided to C&D recycling facilities that implement a sorting program for CCA-treated wood within their day-
to-day operations. Incentives can be provided in the form of tax breaks or in their ability to sell the
sorted wood at a higher profit.

One drawback observed at the current time, are markets for treated wood waste once it is
sorted-out from other wood types. One promising disposal alternative for ultimate disposal is a
controlled incineration process, pyrolysis, which is designed to reduce the volume of CCA-treated
wood waste and contain the metals within the ash. Efforts should focus on identifying commercially-
available pyrolysis systems and on developing markets, such as metals recovery, for the ash residual
from such a process.
IV.6 ACKNOWLEDGMENTS

This research was funded by the Florida Center for Solid and Hazardous Waste Management. Matching funds were provided by Florida Power and Light Company. The authors acknowledge the Executive Director of the Center, Mr. John Schert, and his staff for their suggestions and for their assistance with information dissemination. The authors also thank the following members of the Technical Advisory Committee for their insight and feedback throughout the course of the project: Kevin Archer of Chemical Specialties Inc., Phil Badger of the Southeastern Biomass Energy Program, Lee Casey of Metro-Dade County Department of Solid Waste Management, Kenneth Cogan of Hickson Corporation, David Dee of Landers and Parsons, Keith Drescher of Florida Power and Light, Jeffrey Fehrs an environmental consultant, Bill Gay of Langdale Forest Products, Jim Gabbert of Meyer and Gabbert Recycling, William Krumholz of the Florida Department of Environmental Protection (Ft. Myers), Lisa Martin of the Florida Department of Environmental Protection (Tallahassee), George Parris of the American Wood Preservers’ Institute, Mike Provenza of Robbins Manufacturing, Pete Rosendahl of Florida Crystals Inc., Chih-Shin Shieh of the Florida Institute of Technology, August Staats of Osmose Wood Preserving, Donald Surrency of Koppers Industries, Ram Tewari of the Broward County Commission Solid Waste Operations Division, and George Varn Jr. of Varn Wood Products.

We also gratefully acknowledge Florida Power and Light Company for allowing the research team to utilize their facility to incinerate wood samples. We thank Keith Drescher for coordinating the permit exemption, Bob Graham for coordinating operations during the incinerator activities, and the many other employees of FPL who helped facilitate sample processing. We also appreciate the assistance received from Julie Kyler of ASOMA Instruments who coordinated the x-ray fluorescence experiments #1 and #3 through her company and for the assistance and hospitality provided to the research team during experiment #2. We thank Bill Gay of Langdale Forest Products and Ken Cogan of Hickson Corp. who coordinated the analysis of the retention levels for unburned wood at their respective facilities. We also thank Ken Cogan for “getting-the-ball-rolling” on the chemical stain study by providing the research team with a batch of Chrome Azurol stain and samples of treated wood. We would like to thank Dr. William Vernetson of the University of Florida and Dr. Michael Ames of the Massachusetts Institute of Technology for the neutron activation analysis of the ash samples. Neutron activation analysis was supported by Dept. of Energy grant number DE-FG02-96NE38152.A003. We thank Gene Pasek of Hickson Corp. for the x-ray diffraction analysis on the ash samples. We appreciate the assistance provided by Dr. Matthew Lynn of the University of Miami during EDX analysis of samples. Catalina Santamaria, an undergraduate student at the University of Miami, and Sue Lee, a graduate student from the University of Florida, are also gratefully acknowledged for their help in processing samples and conducting experiments.
REFERENCES


Cooper, P.A., 1993. "Disposal of treated wood removed from service: the issues." Proceedings of the Carolinas-Chesapeake Section of the Forest Products Society. Presented at the May 13, 1993 meeting on Environmental Considerations in the Use of Pressure-TreatedWood Products. Published by the Forest Products Society, Madison, WI.


Gifford, J.S. and Dare, P.H., 1998. Leaching of copper, chromium, and arsenic from ash produced by burning CCA treated wood. Submitted to Toxicological and Environmental Chemistry.


