Final Research Report

ALTERNATIVE FUEL FOR PORTLAND CEMENT PROCESSING

Submitted to

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Prepared by

Anton K. Schindler, Steve R. Duke,
Thomas E. Burch, Edward W. Davis,
Ralph H. Zee, David I. Bransby, Carla Hopkins,
Rutherford L. Thompson, Jingran Duan,
Vignesh Venkatasubramanian, and Stephen Giles.

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Rick Darnell	Lafarge North America, Calera, Alabama
Nick Ewing	Lafarge North America, Calera, Alabama
Simon Ward	Lafarge North America, Calera, Alabama
Munzer Ghosh	Lafarge North America, Whitehall, Pennsylvania
Paul Cunningham	Lafarge North America, Calera, Alabama
Anthony Perry	Lafarge North America, Calera, Alabama
Ken Evans	Systech, Calera, Alabama

ABSTRACT

The production of cement involves a combination of numerous raw materials, strictly monitored system processes, and temperatures on the order of 1500 °C. Immense quantities of fuel are required for the production of cement. Traditionally, energy from fossil fuels was solely relied upon for the production of cement. The overarching project objective is to evaluate the use of alternative fuels to lessen the dependence on non-renewable resources to produce portland cement. The key objective of using alternative fuels is to continue to produce high-quality cement while decreasing the use of non-renewable fuels and minimizing the impact on the environment.

Burn characteristics and thermodynamic parameters were evaluated with a laboratory burn simulator under conditions that mimic those in the preheater where the fuels are brought into a cement plant. A drop-tube furnace and visualization method were developed that show potential for evaluating time- and space-resolved temperature distributions for fuel solid particles and liquid droplets undergoing combustion in various combustion atmospheres.

Downdraft gasification has been explored as a means to extract chemical energy from poultry litter while limiting the throughput of potentially deleterious components with regards to use in firing a cement kiln. Results have shown that the clinkering is temperature independent, at least within the controllable temperature range. Limestone also had only a slight effect on the fusion when used to coat the pellets. However, limestone addition did display some promise in regards to chlorine capture, as ash analyses showed chlorine concentrations of more than four times greater in the limestone infused ash as compared to raw poultry litter.

A reliable and convenient sampling procedure was developed to estimate the combustion quality of broiler litter that is the best compromise between convenience and reliability by means of statistical analysis.

Multi-day trial burns were conducted at a full-scale cement plant with alternative fuels to examine their compatibility with the cement production process. Construction and demolition waste, woodchips, and soybean seeds were used as alternative fuels at a full-scale cement production facility. These fuels were co-fired with coal and waste plastics. The alternative fuels used in this trial accounted for 5 to 16 % of the total energy consumed during these burns. The overall performance of the portland cement produced during the various trial burns performed for practical purposes very similar to the cement produced during the control burn. The cement plant was successful in implementing alternative fuels to produce a consistent, high-quality product that increased cement performance while reducing the environmental footprint of the plant. The utilization of construction and demolition waste, woodchips and soybean seeds proved to be viable replacements for traditional fuels. The future use of these fuels depends on local availability, associated costs, and compatibility with a facility's production process.

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INTRODUCTION

1.1 PROJECT BACKGROUND

In 2010, over 3 billion tons of portland cement were produced globally making it the most widely used and manufactured material in the world (Chen and Juenger 2009; ICR 2011). In the United States, 113 cement plants that operate in 36 states produced 65 million tons of cement in 2010. The United States is the third largest cement producer following China and India (PCA 2010; ICR 2011). The contribution of various countries to the total 3.3 billion tons of cement produced in 2010 is summarized in Figure 1-1.

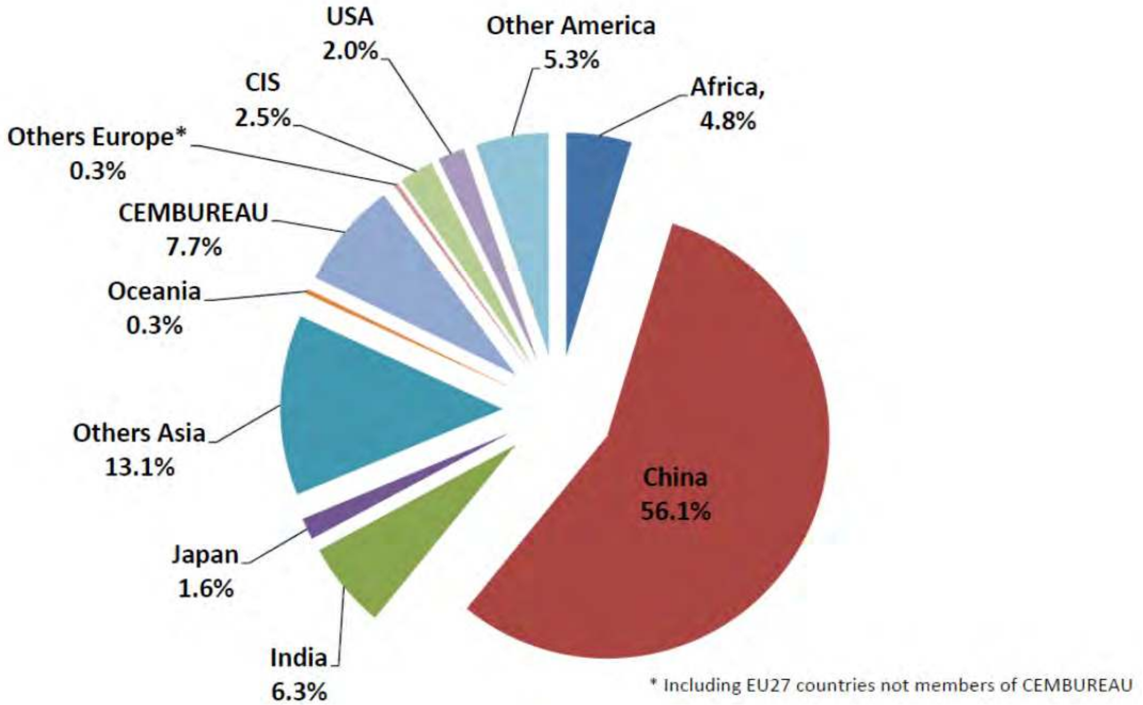


Figure 1-1: World Cement Production in 2010 (Cembureau 2010)

The production of cement involves a combination of numerous raw materials, complex facilities, and strictly monitored system processes. Portland cement is the primary ingredient in concrete, which is used worldwide, as a construction material in order to form buildings, roads, dams, and virtually any super- or substructure used by mankind. During the manufacture of cement, immense quantities of fuels are used in order to reach temperatures necessary to produce cement that bears the ideal chemical composition. Traditionally, fossil fuels have been solely relied upon for the production of cement. Over the past few decades, concerns of sustainability and environmental impact from fossil fuels have influenced the research of and utilization of alternative fuel sources.

Portland cement is produced from several raw material mined from the earth. When mixed in the proper proportions, and exposed to gas temperatures in excess of 1800 °C, the raw materials fuse together to form a product known as clinker (Uliasz-Bocheńczyk 2003). The clinker is then ground with an addition of sulfate to a specific fineness to produce a product known as portland cement. A full-scale cement manufacturing facility is shown in Figure 1.1.

Figure 1-1: Full-Scale Portland Cement Production Facility (Folta 2010)

In order to produce high kiln temperatures, fossil fuels such as coal, petroleum coke, and natural gas are regularly used. It is not uncommon for a modern cement plant to use 1,200 tons of coal every day (Manias 2004). With the rising cost of energy, it is easy to see why fuel costs comprise around 40 percent of a manufacturer’s budget and the incentive to seek less costly fuels (Jackson 1998).

Around the 1970’s, alternative fuels began to be used by the cement industry (Karstensen 2004). Modern facilities typically use alternative fuels to partially replace fossil fuels at rates around 20% (PCA 2009). Alternative fuels are typically waste products from other industries that are destined to be land-filled or incinerated. Examples that have successfully been used in cement manufacture include used oils, municipal solid wastes, tires, solvents, plastic, and biomass (Greco et al. 2004). Not only can waste fuels provide significant savings to a manufacturer, if properly utilized alternative fuels can benefit the community and environment (Mokrzycki and Uliasz-Bocheńczyk 2003). It is, however, necessary to test and thoroughly understand all the attributes of the alternative fuel and its effects on the final product and manufacturing process.

As a means to reduce congestion in landfills, waste incineration has been used for a number of years. Waste incinerators also use fossil fuels in order to destroy the landfill material, but emit more harmful pollutants than cement plants because of lower temperatures and residence times. There is also no final product, like cement, produced from waste incineration.

Regardless of the whether the fuel is a natural resource or a second life for a waste product, the chemical makeup of the fuel and its interaction with the chemical components of the raw materials determine the final chemical composition of the clinker. Also, the majority of the noncombustible components of the fuel and raw material are incorporated in the clinker. Therefore, the use of alternative fuels could alter the chemical composition of cement and thus negatively affect the properties of the cement and concrete. During this study, the chemical composition of each fuel, raw material, and process output were determined. In addition, fresh and hardened concrete property tests were performed to determine if any change in the cement could be directly linked to the use of alternative fuels. If detrimental effects are found within a particular cement, any advantage gained from the utilization of the alternative fuel is lost.

The utilization of alternative fuels has proven to be both beneficial to the cement industry and the environment. It is, however, imperative to fully understand the effects of each new fuel. This study considers three fuels, one of which utilized three different replacement rates. Emissions such as nitrogen oxides, sulfur dioxide, and volatile organic compounds from the firing of raw material and the combustion of fuel can be a significant health risk. Allowable emissions limits set by environmental agencies were continuously monitored throughout each burn. Preliminary testing of alternative fuels provides information about the chemical properties and expected emissions.

The use of alternative fuels for direct burn in cement kilns can be limited by the presence of fuel constituents that negatively impact kiln operation and/or the quality of cement produced. Gasification has the potential to directly remove deleterious constituents that are components of the fuel ash and allows for the possibility of cleanup of the syngas before it is introduced into the cement kiln as fuel. Another objective of one of the phases of this research is to evaluate this potential for fuels that were used in direct-burn trials for this research but where substitution rates were limited because of deleterious components.

1.2 RESEARCH OBJECTIVES

The overarching project objective is to evaluate the use of alternative fuels to lessen the dependence on non-renewable resources to produce portland cement. The key objective of using alternative fuels is to continue to produce high-quality cement while decreasing the use of non-renewable fuels and minimizing the impact on the environment. The objectives of this project are as follows:

1. Collect data on the burn characteristics and thermodynamic parameters with a laboratory burn simulator under conditions that mimic those in the preheater where the fuels are brought into a cement plant.
2. Conduct trial burns at a full-scale cement plant with alternative fuels to examine their compatibility with the cement production process.
3. Determine the feasibility of removing non-volatile and semi-volatile components of alternative fuels through gasification in a small-scale downdraft gasifier.
4. Develop a reliable, but convenient, sampling procedure to estimate the combustion quality of broiler litter that is the best compromise between convenience and reliability by means of statistical analysis.

1.3 RESEARCH PLAN

This project will address the area of renewable energy integration by evaluating the reduction of emissions of air pollutants through increased use of renewable energy sources. A laboratory burn simulator was used to assess the high temperature conversion of a variety of alternate fuels under conditions that mimic those in the cement preheater. Studies were performed with a small-scale downdraft gasifier to identify candidate alternative fuels that have demonstrated deleterious effects in direct burn and then measure the ability of gasification to remove the contaminants. The research with the gasifier focused on determining the feasibility of removing the non-volatile and semi-volatile components of interest through gasification. Broiler litter stacks at commercial broiler farms were sampled and analyzed to determine the nature of the chemical composition of composted broiler litter. Statistical analysis results of these data were evaluated to develop a sampling procedure for estimating the combustion quality of broiler litter that is the best compromise between convenience and reliability.

Trial burns were conducted at a full-scale cement plant to determine the effect of using alternative fuels on cement plant production, the chemical composition of clinker and cement produced, the physical properties of the cement produced, the properties of concrete made from this cement, and the emissions released by the cement plant.

1.4 REPORT ORGANIZATION

This document is organized into five parts, with twelve chapters followed by some appendices. The parts of the report are as follows:

Part 1 - Determine the Burn Characteristics of Alternative Fuels with Burn Simulator,

Part 2 - Full-Scale Trial Burns with Alternative Fuels at Cement Plant,
Part 3 - Evaluate Gasification to Remove Contaminants in Cement Production,
Part 4 - Develop Sampling Procedure to Estimate Combustion Quality of Broiler Litter, and
Part 5 - Feasibility of Using Selected Alternate Fuels in Portland Cement Production.

Chapter 2 contains all the work performed for Part 1 of this research project. A laboratory-scale, drop-tube furnace was designed and manufactured that enabled the research team to mimic conditions of the preheater section of the cement plant. The focus of the work was to develop imaging and visualization methods to obtain images and video of particles and droplets of various fuels undergoing combustion that are of high enough quality and resolution to allow development of three-color pyrometry to determine surface temperatures.

Chapters 3 through 6 contain all the work performed for Part 2 of this research project. Chapter 3 details previous research and literature that pertain to many facets of this phase of the project. The experimental plan used throughout Part 2 of this project is defined in Chapter 4. The data collected during Part 2 are presented, analyzed, and discussed in Chapter 5. The conclusions and recommendations of the work performed for Part 2 are presented in Chapter 6.

Chapters 7 through 11 contain all the work performed for Part 3 of this research project. Chapter 7 contains an introduction, a brief literature review of the issues related to gasification and the use of poultry litter as alternative fuel. Section 7.4 defines the research objectives for Part 3 and Section 7.5 contains the definition of acronyms and abbreviations used in Part 3. Chapter 8 provides background information for Part 3. The experimental setup and procedures used for Part 3 of this project is presented in Chapter 9. The data collected during Part 3 are presented and discussed in Chapter 10. The conclusions and recommendations of the work performed for Part 3 are presented in Chapter 11.

Chapter 12 contains all the work performed for Part 4 of this research project. The experimental procedures used for this effort are defined and the statistical methods used to develop the sampling procedure is presented in detail.

Chapter 13 contains all the work performed for Part 5 of this research project. The work presented in this chapter is aimed at determining factors that may drive the availability and cost of alternative fuels relative to the availability and cost of traditional, non-renewable fuel sources.

The final chapter, Chapter 14, of this report contains the main conclusions and recommendations related to this research project. Conclusions are drawn as they pertain to the objectives. This chapter concludes with recommendations on a number of aspects of this project.

The report also contains some appendices that contain some of the information supporting Part 3.

PART 1

Determine the Burn Characteristics of Alternative Fuels with Burn Simulator

CHAPTER 2

DETERMINE THE BURN CHARACTERISTICS OF ALTERNATIVE FUELS WITH BURN SIMULATOR

The overarching project objective is to evaluate the use of alternative fuels to lessen the dependence on non-renewable resources to produce portland cement. The key objective of using alternative fuels is to continue to produce high-quality cement while decreasing the use of non-renewable fuels and minimizing the impact on the environment. One major facet of the research conducted for this part one of this study is to evaluate individual particles and droplets of fuels undergoing combustion to provide a fundamental understanding of the burn characteristics of the fuels to complement the industrial and pilot scale studies for the same alternative fuels.

2.1 DEVELOPMENT OF A LABORATORY BURN SIMULATOR FACILITY

A laboratory scale drop tube furnace was designed and manufactured by ATS that enables us to mimic conditions of the preheater section of the cement plant. A photograph of the burn simulator system with visualization setup used for this research is shown in Figure 2-1. It can be operated over a wide range of temperatures ranging from 20 °C to 1400 °C and at varying oxygen concentrations ranging from 0 % to above 21 %. A filter at the exit of the drop tube allows collection of uncombusted material. The effluent gases can be vented or sent through a GC. However, the focus of the work completed for this project has been the development of imaging and visualization methods to obtain images and video of particles and droplets of various fuels undergoing combustion that are of high enough quality and resolution to allow development of three-color pyrometry to determine surface temperatures.

The objective of the work document in this section is to obtain burn characteristics and understand the phenomenon in high temperature conversion of the alternate fuels under conditions that mimic those in the cement preheater where the fuels are brought into the industrial process.

2.1.1 Experimental Work

2.1.1.1 Burn Simulator Setup

Samples of alternative fuel types that were used at the cement plant were collected by Auburn laboratories. These alternative fuel samples of switch grass and wood along with coal (used as the standard fossil fuel) were ground to approximately 100 micron sized particles. These fine particles were then dropped or injected into the furnace with a uniquely developed vibrating syringe system. The falling particles were dropped through the furnace glass tube at a variety of operating conditions. Provisions were made to analyze the exit gases in the future by coupling a gas chromatograph to the exit gas stream. Also the drop tube furnace is capable of collecting the uncombusted char on a glass filters: the char and uncombusted material could either be made to undergo chemical analysis or be analyzed by scanning electron microscopy for particle properties.

Experiments were usually conducted at 500 °C, 700 °C and 900 °C at various oxygen concentrations. Particle of coal, wood, and switch grass were dropped through the furnace and uncombusted material was collected on glass filters at the base of the drop tube. The char (effluent particle) samples were collected and analyzed using SEM analysis. SEM images were obtained for the fuel particles before and after combustion.

Figure 2-1: Photograph of the burn simulator system with visualization setup

2.1.1.2 Challenges

Scale formation and at times etching of the glass drop tubes in the furnace seriously inhibits clear imaging. This problem needed to be addressed to allow frequent use of the drop tube furnace. The glass furnace tubes develop scale very quickly on the inside of the tube and more importantly when burning certain materials, especially coal, the glass appears to become etched (scratched) as well. We have been working with the Auburn University glass shop and ATS to determine a low cost means of cleaning or polishing the tube surfaces without damaging the furnace tubes.

We redesigned the effluent piping to incorporate an in-line vacuum pump that enables oxygen and GC sensors to provide useful measurements of gas composition.

2.2 VISUALIZATION STUDIES OF NEW FUEL TYPES UNDERGOING COMBUSTION

The objective of this work is to visualize the alternative fuel particles of 100 micrometers size undergoing combustion inside the drop tube furnace in order to get a better understanding of the mechanisms contributing to effective of combustion at different temperature and oxygen concentrations.

Visualization of particles in combustion was carried out by means of a high speed camera and high magnification lens setup. Both monochrome and high intensity color cameras were employed in combination with varying lens magnification systems to get a good quality image.

2.2.1 Experimental Work

Initial visualization exploration was conducted with a monochrome camera because the simplicity of the camera allowed evaluation of potential for focus clarity and magnification level, and allowed assessment of light intensity. Lens and light settings were then used to evaluate potential for visualization with a Cooke PCO 1200 high speed color camera. The PCO camera is very sensitive to light level and we continue to struggle with the procedures and settings needed to obtain visualizations. The particles fall through the drop tube at high velocities; however motion blur can be eliminated with exposure time settings and high frame rates (up to 3000 frames per second). Unfortunately, focus and light level issues related to use of the new specialized camera with the existing high magnification Questar lens still exist.

2.2.1.1 Solid Fuel Combustion Visualization

Visualizations of combustion of 100 micrometer particles of coal, wood, and switch grass in the drop tube furnace at various temperature and oxygen concentrations were obtained. We had to work with a variety of lens and camera combinations to develop focus techniques that will allow consistent acquisition of color images of particle undergoing combustion. The images thus obtained had sufficient clarity and adjustable degrees of magnification. Figures 2-2 and 2-3 show sample images from experiments with switch grass and wood.

Figure 2-2: Switch grass at 900 C in air (100 micrometer nominal particle)

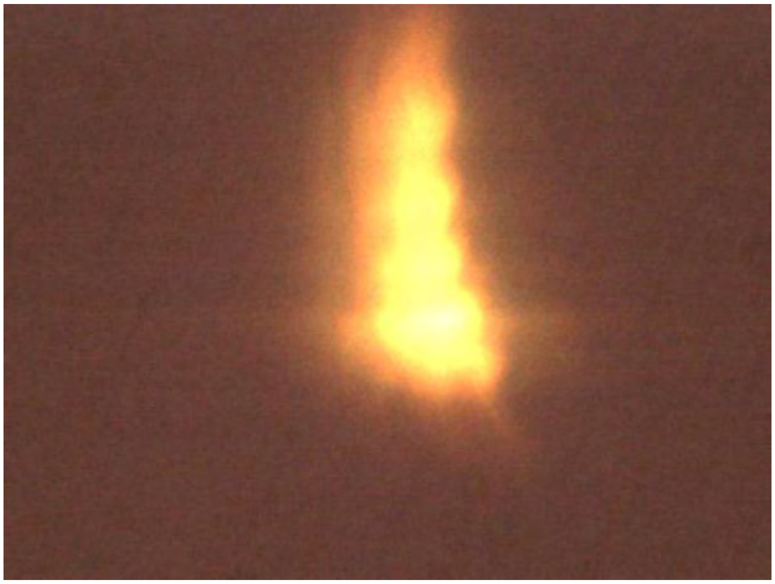


Figure 2-3: Wood at 900 °C in air (100 micrometer nominal particle)

Figure 2-4 shows a time series image of switch grass particles in the top portion of the furnace (short residence time) at 500 frames per second (FPS) from visualizations obtaining high speed images of particles undergoing combustion with the Cooke PCO CMOS camera. The left hand column shows the full frame; the right hand column shows an area of interest to provide detail of particles. The images reveal the high spatial resolution and clear focus that are maintained at the high frame rates. Visualizations such as these can be used to determine particle velocities and average particles temperatures while higher magnification images as above are used for surface temperature distributions.

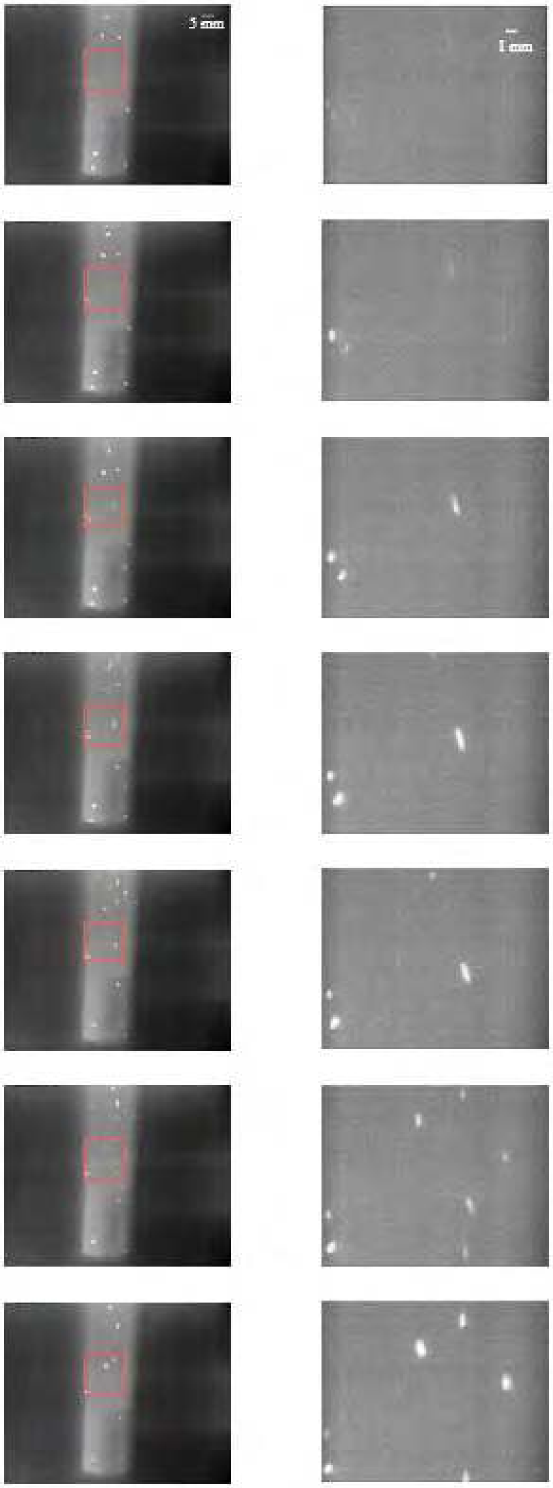


Figure 2-4: The image sequence shows switch grass combusting in the retort at 900 °C and 20.9 % O_2 at 500 FPS

A number of visualizations of combustion of the solid fuel particles (primarily wood and switchgrass) were been obtained. Some of the images were obtained to continue progress on image analysis to determine spatial distribution of temperature on particle; additional images were obtained and have been stored for analysis at a later time. Images that have proven most useful were acquired by use of a new Nikon 105 mm focus lens. This lens allows high magnification, though not as high as the Questar lens, and a greater amount of light (because of its larger aperture) than the Questar lens. Figure 2-5 shows sample images for switch grass captured using Nikon 105 mm lens. Similar images were also obtained for wood and coal.

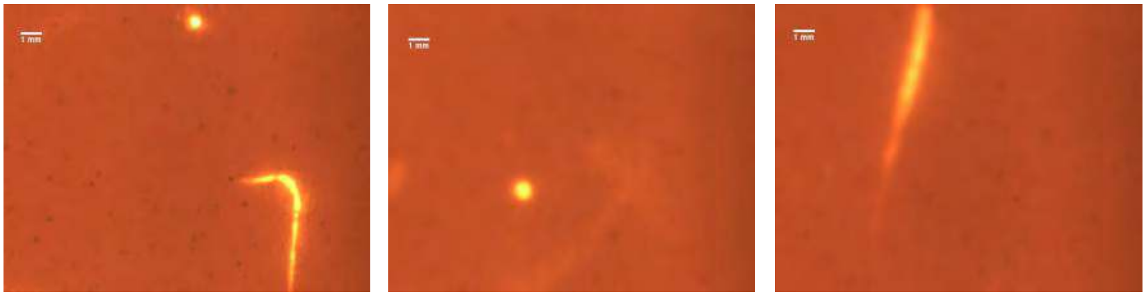


Figure 2-5: Images of switch grass particles undergoing combustion in air at 900 °C

We obtained large sets of visualization data and images of solid fuel particles at various distances from the water cooled injection nozzle and at selected furnace temperatures and oxygen concentrations. A particular camera and lens combination and setting was found to be most suitable in terms of balancing the level of magnification and resolution with the field of view to allow frequent particle visualization capture. Tables 2-1 and 2-2 show sample images (frames) from high resolution video. The table headings show the nominal furnace drop tube temperature along the top heading and numbers 1, 2, and 3 down the left heading column to indicate the position (distance from the injector nozzle) at which the images were taken. Position 1 refers to the top portion of the upper viewing window which corresponds to the nozzle outlet. Position 2 refers to the bottom of the upper window which corresponds to approximately 20 cm from the nozzle outlet. Position 3 refers to the top portion of the middle viewing widow which corresponds to approximately 35 cm from the nozzle outlet.

Observations and visualizations were also made at positions 4, 5, and 6 (bottom of middle window, top of lower window, and bottom of lower window). For the conditions being studies the particle combustion was complete prior to this distance and there was no evidence of continued combustion.

As said earlier, there are lens and camera combinations that provide higher special resolution and magnification. The field of view for such a setup is on the order of a half centimeter square. At the immediate exit of the injection nozzle (position 1), this field of view is sufficient to capture a number of particles as they are emitted from the nozzle. This field of view is insufficient at further distances from the nozzle (position 2 and greater) because of particle motions and erratic trajectories. The field of view for the images shown in Figure 2-4 and 2-5 is approximately 4 cm square and each particle can be resolved with 200 or more pixels, which is sufficient for surface temperature estimation.

Table 2-1: Switch grass combustion images in air at 700 °C, 800 °C, and 900 °C. Numbers 1, 2, and 3 in leftmost column indicate positions down the drop tube of approximately 0, 20, and 35 cm

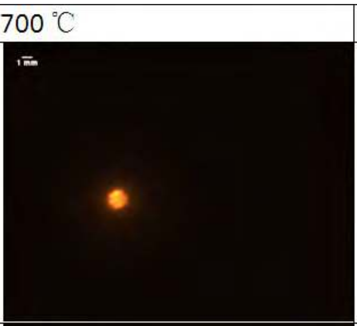
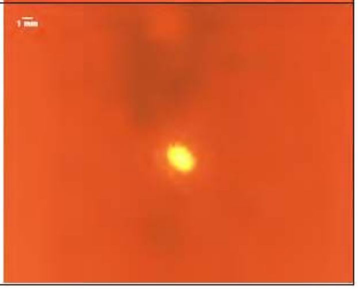
	700 ℃	800 ℃	900 ℃
1			
2			
3			

Table 2-2: Wood combustion images in air at 700 °C, 800 °C, and 900 °C. Numbers 1, 2, and 3 in leftmost column indicate positions down the drop tube of approximately 0, 20, and 35 cm

	700 ℃	800 ℃	900 ℃
1			
2			
3			

Visualizing free falling liquid fuel droplets undergoing combustion in the furnace drop tube of the laboratory burn simulator has been our ultimate goal. We were able to use the new nozzle to inject fuel droplets into the furnace, however the vaporization and combustion events occurred such that we have not been able to obtain clear and high magnification video. Thus, we modified the liquid fuel injector apparatus to allow us to suspend pendant drops of fuel at the tip of a needle of high temperature glass capillary tubing: this provided a stationary droplet in the field of view of the imaging systems and in the high temperature drop tube environment. Experiments conducted in this manner allowed us to select appropriate lighting and focus settings for droplets of various fuels in different environments (temperatures and oxygen concentrations). We determined lighting arrangements to allow visualization of drops in conditions where rapid vaporization occurred in the absence of flame, as well as appropriate camera settings to capture visualization of droplets undergoing combustion. Figure 2-6 shows images of 99% hexadecane droplets undergoing combustion in air at 800 °C

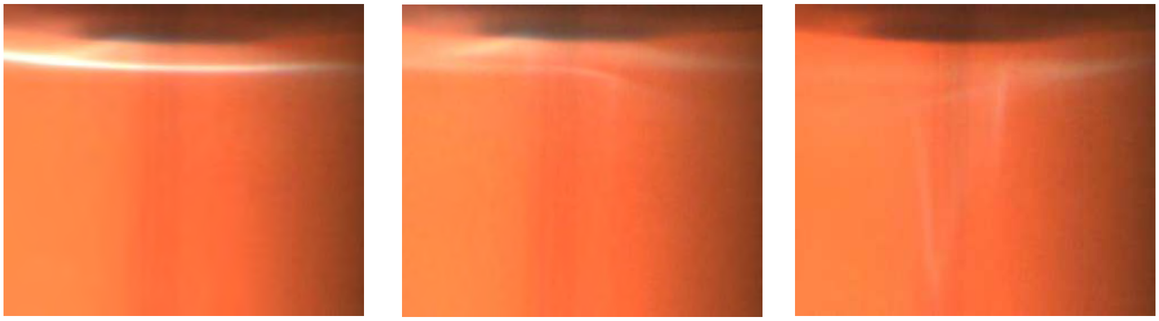


Figure 2-6: Images of 99% hexadecane droplets undergoing combustion in air at 800 °C

Figures 2-7, 2-8, and 2-9 are examples of the visualizations obtained for suspended droplet combustion of cetane, one of the liquids being used as a standard fuel. The figures display selected individual frames from a video sequence. The pendant needle for these experiments is 100 micrometer inside diameter capillary tubing with flow rates varying from 0.6 to 1.0 mL/min. Experiments were conducted in air at 500 °C; the air is drawn down through the drop tube by a vacuum pump (described in previous quarterly reports). Figures 2-7 and 2-8 show examples where combustion of injected fuel takes place very rapidly and as a result the suspended pendant drops are pulled away from the capillary tube to form a jet-like flame. Figure 2-9 shows an example of pendant drop formation followed by vaporization with no visible flame.

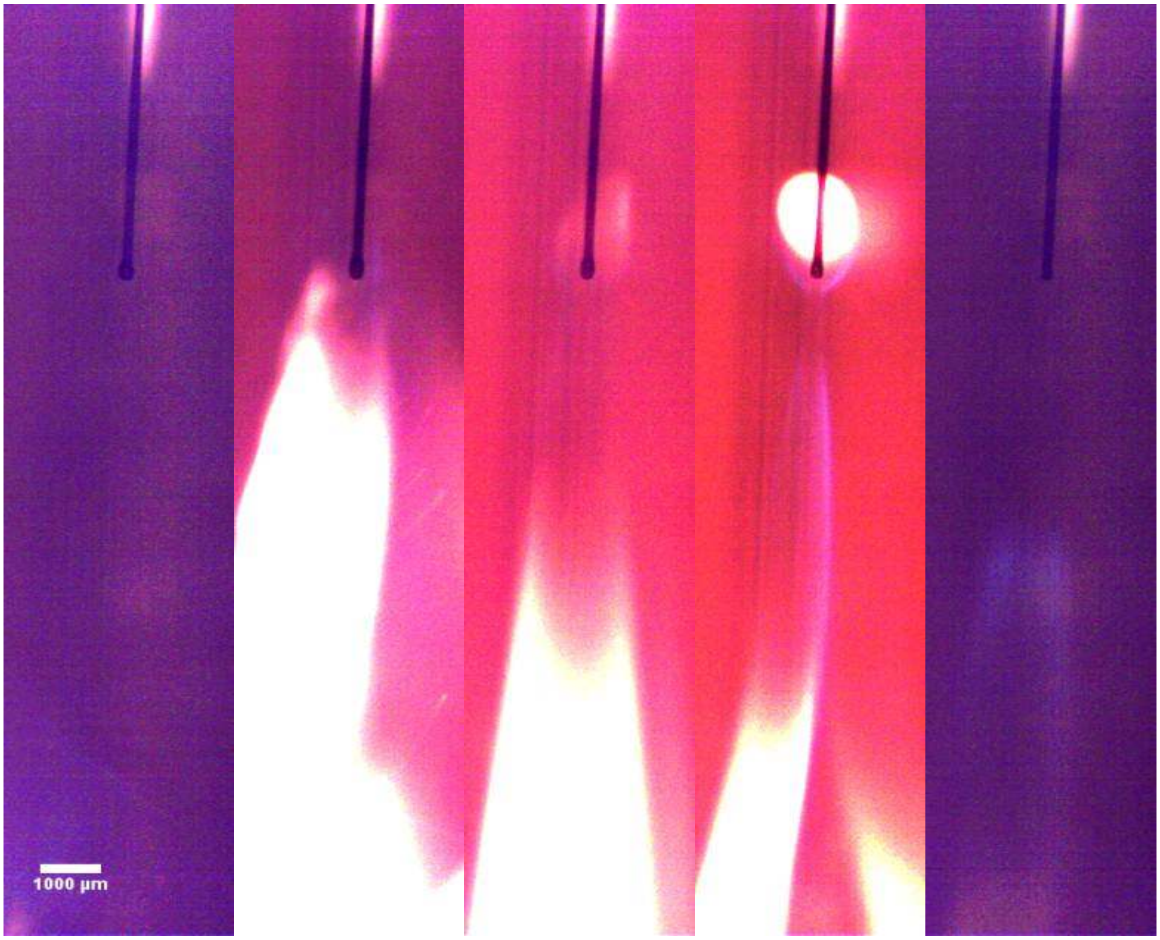


Figure 2-7: Cetane at 500 °C and 20.9% oxygen. Images are displayed at 17 fps and originally taken at 50 fps. The flow rate is 1.0 ml/min.

The visualizations obtained for these and other experiments conducted for fuels injected with the pendant apparatus allowed selection of lenses and camera settings for future studies of liquid fuel drops in the desired free falling state. The images obtained for fuels undergoing combustion at the pendant tip were of sufficient clarity and resolution to be useful in quantitative image analysis the temperature estimation.

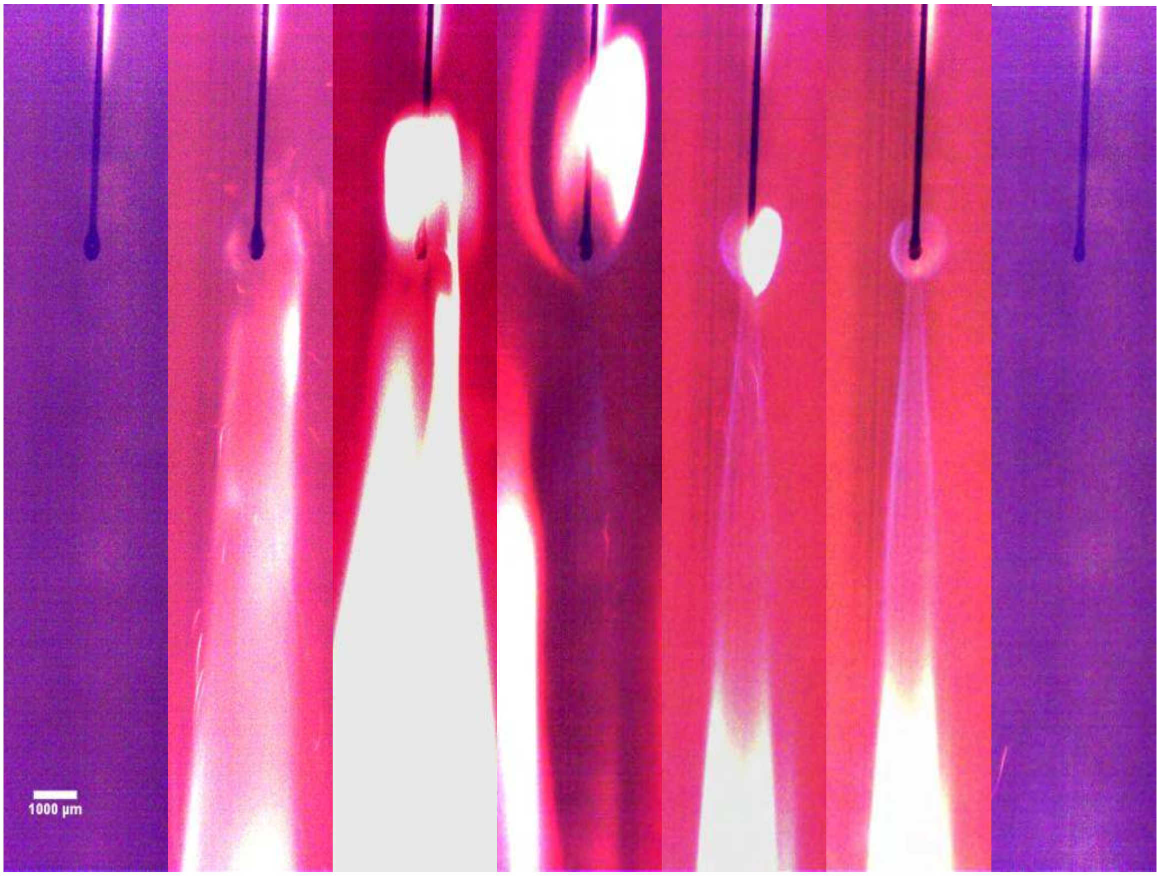


Figure 2-8: Cetane at 500 °C and 20.9% oxygen. Images are displayed at 10 fps and originally taken at 50 fps. The flow rate is 0.6 ml/min.

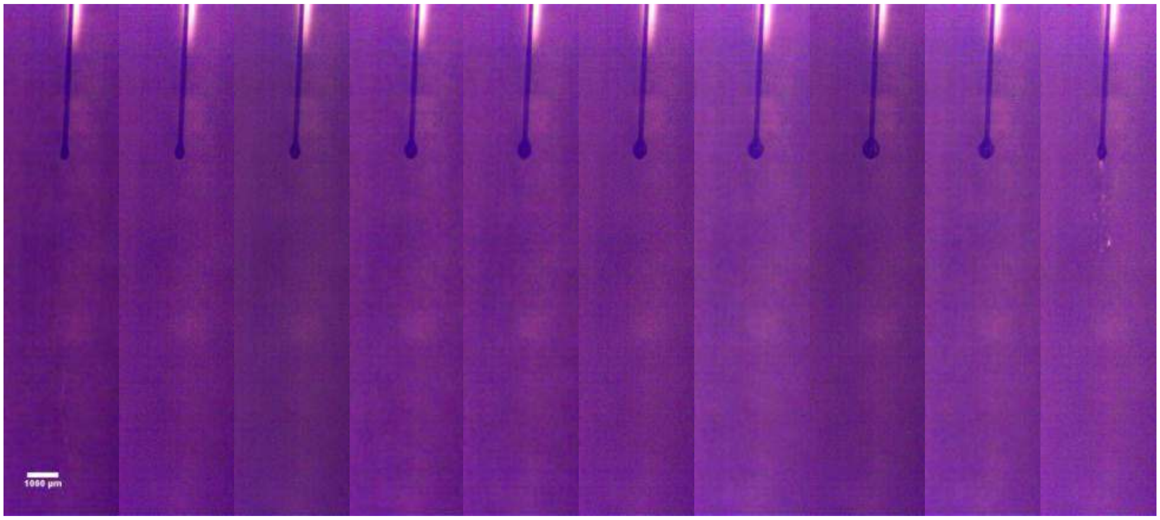


Figure 2-9: Cetane at 500 °C and 20.9% oxygen. Images are displayed at 4 fps and originally taken at 50 fps. The flow rate is 0.8 ml/min.

2.3 OBTAINING SPATIAL TEMPERATURE DISTRIBUTIONS FROM PARTICLE VISUALIZATIONS

The objective of work in this section is to obtain the spatial temperature distributions for particles undergoing combustion by means of visualization. The goal is to use three-color pyrometry to relate the color intensity at each pixel in an image to the temperature at that point.

A MATLAB code was developed to relate the raw intensity information of an image along with the intensity sensitivity of a camera as provided by the manufacturer as inputs. The code utilizes a modified Planck's law equation to provide temperature detail at each pixel. The processing is largely based on Lu et al. 2009.

2.3.1 Experimental Work

The MATLAB code developed handles the high spatial and 30-bit color intensity (high resolution in intensity). The image and video processing software that came with the camera was used to convert 30-bit color intensity to standard 24-bit intensity. Color conversion algorithms were applied directly to the raw digital signal file from the camera to preserve the integrity of the color resolution. Efficient code development and camera signal interpretation has allowed pixel by pixel determination of temperature estimates for the high magnification images of solid fuel particles undergoing combustion. Figures 2-10 and 2-11 show raw visualization images of wood and switch grass particles along with two different types of temperature representations. To obtain these temperature distributions the camera signal ratios were normalized to span from the furnace air temperature (900 °C) and a maximum temperature selected from measurements reported in the literature (2,150 °C).

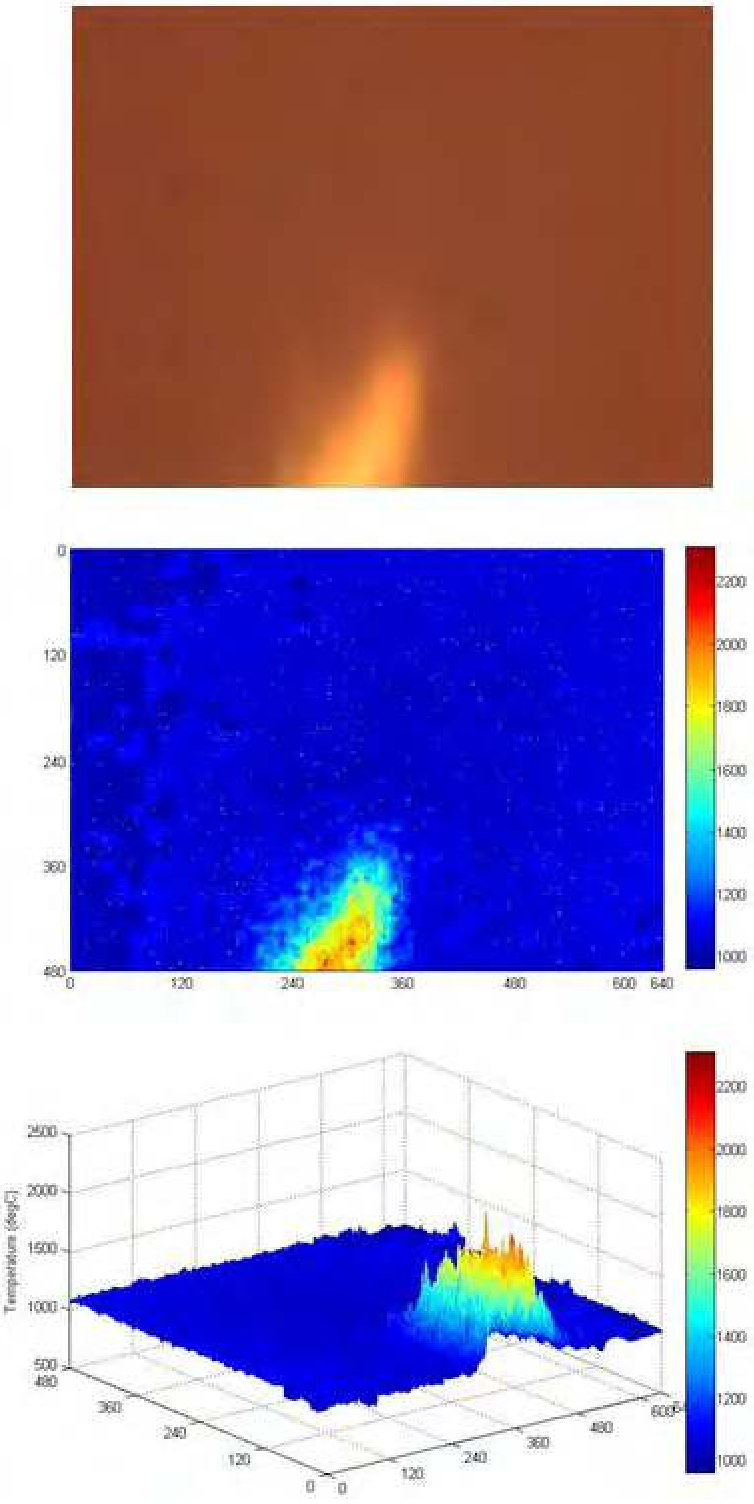


Figure 2-10: Wood combustion image and surface temperature estimates at 900 °C in air

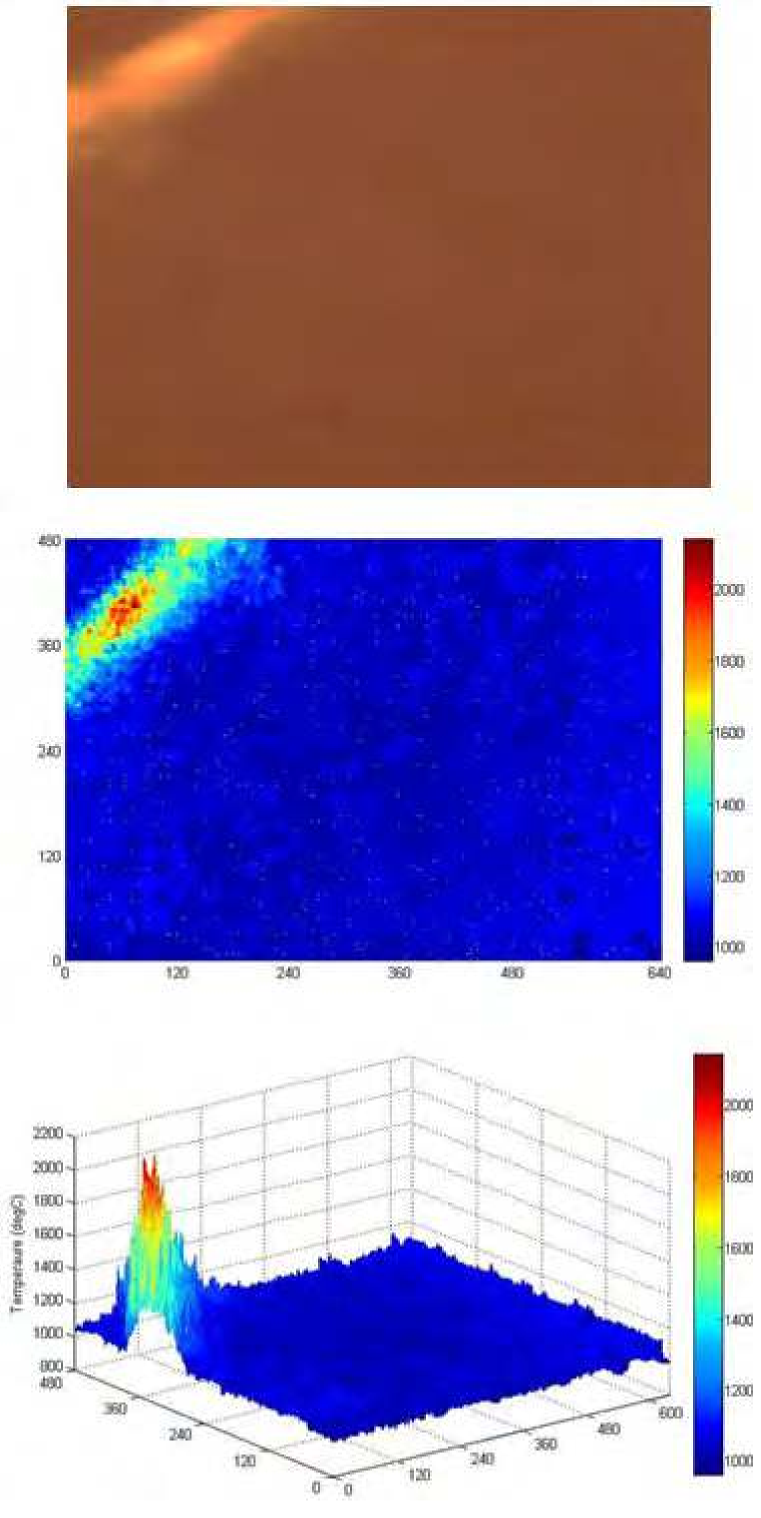


Figure 2-11: Switch grass combustion image and surface temperature estimates at 900 °C in air

At the end of this project, the challenge remained to develop a process to obtain known temperature sources to calibrate the temperature range. As of now, the temperature distributions at this point do not account for particle shape (surface angle with respect to the camera). Table 2-3 shows the average temperatures obtained from analysis of images for particle combustion. The values shown are only preliminary and are displayed to indicate that the temperatures are consistent with those anticipated from literature.

Table 2-3: Particle Average Temperature

Condition	Switch Grass	Wood
Air (20.9% O_2)	1740 °C	1810 °C
5% O_2	1530 °C	Not Applicable

Tables 2-4 and 2-5 show temperature surface distribution estimates for switch grass and wood particles for furnace temperatures of 700 C, 800 °C and 900 °C at various distances from the drop tube nozzle. The raw images were displayed in Tables 2-1 and 2-2.

We incorporated the equation for the wall effect on temperature emission and performed a sensitivity analysis to determine that the wall had less than a 3% influence on temperature determination. Therefore the assumption that wall effect is negligible is reasonable, and this assumption greatly reduced computational time. The temperature distribution calculations reveal that additional smoothing and shape factor considerations need to be incorporated into the image analysis and processing algorithms and the computational processing (MATLAB coding). Nevertheless, the temperature estimations show that the visualization quality and the image processing are capable of obtaining temperatures in the expected range for the wall surroundings and for the maximum temperatures at the particle surface. Further improvements to the image processing are recommended for future research.

Table 2-4: Switch grass combustion temperature distribution for particles in air at 700 °C, 800 °C, and 900 °C. The numbers 1, 2, and 3 along the left column indicate positions down the drop tube of approximately 0, 20, and 35 cm. The z-axis displays temperature in °C and the *x* and *y* axes display pixel numbers.

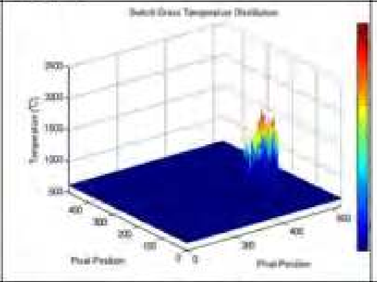
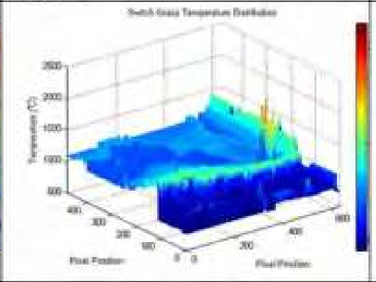
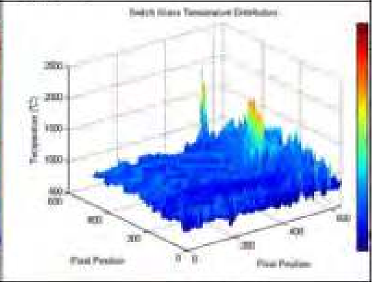
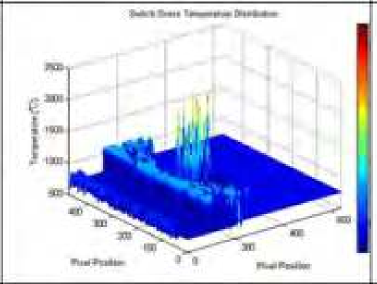
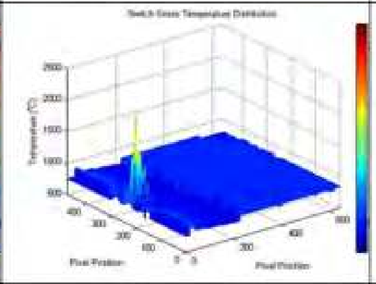
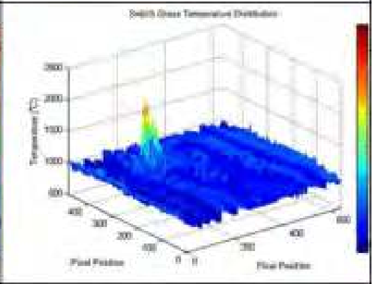
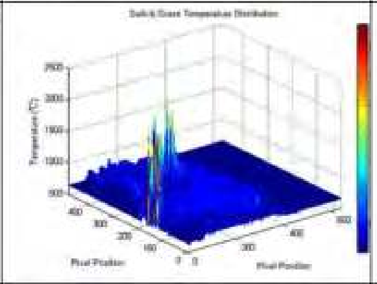
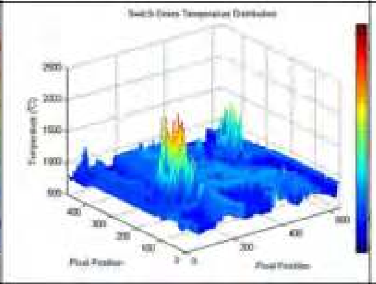
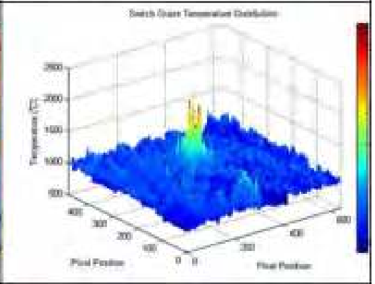
	700 ℃	800 ℃	900 ℃
1			
2			
3			

Table 2-5: Wood combustion temperature distribution in air at 700°C, 800°C, and 900°C. The numbers 1, 2, and 3 along the left column indicate positions down the drop tube of approximately 0, 20, and 35 cm. The z-axis displays temperature in °C and the *x* and *y* axes display pixel numbers.

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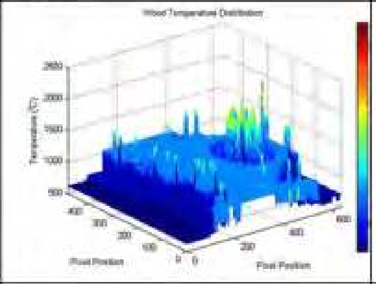
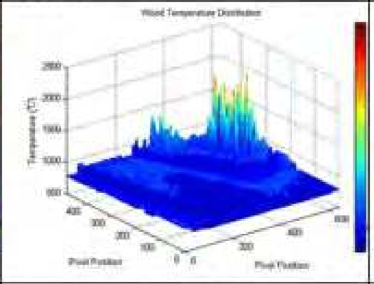
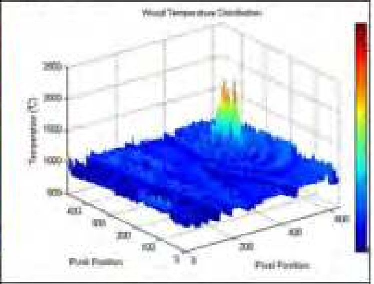
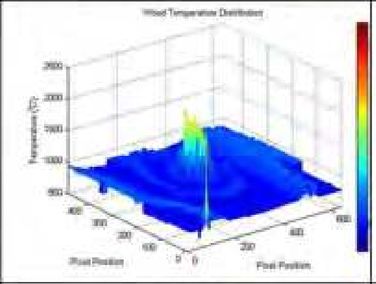
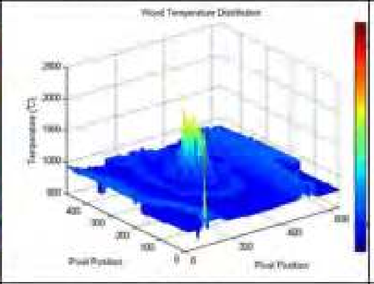
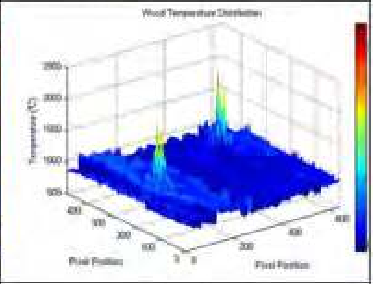
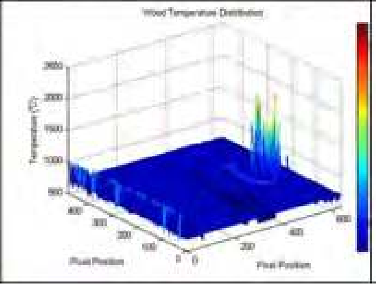
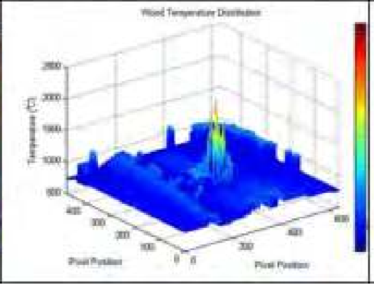
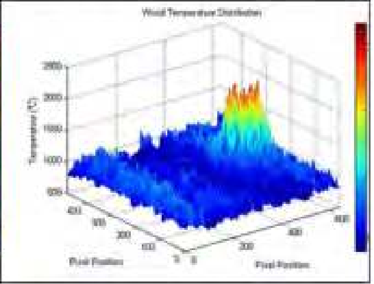
1			
2			
3			

2.4 COMBUSTION OF LIQUID FUELS IN THE FURNACE DROP TUBE

The objective of the work documented in this section is to make modifications to the existing burn simulator system to facilitate combustion studies of alternative *liquid* fuel types.

A microdrop generator was developed for liquid fuels, with the criteria that it would produce on demand uniformly sized microdrops, small enough in diameter to be used with the existing drop tube nozzle in the furnace.

2.4.1 Experimental Work

To develop a microdrop generator for liquid fuels, we built and tested several prototype systems that would produce microdrops on demand which were small enough in diameter to be used with the existing drop tube nozzle in the furnace. The drop tube is approximately 5 cm in diameter but the water-cooled injection nozzle has a 6 mm diameter tube that is 25 cm in length. Furthermore, the visualization system was developed for 100 micrometer solid particles and droplets in liquid fuel sprays tend to be on the order of 100 micrometers. Thus, our intent is to develop a device that generates single drops of liquid on demand that have diameters less than 1 mm and if possible in the 100 micrometer range.

The prototype systems that were set up and tested were based on systems described in *Microdrop Generation* by Lee (2003). Several fluids were used: water, isopropyl alcohol, soy bean oil, corn syrup, and glycerin. The fluids were chosen for ease of use and variation in surface tension, density, and viscosity. Glycerin is the closest to the alternative liquid fuel samples available from the cement plant trials.

2.4.1.1 Prototype Microdroplet Generator

The most straightforward system to start with was simply a syringe pump connected to flat tip needles of varying diameter. Figure 2-12 shows the apparatus and images of a liquid drop produced. An automatic syringe pump was the driving force behind this fluid transport. Different gauges of needles were used, the smallest of which being a 30-gauge (140 μm inner diameter) needle. The droplets that were produced using this apparatus were pendant droplets that grew upon the tip of the needle. The smallest drop size achievable for all of the fluids was just less than 2 mm, with the drop size roughly 6-10 times larger than the needle orifice diameter. Table 2-6 shows fluid properties and the drop size to needle diameter ratio for the 25-gauge needle.

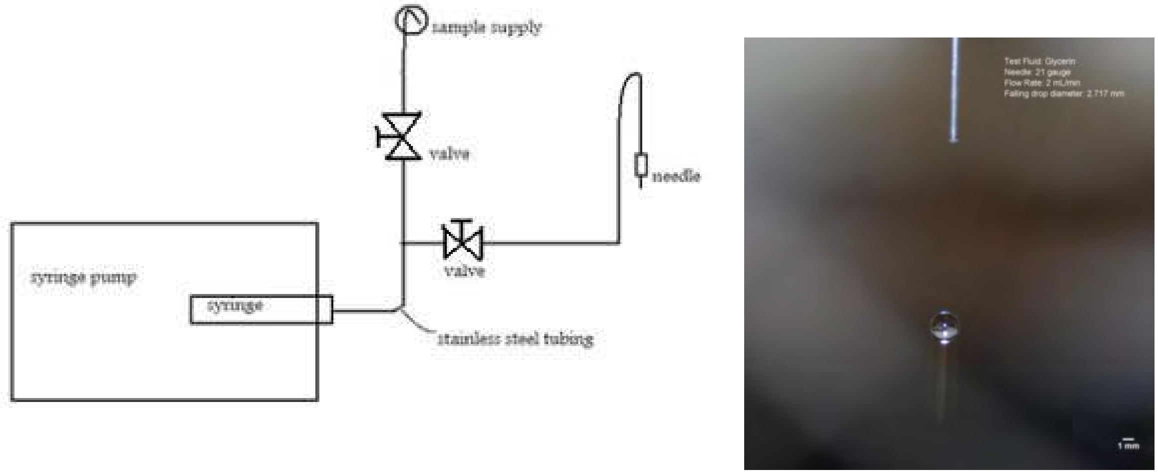


Figure 2-12: Syringe pump drop generation apparatus and image of sample drop of glycerin

Table 2-6: Sample results for drops produced with the syringe pump drop generator

Test Fluid	Surface Tension (mN/m)	Density (g/cm^3)	Viscosity (cp)	Drop Diameter (mm) : 25 Gauge Diameter (mm)
Water	72.58	1.00	1.0	9.88
Glycerin	64.0	1.26	~1200	8.60
S.B. Oil	31.4	.920	79.1	7.51
Iso. Alcohol	23.3	.805	2.2	7.85

As anticipated, surface tension and density affected the drop size, and viscosity affected the ability to pump through the small tubing and needle tips. Droplets produced with this apparatus are easy and readily generated but too large for the present water-cooled injector of the furnace and hence had to be replaced with a better one.

2.4.1.2 Piezoelectric Droplet Generator

As an alternative, we developed a drop generator that uses voltage-driven movement of a piezoelectric disk to generate a pressure pulse and volume displacement in a fluid reservoir connected to a small nozzle. Figures 2-13 and 2-14 show the piezoelectric drop generator system and the overall setup of micro droplet generation respectively. The design is based on the setup documented by Fan et al. (2008).

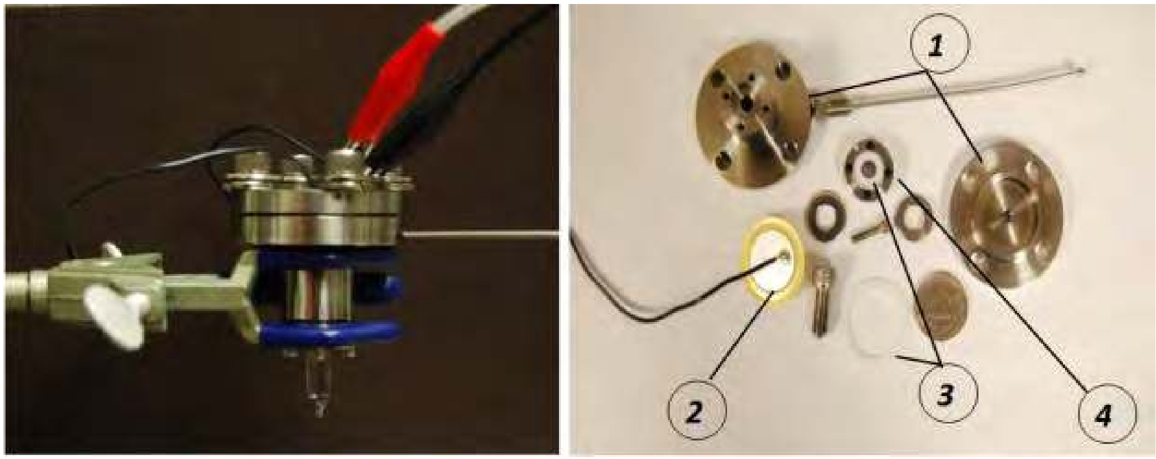


Figure 2-13: The piezoelectric droplet generator and its components. The main parts of the generator are (1) Main body with liquid inlet and upper cover, (2) Piezoelectric disc, (3) Teflon gasket and O-ring, (4) Nozzle holder and (5) Glass nozzle shown at the bottom of the left figure.

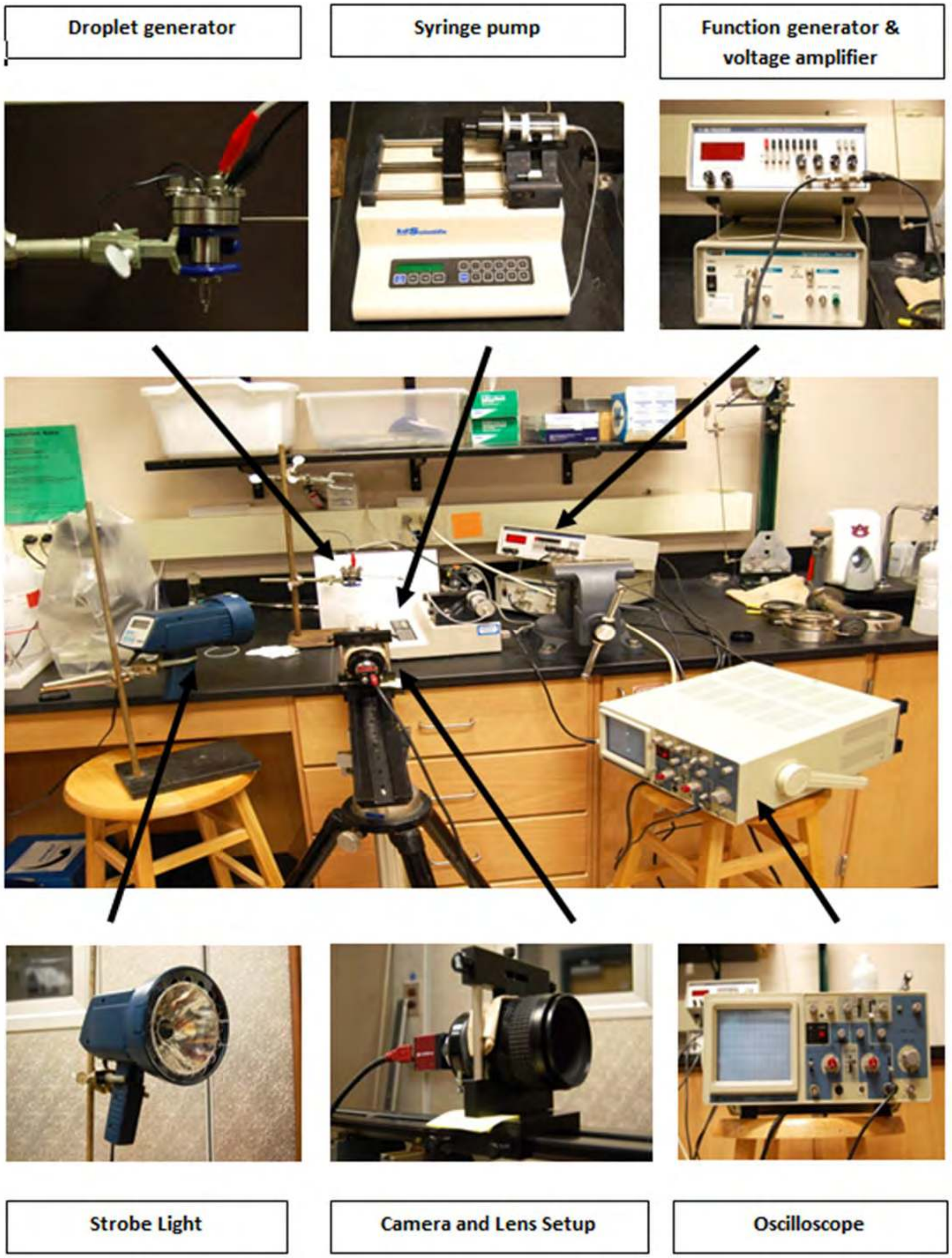


Figure 2-14: Piezoelectric drop generator system

The required metal parts, fittings and the glass nozzles are made out of our own machine shop (Brian Schwieker) and glass shop (W. Sandlin & M. Montgomery) respectively. The other equipment's supplementing the droplet generator are the BK PRECISION 5 MHz Function generator, TEGAM High voltage amplifier, BK PRECISION 20 MHz Oscilloscope, MONARCH NOVA Strobe light, GUPPY F-033 C CCD Camera and NIKON 60mm lens.

The glass nozzles are 31 mm long with tube outer diameter of 6.35 mm. We made several glass nozzles and bored them with inner diameters of 100 μm, 150 μm and 200 μm to study the effect of orifice on droplet size and volume. As shown in Figure 2-15, tapered cross section, short cylindrical holes and smooth edges are important aspects of a nozzle for reliable drop generation.

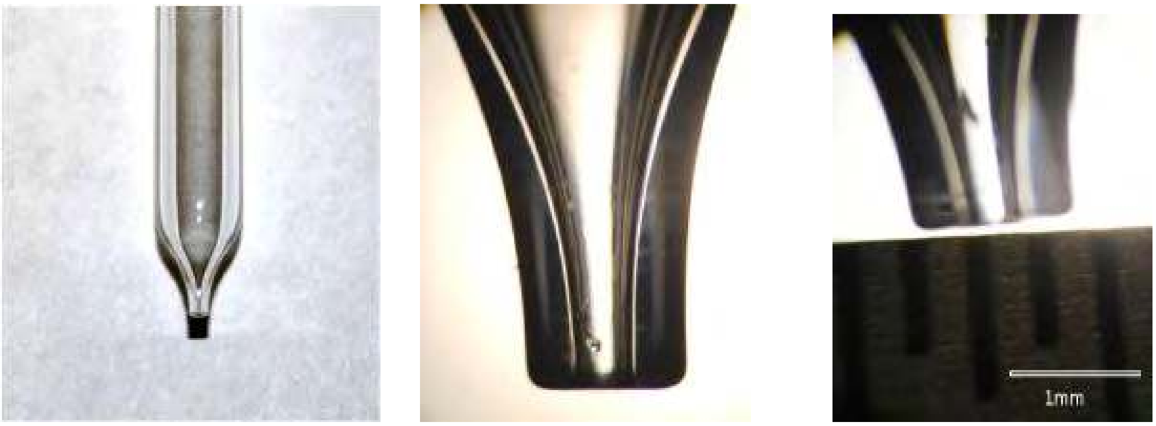


Figure 2-15: Glass nozzles for the piezoelectric drop generator

2.4.1.3 Microdroplet Generation and Testing

Initial studies of microdroplet generation were done with water and isopropyl alcohol. The flow rate of the liquid entering the droplet generator is precisely controlled using the syringe pump while the voltage and frequency of the electric pulse are modulated by means of function generator and the former is measured using an oscilloscope. The camera-lens system is positioned for optimum focus while the strobe light frequency is set for capturing images at a rate of 60 frames per second. Figure 2-16 shows sample of droplets that were generated for various settings of piezoelectric disc voltage and the syringe pump flow rates.

On conducting systematic experiments to determine drop diameters and dropping rates (frequency) for combinations of nozzle tips, voltage applications, flow rates, and fluids, we found that voltage plays an integral part in drop generation by controlling its size as well as the frequency at which the drops produced.

The clamp stand that was holding the droplet generator was replaced with a stable modified optical stand with an E-arm. The stable stand allowed positioning of the apparatus in a nearly exact vertical position thereby reducing the skewness caused due to inappropriate physical positioning. Purchase of a new TEGAM Model 2340 single channel high voltage amplifier (Figure 2-17 a) enabled us to drive the piezoelectric disc for high viscous liquids such as glycerin.

Piezoelectric buzzers of resonant frequency 2 khz (Figure 2-17 b1) and 3.4khz (Figure 2-17 b2) were tried out before settling finally for a 3.9khz one that is presently used. The frequency of piezoelectric buzzer had negligible effect on the droplet generator and that the disk with 3.4 khz resonant frequency was more susceptible to mechanical breakdown.

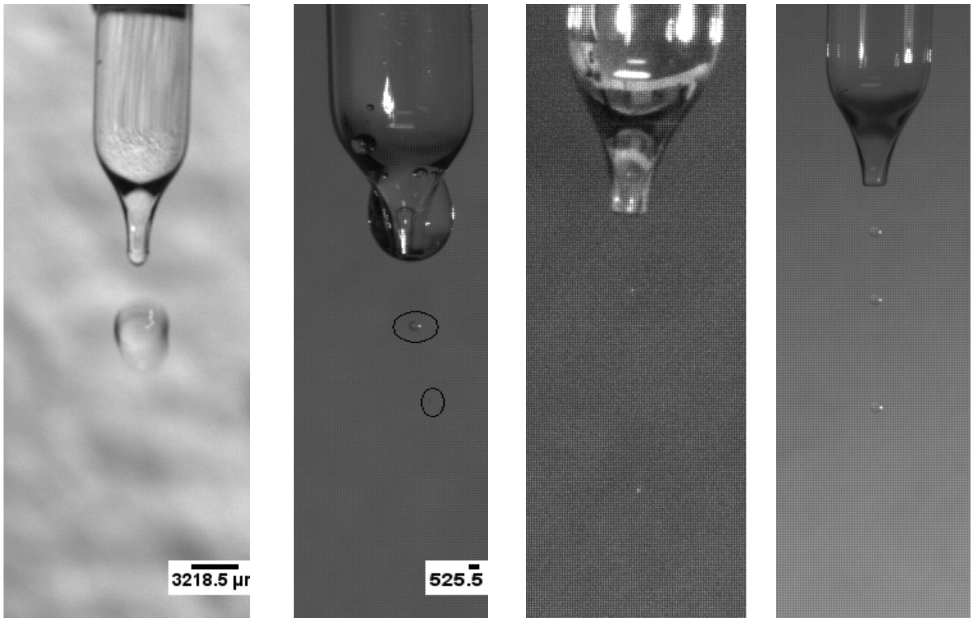


Figure 2-16: Droplets generated for water with low voltage (3 mm diameter, like pendant droplets), water with 12 V and 0.01 µl/min (530 and 140 µm diameter), and isopropyl alcohol with 12 V (240 and 200 µm diameter), and water at 24 V (approximately 700 µm diameter)

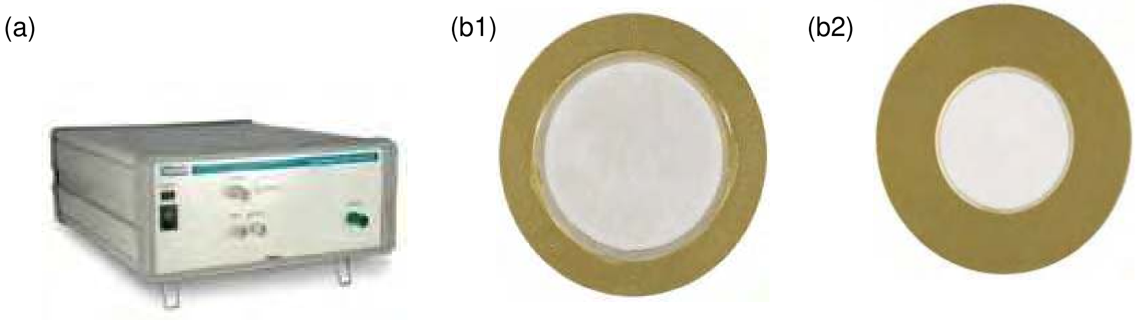


Figure 2-17: (a) TEGAM high voltage amplifier, (b) Piezoelectric buzzers of resonant frequency 2khz (b1) and 3.4khz (b2)

Backlit imaging with semitransparent ground glass as diffuser replaced the earlier used front lit imaging technique for better visualization of microdrops and for ease of acquiring data through image processing. The high speed PCO camera along with a Nikon 105mm lens setup was used for visualization. The images obtained with this setup together with backlit illumination give a clear insight into microdrop generation and enabled us to have a better understanding of the working of droplet generator. Figures 2-18 and 2-19 is a schematic representation of both the microdrop generation setup and piezoelectric droplet generator, respectively.

Following successful generation of microdroplets with water and isopropyl alcohol, we tried 98% Aq. glycerin. With a viscosity of more than 500 mPas and surface tension of 64 m N/m at 20 °C, the drive amplitude was insufficient and the droplet diameter was in several thousand microns. With 70% Aq. glycerin the viscosity of the liquid (at 20 °C) was reduced to around 20mPas yet it proved difficult to eject microdrops with control. The drops were inconsistent in size and skewness, and there was the persistent problem of droplets growing on the tip of the nozzle. On the other hand with 60% glycerin the microdrop generation was comparatively easier, as shown in Figure 2-20. The drive amplitude was lower than that of 70% glycerin. But still the skewing of drops and drop growth on the tip were a concern.

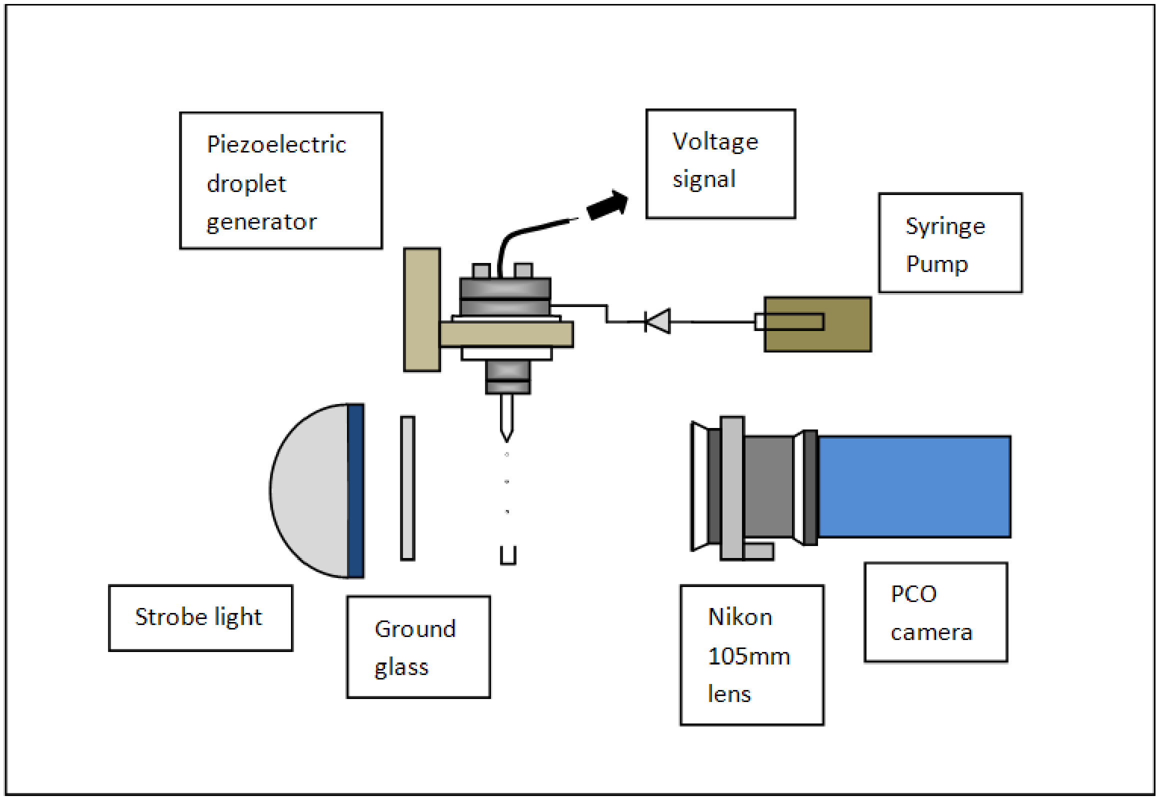


Figure 2-18: Diagram of the microdrop generation setup with the imaging technique

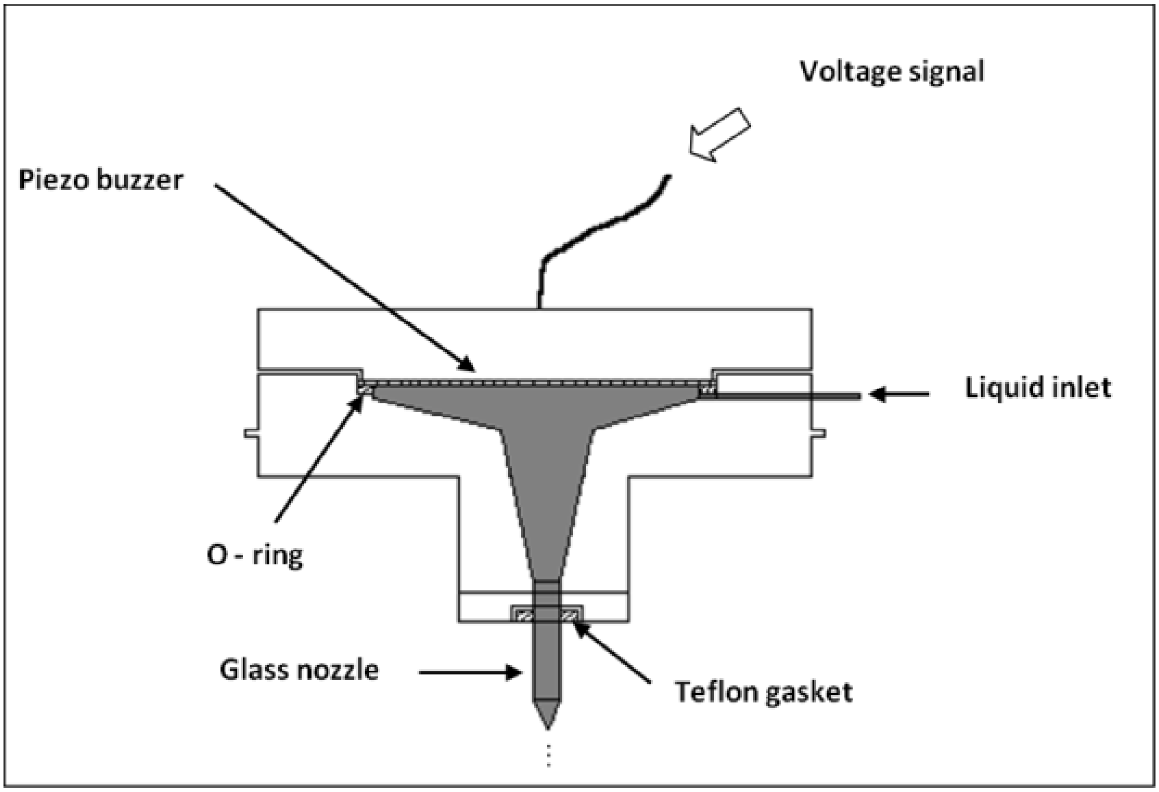


Figure 2-19: Detailed view of piezoelectric droplet generator

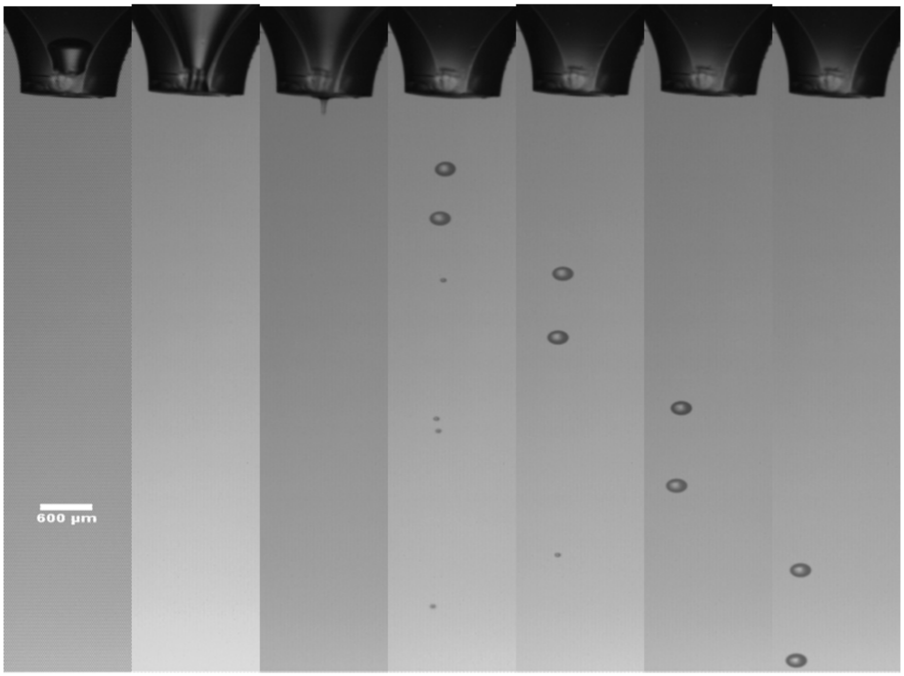


Figure 2-20: Back lit images of 60% aqueous glycerin as it is ejected from the nozzle. Drive voltage of 60V, Flow rate of 0.1 µl/min and drive frequency of 0.4 hz

For a 50% aqueous glycerin solution, microdrops were generated with ease. The droplets were of consistent size, drive amplitude was much lower and the skewness of the drop trajectories was minimal. Figure 2-21 better illustrates the drop skewing (departure from vertical). This skewing is of concern to us because if a droplet has too great of a skew angle it will not be able to travel through the ¼" diameter ejection nozzle in drop-tube furnace. Upon analysis of this image and others in ImageJ, we were able to obtain data concerning droplet diameter and the mean skew angle, which ranged from 1.4 to 2.9 degrees.

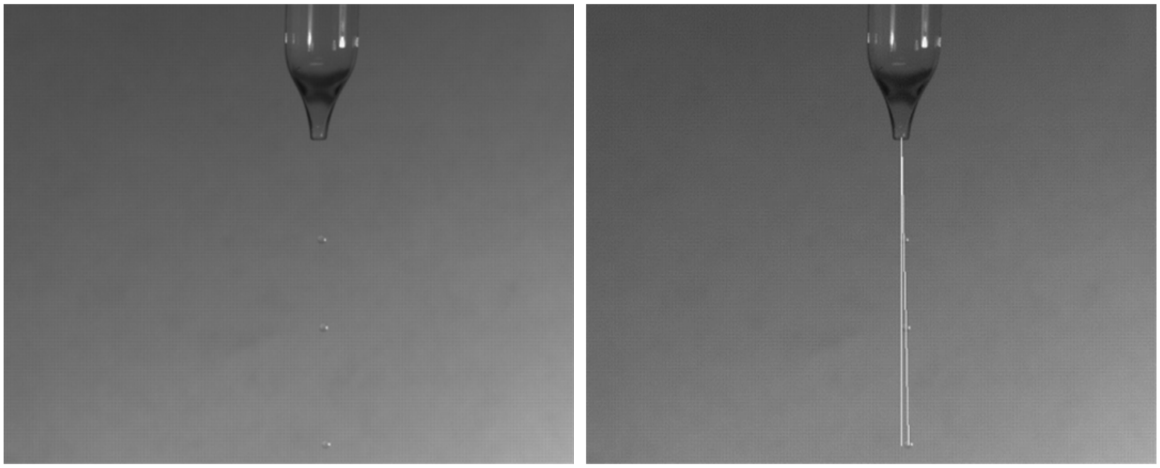


Figure 2-21: Image showing how much the droplet skews as it is ejected

The observed skew angles were deduced to be caused by asymmetric wetting over the ejection orifice, and imperfections in the glass nozzle (Lee 2002). Asymmetric wetting is caused by a slow leak of the fluid from the nozzle. Due to surface tension effects, if the ejection orifice is asymmetrically wetted, a droplet can be skewed as it is being ejected. We took high-magnification images to determine if imperfections in the manufacture of the glass nozzle were present. Figure 2-22 shows images of a 100 micron (left) and 150 micron (right) nozzle. We found that the ejection holes are relatively circular but minor defects in the nozzle tip likely influence the skewing of the drops.

For a systematic study of performance of several liquids, the results of which would give us a high degree of control in generation of microdrops for desired drop diameters and rates was carried out. Sample images from visualizations during these experiments are presented here. Figures 2-23, 2-24, 2-25 show the different sizes of microdrops generated for 60% aq. Glycerin, 70% aq. Glycerin, and Isopropyl alcohol under varying voltage conditions. In general, an increase in voltage signal tends to increase the size of the microdrop generated.

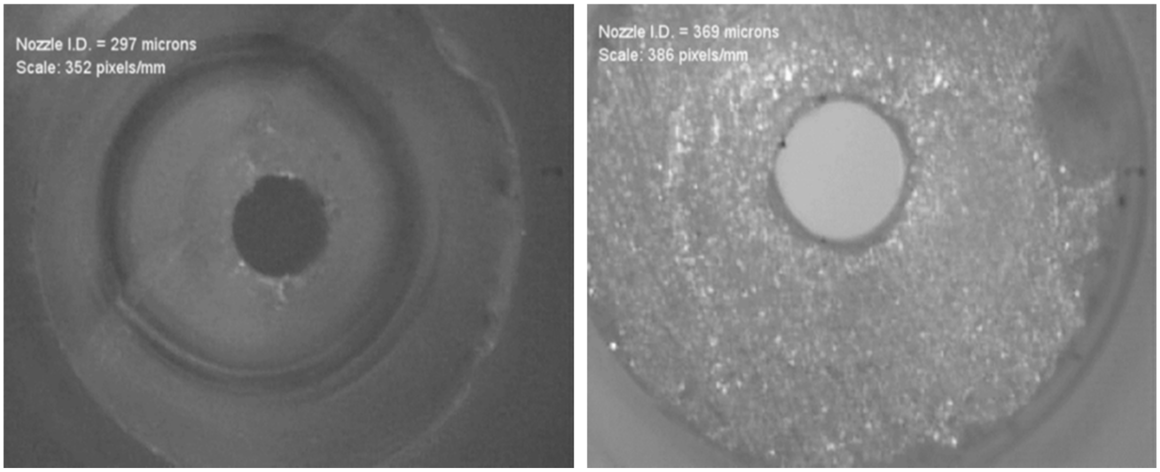
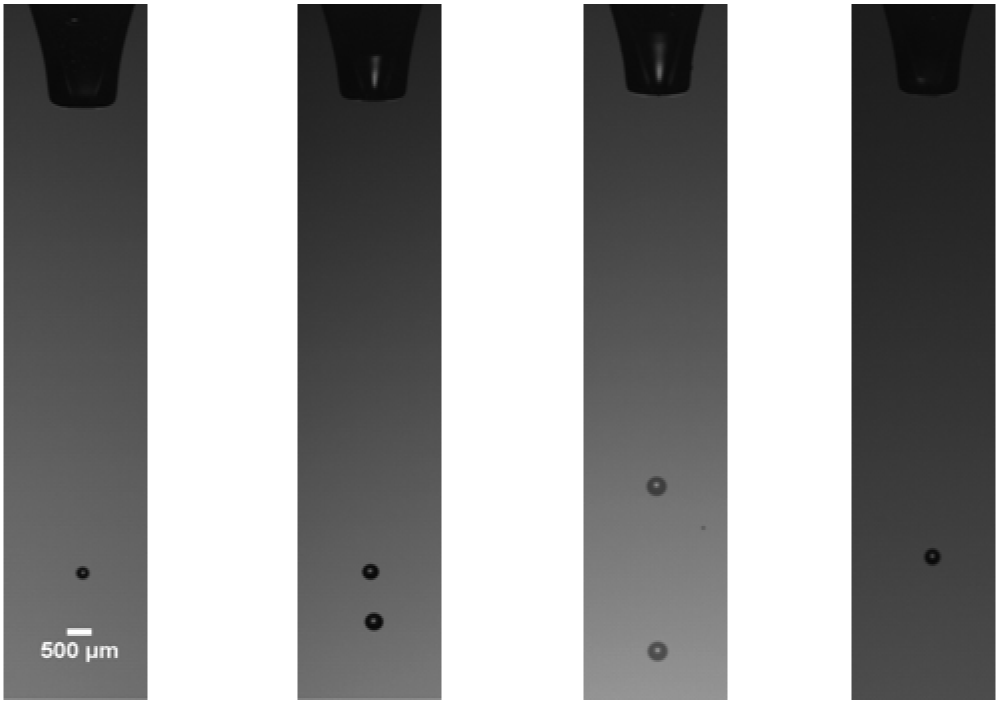


Figure 2-22: High magnification images taken with Questar lens showing nozzle imperfections



Liquid - 60% Aqueous Glycerin, Piezo Conditions (25V, 3.5 Hz, 10 µL/min), Camera (fps - 143), Droplet size – 260 µm.

Liquid - 60% Aqueous Glycerin, Piezo Conditions (37.5V, 3.5 Hz, 10 µL/min), Camera (fps - 143), Droplet size – 340 µm.

Liquid - 60% Aqueous Glycerin, Piezo Conditions (50V, 3.5 Hz, 5 µL/min), Camera (fps - 143), Droplet size – 400 µm.

Liquid - 60% Aqueous Glycerin, Piezo Conditions (62.5V, 3.5 Hz, 5 µL/min), Camera (fps - 143), Droplet size – 345 µm.

Figure 2-23: 60% aqueous glycerin microdroplet generation at different voltages

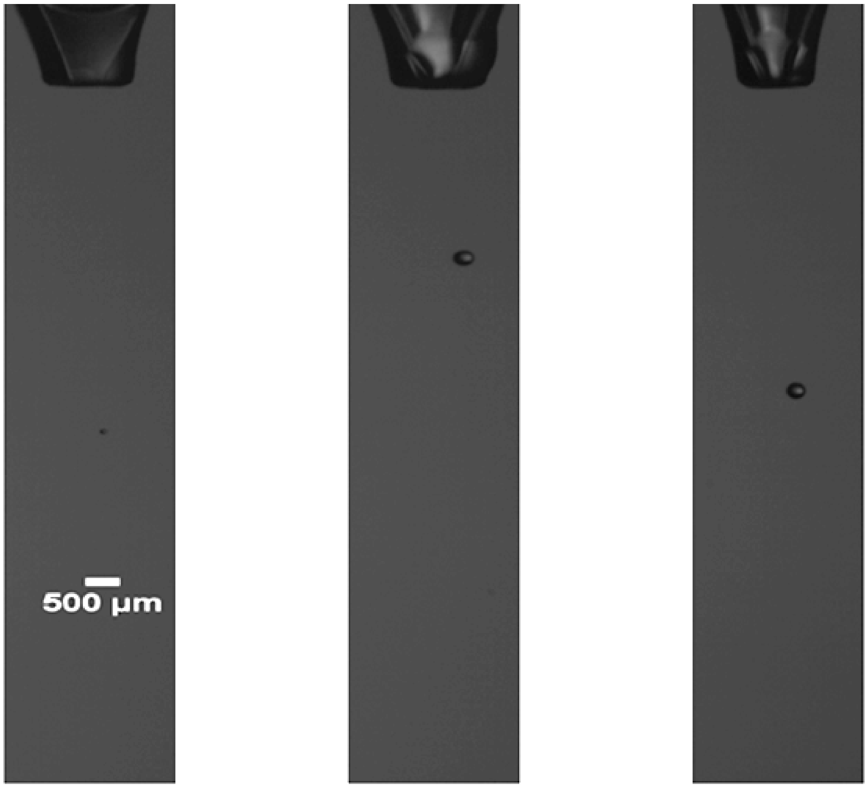
Liquid - 70% Aqueous Glycerin, Piezo Conditions (25V, 3.5 Hz, 10 µL/min), Camera (fps - 250), Droplet size – 258 µm.

Liquid - 70% Aqueous Glycerin, Piezo Conditions (37.5V, 3.5 Hz, 10 µL/min), Camera (fps - 250), Droplet size – 346 µm.

Liquid - 70% Aqueous Glycerin, Piezo Conditions (50V, 3.5 Hz, 10 µL/min), Camera (fps - 250), Droplet size – 467 µm.

Figure 2-24: 70% aqueous glycerin microdroplet generation at different voltages

The liquid alternative fuel of interest is glycerin, and for comparison we selected isooctane (octane number of 100) and hexadecane (cetane number of 100). These liquids are traditional standards for liquid hydrocarbon fuels. We obtained high purity samples of these liquid from VWR. A series of experiments were conducted for the fuels with the piezoelectric generator to determine the conditions and drop sizes that could be produced. Figures 2-26 and 2-27 show droplets of these fuels at selected conditions to illustrate the drop size and consistency. We have not yet analyzed these images to determine exact drop sizes but the scale bar reveals that the drops are easily controlled in the 200 to 400 micrometer range.

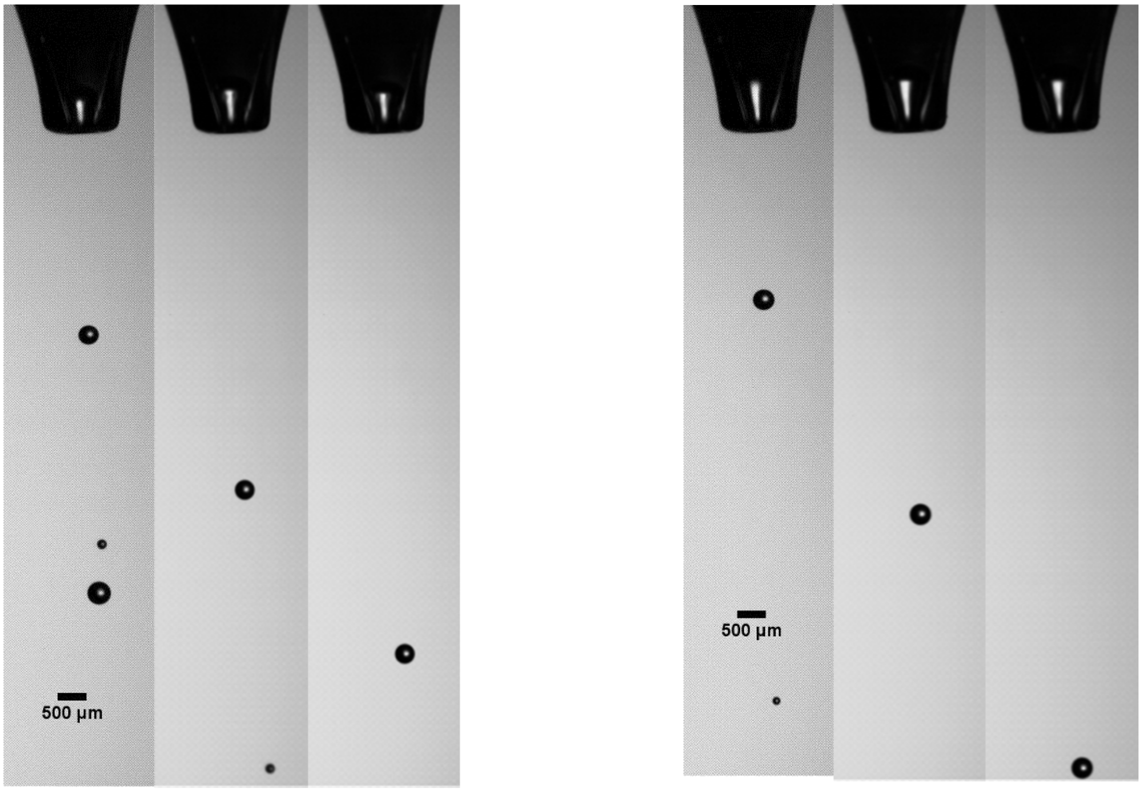


Liquid – Iso Propyl Alcohol, Piezo Conditions (11.5V, 3.5 Hz, 5 µL/min), Camera (fps - 143), Droplet size – 108 µm.

Liquid - Iso Propyl Alcohol, Piezo Conditions (25V, 3.5 Hz, 5 µL/min), Camera (fps - 143), Droplet size – 316 µm.

Liquid - Iso Propyl Alcohol, Piezo Conditions (37.5V, 3.5 Hz, 5 µL/min), Camera (fps - 143), Droplet size – 359 µm.

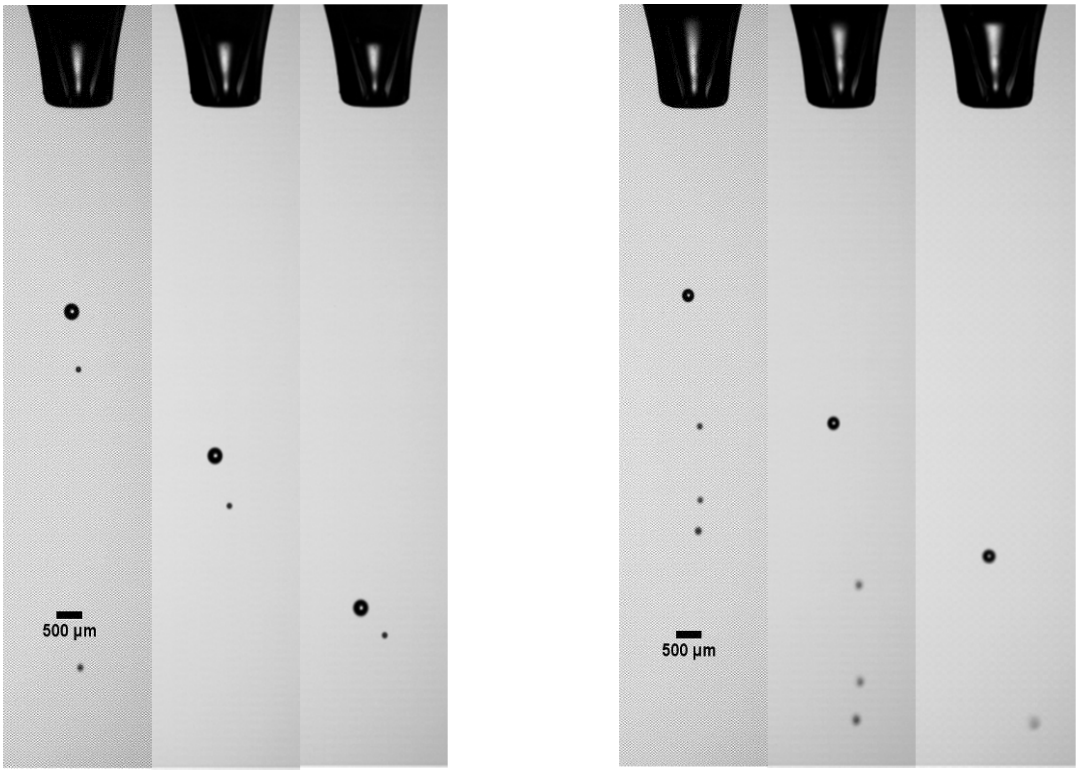
Figure 2-25: Isopropyl Alcohol microdroplet generation at different voltages



Liquid – 99% Hexadecane, Piezo Conditions (25V, 3.5 Hz, 1 µL/min), Camera (fps - 200).

Liquid – 99% Hexadecane, Piezo Conditions (37.5V, 3.5 Hz, 1 µL/min), Camera (fps - 200).

Figure 2-26: 99% Hexadecane microdroplet generation at different voltages



Liquid – Iso-octane, Piezo Conditions (11V, 3.5 Hz, 1 µL/min), Camera (fps - 200).

Liquid – Iso-octane, Piezo Conditions (25V, 3.5 Hz, 30 µL/min), Camera (fps - 200).

Figure 2-27: Iso-octane microdroplet generation at different voltages

A glass model of the central tube of existing stainless steel water-cooled injection nozzle was constructed out our glass shop. The glass tube is about a foot long with an inner diameter of 0.25 inch positioned true to vertical and just below the drop generator nozzle tip. We found that, in spite of some droplets skewing, a good number of drops passed through the ¼ inch tube successfully (Figure 2-28). Analyzing the images obtained at the bottom of the glass tube, we saw two distinct droplet sizes. Our conclusion was that the droplets of smaller size might be due to its collision with the wall of the glass tube or due to the collision with a drop attached to the side of the wall and hence assumed that the larger drops were ones that fell through the tube undisturbed.

Figure 2-28: Images of 50 % glycerin droplets produced at 3.0 Hz, 0.01 µL/min, 55 V drive amplitude. Images are taken using PCO camera with Nikon 105mm lens at 143 FPS

Table 2-7 displays the downward velocity of each droplet. This downward velocity is assumed to be the terminal velocity of the droplet since it has fallen a distance of approximately one foot. The velocity will play an important role when one wants to characterize flame shape during combustion in future.

Table 2-7: Examples of drop diameters and velocities

Drop #	Drop Diameter (µm)	Drop Velocity (m/s)
1	500	1.20
2	440	1.12
3	390	1.05
4	380	1.01
5	380	1.01
6	320	0.87
7	320	0.86
8	300	0.87
9	260	0.73
10	230	0.60

2.4.1.4 Liquid fuel injection

We designed and tested several methods for combining the drop generator with the water cooled injection nozzle at the top of the drop tube of the furnace. A glass injection model with provision for both combustion gas (air) supply and a vertical passage for microdrops was one such design. It is coupled to the existing furnace setup by means of Teflon joints as shown in Figure 2-29. The glass tube coupling, and stainless tube have a bore (inside diameter) of about 6 mm and the total distance that the drops must fall before reaching the furnace retort is about a third of a meter: Our challenge has been to keep the tubes true to vertical and obtain better control over the gas flow but at present we have not been able to consistently get the drops to fall without contacting the tube walls.

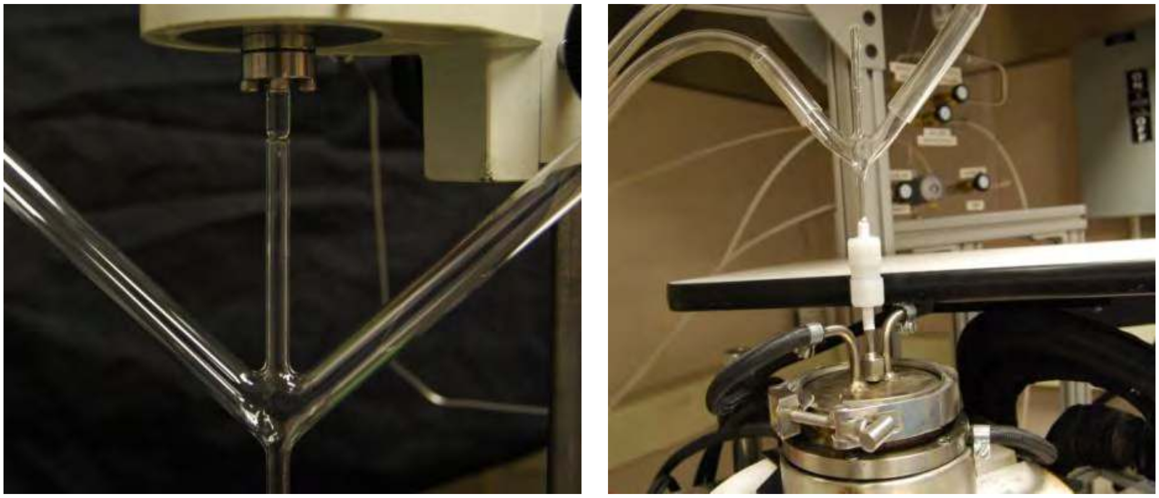


Figure 2-29. Liquid fuel prototype drop generation and injection system

We have not been successful at this point with injection of glycerin through the setup and the existing solid particle injection water-cooled nozzle. It evaporates rapidly and has too high a viscosity. However, we have been able to inject and observe combustion for iso-octane and hexadecane.

The water-cooled injection nozzle that was designed for solid particle injection is not suited for delivery of the liquid fuel drops. The central tube of the injector was too narrow (drops collect along the sides) and the combustion air entered through the same tube that the fuel is delivered. Figure 2-30 shows a schematic diagram of the new nozzle for liquid drops in comparison with the old nozzle, and the key features to note are the drop tube for the fuel and separate tubes for the inlet combustion gas (labeled Air). The Auburn University machine shop has developed engineering drawings for the nozzle and they fabricated it. The new nozzle was tested with the piezo-electric drop generator.

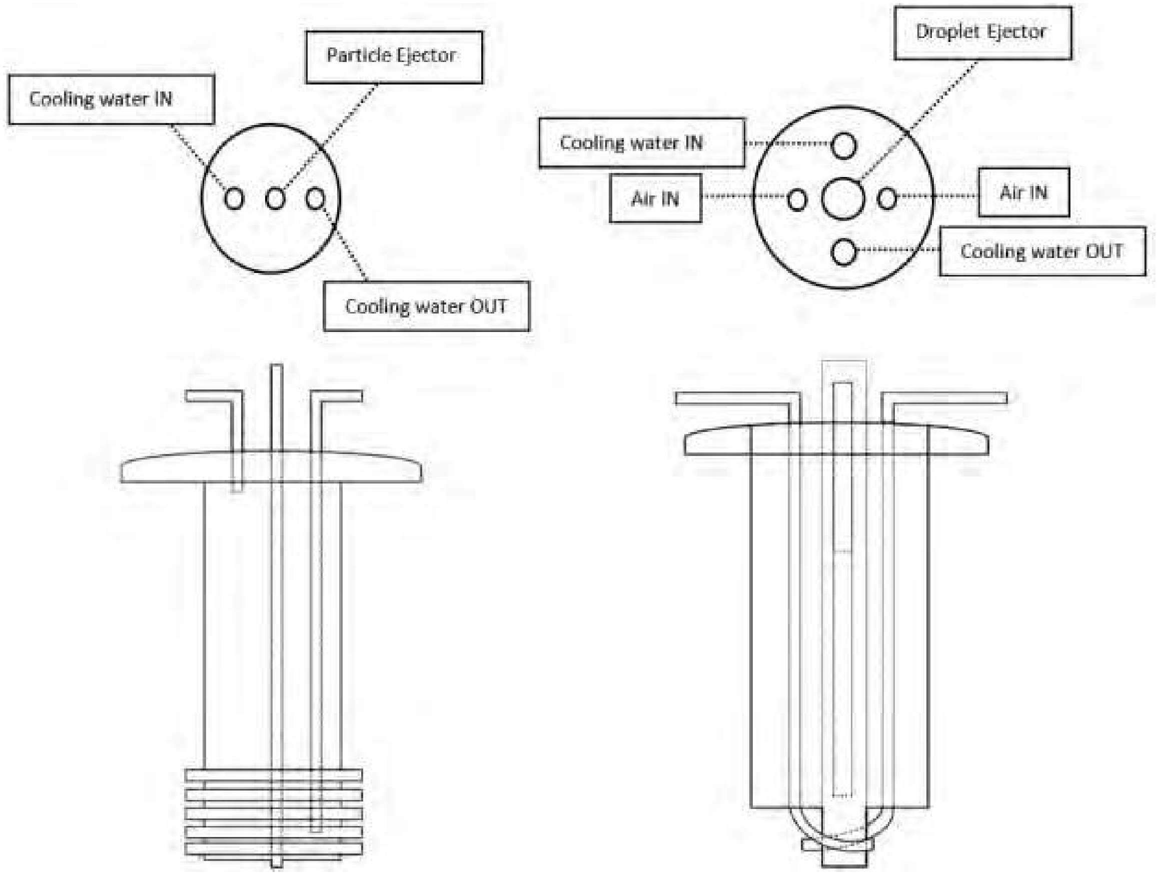


Figure 2-30: Schematic diagram of the liquid fuel water-cooled nozzle recently fabricated (right)

2.5 SUMMARY

Burn characteristics of solid and liquid alternative fuels has been carried out. A laboratory burn simulator system is developed for carrying out the high temperature combustion of fuels. Provisions are made to this burn simulator set up such that we could collect uncombusted char and analyze exhaust gases. Visualization techniques comprising a variety of optical equipment selections (mainly camera and lenses) have been employed to obtain images of solid (coal, wood and switch grass) and liquid (hexadecane) fuels undergoing combustion. Three color pyrometry techniques were used to develop a MATLAB code that would provide spatial and average temperature distribution. Visualization Images of combusting particles along with their surface temperature distribution has been displayed. Piezoelectric droplet ejector was designed to generate microdrops of liquid and has been optimized to produce microdrops for liquids with varying surface tension and viscosity values. Modifications including the design of a new water cooled nozzle have been completed to incorporate liquid fuels on to the drop tube furnace

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2.6 CONCLUSION

A drop tube furnace and visualization method were developed that show potential for evaluating time- and space-resolved temperature distributions for fuel solid particles and liquid droplets undergoing combustion in various combustion atmospheres.

2.7 RECOMMENDATIONS FOR FUTURE RESEARCH

The future research recommended includes continued development of the burn simulator to include effluent gas analysis. Further improvement of visualization quality and inclusion of shape correction for the image processing and analysis are needed.

2.8 RECOMMENDATIONS FOR IMPLEMENTATION

For implementation, a model needs to be developed to apply the temperature distributions to estimations of combustion rates for various fuel types in conditions that mimic those of the cement plant.

PART 2

Full-Scale Trial Burns with Alternative Fuels at Cement Plant

CHAPTER 3

PART 2—INTRODUCTION

3.1 INTRODUCTION

This task primarily involves the subcontractor and will be conducted at a full-scale cement plant. Alternative fuels were selected based on local availability, cost, emissions, and system compatibility. Alternative fuels included in this study are construction and demolition waste, woodchips, and soybeans. Each of these fuels was utilized in order to partially replace and therefore lessen the demand for traditional fuels. Each trial fuel was co-fired with traditional fuels. Lafarge North America's Roberta cement plant, a full-scale cement plant located in Calera, Alabama, produced the cement during each trial. Each trial or burn, as it will be referred from this point forward, was continuous for between 3 and 6 days. A thorough sampling plan was implemented during each of the burns to carry out the objectives listed above. Although each burn utilized a unique fuel, the plant made an effort to maintain consistent conditions in all other aspects of operation.

The first burn conducted, which will be known as the baseline burn, utilized coal and plastics. All the alternative fuel burns are compared to this baseline burn. Although plastics are generally considered alternative fuels, in this study the plastic blend is considered a traditional fuel because it is routinely used by this cement plant. The baseline burn was performed in June of 2010 and lasted 3 days.

The first alternative fuel burn utilized coal, plastics, and construction and demolition waste. The construction and demolition waste consisted of wood paper and plastics. The types of wood utilized include dimensional lumber, plywood, and pallets. The paper included corrugated boxes and miscellaneous paper materials. The plastic consisted of solid and cellular foam and polyethylene film. This burn lasted for 80 hours and also occurred in June of 2010. The first two burns were closely spaced in order to maintain similar plant conditions.

The second alternative fuel burn utilized coal, plastics, and woodchips. This burn was conducted over a 6-day period in July of 2010. This burn was unique to this phase of the project due to the progressively increasing substitution rate of woodchips. This trial burn was broken into three phases. The initial substitution rate of woodchips was 5 percent and every two days thereafter the substitution rate increased by 5 percent. Therefore the average substitution rates for the burn were 5, 10, and 15 percent.

The third and final burn utilized coal, plastics, and soybeans. The soybeans were treated with herbicide. This burn was conducted over a 3-day period in October of 2010.

During each of the burns, samples were collected according to the sampling plan. These samples were transported to Auburn University for further conditioning and testing. The cement plant tested all materials to determine chemical composition except for the fuels used. The cement plant also tested various properties of the final cement to ensure adequate properties were being obtained during production. The final responsibility of the cement plant was to monitor emissions produced during each burn.

Specimens were prepared at Auburn University from each of the samples transported from the cement plant. The specimens were then shipped to the external chemical laboratory for further testing. The external laboratory determined the chemical compositions of each specimen and they conducted proximate, ultimate, and combustion analyses on each fuel.

Auburn University was responsible for the transportation, preparation, and shipment of all specimens. Auburn University also conducted testing on mortar, paste, and concrete to determine the behavior of the cement. Results from each party were collected and analyzed by Auburn University in order to determine the effect of using alternative fuels on portland cement.

3.2 OBJECTIVES OF PART 2

The three fuels investigated during this study were construction and demolition waste, woodchips, and soybeans. The woodchips trial implemented a progressively increasing substitution rate. Each fuel was evaluated separately to assess its viability as a fuel for the production of portland cement. The following assessments were used in order to measure the viability of an alternative fuel:

1. the ability of the cement plant to maintain productive operations,
2. the chemical composition of clinker and portland cement,
3. the physical properties of the portland cement,
4. the properties of concrete made from the portland cement, and
5. the emissions released by the cement plant.

Collaborative efforts between three parties were required to fulfill these objectives. The parties involved included a full-scale cement production facility, and external chemical laboratory, and Auburn University.

The first objective was responsibility of the cement plant personnel. Fuels that produce problems in the manufacturing process cannot be considered as viable replacement options.

The performance of the cement is directly related to its chemical composition and therefore, the chemical components of the cement and clinker needed were determined. Using two laboratories satisfied the second objective as well as provided confidence in accuracy of the data received.

The third and fourth objectives of this study were the primary objectives in this study. The cement plant conducted tests on mortar specimens made from the produced cement. Auburn University conducted testing on mortar, paste, and concrete specimens. The results of these tests were compared to results of similar specimens prepared by each entity from cement produced by only traditional fuels.

The final objective was to monitor emissions released by the cement plant during each trial. The emissions data collection was performed by the cement plant using a continuous emission monitoring system (CEMS). Results from each trial were compared to emissions data collected during a burn that utilized traditional fuels.

3.3 PORTLAND CEMENT PRODUCTION

Portland cement is manufactured by combining raw materials containing calcium, silica, alumina, and iron. After the raw materials are crushed to a specific fineness and blended together, the mixture, or kiln feed, is transported to the kiln where it is heated to temperatures in excess of 1600 °C. This fuses the homogeneous mixture together into a uniform product known as clinker. The clinker is immediately cooled as it exits the kiln and is stored in silos until it is ready to be ground with a predetermined quantity of sulfates. The final product is known as portand cement. Since the quantity of raw materials used is dependent on the material's chemical composition, a facility's geographical location and local industrial conditions determines its use of the raw materials.

Cement is manufactured through a wet or dry process. Dry process manufacturing is the most modern approach and is more fuel efficient and widely used than the wet process. The cement produced from either process is packaged, stored, and sold to consumers.

Figure 3-1 shows a schematic of a typical dry process cement manufacturing facility. Predetermined quantities of raw materials are first fed into grinders that simultaneously crush the raw materials to a certain fineness and create a homogeneous mixture. Next, the raw material is sent through a series of preheaters where the mixture is partially calcined. The calcination process is discussed in more detail in later sections. The mixture in then fed from the preheating tower into the kiln where high temperatures causes the materials to chemically fuse together. Rapid cooling of the fused material forms clinker. The clinker is ground with an addition of gypsum to a specified fineness to form portland cement. Dust, commonly known as cement kiln dust (CKD), is collected through the entire process and is recycled back into the raw feed.

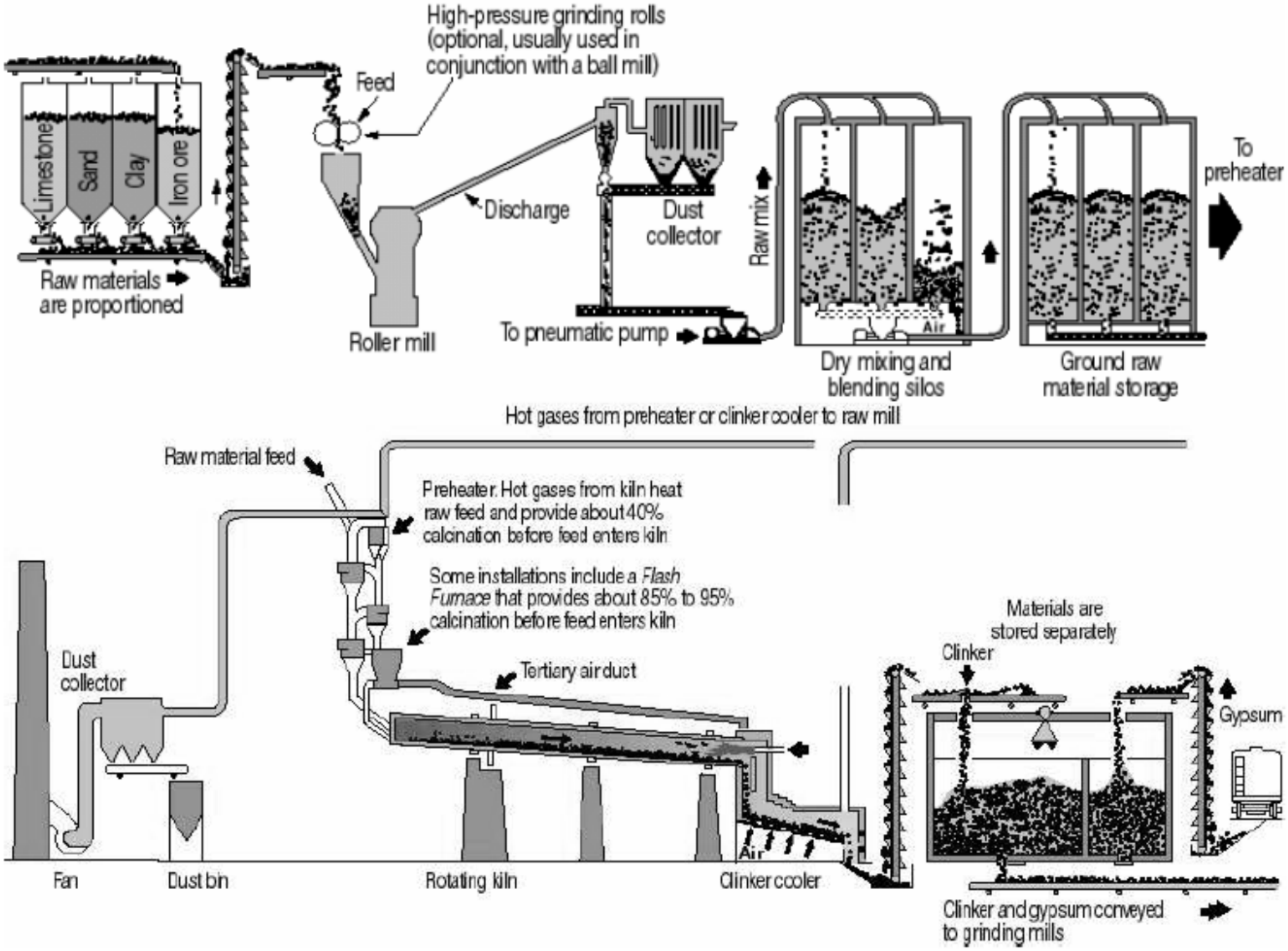

Figure 3-1: Layout of a Typical Dry-Process Portland Cement Production Facility (Kosmatka et al. 2002)

Manufacturing portland cement is highly energy intensive. According to Hendrik and Padovani (2003), an average of 3.2 to 6.3 GJ of energy is required to produce one ton of cement. Since there are multiple methods to achieve each step in production, energy consumption is variable between producers. In Table 3-1 the energy consumption at various stages of the manufacturing process and between manufacturing types are shown. It should be noted the fuel is only used in the kiln and preheater systems. Also, the fuel used in the wet process far exceeds fuel used in the dry process. Additional fuel in the wet process is required to dry incoming material before clinkering can take place in the kiln. Grinding the raw meal and clinker requires the most electricity during the manufacturing process. Over the years, technology has enabled new production methods to be developed that have increased energy efficiency by more than 37% since 1972 (PCA 2010).

3.3.1 Raw Materials

The selection and combination of raw materials is essential to produce clinker with proper hydraulic properties. Typically, 1.7 tons of raw materials are needed to produce 1 ton of cement (Hendrik and Padovani 2003). The primary raw materials used in the production of clinker are calcareous materials (containing calcium carbonates), siliceous material (containing silica), and argillaceous material (containing both silica and alumina) (Miller 2004). These materials are combined to provide the clinker with the appropriate quantities of the following oxides: calcium oxide or lime (CaO = 65% ± 3), silica oxide (SiO = 21% ± 2), alumina oxide (Al_2O_3 = 5% ± 1.5), and iron oxide (Fe_2O_3 = 3% ± 1). The most common sources of each raw material are shown in Table 3-2.

Table 3-1: Approximate Energy Consumption in Cement Making Processes and Process types (Adapted from Worrell et al. 2001)

Process Step	**Fuel use** (GJ/t of cement)	**Electricity use** (kWh/t of cement)	**Primary energy** (GJ/t of cement)
Crushing			
Jaw crusher	-	0.3 - 1.4	0.02
Gyratory crusher	-	0.3 - 0.7	0.02
Roller crusher	-	0.4 - 0.5	0.02
Hammer crusher	-	1.5 - 1.6	0.03
Impact crusher	-	0.4 - 1.0	0.02
Raw meal grinding			
Ball mill	-	22	0.39
Vertical mill	-	16	0.28
Hybrid systems	-	18 - 20	0.32 - 0.35
Roller Press-			
Integral	-	12	0.21
Pregrinding	-	18	0.32
Clinker kiln			
Wet	5.9 - 7.0	25	6.2 - 7.3
Lepol	3.6	30	3.9
Long dry	4.2	25	4.5
Short dry-			
Suspension preheating	3.3 - 3.4	22	3.6 - 3.7
Preheater & precalciner	2.9 - 3.2	26	3.2 - 3.5
Shaft	3.7 - 6.6	NA	3.7 - 6.6
Finishing grinding			
Ball mill	-	55	0.60
Ball mill/separator	-	47	0.51
Roller press/ball mill/separator	-	41	0.45
Roller press/separator/ ball mill	-	39	0.43
Roller press/ separator	-	28	0.31

Table 3-2: Sources of Raw Materials (Kosmatka et al. 2002)

Calcium	Iron	Silica	Alumina	Sulfate
Alkali waste Aragonite Calcite* Cement-kiln dust Cement rock Chalk Clay Fuller's earth Limestone* Marble Marl* Seashells Shale* Slag	Blast-furnace flue dust Clay* Iron ore* Mill scale* Ore washings Pyrite cinders Shale	Calcium silicate Cement rock Clay* Fly ash Fuller's earth Limestone Loess Marl* Ore washings Quartzite Rice-hull ash Sand* Sandstone Shale* Slag Trap rock	Aluminum-ore refuse Bauxite Cement rock Clay* Copper slag Fly ash* Fuller's earth Granodiorite Limestone Loess Ore washings Shale* Slag Staurolite	Anhydrite Calcium sulfate Gypsum*

*Most common sources

Two equally important parameters that must be achieved during the formulation of a raw mix are its burnability and composition. The raw feed must be able to produce an appropriate free lime content under reasonable burning temperatures and time frame (Miller 2004). The chemical composition must also be carefully controlled in order to insure that performance of the cement is adequate. These two parameters are simultaneously controlled by factors such as the C_3S content or the lime saturation factor (LSF), the silica ratio, and the C_3A content or A/F ratio.

According to Miller (2004), about 67% of clinker by mass is composed of lime. It is for this reason that cement production facilities are typically built near large limestone deposits in order to minimize transportation costs of this material. The source of the limestone dictates its composition and thus its contribution to the raw mixture. For example, pure calcium carbonate is added in small amounts while other materials constitute the remainder of the final blend. On the other hand, a lower calcium content limestone known as "cement rock" has a composition that allows it to represent the majority of the raw mix. In-between these two extremes, an intermediate limestone will comprise roughly 80% of the raw mixture. Four different limestone sources arranged according to their CaO content are shown in Table 3-3.

As seen from Table 3-3, the silica ratio also is dependent on the source of limestone. The silica ratio, or silica modulus, is the ratio of silica content to the sum of the contents of alumina and iron. Miller (2004) reported that a silica ratio of 2.62 produces a raw feed with acceptable burnabilty and high-quality clinker. The silica content of the raw mixture must be adjusted by secondary raw materials. Materials such as clay, shale, and fly ash are argillaceous and contribute silica, alumina, and to a lesser extent iron. Lastly, to "fine tune" raw mixtures, corrective materials such as iron ore, bauxite, and sand are used because essentially only one element (iron, alumina, or silica respectively) is dominant.

Table 3-3: Typical Limestone Compositions (Miller 2004)

Elements, as oxides	**Pure Limestone** (mass %)	**Intermediate Limestone** (mass %)	**Siliceous Limestone** (mass %)	**Cement Rock** (mass %)
SiO_2	0.25	6.83	9.05	13.19
Al_2O_3	0.15	2.67	1.03	4.87
Fe_2O_3	0.13	1.14	0.42	1.75
CaO	55.31	48.83	48.83	41.96
MgO	0.40	0.70	0.85	2.00
SO_3	0.02	0.58	0.52	0.83
Na_2O	0.03	0.09	0.11	0.36
K_2O	0.04	0.30	0.35	0.78
Loss on Ignition	43.66	38.85	38.76	34.20
Silica Ratio, S/R	0.89	1.78	6.24	1.99

Once the raw materials are selected and proportioned, grinding and blending occurs prior to kiln entry. Similar to the chemical composition, the burnabilty of the raw feed is also dependant on grinding each material to its optimum fineness (Miller 2004). Raw material that is burned at an appropriate fineness reduces energy costs by using less fuel than a courser fineness (Jackson 1998). Once the appropriate fineness has been obtained, the raw materials are mixed together to form a homogeneous mixture with the predetermined chemical composition (Chatterjee 2004).

The limestone in the kiln feed, on entering zones of higher temperatures in the preheater and kiln, undergoes a process known as calcination. The limestone ($CaCO_3$), is broken down to calcium carbonate (CaO) and carbon dioxide (CO_2). The cement industry has taken measures to reduce CO_2 emissions in order to limit the harmful effects this greenhouse gas has on the environment. Withholding a portion of limestone until the clinker is ground is a typical method to limit carbon dioxide emissions, although the increased CO_2 content of the cement typically alters its primary compounds (Hendrik and Padovani 2003).

3.3.2 Pyroprocessing

Once the raw material is proportioned and ground to the appropriate fineness, the material is heated in a process known as pyroprocessing, which causes chemical and physical changes in the raw materials. The exposure to heat fuses the raw material into a single product known as clinker. Factors such as raw material composition, mineralogical composition, and time and temperature profiles of the material in the kiln all contribute to the complicated endothermic and exothermic reactions that dictate the final performance of the cement (Manias 2004).

Wet and dry kiln systems are the two processing systems used to produce cement. In the 20th century, cement production was dominated by the wet process. However, around the 1970's, as fuel costs rose, the need for a more fuel efficient system sparked the move toward wide spread use of dry kilns. Wet process kilns are less efficient compared to dry process kilns due to the raw feed entering the kiln is in a slurry form requiring additional fuel to drive off moisture prior to combustion. Another disadvantage is that wet process kilns are not capable of the same production levels as dry kilns because of mechanical limitations on equipment size (Manais 2004). For example, a large wet process kiln can produce roughly 1,500 tons per day (tpd) where as a modern, dry process systems exceed 10,000 tpd. Over the years technological innovations have lead to multiple configurations of wet and dry process kiln systems, but all fall into one of the two categories.

Figure 3-2 shows the gas and material temperatures as well as their respective retention times during the pyroporcess. The kiln slope and rotational speed determines the rate raw materials pass through the kiln (Kosmatka et al. 2002). The raw materials enter at the upper end of the kiln and are moved towards the heat source at the lower end by the kiln's rotation. As mentioned earlier, at the point of entry into the kiln, the raw material has already been heated to approximately 850 °C and nearly completed the calcination process (Jackson 1998). The kiln system performs the following material transformations on the raw material starting from the feed end (Manias 2004):

1.	Evaporating free water, at temperatures up to	100 °C
2.	Removal of adsorbed water in clay materials	100 °C – 300 °C
3.	Removal of chemically bound water	450 °C – 900 °C
4.	Calcination of carbonate materials	700 °C – 850 °C
5.	Formation of C_2S, aluminates, and ferrites	800 °C – 1250 °C
6.	Formation of liquid phase melt	>1250 °C
7.	Formation of C_3S	1330 °C – 1450 °C
8.	Cooling of clinker to solidify liquid phase	1300 °C – 1240 °C
9.	Final clinker microstructure frozen in clinker	>1200 °C
10.	Clinker cooled in cooler	1250 °C – 100 °C

During this process, the calcium and other components of the raw mix, combine to form the four major clinker phases: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracacium aluminoferrite (C_4AF) which are commonly referred to as the Bouge compounds (Tennis and Kosmatka 2004). These compounds are often referred to as alite (C_3S), belite (C_2S), aluminate (C_3A), and ferrite (C_4AF). The Bouge compounds typically comprise 90% of cement by mass with calcium sulfate dihydrite, or gypsum filling the remainder (Tennis and Kosmatka 2004).

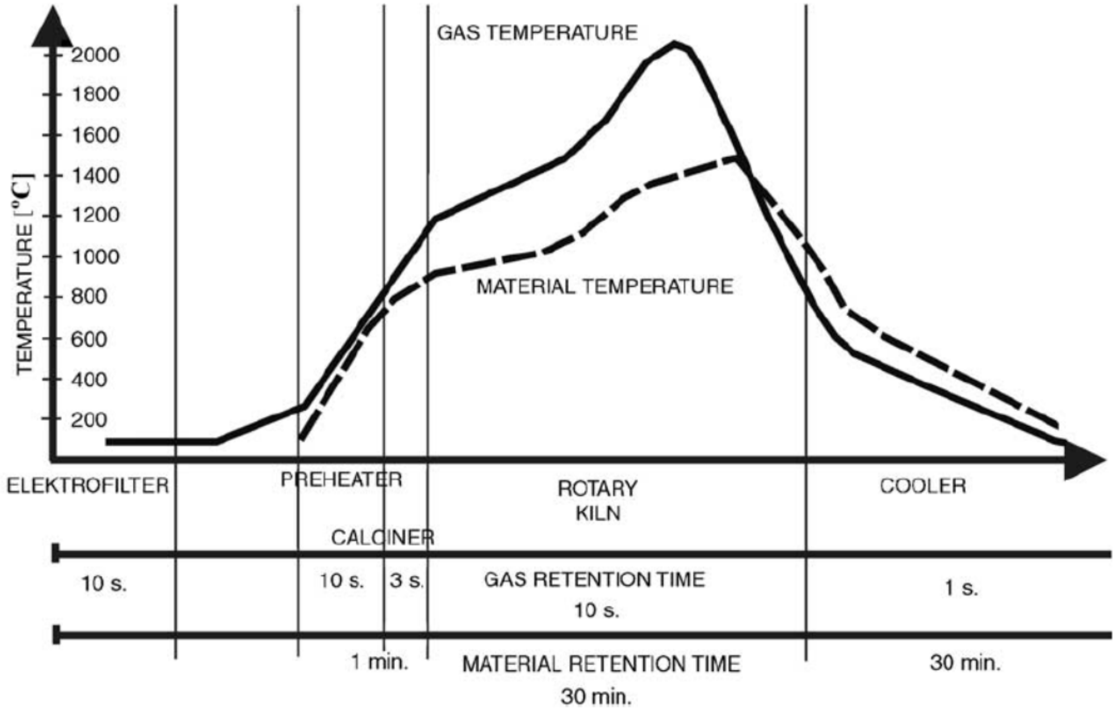

Figure 3-2: Gas and Material Temperature Inside a Typical Cement Kiln (Mokrzycki and Uliasz-Bocheńczyk 2003)

3.3.3 Clinker Cooling

As the newly clinkered material exits the kiln, it enters the clinker cooler. According to Steuch (2004) the most popular cooler in the U.S is the grate cooler, shown in Figure 3-3. Grate coolers are comprised of several perforated, slightly inclined grates that transport the hot bed of clinker across a series of fans that remove heat from the clinker by forcing air up through the bottom of the grates (Jackson 1998).

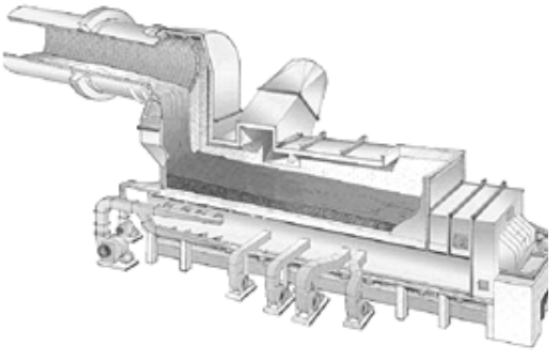

Figure 3-3: Grate Cooler for Cooling Clinker (Network Solutions 2010)

The rate of clinker cooling is just as important as the rate of heating. Jackson (1998) reported that slowly cooling clinker often cause alite to partially transform into belite and free lime, which negatively effects setting and strength properties. Slow cooling also contributes to the formation of large alite and belite crystals that produces a courser, less reactive cement (Manias 2004). By quickly cooling the clinker, the optimal phase composition is secured which results in adequate cementitious properties (Steuch 2004; Jackson 1998).

Another function of the clinker cooler is to recycle the heat extracted from the clinker back into the kiln system. In a modern kiln system, heat extracted from the clinker cooler supplies roughly 20% of the total heat input to the burning zone and 25% of the total heat input to the calciner (Young and Miller 2004).

3.3.4 Grinding and Finishing

The clinker, once cooled, is stored in silos until it is ready for the final step in manufacturing cement: grinding. The finishing mill system reduces the clinker from several centimeters in diameter to a maximum of 100 μm ensuring consistent chemistry throughout (Strohman 2004). Consequently, approximately 30-40% of the total electrical power used for cement production is used in the finishing process. Depending on how the clinker was burned, its chemical composition, and how it was cooled determines the relative ease at which the clinker will grind (Strohman 2004).

The ball mill is the most common type of finishing system, although some facilities utilize roller mills, roller presses, or a combination of these types (Strohman 2004). A ball mill consists of a cylindrical tube that rotates about a horizontal axis. Within the tube several slotted diaphragms separate various sizes of steel balls used to crush the clinker. The cooled clinker enters the initial compartment of the mill and is broken down by large steel balls (90-100 mm). Once small enough, the clinker particles pass through the slotted diaphragm where they are broken down further by smaller balls (13-60 mm) until the required fineness is achieved (Jackson 1998). The finished product's performance is determined partially by the clinker's final gradation.

Calcium sulfate or gypsum is blended with the ground clinker in amounts typically between 3 and 8 percent to retard the formation of aluminate. This temporarily controls the rate of setting and optimizes the strength giving properties of the calcium silicates (Jackson 1998). Without the addition of sulfate, C_3A rapidly forms hydration products leading to accelerated setting times and rendering it insufficient for construction use.

After the gypsum is ground with the clinker, the finished product is portland cement. In order to maintain quality, cement facilities continuously sample the finished product. Parameters such as the Bogue compounds, silica modulus, lime saturation factor, free lime, and sulfate contents are examined to ensure the cement possesses all its intended properties. If the final chemistry is not sufficient, secondary materials are added in order to fix the inadequacies. The finished cement is then ready to be packaged, sold, and shipped to consumers.

3.4 USE OF ALTERNATIVE FUELS IN PORTLAND CEMENT PRODUCTION

Traditionally, cement plants have relied on natural fossil fuels to power the pyroprocessing of raw materials. These fuels include coal, natural gas, and petroleum coke (pet coke). Due to the rising costs of fuels and the fact that up to 40% of a cement facility's budget is fuel costs, manufacturers seek fuels that optimize costs and product quality and minimize environmental impact (Jackson 1998; Greco et al. 2004). Since the 1970's, waste fuels have been utilized by the cement industry for partial replacement of traditional fuels (Karstensen 2004). Today, these waste fuels account for 20-70 % of the total energy demands at a cement facility (PCA 2009). It should be noted that the terms "alternative" and "waste" with respect to fuels are used interchangeably. Although the use of alternative fuels brings many benefits, their overall effects on the manufacturing process, performance of the cement, and environmental impact must be studied before the fuel is routinely utilized.

Coal is the most predominately used fossil fuel in the cement industry. Ancient records date the use of coal back to the Roman Empire and today it is responsible for almost a quarter of the world's energy demands (Greco et al. 2004). In the cement industry, up to 150 kg of coal is needed to produce 1 ton of cement (Mokrzycki and Uliasz-Bocheńczyk 2003). Therefore a kiln capable of producing 10,000 tpd, requires 1,600 tons of coal per day (Manias 2004). With this level of consumption and the fact that the cost of coal has nearly tripled in the past decade, cement manufactures are influenced to research and implement cheaper alternatives to reduce production costs (Shafiee and Topal 2010).

A fuel is any substance that in the presence of an initial "energetic impulse" and oxygen initiates an oxidizing chemical reaction that is rapid, self-sustainable, and exothermic (Greco et al. 2004). Many typical alternative fuels categorized by their origin are shown in Figure 3-4. Lechtenberg (2009) reported that four basic principles for the use of alternative fuels in cement production are as follows:

1. The chemical quality of the fuel has to meet regulatory standards to ensure environmental protection.
2. The calorific quality of the fuel must be stable enough to allow a controlled supply of energy to the kiln to produce homogeneous clinker.
3. The physical form of the fuel has to permit easy handling for transportation and controlled flow into the kiln.
4. The fuels must not introduce any chemical compounds into the clinker that might be deleterious to the stability of the production process or the performance of the product.

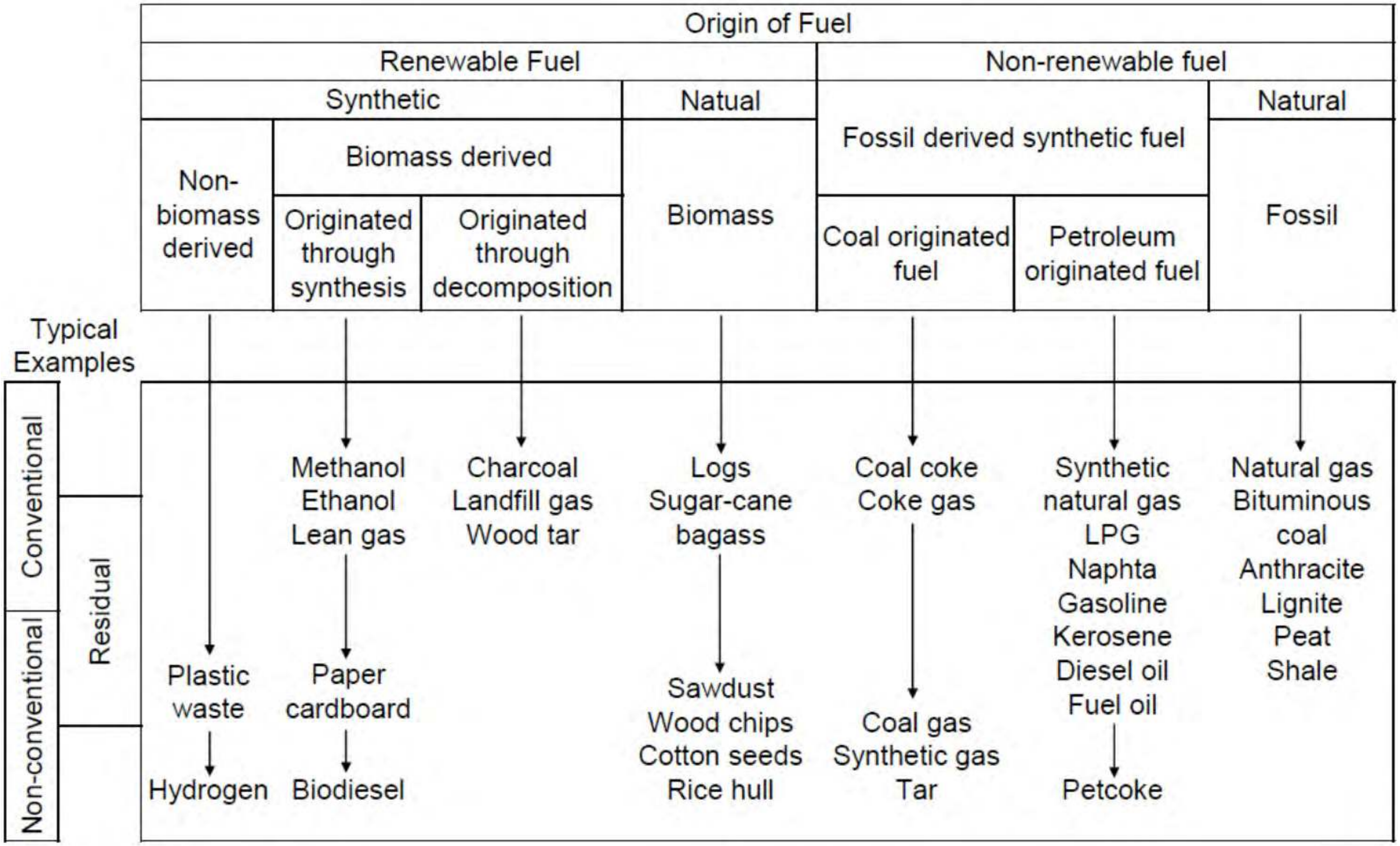

Figure 3-4: Various Fuels and Their Origin (Adapted from Greco et al. 2004)

Alternative fuels are divided into three distinct categories: solid, liquid, and gaseous fuels (Greco et al. 2004; Mokrzycki et al. 2003). Examples of each type of waste fuel commonly used are shown in Table 3-4. Each category requires specific plant modifications in order to condition, dose, and fire the alternative fuel. Replacement levels for alternative fuels vary according to physical and chemical properties and are governed differently from country to country. For example, Conesa et al. (2007) reported, Switzerland has no replacement limit while Spain is limited to 15%. However, appropriate waste fuels could represent 80 to 100 % of fossil fuel replacement according to Willitsch and Strum (2002).

The implementation of waste fuels in the cement industry resulted from diminishing resources and increased fuel costs. The effects are reduced production costs, which create a competitive edge against other cement manufacturers and a decreased environmental impact.

3.4.1 Alternative Fuels in Cement Kilns

To adequately burn waste material, sufficient oxygen and temperature must be supplied as well as retention time, and proper mixing conditions (Karstensen 2008). Greco et al. (2004) reported the following kiln characteristics that render a sufficient environment for waste disposal:

1. The residence time and the temperature exceed minimum environmental regulations,
2. During the firing process, the alkaline environment inside the kiln absorbs the majority of acid gasses produced by the oxidation of sulfur and chlorine,
3. Non-combustible compounds and other metallic oxides do not harm the production or quality of clinker, and
4. The dusting system traps and recycles most other metals.

As stated earlier, it is important to fully understand the chemical composition of a waste material before use. Excess compounds such as sulfur and nitrogen oxides can cause kiln rings and build ups that lead to kiln shutdowns. In addition, extra quality assurance measures should be taken to ensure complete combustion of material and parameter control (Greco et al. 2004). Lastly, emissions must also be carefully monitored due to costly fines completely negating the cost savings of the alternative fuel.

Table 3-4: Typical Waste Fired in Cement Kilns (Adapted from Greco et al. 2004)

Gaseous waste	Landfill gas
Liquid waste	Cleansing solvents
	Paint sludges
	Solvent contaminated waters
	“Slope”– residual washing liquid from oil and oil products storage tanks
	Used cutting and machining oils
	Waste solvents from chemical industry
Solid waste	Farming residues (rice husk, peanut husk, etc.)
	Municipal waste
	Plastic shavings
	Residual sludge from pulp and paper production
	Rubber shavings
	Sawdust and woodchips
	Sewage treatment plant sludge
	Tannery waste
	Tars and bitumens
	Used catalyst
	Used tires

3.4.2 Advantages of Alternative Fuels

There are multiple environmental advantages of substituting alternative fuels in the cement industry. Four simultaneous gains are as follows (Greco et al. 2004):

1. Reduction of production costs,
2. Preservation of fossil fuel reserves,
3. Reduction in the volume of waste disposed through landfill and incineration, and
4. Reduction of green house gasses.

In recent years, the cost of fuel and electricity has increased dramatically. As a result, production costs of cement have also soared. Fossil fuel prices from 1950 to 2008 are shown in Figure 3-5. From this figure one can see that coal prices nearly doubled from 2006 to 2008. In 2011, coal prices exceeded $200 per short ton (McCrae 2011). In an effort to offset these increases, manufacturers employ waste fuels because their cost per unit energy is far below that of fossil fuels (Greco et al. 2004). According to Hendrik and Padovani (2003), some cement plants in the United States are even paid to take waste, which in some cases completely offsets the conventional fuel costs.

Coal, natural gas, and petroleum coke are the predominate fossil fuels used to produce cement. The conservation of fossil fuels is important because they are non-renewable resources. At the present world consumption level, coal reserves will last approximately 119 more years (WCA 2011). Although coal and other fossil fuels are extensively used in the production of cement, electricity and steel, the use of waste fuels reduces the ecological footprint made by the cement industry.

As the world's population continues to grow, landfill space is becoming scarce. Waste incineration is a typical method used to free landfill space. Waste incinerators use large quantities of fossil fuels to reach temperatures of at least 850 °C in order to break down materials. The drawback to waste incinerators is that no product, such as portland cement, is formed from the use of fuel. Waste incineration also produces higher emissions than cement kilns. The material breakdown in a cement kiln is much more complete because of the significantly higher temperatures and the longer residence times. Incidentally, Mokrzycki and Bocheńczyk (2003) point out that it is cheaper to modify an existing kiln to burn waste fuels than it is to build a new incineration plant.

Greenhouse gasses are produced through the firing of raw materials and fuels. Carbon dioxide is one of these gasses that has come to the forefront due to its negative impact on the environment. Carbon dioxide is formed during the production of electricity, calcination of lime, and combustion of carbon-based fuels (Worrell et al. 2001). Green house gasses are of concern because they trap radiation within the atmosphere. Worrell et al. (2001) reported that the use of waste fuels may reduce the carbon dioxide emissions by 0.1 to 0.5 kg/kg of cement compared to traditional fuel emissions.

Alternative fuels can also supplement raw materials in cement production. Jackson (1998) reported that rice husk ash significantly reduces the required additions of silica in the raw feed because of its high silica content (78-90 %). Kääntee et al. (2002) also reported that iron found in the steel belts of automobile tires reduces the required iron in the raw feed.

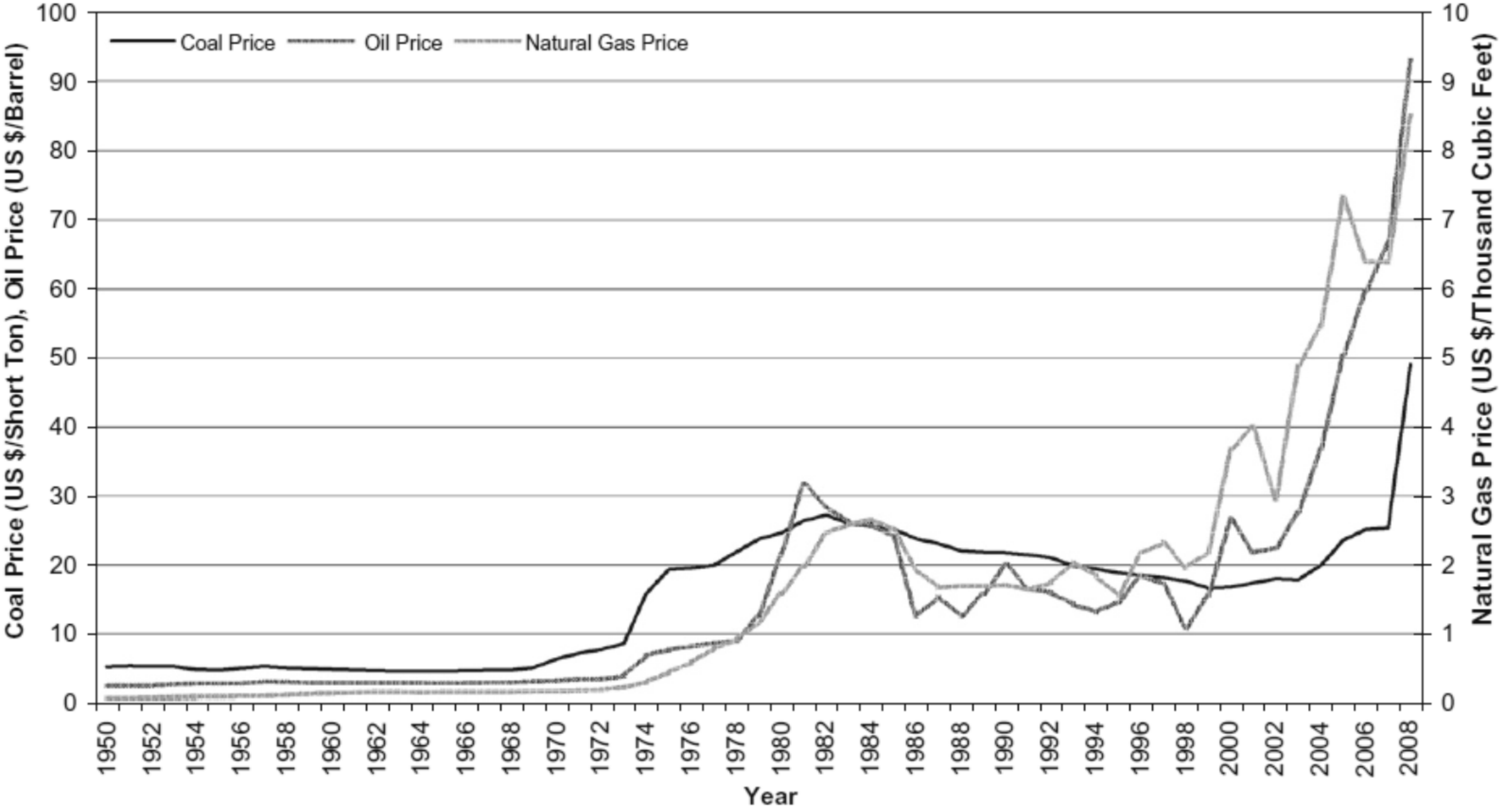

Figure 3-5: Average Yearly Trend of Fossil Fuel Prices (Shafiee and Topal 2010)

3.4.3 Disadvantages of Alternative Fuels

Many factors such as increased emissions, altered clinker composition, and initial investment costs must be considered prior to the implementation of waste fuels. The effects of the disadvantages, if not addressed, can negate all other advantages.

The availability and cost often determines the viability of an alternative fuel (Kääntee et al. 2002). Preliminary conditioning of waste materials such as shredding, drying, and removal of detrimental contents is typically outsourced, but is critical before use and imposes a significant cost to the producer (Greco et al. 2004). The final condition of the waste material determines its energy output and replacement rate. Purchasing and installing mechanical equipment specifically designed to condition, convey, and dose the waste fuel are not only cost intensive, but if the waste material source is depleted or becomes unavailable, the need for the equipment also may become obsolete.

Metering and feeding systems must be installed to covey the waste fuel to the kiln. Although the prices vary according to capacity and precision, state of the art storage, metering, and feeding systems require large initial investments upwards of several million dollars (Lechtenberg 2009). The cost of training personnel to operate the continuous feed systems should also be considered (Willitsch and Strum 2002). The difficulty surrounding the ability to accurately monitor heterogeneous mixtures with varying densities was also noted by Willitsch and Srum (2002).

According to Hendrik and Padovani (2003), waste fuels can induce or increase kiln emissions. Chemical composition of the cement can also be altered by waste fuels. Waste fuels with high chloride concentrations can lead to the formation of sodium and potassium chloride gasses in the kiln and calcium chloride in the clinker. Updates to emission control systems as well as quality control systems may be necessary to ensure emissions remain within limits and the performance of the clinker is no altered. Buildup of chloride gasses in the kiln can also cause blockages in the cyclone pipes and therefore kiln shutdowns (Lechtenberg 2009). Unnecessary kiln shutdowns reduce production rates and are an avoidable loss of revenue.

3.4.4 Alternative Fuel Options

Examples of typical waste fuels and their origins were shown earlier in Table 3-4 and Figure 3-4. These fuels are readily accessible to most geographic locations. Not only must the fuel release large amounts of energy when burnt, but there are a number of other characteristics that the fuel must possess in order to be considered for implementation. In order to validate a waste fuel's potential, the following factors should be considered (Mokrzycki and Uliasz-Bocheńczyk (2003):

1. Physical state of fuel (solid, liquid, gaseous),
2. Content of circulating elements (Na, K, Cl, S),
3. Toxicity (organic compounds, heavy metals),
4. Composition and ash content,
5. Volatile content,
6. Calorific, or heating value,
7. Physical properties (particle size, density, homogeneity), and
8. Moisture Content.

The replacement rate of a fuel is determined by a combination of the parameters listed above and is the reason why knowledge of the fuel's chemical composition is essential (Kääntee et al. 2002). For example, it would not be beneficial or make sense to replace a traditional fuel with an alternate, if the alternative fuel's low heating value requires excessive replacement rates. Although minimum requirements for a waste fuel differ among cement facilities, an example of criteria used by the Lafarge Cement Polska group is shown below (Mokrzycki et al. 2003):

- Heating Value > 6019 BTU/lb (weekly average)
- Chlorine content < 0.2%
- Sulfur content < 2.5%
- Polychlorinated Biphenyls (PCBs) content < 50ppm, and
- Heavy metals content < 2500 ppm, out of which:
  - Hg < 10ppm
  - Cd + Tl + Hg < 100ppm

The heating value, expressed in British Thermal Units (BTU), or calorific value, expressed in calories (cal), is the energy output upon combustion and is a key parameter in determining the viability of a fuel. The conditioning of the waste material before combustion also has a dramatic impact on the performance of the fuel. Material with a high moisture content will release less net energy than a material with a lower moisture content. This is due to extra fuel being required to remove the moisture before combustion. The approximate energy values of typical alternative fuels is shown in Table 3-5. Note the significant difference in energy values between the As-Received and Dry columns. The As-Received energy value is the energy value associated with the fuels natural moisture content.

The alternative fuels utilized in this study include construction and demolition waste, woodchips, and soybean seeds. A brief description of their historical use as alternative fuels will be discussed in the following sections. A comprehensive discussion of other alternative fuels utilized in previous studies is available, but will not be discussed further here.

Table 3-5: Approximate Energy Values of Typical Alternative Fuels (Adapted from Lechtenberg 2009)

Alternative Fuel	**Approximate Energy Value**	
	As-Received BTU/lb (kca/kg)	**Dry** BTU/lb (kca/kg)
Wood	2700 (1500)	6300 (3500)
Cattle dung	1800 (1000)	6700 (3700)
Bagasse	4000 (2200)	7900 (4400)
Wheat and rice straw	4300 (2400)	4500 (2500)
Cane trash, rice husk, leaves, and vegetable waste	5400 (3000)	5400 (3000)
Coconut husks, dry grass and crop residues	6300 (3500)	6300 (3500)
Groundnut shells	7200 (4000)	7200 (4000)
Coffee and oil palm husks	7600 (4200)	7600 (4200)
Cotton husk	7900 (4400)	7900 (4400)
Refused derived fuels from municipal solid wastes	7200 (4000)	8100 (4500)

3.4.4.1 Plastic Solid Waste (PSW) as Fuel

In 2009, just over 12% of the total municipal solid waste generated in the U.S. (243 million tons) were plastics. Global plastic production in 2007 was estimated to be 260 million tons, which is over three times that produced in 1990 (Al-Salem et al. 2010). Siddique et al. (2008) reported that approximately 8% of plastic solid waste is incinerated and 7% is recycled leaving the 85% remainder to be landfilled. Low density polyethylene (LDPE) represents the largest contributor to PSW. Typical sources of PSW include packaging, industrial, and healthcare applications, and many other uses.

In order of free landfill space, multiple recovery methods have been developed. Re-extrusion, mechanical, chemical, and energy recovery are four categories that recycle these materials for productive application. The use of plastics for the manufacture of cement falls under the energy recovery category.

Before solid wastes enter the combustion chamber, the material must be conditioned (Greco et al. 2004). Drying, shredding, and mixing the material are examples of conditioning. It is also necessary to separate incombustible substances such as metals and glass, as well as any materials with organic impurities (Willitsch and Sturm 2002). An optimal moisture content of 0.5 - 2.0 % and maximum edge length of 10 *mm* produce the most desirable results (Greco et al. 2004; Willitsch and Sturm 2002). Feeding systems are also needed to transport the solid material from the storage facility to the preheating tower. The material is typically transported by the use of conveyor belts and injected into the combustion chamber by compressed air. It is also common that plastic solid waste be comprised from multiple sources to create an optimum blend (Greco et al. 2004). A comparison of coal and polyethylene is shown in Table 3-6.

As can be seen in Table 3-6, polyethylene contains significantly more volatile matter than coal. This could adversely affect kiln functionality, emissions, and the replacement rate utilized. The heating value shown represents pure polyethylene, not a PSW blend. Al-Salem et al. (2010) reported that the heating value typical of a PSW blend would be roughly 14,000 BTU/lb.

Table 3-6: Comparison Analysis of Coal and Polyethylene (Adapted from Al-Salem et al. 2010)

Analysis (wt. %)	Coal	Polyethylene
Volatile Matter	33.32	99.87
Ash	7.40	0.13
Fixed Carbon	59.28	–
Carbon	76.76	84.83
Hydrogen	4.70	14.08
Oxygen	8.65	–
Density (kg/m^3)	1300	920
Heating Value (BTU/lb)	11,700	19,300

The main impurities found in plastic solid wastes are chlorine, cadmium, lead, and zinc (Willitsch and Sturm 2002). Plastic solid waste has a high chlorine content with is one of the main contributors to its high volatile content. High chlorine contents are known to lead to blockages in ducts and fans, corrode kiln lining, and reduce the quality of the clinker. Sorting PSW according to chlorine content is one method of managing the chlorine content (Kikuchi et al. 2008). Another benefit of PSW is lower transportation costs. Plastic solid waste has a lesser density than coal, which reduces fuel consumption during transportation (Siddique et al. 2008).

Currently, little research exists discussing the effects that plastics have on portland cement quality and production. In an first phase of this project, two fuel scenarios were evaluated at a full scale cement plant during 3-day trial periods. The baseline burn consisted of only coal, whereas the trial burn consisted of a blend of coal, plastics and waste tires. The results of the trial were that concrete compressive strengths increased slightly, CO emissions were reduced, and NO_x, SO_2, and VOC were increased compared to the coal only burn (Swart 2007). These results, however, are not known to be directly linked to the change in fuel as conditions at the plant throughout the study were inconsistent. In the second phase of this project, Akkapeddi (2008) concluded that the tested alternative fuels could not be linked to changes in cement chemistry.

3.4.4.2 Biomass as Fuel

As the first fuel source harnessed by mankind, biomass fuels are defined as combustible materials that are the result of growing plants or raising animals (Abbas 1996). According to Cuiping et al. (2004), biomass accounts for 14 percent of the world's energy consumption and is used as a primary energy source by more than half the world's population. Biomass fuels are unique with respect to fossil fuels because they are gathered from a large area and transported to a concentrated area for use whereas fossil fuels are produced from a single location (i.e., a coal mine) and dispersed over a large area for use. Typical biomass fuels include wood, rice hulls, coffee grounds, sewage sludge, and manure. Abbas (1996) reported that the energy stored in biomass through photosynthesis is almost 10 times that of the world energy consumption. Biomass fuels with moisture contents less than 10 percent are better suited for thermal energy conversion, while biomass with higher moisture contents produce better results from biochemical processes such as fermentation (Cuiping et al. 2004). Since biomass fuels have lower concentrations of nitrogen and sulfur, oxides produced during the combustion process are significantly less than emissions produced by fossil fuels (Cuiping et al. 2004). Cuiping et al. (2004) also reported that the levels of carbon dioxide produced from the combustion of biomass will not contribute to global warming. The biomass fuels utilized in this study include portions of the construction and demolition waste, wood chips, and soy beans. The following are typical traits of a biomass fuel and the reasons why they are not widely used as reported by Abbas (1996):

1. Has compositional variability similar to coal,
2. Has a lower calorific content than coal – one-half by mass and one-fifth by volume,
3. Contains many of the same potential pollutants (sulfur, nitrogen, chlorine, etc.) found in coal, although in lower concentrations,
4. Expensive storage costs associated with providing a constant supply due to seasonal availability, and
5. Raising crops for energy purposes instead of food production creates a moral dilemma.