This page left intentionally blank
APPENDIX A:
SUPPLEMENTARY TABLES FOR TCLP AND SPLP TESTS
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Total Mass (g)</th>
<th>Mass Retained on Sieve(^1) (g)</th>
<th>Mass Passing Sieve(^1) (g)</th>
<th>Mass Retained on Sieve(^1) (%)</th>
<th>Mass Passing Sieve(^1) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>998.3</td>
<td>248.7</td>
<td>749.6</td>
<td>24.9%</td>
<td>75.1%</td>
</tr>
<tr>
<td>2</td>
<td>674.9</td>
<td>130.9</td>
<td>544.0</td>
<td>19.4%</td>
<td>80.6%</td>
</tr>
<tr>
<td>3</td>
<td>843.4</td>
<td>114.6</td>
<td>728.8</td>
<td>13.6%</td>
<td>86.4%</td>
</tr>
<tr>
<td>4(^2)</td>
<td>235.4</td>
<td>12.2</td>
<td>233.2</td>
<td>5.2%</td>
<td>94.8%</td>
</tr>
<tr>
<td>5</td>
<td>587.9</td>
<td>138.7</td>
<td>449.2</td>
<td>23.6%</td>
<td>76.4%</td>
</tr>
<tr>
<td>6</td>
<td>1203.5</td>
<td>31.9</td>
<td>1171.6</td>
<td>2.7%</td>
<td>97.3%</td>
</tr>
<tr>
<td>7</td>
<td>855.3</td>
<td>43.2</td>
<td>812.1</td>
<td>5.1%</td>
<td>94.9%</td>
</tr>
<tr>
<td>8</td>
<td>841.8</td>
<td>45.2</td>
<td>796.6</td>
<td>5.4%</td>
<td>94.6%</td>
</tr>
<tr>
<td>9</td>
<td>1074.3</td>
<td>403.1</td>
<td>671.2</td>
<td>37.5%</td>
<td>62.5%</td>
</tr>
<tr>
<td>10</td>
<td>627.6</td>
<td>143.4</td>
<td>484.2</td>
<td>22.8%</td>
<td>77.2%</td>
</tr>
</tbody>
</table>

\(^1\) The sieve size used was 4.75 mm.

\(^2\) Sample was later recombined for further analysis because of the small sample mass retained on sieve.

Table A.1: Results of Size Fractionation
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Small or Large Fraction</th>
<th>Mass Used (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPLP</td>
<td>TCLP</td>
</tr>
<tr>
<td></td>
<td>Run A</td>
<td>Run B</td>
</tr>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>100</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>10</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>10</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>10</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>10</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>5</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>5</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>5</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>10</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>10</td>
</tr>
<tr>
<td>2.50 pcf²</td>
<td>----</td>
<td>10</td>
</tr>
</tbody>
</table>

² Note: The size fractions for sample 4 were combined. They were run in triplicate at 10 g each.

Table A.2: The Mass of Samples used in Leaching Procedures
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Small or Large Fraction</th>
<th>Initial pH Run A</th>
<th>Final pH Run A</th>
<th>Initial pH Run A</th>
<th>Final pH Run B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>4.88</td>
<td>6.03</td>
<td>4.90</td>
<td>6.21</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>4.90</td>
<td>6.26</td>
<td>4.93</td>
<td>6.71</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>4.90</td>
<td>5.51</td>
<td>4.91</td>
<td>5.51</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>4.92</td>
<td>6.04</td>
<td>4.90</td>
<td>6.05</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>2.89</td>
<td>5.85</td>
<td>2.89</td>
<td>5.80</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>2.90</td>
<td>5.75</td>
<td>2.90</td>
<td>6.07</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>2.88</td>
<td>6.08</td>
<td>2.87</td>
<td>6.71</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>2.91</td>
<td>6.80</td>
<td>2.87</td>
<td>6.71</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>2.88</td>
<td>5.57</td>
<td>2.89</td>
<td>5.40</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>4.94</td>
<td>5.45</td>
<td>4.94</td>
<td>5.50</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>4.94</td>
<td>5.45</td>
<td>4.94</td>
<td>5.46</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>4.92</td>
<td>5.23</td>
<td>4.92</td>
<td>5.28</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>4.92</td>
<td>5.40</td>
<td>4.92</td>
<td>5.44</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>4.94</td>
<td>6.45</td>
<td>4.94</td>
<td>6.52</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>4.94</td>
<td>5.72</td>
<td>4.94</td>
<td>6.09</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>4.89</td>
<td>6.23</td>
<td>4.89</td>
<td>6.14</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>4.89</td>
<td>5.50</td>
<td>4.89</td>
<td>5.45</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>4.91</td>
<td>5.34</td>
<td>4.91</td>
<td>5.39</td>
</tr>
<tr>
<td>2.50 pcf¹</td>
<td>----</td>
<td>4.92</td>
<td>5.03</td>
<td>4.92</td>
<td>5.01</td>
</tr>
<tr>
<td></td>
<td>----</td>
<td>4.92</td>
<td>5.04</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ Note: The size fractions for sample 4 were combined. They were run in triplicate at 10 g each.

Table A.3: The Initial and Final pH of the Leaching Solutions (TCLP)
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Small or Large Fraction</th>
<th>Final pH Run A&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Final pH Run B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>8.70</td>
<td>8.76</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>8.23</td>
<td>8.13</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>6.48</td>
<td>6.41</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>7.79</td>
<td>7.57</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>11.76</td>
<td>11.75</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>10.63</td>
<td>10.40</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>12.12</td>
<td>12.25</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>10.31</td>
<td>10.33</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>9.78</td>
<td>10.29</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>7.38</td>
<td>7.68</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>7.12</td>
<td>7.25</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>6.32</td>
<td>6.38</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>6.73</td>
<td>6.68</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>9.60</td>
<td>9.39</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>8.45</td>
<td>7.52</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>8.96</td>
<td>9.23</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>7.89</td>
<td>7.85</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>7.75</td>
<td>7.78</td>
</tr>
<tr>
<td>2.50 pcf&lt;sup&gt;2&lt;/sup&gt;</td>
<td>----</td>
<td>4.74</td>
<td>4.75</td>
</tr>
</tbody>
</table>

<sup>1</sup> Note: The initial pH of all SPLP tests was 4.2.