Woodchips are solid fuels made from woody biomass and are a byproduct of the timber industry. Woodchips are typically made from waste wood, saplings, and logging operations. Because it is a renewable energy source and locally available, woodchips are one of the least expensive fuels (Maker 2004). In Table 3-7 woodchip fuel costs are compared to coal, as reported by Maker (2004). Although conventional fuel system require less capital initially than a woodchip system, the substantial cost savings from using woodchips pays for the initial costs in a time period significantly less than the life of the system.

Table 3-7: Comparative Fuel Cost for Woodchips (Adapted from Maker 2004)

Fuel	Fuel price range per ton	Gross fuel cost per MBTU	Net cost per MBTU
Coal	\$100 - \$150	\$4.00 - \$6.00	\$5.70 - \$8.55
Woodchips	\$20 - \$34	\$2.00 - \$3.45	\$3.10 - \$5.30

Note: MBTU – 1 Million BTUs

There are not significant amounts of literature available on the use of woodchips as fuel in cement production. Therefore, only the characteristics and chemical compositions will be discussed in this section.

Much like PSW, woodchips must be conditioned before use. Shredding woodchips to an optimal particle size of 6 mm is a cost intensive process. This conditioning, however, is required to achieve the most efficient feeding and combustion characteristics for the woodchips (Willitsch and Sturm 2002). Another cost associated with biofuel is storage. Proper storage is necessary to minimize smell, bacterial growth, and heat development. Controlling the moisture content is also critical due to lower heating values and inefficient combustion resulting from higher moisture contents.

As stated above, the heating value of woodchips depends heavily on its moisture content. The species of wood also determines the heating value. Maker (2004) reported that the average dry value of a woodchip stream was roughly 8,500 BTUs/lb. Typical dry-sample heating values from certain wood species are shown in Table 3-8.

Table 3-8: Dry Sample Heating Values for Woodchips (Adapted from Maker 2004)

Species	Heating Value		
	Average	Low	High
Hardwoods			
Ash, white	8583	8246	8920
Birch, White	8335	8019	8650
Elm	8491	8171	8810
Hickory	8355	8039	8670
Maple	8288	7995	8580
Oak, red	8364	8037	8690
Oak, white	8490	8169	8810
Poplar	8616	8311	8920
Softwoods			
Cedar, white	8090	7780	8400
Hemlock, eastern	8885	NR	NR
Pine, white	8603	8306	8900

Note: NR -- Not Reported

Dry sample heating values are achieved in a laboratory setting and do not represent actual heating values. Table 3-9 shows the effect that increasing moisture content has on gross heating values. Since this moisture content of wood usually falls between 35 – 40 %, a heating value of 5,100 BTUs/lb is a typical figure for woodchip fuel. In an earlier phase of this project, Akkapeddi (2008) conducted a trial burn that utilized coal, tires, and woodchips. The average moisture content and heating value of the wood specimens tested were 36.5 % and 8,388 BTU/lb., respectively.

Table 3-9: Heating Values for Woodchips Corresponding to Moisture Content (Adapted from Maker 2004)

Species	**Heating Value**		
	Average	**Low**	**High**
Hardwoods			
Ash, white	8583	8246	8920
Birch, White	8335	8019	8650
Elm	8491	8171	8810
Hickory	8355	8039	8670
Maple	8288	7995	8580
Oak, red	8364	8037	8690
Oak, white	8490	8169	8810
Poplar	8616	8311	8920
Softwoods			
Cedar, white	8090	7780	8400
Hemlock, eastern	8885	NR	NR
Pine, white	8603	8306	8900

Note: NR -- Not Reported

A dry chemical analysis of woodchips performed by Teislev (2002) produced the following results: Carbon 50.00%, Hydrogen 6.17%, Oxygen 42.64%, Nitrogen 0.17%, and ash 1.00%. The high amounts of volatiles and low ash content produce favorable results in a kiln atmosphere. The low ash content has minimal effects on the quality of the clinker produced. Woodchips produce NO_x, CO, and VOC emissions during combustion that are comparable to fossil fuels (Maker 2004). Sulfur emissions, however, are basically nonexistent due to woodchip's low sulfur content.

During an earlier phase of this study, a fuel blend of coal, waste tires, and woodchips, was evaluated at a full-scale cement plant during a 3-day trial period. Results were compared to a control condition utilizing only coal and waste tires. According to Akkapeddi (2008), the trial containing woodchips showed an increase in NOx and VOC emissions but a reduction in SO_2 and

CO when compared to the control trial. In addition, cement produced from both trials were used to mix concrete. Compressive strengths were higher in the woodchips trial as compared to the control condition. Though plant conditions may have been inconsistent throughout the study, the change in fuel was thought to be of some contribution to these effects.

The EPA reported that there were 72.7 million acres of soybeans harvested in 2000, making corn and soybeans the largest grown crops in the U.S. Over 50% of the worlds soybeans are grown in the U.S. on over 350,000 farms. In 2010, soybeans accounted for 58% of the world's oilseed production (Soystats 2011). Soybeans have multiple uses including food manufacturing, anti-corrosion agents, soaps, paints, diesel fuel, and livestock feed. Since there is not much literature available for use of soybeans as fuel in the cement industry, only characteristics and chemical composition of soybeans will be discussed in this section.

As shown above in Table 3-9, the fuel's heating value is heavily dependent on its moisture content. Other parameters that are shown in Tables 3-10 to 3-12 can also impact the feasibility of a fuel. A comparison study of 21 agriculture and forestry biomass fuels in China was conducted by Cuiping et al. in 2004. The reported values in Tables 3-10 to 3-12 are the average of three specimens along with their respective standard deviations. Similar parameters for bituminous coal were also presented for comparison.

Table 3-10: Chemical Characteristics of Soybeans and Coal (Adapted from Cuiping et al. 2004)

Test	**Parameter**	**Soybeans**	**Bituminous Coal**
		Value (wt. %)	**Value (wt. %)**
Proximate Analysis	**Ash**	6.08 ± 1.10	20.08 ± 3.49
	Fixed Carbon	15.62 ± .017	49.08 ± 2.12
	Moisture	9.34 ± 1.88	2.83 ± 0.66
	Volatile Matter	68.95 ± 1.74	28.33 ± 1.89
Ultimate Analysis	**Carbon**	43.16 ± 1.13	63.78 ± 2.33
	Hydrogen	6.9 ± 0.13	3.97 ± 0.38
	Nitrogen	0.95 ± 0.28	1.13 ± 0.01
	Oxygen	44.76 ± 2.42	10.08 ± 4.66
	Sulfur	0.2 ± 0.4	0.97 ± 0.19
Heat Value (BTU/lb)		7295	14625

The proximate, ultimate, and combustion analysis of soybeans and coal are shown in **Error! Reference source not found.**Table 3-10. The ash content of bio-fuels is significantly influenced by chemical composition (Cuiping et al. 2004). Operational problems stemming from the chemical composition of the ash include slagging, fouling, sintering, and corrosion. Ash forming elements are shown in Table 3-11. From Table 3-10 it can be seen that compared to coal, soybeans contain higher proportions of hydrogen and oxygen. Cuiping et al. (2004) reported that the higher proportions of hydrogen and oxygen decrease the heating value of a fuel due to carbon – hydrogen and carbon – oxygen bonds containing less energy than carbon – carbon bonds. The significantly lower nitrogen and sulfur content of soybeans when compared to coal is also important for environmental protection. Trace elements found in soybean are presented in Table 3-12.

Table 3-11: Ash-Forming Elements (Adapted from Cuiping et al. 2004)

Ash - Forming Elements	**Soybeans**
	Value (ppm)
Al	1336 ± 1013
Si	14.66 ± 12.57
Ca	16159 ± 1181
Fe	1500 ± 899
K	9986 ± 2773
Mg	7613 ± 996
Na	161 ± 73
P	1559 ± 579

Table 3-12: Trace Elements Found in Soybeans and Coal (Adapted from Cuiping et al. 2004)

Trace Elements	**Soybeans**	**Bituminous Coal**
	Value (ppm)	**Value (ppm)**
As	0.58 ± 0.31	14.5
Ba	56.08 ± 17.78	na
Cd	0.28	0.19
Co	0.56 ± 0.31	8.5
Cr	3.41 ± 1.53	36.8
Cu	10.05 ± 1.75	27.5
Mn	68.33 ± 26.93	na
Mo	2.5 ± 0.36	na
Ni	2.48 ± 1.31	13.9
Pb	12.32 ± 7.39	20.9
Ti	80.68 ± 73.56	na
V	**4.15 ± 4.2**	**76.5**
Zn	**11.96 ± 3.85**	**na**

3.5 EMISSIONS

The cement industry follows guidelines set by local, state, and federal agencies to minimize its environmental impact (Greer et al. 2004). Harmful pollutants emitted into the atmosphere can be transferred directly to humans through air inhalation as well as indirectly through pathways such as drinking water, skin absorption, and contaminated food (Conesa et al. 2008; Schuhmacher et al. 2004). The dominate types of emissions formed during the manufacture of cement are particulate matter (PM), produced from the acquisition and preparation of raw materials, and gaseous pollutants, produced during the pyroprocess. The formation and control of particulate matter is discussed in more detail in latter sections. Jackson (1998) reported that a cement facility producing 1 million tons of cement a year will also produce approximately 1.5 billion cubic meters of gasses. These gaseous pollutants include carbon dioxide (CO_2), nitrogen and sulfur oxides (NO_x, SO_x), volatile organic compounds (VOCs), metals, and other minor pollutants (Greer et al. 2004; Schuhmacher et al. 2004). The quantity and composition of emissions for a particular cement plant are determined by a combination of the physical and chemical properties of the raw materials and fuels as well as the kiln type and configuration.

Air pollution control devices (APCD) are used to control the harmful emissions from the kiln. The most common being electrostatic precipitators (ESP), which are closely spaced, positively charged plates paired with negatively charged woven wires in between the plates. The wires ionize the stack gases, which in turn causes the dust particles in the gas to become negatively charged and stick to the plates. Periodically the plates are cleaned and the waste particles disposed of (Jackson 1998).

Using alternative fuels not only can lower emissions and free space in landfills, but some plants in the United States are reimbursed to take waste. In some cases this revenue offsets the remaining costs of the conventional fuels (Hendrik and Padovani 2003). Cement kilns incinerate waste materials more efficiently, and emit less harmful emissions while producing a final product when compared to a typical waste incinerator that has no final product, burns at a lower temperature, and uses fossils fuels merely to free landfill space. Although the economics of using an alternative fuel can be easily justified, before use, the fuel's environmental effects must also be considered along with its effect on cement quality. The following sections will discuss the primary emission components as they pertain to the scope of this project.

3.5.1 Carbon Emissions

The carbon emissions that the cement industry and environmental agencies are most concerned with are carbon monoxide (CO) and carbon dioxide (CO_2). As previously mentioned, CO_2 is the primary agent responsible for the "greenhouse effect," and is therefore monitored by environmental agencies around the world. Carbon credits are rewarded to companies that do not exceed the emission limits. These credits can be sold or traded to other companies that exceed the carbon emission limits (Lechtenberg 2009). Worrell (2001) reported that the global cement industry contributes roughly 5% to the total anthropogenic CO_2 emissions. The percentages of carbon dioxide produced by particular countries are shown in Figure 3-6.

Carbon monoxide is formed when there is incomplete combustion of carbon-rich fuels due to insufficient oxygen at the combustion site and/or the oxidation process is left incomplete due to rapid cooling (Greer et al. 2004). Carbon dioxide is unavoidable and results from the combustion of carbon rich fuel and the decarbonization of calcareous raw materials. Decarbonization or calcination is the process of heating limestone ($CaCO_3$) and converting into carbon dioxide (CO_2) and calcium oxide or lime (CaO). Decarbonization is typically carried out in the preheater, which may also be known as a precalciner. The calcium oxide (CaO), once in the kiln, becomes one of the primary components of the clinker while the CO_2 is released into the atmosphere. The amount of CO_2 produced is more dependent on the kiln conditions rather than the type of fuel being used (Worrell et al. 2001). The carbon dioxide produced from the fuel and raw materials is roughly equal. It is also accepted that for every ton of clinker produced, one ton of CO_2 is produced (Chen and Juenger 2009; Greer et al. 2004).

There are a number of ways that cement manufactures can reduce their carbon emissions. The use of fly ash and blast furnace slag are typical ways carbon emissions can be reduced. Fly ash, which is a byproduct from coal burning power plants, and blast furnace slag, a byproduct from steel production, are both calcium-bearing waste materials that can be substituted into the raw materials for natural limestone. Fly ash and blast furnace slag can replace a portion of the cement in a concrete mixture and therefore are referred to as supplementary cementitious materials (SCMs). Chen and Juenger (2009) reported that fly ash and blast furnace slag can successfully replace limestone up to 27.5% and 35.0% respectively without compromising the mechanical properties of the cement.

Carbon dioxide emissions can also be reduced with the use of alternative fuels during production. CO_2 emissions can be reduced by 0.1 to 0.5 kg per kg of cement produced by substituting waste fuels for fossil fuels (Worrell et al. 2001). Syverud (1994) reported that in 1987, a plant in Norway partially replaced coal with chipped tires. The CO, NO_x, and SO_x emissions were recorded during the 56-hour study. Reductions of up to 50% were recorded in CO emissions. The Taiheiyo Cement Group, a Japanese company, replaced 20% of raw materials and 9% of fossil fuels with industrial waste and raw materials from around the county. As a result, the carbon dioxide emissions were reduced by 14% (Taniguchi 2001).

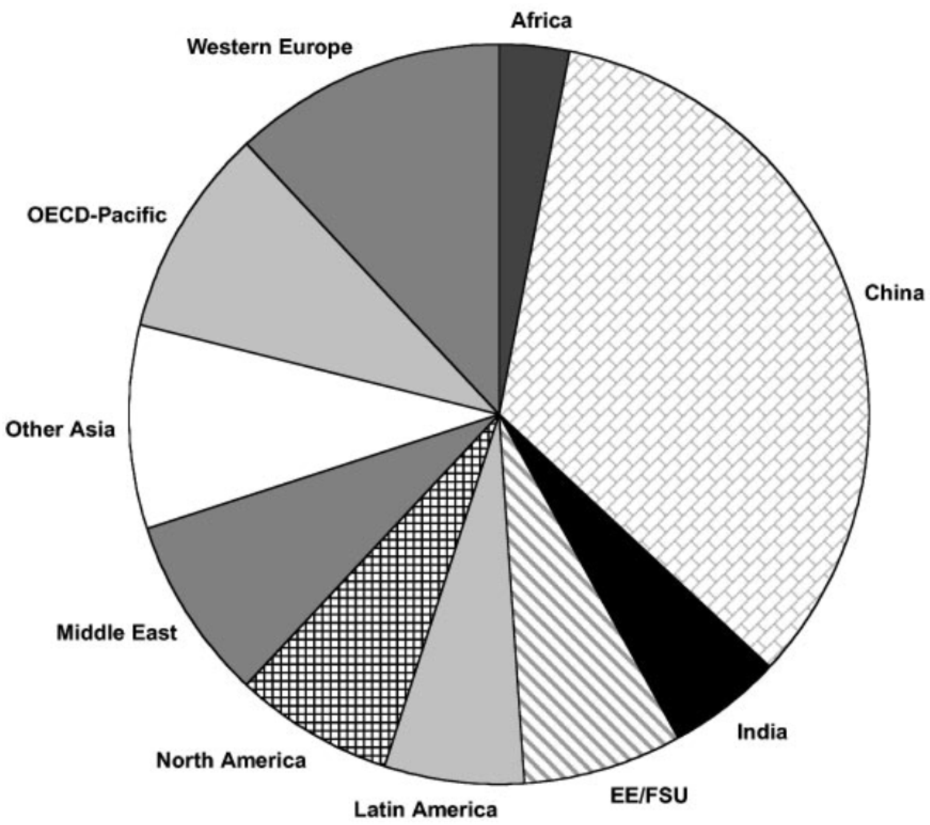

Figure 3-6: Share of Carbon Emissions from Global Cement Production
(Worrell et al. 2001)

3.5.2 Nitrogen Oxide Emissions

Nitrogen oxides (NO_x) are a family of nitrogen-based compounds that are formed through nitrogen oxidation from the combustion of fuels and raw materials in the presence of atmospheric air (Greco et al. 2004; Walters et al. 1999). Nitrogen oxide (NO) and Nitrogen dioxide (NO_2) are the two most common forms of NO_x and comprise roughly 90% and 10% of NO_x respectively (Greer 2004). Once nitrogen oxide is formed, it is quickly oxidized again to form nitrogen dioxide. Naik (2005) reported that for every ton of cement produced, 1.5 to 10 kg of NO_x is emitted into the atmosphere. The fuel type, feed rate, air flow, and kiln temperatures influence the quantity of emissions. In order to accurately document NO_x emissions, several measurements over closely spaced time intervals are needed.

Nitrogen oxides are formed through four mechanisms: thermal, fuel, feed, and prompt (Greco et al. 2004; Hendrik and Padovani 2003). Thermal NO_x makes up around 70% of the total NO_x that occurs when the atmospheric nitrogen begins to oxidize around temperatures of 1200°C. Rapid formation starts to occur at slightly hotter temperatures of 1600°C (Hendrik and Padovani 2003). Thermal NO_x forms around the main burner in the sinistering zone and the amount of thermal NO_x formed primarily depends on the amount of available oxygen.

Fuel NO_x is formed from the oxidation of nitrogen within fuels such as coal during combustion. Fuel NO_x forms at any temperature above the ignition temperature of the fuel. Due to the lower temperatures in the precalciner, the oxidation temperature of thermal NO_x has not been reached. Therefore, fuel NO_x is more prevalent at this location (Greco et al. 2004; Hendrik and Padovani 2003). On the other hand, the quantity of nitrogen is much more prevalent in the atmosphere than in fuel which means that in the sinistering zone thermal NO_x dominates. As mentioned above, the contribution of fuel NO_x is relatively small compared to thermal NO_x. However, Greer (1986) reported that if all other factors controlling NO_x formation are held constant, the total amount to NO_x can be altered by controlling the nitrogen content in the fuel.

Feed NO_x is formed when the nitrogen that is chemically attached to the feed is released and oxidized. Greco et al. (2004) reported that feed NO_x has only been generated in a laboratory by slowly heating raw materials to 300-800°C in the presence of oxygen. Older technology, such as wet and long dry kilns may exhibit an increase in feed NO_x because of the slow temperature rise of the raw material (Greco et al. 2004; Hendrik and Padovani 2003). Feed NO_x has a minimal impact on total NO_x production in the kiln due to the small quantities of the nitrogen present in the feed.

Finally, prompt NO_x refers to NO that is formed in excess of what is expected from thermal NO_x and is generated from fuel derived radicals, a fuel rich flame and elemental nitrogen (Greer et al. 2004; Hendrik and Padovani 2003). Similar to feed NO_x, prompt NO_x are considered minor contributors to total NO_x generation.

Although 70% of NO_x consist of nitrogen oxide, according to Greer (2004), the predominate "environmental evil" is nitrogen dioxide. Nitrogen dioxide creates two main problems. When nitrogen dioxide is mixed with water, nitrous acid (HNO_2) and nitric acid (HNO_3) are formed. The result of these highly corrosive acids is acid rain, which is the main contributor to building and vegetation destruction (Greco 2004). Smog, an atmospheric pollutant, is the resultant of a photochemical reaction between nitrogen dioxide, hydrocarbons, and solar radiation. On November 7, 1997, the Environmental Protection Agency instated a law requiring up to 70% reductions of mass NO_x emissions that would apply to cement plants in 22 states. An emission credit system similar to carbon emission credits was also instated (Walters et al. 1999).

The majority of NO_x produced in cement kilns comes from thermal NO_x. The use of alternative fuels cannot significantly change its concentration in either direction. Fuel NO_x, however, can be controlled by the use of fuels low in nitrogen concentrations. The study conducted by Prisciandaro et al. (2003) shows and increase in NO_x emissions in Plant 1, and a decrease in NO_x emission at Plant 2, as shown in Figure 3-7. Chipped tires were utilized to partially replace coal in the study conducted by Syverud (1994). NO_x emissions were reduced by 45%.

3.5.3 Sulfur Oxide Emissions

In cement manufacturing, sulfur oxides (SO_x) are formed from the combustion of sulfur bearing compounds in the fuels and raw materials (Hendrik and Padovani 2003). The most prevalent SO_x in the cement industry are sulfur dioxide (SO_2) and sulfur trioxide (SO_3), which begin to form at a temperature range of 300 to 600 °C (Greer et al. 2004; PCA 2009). SO_2 is more abundant than SO_3 because it forms at higher temperatures (Greco et al. 2004). Sulfur dioxide is a colorless gas with a strong odor that can be harmful to the respiratory tract of humans and damage vegetation (Greco et al. 2004; Greer 1986). Sulfur dioxide, when combined with water forms sulfuric acid (H_2SO_4) rain (Greco et al. 2004).

Although the amount of SO_x production varies from plant to plant, a large measure, more than 50 to 90% is absorbed by the kiln feed, clinker, cement kiln dust, or left in the kiln as a coating that helps preserve the brink lining (Greer 1986; Hendrik and Padovani 2003). The clinkering process removes the majority of the SO_x build up on the inside of the kiln. This is beneficial to the cement producer because less gypsum can be added later during clinker grinding. If excessive SO_x buildup accumulates on the inside of the kiln, blockages can impede material movement causing kiln shutdowns (Hendrik and Padovani 2003).

During the 56-hour trial Syverud (1994) mentioned earlier, chipped tires were used as an alternative fuel to partially replace coal. Over the 56-hour period, the SO_2 levels dropped 25%. However, the plant experienced operational problems from the rapid increase in SO_3 levels that caused build-up and the smell of sulfur in the preheater.

3.5.4 Other Problematic Emissions

Many other compounds may be created in the kiln system and emitted into the atmosphere in addition to the three predominate emission types previously discussed. There is a lack of literature directly relating alternative fuels and emissions of these compounds, so a brief discussion of their formation and potential dangers will be presented in the following sections.

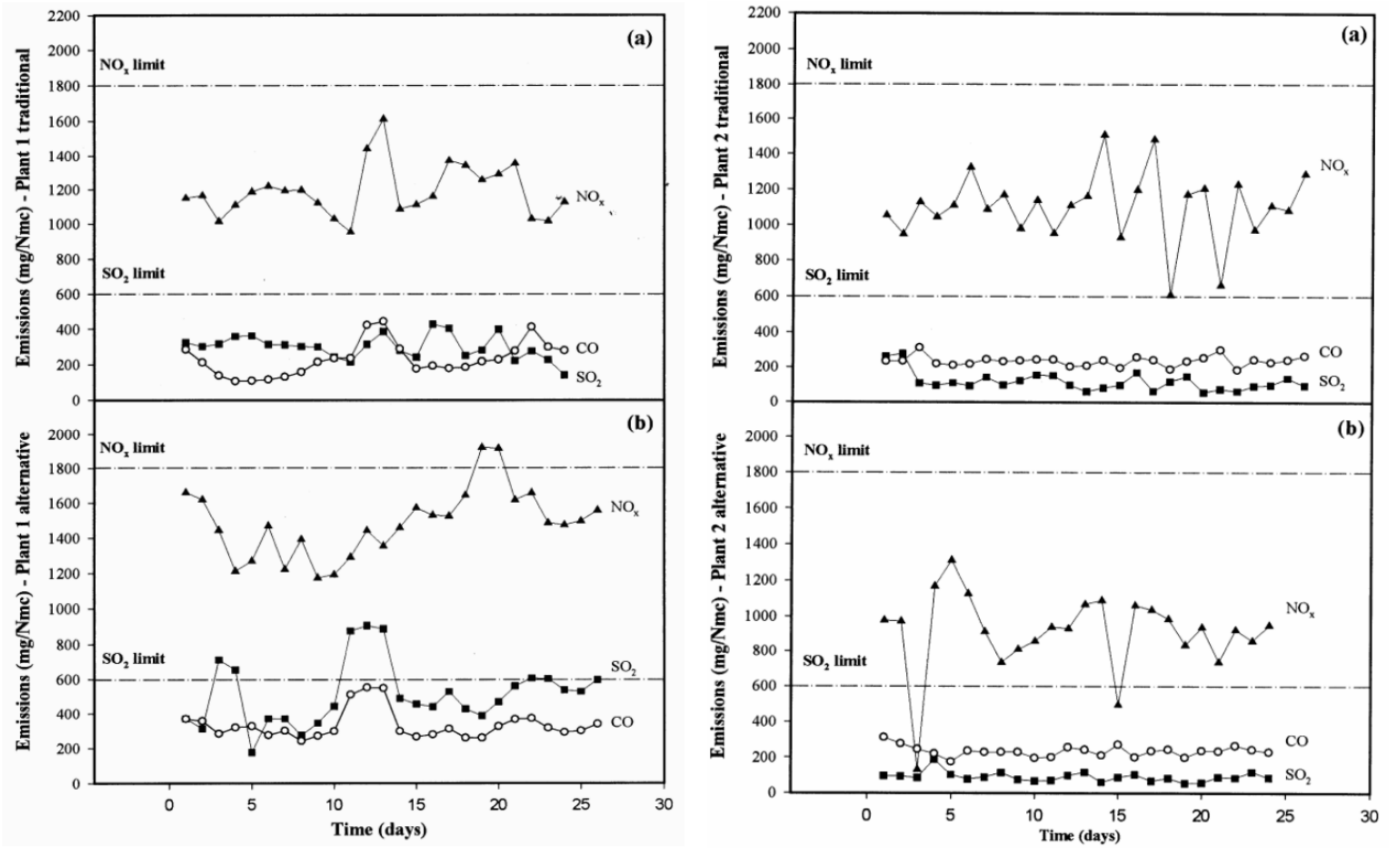

Figure 3-7: Change in Emission Levels Due to Changes in Fuel Types (Prisciandaro et al. 2003)

3.5.4.1 Dioxins and Furans

Polychlorinated dibenzodioxins (dioxins) and polychlorinated dibenzofurans (furans) are byproducts from the combustion of organic compounds mainly found in the raw materials. Dioxins and furans will be denoted PCDD and PCDF respectively hereafter. PCDD and PCDF are considered unintentional persistent organic pollutants (POPs) and measures were taken to minimize these pollutants by the Cement Sustainability Initiative (CSI) (Loo 2007). PCDD and PCDF form between 290-790°C with the latter forming at a temperature greater than 700°C (Bech and Mishulovich 2004). These temperatures concentrate the formation of PCDD/PCDF to the preheater zone and post preheater zone, which includes the particulate matter control device (PMCD). Karstensen (2008) reported that temperatures in the preheater and post preheater zones range from 850-1250°C and 250-290°C respectively. The control of PCDD/PCDF emissions is possible and can be reduced if the number of stages in the preheater is increased, thus reducing the flu gas temperature below the formation threshold of 260°C (Bech and Mishulovich 2004). According to Conesa et al. (2008) and others, the type of fuel used does not significantly impact the amount of PCDD or PCDF formed in the preheater or post preheater (Loo 2008, Karstensen 2008).

Dioxins and furans are transported to humans through the food chain as well as dermal absorption and inhalation (Kirk 2000). PCDD/PCDF are a known animal carcinogen and probable human carcinogen. Once ingested, short term effects of PCDD/PCDF can include allergic dermatitis, eye irritation, and gastrointestinal disturbances. Long term effects include liver and kidney damage and reproductive affects (Kirk 2000).

3.5.4.2 Metals

Metals are present in small concentrations in both fuels and raw materials used during the production of cement (Schuhmacher et al. 2004). Metals that are not adsorbed into the clinker are either collected by particulate matter control devices with the cement kiln dust or emitted to the atmosphere through stack emissions (Conesa et al. 2008). The toxicity of some heavy metals in stack emissions raises concern for public heath. Three classes of metals were formed to differentiate between their toxicity levels. The classes are as follows:

Class I:	Cadmium (Cd), Mercury (Hg), Titanium (Ti)
Class II:	Arsenic (As), Cobalt (Co), Nickel (Ni), Selenium (Se), Tellurium (Te)
Class III:	Lead (Pb), Cromium (Cr), Copper (Cu), Platinum (Pt), Vanadium (V), Tin (Sn), Palladium (Pd), Antimony (Sb), Manganese (Mn), Rhodium (Rh)

Class I contains the metals that are most toxic and Class III contains the least toxic. The volatility of the metals is determined by their behavior in the kiln and how they exit the kiln. The majority of the metals are carried out by the clinker, but metals such as mercury is of concern because it remains volatile, cannot be controlled by dedusting, and exits the kiln in a vaporous form (Conesa et al. 2008). Conditioning alternative fuels by removing metals that could disrupt the mechanical operation or cause environmental concerns is necessary and considered a method for reducing metallic emissions (Bhatty 2004).

3.5.4.3 Particulate Matter and Cement Kiln Dust (CKD)

Particulate matter is created throughout the entire process of cement manufacturing. Grinding, crushing, and pyroprocessing create particles that range from 1-100 μm in diameter (Richards 2004). To add perspective to size, a human hair's diameter is roughly 50 μm (Richards 2004). The dividing line between coarse and fine particles is 10 μm (PM_{10}). The former can cause respiratory problems due to the potentially toxic concentrations of metals and other compounds, while coarse particles tend not to cause health concerns and are considered merely a public nuisance (Hendrik and Padovani 2003). In 1997 the Environmental Protection Agency (EPA) revised the National Ambient Air Quality Standard to include a 50% cut point for particulate matter with diameters less than 2.5 μm ($PM_{2.5}$). The EPA deemed that particles of this size are of greater concern because they can efficiently penetrate deeply into the respiratory track (Richards 2004).

Particulate matter control device (PMCD) is any device such as a fabric filter or electrostatic precipitators (ESP) used to collect cement kiln dust (CKD). Today, these filters are quite efficient and have the ability to collect upwards of 99% of CKD (Hendrik and Padovani 2003). Since the captured CKD is nearly identical chemically to the kiln feed, rerouting it from the baghouse to the kiln reduces energy and material costs (Hendrik and Padovani 2003).

Cement kiln dust is a loosely labeled material referring to the unburned and partially burned particles from the kiln feed, clinker and interior lining of the kiln (Hendrik and Padovani 2003). The particle size and chemistry greatly vary depending on the raw materials, fuel, pyroprocessing type, and equipment layout (Hawkins et al. 2004). Cement kiln dust is typically collected by fabric filters and electrostatic precipitators (ESP) from stack emissions, alkali bypass systems and clinker coolers (Hendrik and Padovani 2003). The majority, if not 100% of CKD, is typically recycled back into the kiln feed unless the alkali or sulfur contents are excessively high. In this case, the CKD is used for other purposes that are discussed later or landfilled (Hawkins et al. 2004).

Although there is not much information on total quantities of CKD produced by cement plants, the Portland Cement Association (PCA) conducted several decade-long U.S. industry-wide surveys to follow the production and disposition of CKD. Hawkins et al. (2004) reported that the total amount of CKD disposed of from 1990 to 2000 decreased by 16% and the CKD landfilled per unit of clinker decreased from 60 kg/Mg to 32 kg/Mg while the quantity of clinker produced over the same time period increased by 55%. A generic chemical breakdown of CKD is shown in Table 3-13.

Table 3-13: Typical Composition of CKD and Portland Cement (Adapted from Greer 2004)

Constituent	CKD (%)	Ordinary Portland Cement (%)
SiO_2	11-16	22
Al_2O_3	3-6	5
Fe_2O_3	1-4	3
CaO	38-50	64
MgO	0-2	1
SO_3	4-18	3
K_2O	3-13	<1
Na_2O	0-2	<1
Cl	0-5	<0.1
Loss on ignition	5-25	1
Free-lime	1-10	2

Cement kiln dust that is not recycled back into the kiln due to high alkali or sulfate concentrations has beneficial uses in alternative applications and industries. Due to high potassium and lime concentrations' ability to counter act acidic soils, CKD is commonly used as a fertilizer. Cement kiln dust is also used for soil stabilization and consolidation for the construction of streets and highways because of lime's ability to harden when exposed to moisture. Other common uses include landfill liners, gas scrubbing, and wastewater neutralization (Hawkins 2004).

3.6 HYDRATION OF PORTLAND CEMENT

The hydration of portland cement begins once water comes in contact with cement. Through exothermic reactions, new hydration products are formed. The role of the hydration products is to glue the aggregates together. The main compounds of cement can be formed into two distinct groups: Calcium Silicates and Aluminates. The Calcium silicate group includes Tricalcium silicate (C_3S) (alite) and Dicalcium silicate (C_2S) (belite). Alite and belite are the primary cement compounds and make up 70 to 75% of cement. They begin to hydrate within an hour of adding water to the cement and are responsible for the rate of strength development (Mehta and Monteiro 2006). The aluminates include tricalcium aluminate (C_3A) and tetracalcuim aluminaferrite (C_4AF). Tricalcium aluminate and tetracalcium aluminoferrite control setting times and account for 25 to 30 percent of portland cement.

Hydration of the aluminates is immediate in the presence of water. Since the aluminates are responsible for setting, this reaction must be retarded in order for cement to be used as a construction material. Typically, gypsum, a source of sulfate, is added to slow the hydration of C_3A and allow time for placement of the concrete. Equation 3-1 shows that calcium sulfoaluminate hydrate (ettringite) is the product formed from the C_3A, water, and gypsum reaction.

$$C_3A + \text{Gypsum} + H_2O \rightarrow \text{Ettringite} + 1350 \quad \text{J/g} \qquad \text{(Eq. 3-1)}$$

Ettringite remains stable as long as sulfates are present. After several hours, all the gypsum is consumed and ettringite becomes unstable and converts into monosulfate hydrate (MSH) (Equation 2). The presence of MSH allows the hydration of C_3A to continue.

$$\text{Ettringite} + C_3A + H_2O \rightarrow \text{MSH} + 0 \quad \text{J/g} \qquad \text{(Eq. 3-2)}$$

The rate of hydration is controlled by the reactivity of the C_3A in the clinker and the availability of sulfate in the solution (Mehta and Monteiro 2006). The effects that different combinations of C_3A and sulfate have on the hydration of cement are shown in Figure 3-8.

As mentioned earlier, the calcium silicates begin to hydrate within an hour of combining water and cement. The silicate hydration equations are shown below:

$$C_3S + H_2O \rightarrow \text{C-S-H} + 3CH + 500 \quad \text{J/g} \qquad \text{(Eq. 3-3)}$$

$$C_2S + H_2O \rightarrow \text{C-S-H} + CH + 260 \quad \text{J/g} \qquad \text{(Eq. 3-4)}$$

Calcium silicate hydrate (C-S-H) and calcium hydroxide are the two reaction products formed. Because varying water cement ratios, age of hydration, and temperature alter the chemical composition of the calcium silicates, a notation is used that does not imply a fixed chemical composition (Mehta and Monteiro 2006). The microstructure of C-S-H is very strong and dense which is the reason for the adhesive properties of silicates. On the other hand, calcium hydroxide is weak and soluble. The hydroxide ions do however minimize corrosion because of a high basic pH.

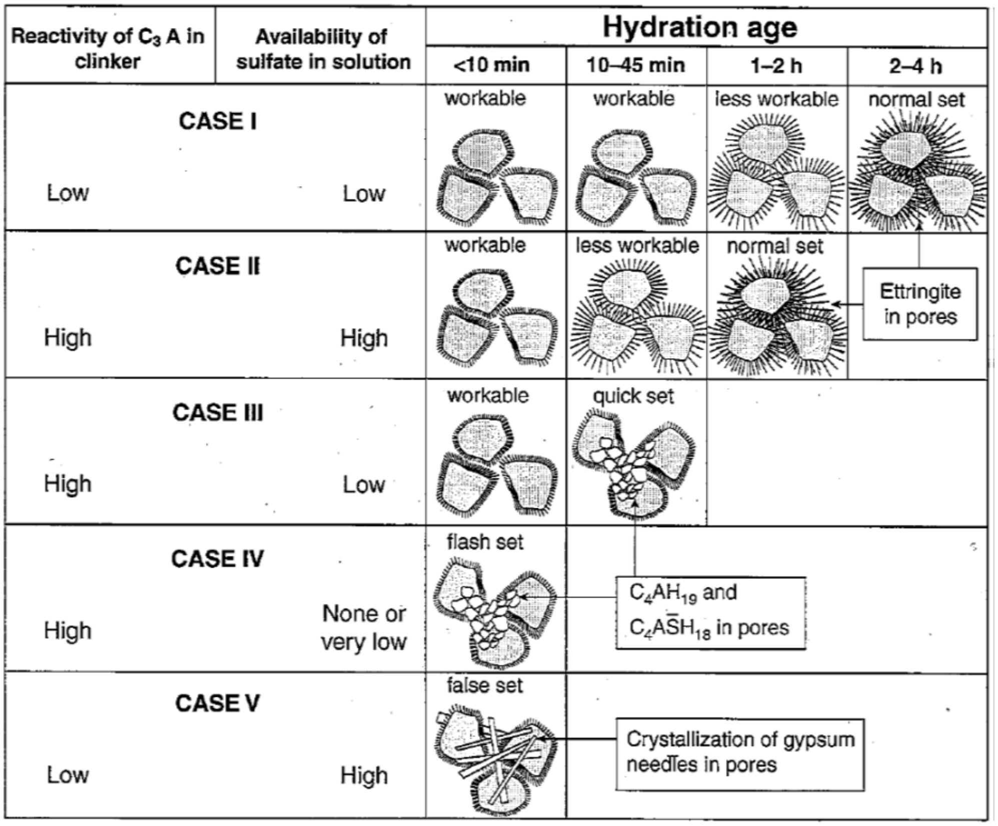

Figure 3-8: Influence of A/S on Setting Characteristics of Portland Cement (Mehta and Monteiro 2006)

3.7 CONCLUDING REMARKS

Fossil fuels have been traditionally used in the production of cement manufacturing. Immense quantities of these fuels are needed to in order to heat the raw materials to temperatures exceeding 1600 °C. As fuel prices continue rise, cement producers have started implementing alternative sources of fuels to reduce cost, emissions, and the demand for fossil fuels.

Waste or alternative fuels are by-products from other industries that come in many forms and can benefit both the cement producer and the environment. Since alternative fuels can replace both fuels and raw materials, production costs can be significantly reduced. Environmental benefits include reduced demand for fossil fuels, landfill waste disposal, and greenhouse gases. However, not all waste fuels are beneficial, and therefore each fuel needs to be thoroughly investigated before utilization.

Utilizing non-traditional fuels or materials in the manufacture of cement introduces new chemical compositions into the kiln environment. These changes could possibly alter the chemical composition of the cement and thus its final cement properties. Also, any variation in the composition of the alternative fuel could have adverse effects on the final cement properties.

If successfully utilizing alternative fuels, the final composition of the cement would be a near match to cement produced with traditional fuels.

Emissions are heavily dependent on the fuels used during production. In the transition from fossil fuels to waste fuels, harmful gases produced in the pyroprocess can be reduced. Testing emissions produced by alternative fuels allows limits to be determined for feasible replacement rates as well as environmental protection. Emissions must also be continuously monitored throughout production to ensure environmental limitations are not exceeded.

Every alternative fuel produces a unique effect on the production of cement and final product. Effects can also differ between cement facilities. The geographical location of the cement plant, availability of fuel alternatives, and plant modification costs are considerations that must be addressed prior to implementing any fuel. Informed use of alternative fuels can benefit not only the manufacturer, but the rest of society.

CHAPTER 4

PART 2—EXPERIMENTAL PLAN

4.1 INTRODUCTION

The production of portland cement is a complex process involving many systems and materials working in synchronization. The objective of this part of the study was to determine if the partial replacement of a traditional fuel by an alternative fuel affects the manufacture and/or the cement performance.

In this study, traditional and alternative fuels were used simultaneously to produce portland cement. Two of the three alternative fuels tested were fired continuously over a 3-4 day period. The third fuel was fired over a 6-day period with the replacement rate of the alternative fuel increasing every two days. Lafarge North America's Roberta cement plant, a full-scale cement manufacturing facility in Calera, Alabama, conducted the trial burns. The cement plant conducted four separate trials, or burns, with each burn utilizing a different alternative fuel. A short description of each burn is provided below. Note that there are three trial burns and one baseline burn. "B" denotes the baseline burn with the remaining letters serving as an acronym for the fuel utilized.

1. B-CP – Coal (C) and plastics (P) were the fuels utilized during this burn period. This was the baseline burn to serve as reference for the construction and demolition (C&D), variable feed wood chips (VF), and soybean seed (Soy) trial burns shown below. This was a 72-hour continuous burn that took place in June of 2010. A sample of the waste plastic blend is shown in Figure 4-1.
2. C&D – Coal (C), plastics (P), and construction and demolition waste (C&D) were the fuels utilized during this trial burn. The types of wood utilized include dimensional lumber, plywood, and pallets. The paper included corrugated boxes and miscellaneous paper materials. The plastic consisted of solid and cellular foam and polyethylene film. This was an 80-hour continuous burn that took place in June of 2010. A sample of the construction and demolition waste is shown in Figure 4-2.
3. VF – Coal (C), plastics (P), and variable feed (VF) woodchips were the fuels utilized during this trial burn. This was a 148-hour, continuous burn that took place in July of 2010. This trial was broken into three phases, each representing an increased substitution percentage of wood chips. The phases are denoted according to their substitution rates as follows: VF 5%, VF 10%, VF15%. A sample of woodchips is shown in Figure 4-3.

4. Soy – Coal (C), plastics (P), and soybean seeds (Soy) were the fuels utilized during this trial burn. This was a 72-hour continuous burn that took place in October of 2010. A sample of the soybean seeds is shown in Figure 4-4.

Figure 4-1: Waste Plastic Blend

Figure 4-2: Construction and Demolition Waste

Figure 4-3: Woodchip Waste

Figure 4-4: Treated Soybean Seeds

The fuels utilized during this phase of the study are categorized in Figure 4-5. Plastics represent a combination of alternative fuels and traditional fuels. Although plastics are considered an alternative fuel by the industry, they are a part of the Roberta Plant's normal operation and thus considered a traditional fuel for this study. Construction and demolition waste, woodchips, and soybean seeds are the only alternative materials evaluated throughout the remainder of this study.

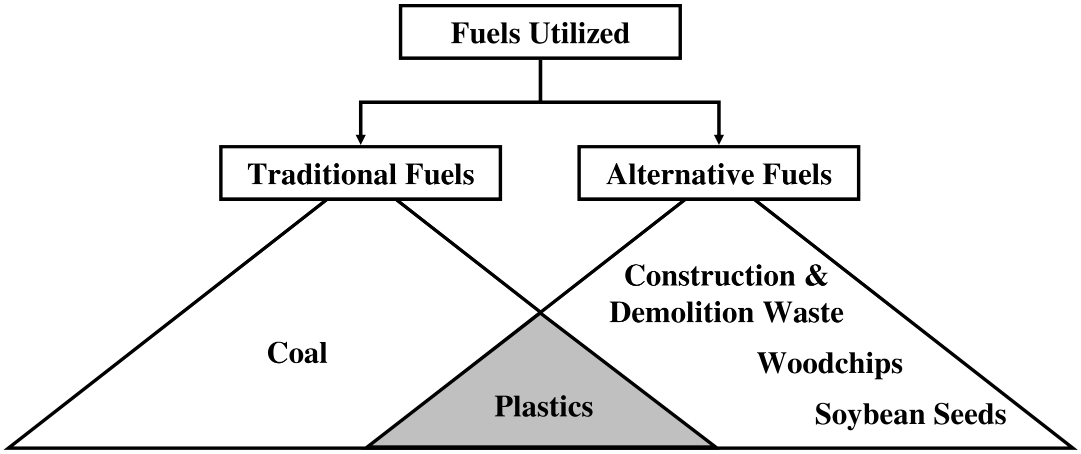

Figure 4-5: Classification of the Fuels Utilized During this Phase of the Study

The first phase of the testing program was to collect samples of all of the materials involved in the process. For convenience and simplicity, a sampling plan was developed to match the materials, sample quantities, and frequencies already established by the cement plant.

The actual testing of the sampled material made up the second half of the testing program. To be as thorough as possible, many different tests were conducted. The specific tests are detailed in the appropriate sections that follow.

4.1.1 Definitions

All materials involved in the manufacturing of cement are collectively labeled as process inputs or process outputs. Process inputs refer to materials placed in the system such as raw material and fuel. Process outputs refer to products that exit the system such as clinker, cement kiln dust (CKD), and emissions. It should be noted that some materials fall into both categories. CKD falls into both categories because the dust is collected throughout the manufacturing process and is typically recycled back into the kiln feed.

The process of sampling refers to methods used to isolate a portion of material from a larger source. A specimen refers to a portion of a sample that will be tested. Discrete and composite specimens were the two types of specimens collected. A discrete specimen refers to a portion of a single sample collected from a single source and time. A composite specimen refers to a portion of multiple samples collected from one source over a particular time period.

4.2 SAMPLING AND TESTING OVERVIEW

A sampling plan was developed and consists of sampling all process inputs and outputs throughout production in order to evaluate the overall effects of utilized alternative fuels. A diagram of this plan is depicted in Figure 4-6. This section provides a general overview of the sampling and testing performed during this study. Sampling and testing are detailed in Sections 4.3 and 5.4, respectively.

Throughout this study, three organizations worked together in order to compile and validate test results and fulfill study obligations. These organizations included the cement plant, an external laboratory, and Auburn University. Many tests were performed by multiple parties in order to validate test results with the exception of the fresh and hardened properties of concrete made from the cement. Auburn University was the only party involved in concrete testing.

Lafarge North America's Robert cement plant was responsible for process input and output sample collection and the manufacturing of the cement. All of the cement was produced and distributed under normal production operations. When necessary, in order to accommodate the alternative fuels, modifications were made by the cement plant. The plant's laboratory conducted chemical analysis on all of the raw materials used in addition to performing tests on cement paste and mortar. Alternative fuels utilized during the burns were not analyzed by the cement plant. The clinker and cement underwent additional testing at the cement plant's specialty lab. Plant emissions were also closely monitored to ensure environmental and production regulations were met.

An external laboratory was used in order to perform chemical analyses on the raw materials, fuels, and final products. The samples collected by the cement plant were shipped to the external laboratory by Auburn University. The results from the external laboratory were used to determine how the alternative fuel affected process inputs and outputs during operation. To determine various parameters of each material, several test methods were used and are explained in Section 4.4.

A chemical analysis was the predominate test conducted on all materials. The cement plant and the external laboratory used X-Ray Fluorescence (XRF) to determine the chemical properties of all the materials except RM3 and the plant emissions. A Prompt Gamma Neutron Activation Analyzer (PGNAA) was used by the cement plant to assess the properties of RM3. In addition to XRF testing, the external laboratory conducted a proximate, ultimate, and combustion analysis as well as determining the ash content for each fuel. Details on emissions testing are detailed in Section 4.4.4.

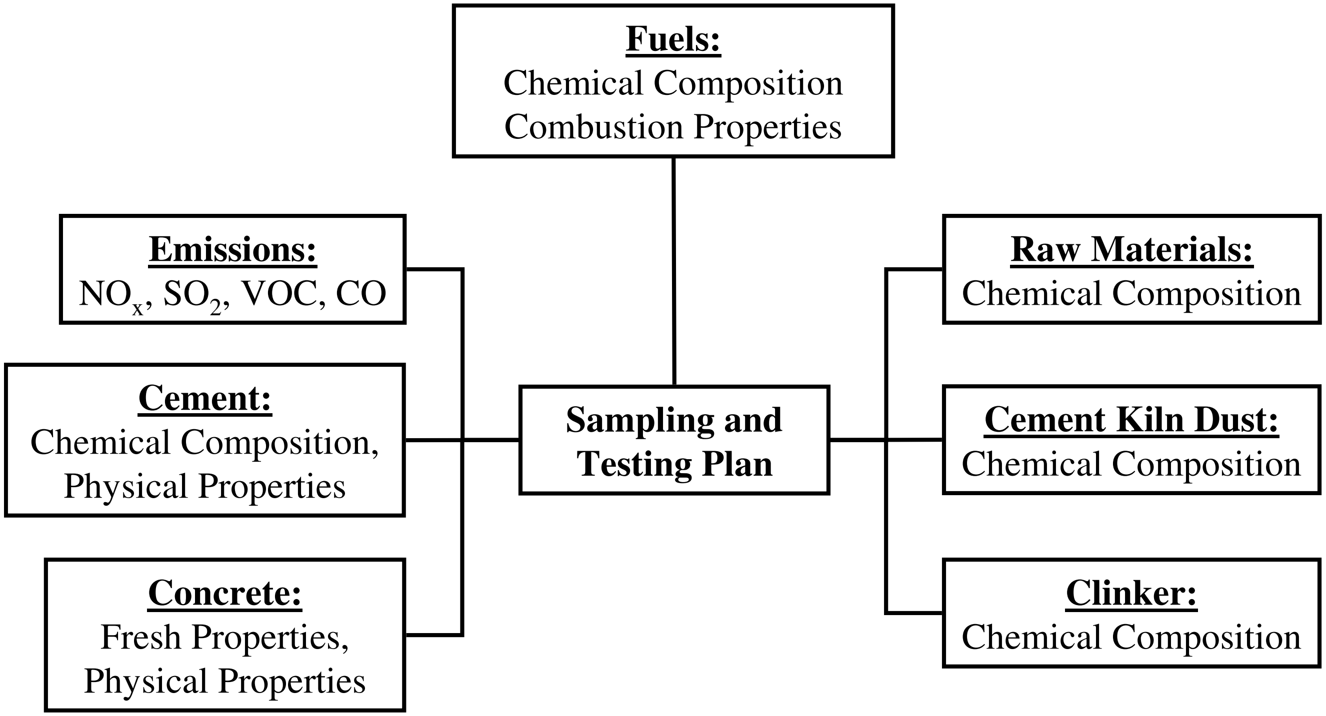

Figure 4-6: Sampling and Testing Plan

Auburn University was the final party involved in this study. Samples collected by the cement plant were collected, conditioned, and shipped to the external laboratory by Auburn University. Cement from each burn was also collected by Auburn University for the purpose of conducting tests on paste, mortar, and concrete. All the results from the cement plant and the external laboratory were collected and compiled by Auburn University in order to be presented in this document.

4.3 SAMPLING

Cement plant personnel collected samples of all materials used during the trial burns. The sampling plan developed by Auburn University followed an in situ-plan used by the cement plant and was modified to include all fuels. The sampling plan used by the cement plant with its respective burn is shown in Table 4-1. All of the process inputs and outputs were collected in one-gallon tin containers with the exception of the cement and liquid fuel. The cement was collected in one-gallon plastic containers and the liquid fuel was collected in 16-ounce, high-density polyethylene bottles.

The projected total number of samples collected during each burn is shown in Table 4-1. It should be noted that fewer samples may have been collected due to the plant's staffing during the burns. The raw materials were sampled once during each burn. The remaining materials were sampled at a regular frequency.

Table 4-1: Sample Collection Plan

Material	**Samples per burn**			
	Trial Burn			
	B-CP (June 2010)	**C&D** (July 2010)	**VF** (July 2010)	**Soy** (Oct. 2010)
RM1 - RM5	1	1	1	1
Kiln Feed	6	6	12	6
Pulverized Coal	6	6	12	6
Cement Kiln Dust	6	6	12	6
Clinker	36	36	72	36
Plastics	24	24	48	24
Alternative Fuel	NA	24	48	24
Material	**Samples per grinding period**			
RM6	6	6	12	6
Cement	10	10	20	10

Notes: RM – Raw Material
NA – Not applicable

For example, the baseline burn lasted 72 hours. Plastics were collected at a frequency of 8 samples every 24 hours, which equals 24 total samples. The frequency at which a sample was taken was determined the expected variability of each material. The plastic feed comprises material from multiple sources that is blended into a homogeneous stream to produce an ideally constant energy value. Plastic samples are taken every 3 hours in order to gain a better understanding of the actual energy values provided by the plastic fuel. Clinker was sampled at the highest frequency because it is the final product before finishing occurs and any chemical variation in the clinker can cause significant changes to final properties of cement. A generic schematic of a cement plant and specific sampling points from which materials are taken is shown in Figure 4-7. In the following section, details are provided for each material sampled.

4.3.1 Sample Collection

From Table 4-1 it can be seen that six raw materials were used during the production of cement at this plant. Due to sources of the raw materials being deemed proprietary information, they will not be disclosed and will be referred to as RM1 – RM6 hereafter. The primary raw material RM3 is quarried and shipped to the plant where it is crushed to a manageable sized and its chemical composition is determined by a Prompt Gamma Neutron Activation Analyzer (PGNAA). From this point the material is either stockpiled or sent directly to the proportioning equipment. The chemical composition of the RM1, RM2, RM4, and RM5 are determined by X-Ray Fluorescence (XRF) and proportioned appropriately to meet the targeted cement chemical composition by the proportioning equipment. Each of the raw materials were sampled at their respective sampling points once per burn. A raw material sampling point is shown in Figure 4-8.

Once proportioned, RM1 - RM5 are sent to the roller mill where the appropriate fineness for optimum burnability is achieved. The raw materials are then sent to the homogenizing silo where they are combined with cement kiln dust (CKD) and mixed to form a homogeneous blend know as kiln feed. Prior to entering the homogenizing silo, the CKD is collected at sampling point 12. The kiln feed is sampled at sampling point 6 before entering into the preheating tower. A kiln feed sampling point is shown in Figure 4-9. During each burn the kiln feed and the CKD were sampled approximately six times each. All fuels were sampled throughout each burn, though the alternative fuels more frequently than the traditional fuels. There are two locations in the kiln system where fuels are introduced.

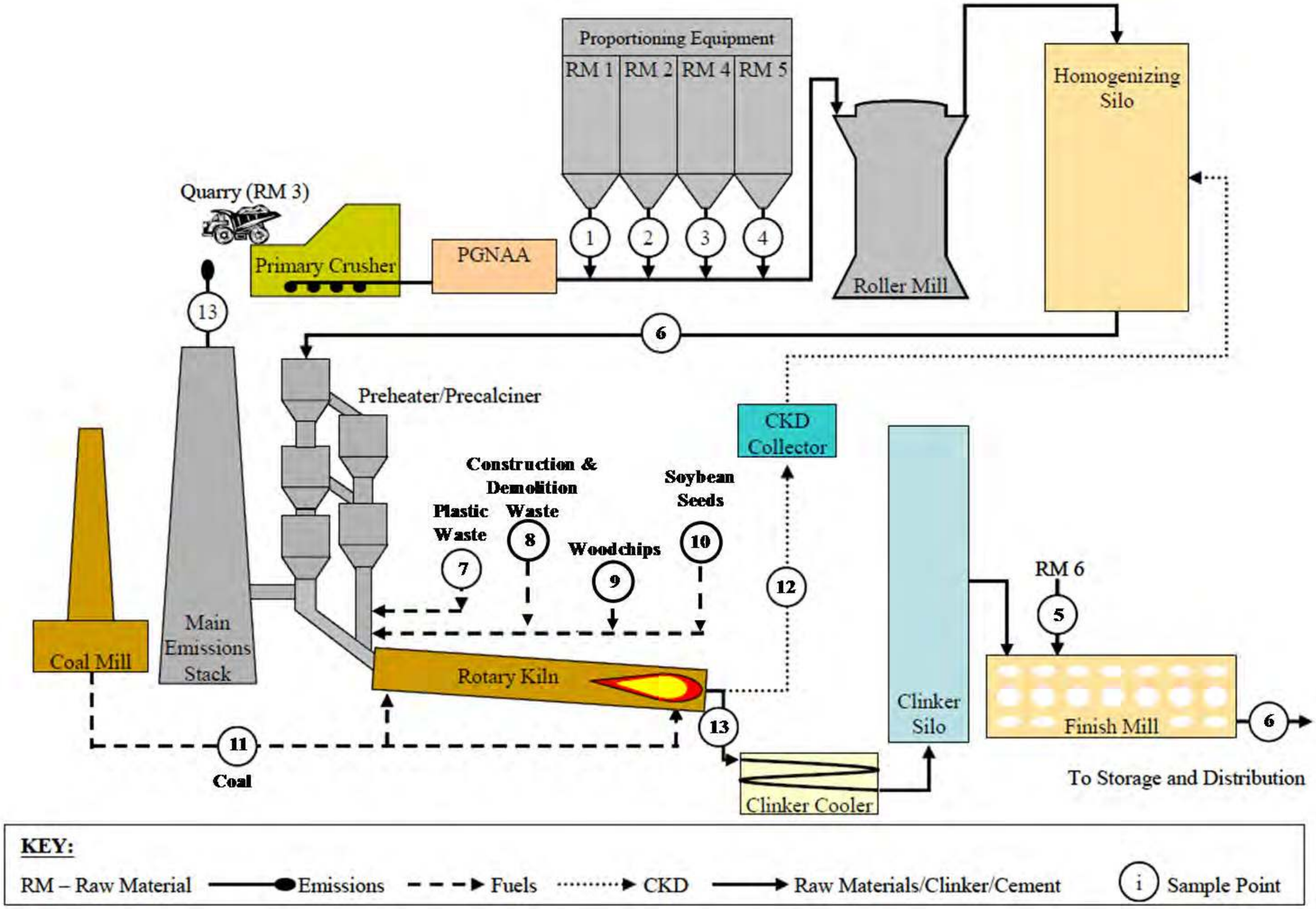

Figure 4-7: Schematic of Cement Plant Operation (Folta 2010)

Figure 4-8: Raw Material Sampling Point

Figure 4-9: Kiln Feed Sampling Point

The upper end of the kiln consumes the majority of the coal and alternative solid fuels such as plastics, woodchips, and C&D waste. These fuels are used to partially calcinate the kiln feed before its entry into the kiln. The remaining coal and liquid fuels are injected into the lower end of the kiln. The burner at the lower end of the kiln is responsible for the remainder of the pyroprocess.

The alternative fuels are transported from the storage facility by conveyer to the alternative fuel injection point depicted in Figure 4-7 at sampling points 7-10 shown in Figure 4-10. Once the ASF is transported to a bin above the injection point, a screw feeds the alternative fuel into the kiln system at a controlled rate.

Coal was collected approximately six times each burn. Samples were taken from sampling point 11 shown in Figure 4-7 by an automated plunger system that removes the pulverized material from the injection stream. The automated plunger system is shown in Figure 4-11. At the lower end of the kiln, the kiln feed has undergone a chemical transformation and has become a homogeneous molten mass known as clinker. The clinker exits the lower end of the kiln and falls onto a revolving grate that cools the clinker. The clinker is sampled at point 13 in Figure 4-7 and the process is depicted in Figure 4-12.

Once the clinker is cooled, it is transferred to a silo until it is ready to be ground. Raw material six is added to the clinker during the finishing process. RM6 is sampled in a similar manor to the raw materials and is collected at sampling point 5 in Figure 4-7. The finished portland cement sample is removed by an automated plunger at sampling point 6 in Figure 4-7. The process is depicted in Figure 4-13.

Figure 4-10: Alternative Fuel Conveyer and Injection System

Figure 4-11: Automated Plunger System

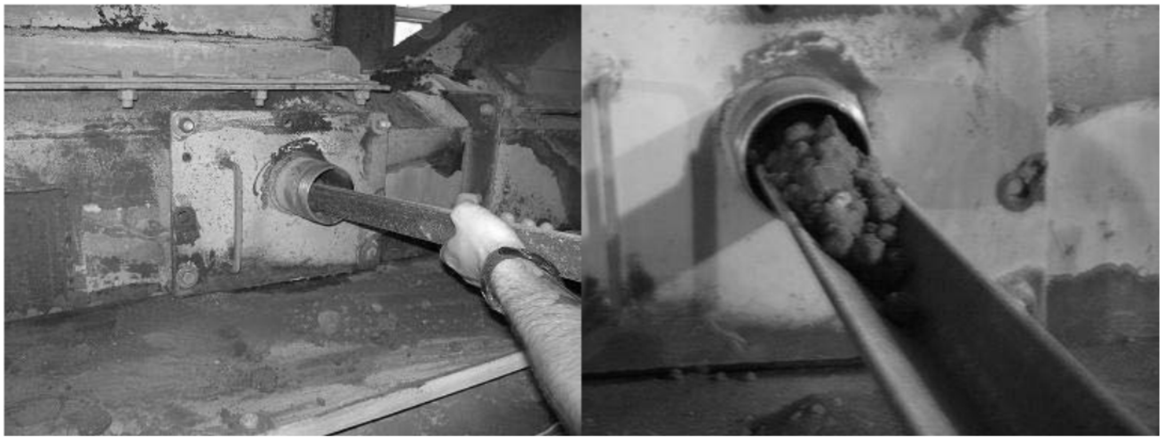

Figure 4-12: Clinker Sampling Point

Figure 4-13: Portland Cement Sampling Point

4.3.2 Sample Conditioning, Shipping, and Storage

Once all the samples were collected from the trial burn at the cement plant, they were transported to Auburn University for further conditioning. All the samples were removed from the aluminum containers and placed into heavy-duty re-sealable bags to prevent the sample's moisture from corroding the insides of the containers and disturbing the *in-situ* chemistry of the material. Each plastic bag was labeled with the material content and the date and time the sample was taken. Samples were then prepared for shipping and testing.

Prior to shipping, the samples were organized into discrete and composite specimens. As previously discussed, a discrete specimen refers to a portion of a sample that was collected from a single source and time period. A composite specimen consists of a single source of material collected over multiple time periods. Regardless of the type of specimen made, the materials were placed into smaller re-sealable plastic bags and labeled with specific identification numbers for reference purposes.

Discrete samples were made from the types of materials that were thought to have the most compositional variability over the burn period. Sample types include the alternative solid fuel, clinker, and CKD. To prepare a discrete specimen, a sample was vigorously shaken and a random portion of material was taken from the original sample, and transferred to a re-sealable bag corresponding to its contents.

Composite samples were made from the types of materials that were thought to have the least compositional variability over the burn period. Sample types include the cement, kiln feed, and coal. Two types of composite samples were prepared. A daily composite specimen consisted of portions of samples collected over a 24-hour time period. A 3-day composite specimen consisted of portions of samples collected over a 72-hour time period. To prepare a composite specimen, a random portion of material was taken from the original samples over a 24-hour or 72-hour time period and transferred to a re-sealable bag corresponding to its contents.

All the specimens were boxed and shipped to appropriate laboratories to undergo chemical analysis. The remaining samples were placed into labeled, steel 55-gallon drums and transported to a temperature and moisture controlled storage facility in the event more specimens were needed for further testing.

4.4 TEST METHODS

In order to evaluate the possible effects of utilizing each alternative fuel, numerous materials in the production process were tested and evaluated. An effort was made to keep production parameters as consistent as possible in order to isolate the trial fuel as the independent variable. It is, however, inevitable that variations in the process conditions exist at a full-scale cement facility, and therefore a certain degree of deviation is expected. As a result, the addition of alternative fuels may only partially contribute to the variability in test results.

Physical properties of the cement were determined by the cement plant and Auburn University. Concrete was also mixed by Auburn University to evaluate its fresh and physical properties. Emissions were monitored by the cement plant to evaluate the impact of alternative fuels, as well as to ensure that environmental regulations were met. Chemical analyses of all the raw materials and finished products were conducted by the cement plant and the external laboratory.

All the test results were gathered by Auburn University in order to present them in this document. Analysis and presentation of results can be found in Chapter 4. The remainder of this chapter details the testing methods used to satisfy the objectives of this study.

4.4.1 Chemical Compositions

The combination of all material inputs determines the chemistry and performance of the process outputs. The primary method for determining chemical makeup was with the use of X-Ray Fluorescence (XRF). Components were reported as either percent by weight (wt. %), or as parts per million (ppm). Percent by weight is the percentage of the total unit weight for a particular parameter in question. Since the parameters in question are typically small, reporting the results in ppm is most convenient.

The cement plant and the external laboratory performed chemical analyses on the materials. There was a slight difference between the standard parameters obtained by the two. The standard parameters collected by both parties are shown in Table 4-2. All the parameters in

Table 4-2 were determined by XRF with the exception of Na_2O_{eq}. Na_2O_{eq} was determined by calculations provided in ASTM C 150 that incorporate the concentrations of Na_2O and K_2O. The detection limits that the external laboratory used for XRF are presented in Table 4-3.

Table 4-2: Standard Chemical Parameters

Standard cement plant parameters	Standard External laboratory parameters	
(wt. %)	(wt. %)	(ppm)
Al_2O_3	Al_2O_3	Arsenic (As)
CaO	CaO	Cadmium (Cd)
Fe_2O_3	Fe_2O_3	Chlorine (Cl)
K_2O	K_2O	Cobalt (Co)
MgO	MgO	Cromium (Cr)
Na_2O	Na_2O	Copper (Cu)
Na_2O_{eq}	P_2O_5	Mercury (Hg)
SiO_2	SiO_2	Molybdenum (Mo)
SO_3	SO_3	Nickel (Ni)
Moisture	TiO_2	Lead (Pb)
LOI	Moisture	Selenium (Se)
	LOI	Vanadium (V)
		Zinc (Zn)

Table 4-3: Approximate XRF Detection Limits Used by External Laboratory

Parameter	Detection Limit (wt. %)	Parameter	Detection Limit (ppm)
Al_2O_3	0.01	Arsenic (As)	2
CaO	0.01	Cadmium (Cd)	3
Fe_2O_3	0.01	Chlorine (Cl)	5
K_2O	0.01	Cobalt (Co)	10
MgO	0.01	Cromium (Cr)	16
Na_2O	0.01	Copper (Cu)	13
P_2O_5	0.01	Mercury (Hg)	0.01
SiO_2	0.01	Molybdenum (Mo)	9
SO_3	0.01	Nickel (Ni)	9
TiO_2	0.01	Lead (Pb)	4
Moisture	0.01	Selenium (Se)	1
LOI	0.01	Vanadium (V)	20
		Zinc (Zn)	9

4.4.1.1 Raw Materials and Kiln Feed

During the burns, there were six raw materials (RMs) collected. Due to the sources of these materials being proprietary and the request of the cement plant they will not be disclosed. RM1 – RM5 were each sampled once per trial before grinding and mixing and discrete specimens for each material was prepared for testing by the external laboratory. RM6 was sampled approximately 6 times during each trial and was sampled prior to being ground with the clinker. A 3-day composite specimen of RM6 was prepared for the external laboratory for each trial.

The kiln feed consisted of a blend of RM1 – RM5 and was sampled approximately 6 times per trial. A 3-day composite specimen was prepared for testing by the external laboratory for each trial. As discussed earlier, with the exception of RM3, RM1 – RM5 were chemically analyzed by the cement plant and external laboratory utilizing XRF to acquire the standard parameter listed in Table 4-2. RM6 is typically not tested by the cement plant. RM3 is analyzed at the cement plant by using a Prompt-Gamma Neutron Activation Analyzer (PGNAA). The PGNAA obtains immediate compositional results that allow the remaining raw materials to be proportioned correctly.

The cement plant did not test all the raw materials during each burn. Reasons for this include the source of the material remaining constant or the tests just never being conducted. All the data provided by the cement plant, however, are the most recent available.

4.4.1.2 Cement Kiln Dust (CKD)

As stated previously, cement kiln dust is a unique material in that it is a process input and a process output. During the pyroporcess, dust is collected and recycled into the kiln feed if its chemical composition is acceptable. Approximately six samples were taken during each trial and tested as discrete specimens by both laboratories. XRF was used to determine each parameter listed in Table 4-2 except for moisture and Loss on Ignition (LOI). The external laboratory was the only entity to include these parameters.

4.4.1.3 Fuel Sources

As shown in Figure 4-1, each alternative fuel was sampled approximately 8 times each day. In addition to using XRF for each fuel, proximate and ultimate analyses were conducted by the external laboratory. A list of parameters for the proximate and ultimate analyses is shown in Table 4-4. A calorific value was also collected by measuring the energy released through combustion. This value was reported on a dry basis and expressed in BTU/lb. The ash resulting from combustion was tested using XRF to determine the parameters listed in Table 4-2.

Coal was sampled six times over each burn period. The external laboratory tested 3-day composite specimens prepared from the samples collected. The results consisted of all the parameters listed in Table 4-2 and Table 4-4, in addition to the combustion and ash analysis previously discussed. Coal was the only fuel that the cement plant tested.

Table 4-4: Proximate and Ultimate Analysis Parameters

Proximate Analysis (wt. %)	Ultimate Analysis (wt. %)
Moisture	Carbon (C)
Ash	Hydrogen (H)
Volatile Matter (VM)	Nitrogen (N)
Fixed Carbon (FC)	Oxygen (O)
	Sulfur (S)
	Ash
	Moisture

Construction and demolition waste was sampled in accordance with Table 4-1. C&D waste was sampled at a relatively high frequency because the fuel was comprised of a blend of material originating from multiple sources. Discrete specimens were prepare from the collected samples and were tested by the external laboratory to acquire all the fuel parameters discussed.

Woodchips were sampled in accordance with Table 4-1. Woodchips were sampled at a relatively high frequency due to their varying moisture contents. Discrete specimens were prepares from the collected samples and were tested by the external laboratory to acquire all the fuel parameters discussed.

Soybeans were sampled in accordance with Table 4-1. Soybeans were sampled at a relatively high frequency in order to identify any compositional variability in the fuel. Discrete specimens were prepared from the collected samples and were tested by the external laboratory to acquire all the fuel parameters discussed.

4.4.1.4 Clinker

Clinker samples were collected approximately every three hours each trial burn. In addition to meeting the parameters listed in Table 4-2, the cement plant calculated the equivalent alkali content and Bogue compounds in accordance with ASTM C 150 (2007). The free lime content (FCaO) of each sample was also determined by the cement plant.

Daily composite samples were prepared by Auburn University and tested by the external laboratory to determine the standard parameters shown in Table 4-2. Based on the data provided, Auburn University calculated the Bogue compounds in accordance with ASTM C 150 (2007).

The cement plant's specialty laboratory was also sent similar composite specimens to determine the four major clinker phases using Rietveld analysis. Rietveld analyses typically provide more accurate results than the Bogue calculations specified by ASTM C 150 (2007).

4.4.1.5 Portland Cement

Portland cement was sampled in accordance with Table 4-1 and tested by the cement plant to obtain the parameter shown in Table 4-2 as well as the equivalent alkali content and Bogue compounds in accordance with ASTM C 150 (2007). The free lime content (FCaO) and Blaine SSA (Specific Surface Area) were also determined by the cement plant for each sample.

Daily composite samples were prepared by Auburn University and tested by the external laboratory to determine the standard parameters shown in Table 4-2 as well as total organic compounds (TOC) using a TOC analyzer. Based on the data provided, Auburn University calculated the Bogue compounds in accordance with ASTM C 150 (2007).

The cement plant's specialty laboratory was also sent similar composite specimens to determine the four major clinker phases using Rietveld analysis. Rietveld analyses typically provide more accurate results than the Bogue calculations specified by ASTM C 150 (2007).

Limestone is commonly added to portland cement to adjust its final composition. The added limestone increases the carbon dioxide (CO_2) of the cement and must be accounted for in the Bogue calculations specified in ASTM C 150 (2007). The cement plant reported this additional parameter for all trial burns.

4.4.2 Cement Physical Properties

The cement plant, Auburn University, and the cement plant's specialty lab determined various physical properties of the cement produced during each trial. For comparison purposes, Auburn University and the cement plant conducted several of the same tests. The cement plant used cement sampled from each trial to conduct their tests. The tests performed by the cement plant, as well as the units and ASTM specifications associated with each test are listed in Table 4-5. Auburn University received bags of cement produced from each trial for further testing. The tests conducted by Auburn University to determine the physical properties of each cement are shown in Table 4-6.

The cement plant's specialty lab received composite specimens of cement comprised of samples collected by the cement plant. In addition to performing the Rietveld analysis, the cement plant's specialty lab also determined the particle size distribution of each cement by laser diffraction.

Table 4-5: Cement Physical Properties Determined by the Cement Plant

Property	ASTM Specification
Air in mortar, %	C 185 (2002)
Blaine specific surface area, m^2/kg	C 204 (2007)
Autoclave expansion, %	C 151 (2005)
Mortar flow, %	C 230 (2003)
Compressive strength, MPa (1, 3, 7, and 28 days)	C 109 (2007)
Normal consistency, %	C 187 (2004)
Gillmore initial set, min. Gillmore final set, min.	C 266 (2008)
Vicat initial set, min. Vicat final set, min.	C 191 (2008)

Table 4-6: Cement Physical Properties Determined by Auburn University

Property	ASTM Specification
Autoclave expansion, %	C 151 (2005)
Mortar flow, %	C 230 (2003)
Compressive strength, MPa (1, 3, 7, and 28 days)	C 109 (2007)
Normal consistency, %	C 187 (2004)
Gillmore initial set, min. Gillmore final set, min.	C 266 (2008)
Vicat initial set, min. Vicat final set, min.	C 191 (2008)
Drying Shrinkage development, %	C 596 (2007)

4.4.3 Concrete Properties

Each trial burn was bagged in accordance with normal procedures at the cement plant. Auburn University collected approximately 15 bags of cement from each trial for mixing and testing concrete. Concrete was mixed in order to establish any link between fuels used to produce the cement and the concrete properties.

Two concretes were developed and used throughout the study. The first concrete (Mix 0.37) had a water cement ratio (w/c) of 0.37 and used No. 78 crushed limestone and natural river sand as aggregate. The second mixture (Mix 0.44) had a w/c of 0.44 and used No. 57 crushed limestone and natural river sand as coarse and fine aggregate, respectively. A summary of mixture proportions for the first and second mix are shown in Tables 4-7 and 4-8.

The concrete produced at Auburn University was mixed in the structures laboratory in accordance with ASTM C 192 (2007). Due to the required volume of Mix 0.37 and 0.44, each mix was divided into two batches of approximately equal volumes. Fresh concrete properties were tested for each batch mixed prior to preparing test specimens listed in Figure 4-9. The tests conducted for each mixture in addition to the ASTM specifications followed for each are shown in Figure 4-9.

The slump and air content of the concrete was tested in both batches in accordance with ASTM C 192 (2007). Tolerances set by Section 9.2 of ASTM C 192 (2007) to ensure consistency between the two batches were obtained.

Table 4-7: Proportions for Mix 0.37 (w/c = 0.37)

Material	Proportion	Volume
Water content	260 lb/yd^3	4.17 ft^3
Cement content	705 lb/yd^3	3.59 ft^3
Coarse aggregate content (# 78 crushed limestone)	1942 lb/yd^3	11.40 ft^3
Fine aggregate content (natural river sand)	1104 lb/yd^3	6.73 ft^3
Total air content	4.0 %	1.08 ft^3
Air-entraining admixture	1.8 oz/yd^3	0.002 ft^3
Water-reducing admixture	35.3 oz/yd^3	0.035 ft^3

Table 4-8: Proportions for Mix 0.44 (w/c = 0.44)

Material	Proportion	Volume
Water content	273 lb/yd^3	4.38 ft^3
Cement content	620 lb/yd^3	3.15 ft^3
Coarse aggregate content (# 57 crushed limestone)	1900 lb/yd^3	10.77 ft^3
Fine aggregate content (natural river sand)	1247 lb/yd^3	7.60 ft^3
Total air content	4.0 %	1.08 ft^3
Air-entraining admixture	1.2 oz/yd^3	0.001 ft^3
Water-reducing admixture	12.4 oz/yd^3	0.012 ft^3

Table 4-9: Concrete Tests

Test	ASTM Specification
Slump	C 143 (2008)
Total air content	C 231 (2008)
Setting Time	C 403 (2008)
Compressive Strength (1, 3, 7, 28, and 91 days)	C 39 (2005)
Drying shrinkage development	C 157 (2006)
Permeability (RCPT)	C 1202 (2007)

Four by eight in. cylinders were prepared for rapid chloride ion penetration testing (RCPT). Ten 6 x 12 in. cylinders were used for compressive testing. One 6 x 12 in. cylinder was used for a semi-adiabatic (heat of hydration) test. Prisms (3 x 3 x 11.25 in.) were prepared for drying shrinkage development. A setting specimen was also prepared in accordance with ASTM C 403 to determine initial and final setting times of the trial cement.

4.4.4 Plant Emissions

In order to satisfy limits set by the Alabama Department of Environmental Management (ADEM), plant emissions were monitored by a Continuous Emissions Monitoring System (CEMS). The main stack emissions monitored were carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO_2) and volatile organic compounds (VOCs). The emissions data, though continuously monitored, was reported in average tons per hour. In order to normalize these data, the production data detailing the amount of clinker produced per hour were used. Emission quantities were reported in tons per ton of clinker. These data were used to evaluate the effects of utilizing alternative fuels.

4.5 CONCLUDING REMARKS

Four individual burns were conducted at a full-scale cement plant during this phase of the alternative fuels study, each yielding portland cement from different fuel scenarios. Two of the trials conducted utilized a constant feed rate. Unique to this study, one trial utilized a variable feed rate which consisted of 5, 10, and 15 percent replacement of woodchips. This chapter described all testing plans and methods used to satisfy objectives of this study.

The cement plant's laboratory and external laboratory were responsible for testing all material input and outputs. Material inputs included raw material, and fuels. Material outputs included CKD, clinker, and cement. Chemical analyses of the input and output materials were used to determine if there were significant differences that could be attributed to the utilization of alternative fuels

Physical properties of cement were tested by the cement plant as well as Auburn University. Cement produced during each trial was collected by Auburn University for fresh and physical concrete property testing.

Emissions were monitored continuously during each trial to ensure environmental regulations were met and evaluate the impact of alternative fuels on portland cement. The emissions monitored during each trial were carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO_x), and volatile organic compounds (VOCs).

CHAPTER 5

PART 2—DATA PRESENTATION AND ANALYSIS

5.1 INTRODUCTION

A summary of all collected data in addition to an analysis and discussion of the results are presented in the chapter. The data pertaining to each material follow the same order of presentation used in Chapter Four. Each material's results as reported from the testing laboratories are discussed separately. Similar analyses between entities are compared where necessary. Results from trial burns are compared to these obtained from the baseline burn.

An analysis plan was developed and is sown in Figure 5-1. It should be noted that the construction and demolition waste, variable feed woodchip, and soybean seed burns represent the trial burns. The trial burns are compared to the baseline burn.

5.2 STATISTICAL ANALYSIS BACKGROUND

In this chapter, data pertaining to each test or parameter are presented. Where more than ten data points are available for a data set, statistical analysis results are also presented for the data.

It should be noted that the term *significant* is used frequently throughout this chapter. This could indicate that there is a large change or difference between two or more results. Also, the terms *statistical* significance and *practical* significance are used. Statistical significance implies the result is supported by statistical analysis and unlikely to have occurred by chance. Practical significance is based on the performance of a cement or concrete. Data may show any combination of these two types of significance.

The normality of all applicable data was tested using the Anderson-Darling test (Gingerich 1995). The Wilcoxon rank-sum test, which is not dependent on sample size or normality, is presented in this chapter for applicable data (Bridge and Sawilowsky 1999).

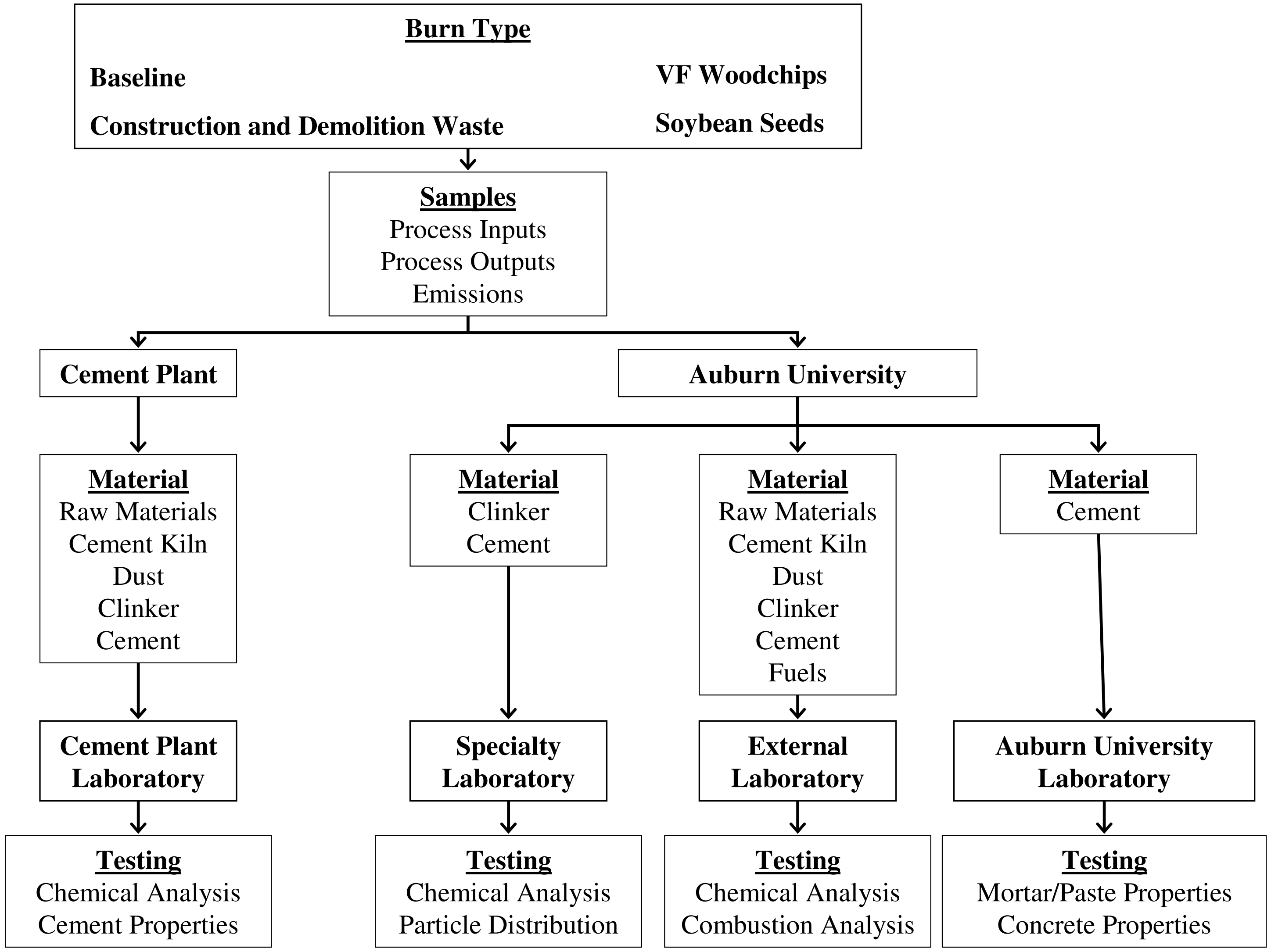

Figure 5-1: Analysis Plan

The Anderson-Darling and Wilcoxon rank-sum tests are both based around two competing hypotheses: a null hypothesis (H_o), which is considered true until statistics proves otherwise, and an alternative hypotheses (H_a) (Gingerich 1995). A p-value is the probability of failing to reject the null hypotheses in favor of the alternative hypothesis. A confidence level of 90 % was used for both statistical tests because most of the sample sizes in this study are small. If the p-value calculated is less than the confidence level, the null hypothesis is rejected for the alternative hypothesis.