<sup>2</sup> Note: The size fractions for sample 4 were combined. They were run in triplicate at 10 g each.

Table A.4: The Final pH of the Leaching Solutions (SPLP)
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Small or Large Fraction</th>
<th>As Conc. Run A (mg/l)</th>
<th>As Conc. Run B (mg/l)</th>
<th>Average As Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>57.0</td>
<td>58.1</td>
<td>57.5</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>124.8</td>
<td>151.4</td>
<td>138.1</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>227.0</td>
<td>235.1</td>
<td>231.0</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>2.2</td>
<td>4.7</td>
<td>3.5</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>0.11</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>8.6</td>
<td>5.0</td>
<td>6.8</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>5.3</td>
<td>6.9</td>
<td>6.1</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>10.3</td>
<td></td>
<td>10.3</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>20.9</td>
<td>23.2</td>
<td>22.0</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>92.8</td>
<td>108.6</td>
<td>100.7</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>91.8</td>
<td>102.5</td>
<td>97.1</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>2.1</td>
<td>3.4</td>
<td>2.7</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>2.4</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>5.2</td>
<td>5.7</td>
<td>5.5</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>3.7</td>
<td>3.5</td>
<td>3.6</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>1.4</td>
<td>2.6</td>
<td>2.0</td>
</tr>
<tr>
<td>2.50 pcf²</td>
<td>----</td>
<td>545.5</td>
<td>473.2</td>
<td>510.6</td>
</tr>
</tbody>
</table>

Table A.5: Results of the TCLP for Arsenic
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Small or Large Fraction</th>
<th>Cr Conc. Run A (mg/l)</th>
<th>Cr Conc. Run B (mg/l)</th>
<th>Average Cr Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>0.33</td>
<td>14.5</td>
<td>7.4</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>25.6</td>
<td>24.0</td>
<td>24.8</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>2.7</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>0.3</td>
<td>&lt;0.10</td>
<td>0.02</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>2.50 pcf$^2$</td>
<td>----</td>
<td>5.4</td>
<td>&lt;0.10</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table A.6: Results of the TCLP for Chromium
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Small or Large Fraction</th>
<th>Cu Conc. Run A (mg/l)</th>
<th>Cu Conc. Run B (mg/l)</th>
<th>Average Cu Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>0.36</td>
<td>0.10</td>
<td>0.23</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>14.3</td>
<td>13.8</td>
<td>14.0</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>3.4</td>
<td>3.7</td>
<td>3.6</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>0.43</td>
<td>0.50</td>
<td>0.47</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>0.06</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>0.09</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>2.0</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>20.7</td>
<td>19.5</td>
<td>20.1</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>3.7</td>
<td>4.1</td>
<td>3.9</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>0.05</td>
<td>&lt;0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>2.50 pcf²</td>
<td>----</td>
<td>14.8</td>
<td>10.8</td>
<td>11.78</td>
</tr>
</tbody>
</table>

Table A.7: Results of the TCLP for Copper
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Small or Large Fraction</th>
<th>As Conc. Run A (mg/l)</th>
<th>As Conc. Run B (mg/l)</th>
<th>Average As Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>63.1</td>
<td>73.1</td>
<td>68.1</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>277.5</td>
<td>307.3</td>
<td>292.4</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>196.3</td>
<td>178.2</td>
<td>187.2</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>1.31</td>
<td>0.22</td>
<td>0.76</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>0.34</td>
<td>0.18</td>
<td>0.26</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>0.53</td>
<td>0.40</td>
<td>0.47</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>0.80</td>
<td>0.63</td>
<td>0.72</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>3.5</td>
<td>2.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>18.7</td>
<td>19.4</td>
<td>19.0</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>101.8</td>
<td>85.5</td>
<td>93.7</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>75.9</td>
<td>80.6</td>
<td>78.2</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>3.07</td>
<td>0.61</td>
<td>1.8</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>1.05</td>
<td>0.88</td>
<td>0.97</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>2.13</td>
<td>1.48</td>
<td>1.81</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>1.61</td>
<td>1.81</td>
<td>1.71</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>1.34</td>
<td>1.07</td>
<td>1.20</td>
</tr>
<tr>
<td>2.50 pcf²</td>
<td>----</td>
<td>551.5</td>
<td>581.0</td>
<td>561.2</td>
</tr>
</tbody>
</table>