The Anderson-Darling statistic for all the applicable data was calculated with Statistical Analysis Software (SAS 9.2) utilizing the following hypotheses:

H_o: The data follow a normal distribution, and
H_a: The data do not follow a normal distribution.

The 90 % confidence level was represented by a limiting alpha value of 0.1. A p-value less than 0.1 indicates that the null hypothesis is likely to be false, and thus the data do not follow a normal distribution. All values resulting from the Anderson-Darling statistic presented in this study that do not follow a normal distribution are indicated by a superscript when presented in tabular from.

The Wilcoxon rank-sum test was used to determine the statistical significance between means of two samples. The Wilcoxon rank-sum test for all the applicable data was calculated with Statistical Analysis Software (SAS 9.2) and utilized the following hypotheses:

H_o: The means of the two data sets are equal, and
H_a: The means of the two data sets are not equal.

The 90 % confidence level was represented by a limiting alpha value of 0.1. A p-value less than 0.1 indicates that the null hypothesis is likely to be false, and thus the means between the trial and the baseline are different. All trial values that possess statistically different means compared to the baseline mean are indicated by a superscript.

5.3 RESEARCH CONDITIONS

The burns conducted for this study were described in Chapter Four. All trial fuels were used to partially replace traditional fuels and were co-fired with traditional fuels over a 3-6 day period. Each 3-day burn lasted between 72 and 80 hours. The variable-feed 6-day burn lasted 148 hours. Although efforts were made to maintain consistent plant conditions, changes that may have occurred include process inputs such as raw material sources, fuel feed rates, and production rates. These changes are unavoidable with respect to the study and necessary for the cement facility to maintain its normal operations. The range of values for the rates of process inputs and outputs are presented in Table 5-1. It should be noted that the alternative solid fuel incorporates the plastic blend as well as the alternative fuel utilized during the burn.

Values presented in Table 5-1 were calculated using production data from the cement plant. The alternative fuel replacement rates were reported in production data obtained from the cement plant.

Table 5-1: Summary of Plant Conditions During Each Burn

Burn	**B-CP**	**C&D**	**VF 5%**	**VF 10%**	**VF 15%**	**Soy**
Period	**Jun-10**	**Jul-10**	**Jul-10**	**Jul-10**	**Jul-10**	**Oct-10**
Kiln Feed (tph)	250-320	250-300	293-301	214-311	250-303	298-321
Clinker Production (tph)	140-250	100-275	184-237	106-264	126-324	152-254
Coal Feed (tph)	13-22	9.1-29	20-23	7.3-34	12-25	7.0-24
Alternative Solid Fuel Blend (tph)	6.5-8.2	6.5-7.9	7.7-7.8	5.6-8.1	6.5-7.8	7.8-8.2
Alternative Fuel Replacement (%)[1]	0	5.0	5.0	12	15	7.0

Note: [1]Replacement % based on average total energy as reported from the cement plant

5.4 DATA PRESENTATION AND ANALYSIS

Specific notations designated for each of the participating parties involved in this study are shown below. Each set of data will be labeled with this notation to identify the origin of the data. The notations that will be used throughout the remainder of this chapter are as follows:

- Cement Plant Results (CPR) refers to the results obtained from the cement plant laboratory,
- External laboratory results (ELR) refers to the data obtained from the external laboratory,
- Specialty lab results (SLR) refers to the results obtained from the cement plant's specialty laboratory, and
- Auburn University results (AUR) refers to the results collected by Auburn University personnel.

The tables and figures presented in this chapter represent a summary of the raw data collected from its corresponding entity. The term *Value* corresponds to a material represented by a single sample. The abbreviation *Avg.* corresponds to the average value representing multiple samples. The percent difference of the trial result relative to the baseline result is abbreviated, *%Diff*. It should be noted that the percent difference compares trial data to the baseline data collected by the same entity.

5.4.1 Chemical Composition of Raw Materials

The results from RM1 – RM6 are reported in Tables 5-2 to 5-7. It should be noted that the raw material values represent one specimen. The percent difference also is provided to compare the trial burn to the baseline. Testing only one specimen between burns can increase the percent difference relative to the baseline due to the fluctuations in material chemistry. Since these data are represented by one specimen, they are not shown in the appendices.

The external laboratory results for raw material 1 are tabulated in Table 5-2. The most noticeable decrease is in the SO_3 content. A decrease in SO_3 could affect emissions and cement physical properties. Notable trace elements include arsenic (As) and mercury (Hg). Their levels significantly vary from the baseline results. The effects from the fluctuations in all raw materials will be determined from the final cement composition.

The external laboratory results for raw material 2 are tabulated in Table 5-2. The most noticeable decrease is in the SO_3 content. A decrease in SO_3 could affect emissions and cement physical properties. Notable trace elements that significantly varied from the baseline include As, Hg, Cu, Ni, Pb, and Zn.

Table 5-2: ELR- Chemical Composition of RM1 for All Burns

Property	**B-CP**	**C&D**		**VF**		**Soy**	
	Value	Value	% Diff.[1]	Value	% Diff.[1]	Value	% Diff.[1]
Al_2O_3 (wt. %)	25.7	NR	-	25.6	-0.3	26.3	2.5
CaO (wt. %)	2.58	NR	-	2.64	2.7	2.67	3.5
Fe_2O_3 (wt. %)	12.1	NR	-	12.2	0.6	11.4	-5.9
K_2O (wt. %)	2.39	NR	-	2.38	-0.6	2.39	0.0
MgO (wt. %)	1.13	NR	-	1.16	2.6	1.17	3.7
Na_2O (wt. %)	0.63	NR	-	0.63	0.2	0.48	-24
P_2O_5 (wt. %)	0.60	NR	-	0.60	0.2	0.64	7.3
SiO_2 (wt. %)	45.0	NR	-	44.8	-0.3	45.2	0.5
SO_3 (wt. %)	0.30	NR	-	0.07	-76	0.03	-91
TiO_2 (wt. %)	1.32	NR	-	1.32	-0.5	1.32	-0.4
Moisture (wt. %)	22.9	NR	-	18.4	-19	16.3	-29
LOI (wt. %)	7.83	NR	-	8.1	3.4	7.9	0.8
As (ppm)	156	NR	-	236	51	449	190
Ba (ppm)	NR	NR	-	NR	-	NR	-
Cd (ppm)	6.00	NR	-	6.00	0.0	6.00	0.00
Cl (ppm)	57.0	NR	-	46.0	-19	22.0	-61
Co (ppm)	63.0	NR	-	65.0	3.2	57.0	-9.5
Cr (ppm)	180	NR	-	283	57	163	-9.3
Cu (ppm)	365	NR	-	381	4.4	253	-31
Hg (ppm)	0.01	NR	-	0.05	920	0.12	2200.0
Mn (ppm)	NR	NR	-	NR	-	NR	-
Mo (ppm)	28.0	NR	-	22.0	-21	22.0	-21
Ni (ppm)	111	NR	-	115	3.6	132	18.9
Pb (ppm)	151	NR	-	158	4.6	343	130.0
Sb (ppm)	NR	NR	-	NR	-	NR	-
Se (ppm)	3.00	NR	-	2.00	-33	2.00	-33
Sr (ppm)	NR	NR	-	NR	-	NR	-
V (ppm)	368	NR	-	355	-3.5	384	4.3
Zn (ppm)	145	NR	-	191	32	200	38

Notes: NR - Not Reported

[1] Relative to B-CP

Table 5-3: ELR- Chemical Composition of RM2 for All Burns

Property	B-CP	C&D		VF		Soy	
	Value	Value	% Diff.[1]	Value	% Diff.[1]	Value	% Diff.[1]
Al_2O_3 (wt. %)	0.30	NR	-	0.27	-12	0.38	27
CaO (wt. %)	55.0	NR	-	54.3	-1.4	53.3	-3.2
Fe_2O_3 (wt. %)	0.10	NR	-	0.09	-14	0.14	36
K_2O (wt. %)	0.06	NR	-	0.06	-2.7	0.08	38
MgO (wt. %)	0.93	NR	-	0.78	-17	1.23	31
Na_2O (wt. %)	0.00	NR	-	0.00	-	0.00	-
P_2O_5 (wt. %)	0.00	NR	-	0.01	-	0.01	-
SiO_2 (wt. %)	1.12	NR	-	1.04	-7.3	1.58	41
SO_3 (wt. %)	0.57	NR	-	0.09	-84	0.08	-86
TiO_2 (wt. %)	0.00	NR	-	0.00	-	0.00	-
Moisture (wt. %)	1.01	NR	-	0.31	-69	2.09	110
LOI (wt. %)	41.8	NR	-	43.4	3.7	43.2	3.2
As (ppm)	13.0	NR	-	13.0	0.0	5.0	-62
Ba (ppm)	NR	NR	-	NR	-	NR	-
Cd (ppm)	6.00	NR	-	6.00	0.0	6.00	0.0
Cl (ppm)	72.0	NR	-	39	-46	40	-44
Co (ppm)	6.00	NR	-	6	0.0	6	0.0
Cr (ppm)	25.0	NR	-	16	-35	22	-12
Cu (ppm)	5.00	NR	-	5	0.0	67	1200
Hg (ppm)	0.01	NR	-	0.03	580	0.08	1400
Mn (ppm)	NR	NR	-	NR	-	NR	-
Mo (ppm)	5.00	NR	-	10.0	100	5.00	0.0
Ni (ppm)	3.00	NR	-	3.00	0.0	24.0	700
Pb (ppm)	5.00	NR	-	5.00	0.0	42.0	740
Sb (ppm)	NR	NR	-	NR	-	NR	-
Se (ppm)	2.00	NR	-	2.00	0.0	2.00	0.0
Sr (ppm)	NR	NR	-	NR	-	NR	-
V (ppm)	8.00	NR	-	10.0	25	5.00	-38
Zn (ppm)	5.00	NR	-	21.0	320	19.0	280

Notes: NR - Not Reported

[1] Relative to B-CP

The external laboratory results for raw material 3 are tabulated in Table 5-4. The most noticeable fluctuations were in the Fe_2O_3, K_2O, MgO, Na_2O, SiO_2, and SO_3 contents. The large fluctuations observed in RM3 are most likely due to testing one sample. Notable trace elements that significantly varied from the baseline include As, Hg, Cu, Ni, and Pb. The external laboratory results for raw material 4 are tabulated in Table 5-5. RM4 stayed fairly consistent over the trial burns. The most noticeable fluctuations were in the K_2O, Na_2O, and SO_3 contents. The only trace element that varied significantly from the baseline was Hg. The external laboratory results for raw material 5 are tabulated in Table 5-6. The most noticeable fluctuations were in the Al_2O_3,

CaO, Fe_2O_3, K_2O, MgO, SiO_2, and SO_3 contents. The large fluctuations seen in RM5 are most likely attributable to testing only one sample. Notable trace elements that significantly varied from the baseline include As, Cr, Hg, Ni, Pb, V, and Zn.

Table 5-4: ELR- Chemical Composition of RM3 for All Burns

Property	B-CP	C&D		VF		Soy	
	Value	Value	% Diff.[1]	Value	% Diff.[1]	Value	% Diff.[1]
Al_2O_3 (wt. %)	9.12	NR	-	6.11	-33	10.0	9.9
CaO (wt. %)	22.6	NR	-	25.6	13	0.50	-98
Fe_2O_3 (wt. %)	1.88	NR	-	3.62	93	10.5	460
K_2O (wt. %)	0.37	NR	-	0.47	28	0.73	96
MgO (wt. %)	2.69	NR	-	0.47	-82	0.34	-88
Na_2O (wt. %)	0.04	NR	-	0.05	23	0.07	97
P_2O_5 (wt. %)	0.09	NR	-	0.03	-66	0.10	13
SiO_2 (wt. %)	38.9	NR	-	40.7	4.4	70.4	81
SO_3 (wt. %)	0.12	NR	-	0.11	-10	0.02	-85
TiO_2 (wt. %)	0.55	NR	-	0.48	-12	1.01	85
Moisture (wt. %)	1.59	NR	-	0.75	-53	2.27	43
LOI (wt. %)	23.5	NR	-	22.3	-5.0	5.96	-75
As (ppm)	21.0	NR	-	38.0	81	60.0	190
Ba (ppm)	NR	NR	-	NR	-	NR	-
Cd (ppm)	6.00	NR	-	6.00	0.0	6.00	0.0
Cl (ppm)	67.0	NR	-	101	51	6.00	-91
Co (ppm)	10.0	NR	-	7.00	-30	32.0	220
Cr (ppm)	62.0	NR	-	130	110	104	67
Cu (ppm)	47.0	NR	-	35	-26	80.0	70
Hg (ppm)	0.01	NR	-	0.03	480	0.09	1800
Mn (ppm)	NR	NR	-	NR	-	NR	-
Mo (ppm)	5.0	NR	-	12.0	140	5.00	0.0
Ni (ppm)	32.0	NR	-	26.0	-19	34.0	6.3
Pb (ppm)	59.0	NR	-	5.0	-92	74.0	25
Sb (ppm)	NR	NR	-	NR	-	NR	-
Se (ppm)	2.00	NR	-	2.00	0.0	2.00	0.0
Sr (ppm)	NR	NR	-	NR	-	NR	-
V (ppm)	87.0	NR	-	137	57	166	91
Zn (ppm)	40.0	NR	-	38.0	-5.0	55.0	38

Notes: NR - Not Reported

[1] Relative to B-CP

The external laboratory results for raw material 6 are tabulated in Table 5-7. The most noticeable fluctuations were in the Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, P_2O_5, and SO_3 contents. The large fluctuations seen in RM6 are most likely from testing one sample. Notable trace elements that significantly varied from the baseline include As, Cr, Cu, Hg, Ni, and Zn. Effects of the increases of trace elements will be determined from the final cement composition.

Table 5-5: ELR- Chemical Composition of RM4 for All Burns

Property	**B-CP**	**C&D**		**VF**		**Soy**	
	Value	Value	% Diff.[1]	Value	% Diff.[1]	Value	% Diff.[1]
Al_2O_3 (wt. %)	2.76	NR	-	2.80	1.4	2.71	-1.8
CaO (wt. %)	18.56	NR	-	20.1	8.1	16.5	-11
Fe_2O_3 (wt. %)	51.03	NR	-	45.8	-10	51.6	1.1
K_2O (wt. %)	0.09	NR	-	0.10	18	0.14	63
MgO (wt. %)	4.01	NR	-	4.6	15	4.56	14
Na_2O (wt. %)	0.04	NR	-	0.04	-1.7	0.09	104
P_2O_5 (wt. %)	0.22	NR	-	0.25	14	0.28	31
SiO_2 (wt. %)	8.80	NR	-	10.1	15	10.6	20
SO_3 (wt. %)	0.57	NR	-	0.57	-0.2	0.36	-37
TiO_2 (wt. %)	0.29	NR	-	0.38	30	0.28	-3.9
Moisture (wt. %)	6.37	NR	-	9.26	45	12.6	98
LOI (wt. %)	12.2	NR	-	13.6	12	11.4	-5.8
As (ppm)	21	NR	-	29	38	19	-9.5
Ba (ppm)	NR	NR	-	NR	-	NR	-
Cd (ppm)	12	NR	-	13	8.3	17	42
Cl (ppm)	240	NR	-	210	-13	254	5.8
Co (ppm)	36	NR	-	42	16.7	56	56
Cr (ppm)	858	NR	-	1600	86	845	-1.5
Cu (ppm)	214	NR	-	209	-2.3	237	11
Hg (ppm)	0.005	NR	-	0.018	260	0.12	2300
Mn (ppm)	NR	NR	-	NR	-	NR	-
Mo (ppm)	18	NR	-	25	39	16	-11
Ni (ppm)	34	NR	-	48	41	78	130
Pb (ppm)	219	NR	-	183	-16	62	-72
Sb (ppm)	NR	NR	-	NR	-	NR	-
Se (ppm)	2	NR	-	2	0.0	2	0.0
Sr (ppm)	NR	NR	-	NR	-	NR	-
V (ppm)	276	NR	-	336	22	278	0.7
Zn (ppm)	1870	NR	-	1790	-4.3	2800	50

Notes: NR - Not Reported

[1] Relative to B-CP

Table 5-6: ELR- Chemical Composition of RM5 for All Burns

Property	B-CP	C&D		VF		Soy	
	Value	Value	% Diff.[1]	Value	% Diff.[1]	Value	% Diff.[1]
Al_2O_3 (wt. %)	0.89	NR	-	1.42	59	3.41	280
CaO (wt. %)	0.12	NR	-	0.35	200	0.53	350
Fe_2O_3 (wt. %)	0.28	NR	-	1.32	370	1.77	540
K_2O (wt. %)	0.09	NR	-	0.13	49	0.30	250
MgO (wt. %)	0.01	NR	-	0.22	1900	0.13	1100
Na_2O (wt. %)	0.00	NR	-	0.03	-	0.05	-
P_2O_5 (wt. %)	0.00	NR	-	0.02	-	0.07	-
SiO_2 (wt. %)	98.1	NR	-	95.6	-2.6	92.5	-5.7
SO_3 (wt. %)	0.16	NR	-	0.05	-69	0.01	-94
TiO_2 (wt. %)	0.12	NR	-	0.19	59	0.24	100
Moisture (wt. %)	20.0	NR	-	3.45	-83	4.86	-76
LOI (wt. %)	0.13	NR	-	0.60	370	0.90	590
As (ppm)	9	NR	-	12	33	18	100
Ba (ppm)	NR	NR	-	NR	-	NR	-
Cd (ppm)	6	NR	-	6	0.0	6	0.0
Cl (ppm)	83	NR	-	52	-37	142	71
Co (ppm)	6	NR	-	6	0.0	6	0.0
Cr (ppm)	11	NR	-	41	270	51	360
Cu (ppm)	34	NR	-	32	-5.9	123	260
Hg (ppm)	0.005	NR	-	0.005	0.0	0.07	1300
Mn (ppm)	NR	NR	-	NR	-	NR	-
Mo (ppm)	5	NR	-	5	0.0	5	0.0
Ni (ppm)	3	NR	-	3	0.0	35	1100
Pb (ppm)	7	NR	-	5	-29	25	257
Sb (ppm)	NR	NR	-	NR	-	NR	-
Se (ppm)	2	NR	-	2	0.0	2	0.0
Sr (ppm)	NR	NR	-	NR	-	NR	-
V (ppm)	8	NR	-	23	190	17	110
Zn (ppm)	8	NR	-	60	650	43	440

Notes: NR - Not Reported

[1] Relative to B-CP

Table 5-7: ELR- Chemical Composition of RM6 for All Burns

Property	**B-CP**	**C&D**		**VF**		**Soy**	
	Value	Value	% Diff.[1]	Value	% Diff.[1]	Value	% Diff.[1]
Al_2O_3 (wt. %)	0.08	0.29	270	0.15	97	0.26	240
CaO (wt. %)	17.2	32.5	88.8	37.9	120	32.8	90
Fe_2O_3 (wt. %)	0.04	0.16	320	0.06	72	0.17	350
K_2O (wt. %)	0.00	0.03	660	0.02	341	0.02	290
MgO (wt. %)	0.12	0.27	120.0	0.26	113	0.31	150
Na_2O (wt. %)	0.00	0.00	-	0.00	-	0.02	-
P_2O_5 (wt. %)	0.00	0.02	280.0	0.01	121	0.01	93
SiO_2 (wt. %)	0.30	0.73	140.0	0.55	81	0.44	46
SO_3 (wt. %)	23.2	44.8	93.6	50.9	120	44.9	94
TiO_2 (wt. %)	0.00	0.00	-	0.00	-	0.00	-
Moisture (wt. %)	24.1	6.93	-71	18.7	-22	0.00	-100
LOI (wt. %)	59.1	21.1	-64	10.1	-83	21.1	-64
As (ppm)	13	5	-62	5	-62	5.00	-62
Ba (ppm)	NR	NR	-	NR	-	NR	-
Cd (ppm)	6	6	0.0	6	0.0	6.00	0.0
Cl (ppm)	58	28	-52	25	-57	68.0	17
Co (ppm)	6	6	0.0	6	0.0	6.00	0.0
Cr (ppm)	5	16	220	34	590	23.20	360
Cu (ppm)	19	5	-74	5	-74	36.0	89
Hg (ppm)	0.008	0.05	550	0.16	1900	0.16	1900
Mn (ppm)	NR	NR	-	NR	-	NR	-
Mo (ppm)	5	5	0.0	5	0.0	5.00	0.0
Ni (ppm)	3	3	0.0	3	0.0	13.0	330
Pb (ppm)	5	5	0.0	14	180	5.00	0.0
Sb (ppm)	NR	NR	-	NR	-	NR	-
Se (ppm)	17	16	-5.9	18	5.9	19.0	12
Sr (ppm)	NR	NR	-	NR	-	NR	-
V (ppm)	5	5	0.0	5	0.0	5.00	0.0
Zn (ppm)	5	12	140	6	20	23.0	360

Notes: NR - Not Reported

[1] Relative to B-CP

5.4.2 Chemical Composition of Kiln Feed

Kiln feed comprises specific proportions of ground raw materials and recycled cement kiln dust and is the primary process input into the kiln system. Changes in the chemical composition of any of the raw material can influence the chemical composition of the kiln feed. Throughout this study, kiln feed was sampled twice per day in order to obtain the average chemical composition. The average percent by weight (*Avg. wt. %*) and the percent difference relative to the baseline (*%Diff.*) for all burns collected by the cement plant are tabulated in Table 5-8. Summary statistics are not presented for the kiln feed due to the limited number of samples collected.

The percent differences between the trial burns and the baseline burn as reported by the cement plant are shown in Figure 5-2**Error! Reference source not found.**. Most of the parameters are seen to be relatively consistent with the baseline conditions. The greatest difference is seen in the increase of SO_3 content over all the burns conducted. This increase may be attributed to the significantly higher sulfite contents of the cement kiln dust for each trial burn compared to the baseline. The SO_3 was elevated in the cement kiln dust over 400 % for all the trial burns. These results are shown in Figure 5-3 B.

The results from the external laboratory are presented in Table 5-9. Compared to the cement laboratory results, the external lab results showed more variability in most compounds in the kiln feed throughout this study. The sulfite levels reported by the external laboratory for the trial burns are similar to the cement plant laboratory findings. Hg and Cr were increased over all burns. Pb, Cu, and Zn varied over all the burns. Cl and V were decreased over the trial burns compared to the baseline's results.

Table 5-8: CPR – Kiln Feed Compositions for All Burns

Property	**B-CP**	**C&D**		**VF 5%**		**VF 10%**		**VF 15%**		**Soy**	
	Average (wt. %)	**Average (wt. %)**	**% Diff.**	**Average (wt. %)**	**% Diff.**	**Average (wt. %)**	**% Diff.**	**Average (wt. %)**	**% Diff.**	**Average (wt. %)**	**% Diff.**
Al_2O_3	3.12	3.29	5.46	3.09	-0.96	3.00	-3.65	2.98	-4.44	3.18	2.17
CaO	42.52	43.27	1.78	42.69	0.41	42.91	0.93	42.88	0.86	42.59	0.17
Fe_2O_3	1.91	1.84	-3.73	1.92	0.59	1.86	-2.66	1.89	-1.46	1.90	-0.59
K_2O	0.29	0.35	19.12	0.31	8.03	0.31	6.69	0.31	5.51	0.28	-4.49
MgO	2.30	2.03	-11.50	2.14	-6.91	2.18	-5.17	2.34	1.76	2.31	0.63
Na_2O	0.05	0.05	-2.86	0.05	3.57	0.05	0.50	0.06	10.00	0.05	-6.67
Na_2O_{eq}	0.24	0.28	15.49	0.26	6.77	0.25	3.69	0.26	6.44	0.23	-4.94
SiO_2	13.56	13.34	-1.63	13.12	-3.27	13.03	-3.90	13.12	-3.25	13.18	-2.82
SO_3	0.15	0.21	43.27	0.17	13.65	0.19	27.63	0.21	39.66	0.19	30.13
LOI	35.87	36.27	1.10	36.05	0.49	36.15	0.77	36.21	0.93	35.95	0.21

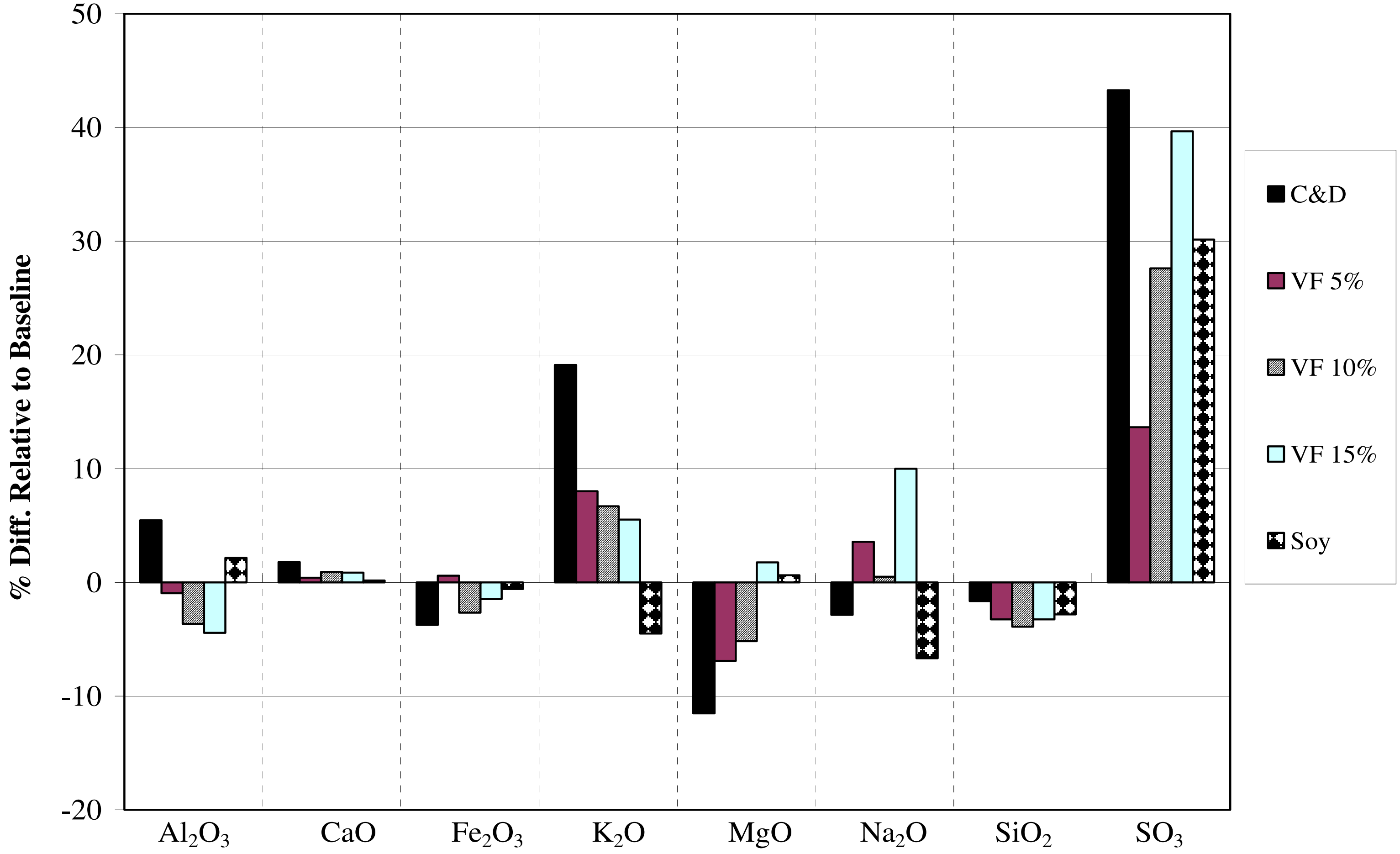

Figure 5-2: CPR – Percent Difference in Kiln Feed Composition Relative to Baseline

Table 5-9 A: ELR – Kiln Feed Compositions and Percentage Difference Relative to Baseline for All Burns

Property	B-CP	C&D		Soy	
	Value (wt. %)	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.
Al_2O_3	3.1	4.6	48.7	3.3	7.5
CaO	42.1	56.7	34.7	41.7	-1.1
Fe_2O_3 (wt. %)	1.9	2.6	34.9	1.9	2.2
K_2O	0.3	0.5	74.1	0.3	4.9
MgO	2.3	2.9	24.5	2.5	7.4
Na_2O	0.0	0.0	12.8	0.0	-16.5
P_2O_5	0.0	0.1	89.5	0.0	40.2
SiO_2	13.8	18.5	34.9	13.7	-0.7
SO_3	0.3	0.2	-16.2	0.2	-38.0
TiO_2	0.1	0.2	35.4	0.2	18.4
Moisture	0.3	0.2	-23.4	0.0	-100.0
LOI	36.0	13.6	-62.2	36.1	0.4
Property	**Value (ppm)**	**Value (ppm)**	**% Diff.**	**Value (wt. %)**	**% Diff.**
As	19.0	5.0	-73.7	13.0	-31.6
Ba	NR	NR	-	NR	-
Cd	6.0	6.0	0.0	6.0	0.0
Cl	110.0	77.0	-30.0	68.0	-38.2
Co	13.0	14.0	7.7	6.0	-53.8
Cr	44.0	58.0	31.8	73.0	65.9
Cu	42.0	5.0	-88.1	69.0	64.3
Hg	0.0	0.0	880.0	0.2	3480.0
Mn	NR	NR	-	NR	-
Mo	9.0	5.0	-44.4	5.0	-44.4
Ni	13.0	16.0	23.1	31.0	138.5
Pb	23.0	81.0	252.2	74.0	221.7
Sb	NR	NR	-	NR	-
Se	2.0	2.0	0.0	2.0	0.0
Sr	NR	NR	-	NR	-
V	51.0	43.0	-15.7	37.0	-27.5
Zn	61.0	65.0	6.6	115.0	88.5

NR – Not Reported

Table 5-9 B: ELR – Kiln Feed Compositions and Percentage Difference Relative to Baseline for All Burns

Property	**B-CP**	**VF 5%**		**VF 10%**		**VF 15%**	
	Value (wt. %)	**Value (wt. %)**	**% Diff.**	**Value (wt. %)**	**% Diff.**	**Value (wt. %)**	**% Diff.**
Al_2O_3	3.1	3.1	-0.2	3.0	-1.8	3.0	-3.3
CaO	42.1	42.5	1.1	42.5	0.9	42.4	0.8
Fe_2O_3 (wt. %)	1.9	1.9	1.0	1.9	0.7	1.9	0.4
K_2O	0.3	0.3	6.4	0.3	7.7	0.3	8.9
MgO	2.3	2.3	-1.8	2.3	1.3	2.4	4.4
Na_2O	0.0	0.0	-0.6	0.0	-17.2	0.0	-33.7
P_2O_5	0.0	0.0	39.1	0.0	29.2	0.0	19.3
SiO_2	13.8	13.4	-2.4	13.4	-2.3	13.5	-2.1
SO_3	0.3	0.2	-26.7	0.2	-27.8	0.2	-29.0
TiO_2	0.1	0.2	8.4	0.2	8.4	0.2	8.4
Moisture	0.3	0.2	-46.5	0.2	-42.4	0.2	-38.3
LOI	36.0	36.0	-0.1	36.0	0.0	36.0	0.0
Property	**Value (ppm)**	**Value (ppm)**	**% Diff.**	**Value (ppm)**	**% Diff.**	**Value (wt. %)**	**% Diff.**
As	19.0	35.0	84.2	30.0	57.9	25.0	31.6
Ba	NR	NR	-	NR	-	NR	-
Cd	6.0	6.0	0.0	6.0	0.0	6.0	0.0
Cl	110.0	115.0	4.5	98.0	-10.9	81.0	-26.4
Co	13.0	11.0	-15.4	9.5	-26.9	8.0	-38.5
Cr	44.0	61.5	39.7	58.0	31.9	54.6	24.1
Cu	42.0	47.0	11.9	43.5	3.6	40.0	-4.8
Hg	0.0	0.0	160.0	0.0	150.0	0.0	140.0
Mn	NR	NR	-	NR	-	NR	-
Mo	9.0	5.0	-44.4	6.0	-33.3	6.0	-33.3
Ni	13.0	10.0	-23.1	10.5	-19.2	11.0	-15.4
Pb	23.0	5.0	-78.3	20.0	-13.0	20.0	-13.0
Sb	NR	NR	-	NR	-	NR	-
Se	2.0	2.0	0.0	2.0	0.0	2.0	0.0
Sr	NR	NR	-	NR	-	NR	-
V	51.0	48.0	-5.9	50.0	-2.0	52.0	2.0
Zn	61.0	54.0	-11.5	58.0	-4.9	62.0	1.6

NR – Not Reported

5.4.3 Chemical Composition of Cement Kiln Dust

Dust collected throughout the pyroprocess is known as cement kiln dust (CKD). Since CKD is primarily comprised of calcinated and partially calcinated kiln feed, it is often recycled into the kiln feed. During this study, CKD samples were collected twice daily and tested as discrete specimens by both chemical analysis laboratories. Statistical analysis was not conducted for the cement kiln dust due to an insufficient number of samples collected.

The average weights and percent difference relative to the baseline for each CKD parameter collected over the duration of this study are presented in Table 5-10. The loss on ignition (LOI) and moisture content parameters of the CKD specimens were not determined by the cement plant. A graphical representation of the percent difference is shown in Figure 5-3. From this figure, it can be seen that most of the parameters show consistency with the baseline burn. The MgO and SO_3 contents are increased from the baseline burn. Both the laboratories show an increase in MgO for the VF 15% burn. RM5 also showed elevated MgO contents relative to the baseline conditions. Similar to the kiln feed, the SO_3 content is drastically elevated over the baseline. External laboratory results also show a significant SO_3 increase over baseline conditions.

The External laboratory results are shown in Table 5-11. All the burns exhibited significant decreases in Hg, Cl, and Pb. The results from Cu, Cr, V, and Zn varied greatly for all the trial burns. Some of the same fluctuations were noticed with the kiln feed as well. This is expected due to typical incorporation of CKD into the kiln feed.

Table 5-10: CPR – CKD Compositions for All Burns

Property	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Average (wt. %)	Average (wt. %)	% Diff.	Average (wt. %)	% Diff.	Average (wt. %)	% Diff.	Average (wt. %)	% Diff.	Average (wt. %)	% Diff.
Al_2O_3	3.70	3.55	-3.92	3.47	-6.06	3.60	-2.68	3.50	-5.32	3.86	4.42
CaO	44.1	46.8	6.25	46.3	5.13	45.6	3.56	45.8	4.02	44.7	1.55
Fe_2O_3	2.03	1.80	-11.2	1.87	-7.5	1.91	-5.93	1.87	-7.82	1.95	-3.54
K_2O	0.38	0.43	11.8	0.40	4.15	0.42	9.39	0.44	15.3	0.40	3.93
MgO	1.44	1.50	4.05	1.61	11.5	1.66	14.8	1.89	31.1	1.63	12.8
Na_2O	0.09	0.09	3.70	0.10	8.33	0.10	13.9	0.10	14.8	0.08	-7.41
Na_2O_{eq}	11.8	11.0	-7.44	11.2	-5.41	11.2	-5.41	11.5	-2.66	10.9	-8.17
SiO_2	0.13	0.97	645	0.83	537	0.82	527	1.13	769	0.68	421

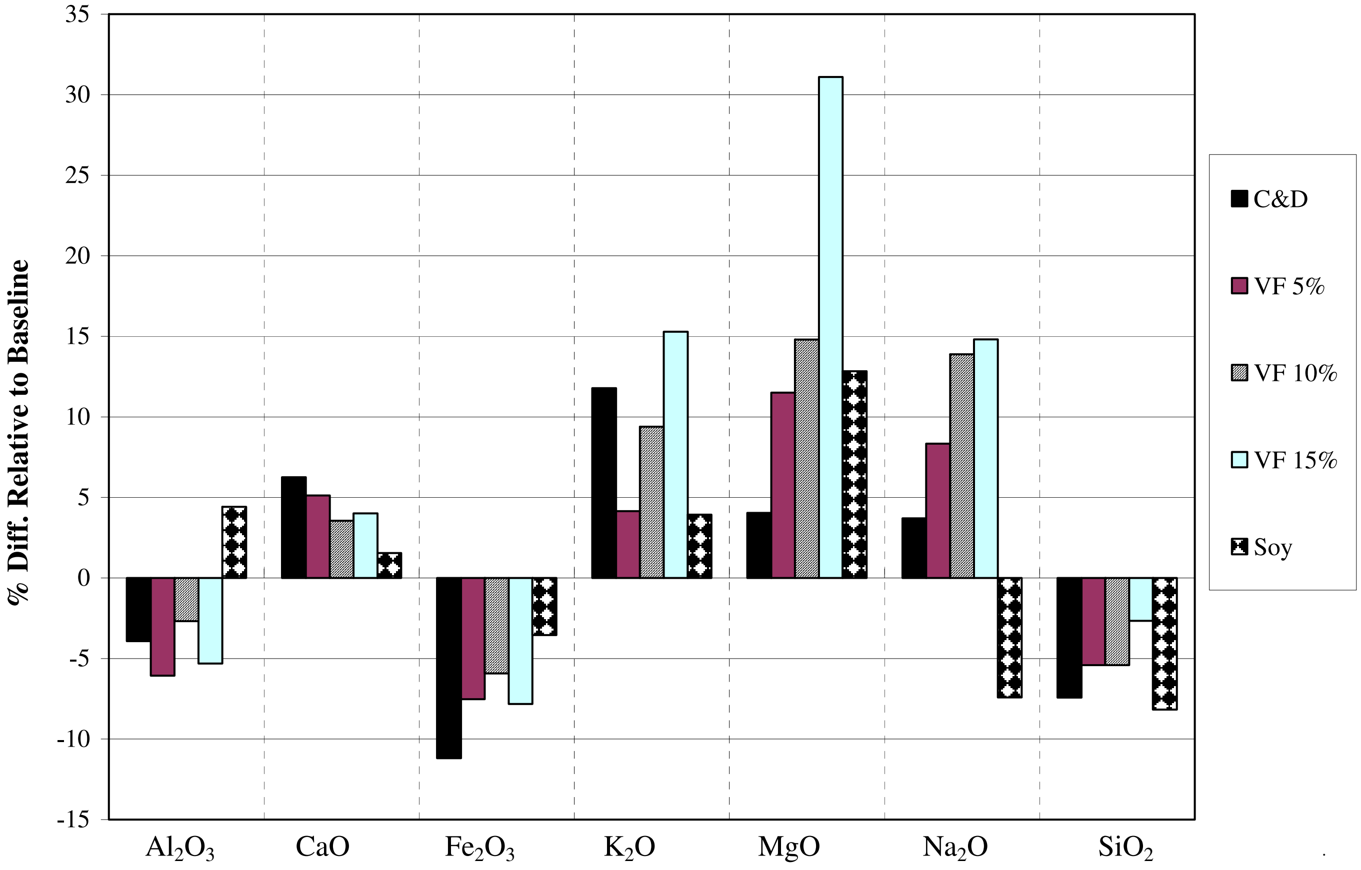

Figure 5-3 A: CPR – CKD Compositions Relative to Baseline for All Burns

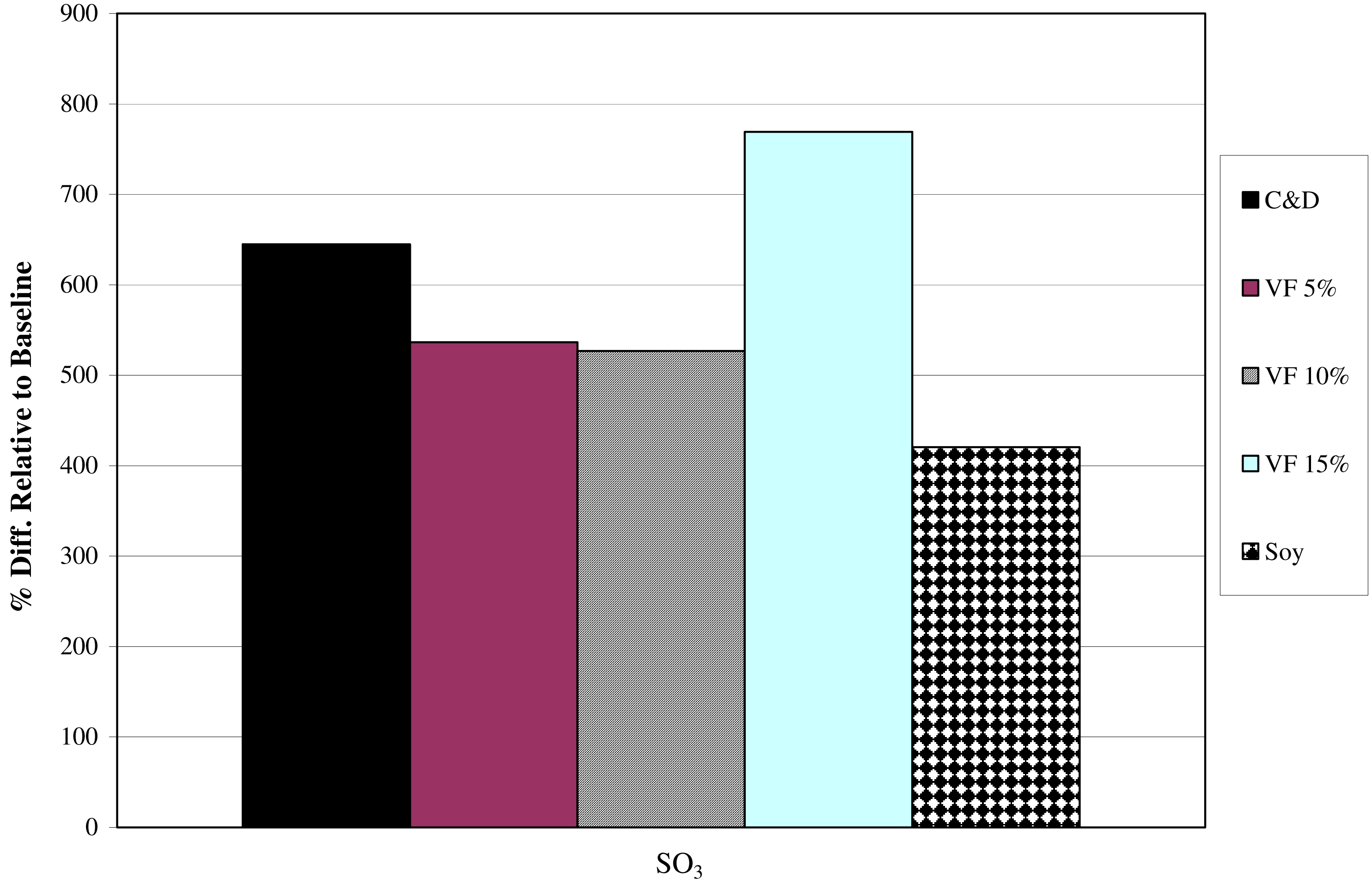

Figure 5-3 B: CPR – CKD Compositions Relative to Baseline for All Burns

Table 5-11 A: ELR – CKD Compositions and Percentage Difference to Baseline for All Burns

Parameter	B-CP	C&D		Soy	
	Value (wt. %)	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.
Al_2O_3 (wt. %)	3.90	3.78	-2.88	4.07	4.54
CaO (wt. %)	43.9	46.0	4.68	44.3	0.94
Fe_2O_3 (wt. %)	1.97	1.83	-7.00	1.94	-1.35
K_2O (wt. %)	0.37	0.36	-2.29	0.35	-4.01
MgO (wt. %)	1.45	1.60	10.1	1.84	27.2
Na_2O (wt. %)	0.05	0.06	21.8	0.04	-26.9
P_2O_5 (wt. %)	0.04	0.13	191	0.06	26.1
SiO_2 (wt. %)	11.6	11.3	-2.95	11.6	-0.28
SO_3 (wt. %)	0.21	0.97	363	0.61	192
TiO_2 (wt. %)	0.19	0.16	-16.06	0.21	11.04
Moisture (wt. %)	0.49	0.18	-63.9	0.10	-78.8
LOI (wt. %)	36.2	33.7	-6.77	34.8	-3.71
As (ppm)	26.7	37.8	41.8	42.2	58.1
Ba (ppm)	NR	NR	-	NR	-
Cd (ppm)	6.00	6.00	0.00	6.00	0.00
Cl (ppm)	229	166	-27.5	117	-48.9
Co (ppm)	11.0	15.0	36.4	12.0	9.09
Cr (ppm)	51.2	87.6	71.2	55.6	8.70
Cu (ppm)	44.5	24.8	-44.4	62.2	39.7
Hg (ppm)	0.51	0.05	-90.5	0.21	-59.4
Mn (ppm)	NR	NR	-	NR	-
Mo (ppm)	6.67	5.00	-25.0	5.00	-25.0
Ni (ppm)	15.7	24.8	58.3	30.0	91.5
Pb (ppm)	46.5	21.8	-53.2	35.8	-23.0
Sb (ppm)	NR	NR	-	NR	-
Se (ppm)	2.00	2.00	0.00	2.00	0.00
Sr (ppm)	NR	NR	-	NR	-
V (ppm)	61.3	65.4	6.63	50.0	-18.5
Zn (ppm)	87.2	77.0	-11.7	124	42.3

Table 5-11 B: ELR – CKD Compositions and Percentage Difference to Baseline for All Burns

Parameter	B-CP	VF 5%		VF 10%		VF 15%	
	Value (wt. %)	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.
Al_2O_3 (wt. %)	3.9	3.78	-2.9	3.92	0.5	3.88	-0.5
CaO (wt. %)	43.9	47.1	7.1	47.40	88.9	46.84	6.6
Fe_2O_3 (wt. %)	2.0	1.86	-5.3	1.93	-1.0	1.93	-2.0
K_2O (wt. %)	0.4	0.36	-1.3	0.42	1.3	0.45	20.7
MgO (wt. %)	1.4	1.60	10.1	1.75	7.6	1.98	36.4
Na_2O (wt. %)	0.0	0.05	-3.9	0.05	0.0	0.05	11.2
P_2O_5 (wt. %)	0.0	0.05	15.5	0.05	0.2	0.05	16.8
SiO_2 (wt. %)	11.6	11.05	-5.0	10.98	-16.6	11.61	-0.2
SO_3 (wt. %)	0.2	0.81	285	1.04	21.3	1.14	444
TiO_2 (wt. %)	0.2	0.19	-0.5	0.19	0.0	0.20	5.3
Moisture (wt. %)	0.5	0.11	-77.6	0.08	-10.5	0.06	-87.7
LOI (wt. %)	36.2	33.1	-8.5	32.2	-102	31.8	-12.1
As (ppm)	26.7	38	43.4	42	394	45	67.5
Ba (ppm)	NR	NR	-	NR	-	NR	-
Cd (ppm)	6.0	6	0.0	6	0.0	6	0.0
Cl (ppm)	229	192	-16.1	245	415	173	-24.3
Co (ppm)	11.0	14	27.3	12	25.7	12	12.1
Cr (ppm)	51.2	71	39.2	61	257	71	38.4
Cu (ppm)	45	70	57.3	37	-183.9	50	13.1
Hg (ppm)	0.5	0	-89.2	0	-12.0	0.02	-95.5
Mn (ppm)	NR	NR	-	NR	-	NR	-
Mo (ppm)	6.7	5	-25.0	8	34.2	8	12.5
Ni (ppm)	15.7	17	8.5	23	180	54	245
Pb (ppm)	46.5	26	-43.5	32	-381	28	-40.9
Sb (ppm)	NR	NR	-	NR	-	NR	-
Se (ppm)	2.0	2	0.0	2	0.0	2	0.0
Sr (ppm)	NR	NR	-	NR	-	NR	-
V (ppm)	61.3	61	-0.1	70	222	274	346
Zn (ppm)	87.2	65	-25.1	79	-218	61	-29.6

5.4.4 Fuel Properties

In this section, chemical compositions and properties of each fuel will be presented and evaluated. Throughout the duration of the study, fuel samples were taken according to the sampling plan defined in Table 4-1. The specifications for the as-received alternative fuels listed below were targeted by this particular cement plant during this study (Akkapeddi et al. 2008).

1. Energy value ≥ 5,000 BTU/lb,
2. Chlorine content ≤ 0.2 %,
3. Sulfur content ≤ 2.0 %
4. Nitrogen content ≤ 1.4 %,
5. Moisture content ≤ 14%, and
6. Ash content ≤ 18 %.

The average heating values and percent utilization are shown in Table 5-12. The as-received heating value is calculated from the moisture content of the material and the dry heating value provided by the external laboratory. It should be noted that the woodchips utilized in the variable feed trials do not meet the minimum energy or moisture content requirements specified in the list above. This is due to the woodchip's high moisture content. With a lesser moisture content, research has proven that higher heating values can be achieved (Maker 2004). The Construction and demolition waste and soybean seed fuels met the target fuel specifications listed above.

Table 5-12: ELR – Fuel Heating Values and Percent Utilization

Fuel	B-CP	C&D	VF 5%	VF 10%	VF 15%	Soy
	Avg. (BTU/lb)[1]	**Avg. (BTU/lb)[1]**	**Avg. (BTU/lb)[1]**	**Avg. (BTU/lb)[1]**	**Avg. (BTU/lb)[1]**	**Avg. (BTU/lb)[1]**
Coal	12090	11860	10860	10840	10820	11460
Plastics	10150	8855	9865	10430	10720	10780
Alt. Fuel	NA	6033	4625	4750	4850	9150
	Utilization (%)[2]	**Utilization (%)[2]**	**Utilization (%)[2]**	**Utilization (%)[2]**	**Utilization (%)[2]**	**Utilization (%)[2]**
Coal	89	84	80	73	70	77
Plastics	11	12	15	15	15	16
Alt. Fuel	0	5	5	12	15	7

Notes: [1] Based on as-received heating values

[2] Utilization % based on average fuel energy as reported from the cement plant

NA – Not applicable

Heating values for each fuel are graphically presented in Figure 5-4. The bar labeled *Alt. Fuel* represents the respective alternative fuel utilized in each trial. During the baseline burn, the only fuels utilized were coal and plastics, thus no alternative fuel bar is shown. Throughout this study, coal and plastics are considered traditional fuels. Coal possessed the highest energy content followed closely by the plastic blend for the traditional fuels. During the variable feed and the soybean seed burns, coal and plastics nearly shared the same energy values. The soybean seeds possessed the highest energy content for the alternative fuels followed by the construction and demolition waste and finally, the woodchips.

The fuel utilization for each burn in this study is graphically presented in Figure 5-5. The percent utilization for each fuel was obtained from average cement plant production data. It should be noted that the percent utilization of the alternative fuel during the variable feed trials increases approximately 5 % during each stage. The waste plastic utilization for all trial burns was held fairly constant. Coal was the most utilized fuel during all burns. The plastics and the trial fuels accounted for approximately 15 – 30 % of the energy used for the pyroprocess.

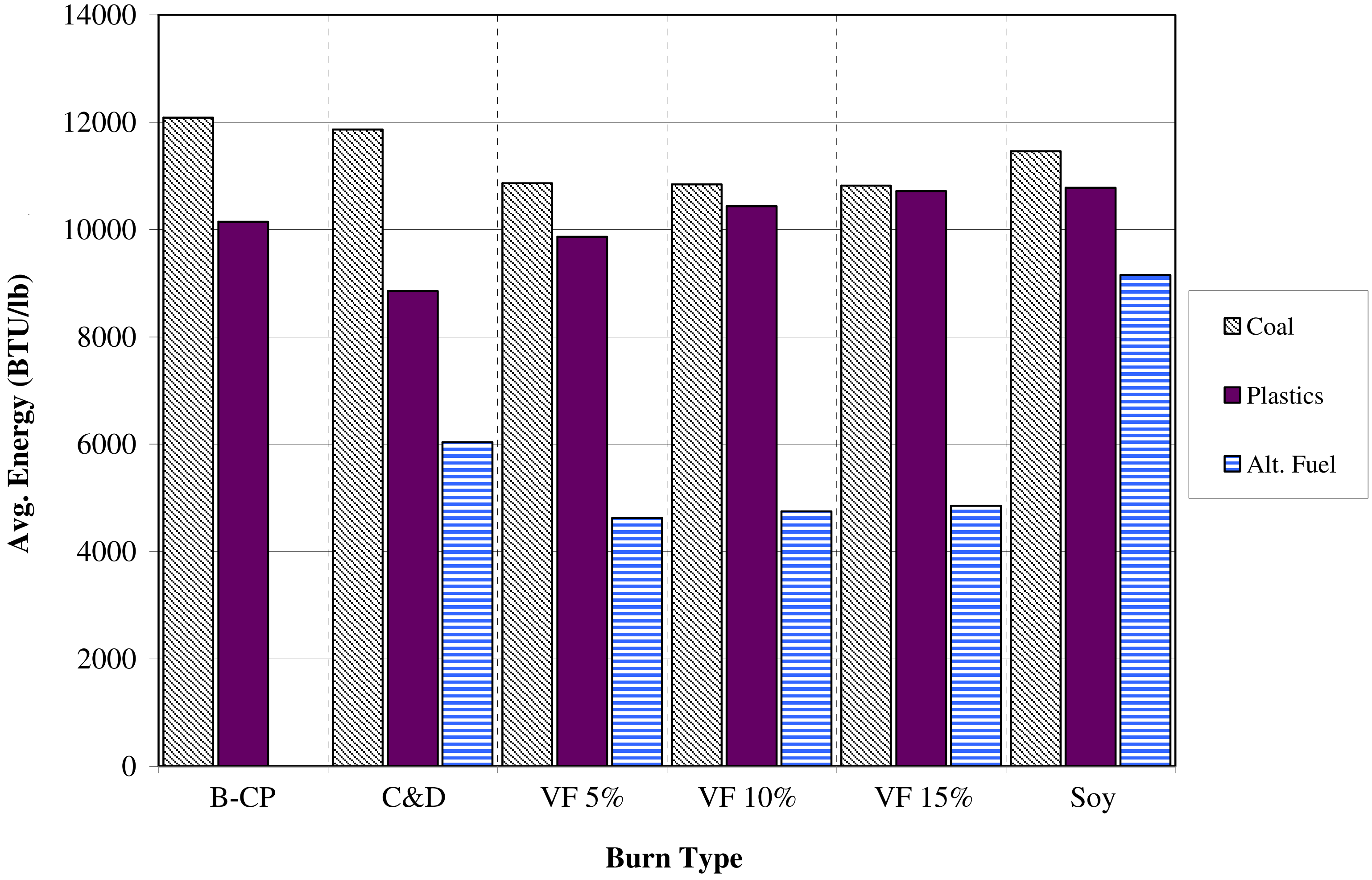

Figure 5-4: Fuel Heating Values Based on As-Received Conditions

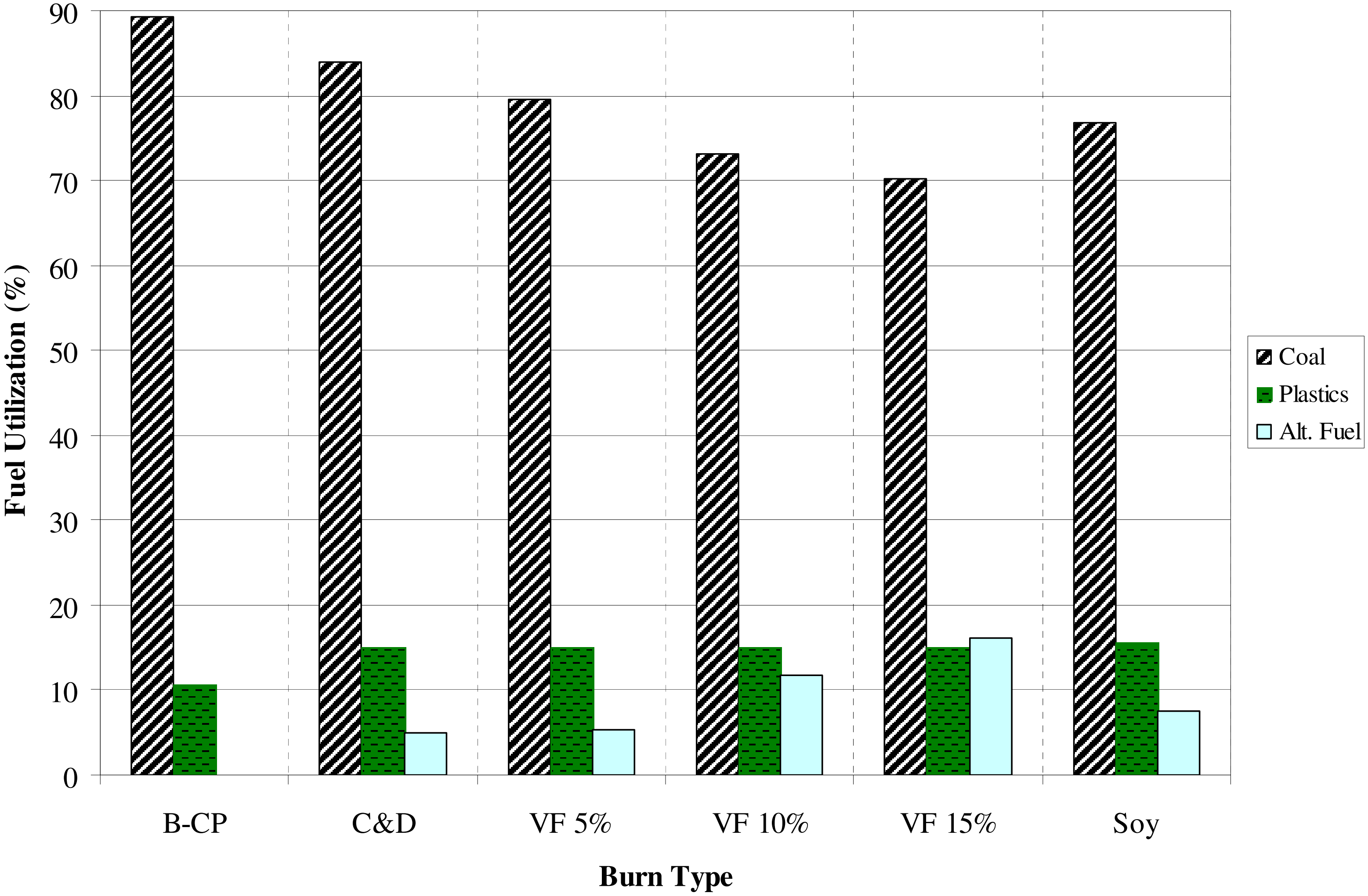

Figure 5-5: CPR – Fuel Utilization for All Burns

5.4.4.1 Coal

Pulverized coal was the most heavily utilized fuel throughout the study. Coal samples were taken twice daily during each burn period. Twenty-four-hour composite specimens were prepared for chemical analysis by the external laboratory. As previously stated, the external laboratory conducted proximate, ultimate, and combustion analyses as well as determined each fuel's standard parameters.

The results from the proximate, ultimate, and combustion analyses of coal are tabulated in Table 5-13. The proximate analysis of coal for all burns appeared to remain fairly consistent except for the moisture content, which possessed a relatively high percent difference for each trial burn compared to the baseline. The results from the ultimate analysis remained consistent for all parameters except for oxygen. Oxygen fluctuated significantly compared to the baseline for all burns. The oxygen content for coal in the construction and demolition waste was lower than the baseline and significantly higher for all three variable feed trials. Sulfur was also increased in the construction and demolition waste burn's coal, but remained fairly constant throughout the remainder of the trial burns compared to the baseline's results. The heating values for the coal remained within 10 % of the baseline's heating values for all trial burns.

Table 5-13 A: ELR – Proximate, Ultimate, and Combustion Analysis of Coal for All Burns

Test	**Parameter**	**B-CP**	**C&D**		**Soy**	
		Value (wt. %)	**Value (wt. %)**	**% Diff.**	**Value (wt. %)**	**% Diff.**
Proximate Analysis	**Ash**	19.5	20.8	6.6	22.5	16
	Fixed Carbon	50.8	50.5	-0.6	49.0	-3.7
	Moisture [1]	1.09	1.49	37	1.17	7.3
	Volatile Matter	29.7	28.7	-3.3	28.6	-3.8
Ultimate Analysis	**Carbon**	70.1	68.3	-2.6	66.8	-4.8
	Hydrogen	3.95	3.62	-8.4	3.48	-12
	Nitrogen	1.34	1.46	9.0	1.43	6.7
	Oxygen	1.52	0.89	-41	1.70	12
	Sulfur	3.58	4.96	39	4.10	15
Heat Value [2] **(BTU/lb)**		12,200	12,000	-1.5	11,600	-5.1

Notes: [1] As Received [2] Dry Basis

Table 5-13 B: ELR – Proximate, Ultimate, and Combustion Analysis of Coal for All Burns

Test	Parameter	B-CP	VF 5%		VF 10%		VF 15%	
		Value (wt. %)	**Value (wt. %)**	**% Diff.**	**Value (wt. %)**	**% Diff.**	**Value (wt. %)**	**% Diff.**
Proximate Analysis	**Ash**	19.5	26.8	37.9	26.8	37.5	26.7	37.1
	Fixed Carbon	50.8	47.0	-7.5	47.4	-6.8	47.8	-6.0
	Moisture [1]	1.09	1.73	58.7	1.80	65.1	1.87	71.6
	Volatile Matter	29.7	26.2	-11.9	25.8	-13.0	25.5	-14.0
Ultimate Analysis	**Carbon**	70.1	61.7	-12.0	62.3	-11.2	62.9	-10.4
	Hydrogen	3.95	3.25	-17.7	3.23	-18.4	3.20	-19.0
	Nitrogen	1.34	1.32	-1.5	1.32	-1.5	1.32	-1.5
	Oxygen	1.52	3.33	119.1	3.07	102.0	2.81	84.9
	Sulfur	3.58	3.54	-1.1	3.32	-7.3	3.10	-13.4
Heat Value [2] **(BTU/lb)**		12,200	11,100	-9.5	11,000	-9.7	11,000	-9.8

Notes: [1] As Received [2] Dry Basis

The results from the standard parameters analysis are shown in Table 5-14. The coal's P_2O_5 content increased for all burns compared to the baseline. The SO_3 content decreased for all burns compared to the baseline. The arsenic (As) concentration of the coal increased in the construction and demolition waste and soybean trials and decreased in all the variable feed trials. The Hg concentration of the coal was reduced in all trials except for the soybean burn in which it was significantly increased. The coal's Pb concentration also increased in the soybean trial compared to the baseline's results.

Table 5-14 A: ELR – Standard Parameters of Coal for All Burns

Test	Property	B-CP	C&D		Soy	
		Value (wt. %)	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.
Standard Parameters	Al_2O_3	14.2	13.9	-2.1	16.9	19
	CaO	11.3	10.5	-6.9	7.77	-31
	Fe_2O_3	23.2	28.2	22	25.4	9.7
	K_2O	2.08	1.93	-7.5	2.29	10.0
	MgO	1.07	1.03	-3.9	1.05	-2.4
	Na_2O	0.24	0.23	-3.4	0.21	-12
	P_2O_5	0.07	0.15	116	0.13	86
	SiO_2	32.6	31.2	-4.0	35.2	8.3
	SO_3	14.3	11.8	-17	10.1	-29
	TiO_2	0.67	0.65	-3.7	0.68	1.9
	Property	**Value (ppm)**	**Value (ppm)**	**% Diff.**	**Value (ppm)**	**% Diff.**
	As	948	1,320	40	1,790	89
	Cd	6	6	0	6	0
	Cl	142	138	-3	145	2
	Co	62	61	-2	46	-26
	Cr	111	144	30	99	-11
	Cu	290	251	-13	223	-23
	Hg	0	0	-32	0	66
	Mo	68	82	21	55	-19
	Ni	118	144	22	112	-5
	Pb	73	62	-15	109	49
	Se	2	2	0	3	50
	V	266	249	-6	248	-7
	Zn	161	211	31	161	0

Table 5-14 B: ELR – Standard Parameters of Coal for All Burns

Test	Property	B-CP	VF 5 %		VF 10 %		VF 15 %	
		Value (wt. %)	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.
Standard Parameters	Al_2O_3	14.2	17.7	25	17.6	24	17.4	23
	CaO	11.3	10.2	-9.7	9.75	-14	9.27	-18
	Fe_2O_3	23.2	16.3	-30	17.3	-25	18.4	-20
	K_2O	2.08	2.52	21	2.46	18	2.39	15
	MgO	1.07	1.30	21.1	1.26	17	1.22	13
	Na_2O	0.24	0.24	-1.9	0.23	-2.5	0.23	-3.2
	P_2O_5	0.07	0.14	99	0.14	97	0.14	96
	SiO_2	32.6	41.8	28	41.4	27	41.1	26
	SO_3	14.31	8.56	-40	8.54	-40	8.53	-40
	TiO_2	0.67	0.90	34	0.90	34	0.90	34
	Property	**Value (ppm)**	**Value (ppm)**	**% Diff.**	**Value (ppm)**	**% Diff.**	**Value (ppm)**	**% Diff.**
	As	948	482	-49	559	-41	635	-33
	Cd	6	6	0	6	0	6	0
	Cl	142	201	42	208	46	214	51
	Co	62	44	-29	47	-25	49	-21
	Cr	111	121	9	128	15	135	21
	Cu	290	188	-35	219	-25	249	-14
	Hg	0	0	-56	0	-51	0	-46
	Mo	68	38	-44	40	-42	41	-40
	Ni	118	94	-20	124	5	153	30
	Pb	73	70	-4	75	3	80	10
	Se	2	2	0	2	0	2	0
	V	266	246	-8	249	-7	251	-6
	Zn	161	142	-12	143	-11	144	-11

5.4.4.2 Waste Plastics

Waste plastics are typically considered alternative fuels when compared with traditional fuels such as coal, petroleum coke, and natural gas. For this study, however, the cement facility regularly co-fires waste plastics with coal. Therefore, the waste plastics are considered a traditional fuel. The waste plastics were sampled in accordance with the sampling plan shown in Table 4-1. Sampling of this fuel was conducted at a higher frequency in order to pinpoint local variations in the fuel's composition. Discrete specimens were prepared from the samples and analyzed by the external laboratory.

The results of the proximate, ultimate, and combustion analyses for waste plastics from the external laboratory are shown in Table 5-15. Overall, the waste plastic's proximate analysis remained fairly consistent over all burns. The moisture content was the only parameter that was significantly reduced in every trial burn when compared to the baseline's results. The ultimate analysis showed that the nitrogen concentration fluctuated significantly between all the trial burns. Sulfur showed increases between 18 to 169 % for all trial burns compared to the baseline's results. The heating values of the waste plastics remained within 20 % of the baseline for all burns. The plastics burnt during the construction and demolition waste trial burn possessed the lowest heating value for all the trial burns.

Table 5-15 A: ELR – Proximate, Ultimate, and Combustion Analysis of Plastics for All Burns

Test	Parameter	B-CP	C&D		Soy	
		Avg. (wt. %)	Avg. (wt. %)	% Diff.	Avg. (wt. %)	% Diff.
Proximate Analysis	Ash	6.82	5.83	-14.5	5.84	-14.4
	Fixed Carbon	10.2	10.1	-0.8	8.65	-15.1
	Moisture [1]	10.5	2.74	-73.8	2.39	-77.1
	Volatile Matter	83.0	84.1	1.3	85.5	3.0
Ultimate Analysis	Carbon	57.3	48.9	-14.7	60.7	6.1
	Hydrogen	5.92	5.34	-9.7	6.33	6.9
	Nitrogen	0.96	0.08	-91.7	1.16	20.7
	Oxygen	28.9	37.0	28.1	25.7	-10.9
	Sulfur	0.17	0.20	17.9	0.21	24.3
Heat Value [2] (BTU/lb)		11,300	9,100	-20	11,000	-3

Notes: [1] As Received [2] Dry Basis

Table 5-15 B: ELR – Proximate, Ultimate, and Combustion Analysis of Plastics for All Burns

Test	Parameter	B-CP	VF 5%		VF 10%		VF 15%	
		Avg. (wt. %)	Avg. (wt. %)	% Diff.	Avg. (wt. %)	% Diff.	Avg. (wt. %)	% Diff.
Proximate Analysis	Ash	6.82	4.51	-33.8	6.61	-3.1	6.88	0.8
	Fixed Carbon	10.18	10.47	2.9	7.66	-24.8	8.28	-18.7
	Moisture [1]	10.45	3.55	-66.0	1.08	-89.7	0.92	-91.2
	Volatile Matter	83.00	85.01	2.4	85.73	3.3	84.85	2.2
Ultimate Analysis	Carbon	57.25	56.67	-1.0	57.81	1.0	57.80	1.0
	Hydrogen	5.92	5.62	-5.0	5.93	0.3	5.70	-3.7
	Nitrogen	0.96	1.10	14.5	1.70	77.0	1.32	37.3
	Oxygen	28.88	31.87	10.4	27.49	-4.8	27.99	-3.1
	Sulfur	0.17	0.22	31.3	0.46	169.0	0.31	84.1
Heat Value [2] (BTU/lb)		11,300	10,200	-10	10,500	-7	10,800	-5

Notes: [1] As Received [2] Dry Basis

The external laboratory's results for the waste plastic's standard parameter analysis are tabulated in Table 5-16. Throughout all the trial burns, the majority of the standard parameters fluctuated significantly compared with the baseline's results. However, these fluctuations did not appear to substantially influence the final cement composition.

Table 5-16 A: ELR – Standard Parameters of Plastics for All Burns

Test	Parameter	B-CP	C&D		Soy	
		Avg. (wt. %)	Avg. (wt. %)	% Diff.	Avg. (wt. %)	% Diff.
Standard Parameters	Al_2O_3	18.6	30.2	63	7.00	-62
	CaO	23.1	31.2	35	43.5	88
	Fe_2O_3	3.34	1.09	-68	1.01	-70
	K_2O	1.57	1.54	-2	2.57	64
	MgO	4.08	8.63	111	18.3	348
	Na_2O	3.06	2.23	-27	1.62	-47
	P_2O_5	0.54	0.58	7	1.86	245
	SiO_2	34.0	21.3	-37	17.0	-50
	SO_3	3.60	1.08	-70	1.20	-67
	TiO_2	3.09	1.67	-46	5.05	63
	Parameter	**Avg. (ppm)**	**Avg. (ppm)**	**% Diff.**	**Avg. (ppm)**	**% Diff.**
	As	42.8	12.0	-72	8.96	-79
	Cd	6.00	6.00	0	6.00	0
	Cl	1320	220	-83	351	-73
	Co	166	68.7	-59	120	-28
	Cr	968	214	-78	261	-73
	Cu	1340	427	-68	420	-69
	Hg	0.02	0.04	76	0.14	511
	Mo	38.9	21.0	-46	19.5	-50
	Ni	364	114	-69	120	-67
	Pb	1682	147	-91	78.3	-95
	Se	2.00	2.00	0	2.00	0
	V	167	80.9	-52	315	88
	Zn	15500	858	-94	2790	-82

Table 5-16 B: ELR – Standard Parameters of Plastics for All Burns

Test	**Parameter**	**B-CP**	**VF 5%**		**VF 10%**		**VF 15%**	
		Avg. (wt. %)	**Avg. (wt. %)**	**% Diff.**	**Avg. (wt. %)**	**% Diff.**	**Avg. (wt. %)**	**% Diff.**
Standard Parameters	**Al_2O_3**	18.6	15.8	-15	18.2	-2	9.94	-46
	CaO	23.1	32.1	39	39.2	70	39.5	71
	Fe_2O_3	3.34	1.86	-44	2.44	-27	2.58	-23
	K_2O	1.57	0.51	-68	0.38	-76	0.32	-80
	MgO	4.08	8.70	113	12.6	209	19.6	381
	Na_2O	3.06	1.76	-42	0.84	-72	0.98	-68
	P_2O_5	0.54	0.56	4	0.31	-43	0.47	-12
	SiO_2	34.0	25.2	-26	87.7	158	16.6	-51
	SO_3	3.60	4.32	20	3.72	3	2.54	-30
	TiO_2	3.09	2.95	-5	3.09	0	4.08	32
	Parameter	**Avg. (ppm)**	**Avg. (ppm)**	**% Diff.**	**Avg. (ppm)**	**% Diff.**	**Avg. (ppm)**	**% Diff.**
	As	42.8	20.3	-53	8.00	-81	19.5	-54
	Cd	6.00	6.00	0	6.00	0	6.00	0
	Cl	1320	532	-60	228	-83	315	-76
	Co	166	95.7	-42	276	67	268	62
	Cr	968	239	-75	1320	36	879	-9
	Cu	1340	453	-66	445	-67	423	-68
	Hg	0.02	0.06	174	0.02	3	0.01	-34
	Mo	38.9	27.0	-31	48.9	26	33.2	-15
	Ni	364	69.7	-81	480	32	404	11
	Pb	1682	196	-88	123	-93	136	-92
	Se	2.00	2.00	0	2.00	0	2.00	0
	V	167	254	52	177	6	260	56
	Zn	15500	1090	-93	400	-97	1060	-93

5.4.4.3 Construction and Demolition (C & D) Waste Trial Burn

Coal, plastics, and construction and demolition waste were the fuels utilized during the C&D burn. The traditional fuel results were reported in the previous section, but are presented in this section with the alternative fuel results for comparison purposes. Chemical analyses of the construction and demolition waste specimens were conducted by the external laboratory and shown in Tables 5-17 and 5-18.

The results of the proximate and ultimate analyses are tabulated in Table 5-17. The proximate analysis results show that the moisture content of the construction and demolition waste was significantly higher than the coal or the plastic results. This, however, is typical of biomass fuels. Conditioning practices such as drying and covered storage are necessary to control the moisture content in order to maximize the heating value of the fuel. The sulfur content should also be noted in the ultimate analysis results. The construction and demolition waste is primarily composed of biomass and therefore possesses significantly lower sulfur contents when compared to coal. The oxygen content of the construction and demolition waste is also significantly higher than that of the coal.

Table 5-17: ELR – Proximate, Ultimate, and Combustion Analysis of All Fuels from C&D Burn

Test	Parameter	Coal	Plastics	C&D
		Value (wt. %)	Avg. (wt.%)	Avg. (wt.%)
Proximate Analysis	Ash	20.8	5.83	14.5
	Fixed Carbon	50.5	10.1	16.1
	Moisture [1]	1.49	2.74	18.4
	Volatile Matter	28.7	84.1	69.4
Ultimate Analysis	Carbon	68.3	48.9	45.2
	Hydrogen	3.62	5.34	5.03
	Nitrogen	1.46	0.08	1.07
	Oxygen	0.89	37.0	34.1
	Sulfur	4.96	0.20	0.12
Heat Value [2] (BTU/lb)		12,000	9,100	7,400

Notes: [1] As Received [2] Dry Basis

The standard parameters of all the fuels in the construction and demolition burn are listed in Table 5-18. The construction and demolition waste possessed the highest concentrations of P_2O_5, SiO_2, Cl, Cr, and Zn. In excess, these parameters can be problematic to both manufacture and performance of the cement.

Table 5-18: ELR – Standard Parameters of All Fuels from C&D Burn

Test	**Property**	**Coal**	**Plastics**	**C&D**
		Value (wt. %)	**Avg. (wt.%)**	**Avg. (wt.%)**
Standard Parameters	**Al_2O_3 (wt. %)**	13.9	30.2	11.8
	CaO (wt. %)	10.5	31.2	13.4
	Fe_2O_3 (wt. %)	28.2	1.09	4.99
	K_2O (wt. %)	1.93	1.54	2.73
	MgO (wt. %)	1.03	8.63	1.90
	Na_2O (wt. %)	0.23	2.23	2.19
	P_2O_5 (wt. %)	0.15	0.58	0.68
	SiO_2 (wt. %)	31.2	21.3	57.9
	SO_3 (wt. %)	11.8	1.08	3.10
	TiO_2 (wt. %)	0.65	1.67	0.72
	As (ppm)	1320	12.00	43.0
	Cd (ppm)	6.00	6.00	6.00
	Cl (ppm)	138	220	776
	Co (ppm)	61.0	68.7	26.5
	Cr (ppm)	144	214	456
	Cu (ppm)	251	427	397
	Hg (ppm)	0.17	0.04	0.05
	Mo (ppm)	82.0	21.0	18.8
	Ni (ppm)	144	114	169
	Pb (ppm)	62.0	147	108
	Se (ppm)	2.00	2.00	2.00
	V (ppm)	249	80.9	72.3
	Zn (ppm)	211	858	2140

5.4.4.4 *Variable Feed Woodchip Trial Burn (VF)*

Coal, plastics, and woodchips were the fuels utilized during the VF 5%, 10%, and 15% burns. Chemical analyses of the variable feed specimens were conducted by the external laboratory and shown in Tables 5-19 and 5-20.

The results of the proximate and ultimate analyses for each of the variable feed replacement rates are tabulated in Table 5-19. Since the sources of the fuels utilized during this burn did not change, the results of the proximate, ultimate, combustion, and standard parameter analyses fluctuate very little. Therefore, the results reported are 6-day averages.

The proximate analysis results show that the moisture content of the woodchips are significantly higher than the coal or the plastic results. This, however, is typical of biomass fuels. As with most bio-fuels, conditioning practices such as drying and covered storage are necessary to control the moisture content (Greco et al. 2004). The sulfur content should also be noted in the ultimate analysis results. Biomass fuels such as woodchips possess significantly lower sulfur contents than traditional fuel sources. Low sulfur fuels are advantageous because they can reduce sulfur emissions in the pyroprocess. The oxygen content of the woodchips is also significantly higher than the oxygen content observed in the coal.

Table 5-19: ELR – Average Proximate, Ultimate, and Combustion Analysis of All Fuels from VF 5 – 15 % Burns

Test	**Parameter**	**Coal**	**Plastics**	**VF Avg.**
		Value (wt. %)	**Avg. (wt.%)**	**Avg. (wt.%)**
Proximate Analysis	**Ash**	26.8	6.0	11.1
	Fixed Carbon	47.4	8.8	16.7
	Moisture [1]	1.80	1.85	38.10
	Volatile Matter	25.8	85.2	72.2
Ultimate Analysis	**Carbon**	62.3	57.4	47.9
	Hydrogen	3.23	5.75	5.15
	Nitrogen	1.32	1.37	0.29
	Oxygen	3.07	29.12	35.54
	Sulfur	3.32	0.33	0.02
Heat Value [2] **(BTU/lb)**		11,000	10,500	7,670

Notes: [1] As Received [2] Dry Basis

The 6-day averages of the standard parameters of all the fuels in the variable feed woodchip burn are listed in Table 5-20. The woodchip waste possessed the greatest concentration of SiO_2 compared to the traditional fuels. On the other hand, the woodchip waste possessed the lowest concentrations of Al_2O_3, SO_3, and V.

Table 5-20: ELR – Average Standard Parameters for All Fuels from VF 5 – 15 % Burns

Test	Property	Coal	Plastics	VF Avg.
		Value (wt. %)	Avg. (wt.%)	Avg. (wt.%)
Standard Parameters	**Al_2O_3 (wt. %)**	17.6	14.6	8.42
	CaO (wt. %)	9.7	36.9	13.1
	Fe_2O_3 (wt. %)	17.3	2.29	8.80
	K_2O (wt. %)	2.46	0.40	1.81
	MgO (wt. %)	1.26	13.7	2.97
	Na_2O (wt. %)	0.23	1.20	0.56
	P_2O_5 (wt. %)	0.14	0.45	0.22
	SiO_2 (wt. %)	41.4	43.2	62.4
	SO_3 (wt. %)	8.54	3.53	0.36
	TiO_2 (wt. %)	0.90	3.38	0.83
	As (ppm)	559	15.9	58.7
	Cd (ppm)	6.00	6.00	6.00
	Cl (ppm)	208	359	238
	Co (ppm)	46.5	213	72.1
	Cr (ppm)	128	812	792
	Cu (ppm)	219	441	219
	Hg (ppm)	0.12	0.03	0.03
	Mo (ppm)	39.5	36.4	27.6
	Ni (ppm)	124	318	294
	Pb (ppm)	75.0	152	110
	Se (ppm)	2.00	2.00	2.00
	V (ppm)	249	230	69.7
	Zn (ppm)	143	852	454

5.4.4.5 Soybean Trial Burn (Soy)

Coal, plastics, and soybean seeds were the fuels utilized during the soy trial burn. Chemical analyses of the soybean seeds specimens were conducted by the external laboratory and shown in Tables 5-21 and 5-22. The results from the proximate and ultimate analyses are tabulated in Table 5-21. From the proximate analysis results, the low ash and moisture content, and high volatile content should be noted. The carbon, nitrogen, and sulfur contents should also be noted in the ultimate analysis results. The heating value of the soybean seeds was within 10 percent of the energy output of the traditional fuels.

The standard parameters of all the fuels utilized in the soybean burn are listed in Table 5-22. The soybean seeds possessed the highest concentrations of K_2O, P_2O_5, and Mo. The soybean seeds possessed the lowest concentrations of Al_2O_3, Fe_2O_3, SiO_2, Cl, Co, Cr, Ni, Pb, and V.