Table A.8: Results of the SPLP for Arsenic

A-9
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Small or Large Fraction</th>
<th>Cr Conc. Run A (mg/l)</th>
<th>Cr Conc. Run B (mg/l)</th>
<th>Average Cr Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>&lt;0.10</td>
<td>69.8</td>
<td>34.9</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>7.8</td>
<td>31.5</td>
<td>19.6</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>58.7</td>
<td>54.2</td>
<td>56.5</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>5.6</td>
<td>5.5</td>
<td>5.6</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>26.4</td>
<td>27.5</td>
<td>27.0</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>4.3</td>
<td>6.7</td>
<td>5.5</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>5.8</td>
<td>9.5</td>
<td>7.6</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>2.7</td>
<td>2.1</td>
<td>2.4</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>1.5</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>0.22</td>
<td>0.64</td>
<td>0.43</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>0.66</td>
<td>0.53</td>
<td>0.60</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>0.23</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>2.50 pcf²</td>
<td>----</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>----</td>
<td>2.7</td>
<td>----</td>
<td></td>
</tr>
</tbody>
</table>

Table A.9: Results of the SPLP for Chromium
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Small or Large Fraction</th>
<th>Cu Conc. Run A (mg/l)</th>
<th>Cu Conc. Run B (mg/l)</th>
<th>Average Cu Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Small</td>
<td>0.12</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>Weathered</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Small</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Untreated</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>Large</td>
<td>0.13</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>Weathered</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>5% CCA a</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>5% CCA b</td>
<td>Large</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>2.50 pcf²</td>
<td>----</td>
<td>46.8</td>
<td>45.5</td>
<td>40.8</td>
</tr>
<tr>
<td></td>
<td>----</td>
<td>30.0</td>
<td>----</td>
<td></td>
</tr>
</tbody>
</table>

Table A.10: Results of the SPLP for Copper
<table>
<thead>
<tr>
<th>Sample</th>
<th>Arsenic</th>
<th></th>
<th>Copper</th>
<th></th>
<th>Chromium</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Spike Conc. (mg/L)</td>
<td>Sample Conc. (mg/L)</td>
<td>% Rec.</td>
<td>Spike Conc. (mg/L)</td>
<td>Sample Conc. (mg/L)</td>
</tr>
<tr>
<td>BLK TCLP 1</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>BLK MS TCLP 1</td>
<td>40</td>
<td>39.585</td>
<td>99%</td>
<td>20</td>
<td>20.25</td>
<td>101%</td>
</tr>
<tr>
<td>10S TCLP</td>
<td>-</td>
<td>1.4125</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>10S MS TCLP 1</td>
<td>60</td>
<td>61.35</td>
<td>100%</td>
<td>20</td>
<td>18.5</td>
<td>92%</td>
</tr>
<tr>
<td>10S MSDUP TCLP 1</td>
<td>60</td>
<td>60.29</td>
<td>98%</td>
<td>20</td>
<td>18.67</td>
<td>93%</td>
</tr>
<tr>
<td>BLK SPLP 1</td>
<td>-</td>
<td>0.054</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>BLK MS SPLP 1</td>
<td>40</td>
<td>39.15</td>
<td>98%</td>
<td>20</td>
<td>21.5</td>
<td>107%</td>
</tr>
<tr>
<td>3S SPLP</td>
<td>-</td>
<td>277.5</td>
<td>-</td>
<td>-</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>3S MS SPLP 1</td>
<td>40</td>
<td>315.2</td>
<td>94%</td>
<td>20</td>
<td>19</td>
<td>94%</td>
</tr>
<tr>
<td>3S MSDUP SPLP 1</td>
<td>40</td>
<td>310.9</td>
<td>83%</td>
<td>20</td>
<td>19</td>
<td>94%</td>
</tr>
<tr>
<td>BLK TCLP 2</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>BLK MS TCLP 2</td>
<td>40</td>
<td>43.4</td>
<td>108%</td>
<td>20</td>
<td>17.25</td>
<td>86%</td>
</tr>
<tr>
<td>1S TCLP</td>
<td>-</td>
<td>41.29</td>
<td>103%</td>
<td>20</td>
<td>17.87</td>
<td>89%</td>
</tr>
<tr>
<td>1S SPLP</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>1S MS SPLP 2</td>
<td>40</td>
<td>40.01</td>
<td>100%</td>
<td>20</td>
<td>21.5</td>
<td>107%</td>
</tr>
<tr>
<td>10L SPLP 2</td>
<td>-</td>
<td>1.34</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>10L MS SPLP 2</td>
<td>40</td>
<td>39.6</td>
<td>96%</td>
<td>4</td>
<td>4</td>
<td>99%</td>
</tr>
<tr>
<td>10L MSDUP SPLP 2</td>
<td>40</td>
<td>38.75</td>
<td>94%</td>
<td>4</td>
<td>3.5</td>
<td>86%</td>
</tr>
<tr>
<td>BLK TCLP 3</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>BLK MS TCLP 3</td>
<td>40</td>
<td>39.63</td>
<td>99%</td>
<td>20</td>
<td>19.25</td>
<td>96%</td>
</tr>
<tr>
<td>10SDUP TCLP 3</td>
<td>-</td>
<td>10.275</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>10S DUP MS TCLP 3</td>
<td>40</td>
<td>48.9</td>
<td>97%</td>
<td>4</td>
<td>3.75</td>
<td>93%</td>
</tr>
<tr>
<td>10S DUP MSDUP TC.3</td>
<td>40</td>
<td>45.78</td>
<td>89%</td>
<td>4</td>
<td>3.83</td>
<td>95%</td>
</tr>
<tr>
<td>BLK SPLP 3</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>BLK MS SPLP 3</td>
<td>40</td>
<td>41.51</td>
<td>104%</td>
<td>20</td>
<td>18.5</td>
<td>92%</td>
</tr>
<tr>
<td>1L SPLP 3</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>1L MS SPLP 3</td>
<td>40</td>
<td>38.76</td>
<td>97%</td>
<td>20</td>
<td>19.675</td>
<td>96%</td>
</tr>
<tr>
<td>1L MSDUP SPLP 3</td>
<td>40</td>
<td>39.12</td>
<td>98%</td>
<td>20</td>
<td>19.775</td>
<td>99%</td>
</tr>
</tbody>
</table>

Table A.11: Quality Assurance Data for TCLP and SPLP Tests
Figure A.1: Arsenic Concentration from TCLP and SPLP Tests for Each Size Fraction
Figure A.2: Chromium Concentration from TCLP and SPLP Tests for Each Size Fraction
Figure A.3: Copper Concentration from TCLP and SPLP Tests for Each Size Fraction
APPENDIX B:
SUPPLEMENTARY TABLES FOR
THE SOLVENT EXTRACTION STUDY
### Table B.1: Percent Copper Removal for Various Solvents

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Total Conc. (mg/kg)</th>
<th>DW</th>
<th>MC</th>
<th>Pero</th>
<th>HH</th>
<th>SHC</th>
<th>Acetic</th>
<th>Citric</th>
<th>HCl</th>
<th>Nitric</th>
<th>TRM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>212</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>11,200</td>
<td>0.1</td>
<td>0.9</td>
<td>0.6</td>
<td>4.3</td>
<td>3.7</td>
<td>8.9</td>
<td>19.3</td>
<td>54.0</td>
<td>66.6</td>
<td>57.8</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>32,300</td>
<td>1.8</td>
<td>1.7</td>
<td>10.1</td>
<td>5.6</td>
<td>5.9</td>
<td>20.8</td>
<td>58.5</td>
<td>76.4</td>
<td>60.7</td>
<td></td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>104,000</td>
<td>0.1</td>
<td>0.7</td>
<td>1.1</td>
<td>4.7</td>
<td>2.8</td>
<td>3.5</td>
<td>15.1</td>
<td>25.8</td>
<td>45.3</td>
<td>46.7</td>
</tr>
<tr>
<td>Weathered</td>
<td>35,000</td>
<td>BD</td>
<td>1.0</td>
<td>1.2</td>
<td>5.1</td>
<td>3.6</td>
<td>3.3</td>
<td>17.5</td>
<td>51.7</td>
<td>62.9</td>
<td>55.9</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>2,040</td>
<td>0.5</td>
<td>0.3</td>
<td>BD</td>
<td>2.7</td>
<td>0.6</td>
<td>17.5</td>
<td>45.8</td>
<td>25.5</td>
<td>26.2</td>
<td></td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>1,600</td>
<td>0.5</td>
<td>3.1</td>
<td>1.6</td>
<td>2.3</td>
<td>13.6</td>
<td>16.4</td>
<td>28.3</td>
<td>65.3</td>
<td>111.2</td>
<td>58.2</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>1,500</td>
<td>BD</td>
<td>2.4</td>
<td>4.6</td>
<td>1.8</td>
<td>13.4</td>
<td>17.1</td>
<td>26.3</td>
<td>56.6</td>
<td>88.0</td>
<td>63.9</td>
</tr>
</tbody>
</table>

BD : Below Detection, Detection Limit = 0.1 mg/L.

### Table B.2: Copper Leachate Concentrations for Various Solvents

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Copper Leachate Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DW</td>
</tr>
<tr>
<td>Untreated</td>
<td>BD</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>0.1</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>0.2</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>3.0</td>
</tr>
<tr>
<td>Weathered</td>
<td>0.2</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>BD</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>0.1</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>BD</td>
</tr>
</tbody>
</table>

BD : Below Detection, Detection Limit = 0.1 mg/L.
### Table B.3: Percent Chromium Removal for Various Solvents