Table 5-21: ELR – Proximate, Ultimate, and Combustion Analysis of All Fuels from the Soy Burn

Test	Parameter	Coal	Plastics	Soy
		Value (wt. %)	Avg. (wt.%)	Avg. (wt.%)
Proximate Analysis	Ash	22.5	5.8	4.60
	Fixed Carbon	49.0	8.6	14.0
	Moisture[1]	1.17	2.39	10.41
	Volatile Matter	28.6	85.5	81.4
Ultimate Analysis	Carbon	66.8	60.7	57.1
	Hydrogen	3.48	6.33	6.83
	Nitrogen	1.43	1.16	6.60
	Oxygen	1.70	25.74	24.6
	Sulfur	4.10	0.21	0.22
Heat Value[2] (BTU/lb)		11,600	11,000	10,000

Notes: [1] As Received [2] Dry Basis

5.4.5 Chemical Composition of Clinker

Clinker is the primary output of the pyroprocess. The cement plant collected approximately 8 samples per day. Composite specimens were analyzed by the cement plant and the external laboratory. The average clinker compositions, determined by the cement plant for each trial burn, are tabulated in Table 5-23 as well as their respective p-values and percent difference relative to the baseline. The p-values were obtained from the Wilcoxon rank-sum test. As discussed previously, this test does not depend on normality and determines if there is a significant difference between the average baseline and trial burn parameters.

Parameter means that show a significant difference to the baseline are noted with a superscript. If the p-value indicates that the two samples populations are not equal (i.e. $p\text{-value} < 0.1$), the degree of difference should be noted and is represented by the trial burn's percent difference relative to the baseline burn. If, however, the p-value indicates that the two samples population means are equal, the degree of difference should disregarded.

Table 5-22: ELR – Standard Parameters of All Fuels from the Soy Burn

Test	Property	Coal	Plastics	Soy
		Value (wt. %)	Avg. (wt.%)	Avg. (wt.%)
Standard Parameters	Al_2O_3 (wt. %)	16.9	7.00	0.27
	CaO (wt. %)	7.77	43.5	8.16
	Fe_2O_3 (wt. %)	25.4	1.01	0.33
	K_2O (wt. %)	2.29	2.57	50.8
	MgO (wt. %)	1.05	18.3	10.2
	Na_2O (wt. %)	0.21	1.62	0.36
	P_2O_5 (wt. %)	0.13	1.86	27.2
	SiO_2 (wt. %)	35.2	17.0	0.80
	SO_3 (wt. %)	10.1	1.20	1.34
	TiO_2 (wt. %)	0.68	5.05	0.12
	As (ppm)	1790	8.96	6.79
	Cd (ppm)	6.00	6.00	6.00
	Cl (ppm)	145	351	97.6
	Co (ppm)	46.0	120	21.13
	Cr (ppm)	98.7	261	28.20
	Cu (ppm)	223	420	101
	Hg (ppm)	0.42	0.14	0.17
	Mo (ppm)	55	20	153
	Ni (ppm)	112	120	68.0
	Pb (ppm)	109	78.3	59.3
	Se (ppm)	3.00	2.00	2.00
	V (ppm)	248	315	5.00
	Zn (ppm)	161	2790	1070

From the data presented in Table 5-23 it can be concluded that the majority of trial burn parameter means are significantly different from the baseline mean data. Due to the small variation in each parameter's data set, the probability of a significant difference between means is increased. The data variation for each parameter is shown in Figure 5-6. Bars extending above and below the mean values denote the 5th and 95th percentiles.

Almost all the primary oxides, such as Al_2O_3, CaO, Fe_2O_3, and SiO_2, in the trial burns possess significantly different means compared to the baseline's results for the trial burns conducted. The primary oxides in the trial burns possess percent differences relative to the baseline burn that are fairly low. The construction and demolition waste Al_2O_3 content increased 9 %, which was the greatest difference compared to the baseline's results.

Table 5-23 A: CPR – Statistical Significance and Percent Difference of Clinker Relative to Baseline Medium

Parameter	B-CP	C&D			Soy		
	Avg. (wt. %)	Avg. (wt. %)	P-value[1]	% Diff.[2]	Avg. (wt. %)	P-value[1]	% Diff.[2]
Al_2O_3	4.65	5.05	<0.0001[3]	8.6	4.83	<0.0001[3]	4.0
CaO	64.5	64.9	0.1211	0.5	65.0	0.0075[3]	0.7
Fe_2O_3	3.31	3.30	0.4086	-0.1	3.43	0.0001[3]	3.7
K_2O	0.47	0.56	<0.0001[3]	17.3	0.49	0.0503[3]	4.3
MgO	3.55	3.06	<0.0001[3]	-13.7	3.50	0.1138[3]	-1.4
Na_2O	0.06	0.06	0.2035[3]	-3.7	0.05	0.0001[3]	-20.9
Na_2O_{eq}	0.37	0.42	0.0001[3]	13.9	0.37	0.7875	0.2
SiO_2	21.4	20.9	0.0001[3]	-2.2	21.0	0.0001[3]	-1.8
SO_3	0.99	1.15	0.375	15.7	1.24	0.0001[3]	25.2
Free CaO	1.30	1.73	0.0424[3]	33.5	1.04	0.1976	-20.0
C_3A	6.72	7.79	0.0001[3]	15.8	7.01	0.0001[3]	4.2
C_4AF	10.1	10.1	0.4139	-0.1	10.4	0.0001[3]	3.7
C_3S	64.5	66.8	0.0002[3]	3.5	67.8	0.0001[3]	5.1
C_2S	12.6	9.49	0.0001[3]	-24.6	9.03	0.0001[3]	-28.2

Notes:

[1] Wilcoxon Rank Sum Test

[2] Difference Relative to Baseline

[3] Data shows Significant Difference Between Means

Table 5-23 B: CPR – Statistical Significance and Percent Difference of Clinker Relative to Baseline

Parameter	B-CP	VF 5%			VF 10%			VF 15%		
	Avg. (wt. %)	Avg. (wt. %)	P-value[1]	% Diff.[2]	Avg. (wt. %)	P-value[1]	% Diff.[2]	Avg. (wt. %)	P-value[1]	% Diff.[2]
Al_2O_3	4.65	4.98	<0.0001[3]	7.2	4.87	<0.0001[3]	4.8	4.81	0.0024[3]	3.5
CaO	64.5	64.4	0.0356[3]	-0.3	64.5	0.0546[3]	0.0	64.2	0.0002[3]	-0.5
Fe_2O_3	3.31	3.44	0.0023[3]	4.1	3.30	0.8977	-0.2	3.37	0.0014[3]	1.8
K_2O	0.47	0.54	<0.0001[3]	14.0	0.52	<0.0001[3]	10.7	0.54	0.0002[3]	14.0
MgO	3.55	3.31	0.0001[3]	-6.9	3.43	0.0001[3]	-3.5	3.65	0.0143[3]	2.8
Na_2O	0.06	0.07	0.0006[3]	17.6	0.06	0.4778	3.7	0.07	0.0885[3]	10.6
Na_2O_{eq}	0.37	0.43	0.0001[3]	14.6	0.41	0.0001[3]	9.6	0.42	0.0001[3]	13.5
SiO_2	21.4	21.0	0.0001[3]	-1.6	21.2	0.0001[3]	-0.8	21.1	0.0003[3]	-1.2
SO_3	0.99	1.11	0.0002[3]	11.9	0.85	0.311	-14.5	1.06	0.0023[3]	7.0
Free CaO	1.30	1.32	0.793	1.3	1.46	0.3822	12.1	1.52	0.374	16.8
C_3A	6.72	7.39	0.0001[3]	9.9	7.33	0.0001[3]	9.0	7.05	0.0016[3]	4.9
C_4AF	10.1	10.5	0.0022[3]	4.1	10.0	0.8877	-0.2	10.2	0.0014[3]	1.8
C_3S	64.5	64.0	0.5556	-0.7	64.1	0.6263	-0.6	63.9	0.2884	-0.9
C_2S	12.6	11.9	0.8376	-5.0	12.4	0.5386	-1.2	12.3	0.8786	-2.6

Notes:

[1] Wilcoxon Rank Sum Test

[2] Difference Relative to Baseline

[3] Data shows Significant Difference Between Means

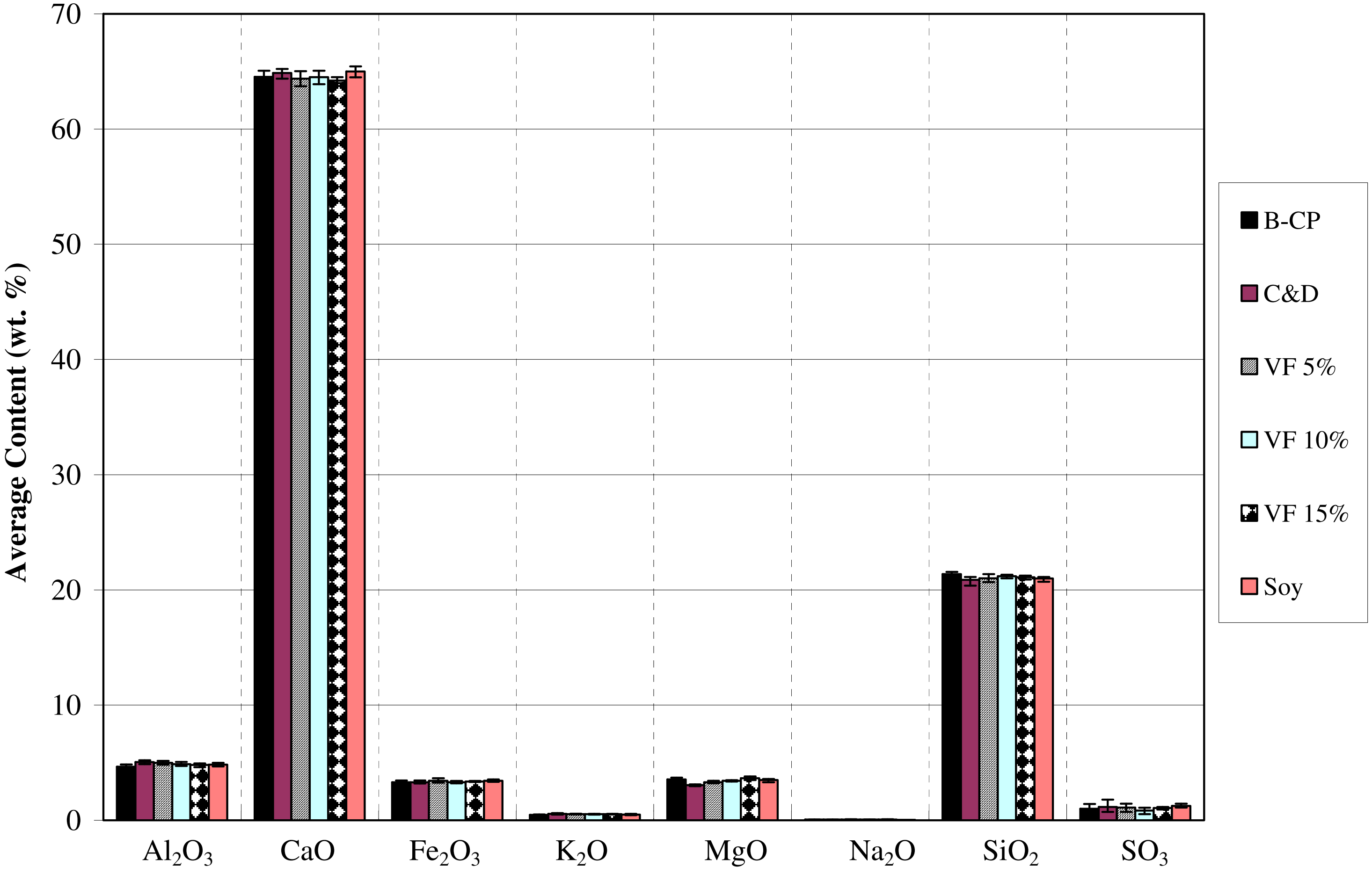

Figure 5-6: CPR – Average Clinker Composition with 5th and 95th Percentiles

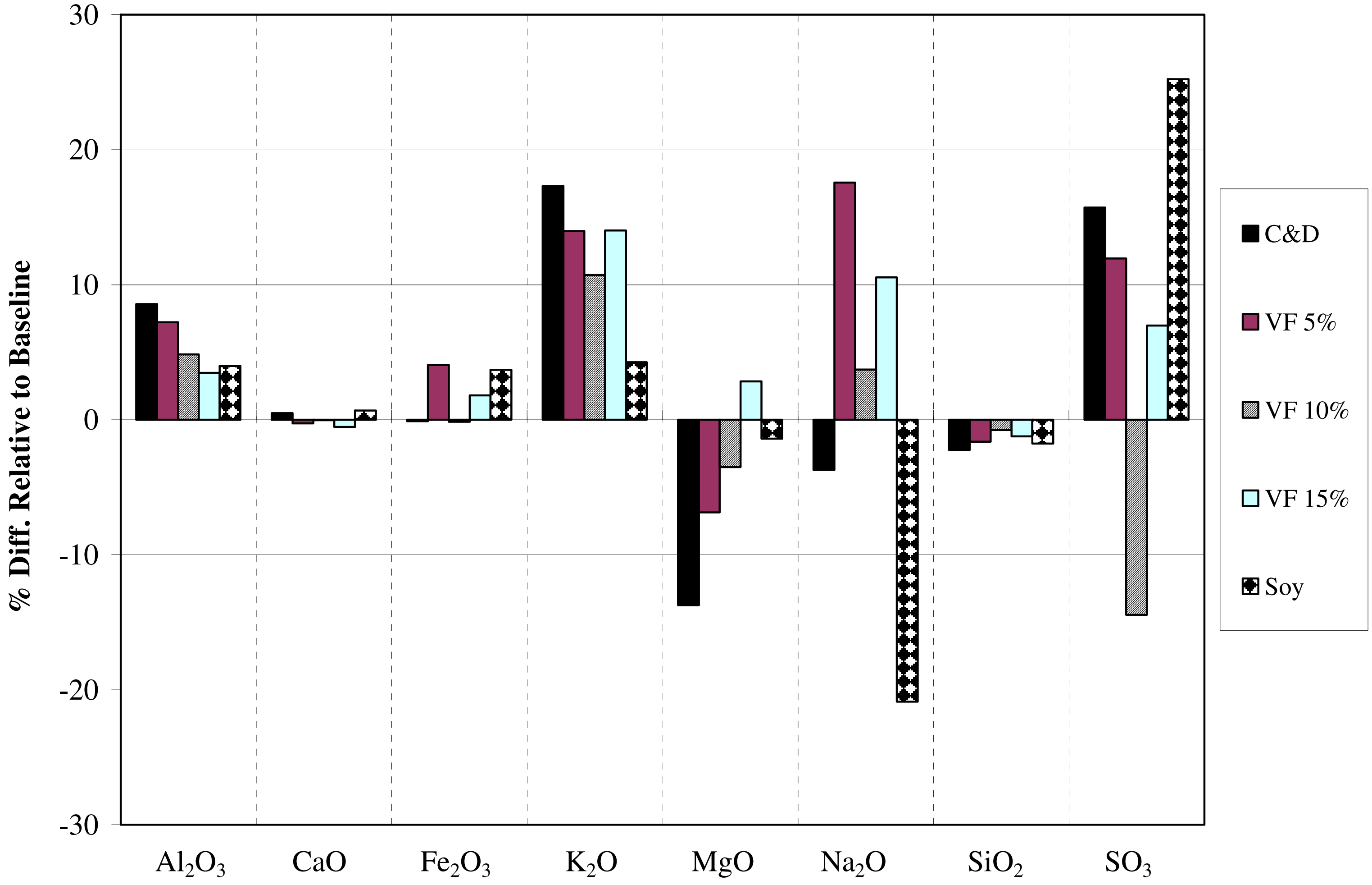

Figure 5-7: CPR – Percent Difference in Clinker Composition Relative to Baseline

The cement plant's Bogue compound results from the trial burns, in most cases, possessed significantly different means when compared to the baseline means. Similarly to the primary oxides, the degree of difference between trial and baseline means was fairly small. The belite content for the soybean trial possessed the largest difference with a decrease of 28 % compared to the baseline result.

The external laboratory tested 24-hour composite specimens prepared from the clinker samples collected during each trial burn. The average chemical composition and the percent difference relative to the baseline for the standard parameters are tabulated in Table 5-24. Due to the limited number of tested specimens, statistical analysis is not presented for these data.

The external laboratory reported values that were similar to the cement plant parameter results in all trials except the baseline burn. In Table 5-24, a significant number of the percent difference values seem extreme; however, these values depend on the baseline results. Observing the similarity between the trial burn results from the external lab and the cement plant results suggests the possibility of error in the external lab baseline chemical analysis results.

Composite clinker specimens were also tested by the cement plant's specialty laboratory. A Rietveld analysis was conducted by the specialty laboratory in order to determine the Bogue compounds. The test results and their percent difference relative to the baseline are tabulated in Table 5-25. The alite content of the variable feed 15 % trial burn cement decreased 24 % compared to the baseline's results. The belite content increased 19 and 42 % for the variable feed 5 and 15 % trial burns, respectively, compared to the baseline. The specialty laboratory also found that belite decreased 18% in the soybean trial. Recall from the clinker chemical composition from the cement plant's results, the belite decreased around 28 %. Ferrite and Aluminate levels were also significantly increased for the construction and demolition waste and variable feed trial burns compared to the baseline's results. The physical properties of the cement will dictate any practical significance and are discussed in the following section.

Table 5-24: ELR – Chemical Composition of Clinker and Percent Difference Relative to Baseline for All Burns

Parameter	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Avg. (wt. %)	Avg. (wt. %)	% Diff.	Avg. (wt. %)	% Diff.	Avg. (wt. %)	% Diff.	Avg. (wt. %)	% Diff.	Avg. (wt. %)	% Diff.
Al_2O_3 (wt. %)	11.8	5.20	-56.0	5.35	-54.8	5.09	-57.0	5.03	-57.5	21.2	79.1
CaO (wt. %)	48.2	64.5	33.8	63.3	31.4	63.5	31.9	63.6	32.0	63.9	32.6
Fe_2O_3 (wt. %)	2.78	3.36	20.9	3.32	19.5	3.12	12.3	3.29	18.7	3.40	22.3
K_2O (wt. %)	0.78	0.52	-34.1	0.44	-43.7	0.50	-35.9	0.41	-47.8	0.44	-43.1
MgO (wt. %)	2.84	3.22	13.2	3.59	26.1	3.67	29.1	3.98	39.8	3.84	34.9
Na_2O (wt. %)	0.10	0.07	-29.0	0.07	-26.6	0.05	-44.0	0.04	-58.3	0.04	-54.1
P_2O_5 (wt. %)	0.04	0.06	43.5	0.07	56.0	0.07	48.9	0.06	44.2	0.07	59.4
SiO_2 (wt. %)	32.1	20.9	-35.0	22.1	-31.0	22.4	-30.2	21.6	-32.6	21.2	-34.0
SO_3 (wt. %)	0.71	1.06	49.0	1.15	61.9	1.10	54.7	1.22	72.1	1.21	71.4
TiO_2 (wt. %)	0.34	0.23	-31.0	0.25	-26.1	0.24	-29.0	0.24	-27.9	0.27	-20.7
Moisture (wt. %)	0.02	0.01	-63.9	0.01	-73.1	0.00	-94.7	0.00	-93.8	0.00	-88.1
LOI (wt. %)	0.21	0.84	303	0.22	7.22	0.12	-42.6	0.41	96.2	0.15	-26.5
As (ppm)	41.5	30.7	-26.1	41.0	-1.20	43.0	3.61	44.5	7.23	61.0	47.0
Cd (ppm)	< 6	< 6	NA	< 6	NA	< 6	NA	< 6	NA	< 6	NA
Cl (ppm)	182	140	-22.9	494	172	691	280	379	108	54.4	-70.1
Co (ppm)	12.3	10.7	-12.9	10.0	-18.4	13.3	8.84	11.5	-6.12	8.60	-29.8
Cr (ppm)	48.5	69.3	43.0	72.2	48.8	65.0	34.0	57.1	17.8	69.8	43.9
Cu (ppm)	51.5	16.0	-68.9	43.0	-16.5	29.7	-42.4	23.0	-55.3	42.8	-16.9
Hg (ppm)	0.14	0.06	-54.9	0.06	-55.2	0.01	-91.4	0.01	-94.5	0.04	-67.3
Mo (ppm)	11.0	< 5	NA	10.0	-9.09	9.33	-15.2	8.50	-22.7	< 5	-54.6
Ni (ppm)	14.8	19.3	31.1	94.0	537	15.0	1.7	11.5	-22.0	29.2	98.0
Pb (ppm)	31.3	47.3	51.1	57.5	83.5	22.3	-28.7	20.0	-36.2	45.6	45.5
Se (ppm)	< 2	< 2	NA	< 2	NA	< 2	NA	< 2	NA	< 2	NA
V (ppm)	54.0	45.7	-15.4	63.7	17.9	59.7	10.5	56.0	3.7	40.4	-25.2
Zn (ppm)	83.3	77.3	-7.1	65.0	-21.9	36.0	-56.8	48.5	-41.7	88.4	6.19

Table 5-25: SLR – Rietveld Analysis of Clinker and Percent Difference Relative to Baseline

Property	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Value (wt. %)	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.
Alite (C_3S) (wt. %)	59.2	55.6	-6.08	53.4	-9.92	55.5	-6.30	44.9	-24.2	62.4	5.31
Belite (C_2S) (wt. %)	22.9	24.8	8.23	27.4	19.4	25.3	10.3	32.5	41.9	18.6	-18.8
Aluminate (C_3A) (wt. %)	3.03	4.12	36.2	3.55	17.4	3.94	30.2	3.81	25.9	3.41	12.6
Ferrite (C_4AF) (wt. %)	10.4	11.0	6.01	11.1	6.92	10.7	3.68	10.9	5.06	10.8	4.02

5.4.6 Chemical Composition of Cement

The final product of the manufacturing process is portland cement. All of the cement produced during the trial burns by the cement plant was indented to meet ASTM C 150 specifications for Type I/II cement. Samples were gathered by the cement plant during each burn period. Composite specimens were prepared and tested by the cement plant and sent to the external laboratory for analysis. Sample sizes were not large enough in order to perform Wilcoxon rank-sum tests for each parameter. Therefore, only the average values and percent difference relative to the baseline test results are presented.

The cement chemical composition data obtained from the cement plant are shown in Table 5-26 and Figure 5-8. Most parameters are fairly consistent throughout trial burns. The average content as well as the 5th and 95th percentiles of the data collected are shown in Table 5-26 and Figure 5-8. Since the data from the trials have a small variance, the percentile bars are nearly equal to the mean value.

All the primary oxides decreased slightly from the reported values from the clinker. The SO_3 contents increased from the clinker results which is due to the addition of gypsum or other sources of sulfates during grinding. The SO_3 contents in the baseline and soybean burn cements slightly exceeded the allowable 3 % maximum to be considered Type I and II cement. A slight excess is permissible, however, if the cement is in compliance with ASTM C 563 and 1038. Overall, the parameter values from the cement plant stayed fairly consistent between the clinker and cement results. The percent difference relative to the baseline, depicted Figure 5-9, shows that the parameters for all the trial burns stayed fairly consistent. The greatest fluctuation was found in the K_2O and Na_2O contents. The K_2O content for the construction and demolition waste trial burn differed by 19 % from the baseline burn. The Na_2O content increased by 14 % and 17 % for the variable feed 5 % and 10 % burns, respectively. The Na_2O content decreased by 12 % in the soy trial burn.

Composite cement specimens were prepared for testing by the external laboratory for every 24-hour period during each burn. The external laboratory results are shown in Table 5-27. The results of each parameter between the external and cement plant laboratories are similar. This provides a high level of confidence in precision of the results.

In the external laboratory results, the primary oxides stayed fairly consistent compared to the baseline. Due to the addition of sulfate during grinding, the SO_3 content in the cement increased from the clinker composition just as it did in the cement plant results. The external laboratory reported that the P_2O_5 content increased over the variable feed 5 and 10 % and soybean seed trial burns compared to the control results. Excessive P_2O_5 concentrations can inhibit the formation of C_3S. However, the external laboratory reported that the C_3S content of the variable feed 5 and 10 % trial burns decreased 17 and 14 %, respectively, compared to the baseline's results. The C_3A concentrations were increased in the construction and demolition waste and variable feed 10 % trial burns compared to the baseline's results.

The trace elements were only tested by the external laboratory and are presented in Table 5-27. The arsenic (As) concentrations decreased for the construction and demolition waste trial burn, stayed relatively the same for the variable feed trial burns, and increased for the soybean seed trial burn compared to the baseline values. The chlorine (Cl) and zinc (Zn) contents were significantly lower in the construction and demolition waste and variable feed trial burns when compared to the baseline. The soybean seed trial burn also had a significantly reduced chlorine content compared to the baseline burn's chlorine content.

The cement plant's specialty laboratory also received cement samples in order to perform a Reitveld analysis. The Reitveld analysis results and their percent difference relative to the baseline are tabulated in Table 5-28. The alite and belite content of the cement remained fairly constant for the construction and demolition waste and variable feed 5 % and 10% trial burns. The soybean seed trial burn cement had the greatest increase in alite of 17 % and the greatest decrease in belite of 20 % when compared to the baseline burn results. The variable feed 15 % trial burn showed a 14% increase in belite compared to the baseline results. The aluminate increased 33 % in the construction and demolition waste trial burn and 24 % in the variable feed 10 % trial burn compared to the baseline results. The remaining trial burn's aluminate levels were comparable to the baseline results. All the aluminate levels were within allowable limits for Type I and II cement according to ASTM C 150. The ferrite level in the soybean seed trial burn had an increase of 6 % over the baseline results, which was the greatest difference in ferrite for all the trial burns. The Bogue compounds in the variable feed 5 % trial burn cement had the lowest percent differences compared to the baseline cement composition. Therefore, the cement from the variable feed 5 % trial burn has the greatest resemblance to the baseline cement. The results from the physical property tests of the trial burn cements will dictate any practical significance between the trial and baseline cements and are discussed in the following section.

Table 5-26: CPR – Average Cement Composition and Percent Differences Relative to Baseline Results

Parameter	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Average (wt. %)	Average (wt. %)	% Diff.	Average (wt. %)	% Diff.	Average (wt. %)	% Diff.	Average (wt. %)	% Diff.	Average (wt. %)	% Diff.
Al_2O_3	4.51	4.95	9.63	4.76	5.58	4.73	4.75	4.73	4.84	4.54	0.55
CaO	62.8	63.1	0.60	62.9	0.24	62.9	0.17	62.6	-0.31	63.4	1.06
CO_2	1.30	1.30	0.00	1.30	0.00	1.30	0.00	1.30	0.00	1.55	19.2
Fe_2O_3	3.11	3.08	-0.90	3.21	3.22	3.11	-0.11	3.18	2.35	3.18	2.43
K_2O	0.44	0.52	19.4	0.48	9.89	0.48	10.3	0.46	5.67	0.45	2.53
MgO	3.44	3.13	-8.91	3.26	-5.38	3.33	-3.36	3.53	2.70	3.40	-1.04
Na_2O	0.07	0.07	0.00	0.08	14.3	0.08	17.0	0.07	0.39	0.06	-12.28
Na_2Oeq	0.35	0.41	15.7	0.39	10.7	0.40	11.4	0.37	4.65	0.35	-0.33
SiO_2	19.9	19.6	-1.66	19.3	-3.32	19.6	-1.63	19.6	-1.49	19.4	-2.71
SO_3	3.18	2.78	-12.6	2.97	-6.73	2.75	-13.7	2.82	-11.27	3.23	1.46
Free CaO	1.20	1.51	25.7	1.03	-14.4	1.02	-15.2	0.78	-35.18	1.16	-3.88
LOI	2.50	2.08	-16.9	2.46	-1.92	2.53	1.04	2.42	-3.55	2.51	0.11
C_3A	6.70	7.90	17.9	7.20	7.43	7.28	8.58	7.16	6.80	6.64	-0.92
C_4AF	9.46	9.37	-0.90	9.76	3.22	9.45	-0.15	9.68	2.35	9.69	2.43
C_3S	53.4	55.7	4.32	57.8	8.26	56.1	5.08	54.3	1.69	58.5	9.57
C_2S	16.8	14.1	-16.0	11.6	-31.0	13.9	-17.7	15.3	-9.10	11.4	-32.1
Blaine SSA (m^2/kg)	387	374	-3.3	379	-2.1	369	-4.7	367	-5.2	385	-0.5

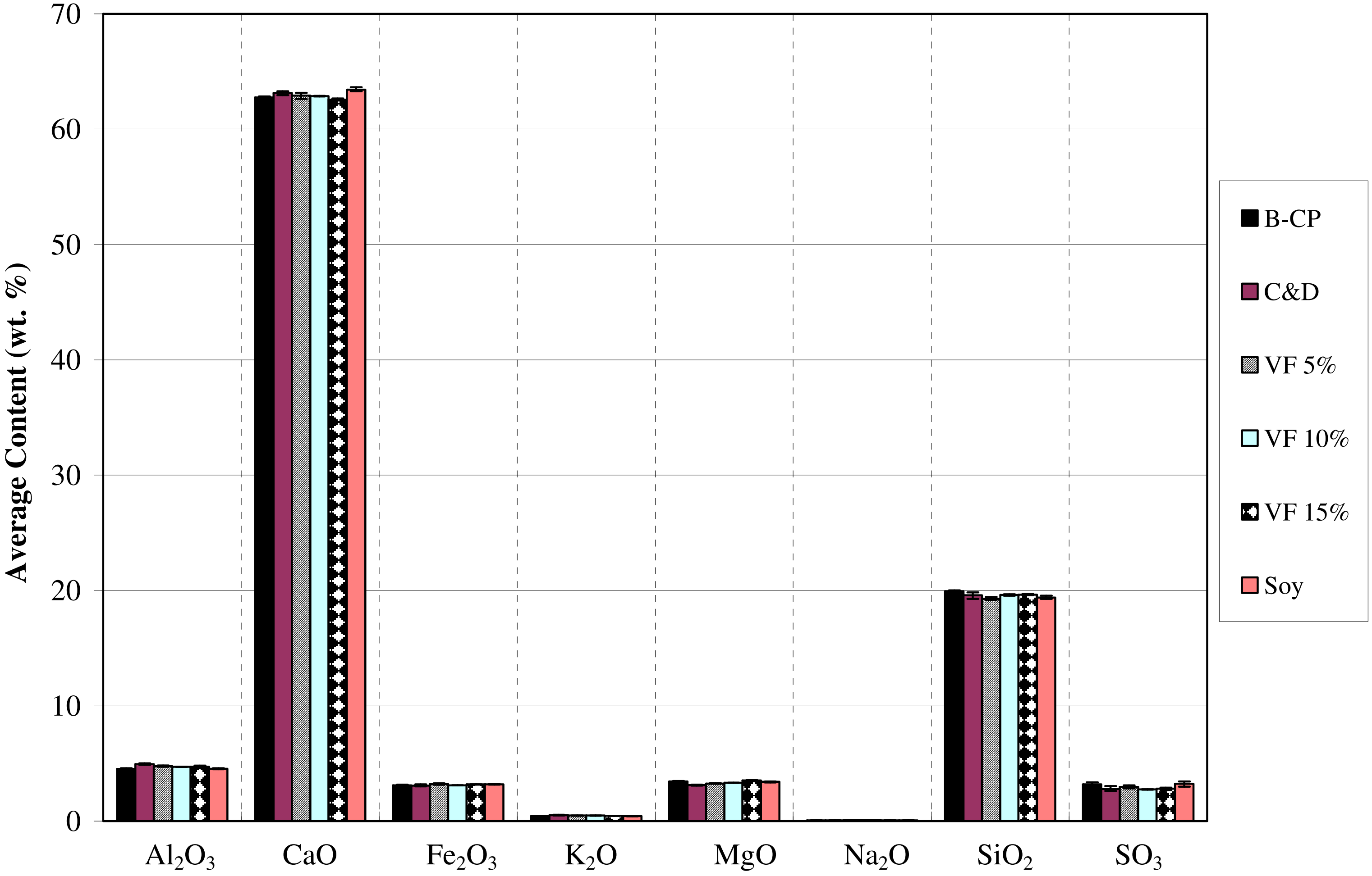

Figure 5-8: CPR – Average Cement Composition with 5th and 95th Percentiles

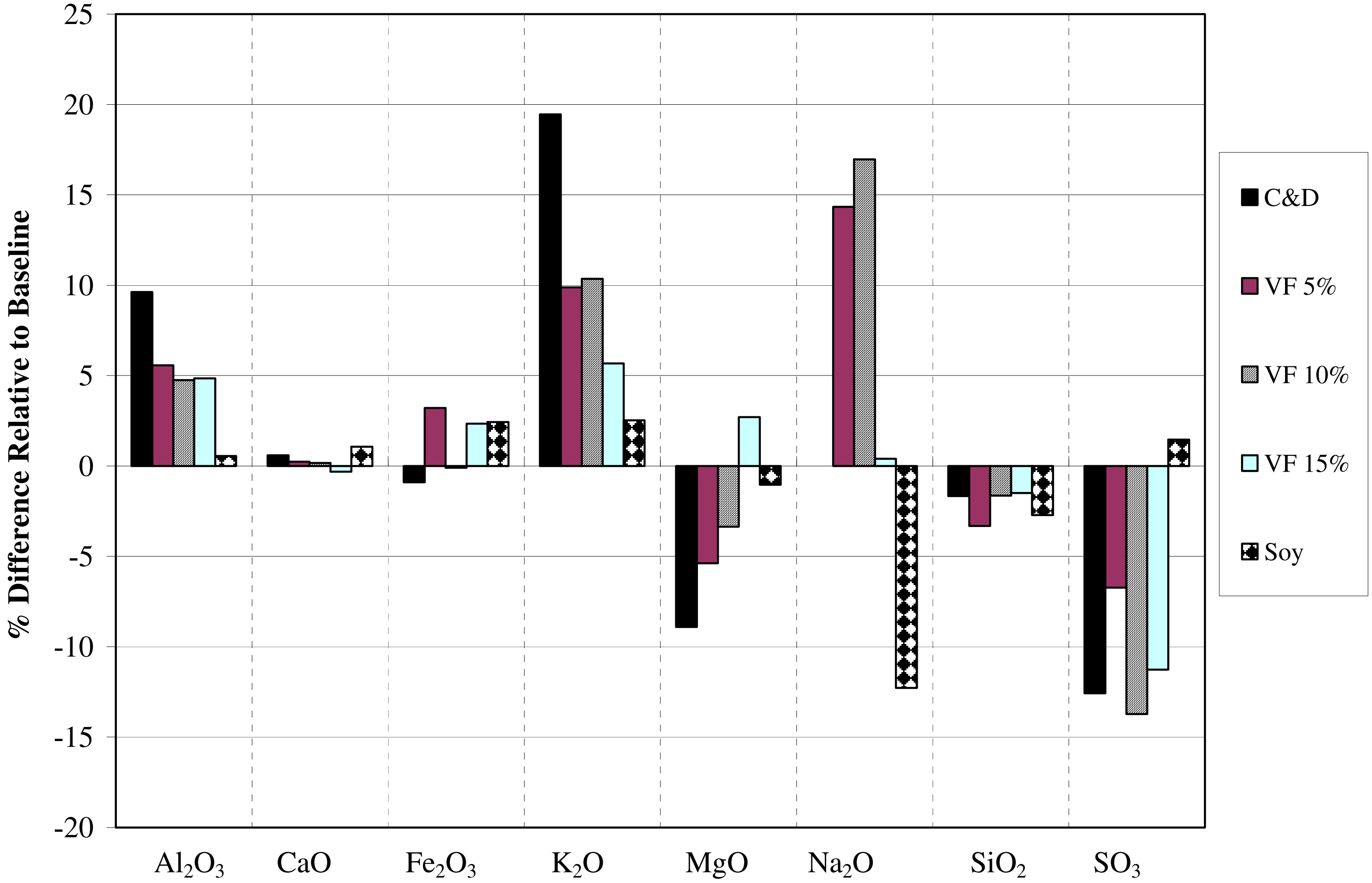

Figure 5-9: CPR – Percent Difference of Cement Composition Relative to Baseline

Table 5-27: ELR – Average Cement Composition and Percent Difference Relative to Baseline Results

Property	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Value (wt. %)	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.
Al_2O_3 (wt. %)	4.64	5.23	12.8	5.00	7.79	5.01	8.01	4.97	7.23	4.88	5.36
CaO (wt. %)	62.4	62.5	0.25	62.0	-0.66	61.9	-0.81	61.6	-1.22	62.4	0.04
Fe_2O_3 (wt. %)	3.08	3.12	1.35	3.19	3.68	3.07	-0.20	3.13	1.56	3.18	3.06
K_2O (wt. %)	0.38	0.47	26.4	0.33	-11.25	0.39	4.01	0.42	11.7	0.33	-13.3
MgO (wt. %)	3.45	3.15	-8.65	3.34	-3.19	3.46	0.11	3.67	6.19	3.65	5.64
Na_2O (wt. %)	0.05	0.06	23.0	0.06	20.6	0.05	0.13	0.06	20.0	0.05	-0.39
P_2O_5 (wt. %)	0.05	0.06	11.8	0.07	27.9	0.07	27.4	0.06	9.08	0.08	44.8
SiO_2 (wt. %)	20.1	20.2	0.62	20.4	1.72	20.4	1.77	20.4	1.83	19.6	-2.46
SO_3 (wt. %)	3.03	2.91	-3.82	3.07	1.31	2.77	-8.43	2.92	-3.40	3.23	6.81
TiO_2 (wt. %)	0.21	0.21	0.13	0.23	5.07	0.23	9.22	0.23	9.07	0.25	17.70
Moisture (wt. %)	0.12	0.19	64.4	0.25	114	0.35	205	0.34	196	0.53	360
LOI (wt. %)	2.55	1.93	-24.1	2.22	-12.61	2.54	-0.19	2.39	-6.17	2.25	-11.77
C_3S (wt. %)	49.0	44.8	-8.71	40.8	-16.8	42.0	-14.2	40.6	-17.3	50.9	3.77
C_2S (wt. %)	20.5	24.1	17.4	27.7	35.2	26.8	30.6	28.0	36.2	17.7	-13.7
C_3A (wt. %)	7.07	8.58	21.3	7.84	10.8	8.07	14.1	7.88	11.4	7.57	7.05
C_4AF (wt. %)	9.38	9.50	1.35	9.72	3.68	9.36	-0.20	9.52	1.56	9.66	3.06
TOC (wt. %)	0.08	1.84	2350	1.50	1900	1.48	1870.0	1.88	2400	0.03	-66.7
As (ppm)	42.5	27.0	-36.5	40.0	-5.88	47.0	10.6	40.0	-5.88	62.5	47.1
Cd (ppm)	6.00	6.00	0.00	6.00	0.00	6.00	0.00	6.00	0.00	6.00	0.00
Cl (ppm)	423	200	-52.8	200	-52.7	163.0	-61.5	135	-68.1	121	-71.4
Co (ppm)	10.0	11.5	15.0	12.0	20.0	6.0	-40.0	17.0	70.0	6.00	-40.0
Cr (ppm)	57.0	64.0	12.3	61.0	7.00	66.7	16.9	84.6	48.4	95.8	68.0
Cu (ppm)	28.0	13.0	-53.6	27.0	-3.57	43.0	53.6	26.0	-7.14	56.5	102
Hg (ppm)	0.01	0.02	250	0.01	0.00	0.01	20.0	0.01	20.0	0.14	2640
Mo (ppm)	5.00	5.00	0.00	5.00	0.00	5.00	0.00	5.00	0.00	5.00	0.00
Ni (ppm)	13.0	19.5	50.0	13.0	0.00	18.0	38.5	12.0	-7.69	27.5	111.5
Pb (ppm)	5.00	51.5	930	102	1940	5.00	0.00	5.00	0.00	15.5	210.0
Se (ppm)	2.00	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00
V (ppm)	58.0	40.5	-30.2	58.00	0.00	51.0	-12.1	60.0	3.45	37.0	-36.2
Zn (ppm)	95.0	73.5	-22.6	62.0	-34.7	41.0	-56.8	66.0	-30.5	87.0	-8.42

Table 5-28: SLR – Rietveld Analysis and Percent Difference of Trial Burn Cement Relative to Baseline Results

Property	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Value (wt. %)	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.	Value (wt. %)	% Diff.
Alite (C_3S)	53.6	51.6	-3.8	51.5	-4.0	51.1	-4.8	50.5	-5.8	62.9	17.3
Belite (C_2S)	23.0	24.3	5.7	25.0	8.7	25.2	9.5	26.1	13.6	18.5	-19.8
Aluminate (C_3A)	3.0	4.0	32.8	3.1	4.8	3.7	23.6	3.0	2.0	3.3	10.3
Ferrite (C_4AF)	10.1	10.2	1.1	10.4	3.3	10.1	0.3	10.2	1.5	10.6	5.9

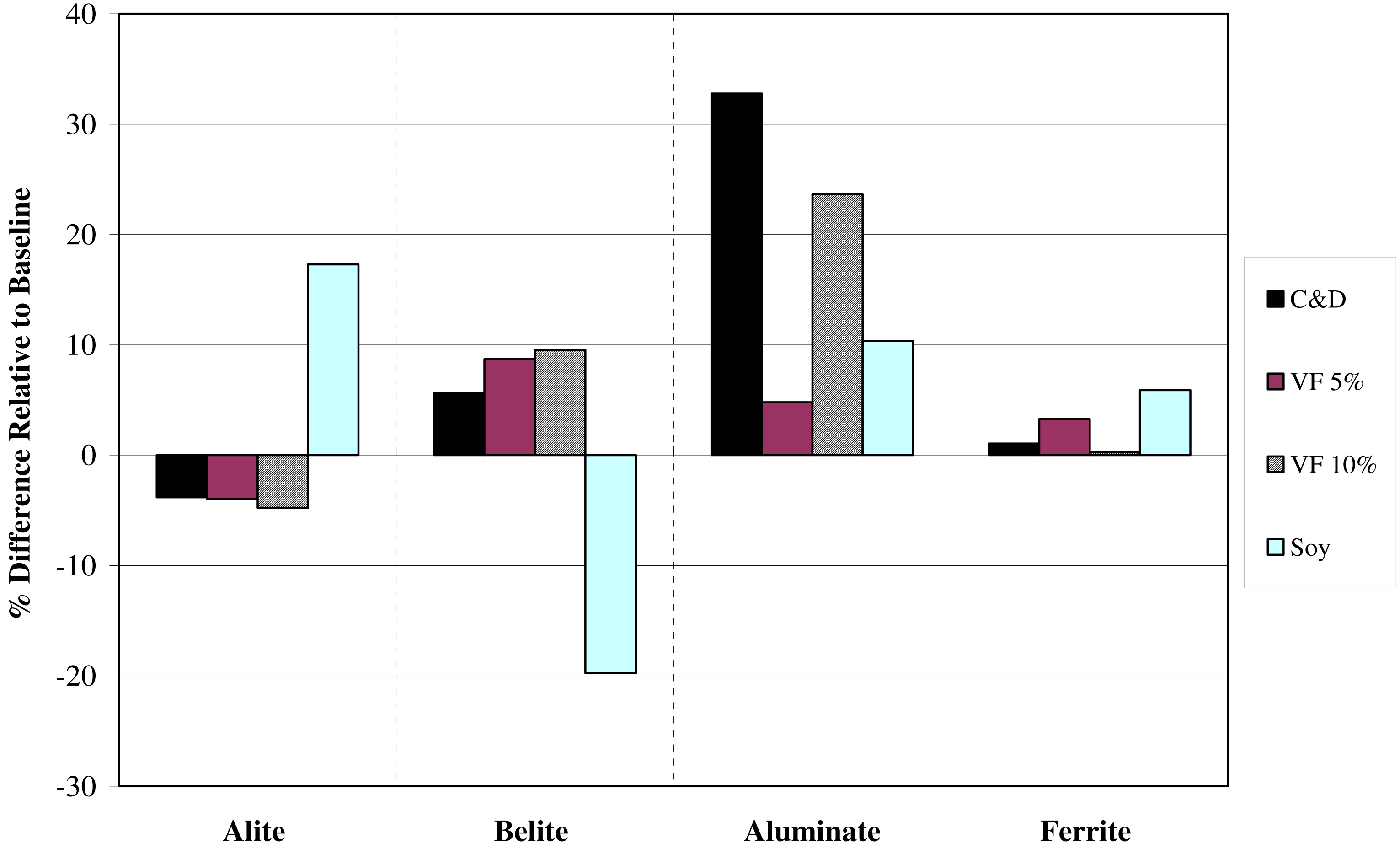

Figure 5-10: SLR – Percent Difference of Bogue Compounds Relative to Baseline

5.4.7 Physical Properties of Cement

On the completion of each burn, cement was tested by the cement plant and Auburn University. The cement plant tested cement specimens for the same properties as Auburn University, except for the additional tests of mortar air content and Blaine specific surface area. Auburn University also tested paste prisms for drying shrinkage development.

The precision requirements for several of the cement properties tested are tabulated in Table 5-29. If results from trial tests fall within the allowable limits set forth by the ASTM specifications, the trial tests results are comparable to the baseline's results. When comparing results between the cement plant and Auburn University, the multi-lab precision limits must be met to be considered similar. Single lab precision limits must be met for specimens tested at Auburn University in order to be considered similar. The percent difference between a trial burn result relative to the baseline burn result will be compared to both single-lab and multi-lab precision limits to determine the level of practical significance. It should be noted that the precision limits for mortar cube strengths are calculated using the d2s%, which is defined as the difference between trial and baseline results divided by their average.

Table 5-29: Precision Requirements for Single and Multiple Laboratories for Cement Physical Properties

Property	ASTM Specification	Single-lab	Multi-lab
Autoclave Expansion	C 151 (2005)	0.07%[1]	0.09%[1]
Mortar flow	C 1437 (2007)	11%[1]	31%[1]
Cube strength	C 109 (2007)	10.7%[2]	18.7%[2]
Dry shrinkage	C 596 (2007)	70με[1]	25.0%[1]

Notes: [1] Difference between two results
[2] Represents d2s% limits as prescribed in Practice C 670

Portland cement results obtained by the cement plant and Auburn University are tabulated in Tables 5-30 and 5-31 and Figures 5-11 through 5-12. The average values and the percent difference relative to the baseline's results for each test are presented in these tables and figures. It should be noted that the percent difference between a trial and a baseline may appear large due to a small baseline value. The percent differences of testing conducted by both the cement plant and Auburn University are plotted in Figures 5-11 and 5-12.

The majority of results from the properties expressed in Tables 5-30 and 5-31 fall within precision requirements for single and multiple laboratories. The tests that fall out of the precision range will be highlighted in this section.

To meet single-laboratory precision requirements for mortar cube flow, the allowable percent difference relative to the baseline burn result is 10 %. The mortar cube flow results from the cement plant for the variable feed 15 % and soybean seed trial burns exceeded the allowable precision limit for single-lab results. The mortar cube flow results from Auburn University for the construction and demolition waste and variable feed 5 % trial burns fell below the allowable precision limit for the single-lab results and therefore the single-lab precision results were not satisfied. The multi-laboratory precision limit for mortar cube flow was satisfied for all burns.

To meet single-laboratory precision limits for mortar cube strengths, the allowable percent difference relative to the baseline burn is 11 %. The allowable percent difference relative to the baseline was calculated from the d2s%. The mortar cube strength results from the cement plant that exceeded the precision limit for 1-day strengths occurred for the construction and demolition waste, variable feed 15 %, and soybean seed trial burns. The cement plant results of mortar cube strength results at later ages did meet the single-laboratory precision limit. The mortar cube strength results from Auburn University all met the single-laboratory precision limit except for the cubes made from the soybean seed trial burn cement. The mortar cubes made from the soybean seed trial burn cement fell significantly below the allowable single-laboratory precision limits over early- and late-age testing. Since the cement plant results showed that the mortar cube prepared from the soybean seed trial cement resembled the baseline strengths, the differences found by Auburn University could be due to error during the preparation or testing these cubes. Therefore, the Auburn University results pertaining to the mortar cube strengths prepared from the soybean seed trial cement will not be presented. All the mortar cube strength results between the cement plant and Auburn University fell within the allowable precision limit for multiple-laboratories except the soybean seed trial burn results. Graphical representations of mortar cube strengths are shown in Figure 5-13 and 5-14.

All the drying shrinkage falls within the single laboratory precision limits except for the prisms prepared with the variable feed 15% cement. The drying shrinkage of the prisms are tabulated in Table 5-31 and graphically represented in Figure 5-15. The dry shrinkage percentage is the strain of the prism recorded in percent. The maximum allowable strains for 14, 21, and 28 days are 730, 850, and 920 $\mu\varepsilon$, respectively. The prisms made with the variable feed 15% possessed strains of 740, 870, and 1020 $\mu\varepsilon$. The drying shrinkage from the concrete specimens will have to be evaluated to determine if the drying shrinkage of the variable feed 15 % trial burn cement is elevated.

A paste setting test from each cement was conducted by the cement plant and Auburn University. ASTM C 191 (2008) reported that when using the manual vicat test method, the allowable single-laboratory precision for the initial and final setting times can vary by 34 and 56 minutes, respectively, and be considered similar. For multiple laboratory precision, the initial and final setting time can vary by 45 and 122 minutes, respectively, and be considered similar. The initial and final setting results from the cement plant can be considered similar to the baseline cement for each trial burn cement. All setting results from Auburn University fell within precision limits. A graphical representation of the cement properties percent difference relative to the baseline for the cement plant and Auburn University results are shown in Table 5-11 and 5-12.

The particle size distribution of each cement produced in this study was determined by laser diffraction at the cement plant's specialty laboratory. The particle size distribution of each cement is shown in Figure 5-16. The graph shows that all the cements in the study were ground to nearly the same size distribution. Thus, differences in cement behavior cannot be attributed to different particle size distributions.

Table 5-30: CPR – Physical Properties of Cement and Percent Difference Relative to Baseline for All Burns

Property	**B-CP**	**C&D**		**VF (5%)**		**VF (10%)**		**VF (15%)**		**Soy**	
	Value	**Value**	**% Diff.**	**Value**	**% Diff.**	**Value**	**% Diff.**	**Value**	**% Diff.**	**Value**	**% Diff.**
Air in Mortar (%)	5.1	6.3	23.5	5.3	3.9	5.3	3.9	5.80	13.7	6.10	19.6
Blaine Specific Surface Area (m^2/kg)	374	372	-0.5	371	-0.8	357	-4.5	374	0.0	376	0.5
Autoclave Expansion (% Exp.)	0.07	0.12	79.7	0.07	-4.3	0.11	65.9	0.08	15.9	0.09	26.1
Mortar flow (%)	106	96.0	-9.4	101	-4.7	105	-0.9	127	19.8	126	18.6
Compressive Strength (MPa)											
1	12.9	15.0	16.3	NR	-	12.6	-2.3	15.0	16.3	16.0	24.3
3	25.8	23.8	-7.8	24.4	-5.6	25.7	-0.6	21.7	-15.9	25.9	0.3
7	29.4	31.4	6.8	31.7	7.7	29.9	1.7	29.3	-0.3	32.3	9.8
28	42.1	40.6	-3.6	44.7	6.1	45.5	8.1	43.2	2.6	44.0	4.5
Normal Consistency (%)	25.4	25.5	0.4	25.7	1.2	25.3	-0.6	25.3	-0.4	25.1	-1.0
Gillmore Initial Set (Min.)	NR	NR	-	NR	-	NR	-	NR	-	NR	-
Gillmore Final Set (Min.)	NR	NR	-	NR	-	NR	-	NR	-	NR	-
Vicat Initial Set (Min.)	122	95	-22.1	121	-0.8	138	12.7	150	23.0	117	-4.4
Vicat Final Set (Min.)	210	195	-7.1	248	17.9	240	14.3	260	23.8	228	8.7

Notes: NR- Not Reported

Table 5-31: AUR – Physical Properties of Cement and Percent Difference Relative to Baseline for All Burns

Property	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Value	Value	% Diff.	Value	% Diff.	Value	% Diff.	Value	% Diff.	Value	% Diff.
Autoclave Expansion (% Exp.)	0.06	0.07	16.7	0.05	-16.7	0.06	0.00	0.08	33.3	0.05	-16.7
Mortar flow (%)	102	89.5	-12.1	74.8	-26.5	102	0.20	104	1.67	96.5	-5.21
Compressive Strength (MPa)											
1	14.2	14.3	0.7	15.3	7.75	13.6	-4.23	13.2	-7.04	11.8	-16.9
3	23.2	24.6	6.0	24.5	5.60	24.3	4.74	22.9	-1.29	19.2	-17.2
7	30.4	31.5	3.6	32.5	6.91	32	5.26	31.2	2.63	26.2	-13.8
28	40.9	45.1	10.3	42.9	4.89	43.4	6.11	44.7	9.29	31.8	-22.2
Normal Consistency (%)	24.5	25.2	2.9	25.0	2.04	24.5	0.00	24.5	0.00	25.0	2.04
Gillmore Initial Set (Min.)	132	190	43.9	137	3.79	145	9.85	134	1.52	200	51.5
Gillmore Final Set (Min.)	222	243	9.5	227	2.25	265	19.4	254	14.4	275	23.9
Vicat Initial Set (Min.)	109	144	32.1	122	11.9	130	19.3	121	11.0	185	69.7
Vicat Final Set (Min.)	207	242	16.9	197	-4.83	220	6.28	209	0.97	250	20.8
Drying Shrinkage (%)											
7	-0.045	-0.045	1.1	-0.047	5.62	-0.049	8.99	-0.050	12.9	-0.048	6.74
14	-0.066	-0.071	6.4	-0.069	4.53	-0.072	8.68	-0.074	12.1	-0.070	4.91
21	-0.078	-0.083	6.1	-0.082	4.49	-0.085	9.29	-0.087	11.5	-0.081	3.85
28	-0.085	-0.090	5.3	-0.090	5.87	-0.096	12.6	-0.102	19.4	-0.089	4.40

Note: NA – Not Available

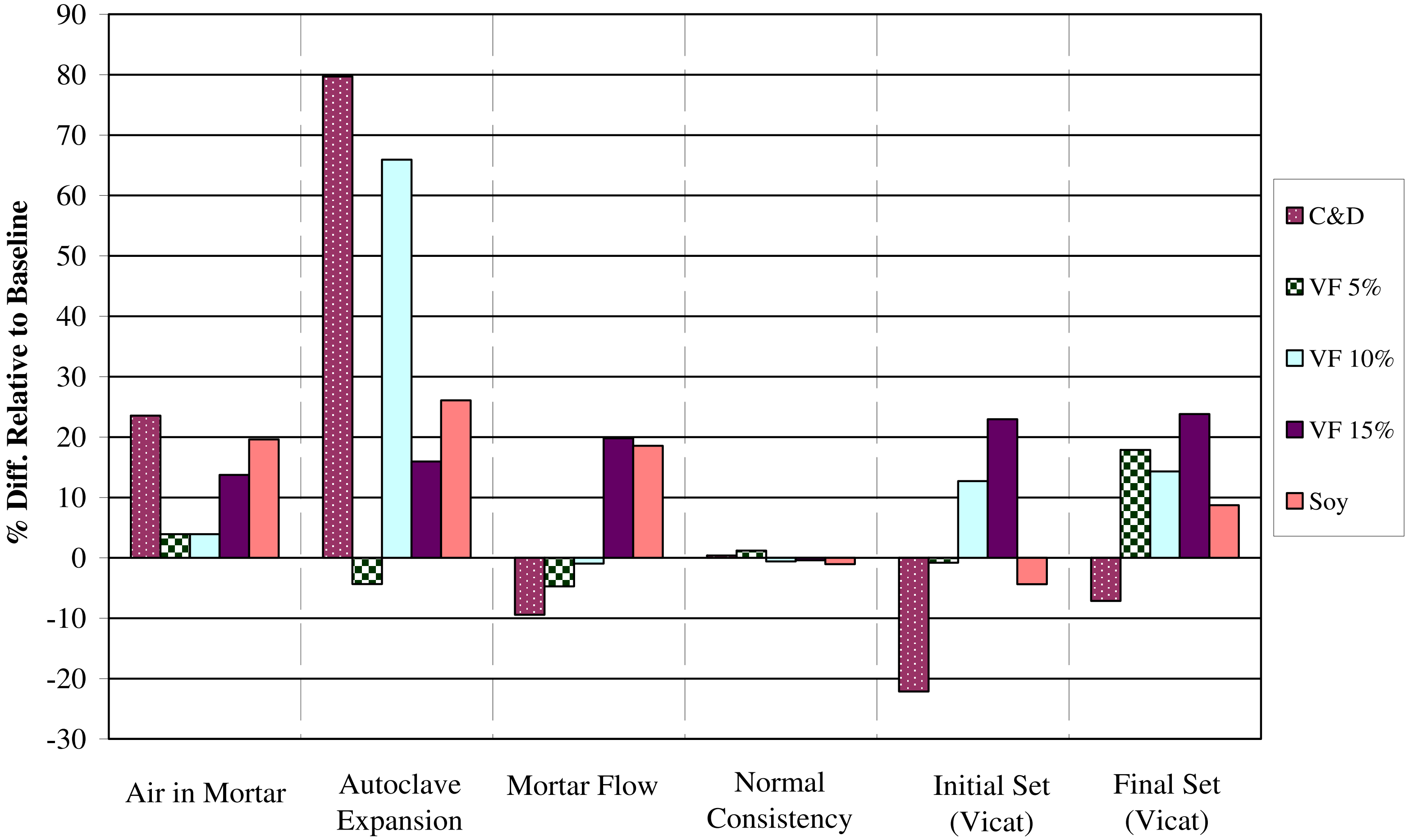

Figure 5-11: CPR – Percent Difference in Cement Properties Relative to Baseline

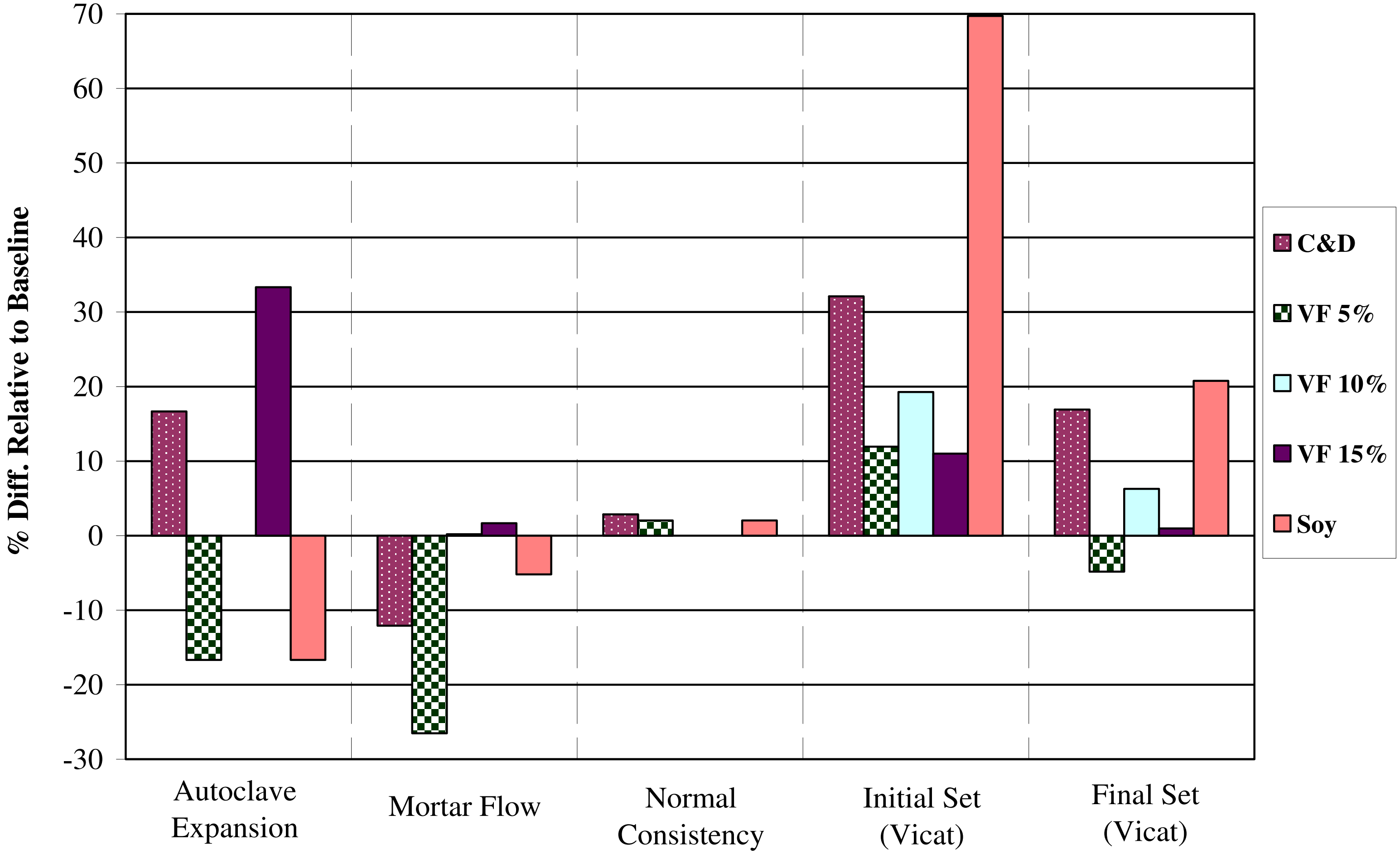

Figure 5-12: AUR – Percent Difference in Cement Properties Relative to Baseline

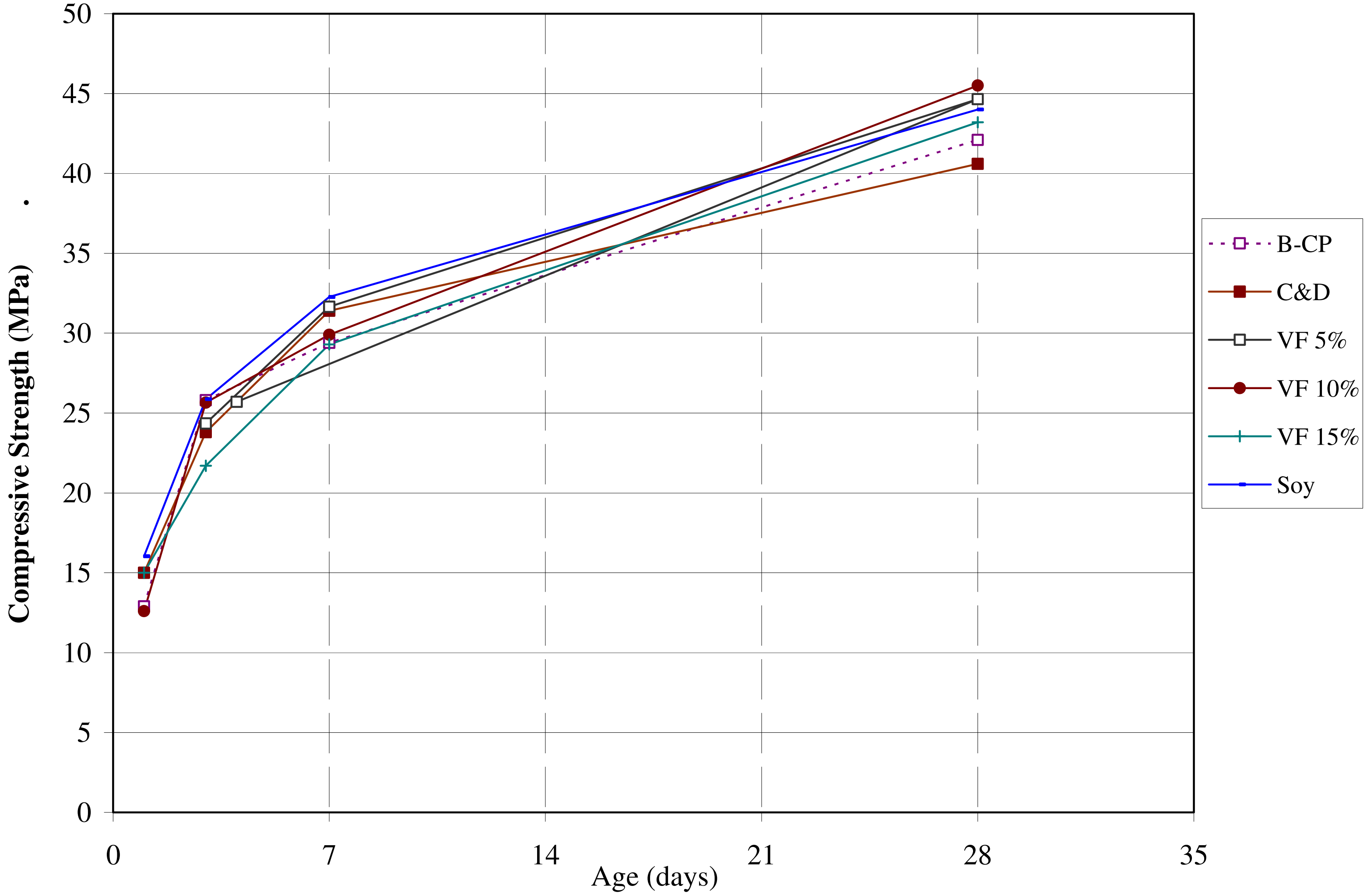

Figure 5-13: CPR – Mortar Cube Compressive Strengths for All Burns

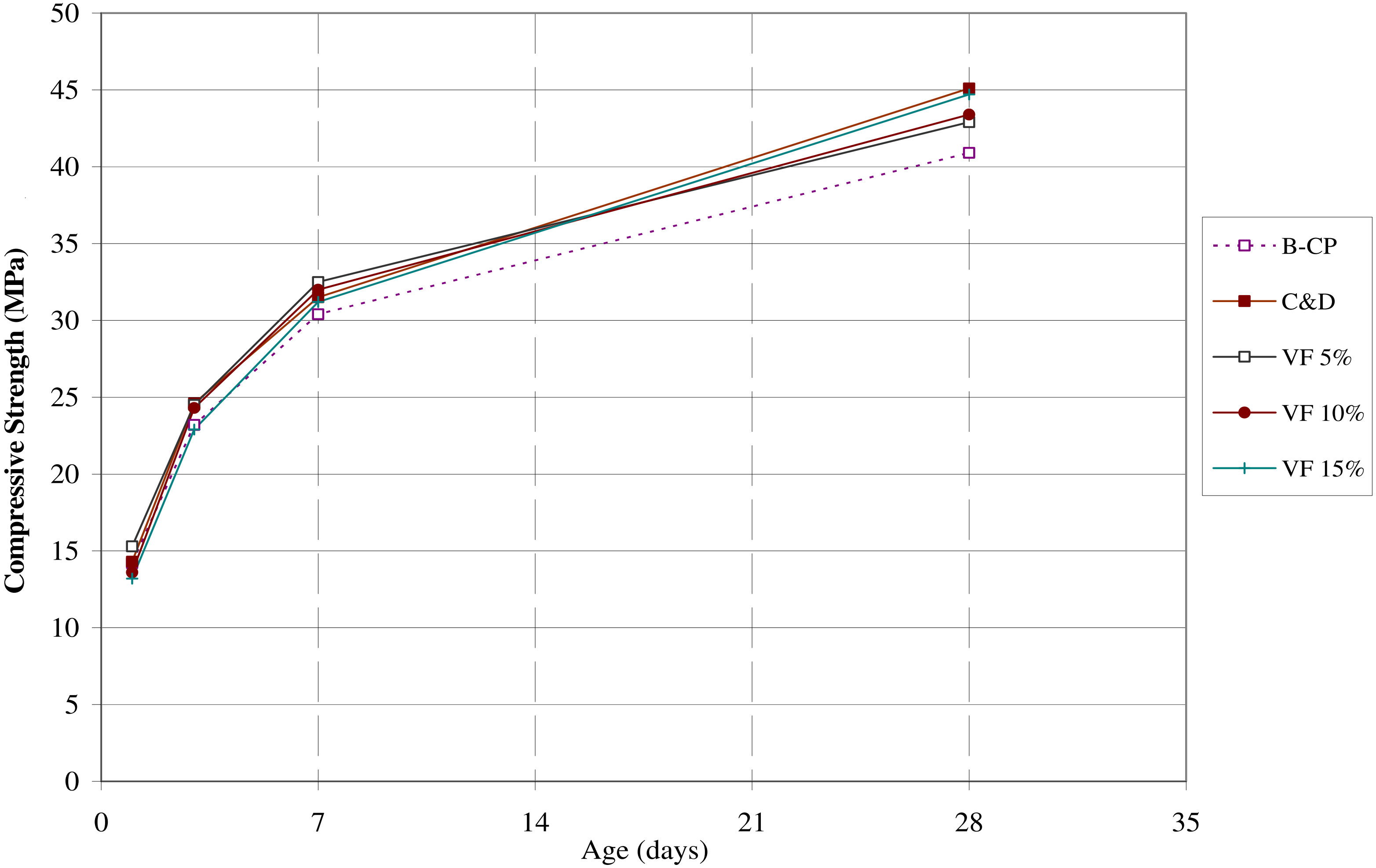

Figure 5-14: AUR – Mortar Cube Compressive Strengths for All Burns

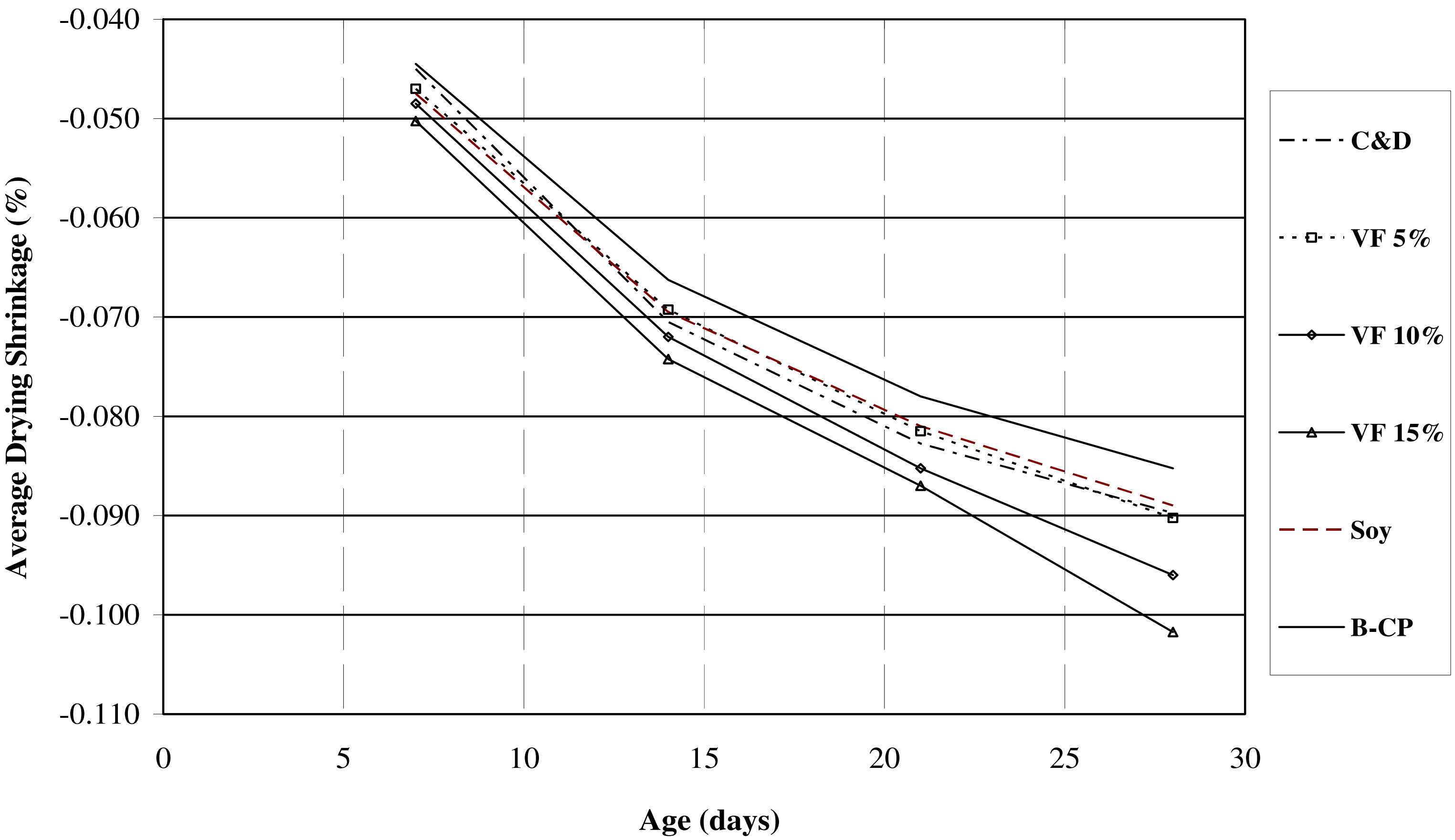

Figure 5-15: AUR – Average Drying Shrinkage of Mortar Prisms for All Burns

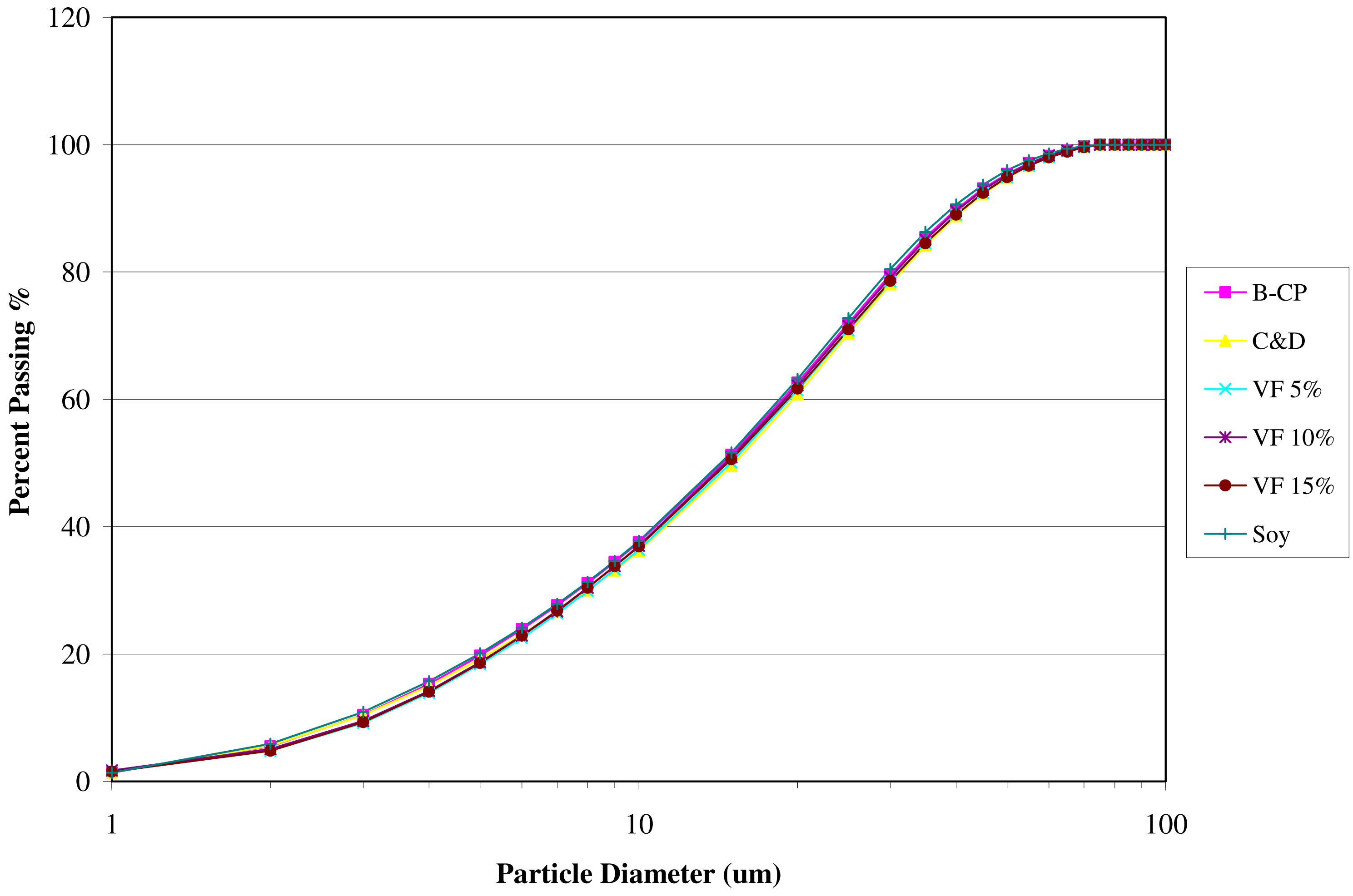

Figure 5-16: SLR – Particle Size Distribution of Cement for All Burns

5.4.8 Concrete Properties

As previously discussed, Auburn University tested properties of concrete prepared from the cement produced during each burn of this study. Two mix designs were utilized. Mix 0.44 and Mix 0.37 have unique water-cement ratios and therefore cannot be directly compared. Trends that are consistent through both mixtures could establish practical significance in the effect that a specific cement has on a specific property. The data from the results will be presented for both mixtures before they are discussed.

Similarly to the cement tests discussed earlier, precision statements acquired from ASTM specifications allow for a specific range of results to be considered comparable when multiple tests are performed. The testing property, ASTM specification, and precision for both single and multiple laboratories are presented in Table 5-32. To assess the practical significance of the trial burn results, the ASTM precision limits are applied to the baseline results. If the test results from a trial burn fall within the baseline burn result's allowable value range, the trial burn and baseline burn results are considered similar. Precision statements from ASTM specifications are given for all concrete tests except setting time. ASTM C 403 (2008) provides precision in terms of difference in setting times. Weakley (2009) conducted a study and reported setting precision in terms of percent difference, which is thought to be more appropriate.

Table 5-32: Single-Lab and Multi-Lab Precision for Concrete Physical Properties

Property	ASTM Specification	Single - lab	Multi-lab
Total air content	C 192 (2007)	0.8%[1]	1.1%[1]
Slump		50.8 mm (2.0 in.)[1]	71.1 mm (2.8 in.)[1]
Unit weight		40.0 kg/m3 (2.5 lb/ft^3)[1]	64.1 kg/m3 (4.0 lb/ft^3)[1]
Initial set	Weakley (2009)	4.8%[3]	10.7%[3]
Final set		3.9%[3]	7.4%[3]
Compressive strength	C 39 (2005)	6.6%[2]	7.8%[2]
Permeability	C 1202 (2007)	42%[2]	51%[2]
Drying shrinkage	C157 (2006)	0.0137%[1]	

Notes: [1] Difference in the average of two results

[2] Acceptable range of values (d2s%) as described in ASTM C 670

[3] Percent difference relative to baseline

5.4.8.1 Concrete Mix 0.44

All physical concrete properties were determined by Auburn University. Concrete Mix 0.44 was a normal-strength mixture possessing a water-cement ratio of 0.44. The average results and percent difference of each trial burn relative to the baseline results from Mix 0.44 are shown in Table 5-33. A graphical representation of the fresh property results of each trial burn's cement relative to the baseline cement's results are shown in Figure 5-17.

Due to the volume of concrete required to conduct the necessary tests and the volume limitations of available mixing equipment, each mixture was divided roughly in half to ensure adequate blending of all materials. The air content, slump, and unit weight recorded in Table 5-33 are the average of two batches of concrete mixed for each trial.

All single-lab precision requirements were met between the individual batches prepared with the cement sampled from each trial.

The air content for Mix 0.44 remained within baseline precision limits for all trial mixtures except VF 10 %, which exceeded allowable limits by 0.1 %. The target air content for each mix was 4.0%. All the trial mixes were within single-lab precision limits if compared to the target air content.

All of the trial concrete slump results were within 1 inch of the baseline mixture and therefore met baseline precision limits. The plot of percent difference, however, is deceiving due to the small baseline slump.

The unit weights of all the trial mixtures were within the allowable ± 2.5 lb difference to the baseline unit weight. The minimal percent differences relative to the baseline for the unit weights of the trial mixtures are shown in **Error! Reference source not found.**Figure 5-17.

Many factors including temperature, water-cement ratio, cement chemistry, and admixtures can affect setting (Odler 1998). Mix 0.44 concrete made with all the trial burn cements failed the baseline concrete setting precision limits except the initial setting time from the construction and demolition waste trial burn concrete. It can be seen in Figure 5-17 that the cement from the variable feed and soybean seed trial burns produced concrete setting times that were significantly retarded, or extended, compared to the baseline concrete setting results. The setting results from the concrete made with the variable feed 10 % trial cement showed between 10 and 39 % longer initial and final setting times than the baseline setting results. To ensure the variable feed 10 % setting results were not erroneous, the tests for this mixture were repeated by making new concrete. Almost identical setting results were found to occur again.