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Total Conc. (mg/kg)</th>
<th>DW</th>
<th>MC</th>
<th>Pero</th>
<th>HH</th>
<th>SHC</th>
<th>Acetic</th>
<th>Citric</th>
<th>HCl</th>
<th>Nitric</th>
<th>TRM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>141</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>20,600</td>
<td>7.7</td>
<td>4.8</td>
<td>0.2</td>
<td>3.0</td>
<td>1.7</td>
<td>4.9</td>
<td>5.9</td>
<td>14.4</td>
<td>23.8</td>
<td>25.2</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>51,100</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>0.1</td>
<td>1.5</td>
<td>0.6</td>
<td>2.0</td>
<td>14.8</td>
<td>17.5</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>174,000</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>2.0</td>
<td>0.3</td>
<td>0.4</td>
<td>4.8</td>
<td>6.8</td>
<td>30.7</td>
</tr>
<tr>
<td>Weathered</td>
<td>51,800</td>
<td>BD</td>
<td>BD</td>
<td>BD</td>
<td>0.1</td>
<td>1.3</td>
<td>BD</td>
<td>1.9</td>
<td>13.1</td>
<td>15.0</td>
<td>28.1</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>2,800</td>
<td>2.6</td>
<td>0.9</td>
<td>0.4</td>
<td>0.9</td>
<td>8.5</td>
<td>1.6</td>
<td>BD</td>
<td>11.0</td>
<td>1.2</td>
<td>11.1</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>1,900</td>
<td>30.9</td>
<td>16.5</td>
<td>29.1</td>
<td>15.1</td>
<td>41.4</td>
<td>8.6</td>
<td>41.3</td>
<td>39.3</td>
<td>56.6</td>
<td>15.1</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>2,700</td>
<td>53.9</td>
<td>29.4</td>
<td>49.3</td>
<td>27.3</td>
<td>56.8</td>
<td>10.7</td>
<td>57.0</td>
<td>54.9</td>
<td>64.9</td>
<td>17.8</td>
</tr>
</tbody>
</table>

BD : Below Detection, Detection Limit = 0.1 mg/L

### Table B.4: Chromium Leachate Concentrations for Various Solvents

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Chromium Leachate Concentration (mg/L) for Various Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DW</td>
</tr>
<tr>
<td>Untreated</td>
<td>BD</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>31.9</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>BD</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>BD</td>
</tr>
<tr>
<td>Weathered</td>
<td>0.4</td>
</tr>
<tr>
<td>C&amp;D1</td>
<td>2.4</td>
</tr>
<tr>
<td>C&amp;D2</td>
<td>11.8</td>
</tr>
<tr>
<td>C&amp;D3</td>
<td>19.4</td>
</tr>
</tbody>
</table>

BD : Below Detection, Detection Limit = 0.1 mg/L
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Total Conc. (mg/kg)</th>
<th>% Arsenic Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DW</td>
<td>MC</td>
</tr>
<tr>
<td>Untreated</td>
<td>28</td>
<td>N/A</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>11,400</td>
<td>4.0</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>42,800</td>
<td>5.2</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>113,500</td>
<td>14.6</td>
</tr>
<tr>
<td>Weathered</td>
<td>34,200</td>
<td>10.9</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>1,700</td>
<td>0.6</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>1,200</td>
<td>1.5</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>1,600</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table B.5: Percent Arsenic Removal for Various Solvents

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Arsenic Leachate Concentration (mg/L) for Various Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DW</td>
</tr>
<tr>
<td>Untreated</td>
<td>BD</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>9.2</td>
</tr>
<tr>
<td>0.60 pcf</td>
<td>44.7</td>
</tr>
<tr>
<td>2.50 pcf</td>
<td>331.1</td>
</tr>
<tr>
<td>Weathered</td>
<td>74.7</td>
</tr>
<tr>
<td>C&amp;D 1</td>
<td>0.2</td>
</tr>
<tr>
<td>C&amp;D 2</td>
<td>0.4</td>
</tr>
<tr>
<td>C&amp;D 3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

BD : Below Detection, Detection Limit = 0.1 mg/L

Table B.6: Arsenic Leachate Concentrations for Various Solvents
APPENDIX C:
SUPPLEMENTARY INFORMATION FOR STUDY WITH CHEMICAL STAINS

1. MSDS Sheets for Reagents used in Chemical Stain Tests
APPENDIX D:
SUPPLEMENTARY INFORMATION FOR XRF STUDY

1. Supplemental tables compiled from experimental set #2
2. ASOMA report from experimental set #1
3. ASOMA report from experimental set #3
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Count Time</th>
<th>Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Untreated</td>
<td>1</td>
<td>2.09</td>
</tr>
<tr>
<td>Untreated</td>
<td>2</td>
<td>18.5</td>
</tr>
<tr>
<td>Untreated</td>
<td>3</td>
<td>22.3</td>
</tr>
<tr>
<td>Untreated</td>
<td>5</td>
<td>24.3</td>
</tr>
<tr>
<td>Untreated</td>
<td>10</td>
<td>23.8</td>
</tr>
<tr>
<td>Untreated</td>
<td>50</td>
<td>26.9</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>1</td>
<td>3.17</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>2</td>
<td>199.3</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>3</td>
<td>233</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>5</td>
<td>304</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>10</td>
<td>322.8</td>
</tr>
<tr>
<td>0.25 pcf</td>
<td>50</td>
<td>382</td>
</tr>
<tr>
<td>2.5 pcf</td>
<td>1</td>
<td>4.18</td>
</tr>
<tr>
<td>2.5 pcf</td>
<td>2</td>
<td>745.5</td>
</tr>
<tr>
<td>2.5 pcf</td>
<td>3</td>
<td>1197</td>
</tr>
<tr>
<td>2.5 pcf</td>
<td>5</td>
<td>1519</td>
</tr>
<tr>
<td>2.5 pcf</td>
<td>10</td>
<td>1753</td>
</tr>
<tr>
<td>2.5 pcf</td>
<td>50</td>
<td>1357</td>
</tr>
<tr>
<td>Weathered</td>
<td>1</td>
<td>4.18</td>
</tr>
<tr>
<td>Weathered</td>
<td>2</td>
<td>890</td>
</tr>
<tr>
<td>Weathered</td>
<td>3</td>
<td>45</td>
</tr>
<tr>
<td>Weathered</td>
<td>5</td>
<td>355</td>
</tr>
<tr>
<td>Weathered</td>
<td>10</td>
<td>299.4</td>
</tr>
</tbody>
</table>