Table 5-33: AUR – Physical Properties and Percent Difference Relative to Baseline for Mix 0.44 Concrete for All Burns

Property	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	AUR	AUR	% Diff.	AUR	% Diff.	AUR	% Diff.	AUR	% Diff.	AUR	% Diff.
Total Air Content (%)	3.9	4.0	2.6	3.8	-2.6	4.8	21.8	4.1	5.1	4.3	10.3
Slump (in)	2.9	2.0	-31.0	2.3	-20.7	3.3	12.1	2.0	-31.0	2.3	-20.7
Unit Weight (lb/ft^3)	150	151	0.5	151	0.2	148	-1.6	150	-0.3	150	-0.4
Initial Set (Min.)	239	238	-0.4	264	10.5	333	39.3	262	9.6	266	11.3
Final Set (Min.)	311	326	4.8	352	13.2	430	38.3	352	13.2	353	13.5
Compressive Strength (MPa)											
1 day	17.2	15.2	-11.6	15.0	-12.8	12.5	-27.3	12.3	-28.5	15.5	-9.9
3 days	25.1	21.5	-14.3	22.7	-9.6	23.0	-8.4	22.1	-12.0	22.8	-9.2
7 days	27.4	27.7	1.1	28.7	4.7	28.3	3.3	28.0	2.2	28.8	5.1
28 days	37.5	35.9	-4.3	37.3	-0.5	39.6	5.6	40.7	8.5	36.1	-3.7
91 days	41.8	40.1	-4.1	42.7	2.2	42.3	1.2	41.7	-0.2	38.5	-7.9
Permeability @ 91 days (Coulombs)	2047	2051	0.2	2449	19.6	2369	15.7	2067	1.0	2449	19.6

Notes: [1]Relative to B-CP

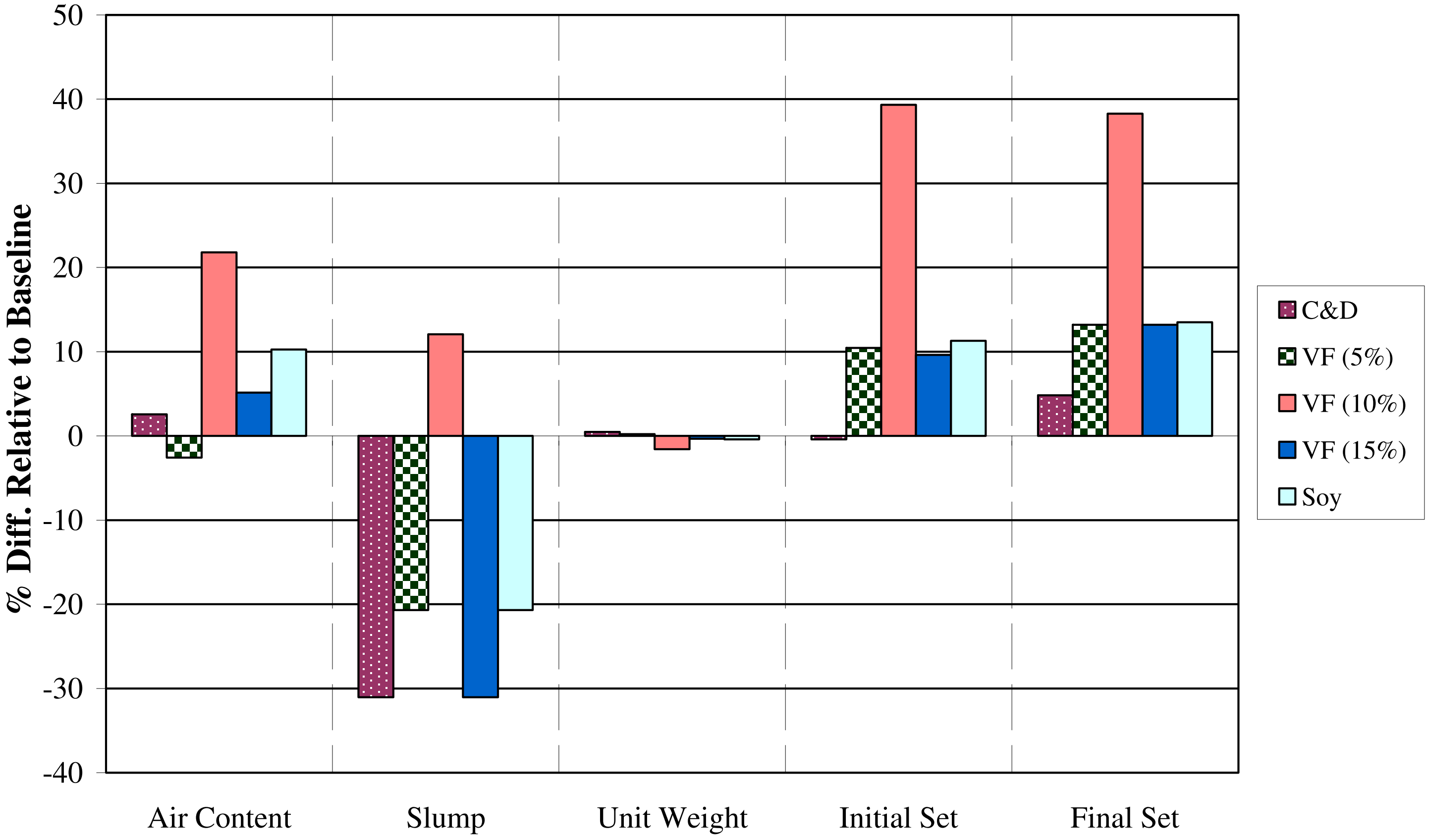

Figure 5-17: AUR – Percent Difference in Physical Properties Relative to Baseline for Mix 0.44 Concrete for Trial Burns

The compressive strength of concrete is significantly affected by its air content. ACI (1992) reported, “Incorporation of entrained air may reduce strength at a ratio of 5 to 7 percent for each percent of air.” To account for the fluctuation of air between each concrete mixture, the trial air content was normalized to the baseline’s air content. The actual compressive strengths for each trial mixture were decreased 5% for every 1% increase in air content that the trial mixture exceeded the baseline’s air content. This provides an adjusted strength for the trial concrete if the baseline and trial mixtures had the same air content. The unadjusted compressive strengths for each trial burn and their percent difference relative to the baseline results are presented in Table 5-33. The air-corrected compressive strengths and their percent difference relative to the baseline results are presented in Table 5-34. The air-corrected compressive strength development results are shown in Figure 5-18. The allowable percent difference relative to the baseline results for trial burns to meet the baseline’s compressive strength precision limit is 7 %.

The air-corrected concrete compressive strength results for the trial burn cements indicate that at early ages, there is a strength loss compared to the baseline strength results. However, the air-corrected compressive strengths for 7 to 91 days for the construction and demolition waste and variable feed trials had similar compressive strengths compared to the results from the baseline trial burn cement. The variable feed 10 and 15 % trial burn strength results decreased between 12 and 30 % at early ages compared to the baseline strength results, which was the largest decrease in strength for any of the trial burns compared to the baseline burn. The air-corrected compressive strengths from the soybean seed trial burn were decreased between 10 and 12 % for 1, 3, and 91-day tests compared to the baseline results.

The drying shrinkage results of concrete prisms from Mix 0.44 are shown in Table 5-35. The average drying shrinkage strain of the concrete prisms and their percent difference relative to the baseline’s results are presented. A plot of the average drying shrinkage strain development over 112 days for all the trial cement’s concrete prisms are shown in Figure 5-19. To meet the allowable precision limit for drying shrinkage, the difference between the trial and baseline results can not exceed 0.0137 %. The concrete prisms with the greatest strain development were made with the baseline burn’s cement. All the trial burn cements used for Mix 0.44 concrete prisms showed average strains that met the precision limits set by the baseline’s drying shrinkage results. Therefore, drying shrinkage is minimally affected by the use of alternative fuels such as construction and demolition waste, woodchips, and soybean seeds to produce portland cement.

Concrete permeability results from Mix 0.44 are shown in Table 5-33. At 91 days, the test results show that the concrete has a moderate permeability. The levels of chloride ion penetration are defined in ASTM 1202 (2007). The concrete made using the soybean seed trial burn cement showed the greatest increase (20 %) of all the trial burns compared to the baseline results. This increase seems significant, but it is within the baseline permeability result’s precision limits and is therefore considered similar.

Table 5-34: AUR – Air-Corrected Compressive Strength and Percent Difference Relative to Baseline for Mix 0.44 Concrete

Concrete Age	**C&D**		**VF 5%**		**VF 10%**		**VF 15%**		**Soy**	
	Avg. (MPa)	**% Diff [1]**	**Avg. (MPa)**	**% Diff [1]**	**Avg. (MPa)**	**% Diff [1]**	**Avg. (MPa)**	**% Diff [1]**	**Avg. (MPa)**	**% Diff [1]**
1 day	15.1	-12.1	15.1	-12.4	12.0	-30.4	12.2	-29.2	15.2	-11.7
3 days	21.4	-14.8	22.8	-9.1	22.0	-12.3	21.9	-12.8	22.3	-11.0
7 days	27.6	0.6	28.8	5.3	27.1	-1.1	27.7	1.2	28.2	3.0
28 days	35.7	-4.7	37.5	0.0	37.9	1.1	40.3	7.4	35.4	-5.7
91 days	39.9	-4.5	42.9	2.7	40.5	-3.1	41.3	-1.2	37.7	-9.7

Notes: [1]Relaive to B-CP

Table 5-35: AUR – Drying Shrinkage Development and Percent Difference Relative to Baseline for Mix 0.44 Concrete for All Burns

Drying Age (days)	**B - CP**	**C&D**		**VF 5%**		**VF 10%**		**VF 15%**		**Soy**	
	Avg. Strain (%)	**Avg. Strain (%)**	**% Diff [1]**	**Avg. Strain (%)**	**% Diff [1]**	**Avg. Strain (%)**	**% Diff [1]**	**Avg. Strain (%)**	**% Diff [1]**	**Avg. Strain (%)**	**% Diff [1]**
4	-0.010	-0.015	46.7	-0.014	43.3	-0.015	46.7	-0.014	40.0	-0.011	6.7
7	-0.013	-0.019	52.6	-0.020	57.9	-0.017	31.6	-0.022	76.3	-0.018	42.1
14	-0.023	-0.025	8.8	-0.027	19.1	-0.023	0.0	-0.027	17.6	-0.025	10.3
28	-0.030	-0.036	18.9	-0.033	8.9	-0.030	0.0	-0.037	23.3	-0.033	10.0
56	-0.038	-0.040	7.1	-0.039	4.4	-0.041	8.0	-0.041	8.0	-0.043	13.3
112	-0.048	-0.046	-4.2	-0.046	-4.2	-0.040	-16.1	-0.045	-4.9	-0.045	-4.9
224	-0.050	-0.047	-5.3	CIP	-	CIP	-	CIP	-	CIP	-

Notes: CIP - Collection in Process

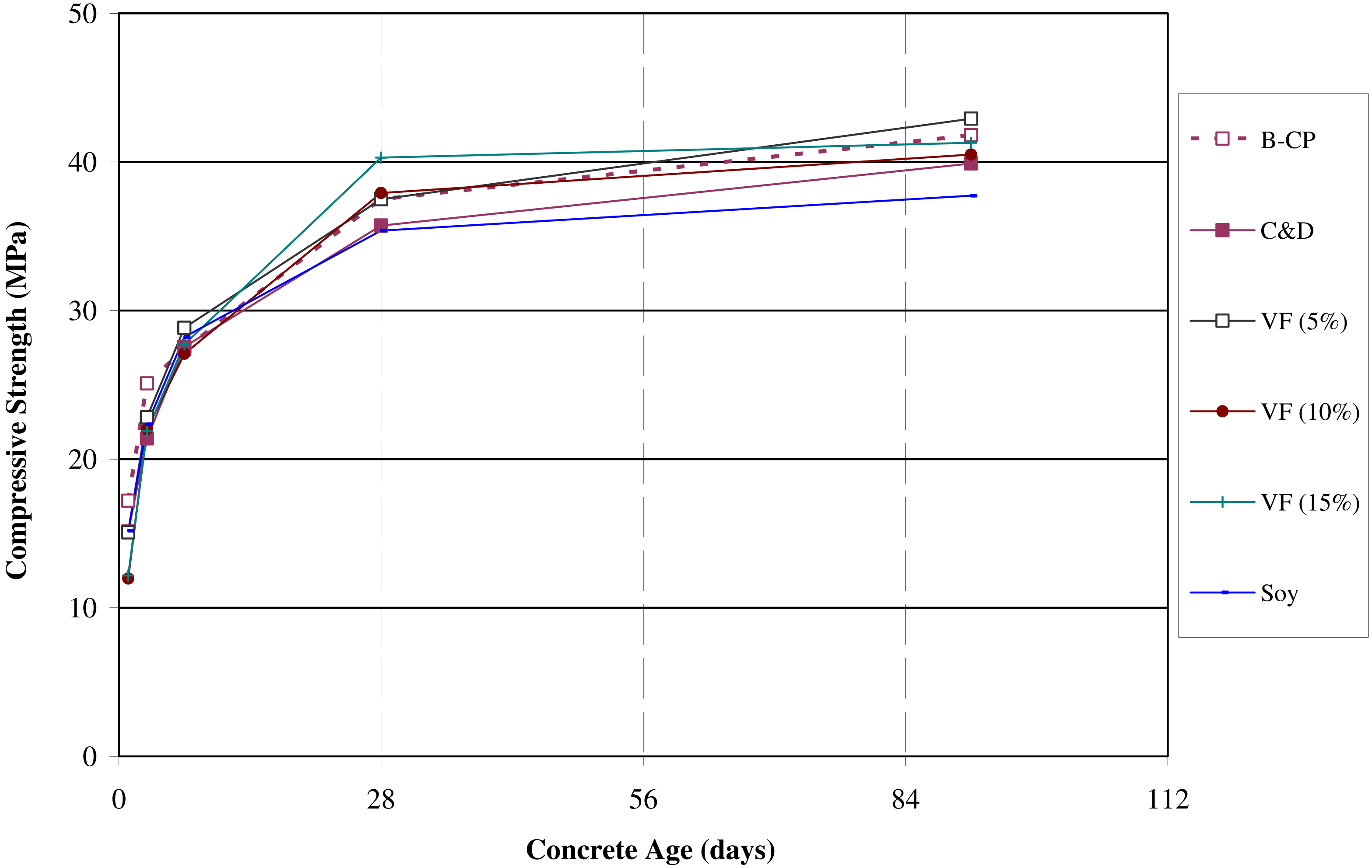

Figure 5-18: AUR – Air-Corrected Compressive Strengths for Mix 0.44 for All Burns

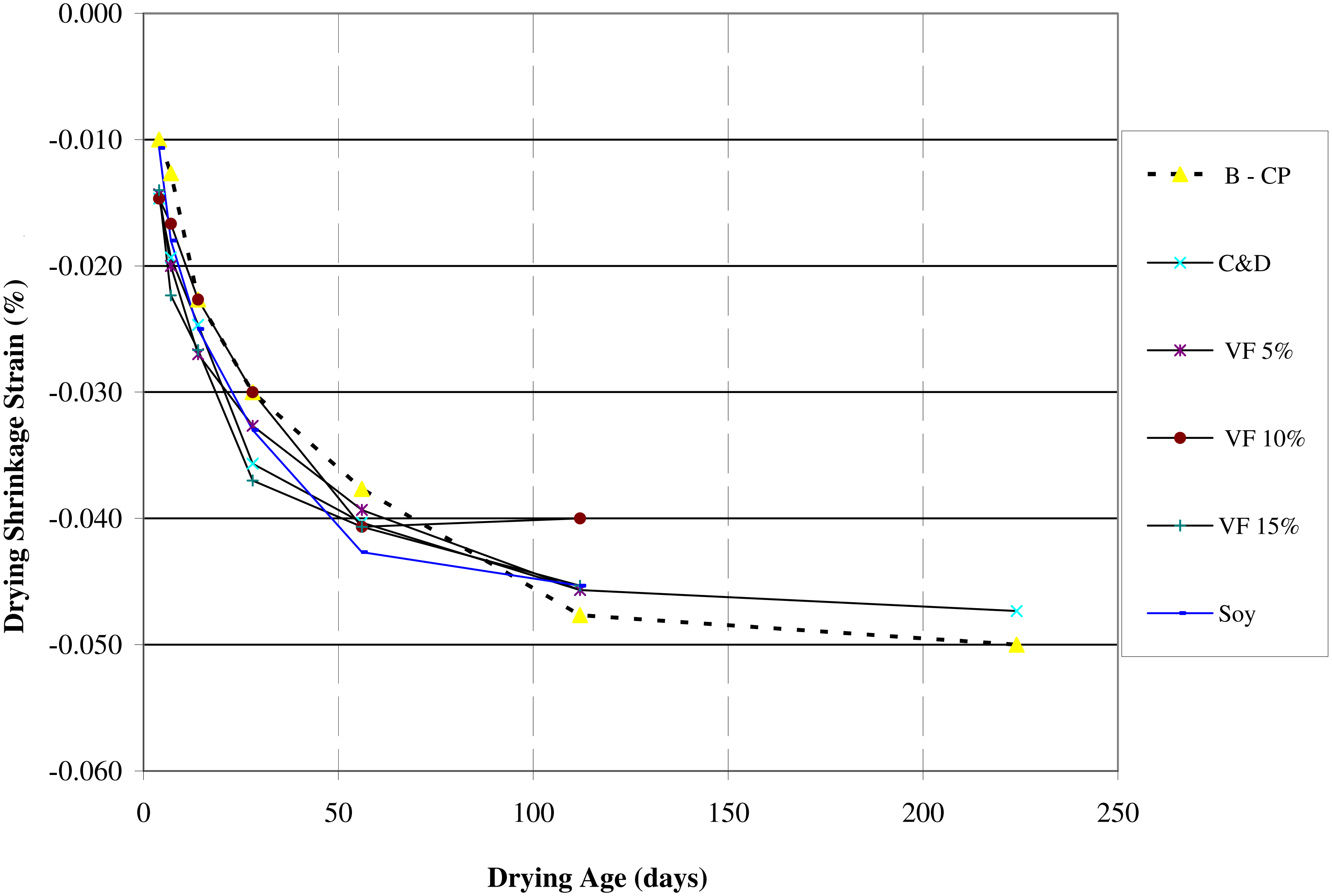

Figure 5-19: AUR – Drying Shrinkage Development of Concrete Prisms for Mix 0.44 Concrete

5.4.8.2 Concrete Mix 0.37

All physical concrete properties were determined by Auburn University. Concrete Mix 0.37 was a high-strength mixture possessing a water-cement ratio of 0.37. The average results and percent difference of each trial burn relative to the baseline results from Mix 0.37 are shown in Table 5-36. A graphical representation of the fresh property results relative to the baseline is shown in Figure 5-20.

This is a high-performance concrete, and its fresh properties are highly dependent on the functionality of chemical admixtures. Therefore, the results are more variable for the mixture than Mix 0.44.

Due to the volume of concrete required to conduct the necessary tests and the volume limitations of available mixing equipment, each mixture was divided roughly in half to ensure adequate blending of all materials. The air content, slump, and unit weight shown in Table 5-36 are the average of two batches of concrete mixed for each trial. All single lab precision requirements were met between the individual batches prepared for each trial.

The air content for Mix 0.37 decreased significantly over all trials and are outside the allowable precision limits for the baseline concrete. Interactions between the high-range water-reducing admixture and the cement and/or the air-entraining admixture used in each 0.37 concrete mixture could be the cause for the fluctuation in air content. The target air content for each mix was 4.0 %. The trial mixture made with the construction and demolition waste trial burn cement was 0.2 % outside the baseline's allowable precision limit of 0.8 % and was the only trial mixture to fall outside the precision limits.

The Mix 0.37 trial mixtures failed to meet slump precision requirements when compared to the baseline. The slump test results showed a significant decrease in slump for all trial burn mixtures. The low air content for each trial mixture is one of the possible causes for the low slump in each trial. If the precision statement for concrete slump is converted into an allowable percentage relative to the baseline, the limiting value is ± 42.6%. From Figure 5-20, VF 5 % shows the largest decrease in slump relative to the baseline. This concrete mixture was repeated in order to rule out possible human error that may have occurred during the initial mixture. The results from the repeated concrete tests were within precision limits when compared to all the original results obtained.

The unit weight results of the variable feed trials and the soy trial slightly exceeded the allowable limits to be deemed similar to the baseline. The small percent differences relative to the baseline for all the trial mixtures unit weight are presented in Figure 5-20. The increase in unit weight can be attributed to the lower air contents of the trial mixtures relative to the baseline mixture.

Many factors including temperature, water-cement ratio, cement chemistry, and admixtures control setting (Odler 1998). The concrete produced from the variable feed 5 % trial burn cement was the only trial concrete that met the setting precision limits when compared to the baseline setting results. From Figure 5-20, it can be seen that the setting times for concrete made with the construction and demolition waste, variable feed 15 %, and soybean seed trial burn cement's were reduced compared to the baseline setting results. The concrete produced from the variable feed 10 % trial burn cement significantly increased for initial and final setting times compared to the baseline burn setting results.

The air-corrected compressive strengths were calculated in the same manner as described for Mix 0.44. The unadjusted compressive strengths for each trial burn and their percent difference relative to the baseline results are presented in Table 5-36. The air-corrected compressive strengths and their percent difference relative to the baseline results are presented in Table 5-37. The air-corrected compressive strength development data for Mix 0.37 are shown in Figure 5-21. The allowable percent difference relative to the baseline results for trial burns to meet the baseline's compressive strength precision limit is 7 %.

The compressive strengths from the concrete prepared with the construction and demolition waste burn cement was the most comparable to the baseline. One-day compressive strength results from concrete made using cement from the variable feed 10 and 15 % trial burns showed reductions of 20 and 18 %, respectively, compared to the baseline compressive strength results. Seven to 91-day day compressive strength results from concrete made using cement from the variable feed 5 and 15 % and the soybean seed trial burns increased 8 to 20 % compared to the baseline results. The late-age compressive strength results from the variable feed 10 % trial burn are similar to the baseline strength results. Compressive strength results from concrete made using cement produced during the soybean trial burn exhibited slightly higher strengths over the majority of testing ages compared to the baseline.

Drying shrinkage results of concrete prisms from Mix 0.37 are shown in Table 5-38. The average drying shrinkage strain of the concrete prisms and their percent difference relative to the baseline's results are presented. A plot of the average drying shrinkage strain development over 112 days for all the trial cement's concrete prisms are shown in Figure 5-22. To meet the allowable precision limit for drying shrinkage, the difference between the trial and baseline results cannot exceed 0.0137 %. The concrete prisms with the greatest drying shrinkage strain development were made with the baseline burn's cement. The concrete prisms made with the soybean seed trial burn cement fell below the allowable precision limit for the 112-day test. All the other the trial burn cements used for Mix 0.37 concrete prisms showed average strains that met the precision limits set by the baseline's drying shrinkage results. Therefore, overall drying shrinkage is minimally affected by the utilization of alternative fuel cements.

Concrete permeability results from Mix 0.37 are shown in Table 5-35. At 91 days, the test results show that the concrete has a low permeability. The levels of chloride ion penetration are defined in ASTM 1202 (2007). The concrete made using the soybean seed trial burn cement showed the greatest increase (19 %) of all the trial burns compared to the baseline results. The concrete permeability that was made from the soybean seed cement is within the baseline permeability result's precision limit and is therefore considered similar.

Table 5-36: AUR – Physical Properties and Percent Difference Relative to Baseline for Mix 0.37 Concrete for All Burns

Property	B-CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	AUR	AUR	% Diff.	AUR	% Diff.	AUR	% Diff.	AUR	% Diff.	AUR	% Diff.
Total Air Content (%)	5.8	5.0	-14	3.5	-40	4.7	-20	4.5	-22	3.5	-40
Slump (in)	4.7	3.4	-28	0.5	-89	2.5	-47	2.3	-52	1.5	-68
Unit Weight (lb/ft^3)	146	147	1.0	150	2.9	148	1.2	149	2.1	150	2.9
Initial Set (Min.)	224	205	-8.5	217	-3.1	266	18.8	208	-7.1	187	-16.5
Final Set (Min.)	301	282	-6.3	301	0.0	351	16.6	282	-6.3	254	-15.6
Compressive Strength (MPa)											
1 day	24.2	22.7	-6.2	23.6	-2.5	18.3	-24.4	18.7	-22.7	23.6	-2.5
3 days	32.8	31.3	-4.6	31.3	-4.6	27.9	-14.9	29.4	-10.4	29.8	-9.1
7 days	36.6	36.5	-0.3	39.3	7.4	34.3	-6.3	37.3	1.9	36.4	-0.5
28 days	45.0	44.5	-1.1	48.3	7.3	44.5	-1.1	47.9	6.4	44.7	-0.7
91 days	50.6	50.1	-1.0	53.4	5.5	49.2	-2.8	51.2	1.2	49.4	-2.4
Permeability @ 91 days (Coulombs)	1762	1846	4.8	1717	-2.6	1939	10.0	1715	-2.7	2100	19.2

Notes:

CIP - Collection in Progress

NC - Not Collected

NA - Not Applicable

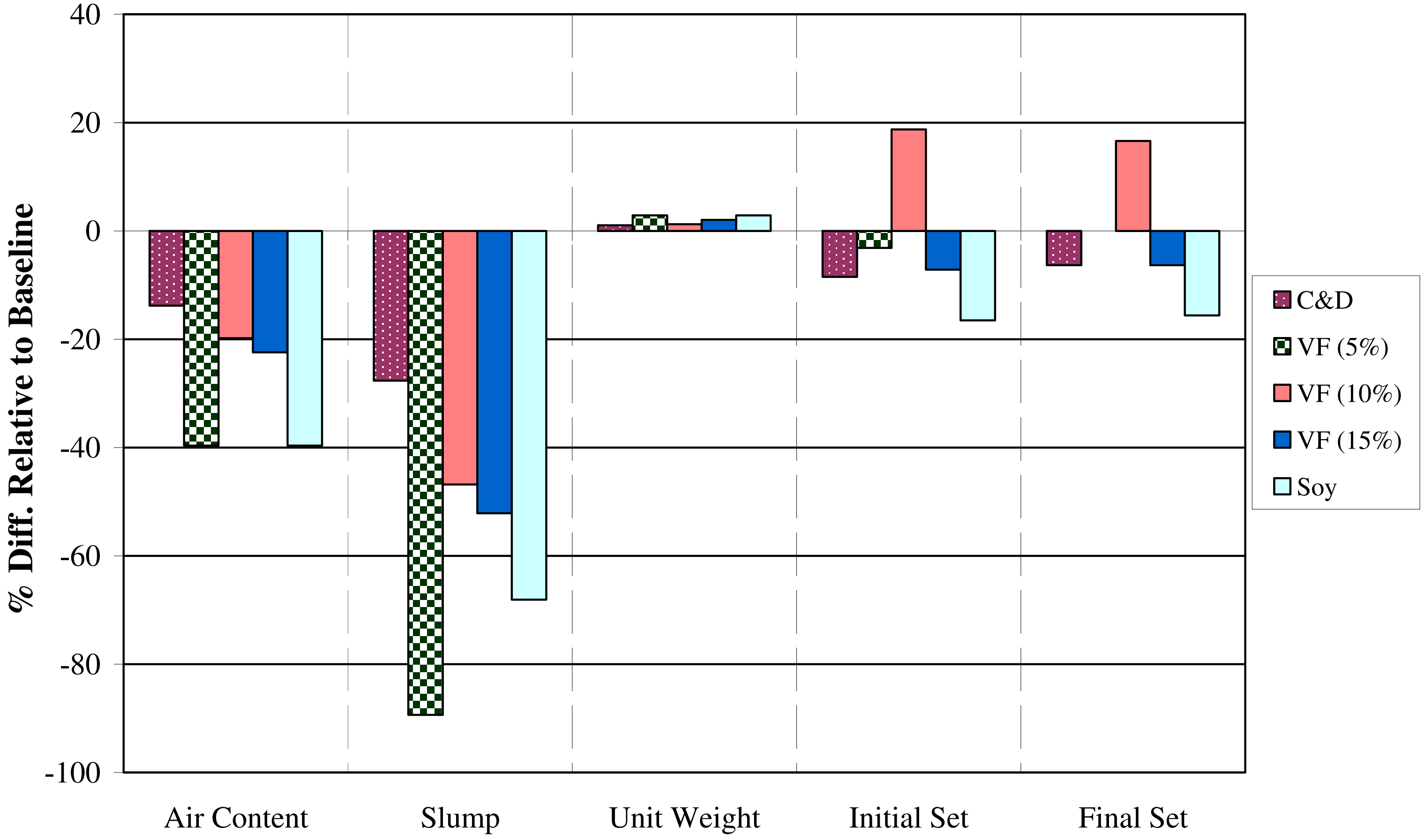

Figure 5-20: AUR – Percent Difference in Physical Properties Relative to Baseline for Mix 0.37 Concrete for Trial Burn

Table 5-37: AUR – Air-Corrected Compressive Strength and Percent Difference Relative to Baseline for Mix 0.37 Concrete

Concrete Age	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Avg. (MPa)	% Diff [1]	Avg. (MPa)	% Diff [1]	Avg. (MPa)	% Diff [1]	Avg. (MPa)	% Diff [1]	Avg. (MPa)	% Diff [1]
1 day	23.6	-2.4	26.3	8.7	19.4	-20.0	19.9	-17.7	26.3	8.7
3 days	32.6	-0.8	34.9	6.4	29.5	-10.0	31.3	-4.5	33.2	1.3
7 days	38.0	3.7	43.8	19.7	36.3	-0.9	39.7	8.5	40.6	10.9
28 days	46.3	2.8	53.9	19.7	47.1	4.6	51.0	13.4	49.8	10.8
91 days	52.1	3.0	59.5	17.7	52.0	2.8	54.5	7.8	55.1	8.9

Notes: [1] Relaive to B-CP

Table 5-38: AUR – Drying Shrinkage Development and Percent Difference Relative to Baseline for Mix 0.37 Concrete for All Burns

Drying Age (days)	B - CP	C&D		VF 5%		VF 10%		VF 15%		Soy	
	Avg. Strain (%)	Avg. Strain (%)	% Diff [1]	Avg. Strain (%)	% Diff [1]	Avg. Strain (%)	% Diff [1]	Avg. Strain (%)	% Diff [1]	Avg. Strain (%)	% Diff [1]
4	-0.015	-0.018	17.8	-0.017	15.6	-0.013	-15.6	-0.014	-8.9	-0.015	2.2
7	-0.021	-0.022	8.1	-0.020	-1.6	-0.017	-16.1	-0.018	-12.9	-0.021	0.0
14	-0.029	-0.029	1.2	-0.030	5.8	-0.026	-10.5	-0.026	-8.1	-0.027	-5.8
28	-0.038	-0.036	-4.4	-0.040	4.4	-0.034	-10.5	-0.032	-14.9	-0.036	-6.1
56	-0.048	-0.046	-4.2	-0.046	-3.5	-0.042	-11.8	-0.040	-17.4	-0.040	-17.4
112	-0.058	-0.053	-8.7	-0.050	-12.7	-0.049	-15.6	-0.045	-22.5	-0.043	-25.4

Notes: [1] Relative to B-CP

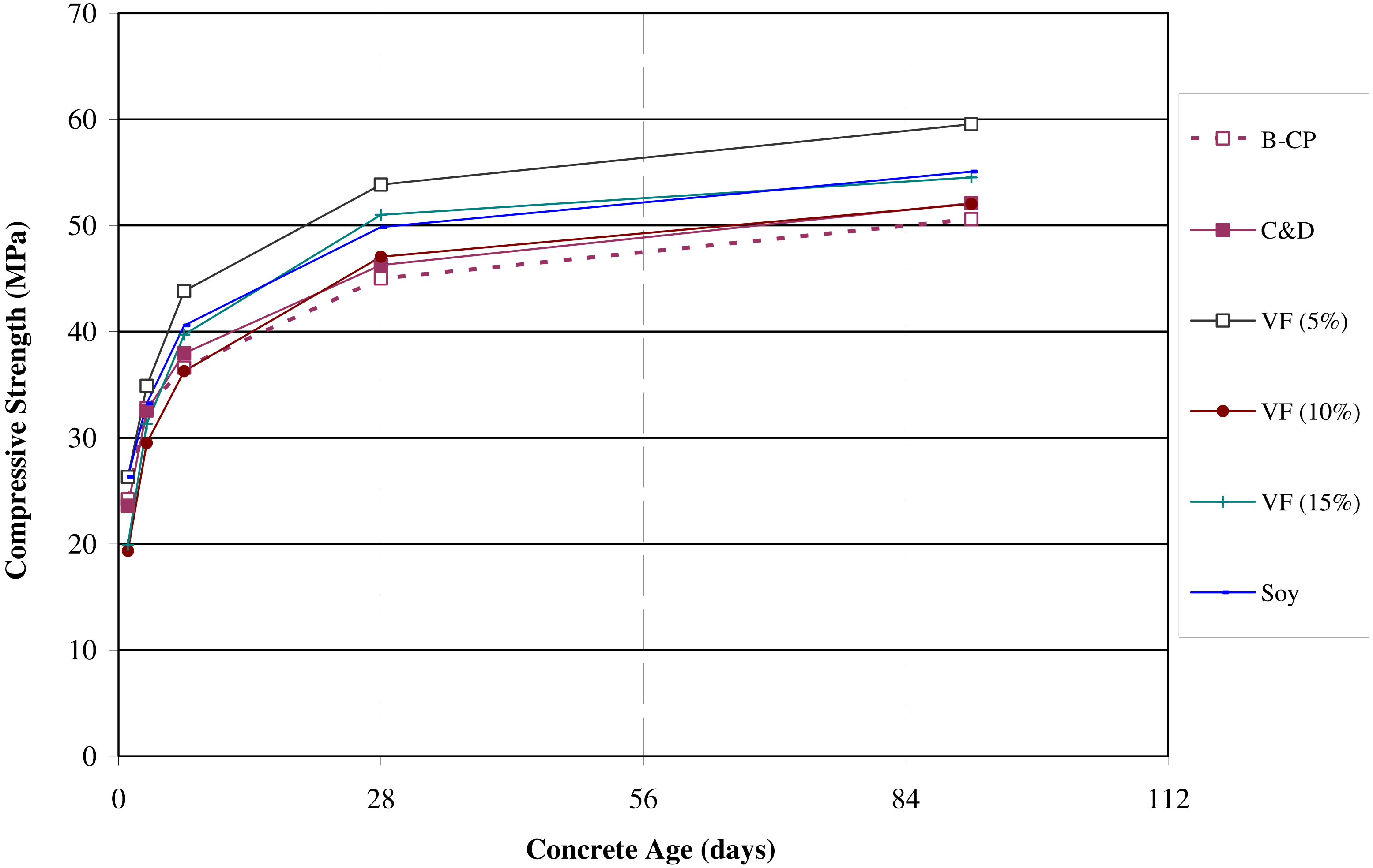

Figure 5-21: AUR – Air-Corrected Compressive Strengths for Mix 0.37 for All Burns

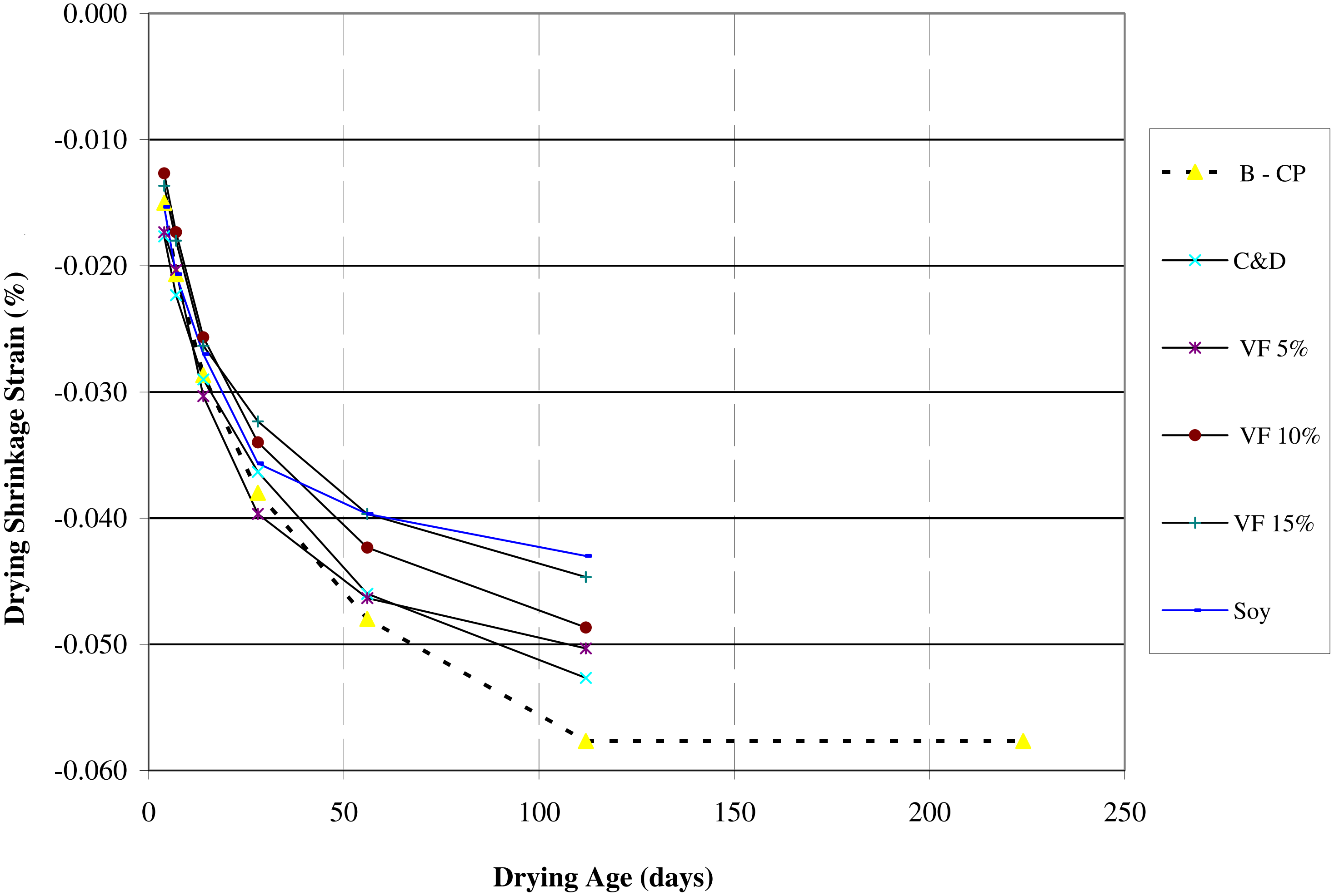

Figure 5-22: AUR – Drying Shrinkage Development of Concrete Prisms for Mix 0.37 Concrete

5.4.9 Comparison of Paste, Mortar, and Concrete Properties

The properties of paste, mortar, and concrete that were made with the cement of each trial burn are compared in this section. A brief review of the test results is presented followed by a discussion of any trends that are consistent between the paste, mortar, and concrete results.

The physical changes observed from the cement and concrete testing are presented in Tables 5-39 through 5-43. The number of tests conducted for a particular property as well as the medium of the observed effect (paste, mortar, or concrete) are presented in order to add perspective to the observed effects. Each arrow indicates a significant change in an individual test compared to the baseline's results. A trial test result is considered significantly different from the baseline result if the trial's result falls outside the baseline's allowable range of values. These values are specified by the test's ASTM precision statement. The results that are not significantly different are not reported unless all the test results for a particular property show similarities to the baseline result.

The physical properties of the paste, mortar, and concrete made with the construction and demolition waste trial burn cement are presented in Table 5-39. The concrete setting time and mortar cube flow are the only properties that did not show similarities to the baseline's results. Both mortar setting results for initial and final setting tests were comparable to the baseline's results. The chemical admixtures used in each concrete mixture could have caused the fluctuations observed in the setting times.

The physical properties of the paste, mortar, and concrete made with the variable feed 5 % trial burn cement are presented in Table 5-40. The decreased slump and increased unit weight compared to the baseline could be caused by the decrease in air content observed in the Mix 0.37 concrete mixture. Since the mortar setting times were comparable to the baseline's results, the concrete's chemical admixtures could be the cause of the concrete's retarded setting times. Two concrete 28-day strength results showed strength increases compared to the baseline's results. Both the mortar cube 28-day strength results were comparable to the baseline's results.

The physical properties of the paste, mortar, and concrete made with the variable feed 10 % trial burn cement are presented in Table 5-41. The air content tests did not produce any trends that were consistent over the mortar and concrete testing. The concrete setting and 28-day strengths showed increases in two tests. Since increases in the mortar setting and 28-day strength tests did not show increases, the increases seen in the concrete tests could have been caused by admixture-cement interactions.

Table 5-39: Summary of Physical Properties of Cement and Concrete from the C&D Trial Burn

Property	No. of Tests	Trend or Effect Relative to B-CP	Medium of Observed Effect	Likely Cause
Air Content	3	CTB	NA	NA
Slump	2	CTB	NA	NA
Unit Weight	2	CTB	NA	NA
Initial Set (↓ = accelerated)	4	↓↑	Concrete	Chemical Admixtures
Final Set (↓ = accelerated)	4	↓↑	Concrete	Chemical Admixtures
Strength (28-day)	6	CTB	NA	NA
Autoclave Exp.	2	CTB	NA	NA
Mortar Flow	2	↓	Mortar	Unknown
Normal Consistency	2	CTB	NA	NA
Drying Shrinkage	3	CTB	NA	NA
Permeability	2	CTB	NA	NA
Blaine SSA	1	CTB	NA	NA

Notes:
CTB – All tests are comparable to baseline's results
NA - Not Applicable

Table 5-40: Summary of Physical Properties of Cement and Concrete from the VF 5% Trial Burn

Property	No. of Tests	Trend or Effect Relative to B-CP	Medium of Observed Effect	Likely Cause
Air Content	3	↓	Concrete	Unknown
Slump	2	↓	Concrete	Low Air Content
Unit Weight	2	↑	Concrete	Low Air Content
Initial Set (↓ = accelerated)	4	↑	Concrete	Chemical Admixtures
Final Set (↓ = accelerated)	4	↑	Concrete	Chemical Admixtures
Strength (28-day)	6	↑↑	Concrete	Chemical Admixtures
Autoclave Exp.	2	CTB	NA	NA
Mortar Flow	2	↓	Mortar	Unknown
Normal Consistency	2	CTB	NA	NA
Drying Shrinkage	3	CTB	NA	NA
Permeability	2	CTB	NA	NA
Blaine SSA	1	CTB	NA	NA

Notes:
CTB – All tests are comparable to baseline's results   NA - Applicable

Table 5-41: Summary of Physical Properties of Cement and Concrete from the VF 10% Trial Burn

Property	**No. of Tests**	**Trend or Effect Relative to B-CP**	**Medium of Observed Effect**	**Likely Cause**
Air Content	3	↓↑	Concrete	Unknown
Slump	2	↓	Concrete	Low Air Content
Unit Weight	2	CTB	NA	NA
Initial Set (↓ = accelerated)	4	↑↑	Concrete	Chemical Admixtures
Final Set (↓ = accelerated)	4	↑↑	Concrete	Chemical Admixtures
Strength (28-day)	6	↑↑	Concrete	Chemical Admixtures
Autoclave Exp.	2	CTB	NA	NA
Mortar Flow	2	CTB	NA	NA
Normal Consistency	2	CTB	NA	NA
Drying Shrinkage	3	CTB	NA	NA
Permeability	2	CTB	NA	NA
Blaine SSA	1	↓	NA	NA

Notes:
CTB – All tests are comparable to baseline's results NA - Not Applicable

The physical properties of the paste, mortar, and concrete made with the variable feed 15 % trial burn cement are presented in Table 5-42. The air content tests did not produce any trends that were consistent over the mortar and concrete testing. The initial and final setting times for the concrete mixtures were not consistent with each other or the mortar setting results. Three of the four 28-day concrete strength results showed increases. This increase could be an effect of the chemical admixtures since the mortar 28-day results were comparable to the baseline's strength results. The increased drying shrinkage of the mortar specimens relative to the baseline's results could be caused by the increased cube flow. The drying shrinkage of the concrete specimens, however, did not significantly fluctuate from the baseline's results.

Table 5-42: Summary of Physical Properties of Cement and Concrete from the VF 15% Trial Burn

Property	No. of Tests	Trend or Effect Relative to B-CP	Medium of Observed Effect	Likely Cause
Air Content	3	↓	Concrete	Unknown
Slump	2	↓	Concrete	Low Air Content
Unit Weight	2	↑	Concrete	Low Air Content
Initial Set (↓ = accelerated)	4	↓↑	Concrete	Chemical Admixtures
Final Set (↓ = accelerated)	4	↓↑	Concrete	Chemical Admixtures
Strength (28-day)	6	↑↑↑	Concrete	Chemical Admixtures
Autoclave Exp.	2	CTB	NA	NA
Mortar Flow	2	↑	Mortar	Unknown
Normal Consistency	2	CTB	NA	NA
Drying Shrinkage	3	↑	Mortar	Increased Cube Flow
Permeability	2	CTB	NA	NA
Blaine SSA	1	CTB	NA	NA

Notes:
CTB – All tests are comparable to baseline's results   NA - Not Applicable

The physical properties of the paste, mortar, and concrete made with the soybean seed trial burn cement are presented in Table 5-43. The decrease air content observed in the Mix 0.37 concrete mixture could be the cause of the observed decrease slump and increase in unit weight. There were no defined trends that were observed in the mortar or concrete setting times. One of the two mortar setting tests showed acceleration compared to the baseline's mortar setting results. Both the final mortar setting time tests, however, were comparable to the baseline's mortar setting results. The 28-day mortar and concrete strength results were comparable to the baseline's strength results for 5 of 6 tests. The mortar cube flow was increased in one of two tests. The mortar drying shrinkage, however, was not affected by the increased cube flow.

Table 5-43: Summary of Physical Properties of Cement and Concrete from the Soy Trial Burn

Property	**No. of Tests**	**Trend or Effect Relative to B-CP**	**Medium of Observed Effect**	**Likely Cause**
Air Content	3	↓	Concrete	Unknown
Slump	2	↓	Concrete	Low Air Content
Unit Weight	2	↑	Concrete	Low Air Content
Initial Set (↓ = accelerated)	4	↓ ↑↑	Paste and Concrete	Chemical Admixtures
Final Set (↓ = accelerated)	4	↓↑	Concrete	Chemical Admixtures
Strength (28-day)	6	↑	Concrete	Chemical Admixtures
Autoclave Exp.	2	CTB	NA	NA
Mortar Flow	2	↑	Mortar	Unknown
Normal Consistency	2	CTB	NA	NA
Drying Shrinkage	3	CTB	NA	NA
Permeability	2	CTB	NA	NA
Blaine SSA	1	CTB	NA	NA

Notes:
CTB – All tests are comparable to baseline's results   NA - Not Applicable

5.4.9.1 Workability

The cement plant and Auburn University conducted several tests to determine the workability of each trial cement. The cement plant and Auburn University determined each trial cement's normal consistency and mortar flow. Auburn University also measured the slump of each concrete mixture made with the trial cements.

The results from the cement plant and Auburn University showed that all trial burn cement's normal consistency were similar to the baseline cement's results. The cement plant's results for mortar flow showed increases with the mortar made from the variable feed 15 % and soybean seed trial burn cements. Auburn University's mortar flow test results did not indicate increases for the variable feed 15 % and soybean seed trial burn cements. Auburn University found mortar flow decreases of 12 and 27 % with mortar made with the construction and demolition waste and variable feed 5 % trial burn cements, respectively. The concrete slumps measured for all Mix 0.44 trial mixtures were similar to the baseline's slump results. The concrete Mix 0.37 slumps made from the variable feed and soybean seed trial burn cements showed decreases between 47 and 89 %, respectively, compared to the baseline's slump results. The air contents of the Mix 0.37 concrete mixtures were significantly decreased compared to the baseline. The reduced air contents in the trial mixtures are thought to have reduced the slump of the Mix 0.37 concrete. There were no consistent trends in the tests defining workability that were found in the paste, mortar and concrete results. Therefore, the workability of paste, mortar and concrete are minimally affected by the use of the trial burn cements.

5.4.9.2 Setting

The cement plant and Auburn University conducted paste setting tests on all the cements produced during the trial burns. Auburn University also tested Mix 0.44 and Mix 0.37 concrete setting times that were made with the trial burn cements. The Vicat paste setting tests were conducted using ASTM C 191, and the concrete setting tests were conducted using ASTM C 403.

Both the cement plant and Auburn University results showed that the Vicat paste setting times for all the trial cements were similar to the baseline's paste setting results. The Mix 0.44 concrete setting results showed 10 to 39 % retardation compared to the baseline results for the concretes made with the variable feed trial burn cements. The Mix 0.37 concrete setting results made with the variable feed 10 and 15 % trial burn cements showed retardation and slight acceleration compared to the baseline burn's concrete setting results, respectively. The setting times for the Mix 0.37 concrete made with the construction and demolition waste and soybean seed trial burn cements were accelerated compared to the baseline's results.

The aluminate content of the construction and demolition waste and the variable feed 10 % trial burn cements increased 33 and 24 %, respectively, compared to the baseline's aluminate content. However, the Vicat paste setting times for the construction and demolition waste and variable feed 10 % trial burns did not seem to be affected by the aluminate increase and were similar to the baseline's results. The behavior of the concrete setting times are also not fully described by the aluminate content found in the trial burn cements. Other factors such as admixture-cement interaction, temperature, and the water-cement ratio can influence concrete setting times. There were no consistent trends that appeared in both the paste and concrete setting results. Since all the trial paste setting tests were similar to the baseline's paste setting results and the paste setting results were not influenced by the addition of admixtures, the effects of the trial fuel cements had minimal impact on setting results.

5.4.9.3 Strength

The cement plant and Auburn University conducted compressive strength tests on mortar cube specimens in order to determine the strength properties of the trial burn cements. Auburn University tested the compressive strength development of the concrete made with cement produced during the trial burns.

One-day compressive strength values for Mix 0.44 for the variable feed 15 % trial burn cements was reduced by 29, compared to the baseline's cement result. Since the mortar cube results made with the variable feed 15 % cement did not show 1-day reductions in strength, no trend could be established. Concrete Mix 0.37 compressive strengths made from variable feed 10 and 15 % trial cements showed reductions of 20 and 17 % in strength compared to the baseline's results for tests, respectively. Here again, the mortar cubes made from variable feed

10 and 15 % trial burn cement did not show 1-day reductions in strength and therefore trends cannot be established.

The cement plant and Auburn University found that the 28-day mortar cube compressive strength results were similar to the baseline's results at this age. Twenty-eight-day Mix 0.44 concrete compressive strengths made with all the trial burn cements were similar to the baseline's 28-day compressive strength. Mix 0.37 concrete compressive strengths made with variable feed 5 and 15 % and soybean seed trial burn cements showed increases in strength between 10 and 20 % compared to the baseline's results for 28-day tests. The strength differences between the concrete and mortar results could be influenced by admixture-cement interactions and differences in air content. Since chemical admixtures were not used in the mortar specimens, their strength results are more representative of the trial cement's strength attributes than the concrete strength results. Given that the majority of trial mortar cube compressive strengths were similar to the baseline's results, the effect that the trial fuels had on the cement is concluded to be minimal.

In an earlier phase of this project woodchips were used as an alternative fuel and co-fired with coal and tires. The mortar cube strengths from the earlier trial and the cubes made with the variable feed 10 % trial burn cement all fell within 12 % of each other. The 28-day strength difference between the two trial's mortar cube strength was 5 %. The Mix 0.44 concrete compressive strengths made from the previous woodchip trial burn and the variable feed 10 % trial burn were also compared. The 1- and 28-day strengths showed a 16 % and 7 % difference, respectively. The 1-day strength showed the largest difference in strengths over all the testing dates.

5.4.9.4 Drying Shrinkage

Mortar and concrete specimens were prepare with the cement produced during the trial burns in order to measure the drying shrinkage characteristics of the cement. The mortar specimens that were made with the cement produced in the variable feed 15 % trial burn showed the largest drying shrinkage strains compared to the baseline's strains. The remaining trial cements produced mortar strains that were similar to the baseline results. The concrete specimens that were made with the variable feed 15 % trial burn cement were similar to the baseline's concrete strains for both Mix 0.44 and 0.37. There were no consistent trends for drying shrinkage that were found in both the mortar and concrete testing results. Therefore, mortar and concrete drying shrinkage are minimally affected by the trial burn cements.

5.4.9.5 Permeability

Rapid chloride ion penetration tests were performed to obtain a measure of the concrete's permeability of the specimens made with the cement produced during the trial burns. Mix 0.44 produced moderate permeability concrete at 91-days of curing with each trial cement tested. Mix 0.37 produced low permeability concrete at 91-days of curing with each trial cement tested. A lower permeability was expected from Mix 0.37 because it was a lower water-cement ratio concrete than Mix 0.44. The fluctuation between trial cement and the baseline cement specimen results were minimal for Mix 0.44 and 0.37 permeability tests. The permeability of the concrete specimens tests do not appear to be affected by the trial burn cements.

5.4.10 Plant Emissions

Pollutants emitted from cement manufacturing facilities during production have raised environmental concerns about the sustainability of the cement manufacturing process. Emissions during this study were closely monitored by a Continuous Emission Monitoring System (CEMS) that recorded data in five-minute intervals. The emissions of the cement plant used are regulated by emission limits set by the Alabama Department of Environment Management (ADEM).

Emission data from the cement plant were reported in tons of emissions per hour. Auburn University normalized the emission data to account for variations in production rate of clinker. Therefore, the emission data are presented in tons per ton of clinker. Results are presented in Table 5-44. The percent differences between the emissions from trial burns and the emissions from the baseline burn are shown in Figure 5-23.

Similar to the clinker data, the emission results were statistically analyzed using the Wilcoxon rank-sum test. If the Wilcoxon test showed a difference between the trial and baseline means, the percent difference relative to the baseline's result establishes the degree of difference. If the statistical analysis does not show a difference between the baseline and trial means, the percent difference is not meaningful.

The p-values calculated for the nitrogen oxides showed that all the trial burns except for the soybean seed trial burn have significantly different means compared to the baseline's NO_x mean. The nitrogen emissions were reduced for the construction and demolition waste and the variable feed burns compared to the baseline burn.

Thermal nitrogen oxides constitute around 70% of the the total NO_x emissions and are created when atmospheric nitrogen begins to oxidize (Hendrik and Padovani 2003). Thermal NO_x is controlled by the amount of available oxygen during the pyroprocess (Greer et al. 2004). The type of alternative fuels utilized has not been shown to alter the overall nitrogen oxide emission. The decrease in NO_x, therefore cannot be attributed to any of the trial fuels due to not knowing the oxygen levels in the kiln during each burn.

The p-values calculated for sulfur dioxide show that all the burn means are significantly different compared to the baseline mean. As shown in Figure 5-23, the SO_2 emission levels for the construction and demolition waste and soybean seed trials increased compared to the baseline SO_2 level. Conversely, the SO_2 emission levels decreased for the variable feed 5 and 10 % woodchip trial burns. Sulfur dioxides are formed from raw materials and fuels (Hendrik and Padovani 2003). The concentrations of sulfur within the alternative fuels are small compared to the traditional fuels and the raw materials. Therefore, the trial alternative fuels seem to have little effect on the SO_2 emissions. In the previous woodchip trial, the SO_2 level fell between the variable feed 5 and 10 % trial burn SO_2 values. This is notable because the woodchip replacement rate during the previous woodchip trial was 7 %. The kiln feed for the construction and demolition waste trial burn had a 43% increase in sulfur relative to the baseline. The coal used for the construction and demolition waste trial burn also had a 38 % increase in sulfur. The kiln feed and coal sulfur contents were also elevated for the soybean seed trial burn. The increase in sulfur content in the kiln feed and coal could be the cause of the elevated SO_2 content shown in Figure 5-23 for the construction and demolition waste and soybean seed trial burns. The sulfur content in the kiln feed and coal was slightly elevated and decreased, respectively for the variable feed trial burns.

The p-values calculated for the volatile organic compounds (VOC) show that all the burn means are significantly different. The percent difference relative to the baseline of the volatile organic compound emissions for all the trial burns are shown in Figure 5-23. The volatile organic emissions were significantly reduced throughout all the trials compared to the baseline. Compared to the previous woodchip trial burn VOC level, the variable feed 5 and 10 % trial burn CO levels were reduced 48 and 67 %, respectively. Volatile organic compounds are formed from combustion of organic material within the raw materials and fuels. Research has shown that system design and control, such as the number of stages in the preheater and the exiting flu-gas temperatures, dictate the formation of dioxin and furan formations more so than the fuels utilized (Bech and Mishulovich 2004; Loo 2008).

The p-values calculated for the carbon monoxide (CO) show that the construction and demolition waste and variable feed 15 % woodchip trial burns are significantly different. The variable feed 5 and 10 % and the soybean seed trial burns have statistically similar means to the baseline, and therefore their percent differences relative to the baseline are negligible. The carbon monoxide content in the variable feed 15 % trial burn was decreased by 19 % compared to the baseline, which was the greatest difference for all the trial burns. Compared to the previous woodchip trial burn CO level, the variable feed 5 and 10 % trial burn CO levels were each reduced 34 %.

Table 5-44: CPR – Emission Wilcoxon Rank Sum Results and Percent Difference Relative to Baseline

Emissions		NO_x (10^{-3}) (tons/ton clinker)	SO_2 (10^{-5}) (tons/ton clinker)	VOC (10^{-5}) (tons/ton clinker)	CO (10^{-4}) (tons/ton clinker)
B-CP	**Avg.**	0.95	1.0	4.26	3.85
C&D	**Avg.**	0.81	1.55	1.44	3.68
	P-value[1]	0.0001[2]	0.0001[2]	0.0001[2]	0.0075[2]
	%Diff	-14.65	63.43	-66.29	-4.45
VF 5%	**Avg.**	0.76	0.25	1.34	3.93
	P-value[1]	0.0001[2]	0.0001[2]	0.0001[2]	0.1729
	%Diff	-20.34	-73.72	-68.45	2.17
VF 10%	**Avg.**	0.83	0.42	0.85	3.89
	P-value[1]	0.0001[2]	0.0001[2]	0.0001[2]	0.5137
	%Diff	-13.03	-55.50	-80.04	1.15
VF 15%	**Avg.**	0.87	1.11	1.67	3.13
	P-value[1]	0.0077[2]	0.0074[2]	0.0001[2]	0.0001[2]
	%Diff	-8.53	17.15	-60.79	-18.74
Soy	**Avg.**	1.15	1.68	3.33	3.86
	P-value[1]	0.7471	0.001[2]	0.0001[2]	0.4990
	%Diff	20.83	76.58	-21.79	0.20

Notes:

[1] Based on Wilcoxon rank-sum

[2] Significantly different means

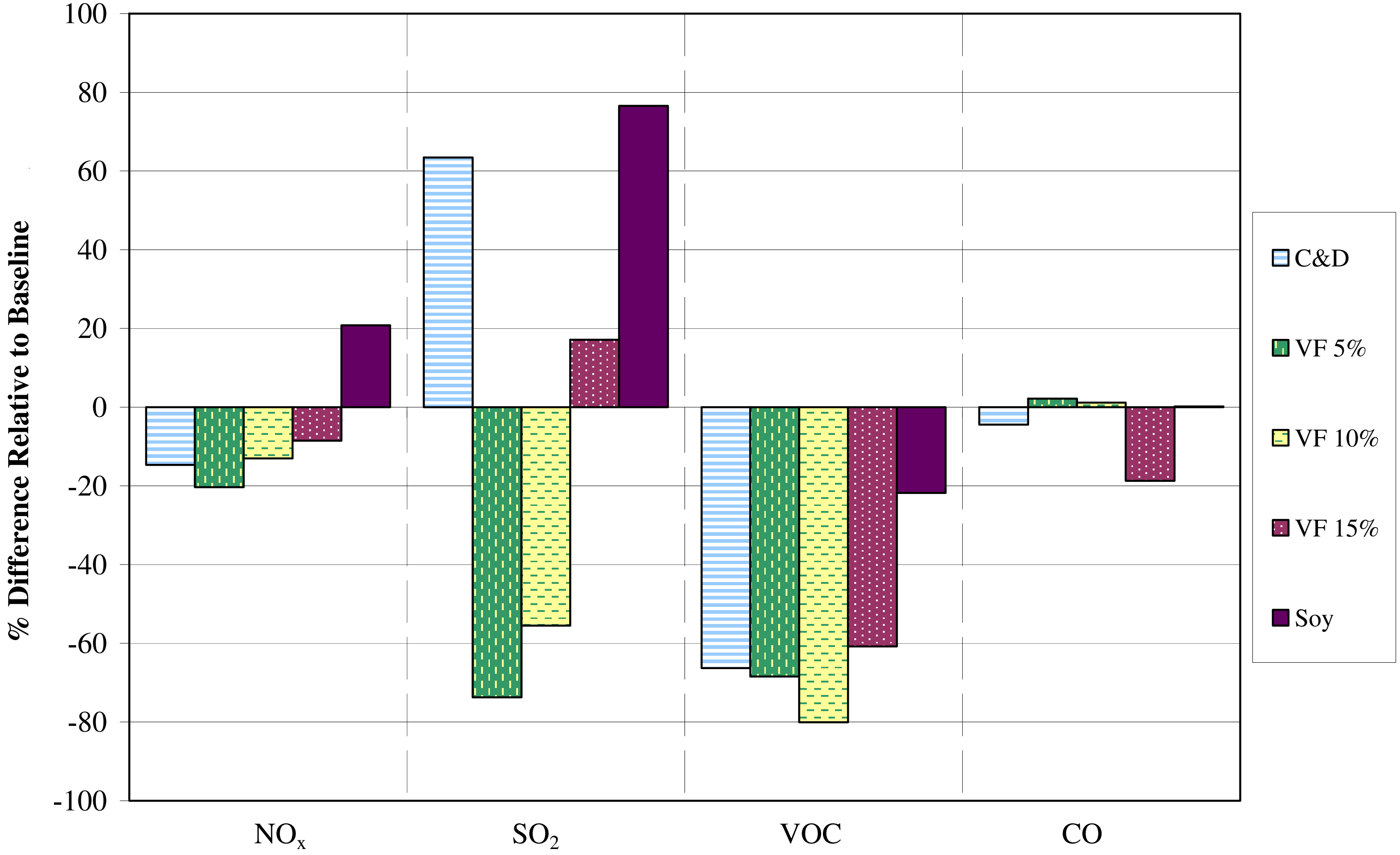

Figure 5-23: Percent Difference Relative to Baseline Emissions for All Burns

CO emissions remained within -19 to 2 % of the baseline CO emissions. Research has shown that carbon monoxide develops from the incomplete combustion of carbon rich fuels due to insufficient oxygen at the combustion site (Greer et al. 2004). Coal has the highest carbon content of all the fuels used. The ultimate analysis showed that the carbon content of the coal fluctuated more than the carbon contents of the plastic blend and trial fuels. Since coal was the most utilized fuel during all the trial burns, the effects from changes in the coal's chemical composition are more likely to influence emission results than the plastic blend or the trial fuels. As previously mentioned, the carbon monoxide emitted from the construction and demolition waste and the variable feed 15 % burns were the two trials with differing means compared to the baseline. Although the coal composition for the construction and demolition waste possessed a negligible percent difference to the baseline, the variable feed 15 % showed a decrease of about 10 % in carbon content. This could explain a portion of the overall decrease in carbon monoxide within the variable feed 15 % trial burn.

The ADEM limits pertaining to each emission monitored by the cement plant are tabulated in Table 5-45. The emission limits are reported in tons per 30 days or tons per hour. Utilizing the cement plant's production rates from each trial, the emission limits were converted to ton of emission per ton of clinker. The average of each emission for all the burns is presented at the bottom of Table 5-45 and shown in Figure 5-24.

The average, 5th and 95th percentiles of each emission for all burns are shown in Figure 5-24. All the emissions remained within limits except for the volatile organic compounds within the baseline and soybean seed burns. As previously stated, controlling the VOC emissions relies more on system control than fuel utilization and this apparent non-compliance cannot be attributed to the use of the trial fuels.

Table 5-45: ADEM Emission Limits and Normalized Limits for Each Burn

ADEM Limits (2007-2010)					
Emission		**NO_X**	**SO_2**	**VOC**	**CO**
Limit (tons/30 days)		221	202	4.8	NA
Limit (tons/hr)		0.307	0.282	0.007	0.36
B-CP	**tons clinker/hr[1]**	198.3			
	Limit (tons/ton clinker)	1.55E-03	1.42E-03	3.53E-05	1.82E-03
C&D	**tons clinker/hr[1]**	218.6			
	Limit (tons/ton clinker)	1.40E-03	1.29E-03	3.20E-05	1.65E-03
VF	**tons clinker/hr[1]**	219.9			
	Limit (tons/ton clinker)	1.40E-03	1.28E-03	3.18E-05	1.64E-03
Soy	**tons clinker/hr[1]**	225.4			
	Limit (tons/ton clinker)	1.36E-03	1.25E-03	3.11E-05	1.60E-03
Average Limit (tons/ton clinker)[1]		1.43E-03	1.31E-03	3.26E-05	1.67E-03

Notes: [1] Based on Average Production Data

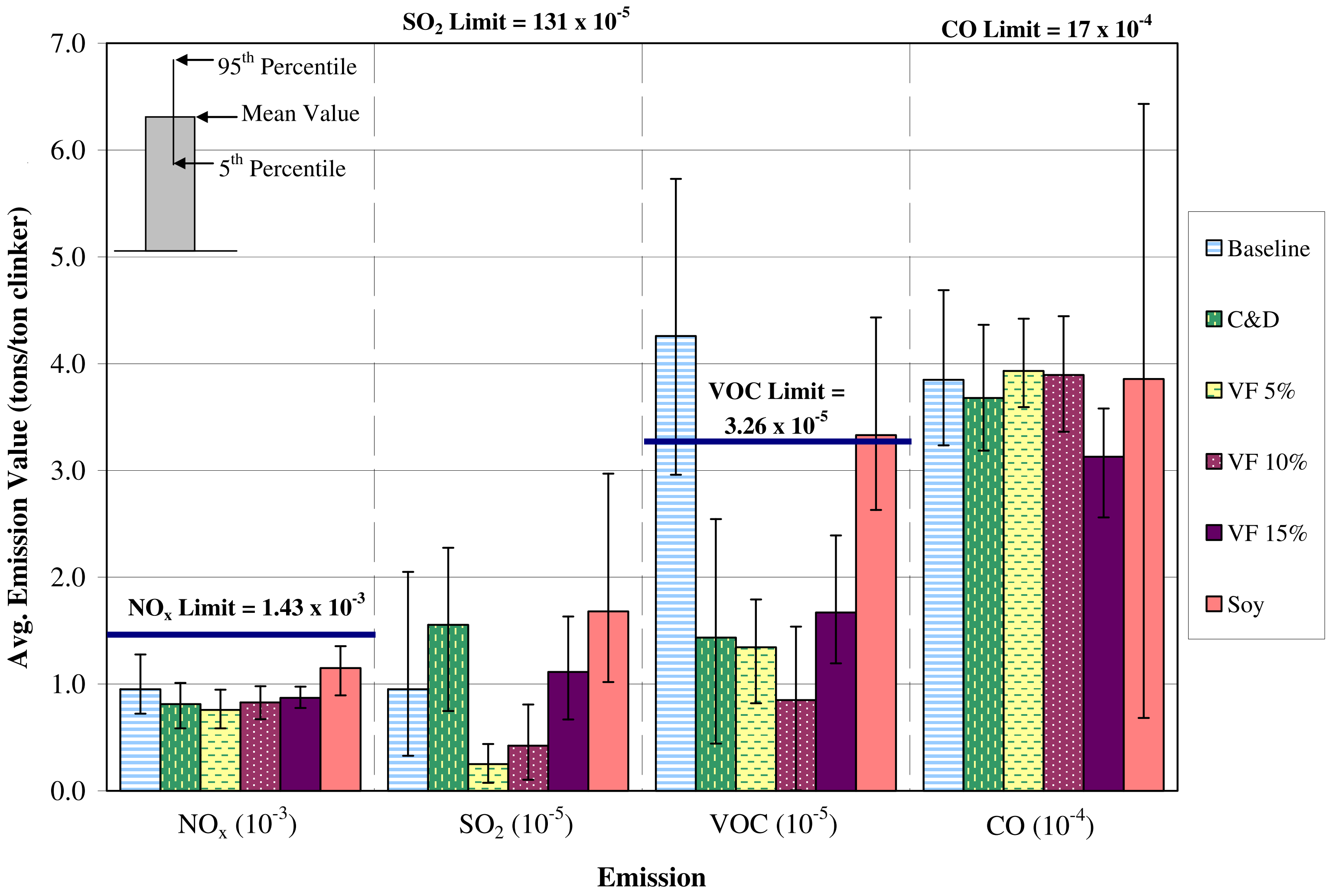

Figure 5-24: Average Normalized Plant Emissions with ADEM Limits for All Burns

5.5 CONCLUDING REMARKS

The complex nature of cement manufacturing and inherent variability in the chemical composition of raw materials and fuels create challenges attributing the effects of one process input to the overall production and performance of the cement. However, multiple conclusions have been formed regarding the utilization of alternative fuels in the manufacture of portland cement.

The ability of the cement plant to maintain production rates and efficiently process and dose the trial fuels were the initial objectives of this study. The processing ability of the available equipment is one factor that limits substitution rates. The construction and demolition waste and woodchip burns did not cause any feed problems. Several cement plant personnel experienced allergic reactions due to handling and de-dusting the soybean seeds. This was most likely due to the herbicide on the soybean seed. This problem, however, was eliminated with the use of proper personal protective equipment.

The energy value associated with each fuel was also an important aspect in determining the viability of the alternative fuel source. The energy values of the fuels utilized during all the trials of this study were less than those of the traditional fuels. The as-received energy values for each fuel utilized during this study were as follows:

1. Coal: 10,820 to 12,090 with an average of 11,320 BTU/lb,
2. Plastics: 8,855 to 10,780 with an average of 10,130 BTU/lb,
3. Construction and Demolition waste: 3,370 to 8,180 with an average of 6,050 BTU/lb,
4. Woodchips: 3,355 to 6,996 with an average of 4,736 BTU/lb, and
5. Soybean seeds: 8,977 to 9,375 with an average of 9,150 BTU/lb.

The coal had the highest energy content followed by the plastic waste and alternative fuels. The high energy content of the plastic waste is one reason it has been utilized for a number of years and is considered a traditional fuel for this study. The soybean seeds possessed the highest energy values for the alternative fuels followed by the construction and demolition waste and woodchips. The minimum and maximum heating values are expressed to show the fluctuation in energy values associated with each fuel. Moisture content greatly affects the energy content of a fuel. Coal, plastics, and soybean seeds all possessed fairly stable moisture contents and thus the ranges of energy values are significantly lower than the construction and demolition waste and the woodchip fuels heating ranges.

A goal of this this part of the study was to determine if the utilization of alternative fuels had a direct impact on the chemical composition of the portland cement. The kiln feed and the cement kiln dust were compared to their respective baseline values and found to be consistent with the exception of an elevated SO_3 content found in all the trial burns kiln feed. A probable cause for the increase in SO_3 was the elevated SO_3 contents found in the of cement kiln dust, which is recycled into the kiln feed.

The statistical analysis performed on the clinker data showed that the majority of parameter means were significantly different than the parameter means of the baseline burn. This was expected because of the narrow range of values surrounding the mean of each parameter. Of the parameter means that showed significant differences, however, the percent difference between the trial and baseline parameter means were small for most parameters. This indicates a fair amount of consistency throughout the trial burns. An example of the consistency that was maintained over all the trial burns can be seen in the chemical composition of the cement's primary oxides levels, Al_2O_3, CaO, Fe_2O_3, and SiO_2 compared to the baseline cement. All of the primary oxide levels are within 10 % of the baseline's results. There were minimal fluctuations found in the cement Bogue compounds. The alite content increased 17 % in the cement produced during the soybean seed trial burn and the aluminate content of the construction and demolition waste and variable feed 10 % trial cements also increased compared to the baseline alite content. The Bogue compounds are influenced by multiple variables such as process inputs, kiln temperature, and clinker cooling rates. Because of the inherent variability throughout portland cement production, changes in cement chemistry are difficult to link to the utilization of a particular fuel.

The physical property results from the cement plant and Auburn University were compared. If consistent changes were observed between a trial and the baseline result throughout paste, mortar, and concrete testing, the property change could be verified and attributed to the trial cement. The majority of paste and mortar physical properties tested were similar to the baseline's paste and mortar results. Since the paste and mortar testing did not use the admixtures found in the concrete mixtures, the paste and mortar tests were thought to better represent the actual behavior of the trial cements. Overall, it was found that the trial burn cements had minimal effects on workability, setting time, strength, drying shrinkage, and permeability compared to the baseline cement.

The statistical analysis conducted for the NO_x emission showed significant differences between the trial and baseline means for all burns except the soybean seed trial. The NO_x, however, were reduced for the construction and demolition waste and variable feed trails. Since the majority of NO_x develops from the oxidation of atmospheric nitrogen, conclusions about the effects of alternative fuels cannot be drawn without reports of oxygen levels in the kiln during the pyroprocess.

Statistical analysis also showed significant differences between the baseline and trial means for SO_2. The increase of SO_2 in the construction and demolition waste and soybean seed trials was thought to be caused by the elevated sulfur contents found in the kiln feed and coal. Because of the low sulfur content of woodchips, the increase in SO_2 from the variable feed 5 % to the 15 % trial burn is probably not due to the increase in woodchip substitution. The kiln feed of the variable feed burns, however, showed progressively increasing SO_3 levels compared to the baseline.

All the trials showed significantly different means for the volatile organic compound emissions. The VOC's were reduced for all burns compared to the baseline's VOC levels. Research has proven that control of volatile organic emissions depend more on system design and control than fuels utilized.

Statistical analysis of the carbon monoxide results for all burns showed that only the construction and demolition waste and variable feed 15 % possessed significantly different means compared to the baseline. The degree of difference between the construction and demolition waste and the baseline, however, was almost a negligible. The decrease seen in the variable feed 15 % trial is thought to be partially caused by a 10 % decrease in the carbon content of the coal utilized during that trial.

Throughout this chapter, several physical changes in the cement could be attributed to changes in chemical composition. It is, however, unfortunate that the variability in the production of portland cement makes connecting changes in cement chemistry or physical properties directly to the utilization of alternative fuels a difficult task. This study did not find conclusive evidence that the changes in cement chemistry and performance were solely due to the utilized alternative fuels. The implementation of trial fuels in this study successfully decreased the quantity of the traditional fuels required and produced cement with equal if not slightly improved properties.

CHAPTER 6

PART 2—SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

6.1 SUMMARY

Alternative fuels included in this study are construction and demolition waste, woodchips, and soybean seeds. Each of these fuels was utilized in order to partially replace and therefore lessen the demand for traditional fuels. Each trial fuel and was co-fired with coal and a waste-plastic blend. In this phase of this study, the waste-plastic bend is considered a traditional fuel since it is used during normal operation at the cement plant.

The first alternative utilized over a 3-day burn period was construction and demolition waste (C&D). The construction and demolition waste consisted of wood, paper, and plastics. The second trial utilized woodchips (VF) and was conducted over a 6 -day period. This burn was unique to this study due to the progressively increasing substitution rate of woodchips. The third and final burn, which utilized soybean seeds, was also conducted over a 3-day burn period. Although this burn took place several months after the baseline, the conditions at the cement plant were maintained to the best of the staffs' ability. A baseline or control burn consisting of just coal and the waste plastic blend occurred prior to the trial burns.

During each trial burn, samples of process inputs and outputs were sampled by the cement plant. The chemical compositions of the samples were determined by two testing agencies. The chemistry of the process inputs and outputs for each trial burn were compared to the baseline's burn results. Since chemical changes in clinker can be caused by the incorporation of noncombustible materials, an attempt was made to establish connections between the clinker chemistry and the alternative fuel. Cement physical properties were determined by two agencies. Fresh and hardened concrete properties were determined by one party. Finally, emissions were monitored by the cement plant during each trial burn. These emissions were compared to the baseline's emissions in order to determine if any correlations could be established between the alternative fuels and their emission profiles.

6.2 CONCLUSIONS

The ability of the cement plant to maintain production rates and efficiently process and dose alternative fuels was the initial objective of this study. The processing ability of the available equipment is one factor that limits substitution rates. The construction and demolition waste and woodchip burns did not cause any feed problems. Several cement plant personnel experienced minor allergic reactions due to handling and de-dusting the soybean seeds. This problem; however, was eliminated with the use of proper personal protective equipment.

The energy value associated with each fuel was also an important aspect in determining the viability of the fuel. The energy values of the alternative fuels utilized during this study were less than those of traditional fuels. The as-received energy values for each fuel utilized during this study are presented in Section 5.4.4.

When assessing the feasibility of the alternative fuel, the unit cost of the fuel is an important parameter. Although some of the alternative fuels possess energy values that are roughly half that of the traditional fuels, the price for traditional fuels is typically significantly more than alternative fuels. Due to fuel cost data being proprietary knowledge, the feasibility of the trial alternative fuels based on price could not be evaluated or compared.

The utilization of each fuel remained fairly consistent over the burn periods. Coal accounted for almost 90 percent of the required energy during the baseline burn, but was reduced to 70 percent during the variable feed 15 percent trial burn. The plastic blend accounted for roughly 15 percent of the required energy for all trial burns. Alternative fuels accounted for 5, 5.4, 11.8, 16, and 7.5 percent of the total energy for the construction and demolition waste, variable feed 5, 10, and 15 percent, and soybean seed burns, respectively. Since the alternative fuels and waste plastic blend only accounted for 20-30 percent of the total fuel energy, only parameters possessing significant differences to the baseline have the possibility to affect the cement and concrete properties.

Another goal of this part of this study was to determine if the utilization of alternative fuels had a direct impact on the chemical composition of the portland cement. The kiln feed and the cement kiln dust results were compared to their respective baseline values and found to be consistent over all trials with the exceptions of elevated SO_3 and P_2O_5 concentrations. A probable cause for the increase in SO_3 was significantly elevated SO_3 contents found in the cement kiln dust. Cement kiln dust is routinely recycled into the kiln feed because it contains many of the same chemical properties that are found in the kiln feed. Since none of the raw materials possessed elevated SO_3 concentrations, the cement kiln dust SO_3 content was more than likely increased by the utilized fuels. It was, however, determined from the standard parameters that the SO_3 content for the coal and plastics decreased over all the trials compared to the baseline. Also, the alternative fuels did not possess excessive SO_3 concentrations. Therefore, the source of increase in the cement kiln dust was not determined.

The external laboratory reported significant increases in P_2O_5 for all trial burns. Slightly increased P_2O_5 levels were also found in the cement kiln dust. In the trial burns, coal possessed significantly elevated levels of P_2O_5 compared to the baseline's coal level. The construction demolition waste contained approximately 3 and 2 times the P_2O_5 content compared to the woodchip and soybean seed trials, respectively. Though the construction and demolition waste fuel possessed the highest P_2O_5 content for the alternative fuels tested, their contribution to the overall P_2O_5 content of the clinker and cement was minimal. The combination of materials and fuel led to the increased P_2O_5 levels found in the clinker and cement.

The statistical analysis performed on the clinker data and it showed that the majority of results from the trial burns had significantly different means. However, because of the inherent variability throughout portland cement production process, changes in cement chemistry are difficult to link to the utilization of a particular fuel.

Additional objectives of this phase of the study were to evaluate if the utilization of the trial fuels directly impacted the physical properties of the portland cement or the concrete that was prepared with the trial burn cements. Overall, it was found that the trial burn cements had minimally different effects on workability, setting time, strength, drying shrinkage, and permeability compared to the baseline cement.

Another objective of this phase of the study was to assess the impact of alternative fuels on emissions produced by the cement plant. The Nitrogen Oxides (NO_x), sulfur dioxide (SO_2), and carbon monoxide (CO) emissions were within acceptable emission limits except for the volatile organic compounds (VOC) produced during the baseline and soybean seed trial burns. The production of volatile organic compounds is more dependent on system design and control than the type of fuel used. The trial fuels utilized were not found to greatly affect the quantity of emission produced.

The cement plant was successful in implementing alternative fuels to produce a consistent, high-quality product that increased cement performance while reducing the environmental footprint of the plant. The utilization of construction and demolition waste, woodchips and soybean seeds proved to be viable replacements for traditional fuels. The future use of these fuels depends on local availability, associated costs, and compatibility with a facility's production process.

6.3 RECOMMENDATIONS

A major factor limiting the effectiveness of this study was the fairly low substitution rate of the alternative fuels. Coal accounted for 70 to 90 percent of the total energy consumed during production. The alternative fuels tested during this study contributed only 5 to 16 percent of the total energy used during the pyroprocess. Changes in cement chemistry could not be solely attributed to the alternative fuels. This was due to observed cement physical changes paralleling significant fluctuations in kiln feed or coal chemical compositions. Increasing the substitution rate would allow the trial fuel's effects to be more pronounced and thus provide a better understanding of the interactions that occur between a utilized fuel and the performance of the portland cement.

If the minimum substitution rates were increased, as well as implementing a variable feed approach similar to the woodchip trial performed in this study, an optimum replacement rate could be established.

Although a thorough sampling plan was developed for each burn, determining the effects of the alternative fuels on the cement chemistry and performance proved a difficult task. If the sampling plan was expanded to include enough samples of kiln feed, coal, and cement kiln dust to perform statistical analysis, a greater understanding of the consistency of these process inputs throughout a trial burn could be achieved. Increasing the number of specimens tested could also limit the number of inconsistent results between testing agencies. A sampling plan, however, is often limited by available funding, personnel, and time.

There were several trends that could not be explained regarding the emissions produced during the trial burns. Oxygen levels should be measured within the kiln. Knowing the oxygen level present in the pyroprocess, which significantly effects the emissions formed, could be beneficial in order to explain the fluctuations observed in the NO_x, SO_2, and CO emissions.

PART 3

Evaluate Gasification to Remove Contaminants in Cement Production

CHAPTER 7

PART 3—INTRODUCTION

7.1 POULTRY LITTER

Poultry litter is a waste product of the poultry industry that comes from floor-raised birds (primarily broilers) and consists of their manure, bedding material (usually wood shavings), waste feed, and feathers. According to the USDA, over 8 billion broilers (47.7 billion pounds) were produced in the US in 2009, and approximately half of all broiler production was from Alabama, Georgia, Arkansas, and Mississippi alone (USDA 2010). Using an estimate of .52 lb litter/lb bird recommended by Alabama Cooperative Extension System, that translates to 12.4 million tons of litter produced annually (aces.edu 1996). The most common use for this litter is as a soil amendment in farming (Kelleher 2002). However, due to high transportation costs most of the litter is applied only to neighboring farmlands leading to nutrient buildup and runoff, most notably of phosphorus, causing excess algae growth, disruption of local ecosystems, and drinking water pollution (Kelleher 2002; Adams 2005; Bock 2004). Because of these harmful effects garnered over time, there is much interest in finding other outlets for this waste product.

7.2 CEMENT KILN

One proposed alternative use for poultry litter is as a fuel. It has an average higher heating value (HHV) of ~14 MJ/dry kg which is comparable to ~20 MJ/dry kg for wood and about half that of coal (Kelleher 2002). A current major waste and alternative solid fuel consumer and potential venue for poultry litter utilization is the cement production industry. Portland cement is manufactured by heating limestone, primarily calcium carbonate ($CaCO_3$), to temperatures up to 1450˚C to form calcium oxide (CaO) as well as calcium silicates and aluminates in a process called calcination (Kaantee et al., 2004). These temperatures are achieved by burning large amounts of primarily non-renewable fossil fuels such coal, petroleum coke, gas, or oil in a massive rotating kiln as shown in Figure 1-1.

It is in the cement producer's interest both economically and environmentally to supplement some energy needs with alternative, renewable fuels. Types of alternative fuels vary depending on availability relative to plant location, but some examples include: waste oils, landfill gas, bark, paper, tires, and plastics (Mokrzycki et al. 2003). A good alternative fuel will have sustained availability and be economically beneficial to the cement producer, and in areas such as the southeast and where plants are in close proximity to poultry farms, poultry litter fulfills those requirements well. While these fuel selection requirements are not very discriminating, some further process-specific limitations do exist. The alternative fuel introduced must not adversely affect the kiln functionality or the quality of the cement product, and while the robust nature of the process makes this a generally undemanding requirement, negative effects can be garnered from excess heavy metal, alkali, sulfur, or chlorine content. Chlorides, sulfides, and alkalis become circulating elements in the kiln, volatilizing in hotter portions while condensing in cooler portions, leading to the formation of kiln ring build-ups and subsequent, costly shut-downs (Mokrzycki et al. 2003; Folta 2010). Every cement manufacturing facility has its own unique standards to determine the quantity of these deleterious components that is permissible, but the high level of alkalis and chlorine found in poultry litter either prevents or severely limits its substitution rate almost universally. Therefore, in order to gain the distinct economic and environmental advantages presented by poultry litter use, an intermediate step of biomass gasification is presented as a means to extract the chemical energy for use in the cement kiln while limiting the throughput of undesirable elements.

7.3 GASIFICATION

Thermochemical gasification via partial oxidation is a relatively old technology; it has been in existence for over 150 years (Beenackers et al. 1984). The overall goal is to convert the solid biomass energy into a gaseous form with minimal loss, usually 10-30%, in order to gain the many advantages which gas possesses over solid fuel (Reed 1981). A possible secondary goal is to remove unwanted components from the fuel source, such as sulfur, as in coal gasification (Beenackers et al. 1984). This is the feature of interest relevant to the implementation of poultry litter energy in the cement kiln. There are many types of gasifiers, each typified by the oxidizer employed; the orientation and flow of products relative to inputs; or the use of fluidized beds versus static, packed fuel beds (Beenackers et al. 1984). A commercially available, relatively simple, low-tar production option is a downdraft gasifier. This vertically-oriented setup draws both the oxidizer (air in this case) and the feedstock in through the open top. The consumption of the biomass then occurs along the throat of the gasifier, proceeding to the grate at the bottom where the hot synthesis gas (syngas) exits, ready for use. The gasification process can be broken down into several stages as it progresses from the entry to the exit of the gasifier: thermal decomposition, or pyrolysis, in which the volatiles are driven off producing pyrolysis vapors and tars; char oxidation, in which char remnants from the pyrolysis zone react with remaining oxygen and other gases and are gasified in both endothermic and exothermic reactions; and char reduction, in which remaining carbon content is consumed through primarily endothermic reactions (Buekens et al. 1984; Gasification 2011). While the exact chemistry of this process is highly complex, there are several principal reactions vital to the formation of the syngas products that are well agreed upon and used commonly when mathematically modeling biomass gasification (Buekens et al. 1984; Priyadarsan et al. 2004; Giltrap et al. 2003; Wang et al. 1993):

Heterogeneous Reactions (Solid and gas reactants)

$C + \frac{1}{2}O_2 \rightarrow CO$ $\Delta H = -110.6$ kJ/mol

$C + O_2 \rightarrow CO_2$ $\Delta H = -393.8$ kJ/mol

$C + CO_2 \rightarrow 2CO$ $\Delta H = +172.6$ kJ/mol

$C + H_2O \rightarrow CO + H_2$ $\Delta H = +131.4$ kJ/mol

$C + 2H_2 \rightarrow CH_4$ $\Delta H = -74.9$ kJ/mol

Homogeneous Reactions (Gas reactants)

$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H = -41.2$ kJ/mol

$CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H = +201.9$ kJ/mol

The gas produced with the downdraft, air-oxidation gasifier is ‘low joule’ or ‘low energy’ gas, relative to other methods of gasification or pure pyrolysis, and is best employed in a ‘closely coupled’ arrangement for immediate use to preserve efficiency (Beenackers et al. 1984; Reed 1981). This arrangement would be ideally suited in preparing potentially harmful fuels, specifically poultry litter, for use in a cement kiln and, therefore, is the focus of the current study.

7.4 OBJECTIVE STATEMENT FOR PART THREE

In a previous study conducted at the Roberta Plant (Folta 2010), poultry litter was the only alternative fuel where the direct burn substitution rate was limited due to fuel components that would negatively impact kiln operation. Poultry litter has high levels of chlorine, sodium, potassium, and phosphorus. For the Lafarge facility, which was the test facility for this project, the limiting factor was the chlorine content of the poultry litter. Depending on the composition of the limestone feedstock composition, any of these constituents could become the limiting factor so the potential of gasification to capture each of these constituents is of interest.

Downdraft biomass gasification of pelletized poultry litter was a proposed solution to this problem as a means to produce a clean, consistent product gas for injection into the kiln. In this phase of the study, this process has been analyzed through experimentation on a pilot-scale 65 Nm^3/hr (Normal m^3/hr at 0˚C, 101.3 kPa) syngas production downdraft gasifier to determine its effectiveness and consistency. The low ash fusion temperature and high alkali content of poultry litter proved to be difficult obstacles to overcome as ash clinker formation is an issue. Experiments with temperature depression via flue gas recirculation as well as experiments employing an additive (limestone) to prevent fusion and aid in chlorine retention in the ash have been carried out. Flue gas recirculation allowed the reduction of the gasifier secondary air oxygen concentration by 40-45%, yielding an approximately 100˚C depression in average temperature. Results have shown that the clinkering is temperature independent, at least within the controllable temperature range. Limestone was found to have only a slight effect on the fusion when used to coat poultry litter pellets. However, limestone addition did display some promise in regards to chlorine capture, as ash analyses showed chlorine concentrations of more than four times greater in the limestone infused ash as compared to raw poultry litter. Experiments were also conducted to explore the effectiveness of mixing limestone with raw poultry litter, the object being to coat more surface area and have a more even mixture. These resulted in the most consistent experiments with no ash clinkering.

Once consistent gasification of raw poultry litter was achieved through a combination of woodchip dilution (60% woodchips:40% poultry litter) and addition of limestone at 5% of the wet poultry litter mass, experiments were performed to determine the capture rates of the contaminants pertinent to cement kilns. Limestone percentage was varied to explore its effect on chlorine retention at three different set points. It was found that limestone percentage, at least within the tested range, had little effect on neither the retention of contaminants nor distribution of contaminants through the gasifier system. On average, 89% of the chlorine was retained in the gasifier char, as was 94% of both the potassium and sodium, and 100% of the phosphorus. A contaminant concentration profile, developed from analyses of char samples from different sections of the gasifier system, showed that 69.1% of the chlorine retained was captured past the gasifier grate and 52.6% was captured in the significantly cooler filter box and heat exchanger sections of the gasifier system. Additionally, peaks in concentration of sulfur and potassium were observed in these same sections. From these results, it was concluded that cooling and filtering the syngas in the range of 60-110˚C obtains the maximum removal of contaminants from the syngas stream.

7.5 ABBREVIATIONS FOR THIS PART OF THE REPORT

Acronyms

CPC	Community Power Corporation
HEX	Heat Exchanger
HHV	Higher Heating Value
LHV	Lower Heating Value
LOI	Loss on Ignition, % mass
MW	Molecular Weight, g/mole
PL	Poultry Litter
WAL	Wyoming Analytical Labs

Symbols

A	Atomic Weight, g/mole
U_i	Uncertainty of *i*, same units as *i*
ΔH	Change in Enthalpy, kJ/mole
n	Number of moles
Nm^3/hr	Normal cubic meters per hour, at 0˚C and 101.3 kPa (1 atm)
P	Pressure, Pa
R_U	Universal Gas Constant, $\frac{\mathrm{J}}{\mathrm{mole \cdot K}}$
T	Temperature, K
V	Volume, m^3

CHAPTER 8

PART 3—BACKGROUND

8.1 POULTRY LITTER COMPOSITION

Poultry litter is a non-homogeneous mixture of bedding, feathers, excrement, and feed. Because of this, no two samples are exactly alike and, thus, a model or standard definition doesn't exist. Proximate and ultimate analyses, on a dry basis, from different farms are usually relatively similar, but can have as much as a 20-30 average percent difference between parameters (Reardon et al. 2001; Li et al. 2008; Primenergy 2008). A comparison of several proximate analyses and ultimate analyses of different litter samples from the literature is presented in Tables 8-1 and 8-2.

Table 8-1: Proximate analyses (% mass, dry basis) of five litter samples from the literature

Fuel	**Li et al. (2008)**	**Schaffer (2006)**	**Reardon et al. (2001) (raw litter sample)**	**Reardon et al. (2001) (pelletized sample)**	**Primenergy (2008)**	***Average***
Ash	27.96	32.65	21.9	26.5	20.61	**25.9**
Volatile Matter	65.16	53.96	62.7	59.8	45.64	**57.5**
Fixed Carbon	6.88	13.39	15.4	13.7	33.75	**16.6**
Total	100.0	100.00	100.0	100.0	100.00	**100.0**

It can be seen from the tables that while the samples do compare relatively well to the calculated average, the differences between individual samples may be significant. Differences become even more apparent when comparing the ash analyses of poultry litter samples. There can exist as much as a 40-50 average percent difference between the oxide concentrations of two separate samples. Table 8-3 shows the comparison between five ash component analyses found in the literature and the average of these values.

While the exact concentration of each element (presented here as their oxide) can be very different for each sample, the species with the highest concentrations tend to be CaO, K_2O, P_2O_5, and SiO_2. The relatively high concentrations of K and P, along with nitrogen, are what make poultry litter an attractive soil amendment. However, the high ratio of P to N and the high water-solubility of the phosphorus-containing compounds is what causes the phosphorus concentrations to build up in the soil over time and run off into watersheds and water supplies (Bock 2004; Codling 2005).

Table 8-2: Ultimate analyses (% mass, dry basis), chlorine content, and heating value of six litter samples from the literature

Fuel	**Li et al. (2008)**	**Schaffer (2006)**	**Reardon et al. (2001) (raw litter sample)**	**Reardon et al. (2001) (pelletized sample)**	**Primenergy (2008)**	**Bock (2004)**	***Average***
Carbon	28.2	35.03	36.6	33.7	40.89	37.8	**35.4**
Hydrogen	5.0	4.50	4.9	4.5	4.86	5.1	**4.8**
Oxygen	35.0	21.51	32.0	29.3	28.66	31.1	**29.6**
Nitrogen	3.4	4.06	3.9	5.0	4.30	3.8	**4.1**
Sulfur	0.9	1.14	0.78	0.95	0.68	0.4	**0.8**
Ash	27.7	32.65	21.9	26.5	20.61	21.8	**25.2**
Total	100.2	98.89	100.08	99.95	100	100	**99.9**
Chlorine	1.16	1.11	Not reported	Not reported	0.051	1.0	**0.8**
MJ/kg	13.31 (LHV)	Not reported	14.82 (LHV)	13.62 (LHV)	15.99 (HHV)	14.87 (HHV)	**15.43 (HHV)**

Table 8-3: Ash analyses (% mass, ignited basis) of five litter samples from the literature

Oxide	**Li et al. (2008)**	**Schaffer (2006)**	**Primenergy (2008)**	**Bock (2004)**	**Codling (2005)**	***Average***
Al_2O_3	4.9	3.45	0.84	1.9	1.73	**2.6**
CaO	13.5	15.00	23.60	17.3	17.63	**17.4**
Fe_2O_3	2.1	1.14	0.85	1.2	1.03	**1.3**
K_2O	12.2	8.68	20.51	16.3	6.06	**12.7**
MgO	4.6	3.62	7.76	5.0	3.96	**5.0**
Na_2O	5.8	4.58	7.04	9.2	N/A	**6.7**
P_2O_5	15.3	10.90	24.62	24.4	17.39	**18.5**
SO_3	5.8	7.11	6.60	6.7	N/A	**6.6**
SiO_2	35.6	38.40	7.46	8.1	N/A	**22.4**
TiO_2	0.2	N/A	0.07	0.2	N/A	**0.2**
Total	100.0	92.88	99.35	90.3	47.79	**93.4**

The high variance in poultry litter composition, specifically of the ash components, is due to many variables involved in how the birds are raised and the individual farm's practices. Commercial poultry houses have dirt floors, so some components of litter come from varying amounts of dirt mixed in by humans when cleaning the pens or by the birds themselves (Price, 2010). This inconsistency between farms most likely accounts for the high variability in silica (SiO_2) content found in the literature. Wood shavings are typically used as bedding in the pens and make up a substantial portion of the litter, and therefore the type of wood used has an effect on the poultry litter composition. The diet of the birds, in the form of unconsumed feed or through their excrement, contributes to the composition as well. A listing of ash components, other elements of interest, and their origins is displayed in Table 8-4. The table was compiled after consulting Carla Price, a nutritionist for Sanderson Farms, but can also apply to other production facilities as well. The broilers' primary diet consists of corn, soy and water and is supplemented with meat meal (ground up chicken parts).

Table 8-4: Origins of poultry litter components relevant to cement kiln implementation. Element % are elemental, not oxide (Price 2010; Misra et al. 1993)

Element	Possible Origin
Al	• In soil • In alum (Aluminum Sulfate), used to keep ammonia levels of litter down • Generally ~0.1-0.7% of wood ash
Ca	• In feed for bone strength • 40g per bird over lifetime, large amount retained • Generally the largest ash component in wood (~20-35%)
K	• High concentration (2-3%) in soy fed to birds • Generally second largest ash component in wood (~5-15%)
Mg	• Fed as a trace mineral • Also in meat meal • Generally the third largest ash component in wood (~3-9%)
Na	• In feed • 10g per bird over lifetime, some retained • Trace element in wood
P	• In feed for bone strength • Generally ~1% of wood ash
S	• Not in the diet • Generally ~1% of wood ash
Si	• In dirt, sand and water • In wood ash
Cl	• Fed as trace mineral • In water, extra added to poultry farm supply if experiencing health issues

8.2 UNDESIRABLE ELEMENTS IN CEMENT KILNS

The exact alternative fuel standards and composition limits for a given kiln vary depending on the cement plant and are usually trade secrets. However, a few examples have been published and general guidelines are known about which elements in excess are harmful to cement product or the kiln itself. For example, the alternative solid fuels used by the Lafarge Cement Polska group in Poland must meet the following requirements (Folta 2010):

- Heating value > 14.0 MJ/kg (weekly average)
- Chlorine content < 0.2%
- Sulfur content < 2.5%

Using these values as a general guideline, it can be seen that poultry litter barely satisfies the energy requirement, easily satisfies the sulfur requirement, and fails the requirement for chlorine with an average from the literature of about 1%. Although not included in this list, much attention is also paid to the alkalis in the fuel which become circulating elements in the kiln, alongside sulfur and chlorine. A list of elements found in poultry litter and their effects on the cement manufacturing process can be seen in Table 8-5. It is evident that the elements whose throughput it is most important to reduce are Cl, K, Na, and S.

Table 8-5: List of elements relevant to cement manufacturing that are present in poultry litter and their effects, adapted from Bhatty (2004)

Element	Effects on Cement Production
Chlorine, Cl	• Circulating element • Forms alkali chlorides • Causes ring formation in kiln and blockages • Causes pre-heater buildup
Magnesium, Mg	• Improves burnability of clinker • Goes into aluminate and ferrite phases • In excess may affect concrete behavior
Phosphorus, P	• Reduces negative effects of alkalis on cement strength • In excess can decrease concrete strength
Potassium, K	• Circulating element • Forms chloride and sulfate compounds in kiln
Sodium, Na	• Circulating Element • Forms chloride and sulfate compounds in kiln
Sulfur, S	• Can be a circulating element • Forms alkali sulfates, necessary in removal of alkalis from the kiln • Excess leads to ring formation and blockages

It can be seen that any alternative fuel with concentrations of harmful elements exceeding that of the primary fuel will be restricted in its substitution rate, the elements in question becoming the limiting factor. Conversely, any deleterious components with a lower concentration than in the primary fuel become less important. Comparing samples of coal and petroleum coke used in the Lafarge Roberta cement plant to an average of poultry litter samples from the literature on a mass basis (Table 8-6) and energy basis (Table 8-7) it becomes apparent that sulfur is not a limiting factor and is insignificant next to the concentrations in coal and coke. Making a comparison on an energy basis is pertinent because substitution rates are based on energy content, not mass (Folta 2010). It was reported by Folta (2010) that over a series of five burns, the energy supplied by coal was between 35-60% of the total, coke was 20-37%, and a combination of tires, plastics and alternative fuel was 18-30% of the total kiln energy consumption.

Table 8-5: Comparison of poultry litter composition (% mass, dry) to coal and coke samples used at the Lafarge Roberta plant (Folta 2010)

	Average Litter Composition from Tables1,2 & 3	**Coal**	**Coke**
Proximate Analysis, % mass, dry			
Ash	25.9	24.9	8.81
volatile matter	57.5	25.4	12.9
Fixed Carbon	16.6	49.7	78.3
Total	100.0	100.0	100.0
Ultimate and Elemental Analysis, % mass, dry			
Carbon	35.4	64.50	78.7
Hydrogen	4.8	3.24	2.7
Oxygen	29.6	2.84	1.81
Nitrogen	4.1	1.02	1.23
Sulfur	0.8	3.47	6.74
Chlorine	0.8	0.059	0.013
Al	0.36	2.98	0.53
Ca	3.22	1.98	1.67
Fe	0.24	1.74	0.42
K	2.73	0.60	0.13
Mg	0.78	0.18	0.07
Na	1.29	0.05	0.02
P	2.09	0.02	0.00
(SO_3 in ash) S	0.68	0.03	0.74
Si	2.71	5.89	1.13
Ti	0.03	0.16	0.03
MJ/kg	15.43 (HHV)	26.45 (HHV)	32.25 (HHV)

Table 8-6: Comparison of poultry litter composition (g/MJ, dry) to coal and coke samples used at the Lafarge Roberta plant (Folta 2010)

	Average Litter Composition from Tables1,2 & 3	Coal	Coke
Proximate Analysis, g/MJ dry			
Ash	16.79	9.41	2.73
volatile matter	37.27	9.60	4.00
Fixed Carbon	10.76	18.79	24.28
Total	64.81	37.81	31.01
Ultimate and Elemental Analysis, g/MJ dry			
Carbon	22.94	24.39	24.40
Hydrogen	3.11	1.22	0.84
Oxygen	19.18	1.07	0.56
Nitrogen	2.66	0.39	0.38
Sulfur	0.52	1.31	2.09
Chlorine	0.52	0.022	0.004
Al	0.23	1.13	0.16
Ca	2.09	0.75	0.52
Fe	0.15	0.66	0.13
K	1.77	0.23	0.04
Mg	0.51	0.07	0.02
Na	0.83	0.02	0.01
P	1.36	0.01	0.00
(SO_3 in ash) S	0.44	0.01	0.23
Si	1.76	2.23	0.35
Ti	0.02	0.06	0.01

Having compared the composition of poultry litter to the standard fuels, observed an example of limits, and examined the effects of certain elements on cement kilns, it becomes evident that the most important components to limit introduction into the kiln are Chlorine, Sodium, and Potassium. This study will focus on these elements, but attention will be paid to other components previously mentioned as potentially harmful.

8.3 CHLORINE AND ALKALI RELEASE FROM BIOMASS UNDER GASIFICATION AND COMBUSTION CONDITIONS

There is little documentation as to the study and quantification of the capture rates of the unwanted constituents of interest to the cement manufacturing process by means of downdraft gasification, especially with regards to poultry litter. However, some work has been done in examining chlorine and alkali release from other types of biomass under similar pyrolytic and gasification conditions. It has been found that in gasification of biomass HCl and KCl are the dominating chlorine-containing species released in the gas and are formed during the pyrolysis and char oxidation phases. Chlorine exists in several forms in biomass but it is believed that a significant portion is present as the salt KCl which is assumed to begin volatilization above its melting point of approximately 750 ˚C (Bjorkman et al. 1997). It was found in experiments performed by Bjorkman, et al. that under pyrolysis conditions using N_2, switchgrass retained its chlorine at all temperatures above 400˚C far better than the two types of coal tested (Figure 8-1), an positive initial sign for the retention of this harmful component of poultry litter in the ash.

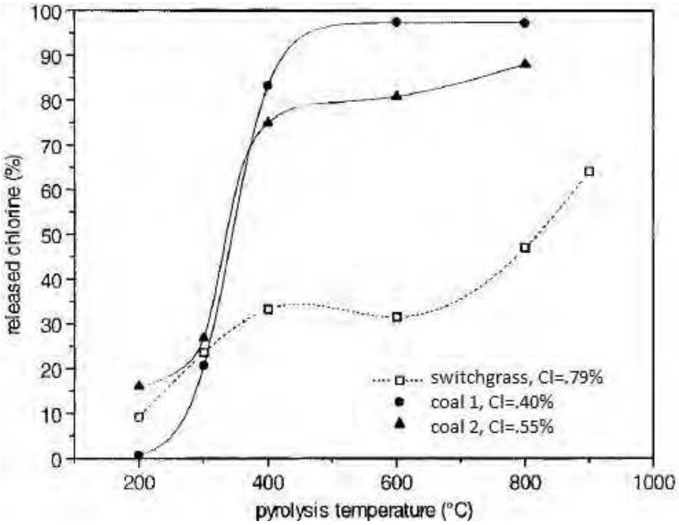

Figure 8-1: % Cl released by switchgrass and coal at varying pyrolysis temperatures (Bjorkman, et al. 1997)

It was also found that using CO_2 in place of N_2, the same experiments yielded higher chlorine release at temperatures above 800˚C (Bjorkman et al. 1997). Additionally, chlorine presence in biomass is known to facilitate the volatility and mobility of many inorganic elements, specifically alkali metals. Chlorine, in fact, has as much effect on the amount of alkali vaporized during combustion as does the alkali concentration (Jenkins et al. 1998). It has been found that in combustion of switchgrass, the dominant alkali containing gas species is KCl, followed by either KOH or NaCl at 1100˚C or 800˚C, respectively (Dayton et al. 1995).

In experiments employing an ashing furnace, it was found by Misra et al. (1993) that varying temperatures from 600-1300˚C when combusting wood sees a loss of K and S with increase in temperature but a retention of Na, Mg, P, Mn, Al, Fe, and Ca. K concentration drops off significantly above 800-900˚C, while S decreases, although less severely, above 1000-1100˚C. All results were normalized with respect to Ca which was assumed to be constant. A similar experiment was performed by Adams (2005) with poultry litter, the temperature varying from 450-1000˚C. Sulfur was not analyzed and different results were found. K, Na, Mg, Al, Fe, and Mn all decreased with increasing temperature, K the most severe. However, P and Ca were still retained.

8.4 GASIFICATION OF POULTRY LITTER

In the literature, gasification trials using poultry litter have been run in both bench-scale and pilot-scale arrangements with varying degrees of success. In all cases slagging or clinkering (fusion) of the poultry litter during gasification was an issue that had to be addressed (Reardon et al. 2001; Schaffer 2006; Priyadarsan et al. 2004). It was found by Community Power Corporation (CPC) that using pelletized litter with reduced moisture and limiting the superficial velocity (volume flow rate of gas produced/gasifier cross-sectional area, measured in m/s) of the gasifier provided the best results in a bench-scale downdraft gasifier. This is said to control the temperature at the pyrolysis front, and without these measures, clinker formation was an issue. A pilot scale trial using 12.5% moisture pellets was run for 5 hours, producing 45 Nm^3/hr (Normal m^3/hr at 0˚C, 101.3 kPa) of syngas with a lower heating value of 4.79 MJ/Nm^3. However, no mention was made of the state of the gasifier char remaining upon completion of the run, as to whether fusion occurred or not (Reardon et al. 2001). In another study, using a fixed-bed, counter-current updraft gasifier, in which the fuel entry and syngas exit is at the top and oxidizer entry is at the bottom, it was found that gasifying pure poultry litter resulted in a large agglomeration forming inside the gasifier. However, mixing the poultry litter with a fuel less prone to slagging, cow manure, in a 50:50 weight ratio char fusion was negligible (Priyadarsan et al. 2004).

8.5 REASONS FOR CLINKER FORMATION AND POSSIBLE SOLUTIONS

The clinkering problems encountered when gasifying poultry litter are attributed the interaction between the alkali metals, chlorine, and silica present in the fuel (Bjorkman et al. 1997; Jenkins et al. 1998). The root of the problem is thought to be caused by either one or both of two reactions. The first is the formation of alkali silicates from a reaction of alkali metals and silica. Alkali silicates can soften or melt at temperatures as low as 700˚C depending on the composition, and most poultry litter is high in both alkalis (K and Na) and silica (SiO_2). The second is the formation of alkali sulfates from alkali and sulfur (Jenkins et al. 1998). As mentioned previously, chlorine aids immensely in the volatilization and transport of alkalis, particularly potassium, conveying them to surfaces where ash deposition occurs (Jenkins et al. 1998). Potential solutions to this problem are co-gasification with other fuels, temperature reduction, and, as suggested by several sources, addition of up to 5% limestone or dolomite (Bock 2004; Reardon et al. 2001; Coda et al. 2001).

8.6 LIMITING THE RELEASE OF CHLORINE AND ALKALIS

The addition of limestone in a combustion or gasifier environment can promote the capture and sequestration of volatilized chlorine. This aids in both the minimization of ash clinkering as well as potentially limiting the throughput of chlorine in the product gas with consideration to cement kiln usage. It has been proposed that gaseous chlorine is removed through the following path during combustion:

$$CaO(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g)$$

It has been suggested through thermodynamic modeling that this equation is favored more at lower temperatures (550-700˚C) and when high HCl and low H_2O are present in the flue gas (Coda et al. 2001). The use of limestone also would be convenient if needed at a cement production facility, as this is one of the primary raw materials employed in cement manufacture.

In the endeavor to mitigate alkali release, it has been shown that simply cooling and filtering the product gas at 400-500˚C (cooler than the melting point of the alkali-containing salts) can have a dramatic effect on the gas alkali concentration (Salo et al. 1998). This effect can be seen in Figure 8-2 where the alkali concentration (Na + K) in the product gas from a fluidized bed gasifier is plotted relative to temperature for many different solid fuels. The points on the right side of the graph are samples taken before the gas cooler and those on the left from after the gas cooler.

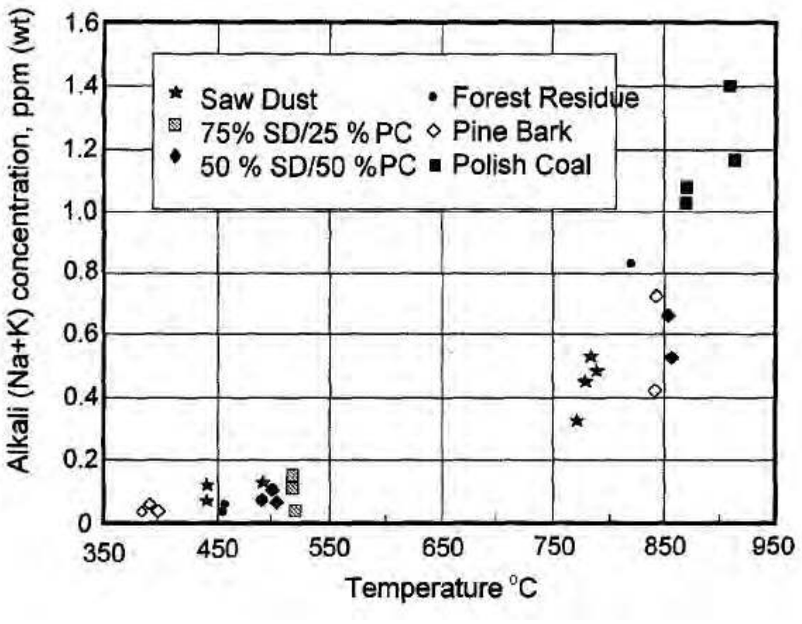

Figure 8-2: Alkali concentration in fluidized bed product gas before and after the gas cooler for various fuels (Salo et al. 1998)

In this study, various experiments were performed initially utilizing methods drawn from the literature as well as methods devised based on known fuel characteristics in an attempt to inhibit the fusion of the poultry litter during gasification in order to consistently gasify it (Sections 9.2.1 and 9.1). Specifically, trials were run experimenting with dilution of the fuel using non-sintering material, attempting to lower the average gasifier temperature using flue gas recirculation, and utilizing limestone as an anti-fusion and potential chlorine-capturing additive. This was done with the end goal of quantifying the alkali, chlorine and other potentially interesting elements released in the gasification of poultry litter, and as such, attention was paid to these properties along the way.

The next set of experiments in this study were performed to actually quantify the contaminant retention and sequestration garnered by the use of a gasifier while extracting the chemical energy from poultry litter (Sections 9.2.2 and 10.2).

CHAPTER 9

PART 3—EXPERIMENTAL SETUP AND PROCEDURE

9.1 EXPERIMENTAL SETUP

9.1.1 Gasifier

This study was conducted using a Community Power Corporation (CPC) Biomax 25 downdraft, co-current gasifier shown in Figure 9-1. This unit is fully automated utilizing a Labview interface and designed to gasify 22kg/hr (~50lbs/hr) of dry biomass and produce 65 Nm^3/hr (~2300 std ft^3/hr) of syngas with a nominal energy content of 4.8 MJ/Nm^3 (~130 Btu/Std ft^3). The produced gas is pulled through a shell and tube, air-cooled heat exchanger and dry bag filter and can either be flared or used to run an internal combustion engine to generate up to 25kW of electricity. The heat removed from the syngas by the heat exchanger is used either to dry the feedstock in the storage bins or to heat the control room. A screenshot of the Labview gasifier schematic can be seen in Figure 9-2.

Figure 9-3: CPC mobile gasifier unit parked outside of the Alabama Capitol Building

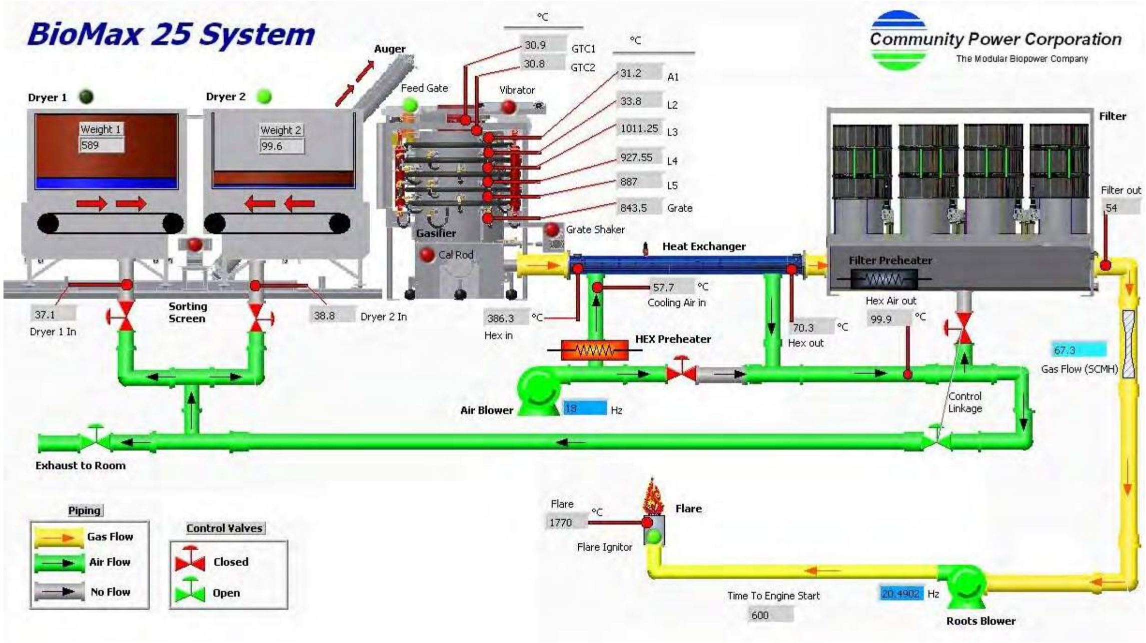

Figure 9-4: Labview schematic of Biomax 25 Gasifier

The gasifier is an open top design, which is where both the primary air and biomass enter. The inside dimensions of the gasifier throat are 130 cm height and 35 cm diameter. The biomass level inside the gasifier is constantly maintained using distance sensors which activate the onboard feed system. Secondary air is injected through five levels of nozzles spaced equally along the height of the gasifier and controlled by proportional valves in order to control the gasifier temperature and syngas composition. The gasifier temperature is monitored using k-type thermocouples (±2.2˚C) at each of the 5 levels, at the grate, and at two locations above the nozzles as shown in Figure 9-3.

Pressure drop is also measured across the gasifier and across the grate using onboard digital manometers and the oscillation of the grate is varied according to the degree of pressure drop. Syngas flow rate is measured via the onboard venturimeter and corrected to 0˚C, 101.3 kPa (1 atm). All pressures, temperatures, and gas flow rates are recorded by the onboard computer every 10 seconds.

Because the gasifier is fully automated, operating parameters such as temperature are controlled to stay within a desired range. Variations in secondary air amount, grate shaker speed/interval, heat exchanger blower speed, and other controls are made by the onboard computer to keep the gasifier as close to steady-state as possible during operation. An average temperature profile in the gasifier from a standard woodchip-fed run can be seen in Figure 9-4. The temperature profile through the rest of the gasifier during the same run can be seen in Figure 9-5.

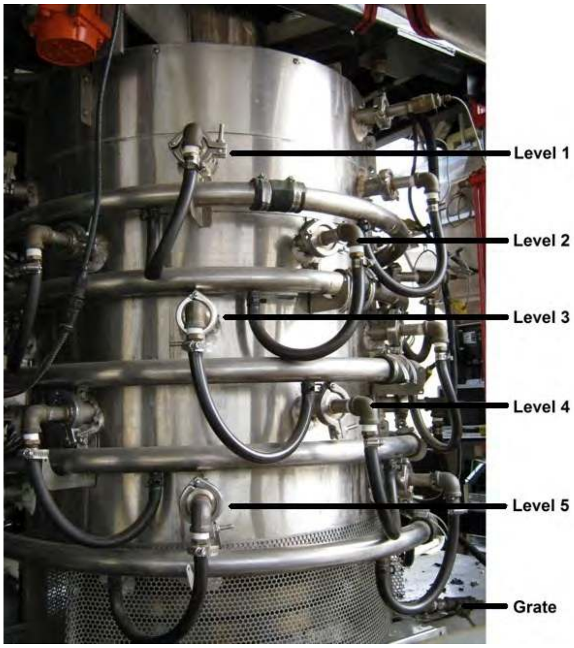

Figure 9-5: Gasifier with secondary air injection levels and grate level labeled

Figure 9-6: Average temperature profile inside the gasifier during a standard woodchip run

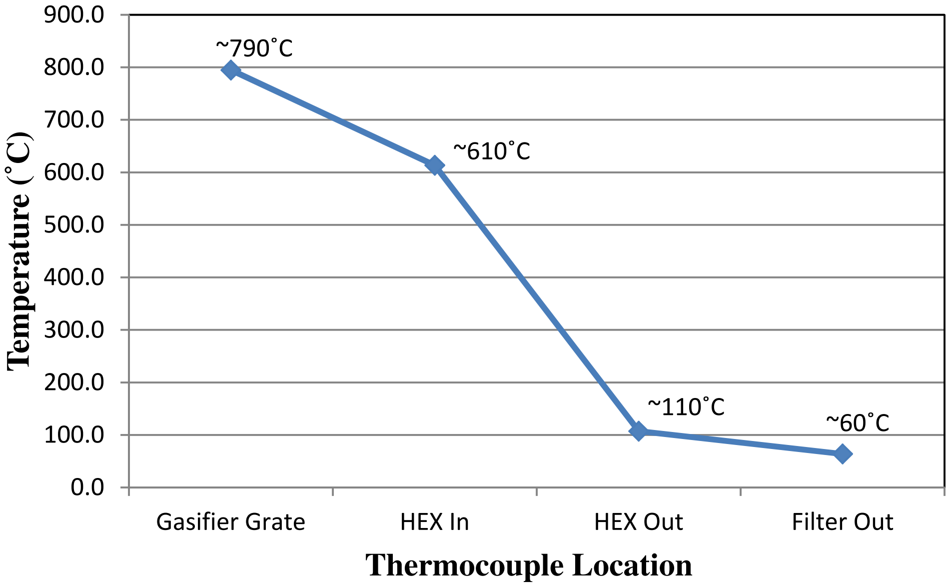

Figure 9-7: Average temperature of the syngas at different locations in the system starting at gasifier exit, proceeding through the heat exchanger (HEX), and finally after the filter

Additionally, syngas composition, and consequently the syngas higher heating value (HHV), are intended to stay within a desired range during steady-state operation. A typical run employing pine chips sees an average dry syngas composition (by volume) and volumetric HHV of approximately:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m^3]
0.5	20	12	1.5	18	5.4

*Syngas over duration of a typical run can be seen in Appendix D, Figure D-1

The O_2 concentration in the syngas is a result of tiny air leaks in the system and is higher if the gasifier differential pressure is elevated. The moisture percentage in the syngas varies with the feedstock moisture and is typically in the range of 5-10% (by volume).

Ash sampled at the end of experiments was collected at several locations in an attempt to capture all of it. Before all experiments, ash was purged from every location using the same methods. Charred woodchips were removed from the top of the gasifier using a Shop-Vac down to around level 4 (see Figure 9-3). Ash remaining in the gasifier was collected by removing bolts and opening the gasifier at a sealed seam 10 cm (4 inches) above the grate (Figure 9-6).

Figure 9-8: Gasifier opened at seam 10cm above the grate

Below the gasifier grate is a round chamber (Figure 9-7) where the heavier ash tends to settle as opposed to becoming entrained and continuing through the pipe (slanted inlet, right side of Figure 9-7) towards the heat exchanger. Some ash settles in the bend just before the heat exchanger. This is accessed through a port at the heat exchanger entrance (Figure 9-8).

Figure 9-9: Chamber below grate, slanted entrance to tube leading to heat exchanger at right. Larger, heavier ash particles settle here

Figure 9-10: Access port at heat exchanger entrance, Shop-Vac in use

More ash settles in the heat exchanger itself and in the pipe leading from heat exchanger to filter box. This is accessed by removing the pipe bend from the end of the heat exchanger (Figure 9-9, bottom right) and using a Shop-Vac to retrieve ash from the individual tubes in the shell and tube heat exchanger (Figure 9-9, just visible at left inside the heat exchanger exit). The Shop-Vac is also used to remove ash from the pipe leading to the filter box.

Figure 9-11: Heat exchanger exit, tubes visible inside at left. Pipe bend and flexible hose leading to filter box at right

The rest of the ash is captured in the filter box by the self-cleaning, dry bags (Figure 9-10). Ash is collected from the filter box using the onboard auger that runs the length of the filter box bottom. The sides of the filter box are v-shaped, funneling ash to the half-pipe containing the auger at bottom.

Figure 9-12: Filter box with doors open. Bags are inverted inside barrels by syngas flow

9.1.2 Gas Analysis

During all experiments the syngas was continuously side-stream sampled and analyzed through a valve located after the heat exchanger and filter box, so the gas was cooled to approximately 60˚C and relatively clean. The sample flow is as shown in Figure 9-11.

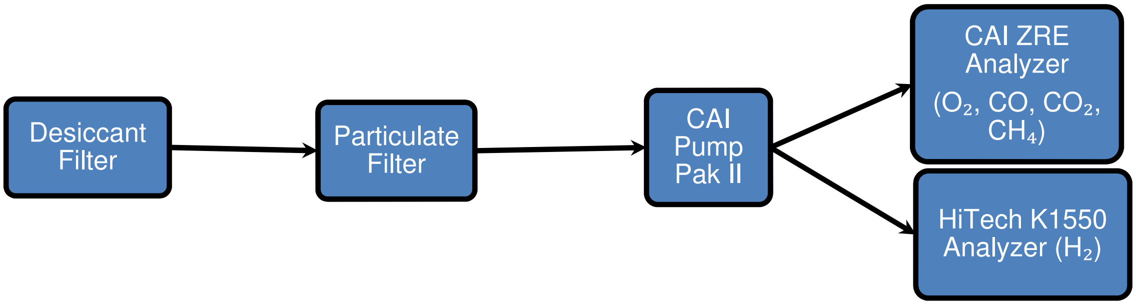

Figure 9-13: Gas analysis flow diagram

The two gas analyzers used were a California Analytical Instruments model ZRE and a HiTech Instruments K1550. The ZRE measured CO (±0.6%), CO_2 (±0.6%), and CH_4 (±0.3%) using Non-Dispersive Infrared (NDIR) method and O_2 (±0.5%) by means of a fuel cell (Figure 9-12, bottom). The K1550 measured H_2 (±2%) using thermal conductivity (Figure 9-12, top right). Gas composition data was recorded every 15 seconds using an Omega OMB-DAQ-56 connected to the analog 4-20mA outputs of the instruments.

Figure 9-14: Gas analyzer train used during experiments. HiTech K1550 top right, California Analytical ZRE bottom, California Analytical Pump Pack II middle

A dew point meter was used in the quantification of contaminant retention experiments (Sections 9.2.2 and 10.2). The meter was a GE DewPro MMR101 (Figure 9-13) that measured percent volume H_2O and was linked to the Omega-DAQ-56 through a 4-20mA loop. The probe was mounted directly in the syngas stream, just before the gas analyzer sampling port.

Figure 9-15: DewPro MMR101 used in contaminant quantification experiments, measures % volume moisture

The ZRE and K1550 analyzers were calibrated less than 1 week before each experiment using both zero and span gases. The DewPro analyzer was received factory-calibrated and requires re-calibration every two years, and thus was not re-calibrated during the study.

9.1.3 Feedstock/Ash Analysis

All biomass and ash analyses were performed by Wyoming Analytical Laboratories (WAL) in accordance with the corresponding ASTM standard except moisture analyses and woodchip char ash analyses performed during the quantification of contaminant retention experiments (Sections 9.2.2 and 10.2). For the analyses that were performed in-house during these experiments, moisture was analyzed according to ASTM Method E 871. Ash was analyzed according to ASTM Method D 1102, with the maximum temperature being 750˚C, as used and suggested by WAL.

9.2 PROCEDURE

9.2.1 Exploration of Poultry Litter Gasification Procedure

The first set of experiments was performed with the goal of consistently gasifying poultry litter. The literature showed this to be either difficult or was ambiguous as to whether poultry litter gasification could actually be sustained. In this study, various experiments were performed utilizing methods drawn from the literature as well as methods devised based on known fuel characteristics in an attempt to inhibit the fusion of the poultry litter during gasification. Specifically, trials were run experimenting with dilution of the fuel using non-sintering material, attempting to lower the average gasifier temperature using flue gas recirculation, and utilizing limestone as an anti-fusion and potential chlorine-capturing additive.

Poultry litter pellets were used for all tests initially (Figure 9-14a). The size and shape of the pellets, coupled with their ease of handling and relative homogeneity, made them a better candidate than raw poultry litter for the type of gasifier and feed system being used. Pellets used were manufactured by Organic Growing Systems, Monticello, MS.

Figure 9-16: a) Poultry litter pellet detail

Figure 9-14 b) Raw poultry litter

Later experiments employed the use of raw poultry litter, acquired from the Auburn University Poultry Science Department Research Farm (Figure 9-14b). In cases where poultry litter was diluted with pine woodchips or mixed with limestone, relatively consistent homogeneity in the mixed feedstock was achieved by employing the use of a portable, clean cement mixer.

For all experiments, the gasifier was started using a combination of natural charcoal and pine chips and allowed to come to steady-state operation, taking approximately one half hour, before the feedstock of interest was fed. All feedstocks tested were run for at least three hours so the effects of the fuel being tested would be amplified relative to the woodchips and charcoal used for startup.

In an attempt to lower and control the average gasifier temperature, trials were run using flue gas as a diluent, supplementing the secondary air. Early gasification trials with poultry litter pellets displayed a tendency to hang up on, and adhere to, the secondary air injection nozzles (can be seen in Figure 9-3). In the oxygen deficient environment of the gasifier, the highest reaction rates, and thus the highest temperatures, would be where oxygen is most available.

Limiting the local "hot-spots" generated at the secondary air injection sites was seen as a potential solution. The experimental setup consisted of generating and cooling flue gas using an Eccotemp L10 propane water heater and feeding it into the secondary air blower inlet (Figure 9-15). The amount of flue gas generated was controllable by the propane valve and the O_2 and CO_2 content of the secondary air mixture could be measured with a second gas analyzer sampling after the blower. This analyzer was manufactured by NOVA Analytical Systems.

Figure 9-17: Propane water heater used for flue gas generation

9.2.2 Quantification of Contaminant Retention Procedure

These later experiments were executed after consistent gasification of poultry litter was achieved. They were performed with the goal of quantifying the retention of the deleterious components pertinent to the cement kiln in the ash. It was found in the first set of experiments (Section 4.2.1 and 5.1), that in order to gasify the litter consistently, raw poultry litter had to be mixed with approximately 5% powdered limestone (by mass, relative to wet poultry litter, or ~6.5% relative to dry litter) and diluted with pine chips to about 40%. In the Quantification of Contaminant Retention experiments, the limestone ratio functioned as the independent variable and two runs each were performed using 3.71, 5.71, and 7.71 percent lime relative to wet poultry litter mass. These slightly higher percentages were selected to account for the lower moisture content of the poultry litter used in these runs versus that used in the Exploration of Poultry Litter Gasification experiments (sections 9.2.1 and 10.1.4), as well as to allow for rounded-off, easy to work with weights of feedstocks (can be seen in Tables A-3 to A-8). Also, to account for the lower moisture content, all runs were performed with the raw litter diluted by pine chips to a 35:65 ratio (litter:woodchips) instead of the 40:60 ratio used previously. As in section 10.1.4, 200 lbs (90.72 kg) of woodchips were fed into the gasifier following the poultry litter/limestone/woodchip mixture to ensure complete gasification of the fuel of interest. Despite this excess biomass, poultry litter would still be dominant source of the chlorine and alkali components in the resulting gasifier char due to the low ash content of the woodchips. All char produced was collected, sampled, and sent for analysis after every experiment. These analyses were then compared in a mass balance to the composition of the incoming feedstocks to determine the retention rate of contaminants pertinent to cement kilns. Additionally, char from three of the experiments was sampled and analyzed by location from the heat exchanger, filter box, and below the gasifier grate in order to examine the effects of temperature variation on char composition.

Preliminary preparation consisted of acquiring a large amount of raw poultry litter from the Auburn Poultry Science Research Farm from the same pile and mixing well for batch homogeneity. This batch would be used for all runs. A consistent, homogeneous batch of pine woodchips was also delivered and used for all runs. Powdered limestone and natural charcoal were purchased by the bag and are assumed to be consistent in composition from bag to bag. Poultry litter, woodchip, and charcoal samples were taken and sent to Wyoming Analytical to have proximate, ultimate, chlorine, Btu, and ash analyses performed. A sample of limestone was sent to WAL to have an ash analysis performed.

The following setup was consistent between experiments, the only variable being limestone percentage:

- Prior to each experiment, the gasifier system was purged using a Shop-Vac and the onboard auger, as shown in Section 9.1.1.
- The feedstock mixture was prepared using a cement mixer, weights measured with an electronic scale. First all the litter and lime were mixed separately, then added to the woodchips in the following amounts:
    - 130 lbs (58.97 kg) pine woodchips
    - 70 lbs (31.75 kg) raw poultry litter
    - 2.6/4/5.4 lbs (1.17/1.81/2.45 kg) powdered limestone
- 200 lbs (90.72 kg) of woodchips were weighed, to be fed after the poultry litter mixture in order for the litter to fully gasify
- The gasifier was filled to level 1 with charcoal from a bag, the weight taken before and after, and the difference recorded as the charcoal weight
- The gasifier was filled the rest of the way with woodchips, the weight recorded
    - Woodchips were kept at ready to be fed as the gasifier warmed up until the poultry litter mixture was fed

- Representative samples were collected and analyzed for moisture content, according to ASTM E 871:
    - Charcoal
    - Warm-up Woodchips
    - Poultry Litter
    - Woodchips mixed with poultry litter/Woodchips fed after poultry litter mix (same batch used for both)

The following procedure was consistent between experiments:

- The gasifier was started, buckets of woodchips weighed, recorded, and added to maintain proper level in the gasifier until temperatures reached steady state
- When the gasifier operation reached steady state (about one half hour after starting), the poultry litter/limestone/woodchip mixture was started feeding (automatically, by the feed system)
    - The time was recorded when the first bit of the mixture dropped into the gasifier
    - The time was recorded when the last bit of the mixture dropped into the gasifier
- After the last of the mixture was fed, the 200 lbs of woodchips were started feeding using the automatic feed system
    - The woodchips and poultry litter chunks that (together with associated limestone percentage) that were sorted by the sorting screen were separated and weighed to be subtracted from the input amount
- After the last of the 200 lbs of woodchips were fed, the flame front was allowed to advance to the top, charring all the raw chips and consuming any remaining moisture. As soon as this occurred, the gasifier was turned off, sealed and allowed to cool overnight.
    - Woodchips that were sorted by the sorting screen were weighed and recorded to be subtracted from the 200 lb total

The following data collection methods were consistent between experiments:

- Syngas was side stream sampled, dried, analyzed, and recorded continuously from the first steady-state before litter/limestone/woodchip addition until end of run for: O_2, CO, CO_2, CH_4, and H_2
- Moisture of syngas was probe monitored and recorded continuously
- Gasifier performance data was recorded by the onboard computer continuously
- At least 24 hours after every experiment (to allow cool-down), ash was collected from the various collection points (Section 9.1.1), weighed, and sampled.
    - The char from the 200 lbs of woodchips was collected from the top of the gasifier, down to level 5, and labeled ‘Woodchip Char’
    - The rest of the gasifier char was collected (Figure 9-6), sample labeled ‘Rest of Gasifier’. The gray, amorphous poultry litter/limestone ash was separated by hand for the first three runs, sample labeled ‘PL Ash’
    - The char below the gasifier grate was collected (Figure 9-7) and combined with the char collected from just before the heat exchanger entrance (Figure 9-8), sample labeled ‘Below Grate’
    - The char was collected from inside and at the exit of the heat exchanger using a Shop-Vac (Figure 9-9), labeled ‘HEX’
    - The char was collected from the filter box using the onboard auger, labeled ‘Filter’

Two experiments were run for each limestone percentage (3.71, 5.71, and 7.71 % limestone). In one experiment for each set point, representative ash and char samples were taken from each of the above locations for comparison of variation in ash composition through the gasifier. In the other three experiments, ‘Rest of Gasifier’ and ‘PL Ash’ were combined and analyzed as one sample labeled ‘Gasifier’. Also, ‘Filter’, ‘HEX’ and ‘Below Grate’ were combined and analyzed as one sample labeled ‘After Grate’. For all experiments, a sample from the ‘Woodchip Char’ was analyzed for Loss on Ignition (LOI), as dictated in Section 9.1.2.

9.2.3 Data Analysis

The data collected for each experiment was analyzed using various methods in order to understand and interpret the results. Syngas volume percentage was used to calculate syngas

HHV and biomass and ash analyses were used to perform mass balances. In performing these analyses, several assumptions were made:

- Only species present in syngas are O_2, CO, CO_2, CH_4, H_2, N_2, and H_2O
- All gases behave as ideal
- All biomass and limestone is homogeneous in composition, on a dry basis
- CO_2 in limestone is fully consumed during gasification
- Limestone and poultry litter, after being mixed, travel together in the same wet weight ratio as they were combined for each experiment (This assumption is used to factor in sorted litter and residual litter in the storage bins)
- The ash content of the 'Woodchip Char' has the same composition as the ash content of the raw woodchips

When calculating composite syngas HHV, the HHV per unit mass (kJ/kg) of each of the combustible components (CO, CH_4, and H_2) were referenced from Turns (2000) and Glassman (2008). To get the volumetric heating value of each gas, the HHV's of each gas were converted to a molar basis and then multiplied by the molar density of an ideal gas at 0˚C, 1 atm (the standard to which the gasifier flow is corrected to).

$$ideal\ gas\ molar\ density_{0^\circ C,1\ atm} = \frac{n}{V} = \frac{P}{R_U \cdot T} = 44.615\left[\frac{mole}{m^3}\right] \qquad \text{Equation 9.1}$$

$$P = 101{,}325\ \text{Pa}$$

$$R_U = 8.3145\ \frac{J}{mole \cdot K}$$

$$T = 273.15\ \text{K}$$

$$Species\ HHV\left[\frac{KJ}{m^3}\right] = \frac{\left(Species\ HHV\left[\frac{KJ}{kg}\right]\right)\cdot\left(Species\ MW\left[\frac{kg}{kmole}\right]\right)\cdot\left(44.615\left[\frac{mole}{m^3}\right]\right)}{1000\left[\frac{mole}{kmole}\right]} \qquad \text{Equation 9.2}$$

The composite HHV at 0˚C, 1 atm is then just the molar fraction (or volume fraction as dictated by the gas analyzers) of each gas multiplied by its corresponding volumetric HHV and summed up.

$$Syngas\ HHV\ \left[\frac{KJ}{m^3}\right] = (Mole\ fraction\ CO)\cdot\left(CO\ HHV\ \left[\frac{KJ}{m^3}\right]\right) + (Mole\ fraction\ CH_4)\cdot\left(CH_4\ HHV\ \left[\frac{KJ}{m^3}\right]\right) + (Mole\ fraction\ H_2)\cdot\left(H_2\ HHV\ \left[\frac{KJ}{m^3}\right]\right) \quad \text{Equation 9.3}$$

To find the element mass percentage (% E) from the corresponding oxide mass percentage (% E_xO_y), the oxide mass percent was multiplied by the ratio of element's weight in one molecule of the oxide to the molecular weight of the oxide.

$$\%\,E = \left(\%\,E_xO_y\right)\cdot\frac{x\cdot A_E}{(x\cdot A_E)+(y\cdot A_O)} \quad \text{Equation 9.4}$$

A_E=Atomic Weight of Element

A_O=Atomic Weight of Oxygen (15.999)

In the Exploration of Poultry Litter Gasification Section (Section 10.1), experiments were performed examining methods to achieve consistent gasification of poultry litter. Replications of experiments were performed only if results from initial experiments were deemed promising. With this in mind, early experiments only were performed once or twice, but later experiments saw more iterations as results were approaching the performance and consistency desired. In the Quantification of Contaminant Retention Study (Section 10.2) six total experiments were performed, two at each limestone set point. This allowed averages to be calculated and trends observed both overall and at each variable each set point.

CHAPTER 10

PART 3—RESULTS AND DISCUSSION

10.1 EXPLORATION OF POULTRY LITTER GASIFICATION

The proximate, ultimate, and ash analyses of the poultry litter pellets used in the experiments are shown in Tables 10-1 to 10-3. This composition is typical for poultry litter. The silica percentage in the ash is relatively high, but this varies from farm to farm depending on the amount of dirt that gets mixed with the litter in the pens. Na_2O is slightly lower than the average expected quantity as well, usually in 5-9% range. Additionally, ash fusion analyses showed initial deformation occurring at 1120˚C in a reducing atmosphere and 1149˚C in an oxidizing environment.

Table 10-7: Poultry litter pellet proximate analysis

Parameter	% as received	% dry basis
Moisture	11.32	-
Ash	25.12	28.33
Volatile matter	52.54	59.25
Fixed carbon, by dif.	11.02	12.42
HHV [MJ/kg]	12.40	13.98

Table 10-8: Poultry litter pellet ultimate analysis

Parameter	% dry basis
Hydrogen	3.44
Carbon	36.72
Nitrogen	1.44
Oxygen, by diff.	28.45
Sulfur	0.77
Chlorine	0.847
Ash	28.33

Table 10-9: Poultry litter pellet ash analysis

Oxide	% ignited basis
SiO_2	45.30
Al_2O_3	2.48
Fe_2O_3	1.08
CaO	11.93
MgO	4.75
Na_2O	4.37
K_2O	13.00
TiO_2	0.28
MnO_2	0.34
P_2O_5	10.56
SrO	0.03
BaO	0.05
SO_3	5.82

10.1.1 Initial Tests and Woodchip Dilution

An initial feasibility test was performed employing the poultry litter pellets in the standard gasifier setup. The gasifier was started using woodchips and after steady-state operation was reached, the pellets were fed for several hours. However, upon inspection after the run, the entire gasifier was clogged with solid poultry litter clinkers, shown in Figure 10-1, that had to be removed with an air chisel.

Figure 10-18: Poultry litter clinker from initial trial, ~18 cm wide

This result was in agreement with most of the literature and showed the need for additional measures to be taken when attempting to gasify poultry litter consistently. Accordingly, the next runs were performed using a mixture of poultry litter pellets diluted with woodchips (the typical feedstock used in this gasifier), and with an eye to reducing the temperature of the gasifier through limited superficial velocity and reduced secondary air flow.

The first of these runs was a test to explore exactly what level of control over the gasifier temperature existed. The fusion of the pellets was most likely due to their low ash fusion temperature, a contribution of the alkali metals, chlorine, and silica present in poultry litter. Lowering the temperatures in the gasifier, especially the peak temperatures, was thought to alleviate at least some of the clinkering. Several trials were conducted running only woodchips and attempting to stabilize reduced temperatures.

The initial attempt consisted of simply reducing the set point temperatures in each stage of air injection for the gasifier. Although the peak temperature was reduced with this technique, the operation was not stable and the flame front rose to the top of the downdraft gasifier. This occurred because as air injection is reduced at each level (to reduce the temperature in that level), additional air was added at the uncontrolled gasifier inlet (top) to provide the total flow rate of air required for the syngas production rate specified (65m^3/hr).

In subsequent trials, to reduce the gasifier superficial velocity, the lower set point temperatures were used in conjunction with lower syngas flow rates until the syngas flow rate was reduced to 40m^3/hr (the minimum allowed by the gasifier). The net reduction in average reaction temperature was less than 50˚C using this technique.

The next runs were conducted to determine if the clinkering tendency of poultry litter could be mitigated by diluting the poultry litter pellets with wood chips. Trials with 20 percent and 40 percent poultry litter (by weight) in wood chips were conducted. Initially the trial with 20 percent poultry litter appeared to be successful and produced no external operating anomalies such as increased pressure drop across the gasifier. Consequently, without purging the existing material, a trial using 40 percent poultry litter was conducted. During each of these trials a suitable quality syngas was produced for the duration. However, as the 40% trial progressed, the operating temperature profile and the gasifier pressure drop became unstable and the trial was aborted. The gasifier was then cleaned and the ash was found to contain significant quantities of clinkered poultry litter pellets (Figure 10-2).

Subsequent trials and analyses showed that clinkering was actually occurring with the 20 percent trial but the low concentration of poultry litter pellets and the long residence time in the gasifier caused the problem to not be evident during the roughly 4-hour initial trial.

Additional tests were performed attempting to limit the gasifier temperature while feeding poultry litter by adjusting set-points, depressing overall gas flow rate, using wet woodchips to depress the flame front, and combinations of each. None of these options yielded either stable operation or a reduction of the pellet clinkering.

Figure 10-19: Poultry litter pellet clinkers from 40% pellet run

However, a pattern was observed in the clinker formation and location throughout the runs. Clinkers tend to be on the order of 6-8 cm in diameter, or roughly the size of a baseball. The pellet agglomerations tended to be found hung-up between levels 3-4 or 4-5 (Figure 10-3). This trend appeared to be independent of trial length or dilution percentage.

Figure 10-20: View from top of gasifier of poultry litter pellet clinkers hung up between levels 3 and 4 after loose biomass char had been removed. Level 5 is obscured by clinkers

10.1.2 Flue Gas Recirculation

According to the ash fusion analysis conducted by Wyoming Analytical Laboratories, initial deformation was found to be occurring at1120˚C in a reducing environment and 1149˚C in an oxidizing environment. Both of these temperatures, however, are greater than any observed in the gasifier under normal operating conditions. A plot of the average temperature profile inside the gasifier over a typical 4 hour run can be seen in Figure 10-4. Levels 1-5 correspond to thermocouples located at the 5 levels of secondary air injection.

Figure 10-21: Average gasifier temperature profile during a typical run with pine chips

While this represents the average over time, it should be noted that peak temperatures observed during standard operation seldom eclipse 950˚C and never exceed 1100˚C unless the flame front escapes the gasifier top and is recorded by the top-most thermocouple.

Given these observations, it was perplexing as to why pellet adhesion was occurring with such severity at these low temperatures despite the efforts put forth to abate them. However, when examining the clinkers formed during some of the experiments, it was discovered that several had distinct impressions corresponding to the shape of the secondary air injection nozzles (Figure 10-5).

This gave rise to the theory that local ‘hot spots’ exceeding the ash fusion temperature were to blame for the clinker formation. In the reducing environment of the gasifier, the highest temperatures would be where oxygen is most available and actual combustion could occur locally. Limiting this oxygen supply through the use of a diluent, the most practical option being flue gas, was a prospective solution. In addition to diluting the throughput of oxygen to the gasifier char, the primary species present in flue gas (CO_2 and H_2O) could potentially participate in two of the dominant endothermic reactions to actually lower the temperature locally (Buekens, et al., 1984)(Priyadarsan, et al., 2004):

$C + CO_2 \rightarrow 2CO + 14.42$ MJ/ kg of carbon gasified

$C + H_2O \rightarrow CO + H_2 +10.92$ MJ /kg of carbon gasified

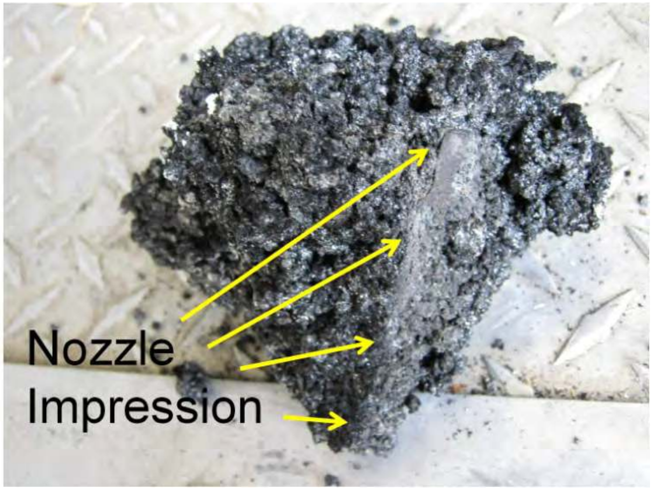

Figure 10-22: Impression of nozzle in poultry pellet clinker

To easily produce, control, and cool a flue gas stream, a propane water heater was used, as detailed in the Experimental Setup section. The lowest average gasifier operating temperature profile obtained is shown in Figure 10-6, for comparison to the standard profile from Figure 10-4.

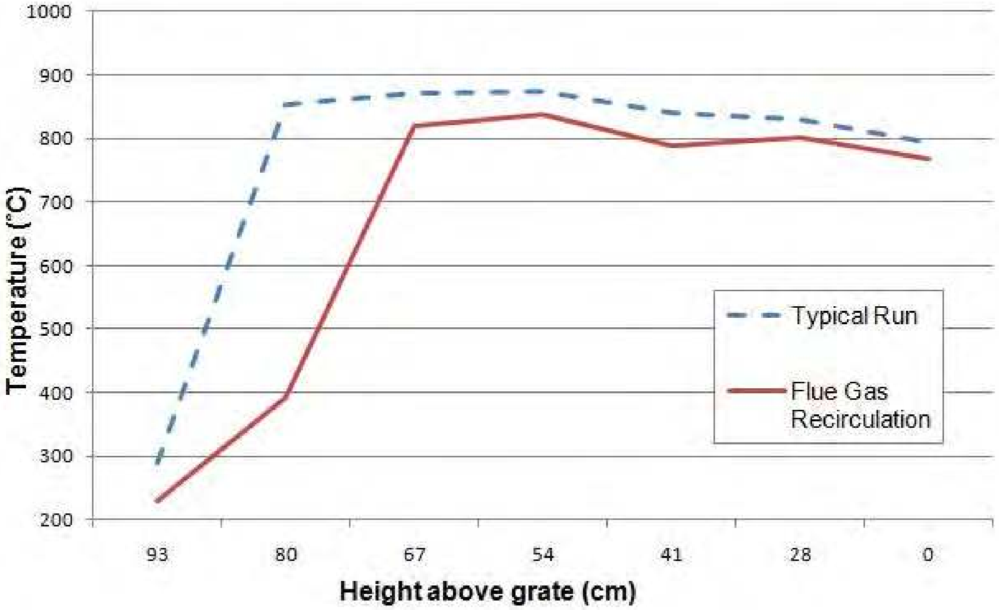

Figure 10-23: Average gasifier temperature profile during flue gas recirculation poultry litter

The overall average temperature of the gasifier achieved using this method was 662˚C, 102˚ cooler than the 764˚C average of the typical run. This was obtained by reducing the syngas production rate to 55Nm³/hr (from the standard 65) to limit the superficial velocity through the gasifier and by diluting the secondary air by an average of 42.5%. That is, the average O_2 reading of the secondary air was 12%, 42.5% less than the 20.9% concentration of the measured ambient air. This test was conducted using a 40% mixture of poultry litter pellets to pine chips by weight for a duration of 3 hours and 20 minutes.

A negative effect manifested in the use of flue gas injection was a reduction in syngas quality. During a standard run with the gasifier using pine chips, the average dry syngas composition (by volume) that can be expected and corresponding higher heating value is approximately:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m^3]
0.5	20	12	1.5	18	5.4

*Syngas over duration of a typical run can be seen in Appendix D, Figure D-1

A composition along these lines was observed when gasifying the 40% poultry litter pellet mixture under normal operation in a previous experiment that resulted in clinker formation. However, use of the flue gas recirculation technique resulted in an inferior average syngas composition and consequently an approximately 25% reduction in higher heating value:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m^3]
1.3	13.1	14.3	1.1	15.2	4.0

*Syngas performance over duration of run can be seen in Appendix D, Figure D-2

Despite the successful overall reduction in temperature, examination after the experiment showed that clinkering of the poultry litter pellets was neither eliminated nor significantly reduced. Clinkers were still recovered that had impressions of the nozzles, similar to Figure 10-5.

From the experiments run and observations made, it can be seen that the fusion experienced by the poultry litter pellets in the gasifier is temperature independent, at least within the controllable range.

10.1.3 Limestone Additive

The next option, as described in the literature, was the use of limestone additive to prevent fusion of gasified litter (Bock 2004; Reardon et al. 2001; Coda et al. 2001). A further benefit of the addition of limestone to the gasifier environment was the potential for the capture and retention in the ash of volatilized chlorine. Powdered limestone was used for the experiments and the analysis is shown in Table 10-4.

The analysis shows that the limestone used was of good quality, being high in calcium carbonate and low in silica and other constituents. As recommended in the literature, 5% by weight (limestone/litter) powdered limestone was used to evenly coat the poultry litter pellets in a cement mixer. This mixture was then diluted to 40% by weight with pine chips to prevent extreme blockage if the experiment was unsuccessful. Ninety kg of this mixture was fed for four hours with very little departure in gasifier performance or syngas composition from a standard woodchip feedstock run. Upon examination of the char, it was discovered that although clinkers had been formed, most were smaller in size than usual (4-5 cm diameter) and two larger ones (12-14 cm) had proceeded beyond the lowest level of nozzles, where few usually advance.

Table 10-10: Powdered limestone analysis

Oxide	% dry basis
SiO_2	1.60
Al_2O_3	0.51
Fe_2O_3	0.59
$CaCO_3$	81.86
$MgCO_3$	15.01
Na_2O	0.01
K_2O	0.17
TiO_2	0.05
MnO_2	0.06
P_2O_5	0.05
SrO	0.07
BaO	0.01
SO_3	0.16

A second, identical experiment was run and after 90 kg of the mixture was gasified, pine chips were fed for an additional four hours in an attempt to flush the poultry litter mixture through the gasifier. A significant amount of poultry litter pellets did feed past the last air injection nozzles, but they were found in the form of a large agglomeration containing both woodchip and pellet remains. However, the furthest advancing, pellet-containing part of this agglomeration appeared to blend seamlessly into a layer of easily crumbled, dense, gray, amorphous ash approximately 4 cm above the grate. This suggested that the pellets, having been fully depleted of their carbon content, no longer possessed the extreme traits of fusion displayed when found higher in the gasifier. A sample of this ash was analyzed and was found to contain oxides associated with both the limestone and poultry litter ash as well as a chlorine concentration of 3.57% (Table 10-5).

The chlorine concentration found (3.57%) is more than four times that of the raw poultry litter pellets (0.847 %) and indicates the successful capture of a measurably significant portion. This was a promising result with regards to the end goal of limiting chlorine volatilization and entrainment in the product gas. The clinkering issue, however, demanded further attention if poultry litter was to be gasified consistently, leading to the set of experiments described next.

Table 10-11: Dense, gray, easily crumbled, amorphous ash analysis

Oxide	% dry basis
SiO_2	24.50
Al_2O_3	1.30
Fe_2O_3	1.25
CaO	37.78
MgO	2.49
Na_2O	0.89
K_2O	15.18
TiO_2	0.16
MnO_2	1.34
P_2O_5	1.99
SrO	0.17
BaO	0.30
SO_3	4.09
Loss on ignition	8.55
Chlorine	3.57

10.1.4 Raw Poultry Litter and Limestone Addition

A trial of raw, un-pelletized, woodchip-diluted poultry litter was seen as an alternative to the dense, seemingly non-porous litter pellets. This mixture would offer a more even distribution of the litter as well as allow easier carbon conversion. Results from previous runs using poultry litter pellets indicated that long residence times were necessary if total carbon conversion was to be achieved. This is due most likely to the low porosity of the highly compacted pellets limiting the gas diffusion and isolating reactions to the surface of the pellets. Additionally, trials could be run using the limestone additive mixed more evenly with the problem feedstock, as opposed to only coating the surface of pellets. Dilution of the raw litter with woodchips would be necessary for implementation in the downdraft gasifier and feed system due to the high percentage of fines.

Ninety kilogram of the 20% raw litter mixture fed for three hours for a total mass flow rate of 30 kg/hr. Over 90 kg of woodchips were fed for four hours following the poultry litter mixture to assure advancement of the mixture to the grate and allow for accurate assessment of performance following the trial.

The trial performed well and a syngas similar to pure woodchips was produced for the duration of the run. Only two small clinkers resulted from this experiment, and both were found past the last level of nozzles inside the gasifier, indicating clean passage through the area where pelletized litter had been hung up.

A second experiment of 40% litter was run to determine the upper limit of raw poultry litter substitution. This was found to be too much for the gasifier, producing a large agglomeration between levels four and five.

To test the effect of limestone addition, 5% lime (to raw litter weight) was evenly mixed with the raw litter before being diluted to 40% with woodchips. Since 40% un-amended litter appeared to exceed the upper limit, this concentration would be a good benchmark for comparison. The mixture was found to gasify much better than either the litter without lime or the pelletized litter mixed with lime. No clinker formation was found to occur, only the existence of an amorphous, grey, crumbly ash (Figure 10-7). This ash was easily broken up by hand and was likely to continue through the gasifier without much issue.

During the experiment a large pressure drop across the gasifier built up, but was alleviated by the continuing oscillation of the grate shaker. Even if this pressure drop proves to be persistent, operation was reliable and steady enough to conduct further tests in quantifying deleterious species capture rates.

An identical experiment was performed to test how consistent this method was and very similar results were found. The syngas composition and resulting HHV were slightly compromised by air leaks resulting from the elevated gasifier differential pressure (seen in Appendix D, Figure D-3), but gasifier performance was satisfactory for beginning the Quantification of Contaminant Retention Study.

Figure 10-24: Easily crumbled, grey amorphous ash from raw poultry litter with limestone

10.1.5 Summary of Results

A summary of the primary techniques explored in the study is presented in Table 10-6.

Table 10-12: Summary of primary experiments and results, avg. syngas HHV≈5.4 MJ/m³

Technique Used	Gasifier Char State	Syngas Quality	Notes
20% pellets, 80%woodchips	6-8cm clinkers, nozzle impressions	Average	
40% pellets, 60%woodchips	6-8cm clinkers, nozzle impressions	Average	
Flue gas recirculation, 40% pellets	6-8cm clinkers, nozzle impressions	Below average, 4.0 MJ/m³	~100˚C reduction in avg. temp.
Limestone addition, 40% pellets	4-5cm clinkers, agglomeration past nozzles	Average	
20% raw litter, 80% woodchips	Minimal clinker formation and only past the nozzles	Average	
40% raw litter, 60% woodchips	Large agglomeration	Average	
Limestone addition, 40% raw litter	No clinkers: amorphous, grey, crumbly ash	Below average, ~4.0 MJ/m³	Reduction in syngas quality due to increased gasifier pressure and resulting air leak

10.2 QUANTIFICATION OF CONTAMINANT RETENTION STUDY

The goal in these experiments was to quantify the percentage of contaminants retained in the ash when gasifying poultry litter. The proximate, ultimate, and ash analyses of the charcoal, woodchips, and raw poultry litter used in these tests are presented in Tables 10-7 to 10-9. The limestone used was the same as that in Sections 10.1.3-10.1.4 and can be seen in Table 10-4. The raw poultry litter has a lower ash content and a higher HHV than the pelletized litter used previously, making it a better fuel candidate from the beginning. When compared to the average from the literature (Section 10.1), the ash is still low, but HHV is average. The sulfur and chlorine content are lower than average as well. The silica content is lower than the poultry litter pellets, potentially aiding in its resistance to clinkering (as discussed in Section 8.5).

Table 10-13: Proximate analysis of charcoal, woodchips, and poultry litter (% dry basis)

Parameter	Charcoal	Woodchips	Poultry Litter
Ash	5.64	0.28	19.63
Volatile matter	16.81	81.71	63.99
Fixed carbon, by dif.	77.55	18.01	16.38
HHV [MJ/kg]	30.17	19.40	15.48

Table 10-14: Ultimate analysis of charcoal, woodchips, and poultry litter (% dry basis)

Parameter	Charcoal	Woodchips	Poultry Litter
Hydrogen	1.88	5.03	3.87
Carbon	80.44	49.33	36.69
Nitrogen	0.52	0.53	0.77
Oxygen, by dif.	11.49	44.70	38.44
Sulfur	0.01	0.13	0.10
Chlorine	0.0221	0.0030	0.502
Ash	5.64	0.28	19.63

Table 10-15: Ash analysis of charcoal, woodchips, and poultry litter (% Ignited Basis)

Oxide	Charcoal	Woodchips	Poultry Litter
SiO_2	6.51	13.99	25.96
Al_2O_3	0.43	2.99	2.87
Fe_2O_3	0.97	6.55	1.47
CaO	78.06	35.50	28.29
MgO	2.15	11.95	4.65
Na_2O	0.90	1.78	3.33
K_2O	5.16	12.50	11.31
TiO_2	0.00	0.00	0.07
MnO_2	2.04	3.73	0.23
P_2O_5	1.07	5.81	15.83
SrO	0.29	0.16	0.03
BaO	0.43	0.47	0.00
SO_3	1.91	4.39	3.52
Chlorine	0.07	0.22	3.13
Total	99.98	99.99	100.00

The low Ash and Chlorine content of the charcoal and woodchips relative to the litter, paired with the low alkali and phosphorus content of the charcoal ensured that the poultry litter was by far the dominant source of Na, K, P, and Cl in the experiments. For all experiments, poultry litter accounted for 90.6±0.6% Na, 83.6±0.9% K, 95.5±0.2% P, and 93.6±0.4% Cl fed into the gasifier (Appendix A, Tables A-3 to A-8).

Results between experiments were very similar from a gasifier performance, qualitative analysis, and syngas production standpoint. During all runs, gasifier differential pressure started climbing after the poultry litter mixture had been feeding for about one hour, due to the large amount of fines present in poultry litter. By one and a half hours it had reached 25" H_2O (6.2 kPa), the maximum in the measured range for the onboard manometer, where it remained for the duration of the test. Consequently, air was drawn into the system anywhere there were small leaks and syngas quality suffered. It was discovered after sampling syngas from different parts of the system that the primary source of the leak was somewhere in the filter box. The dry average syngas composition and HHV during the feeding of the litter/limestone/woodchip mixture for one of the experiments (8.95% limestone/dry litter) is as follows:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m³]
5.6	14.9	8.5	0.8	12.1	3.8

*Syngas variation during this typical run can be seen in Appendix D, Figure D-4

This result was very typical for all experiments. Since it was found that all O_2 was entering through leaks in the filter box, and assuming that 3.76 moles of N_2 entered for every mole of O_2 in air, a corrected syngas composition and corresponding HHV could be calculated:

O_2 [%]	CO [%]	CO_2 [%]	CH_4 [%]	H_2 [%]	HHV [MJ/m³]
0.0	20.4	11.6	1.1	16.6	5.1

This corrected composition and HHV is what would be achieved if leaks were eliminated from the system and is very comparable to the standard woodchip syngas composition as described in Section 4.1.1. However, the root of the problem is the high pressure across the gasifier which is an issue that needs to be addressed if gasifying poultry litter is to be further pursued.

Ash recovered from each section of the gasifier was visibly identical between experiments, the only minor difference being 'PL Ash' crumbling slightly less easily at the 3.71% limestone set point, perhaps indicating an approach towards the threshold of clinkering for a minimum amount of limestone. A sample of the 'Woodchip Char' collected from the top of the gasifier using a Shop-Vac can be seen in Figure 10-8. A dime is pictured as a size reference.

When the gasifier was opened at the seam above the grate, the distinction between what appears to be the poultry litter and limestone ash and the charred wood and charcoal was evident. The poultry litter ash, as previously described in Section 10.1.4, is gray, crumbly and amorphous in nature, and can be seen as the light gray sections of ash in Figure 10-9.

Figure 10-25: 'Woodchip Char' sample, collected from the top of the gasifier

Figure 10-26: Ash mound as seen when gasifier is opened at crack above grate. Poultry litter ash is the light gray section in the middle of the mound

After being separated from the charcoal and wood char by hand and crumbled, the poultry litter and limestone ash can be seen in Figure 10-10. This was separated, weighed, and sent for analysis as 'PL Ash' in the first experiment for each of the three limestone set points (3.71, 5.71, and 7.71 % Limestone/Wet Litter), but mixed with the rest of the gasifier char for the second. The charcoal and wood char not included in the 'PL Ash' sample was labeled 'Rest of Gasifier' and can be seen in Figure 10-11.

Figure 10-27: Crumbled poultry litter ash as sent for analysis in one experiment for each limestone set point (3.71, 5.71, and 7.71 % Lime/Wet PL), labeled 'PL Ash'

Figure 10-28: 'Rest of Gasifier' sample, comprised mostly of charcoal and wood char

The char that settled in the chamber below the gasifier grate and just before the heat exchanger, a section where syngas is between 600-750˚C, was labeled 'Below Grate' and can be seen in Figure 10-12.

Figure 10-29: Char collected from chamber below gasifier grate, labeled ‘Below Grate’

The char that settled inside and just after the exit of the heat exchanger was labeled ‘HEX’ and can be seen in Figure 10-13. It is much finer than that below the grate. Syngas in this section is cooled from 600-630˚C down to 100-110˚C.

Figure 10-30: Char from inside and just after the heat exchanger, labeled ‘HEX’

The final place char is found is the filter box, samples labeled ‘Filter’. This char is very similar to the ‘HEX’ sample, only slightly darker and more powdery (Figure 10-14). Syngas in this section is filtered through bags and cools from 100-110˚C to 50-60˚C.

Figure 10-31: Char collected from filter box, labeled 'Filter'

In the second experiment for each of the three limestone percentages (3.71, 5.71, and 7.71 %), the char comprising the 'Below Grate', 'HEX', and 'Filter' samples was combined, mixed, and then sampled as 'Past Grate'. In these same three experiments, all char labeled 'PL Ash' and 'Rest of Gasifier' was combined, mixed, and sampled as 'Gasifier'.

10.2.1 Contaminant Mass Balances

The procedure followed was that dictated in Section 9.2.2, however after the first four experiments it was discovered that a small amount of the biomass fines were falling below the conveyer in the onboard feed system and never making it into the gasifier. Therefore, during the final two experiments, the small portion of poultry litter mixture that fell through was collected and weighed as was the small portion of the 200 lbs (90.72 kg) of woodchips fed after the poultry litter mixture using the onboard conveyer. The two runs yielded similar results with 4.64 lbs of woodchips and 10.05 lbs of poultry litter mix being collected for one and 5.10 lbs of woodchips and 12.75 lbs of poultry litter mix collected for the other. The average of these two (4.86 lbs woodchips and 11.40 lbs of PL mix) was then assumed as the loss for each of the previous four experiments. To find the composition of the PL mix that was recovered, it was assumed that the same ratio of woodchips fell through from both the 200 lbs woodchip batch and from the woodchips in the poultry litter mixture (130 lbs). This amount (i.e., for the average: $\frac{4.86}{200} \cdot 130$) was then subtracted from the PL mix recovered and what remained was assumed to be poultry litter and lime present in the same ratio as they were mixed for each experiment (i.e. 3.71, 5.71, or 7.71% Limestone/Wet PL).

The analyses for each of the raw feedstocks (charcoal, woodchips, poultry litter, and limestone), coupled with the experimentally found moisture content, predetermined weight, and experimental losses were used to determine the total amount of each contaminant of interest (K, Na, P, Cl) and a tracer element (Ca) fed into the gasifier. In the same manner, using the mass of ash collected, lab analyses, and experimentally determined LOI's the amount of each contaminant and tracer mineral recovered in the ash was determined. Ratios of mass recovered in char to mass fed into the gasifier were then calculated for each element in every experiment, giving a retention percentage of the elements when gasified. Additionally, total ash content fed into the gasifier was calculated from the feedstock weight and ash analysis, as was total ash content recovered from the char. These values were then compared and used to calculate a percent difference of total ash content collected to total ash content expected. These mass balances and analyses can be seen in Appendix A.

Not factoring in the assumed and measured losses from the onboard conveyor, the retention percentage of each element for every experiment can be seen in Table 10-10, arranged in order of increasing Limestone/Dry poultry litter percentage. The average retention percentage at each Limestone/Wet Poultry Litter set point can be seen in Table 10-11.