Table D.1: Counts for Various Samples for Different Count Times, All Samples Whole
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Count Time (s)</th>
<th>Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Untreated</td>
<td>2</td>
<td>16.7</td>
</tr>
<tr>
<td>0.25</td>
<td>2</td>
<td>73.2</td>
</tr>
<tr>
<td>0.60</td>
<td>2</td>
<td>147.9</td>
</tr>
<tr>
<td>2.5</td>
<td>2</td>
<td>423</td>
</tr>
<tr>
<td>Weathered</td>
<td>2</td>
<td>143</td>
</tr>
<tr>
<td>Untreated</td>
<td>3</td>
<td>16.3</td>
</tr>
<tr>
<td>0.25</td>
<td>3</td>
<td>67.7</td>
</tr>
<tr>
<td>0.60</td>
<td>3</td>
<td>277</td>
</tr>
<tr>
<td>2.5</td>
<td>3</td>
<td>451</td>
</tr>
<tr>
<td>Weathered</td>
<td>3</td>
<td>155</td>
</tr>
<tr>
<td>Untreated</td>
<td>10</td>
<td>27.3</td>
</tr>
<tr>
<td>0.25</td>
<td>10</td>
<td>159</td>
</tr>
<tr>
<td>0.60</td>
<td>10</td>
<td>362</td>
</tr>
<tr>
<td>2.5</td>
<td>10</td>
<td>746</td>
</tr>
<tr>
<td>Weathered</td>
<td>10</td>
<td>286</td>
</tr>
</tbody>
</table>

Table D.2: Counts for Various Samples for Different Count Times, All Samples Shredded
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Count Time (s)</th>
<th>Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent CCA-Treated Wood, 0% 0.25 pcf</td>
<td>5</td>
<td>28.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>56.7</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 1% 0.25 pcf</td>
<td>5</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.0</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 10% 0.25 pcf</td>
<td>5</td>
<td>29.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78.8</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 15% 0.25 pcf</td>
<td>5</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>79.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>133</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 20% 0.25 pcf</td>
<td>5</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>79.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>103</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 25% 0.25 pcf</td>
<td>5</td>
<td>51.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>153</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 50% 0.25 pcf</td>
<td>5</td>
<td>64.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>135</td>
</tr>
<tr>
<td></td>
<td></td>
<td>247</td>
</tr>
<tr>
<td>Field Sample, Site A, 3-4% CCA</td>
<td>5</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35.7</td>
</tr>
<tr>
<td>Field Sample, Site B, 5% CCA</td>
<td>5</td>
<td>23.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.6</td>
</tr>
<tr>
<td>Field Sample, Site C, 20% CCA</td>
<td>5</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>56.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>74.3</td>
</tr>
<tr>
<td>Field Sample, Site D, &lt;8% CCA</td>
<td>5</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40.2</td>
</tr>
<tr>
<td>Field Sample, Site E, 6-8% CCA</td>
<td>5</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>42.6</td>
</tr>
<tr>
<td>Field Sample, Site F, 8% CCA</td>
<td>5</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48.1</td>
</tr>
<tr>
<td>Field Sample, Site G, 6% CCA</td>
<td>5</td>
<td>13.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29.4</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 1% 0.25 pcf</td>
<td>2</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>73.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>156.3</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 10% 0.25 pcf</td>
<td>2</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37.5</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 50% 0.25 pcf</td>
<td>2</td>
<td>29.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>84.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>146</td>
</tr>
<tr>
<td>Field Sample, Site A, 3-4% CCA</td>
<td>2</td>
<td>16.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.5</td>
</tr>
<tr>
<td>Field Sample, Site B, 5% CCA</td>
<td>2</td>
<td>20.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45.4</td>
</tr>
<tr>
<td>Field Sample, Site C, 20% CCA</td>
<td>2</td>
<td>33.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65.3</td>
</tr>
<tr>
<td>Field Sample, Site D, &lt;8% CCA</td>
<td>2</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>81.6</td>
</tr>
<tr>
<td>Field Sample, Site E, 6-8% CCA</td>
<td>2</td>
<td>30.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70.7</td>
</tr>
<tr>
<td>Field Sample, Site F, 8% CCA</td>
<td>2</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>47.0</td>
</tr>
<tr>
<td>Field Sample, Site G, 6% CCA</td>
<td>2</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.0</td>
</tr>
</tbody>
</table>

Table D.3: Data Utilized for Estimating the Detection Limit of In Shredded Mixtures Before Extensive Instrument Calibration
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent CCA-Treated Wood, 0% 0.25 pcf</td>
<td>6 3 0</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 1% 0.25 pcf</td>
<td>4 1.5 1.5</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 2% 0.25 pcf</td>
<td>5.5 3 2</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 3% 0.25 pcf</td>
<td>12 9 9</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 4% 0.25 pcf</td>
<td>19 20 21</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 5% 0.25 pcf</td>
<td>12 10 7</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 10% 0.25 pcf</td>
<td>12 13 11</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 15% 0.25 pcf</td>
<td>15 15 14</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 20% 0.25 pcf</td>
<td>19 18 18</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 50% 0.25 pcf</td>
<td>44 45 46</td>
</tr>
<tr>
<td>Field Sample, Site A, 3-4% CCA</td>
<td>8 4 0</td>
</tr>
<tr>
<td>Field Sample, Site B, 5% CCA</td>
<td>14 10 7</td>
</tr>
<tr>
<td>Field Sample, Site C, 20% CCA</td>
<td>17 15 10</td>
</tr>
<tr>
<td>Field Sample, Site D, &lt;8% CCA</td>
<td>12 9 3</td>
</tr>
<tr>
<td>Field Sample, Site E, 6-8% CCA</td>
<td>14 9 5</td>
</tr>
<tr>
<td>Field Sample, Site F, 8% CCA</td>
<td>15 9 6</td>
</tr>
<tr>
<td>Field Sample, Site G, 6% CCA</td>
<td>19 10 5</td>
</tr>
</tbody>
</table>

Table D.4: Data Utilized for Estimating the Detection Limit of In Shredded Mixtures, After Extensive Instrument Calibration, Count Time 25s
### Table D.5: Additional Data Collected on Shredded Mixtures Using Arsenic as the Indicator Metal.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Extensive Calibration</th>
<th>Count Time (s)</th>
<th>Counts as As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent CCA-Treated Wood, 1% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>6.24</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 2% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>17.0</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 3% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>21.4</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 4% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>30.6</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 5% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>46.0</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 10% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>41.4 [78.2]</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 15% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>50.5</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 20% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>71.1</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 25% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>89.5</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 50% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>277</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 100% 0.25 pcf</td>
<td>No</td>
<td>50</td>
<td>453</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 0% 0.25 pcf</td>
<td>Yes</td>
<td>3</td>
<td>0.40</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 3% 0.25 pcf</td>
<td>Yes</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 5% 0.25 pcf</td>
<td>Yes</td>
<td>3</td>
<td>1.4</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 25% 0.25 pcf</td>
<td>Yes</td>
<td>3</td>
<td>19</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 0% 0.25 pcf</td>
<td>Yes</td>
<td>10</td>
<td>0.50</td>
</tr>
<tr>
<td>Percent CCA-Treated Wood, 5% 0.25 pcf</td>
<td>Yes</td>
<td>10</td>
<td>2.9</td>
</tr>
<tr>
<td>Sample I.D.</td>
<td>Plastic Shield</td>
<td>Distance (cm)</td>
<td>Counts</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>---------------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Untreated Wood</td>
<td>No</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Untreated Wood</td>
<td>No</td>
<td>1.1</td>
<td>24</td>
</tr>
<tr>
<td>Untreated Wood</td>
<td>No</td>
<td>1.6</td>
<td>15</td>
</tr>
<tr>
<td>Untreated Wood</td>
<td>No</td>
<td>2.5</td>
<td>11</td>
</tr>
<tr>
<td>CCA-Treated Wood, 0.25 pcf</td>
<td>No</td>
<td>0</td>
<td>294</td>
</tr>
<tr>
<td>CCA-Treated Wood, 0.25 pcf</td>
<td>No</td>
<td>1.0</td>
<td>251</td>
</tr>
<tr>
<td>CCA-Treated Wood, 0.25 pcf</td>
<td>No</td>
<td>1.6</td>
<td>160</td>
</tr>
<tr>
<td>CCA-Treated Wood, 0.25 pcf</td>
<td>No</td>
<td>2.2</td>
<td>119</td>
</tr>
<tr>
<td>CCA-Treated Wood, 0.25 pcf</td>
<td>No</td>
<td>2.8</td>
<td>82</td>
</tr>
<tr>
<td>CCA-Treated Wood, 0.25 pcf</td>
<td>Yes</td>
<td>2.8</td>
<td>20</td>
</tr>
<tr>
<td>CCA-Treated Wood, 0.25 pcf</td>
<td>Yes</td>
<td>0</td>
<td>30</td>
</tr>
</tbody>
</table>

Table D.6: Distance Study on Whole Wood Samples, Count time 5 s
ASOMA report from experimental set #1
ASOMA report from experimental set #3