Table 10-16: Retention percentage of notable elements, not accounting for conveyor losses

Limestone/Wet PL (%)	Limestone/Dry PL (%)	P	K	Cl	Na	Ca
3.71	4.24	83.2%	80.4%	63.3%	73.5%	74.5%
3.71	4.31	112.4%	91.9%	92.7%	101.4%	104.8%
5.71	6.49	91.7%	90.4%	89.3%	89.2%	89.6%
5.71	6.69	100.3%	80.8%	73.1%	96.1%	90.6%
7.71	8.92	71.9%	81.0%	76.4%	60.9%	65.5%
7.71	8.95	88.3%	86.4%	82.0%	84.8%	83.9%
	Average:	91.3%	85.2%	79.5%	84.3%	84.8%

Table 10-17: Average retention percentage of notable elements at the three limestone set points, not accounting for conveyor losses

Limestone/Wet PL (%)	P	K	Cl	Na	Ca
3.71	97.8%	86.1%	78.0%	87.4%	89.7%
5.71	96.0%	85.6%	81.2%	92.6%	90.1%
7.71	80.1%	83.7%	79.2%	72.8%	74.7%

To compare the effect of factoring in the conveyor losses, Table 10-12 shows the absolute percent difference between total ash content put into the gasifier and total ash content recovered in the char, with and without the conveyor losses factored in. It also shows the percentage of the total input ash content that the conveyer losses account for in each run.

It can be seen that including the conveyer losses gains an average 6.0% improvement in ash percent difference for all runs. Also, the losses account for an average 9.6% of the input ash. Because of this, all results presented henceforth will have the conveyor losses factored in.

Table 10-18: Percent of total input ash content accounted for by conveyer losses and absolute % difference between total input ash and output ash with and without conveyor losses factored in

Limestone/Wet PL (%)	Limestone/Dry PL (%)	% of input ash	Abs. % Diff. betweent total ash in and total ash out	
			With losses factored in	Without losses factored in
3.71	4.24	9.4%	12.6%	20.8%
3.71*	4.31*	8.1%	7.7%	1.0%
5.71	6.49	9.2%	0.2%	9.4%
5.71	6.69	9.5%	0.4%	9.1%
7.71*	8.92*	12.2%	25.4%	33.4%
7.71	8.95	9.2%	7.8%	16.3%
	Average:	9.6%	9.0%	15.0%

Note: Designates runs where conveyer losses were collected and weighed, losses for all others are the average of the two

The retention percentage of notable elements, losses factored in, is presented in Table 10-13. Compared to Table 10-10, phosphorus is 6.3% closer and calcium is 7.4% closer on average to 100% retention. In the literature (Section 8.3) it was found that P and Ca did not volatilize at gasification or combustion temperatures and thus are expected to be accounted for fully in the gasifier char. Ca particularly is expected to be fully retained in the ash and was used in the literature as a foundation for normalizing data. The average retention percentage at each limestone set point can be seen in Table 10-14.

The data from Tables 10-13 to 10-14 are presented graphically in Figures 10-15 to 10-17, plotted as percent retention vs. limestone percent (on a wet litter basis). The data points for the two runs at each limestone set point are displayed as diamonds, and the average for those points is shown as an asterisk with a curve fit.

Table 10-19: Retention percentage of notable elements, conveyor losses factored in

Limestone/Wet PL (%)	Limestone/Dry PL (%)	P	K	Cl	Na	Ca
3.71	4.24	93.7%	89.4%	71.0%	82.2%	81.0%
3.71	4.31	124.4%	100.5%	102.5%	111.7%	112.4%
5.71	6.49	102.9%	100.1%	100.0%	99.5%	97.3%
5.71	6.69	112.5%	89.7%	81.9%	107.3%	98.8%
7.71	8.92	82.0%	91.2%	87.0%	69.0%	72.6%
7.71	8.95	98.9%	95.7%	91.7%	94.5%	91.3%
	Average:	102.4%	94.4%	89.0%	94.0%	92.2%

Table 10-20: Average retention percentage of notable elements, conveyor losses factored in

Limestone/Wet PL (%)	P	K	Cl	Na	Ca
3.71	109.0%	95.0%	86.8%	97.0%	96.7%
5.71	107.7%	94.9%	91.0%	103.4%	98.1%
7.71	90.5%	93.4%	89.3%	81.7%	81.9%

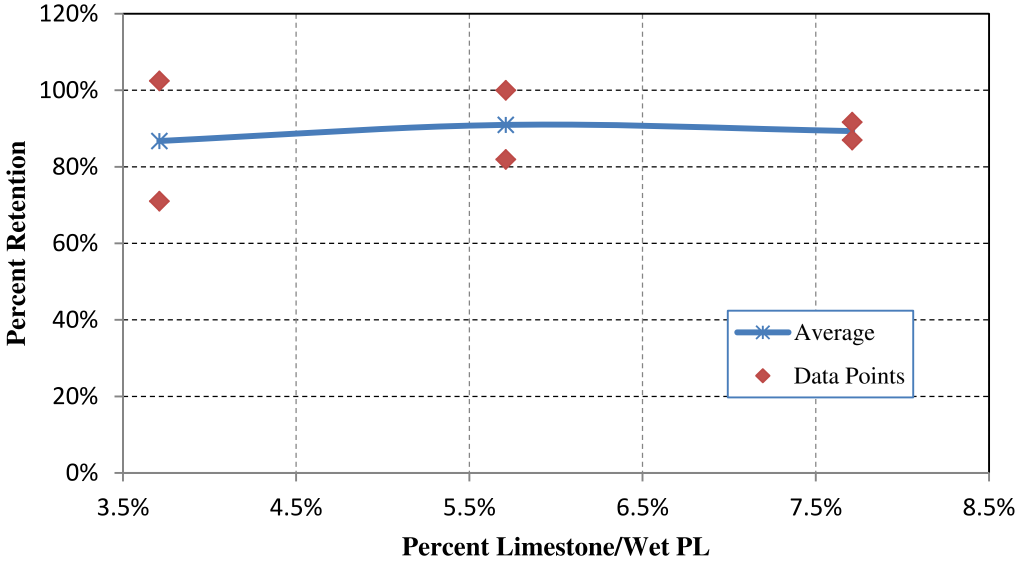

Figure 10-32: Chlorine Retention vs. Limestone Percentage

Chlorine is retained quite well, the average being 89.0%. The average at each set point doesn't vary much from the overall average, indicating little effect of limestone percentage on chlorine retention, at least within the range tested. The average potassium retention appears steady between limestone percentages, straying little from the overall average of 94.4%. The trend lines for Na, P, and Ca, however, all decline quite substantially with increasing limestone percentage. It may be possible for Ca that as more limestone is mixed with the raw poultry litter, there is also more that is lost as dust while mixing or that falls through the conveyor while feeding. However, phosphorus shows a similar decrease and the extremely low P content in limestone (0.05% dry basis, Table 10-4.) prevents that theory for accounting for the losses of both of these elements that were expected to be fully retained. Analyzing the numbers from Tables 10-13 and 10-12 it can be seen that the experiment contributing most to the low average of Na, P, and Ca at 7.71% limestone also has the largest percent difference between total ash in and out: 25.4% even after including the conveyor losses. Additionally, it can be observed from Table 10-13 that the calcium retention percentage for each experiment is very indicative of the percent retention of the other elements for that run. For example, in an experiment when Ca is lower than the average, all other parameters are lower than average as well. The same trend can be observed for the experiment with a Ca balance of greater than 100%. With these observations in mind, and borrowing the technique discussed from the literature, each experiment was normalized to the expected value of 100% Ca (Misra et al. 1993). Table 10-15 shows the retention percentage for all experiments when the results for each experiment were normalized to Ca. The average retention percentage at each % Limestone/Wet Litter set point can be seen in Table 10-16.

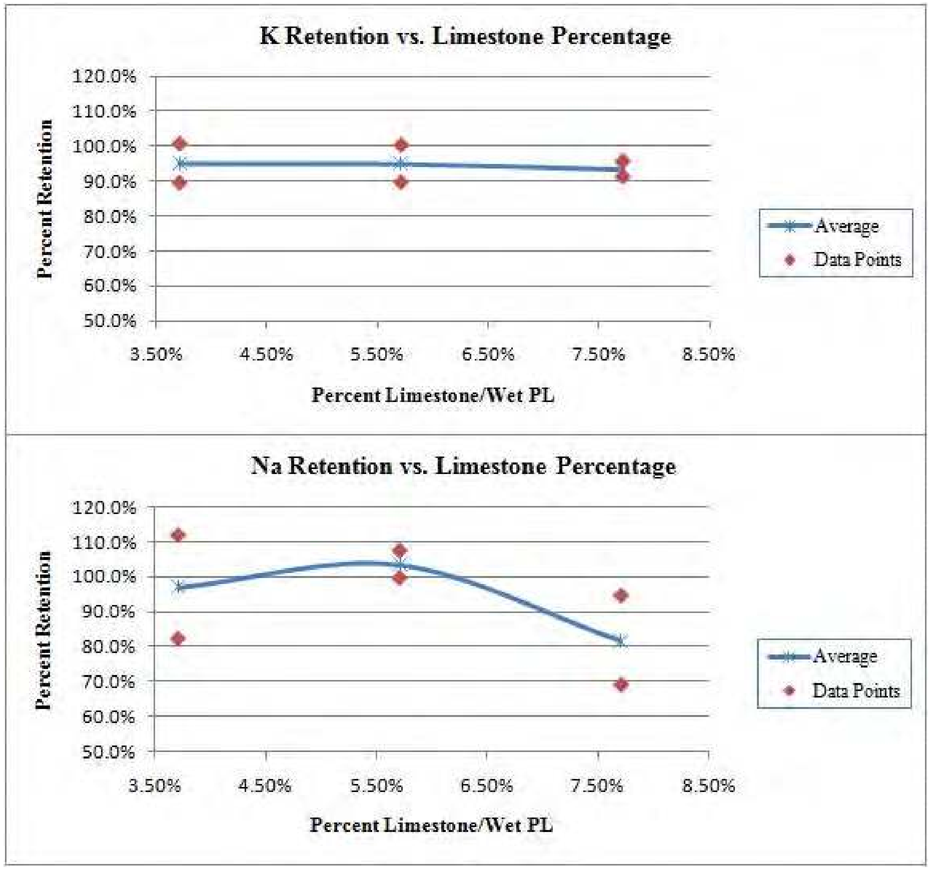

Figure 10-33: Alkali Retention vs. Limestone Percentage

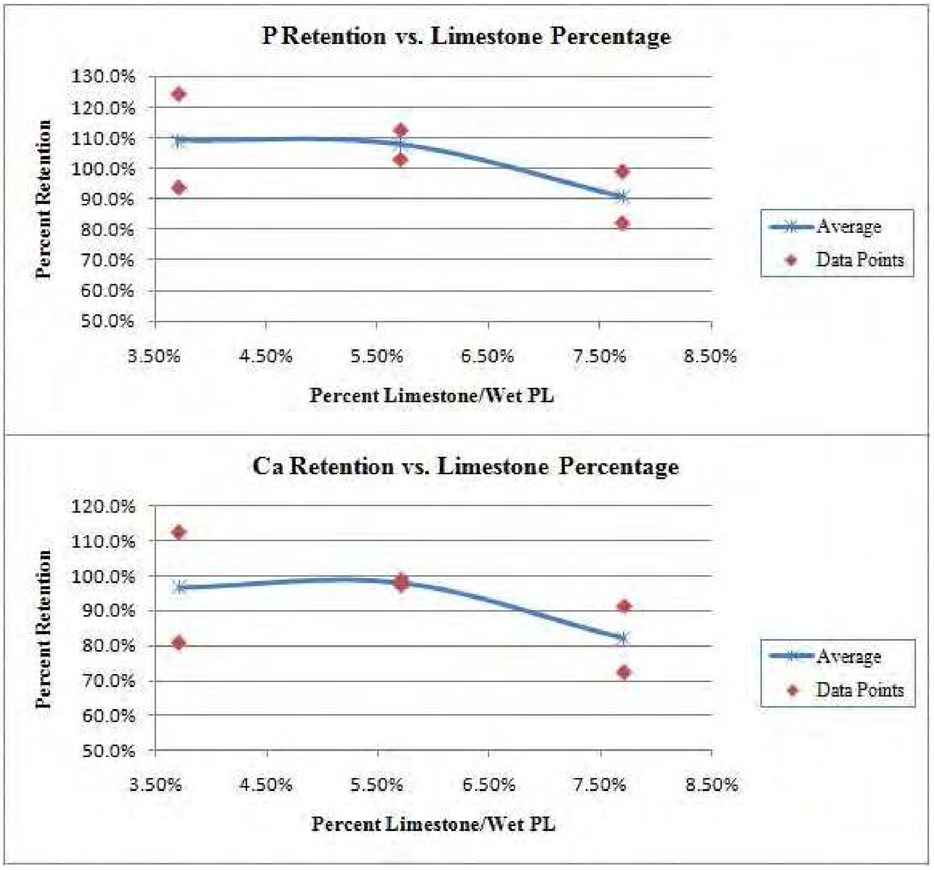

Figure 10-34: Phosphorus and Calcium Retention vs. Limestone Percentage

Table 10-21: Retention percentage of notable elements, normalized to Ca

Limestone/Wet PL (%)	Limestone/Dry PL (%)	P	K	Cl	Na	Ca
3.71	4.24	115.7%	110.4%	87.7%	101.5%	100.0%
3.71	4.31	110.7%	89.5%	91.2%	99.4%	100.0%
5.71	6.49	105.7%	102.9%	102.7%	102.3%	100.0%
5.71	6.69	113.8%	90.7%	82.9%	108.6%	100.0%
7.71	8.92	113.0%	125.7%	119.9%	95.2%	100.0%
7.71	8.95	108.3%	104.7%	100.4%	103.4%	100.0%
	Average:	111.2%	104.0%	97.5%	101.7%	100.0%

Table 10-22: Average retention percentage of notable elements, normalized to Ca

Limestone/Wet PL (%)	P	K	Cl	Na	Ca
3.71	113.2%	100.0%	89.5%	100.5%	100.0%
5.71	109.8%	96.8%	92.8%	105.4%	100.0%
7.71	110.7%	115.2%	110.1%	99.3%	100.0%

The data from Tables 10-15 and 10-16 is presented graphically in Figures 10-18 and 10-19, plotted as percent retention vs. limestone percent (on a wet litter basis). The data points for the two runs at each limestone set point are displayed as diamonds, and the average for those points is shown as an asterisk with a curve fit.

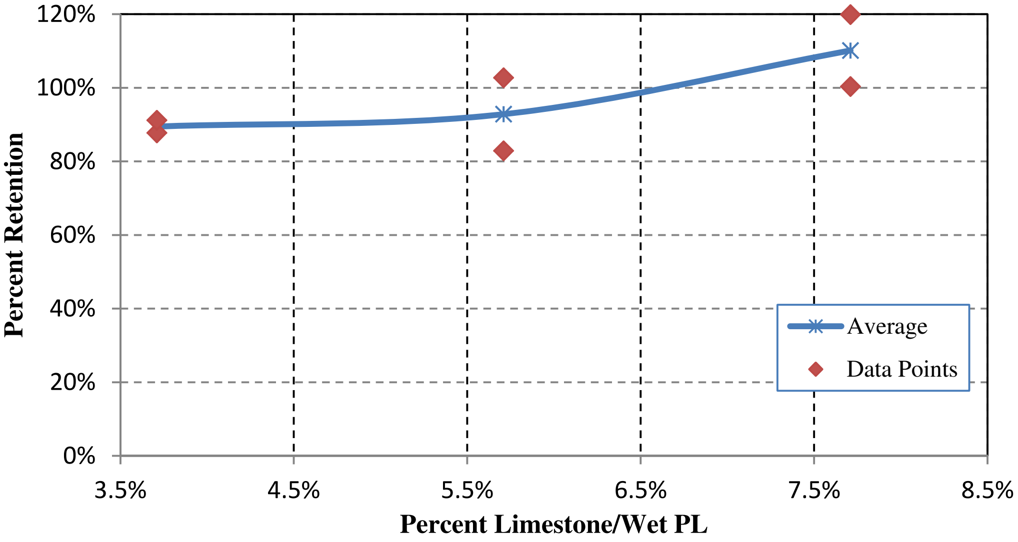

Figure 10-35: Chlorine Retention vs. Limestone Percentage, Normalized to Calcium

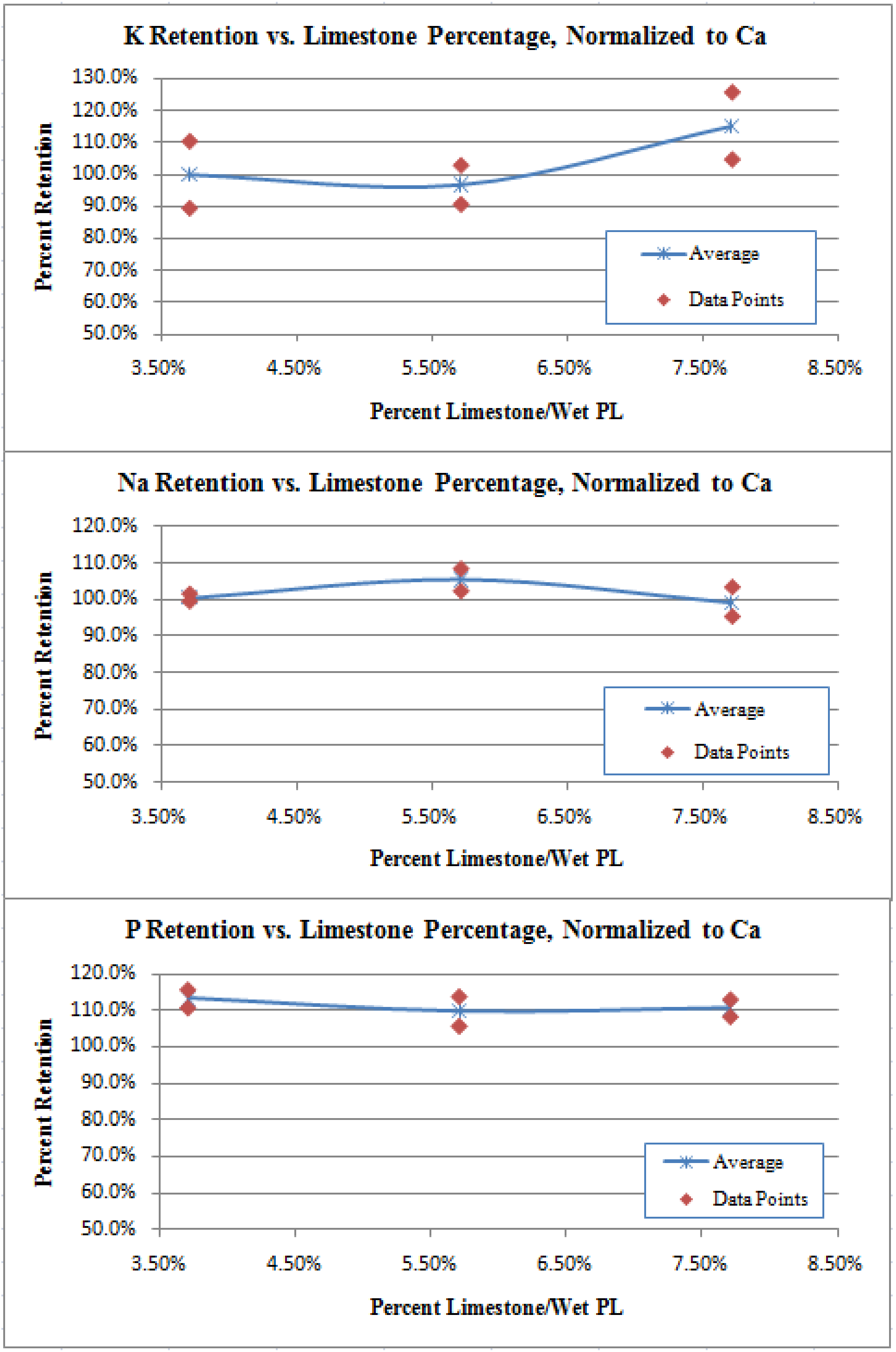

Figure 10-36: Potassium, Sodium, and Phosphorus Retention vs. Limestone Percentage

Normalizing to calcium tightened up most of the data points. The span between the two data points at each limestone percentage improved on average from 16.8% to 11.0% for every element excluding Ca. The phosphorus trend line is now flattened out and the average retention at the 7.71% limestone set point is in line with the averages at 3.71% and 5.71%, which both changed very little. However, now all data points for P as well as several for Na, K, and Cl are above 100%. The trend lines for both Cl and K appear to indicate an increase in retention with an increase in limestone addition, which was the hypothesized result (an increase in Cl capture by the limestone limiting K reaction and volatilization with Cl), however the peak for both is at least 110%.

Overall, it is difficult to say whether the trend lines actually represent a trend, due to limited number of data points and the substantial scatter of the points. However, on average, nearly all of the contaminates appear to be captured. The lowest average retention percentage over all runs, regardless of losses included or normalization, was Cl and at worst the average retention percentage was 78.0% (for 3.71% limestone, not including conveyor losses). Including the known conveyor losses, an average 89.0% Cl was captured over all runs and at least 94.4% on average was captured of P, K, and Na. When normalized to calcium, an average 97.5% Cl was captured and at least 100% on average was captured of P, K, and Na.

10.2.2 Contaminant Distribution

In one of the experiments at each of the three limestone percentages, the char collected from each section of the gasifier was weighed and analyzed separately, instead of combining and mixing it. Doing this allowed insight into the distribution of elements throughout the gasifier. Figure 10-4 shows the average temperature of the syngas as it proceeds from the grate through the heat exchanger and finally out of the filter box. This temperature profile is significant when compared with the contaminant profiles. Figures 10-20 to 10-22 show the mass percent of K_2O, Na_2O, P_2O_5, SO_3, and Cl in the ash of the char samples at the three limestone/wet poultry litter percentages.

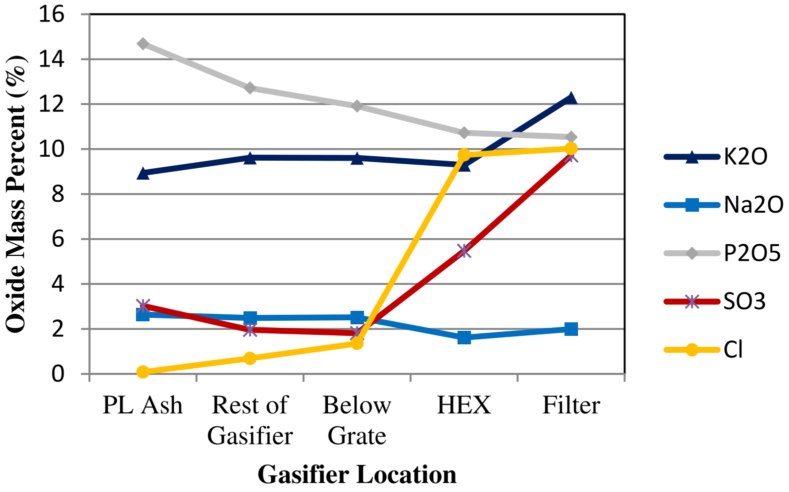

Figure 10-37: Mass percent of oxides in char ash throughout the gasifier, at 3.71% limestone/wet litter

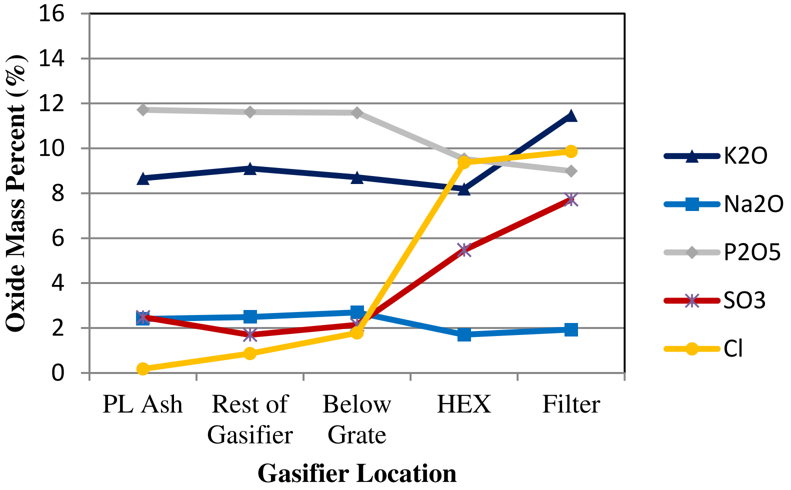

Figure 10-38: Mass percent of oxides in char ash throughout the gasifier, at 5.71% limestone/wet litter

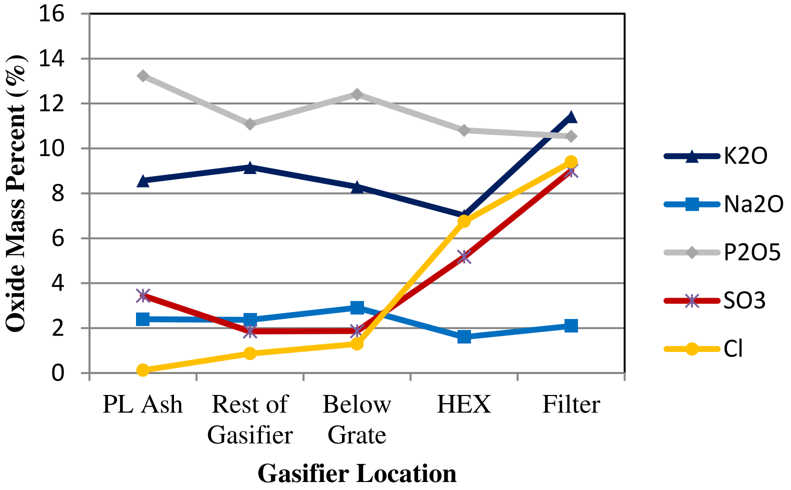

Figure 10-39: Mass percent of oxides in char ash throughout the gasifier, at 7.71% limestone/wet litter

While the limestone percentage doesn't appear to have an effect on the contaminant profile, it is obvious from the three figures that there is a trend in element concentrations. Na_2O and P_2O_5 decrease slightly and seem to mirror each other as you progress through the gasifier. K_2O concentration decreases slightly and then spikes at the Filter location. SO_3 and Cl both increase significantly at the heat exchanger (HEX) and Filter. While sulfur is not one of the main contaminants of interest, the concentration trend was noteworthy and validated presentation. The trend observed for both Cl and S, and to a lesser extent K, is an increase in concentration in the cooler parts of the gasifier. The syngas in the heat exchanger cools from ~610˚C down to ~110˚C and in the Filter down to ~60˚C. At these temperatures some of the volatilized elements appear to be re-condensing and getting sequestered in the char. A second, even more telling graph can be seen in Figures 10-23 to 10-25, which shows the percentage of total mass collected of each major element at four locations in the gasifier system: Inside the Gasifier, Below the Grate, in the Heat Exchanger, and in the Filter Box.

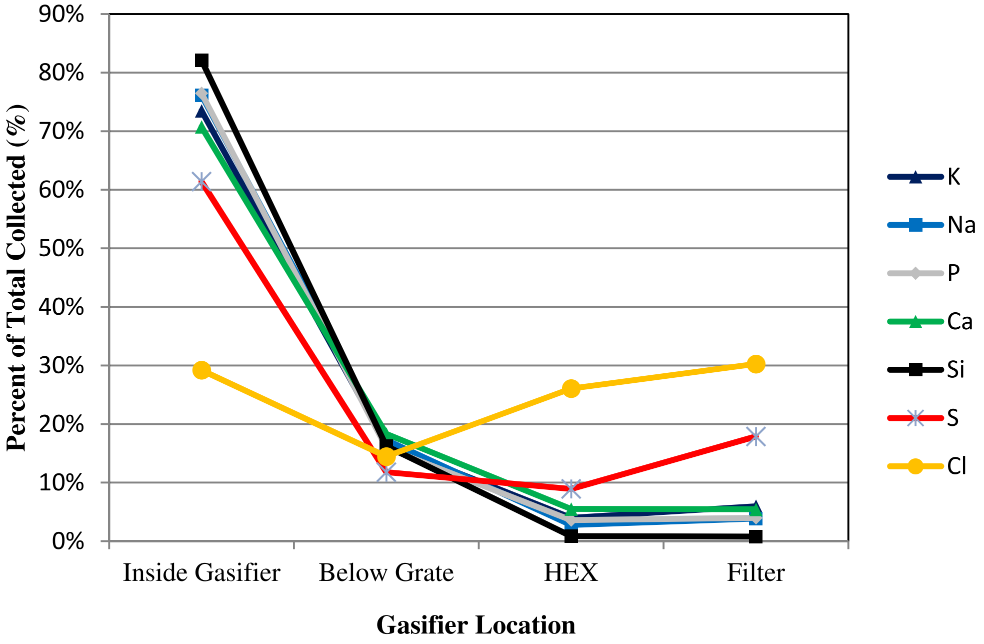

Figure 10-40: Percentage of total mass collected of each element at different locations in the gasifier, at 3.71% limestone/wet litter

Once again, limestone percentage does not appear to have an effect on the distribution, however the distribution is very consistent for each element between the three experiments. Almost all the elements follow a similar pattern: about 70% or more is recovered Inside the Gasifier, between 18% and 23% is recovered Below the Grate, and between 1% and 8% is recovered in the Heat Exchanger and Filter Box. The outliers are chlorine and sulfur, who both appear to volatilize and migrate more readily than the other elements, leaving the gasifier but re-condensing and getting captured in the cooler Heat exchanger and Filter Box sections of the gasifier system. On average, 69.1% of the chlorine was captured past the gasifier grate, and 52.6% was captured in the Heat Exchanger and Filter Box. The average retention of 30.9% of the Cl inside the gasifier agrees well with results of Bjorkman, et al. in Figure 8-1, showing the retention of ~37% when pyrolyzing switchgrass at 900 ˚C. From Figures 10-20 to 10-25, the conclusion can be drawn that cooling and filtering the syngas is necessary for the maximum capture and retention of chlorine and sulfur in the char. While potassium follows the same trend as the other elements in Figures 10-23 to 10-25, the consistent increase in concentration at the Filter Box location in Figures 10-20 to 10-22 suggest that cooling the syngas to between 60-

100˚C aids in the retention of this element as well, which according to the literature is most likely in the form of KCl. The ratios of Cl to K in the Filter location and HEX location allow this as a possibility, but can neither explicitly confirm nor deny it.

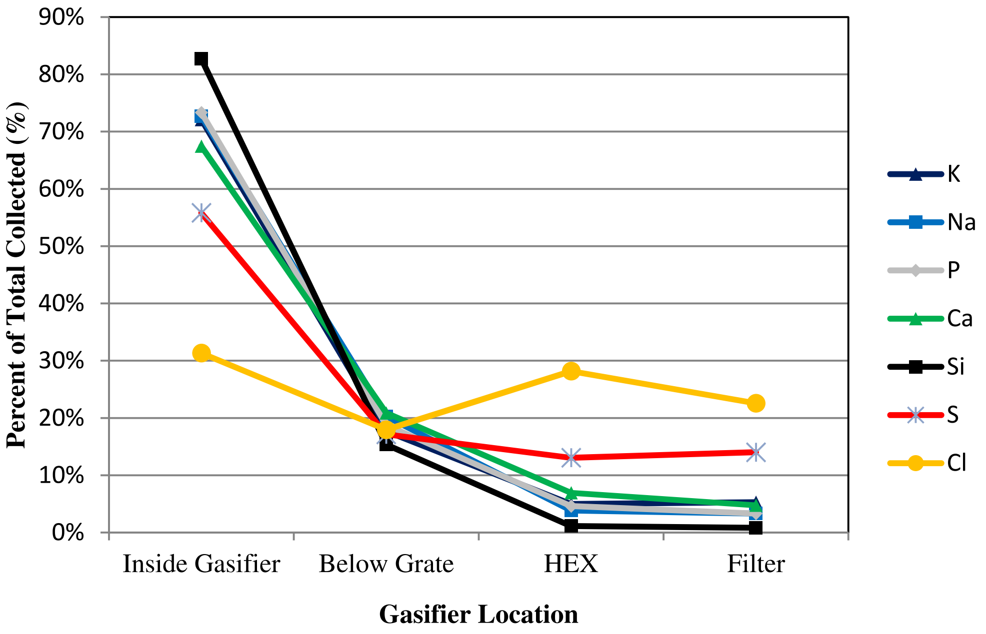

Figure 10-41: Percentage of total mass collected of each element at different locations in the gasifier, at 5.71% limestone/wet litter

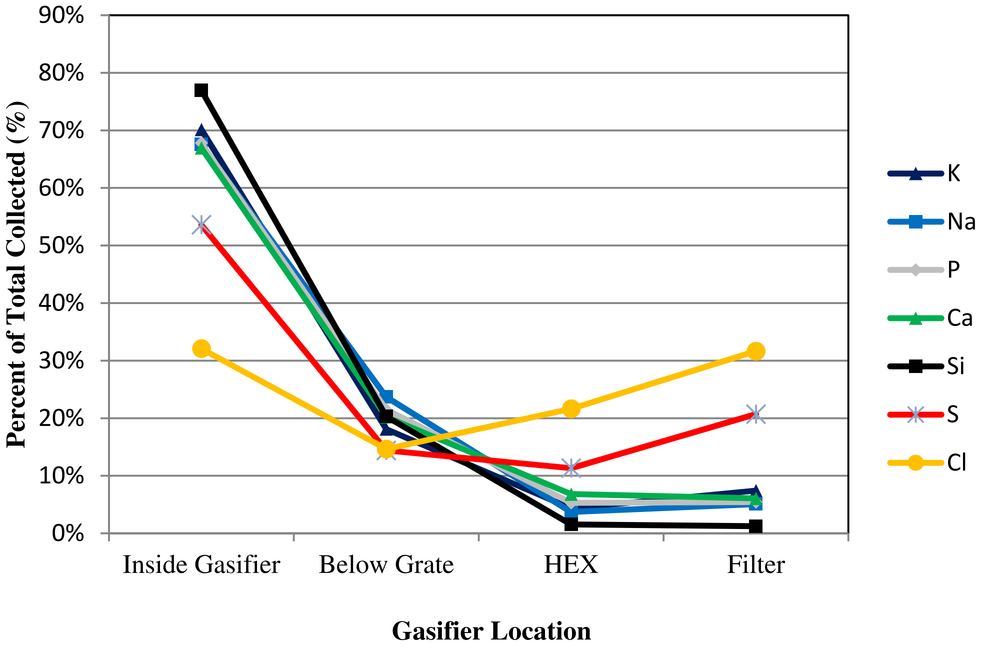

Figure 10-42: Percentage of total mass collected of each element at different locations in the gasifier, at 7.71% limestone/wet litter

10.2.3 Conclusions, Recommendations, and Sources of Error

Through experimentation, it was shown that downdraft gasification is effective as a means of sequestering contaminants harmful to the cement manufacturing process while extracting the usable chemical energy from poultry litter in the form of syngas. Conservatively, 89% of the chlorine can be retained in the char, as well as 94% of the potassium and sodium, along with 100% of the phosphorus. It does, however, appear to be necessary to cool and filter the syngas in the range of 60-110˚C to obtain maximum removal of the contaminants, particularly Cl and K, from the syngas stream. Although sulfur is not a contaminant of high interest when compared to the coal and coke used in the cement kiln, results show that cooling and filtering the syngas limits its throughput as well. Variation of limestone percentage did not appear to have a large effect on the capture rates, at least within the range tested, although the low set point of 3.71% limestone to wet poultry litter (4.24-4.31% dry) seemed to approach the minimum limestone percentage necessary to avoid clinkering. As a result, a limestone percentage in the range of the middle set point (5.71% limestone to wet poultry litter, 6.5-6.7% dry) emerged as the preferred amount, limiting the use of an extra additive while providing a factor of safety against clinkering issues.

It is yet to be determined, however, the effectiveness of the techniques used in the experiments towards gasifying poultry litter of higher ash or chlorine contents. The raw litter used successfully in the experiments had an ash content of about 20% on a dry basis. As seen in the literature as well as the litter pellets used for earlier tests, ash content can be as high as 33% on a dry basis, with an average in the literature of 25.2%. With this in mind, the recommended ratio of 6.5-6.7% limestone to dry litter found in the experiments would be about 33-34% limestone to poultry litter ash. Additional considerations to explore are: methods of eliminating the high pressure drop across the gasifier due the poultry litter fines; further experimentation with poultry litter pellets, perhaps with limestone pre-mixed in; use of different gasifier types; and measurement of the concentration of contaminants in the syngas itself to round out the mass balance and verify retention in the char.

There were many potential sources of error encountered in the experiments. Due to the large scale of experiments and small size of the biomass and char samples analyzed, much of the accuracy depended on the mixing and sampling involved. While mixing or sampling fine char such as that collected from the heat exchanger or filter box (seen in Figures 10-13 and 10-14) probably resulted in an accurate representative sample, char such as that marked 'Rest of Gasifier' was very non-homogeneous (as seen in Figure 10-11) and a given sample could vary highly in its accuracy of representation. While the ash analyses didn't vary greatly between experiments, the LOI varied by as much as 20% in one case between similar samples. An example of a problem encountered when mixing is the presence of white, 1.5" (3.8 cm) deposits found inside the gasifier, circled in Figure 10-26).

Figure 10-26: Ash mound found when gasifier is opened at seam above the grate, white deposits circled

Three to four of these deposits were found in every experiment and an attempt was made to crush them before mixing and retrieving a sample. One deposit was collected and sent for analysis, showing it had only a 2.22% LOI and was comprised of 57.91% CaO and 40.34% MgO on an ash basis. If these deposits were not crumbled and fully mixed in on every run, Ca recovery in the char would be lower than it should be. Another source of error was losses in the form of dust and fines. As reported, fines from the feedstock fell below the conveyer in the onboard feed system, yet they were only collected and quantified for two of the experiments. Dust was observed to be created and carried away with the wind during the mixing of limestone, poultry litter, and woodchips before each experiment as well as during the experiments when being fed into the gasifier. The feedstock with the finest particles was the limestone, and if this accounted for most of the dust loss there would also be a preferential loss of Ca before entry into the gasifier. This may account for the lower than expected Ca retention in some of the runs, as well as the retention rates greater than 100% when normalized to Ca. Overall, these factors most likely account for the scatter observed in the data points when calculating mass balances.

CHAPTER 11

PART 3—CONCLUSIONS AND RECOMMENDATIONS

11.1 SUMMARY OF WORK AND CONCLUSIONS

Downdraft gasification has been explored as a means to extract chemical energy from poultry litter while limiting the throughput of potentially deleterious components with regards to use in firing a cement kiln. Experiments with temperature depression via flue gas recirculation, feedstock dilution using woodchips, and experiments employing limestone as an additive to prevent fusion and aid in chlorine retention in the ash have been carried out. Flue gas recirculation allowed the reduction of the gasifier secondary air oxygen concentration by 40-45%, yielding an approximately 100˚C depression in average temperature. Results have shown that the clinkering is temperature independent, at least within the controllable temperature range. Limestone also had only a slight effect on the fusion when used to coat the pellets. However, limestone addition did display some promise in regards to chlorine capture, as ash analyses showed chlorine concentrations of more than four times greater in the limestone infused ash as compared to raw poultry litter. Experiments were conducted to explore the effectiveness of mixing limestone with raw poultry litter, the object being to coat more surface area and have a more even mixture. These resulted in the most consistent experiments with no ash clinkering.

Once consistent gasification of raw poultry litter was achieved through a combination of woodchip dilution (60% woodchips:40% poultry litter) and addition of limestone at 5% of the wet poultry litter mass (~6.5% Limestone/Dry Poultry Litter), experiments were performed to determine the capture rates of the contaminants pertinent to cement kilns. Limestone percentage was varied to explore its effect on chlorine retention at set points of 3.71, 5.71, and 7.71% limestone to wet poultry litter, the middle quantity slightly inflated from the previously used 5% to account for lower moisture of the litter used in these experiments. It was found that limestone percentage, at least within the tested range, had little effect on neither the retention of contaminants nor distribution of contaminants through the gasifier system. On average, 89% of the chlorine was retained in the gasifier char, as was 94% of both the potassium and sodium, and 100% of the phosphorus. When data was normalized to 100% calcium retention (expected from the literature), an average 100% of the Na, K, and P were shown to be retained, as well as 97.5% of the Cl. The contaminant profile, developed from analyses of char samples from different sections of the gasifier system, showed that 69.1% of the chlorine retained was captured past the gasifier grate and 52.6% was captured in the significantly cooler Filter Box and Heat Exchanger sections of the gasifier system. Additionally, peaks in concentration of sulfur and potassium were observed in these same sections. From these results, it appears necessary to cool and filter the syngas in the range of 60-110˚C to obtain maximum removal of Cl, as well as K and S, from the syngas stream.

11.2 RECOMMENDATIONS FOR FUTURE RESEARCH

Before implementing poultry litter gasification, further research should be performed. Based on the research in this report, the following recommendations can be made:

1. The high pressure drop across the gasifier when using raw poultry litter should be examined and methods of alleviating this explored. One suggestion is making poultry litter and limestone pellets, pre-mixed in the correct ratio.
2. Other methods of gasification should be explored to compare their effectiveness in capturing contaminants as well as ease and consistency of operation using poultry litter. Design of a specialized gasifier around the high ash content, easily-clinkering poultry litter feedstock could be explored.
3. Ways of increasing the percentage of poultry litter fed into the gasifier while maintaining stable performance should be explored.
4. A study measuring the concentration of contaminants in the syngas itself could be performed to close in the mass balance and verify retention of contaminants in the char.
5. The degree to which the syngas needs to be cooled and filtered to remove the maximum amount of contaminants should be examined.

11.3 RECOMMENDATIONS FOR IMPLEMENTATION

The following recommendations are made toward implementing gasification of poultry litter as a cement kiln fuel supplement:

1. Using a downdraft gasifier, it is necessary to dilute raw poultry litter to 35-40% and add 6.5% limestone/dry litter weight to prevent clinker formation and consistent syngas production.
2. Contaminant retention appeared to be independent of limestone percentage, so addition of ~6.5% limestone/dry litter weight is the recommended ratio to limit the use of unnecessary extra additive while providing a factor of safety against clinkering issues.
3. Conservative contaminant retention percentages to expect when using the methods in this report are: 89% chlorine retention, 94% potassium and sodium retention, and 100% phosphorus retention.
4. Cooling and filtering the syngas at 60-100˚C appears to be necessary in capturing the maximum amount of contaminants.

PART 4

Develop Sampling Procedure to Estimate Combustion Quality of Broiler Litter

CHAPTER 12

DEVELOP SAMPLING PROCEDURE TO ESTIMATE COMBUSTION QUALITY OF BROILER LITTER

12.1 INTRODUCTION

Broiler litter is defined as the combination of bedding material (such as wood shavings), excreta, feathers, wasted feed and wasted water. There are approximately 100,000 broiler houses in the US. Each broiler house may contain flocks of 10,000 to 30,000 birds and produce 5 to 6 flocks per year, with an average litter production of 1.25 tons per 1,000 birds. Building structures commonly located on broiler farms are shown in Figure 12-1. The primary method of broiler litter disposal is land application. With growing concerns of environmental thresholds in nutrient management, other methods must be developed. Technologies exits that utilize animal waste material for the production of heat and/or electricity. However, heterogeneity in the chemical composition of broiler litter makes it difficult to optimize its use as a commercial combustion fuel. Therefore, the objective of this task was to develop a reliable but convenient sampling procedure to estimate the combustion quality of broiler litter, thus facilitating pricing the material according to quality.

Pine shavings and coarse pine sawdust are currently the most popular bedding material. As a result of the availability and expense of these materials, poultry producers have developed new methods in the removal of litter. In particular, built-up litter management is the practice that has become standard in the poultry industry. Initially, litter is place on the dirt floor at a depth of about 6 inches. Between flocks, the top 2-inch layer of litter is scraped to remove “cake” which is the excessively moist material around the drinkers and feeders. This type of litter management results in de-caking the house of crusted litter, preheating and ventilating the house prior to each flock to purge existing ammonia and top dress with 2 inches of fresh pine shavings. Complete litter removal occurs only once per year.

Fig. 12-1a: Ten-day old Chicks

Fig. 12-1b: Twenty day old chickens

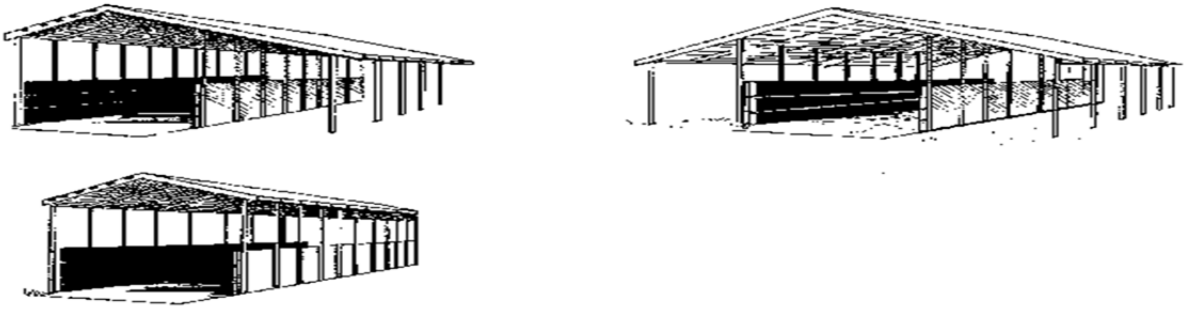

Fig. 12-1c: Types of commodity sheds used in the poultry industry for deep stacking litter

Figure 12-1: Building structures commonly located on broiler farms

12.1.1 Objectives

The objective of the work document for this phase is to develop a reliable, but convenient, sampling procedure to estimate the combustion quality of broiler litter that is the best compromise between convenience and reliability by means of statistical analysis.

Data were collected to estimate variability within several broiler litter stacks, within a single stack over time, and across farms.

12.2 EXPERIMENTAL PROCEDURE

Work for this phase was divided into the following two sub-tasks:

Subtask 1 - Sample and Analyze Broiler Litter Stacks

Broiler litter stacks at 8 commercial broiler farms that were 2-8 weeks old were sampled intensely by taking multiple 200-300-gram samples from both the surface and inside of the stack. Samples were then analyzed for energy and moisture content, ash, and elemental content, including N, P, K, S and Cl by means of standard procedures for analysis with near infrared spectroscopy. These data provide an estimate of variability within several stacks, within a single stack over time, and across farms.

Subtask 2 - Develop Sampling Procedure

A sampling procedure was developed to rapidly estimate combustion quality of broiler litter that is the best compromise between convenience and reliability will be developed by means of statistical analysis.

More specifically, poultry farm selection was determined by a certified animal waste vendor located in Greenville, Alabama. All poultry farms utilized propane for heating, well water, and pine shavings for bedding material. Bird growth period and litter compost duration varied among farms. All farms stored litter in a three-sided commodity shed measuring 40 ft x 60 ft with a 12 ft ceiling height, and with side walls to prevent weathering and leaching into adjacent farm lands and ground water. All litter piles were deep stacked, a method of composting-ensiling litter that heats to a temperature of between 140 and 160 °F. Deep stacked litter can be 10 ft high at the peak of the stack to ensure a critical mass for heating.

To account for variability within each litter stack samples were taken at three depths (surface, 2 ft and 4+ft) and in nine locations within each stack. Samples were taken utilizing a 4 inch x 8 inch hand auger as shown in Figure 12-2. Sampling at different depths is important, because stacks heat up during storage, with temperature ranging from ambient at the surface to over 160 °F inside the stack. The sampling process resulted in 27 samples per stack and 216 total samples from the eight poultry farms.

Standard American Society for Testing and Materials (ASTM) methods were used for all analyses. Samples were frozen until analyses were performed. Samples were dried at 45 C for 24 hours and ground to 4 mm followed by further reduction to less than 1 mm. All lab analyses were performed in duplicate. Broiler litter proximate, ultimate, and compositional lab analyses were completed utilizing the following equipment; Dionex ICS-3000 filtered with a Millipore 0.45 um screen, Elementar Vario Macro NCS, Varian Vista MPX Radical ICP, and Perstorp Analytical NIR System with appropriate ASTM protocols (Figure 12-3a). Energy values were measured using an IKA C2000 Bomb Calorimeter. Mineral content analyses included the following elements: Al, B, Cu, Ca, Fe, Mg, Mn, Mo, Na, K, P, S, and Zn and were measured with an Elementar Vario Macro NCS and Varian Vista MPX Radical ICP (Figure 12-3b).

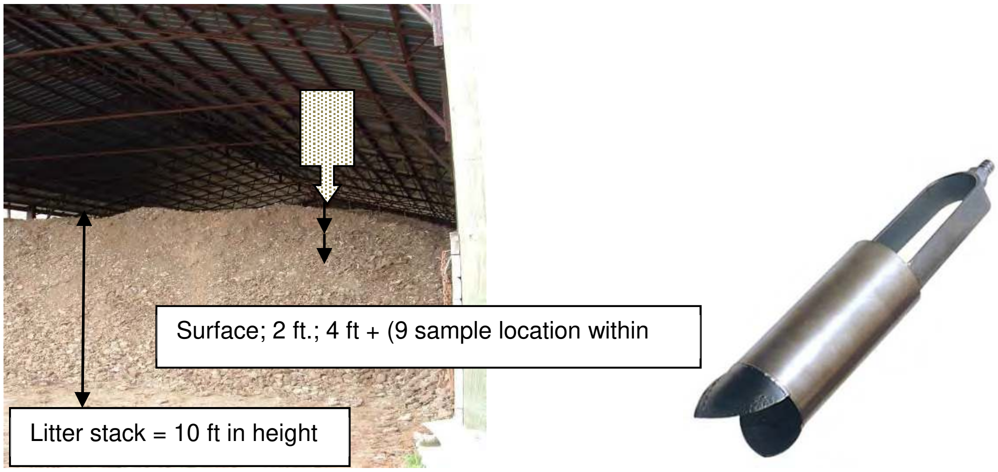

Figure 12-2: Sampling method using a hand auger

Dionex ICS-3000 Millipore Filtration System Perstorp NIR System

Figure 12-3a: Equipment used for sample analysis

Elementar Vario Macro NCS Varian Vista MPX Radical ICP IKA C2000 Bomb Calorimeter

Figure 12-3b: Equipment used for sample analysis

Data were analyzed using Mixed Models procedures as implemented in SAS® PROC MIXED. Farm and Depth and their interactions were treated as fixed effects. Sampling site within farm was treated as random effect. Two-way farm x depth interaction means were calculated along with least significant difference (alpha = 0.05). Pearson product moment phenotypic correlations and associated P-values were calculated to demonstrate the interdependence of certain response variables.

12.3 RESULTS AND DISCUSSION

Main effects and interactions are presented in Table 12-1 and parameter values are presented in Tables 12-2 through Table 12-6. Correlation Parameters related to BTU values are presented in Table 12-7. NIR prediction equations are presented in Table 12-8. Largest differences observed were between surface and inner samples, which might be expected. Variation among farms was surprisingly low, with age of stack being the most important factor.

12.3.1 Sampling Procedure

The most important aspect of sampling procedure is the number of samples needed for a reliable estimate of the mean, or “true” value. Statistical analysis was performed to generate the lowest number of samples needed to estimate a mean, plus or minus 20%, for each of the components measured. Due to differences in the variation of the different components across samples, this minimum number ranged from 1 to 8 samples (Table 12-9). Therefore, based on our study, we conclude that 8 samples drawn from about 24-inches deep in the stack will provide a reliable estimate of the mean of all composition components in the broiler litter sources evaluated, and this number is likely to be appropriate for most stacks.

Table 12-1: Testing Performed for work in this task

Equipment	Parameter	Effect significant at P < 0.05		
		Farm	**Depth**	**Farm*Depth**
NIRS	ADF	1	1	0
	ADL	1	1	0
	NDF	1	1	0
	Ash	1	0	0
	C	1	0	0
	S	1	1	1
	N	1	1	1
ICAP	Ca	1	0	0
	K	1	1	0
	Mg	1	0	0
	P	1	0	1
	Al	1	1	0
	Cu	1	0	0
	Fe	1	1	0
	Mn	1	0	0
	Mo	1	0	0
	Zn	1	0	0
	B	1	1	0
Anion	SO4	1	0	1
	SO4_S	1	0	1
	CL	1	1	1
	NO3	1	0	0
	PO4	1	0	0
Bomb Calorimeter	BTU	1	1	1
	DM	1	0	1
	pH	1	1	1
	NH3	1	0	1

Table 12-2: Parameter values obtained by NIRS Analysis (% DM)

	ADF			ADL				NDF				Ash
Farm	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"
1	24	25	24	5	6	6	32	30	31	34	31	31
2	34	31	31	9	9	9	42	39	39	31	28	30
3	37	35	35	10	8	8	41	32	32	35	41	38
4	32	28	28	8	7	7	39	32	35	36	35	34
5	31	30	29	8	7	7	42	37	39	30	30	29
6	24	23	23	5	5	5	45	44	45	23	23	23
7	24	23	23	6	6	6	32	31	32	38	39	38
8	31	27	27	9	7	8	47	39	40	29	26	28
Highest	37	35	35	10	9	9	47	44	45	38	41	38
Lowest	24	23	23	5	5	5	32	30	31	23	23	23
LSD 0.05	3				1			4			3	
P-values from Analysis of Variance												
Interaction	0.4936			0.1013			0.1568			0.0726		
Farm	<0.0001			<0.0001			<0.0001			<0.0001		
Depth	<0.0001			0.0005			<0.0001			0.6665		

Table 12-2. …continued (% DM)

	Carbon			Sulfur			Nitrogen		
Farm	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"
1	33.5	33.0	33.7	1	1	1	3	3	3
2	37.8	38.0	37.6	1	1	1	3	3	3
3	35.4	32.2	33.0	1	1	1	3	3	3
4	33.7	33.5	33.6	1	1	1	3	3	3
5	37.0	36.2	36.9	1	1	1	3	3	3
6	34.8	35.0	35.4	1	1	1	3	3	3
7	32.5	32.4	32.7	1	1	1	3	3	3
8	38.7	37.2	37.3	1	1	1	3	3	3
Highest	38.7	38.0	37.6	1	1	1	3	3	3
Lowest	32.5	32.2	32.7	1	1	1	3	3	3
LSD 0.05	2.12			0			0		
P-values from Analysis of Variance									
Interaction		0.5553			0.0036			0.0060	
Farm		<0.0001			<0.0001			<0.0001	
Depth		0.0962			<0.0001			<0.0001	

Table 12-3: Parameter values obtained by ICAP Analysis (% DM)

	Ca			K				Mg			P		
Farm	Surface	12'	24"	Surface	12'	24"		Surface	12'	24"	Surface	12'	24"
1	4	4	4	4	4	4	1	1	1		2	2	2
2	3	3	3	4	4	4	1	1	1		2	2	2
3	3	4	4	3	3	3	1	1	1		2	2	2
4	4	4	4	4	4	4	1	1	1		3	2	3
5	4	4	4	4	4	4	1	1	1		2	2	2
6	3	3	3	4	4	4	1	1	1		2	2	2
7	7	7	7	4	4	4	1	1	1		2	2	2
8	4	4	4	4	4	4	1	1	1		2	2	2
Highest	7	7	7	4	4	4	1	1	1		3	2	3
Lowest	3	3	3	3	3	3	1	1	1		2	2	2
LSD 0.05	0			0			0				0		
P-values from Analysis of Variance													
Interaction		0.9059			0.4143			0.0797				0.0130	
Farm		<0.0001			<0.0001			<0.0001				<0.0001	
Depth		0.6785			0.0349			0.6765				0.2013	

Table 12-4: Parameter values obtained by ICAP Analysis (ppm DM)

	Al			B			Cu			Fe		
Farm	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"
1	4244	5016	4135	113	91	95	230	232	236	2732	2735	2526
2	3233	3034	2960	58	51	58	146	150	145	2735	2868	2741
3	3006	5058	3746	48	49	55	127	149	141	1875	2895	2133
4	2865	3341	2721	80	64	72	133	121	118	1710	2016	1656
5	2069	2640	2030	68	61	65	132	140	130	2272	2866	2372
6	579	576	457	89	63	67	218	225	221	801	879	729
7	4092	4356	4077	106	85	96	233	218	223	2864	3082	2958
8	786	740	751	66	55	62	172	163	154	1197	1154	1148
Highest	4244	5058	4135	113	91	96	233	232	236	2864	3082	2958
Lowest	579	576	457	48	49	55	127	121	118	801	879	729
LSD 0.05	1009			11			29			537		
P-values from Analysis of Variance												
Interaction		0.2044			0.1110			0.9210			0.6285	
Farm		<0.0001			<0.0001			<0.0001			<0.0001	
Depth		0.0030			<0.0001			0.7031			0.0069	

Table 12-4: … continued (ppm DM)

	Mn			Mo			Zn		
Farm	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"
1	564	563	564	6	5	6	488	483	486
2	535	553	547	6	6	7	460	465	460
3	611	679	641	4	3	4	447	480	505
4	692	715	689	5	5	4	660	614	620
5	642	667	633	9	8	8	607	592	576
6	566	508	557	9	7	8	590	558	554
7	757	709	752	8	9	10	688	650	674
8	633	602	679	8	7	10	628	580	604
Highest	757	715	752	9	9	10	688	650	674
Lowest	535	508	547	4	3	4	447	465	460
LSD 0.05	56			2			38		
P-values from Analysis of Variance									
Interaction		0.2112			0.2332			0.0996	
Farm		<0.0001			<0.0001			<0.0001	
Depth		0.7200			0.1719			0.0507	

Table 12-5: Parameter values obtained by Anion Analysis (ppm as is basis)

	CL			NO3			PO4			SO4_S		
Farm	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"
1	7405	8294	7980	527	668	778	1792	2088	1908	2435	2847	2558
2	7542	7927	9024	595	474	669	3272	3359	3549	2460	2492	2793
3	5623	5315	6778	1227	1421	1308	2433	2470	2601	2590	2918	3445
4	6195	7137	7513	622	845	810	2584	2594	2740	2298	2745	2815
5	6874	5332	5521	758	344	330	1934	2206	1613	3225	2145	2664
6	7458	7074	7464	778	760	666	1245	1277	1280	2542	2409	2577
7	6399	6992	6406	1170	1125	1278	1546	1605	1476	2304	2471	2270
8	4836	6346	6003	588	453	489	1300	1408	1402	2089	2368	2425
Highest	7542	8294	9024	1227	1421	1308	3272	3359	3549	3225	2918	3445
Lowest	4836	5315	5521	527	344	330	1245	1277	1280	2089	2145	2270
LSD 0.05	1071			344			424			518		
P-values from Analysis of Variance												
Interaction		0.0035			0.2206			0.8078			0.0029	
Farm		<0.0001			<0.0001			<0.0001			0.0901	
Depth		0.0260			0.8686			0.4068			0.0854	

Table 12-6. Parameter values obtained by other analysis

	BTU/lb			Pct_DM			pH			NH3 ppm as is basis		
Farm	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"	Surface	12'	24"
1	5500	6584	6883	59	63	61	9	8	8	2078	2766	2582
2	7974	8220	9216	54	60	60	9	9	9	3285	2919	2926
3	8396	6674	7390	82	81	80	9	9	9	704	1793	1897
4	7329	7044	7924	49	63	62	9	9	9	1703	1871	1272
5	8187	8880	8640	73	58	59	9	9	9	1866	2138	1801
6	8284	8282	8828	67	68	66	9	9	9	1689	1655	1893
7	5930	6923	7481	70	71	70	9	9	9	1128	1411	1363
8	8661	8147	8856	49	55	56	9	8	8	3271	2132	1523
Highest	8661	8880	9216	82	81	80	9	9	9	3285	2919	2926
Lowest	5500	6584	6883	49	55	56	9	8	8	704	1411	1272
LSD 0.05	813			5			0			446		
P-values from Analysis of Variance												
Interaction		0.0014			<0.0001			0.0126			<0.0001	
Farm		<0.0001			<0.0001			<0.0001			<0.0001	
Depth		0.0002			0.2349			0.0001			0.1256	

Table 12-7: Correlation Parameters

	Correlation with	
From	BTU	pH
Ash	**-0.64**	0.35
	0.001	0.095
Carbon	**0.77**	-0.09
	<.0001	0.679
ADF	0.25	0.31
	0.248	0.135
ADL	0.30	0.19
	0.152	0.366
NDF	**0.76**	0.16
	<.0001	0.446
Ammonia	0.16	-0.31
	0.460	0.139
Pct_DM	-0.23	0.36
	0.270	0.084

Table 12-8: Regression Equations developed from NIRS analysis of broiler litter

Component	Range (% of dry matter)	Mean	SD	R^2 for prediction equation
Nitrogen	2.1 - 3.74	3.24	0.26	0.852
Carbon	26.69 - 44.85	35.02	2.77	0.803
Sulfur	0.88 - 1.15	1.00	0.05	0.203
Neutral detergent residue	11.19 - 63.54	37.26	7.11	0.874
Acid detergent residue	17.83 - 48.36	28.18	5.48	0.803
Acid resistant residue	2.32 - 15.79	7.12	1.93	0.775

Table 12-9: Smallest sample size at which the % deviation from TRUE is < ±20%

Component	Sample Size	Smallest	Largest
ADF	4	0.83	1.19
ADL	6	0.81	1.17
Ammonia	8	0.88	1.11
Ash	6	0.85	1.16
B	7	0.80	1.11
BTU	5	0.85	1.16
CL	6	0.84	1.16
Ca	6	0.82	1.16
Carbon	3	0.85	1.18
Cu	7	0.83	1.12
Fe	8	0.80	1.07
K	3	0.80	1.19
Mg	4	0.83	1.16
Mn	4	0.83	1.18
Mo	8	0.87	1.12
NDF	6	0.81	1.19
Nitrogen	2	0.85	1.18
P	4	0.80	1.19
Pct_DM	6	0.83	1.16
SO_4	8	0.91	1.12
SO_4S	8	0.91	1.12
Sulfur	1	0.89	1.11
Zn	4	0.82	1.17
pH	2	0.87	1.07

PART 5

Feasibility of Using Selected Alternate Fuels in Portland Cement Production

CHAPTER 13

FEASIBILITY OF USING SELECTED ALTERNATE FUELS IN PORTLAND CEMENT PRODUCTION

13.1 INTRODUCTION

The purpose of the work document in this part was to evaluate the feasibility of using alternative fuels for cement production. The technical feasibility of producing cement with the required properties at required rates was evaluated in other portions of the work. Thus, the effort undertaken in task six has focused on determining factors that may drive the availability and cost of alternative fuels relative to the availability and cost of the current fuel source, coal. The factors include competitive uses (both current and potential), regional availability (long logistic lines can significantly impact cost), current market cost, equipment modification required for utilization, and impact on CO_2 reduction. Impact on CO_2 production may result in cost benefits depending on the regulatory statutes with regard to CO_2 production. In addition to the six primary alternative fuels originally identified for evaluation at Lafarge several other potential alternative fuels were examined as part of this effort.

13.1.1 Objectives

To provide information related to the economic viability of long term use of alternative fuels.

13.1.2 Research Approach

The work in this part consisted mainly of analyzing data previously collected. The approach was to locate and review publically available data on the availability, alternative uses, and costs of alternative fuels. A summary table was prepared which summarizes pertinent data related to economic viability and technical challenges for several alternative fuels.

13.2 SUMMARY OF WORK

In total 13 potential alternative fuels were examined during the course of this work. Nine of these materials have been tested at Lafarge. The fuel values range from ~4,000 to 14,500 BTU/lb. The most common issue identified with the long term use is the moisture content of the fuel. This issue can be overcome by careful raw material management (segregation, predrying, and storage.) For many of the fuels competitive energy generation processes exist. These competitive processes are likely to become more significant as energy cost rise.

13.2.1 Broiler Litter

Broiler / poultry litter is the material used as bedding, placed on the floor, in poultry farms to make the collection and disposal of waste more manageable. The litter serves to adsorb the waste products thereby making their collection and disposal easier. Some litter types have been shown to improve the flock's health by reducing the levels of ammonia exposure. There are several types of material commonly used for broiler litter; wood shavings, sawdust, peanut hulls, sugar cane, straw, etc. Regardless of the starting material used at the time of collection the litter primarily consists of poultry manure, the original litter material, feathers, and dropped feed. The five largest producers of poultry litter, broiler and turkey litter combined, are Arkansas, Georgia, Alabama, Mississippi, and North Carolina. These states combined produce roughly 6.2 million tons per year of poultry litter from broiler and turkey operations (Perera et al 2011). Recent reports indicate that the amount of poultry litter produced from broiler production operations in the south east range from ~1.2 million tons per year in Arkansas and Alabama (Perera et al 2011; AEDC 2011), to less ~50,000 tons per year in Florida (Perera et al 2011).

There are several competitive uses for broiler litter. These include cattle feed, fertilizer use, and fuel. As a cattle feed poultry litter is used as a cost-saving measure (Bagley and Evans 1995). The main issue with this use is related to the spread of bovine spongeform encephalopathy (BSE), however as of the 2008 FDA regulations its use as a feed material had not been banned. As a fertilizer poultry litter is less concentrated than chemical fertilizers, thus transportation cost limits its use to dairy and beef farms near the poultry farm. In areas where there are insufficient nearby agricultural uses of poultry litter excess litter is produced and its disposal can become problematic.

The cost of transportation of the relatively low fertilizer and feed value poultry litter has resulted in the development of the use of poultry litter as a fuel source, both in small scale biomass systems for the production of heat for the poultry farm and larger direct burn systems for the production of electricity. Potential conversion processes include anaerobic digestion, direct combustion, co-firing, and gasification. There have been several studies on the anaerobic digestion of poultry litter (Safley et al. 1987; Collins et al. 2000; and Kelleher et al. 2002). These studies provide information on the design, cost, and feasibility of using anaerobic digestion to extract energy from poultry litter. Direct combustion utilizes the heat generated during the combustion of the fuel with excess air to produce steam used to drive turbine generators. There are several examples of commercial scale direct fired systems used to produce electricity from poultry waste, in conjunction with other biomass fuels, to produce electricity, including several in the UK and two recently announced plants in the US both in North Carolina (Firbowatt 2011). Co-fired systems involve the blending of a biomass source with a “traditional” fuel source such as coal. Several studies have been performed evaluating the co-firing of biomass with coal, but limited information exists on the use of poultry litter as a co-fired biomass material.

Poultry litter contains ~5,000 BTU/lb. There are several issues with the direct burning of poultry litter in cement kilns The most important is the Chlorine content of this material. High chlorine content affects the cement properties and as a result direct burn of poultry litter is not feasible. As pointed out elsewhere in this report a gasification system could be used to extract usefull energy from the litter and minimize the effect of chlorine content. In the gasification process heat, steam, and pressure are used to extract hydrogen from the organic material. The hydrogen is then collected and burned to produce energy. The main benefit of this process is that the gas can be directly fired in a gas turbine for power generation. Gasification of poultry litter at a small scale has been previously demonstrated (Flora and Riahi-Nezhad 2006). Despite the nascent stage of utilization for this purpose, the extraction of energy from poultry litter is a potentially significant competitor to its use a fuel source in cement kilns. A 2006 report to the South Carolina Energy Office indicates that the value of poultry litter for the production of electricity ranged from \$30 to \$57 / ton depending on the type of conversion process used.[9]

13.2.2 Post-Industrial Plastic Waste

Post-industrial plastic waste consists of trim scrap, off spec production, over production of material at converting and assembly facilities and of post-industrial use plastic for example packaging overwrap from large shipments. For example, automotive carpets are produced and shipped as full width rolls to automotive production facilities. At these facilities, the carpet is cut to size and installed in the vehicles. The trim pieces are scrap and cannot be used. Another example is the production of plastic bottles by the extrusion blow molding process. The process itself results trimmed material. Often this material can be recycled in house but if the color is unusual or degradation has occurred the material is scrapped. The injection molding process used to produce automotive bumpers and the extrusion process used to produce automotive fuel tanks are another source of scrap material. The energy content of plastic depends on the type with typical values in the range of 10,900 (PET) to 18,700 (HDPE) BTU/lb. In the existing study post-industrial carpet scrap from the automotive industry was tested for fuel value and was found to contain ~12,750 BTU/lb. The main issue with the use of post-industrial plastic waste is the need to grind the material to achieve consistent feed rates. However, commercial scale grinders are common and more than capable of grinding post-industrial plastics to a uniform size.

Given the relatively high fuel value of plastic waste and the relative ease of converting this material to energy there is the potential for significant competition for the available supply. A recent report by the American Plastics Council indicates that there are five main plastic to energy conversion technologies currently being explored in the US not including the direct burn of these materials; anaerobic digestion, thermal depolymerization, pyrolysis, pyrolysis/high temperature gasification, and low temperature gasification (ACC 2011). There are currently 86 energy recovery facilities in the US (ACC 2012). Combined these facilities can burn ~ 97,000 tons of materials per day. However, this capacity is utilized for post-consumer waste in addition to post industrial waste.

13.2.3 Tires

Roughly 280 million tires are scrapped each year in the US alone. The majority component of tires is vulcanized rubbers and polyester or nylon based tire cord. The energy content of tire is ~14,000 BTU/lb. Current uses for this scrap includes energy conversion through processes similar to those used for waste plastics and conversion of the tire to rubber powder that is used for modification of plastics, asphalt, and portland cement. In addition, shredded tires are used as subgrade fill and backfill for walls and bridge abutments as well as several other civil engineering applications. The main issue with the use of tires in cement kilns is the tendency for scrap tires to hold water during collection and storage due to their shape. This water must be dried prior to introducing the material to the kiln. As a result much of the energy generated by direct burning is used to volatize water and is not available to the process. Handling whole tires is problematic and must be done manually at the facility were the evaluations were done. These issues can be overcome by grinding, dewatering, and storing the shredded tires prior to burning. However, these processes increase costs and storage during dewatering could consume significant land area. One issue directly related to the use of tire scrap in cement kilns is the buildup of sulfur. A report by Miller et. al. (2001) published by the Portland Cement Association, provides guidance to cement kiln operators on the control and removal of sulfur compounds. However, many of these control measures increase production cost. As a result, the direct burn of tire scrap will be limited to relatively low rates of co-fire by sulfur issues even if issues with dewatering and storage can be mitigated.

13.2.4 Wood Chips (forest trimmings) and Railroad Ties

Large scale harvesting of lumber results in a significant amount of trimmed material. Small branches are trimmed and left on the forest floor. Over time these breakdown and are reintegrated into the soil. However, there is the potential to collect this material, that collected in municipalities, during storm clean up or regular maintenance for example, and the trim produced during roadway and power line maintenance. The latter two sources of material are normally made available as mulch for the local population. However, significantly more material is produced that is used. Conversion of this material to energy is one potentially renewable source of energy. The main issues with using this material at the cement plant were related to storage and handling. Wood can contain ~ 50 moisture, drying and maintaining a low moisture level is critical for the use of this material. High water content limits the utility of the material and inconsistent moisture levels make handling and correct loading difficult.

Railroad ties are produced during the replacement or removal of old railways. The US railroad tie industry produces roughly 20 million ties annually. About 14 million of those, 6.5 million in the eastern US, are used as replacement ties during rail bed repair (Gauntt 2011). Replaced ties are recycled for use in other rail beds (~5%), ~ 50% are recycled as landscape timbers or used as fuel in co-generation plants, the rest are currently landfilled. The roughly 6 million railroad ties landfilled each year represent a significant source of material, ~7.2 x 10^6 million BTU per year. However, this does not account for transportation cost.

Wood has an energy content of ~4,000 BTU/lb relatively low compared to other potential material. In addition, as a biological material it contains a significant amount of moisture when harvested. As a result the material should be air dried for several months before burning to maximize the useful energy recovered.

13.2.5 Switch Grass and Straw

Switch Grass and Straw are two renewable energy sources. Switch grass in particular has been investigated for the production of ethanol. However, some researchers have found a negative energy balance when used for production of ethanol (Pimentel and Patzek 2005). Direct burning of pelletized switch grass however returns an 11 to 1 return on energy required for production. The difference is related to the extra cost for conversion to ethanol and the significant fraction of dry weight that cannot be converted to liquid fuel. Thus direct burn in cement kiln offers an attractive possibility for the utilization of this fuel as a much higher fraction of dry weight can be converted to heat energy. The main issues with dealing utilizing switch grass as an alternate fuel source in cement plants are related to feeding systems that can handle the relatively low density of the material, 5 – 10 lb/cu ft and the need to keep the material dry. Excessive moisture in the material will significantly reduce the usable heat that can be generated by directly burning the product. The density of raw switch grass is relatively low and the low energy density results in a significantly sized storage facility for stockpiling the material for continuous use.

13.2.6 Construction and Demolition Waste and Municipal Solid Waste

Construction and Demolition Waste contains ~6,300 BTU/lb and Municipal solid waste contains ~5,800 BTU/lb. Construction and Demolition waste contains materials such as wood board, particle board, sheet rock and similar construction materials. Municipal solid waste is commonly known as trash or garbage and is collected curbside by municipalities. Much of this material is sent directly to landfill. However, as environmental awareness has grown and the cost of landfill disposal has grown significant efforts have been made to divert fractions of this waste to alternative uses. Recycling initiatives and hand sorting operations segregate recyclable polymers, metals, glass and paper. However, a significant fraction of material remains consisting of food waste, currently non-recycled plastics, and other materials intermingled with food and biological waste to the point that they cannot be efficiently recycled. This material is land filled or, increasingly, used to generate energy. There are several methods to generate energy from municipal solid waste such as pyrolysis, gasification, landfill gas capture, and direct burn.

Often this waste stream contains a significant fraction of moisture. Thus, it poses issues similar to those described for tires and wood products above. In addition, these streams could contain PVC based plastics. In the construction industry PVC is found in profiles such as the window edging, it is also used in toys, credit cards and many other semi durable consumer goods that may appear in municipal waste streams. This issue with PVC is the high chlorine content. As municipal waste would be expected to be a highly variable material supplies with high PVC fractions would need to be identified and rejected or blended with low PVC containing sources to mitigate the potential for high levels of Chlorine. Finally, these sources will contain metals and a system for removing the metal contaminates before introduction to the kiln would need to be developed.

13.2.7 Liquid Waste Fuel

Liquid waste fuel consist of spent cooking oils and liquid waste by products from the food service industries. These materials are primarily cooking oils and fats and contain ~7,700 BTU/lb of material. In addition, they are relatively dense, ~78 lbs/ cu ft, and easy to handle. Currently these materials are collected and either reprocessed or landfilled. As energy cost increase more effort is made to reclaim energy from this waste product, either by direct burn or conversion to biodiesel. This material was tested during the course of this study and no significant handling or processing issues were identified. Cement quality is described elsewhere in this report.

13.3 CONCLUSIONS

The main issue with many of the potential alternative fuels is high moisture content. To mitigate this issue at the plant appropriate processes will need to be developed that may include dewatering, grinding, drying, storage, and blending to mitigate moisture issues. However, all the identified alternative fuels have potential competitive uses and many of them are being explored for commercial energy generation schemes, as direct fire for turbine boilers, in gasification systems, or as raw material sources for biodiesel. As energy cost increase there will be an increasing competitive demand for these materials. Mitigating this effect is the cost of transporting many of the lower density materials to energy production facilities. As energy cost increase, transportation cost increase. As a result cement kilns located nearer to the source of the alternative fuel supply may have an advantage in the use of these alternative fuels.

Table 13-1: Summary of Collected Data for use in Feasibility Evaluation

ALTERNATIVE FUEL	HEATING VALUE BTU/lb	SOURCES / TYPES	REGIONAL AVAILABILITY	RELATIVE COST PER TON	POTENTIAL COMPETITORS FOR MATERIAL	EQUIPMENT MODIFICATIONS / SPECIAL HANDLING REQUIREMENTS	TESTED RATES BTU%	TESTED RATES Ton/hr	DENSITY lbs/ft3	ISSUES	RELATIVE COST OF CO2 REDUCTION
Coal (reference)	11,698 - 12,624 [1]										
Broiler Litter	5,000[2]	Poultry farms	South East	Intermediate	Cattle feed (FDA considering regulating)	Gasification system will reduce issues	5.0 - 7.5	1.7 - 3.0	~42	Alkali metals Phosphorus Chlorine	Intermediate
Post-Industrial Plastic Waste	6,850 - 9530[1]	Auto Carpet Trimmings Auto Door Panels and Dash Boards Polyester and Nylon fibers	Nationwide Large Cities	High	Power generation New carpet recycling efforts Export to china	debailing, grinding, and delivery systems	5 – 15	2.5 – 3.5	5.26	Low density limits feed rate	Low
Tires	13,710 - 14,540[1]	Municipal and industrial collection centers	Nationwide	Low	Landfill caps Power generation Pulp and paper mills	delivery system for whole tires	2.0 - 8.0	0.3 - 4.0	Whole tire 6 – 20 Ground tire ~0.9	Sulfur build up	Low
Wood Chips (Forest Trimmings)	3,491 – 4,140[1]	Municipal collection Industrial collection	South East Mid West North West	Low	Lawn and Garden Biomass energy production	Storage and delivery system	0.8 – 5.8	1.7 – 3.6	15 - 25	Moisture Content	Intermediate
Switch Grass	4,100[2]	Farmed	Nationwide but limited	Very High	Biomass energy production	Storage and delivery system	2.5 - 8.5	1.2 – 4.0	5 - 10	Moisture Content	High
Straw	higher heating (6,318 - 7,355) [1]	Farmed	Nationwide	High	Biomass energy production Animal feed and bedding	Storage and delivery system	Not Tested	Not Tested	5 – 10	Moisture Content	High
Construction and Demolition Waste	6,300[1]	Industrial collection	Large Cities	Intermediate	None Identified	Storage and delivery system	15	4.6	15 - 25		Not evaluated
Municipal Solid Waste	5,800[2]	Municipal collection	Large Cities	High	None Identified	Removal of metal	Not Tested	Not Tested	-	High Chlorine Content	Intermediate
Railway ties	5,641 - 6,774[1]	Industrial collection	Nationwide	Very High	Lawn and Garden	Removal of metal	6.7 – 9.3	2.8 – 3.7	Whole ~75 Chipped ~22 @ 50% moisture	Moisture Content	High
Liquid waste fuel	7,700[1]	Industrial and food service	Nationwide	Very High	Biodiesel production	Modification to Kiln fuel port	0 – 38.4	0 – 20.4	~78		Not evaluated
Corn and Soy Bean Waste	~7,000[1]	Farm and processing by product	Mid West – Corn South East – Soy Beans	Low	Biomass energy production	Storage and delivery system	7.5	2.1	~40		High
Asphalt Regrind	4,000 - 7,200[2]	Shingles, road repaving projects	Nationwide	Low	Pavement	Need to remove metal and aggregate	Not Tested	Not Tested	~45		Not evaluated
Oil Sand (Direct Burn)	~3,500[2]	Mined	North west / Canada	Intermediate	Liquid Fuels		Not Tested	Not Tested	-~120		Not evaluated

CHAPTER 14

CONCLUSIONS AND RECOMMENDATIONS

14.1 CONCLUSIONS

Based on the work document in this report, the following conclusions can be drawn:

1. A drop tube furnace and visualization method were developed that show potential for evaluating time- and space-resolved temperature distributions for fuel solid particles and liquid droplets undergoing combustion in various combustion atmospheres.
2. The processing ability of the available equipment at a cement plant is a factor that limits substitution rates. The construction and demolition waste and woodchip trial burns conducted during this project did not cause any feed problems. Several cement plant personnel experienced minor allergic reactions due to handling and de-dusting the soybean seeds. This problem; however, was eliminated with the use of proper personal protective equipment.
3. The energy values of the alternative fuels utilized during this study were less than those of traditional fuels. The as-received energy values for each fuel utilized during this study were as follows:
    - Coal: 10,820 to 12,090 with an average of 11,320 BTU/lb,
    - Plastics: 8,855 to 10,780 with an average of 10,130 BTU/lb,
    - Construction and Demolition waste: 3,370 to 8,180 with an average of 6,050 BTU/lb,
    - Woodchips: 3,355 to 6,996 with an average of 4,736 BTU/lb, and
    - Soybean seeds: 8,977 to 9,375 with an average of 9,150 BTU/lb.
4. When assessing the feasibility of the alternative fuel, the unit cost of the fuel is an important parameter. Although some of the alternative fuels possess energy values that are roughly half that of the traditional fuels, the price for traditional fuels is typically significantly more than alternative fuels. Due to fuel cost data being proprietary knowledge, the feasibility of the trial alternative fuels based on price could not be evaluated or compared.
5. The utilization of each fuel remained fairly consistent over the burn periods. Coal accounted for almost 90 percent of the required energy during the baseline burn, but was reduced to 70 percent during the variable feed 15 percent trial burn. The plastic blend accounted for roughly 15 percent of the required energy for all trial burns. Alternative fuels accounted for 5, 5.4, 11.8, 16, and 7.5 percent of the total energy for the

construction and demolition waste, variable feed 5, 10, and 15 percent, and soybean seed burns, respectively.

6. Another goal of this part of this study was to determine if the utilization of alternative fuels had a direct impact on the chemical composition of the portland cement. The kiln feed and the cement kiln dust results were compared to their respective baseline values and found to be consistent over all trials with the exceptions of elevated SO_3 and P_2O_5 concentrations.
7. Significant increases in P_2O_5 in the clinker and cement was obtained for all trial burns. In the trial burns, coal possessed significantly elevated levels of P_2O_5 compared to the baseline's coal level. The construction demolition waste contained approximately 3 and 2 times the P_2O_5 content compared to the woodchip and soybean seed trials, respectively. Though the construction and demolition waste fuel possessed the highest P_2O_5 content for the alternative fuels tested, their contribution to the overall P_2O_5 content of the clinker and cement was minimal. The combination of materials and fuel led to the increased P_2O_5 levels found in the clinker and cement.
8. The statistical analysis performed on the clinker data and it showed that the majority of results from the trial burns had significantly different means. However, because of the inherent variability throughout portland cement production process, changes in cement chemistry are difficult to link to the utilization of a particular fuel.
9. Additional objectives of this phase of the study were to evaluate if the utilization of the trial fuels directly impacted the physical properties of the portland cement or the concrete that was prepared with the trial burn cements. Overall, it was found that the trial burn cements had minimally different effects on workability, setting time, strength, drying shrinkage, and permeability compared to the baseline cement.
10. Another objective of this phase of the study was to assess the impact of alternative fuels on emissions produced by the cement plant. The Nitrogen Oxides (NO_x), sulfur dioxide (SO_2), and carbon monoxide (CO) emissions were within acceptable emission limits except for the volatile organic compounds (VOC) produced during the baseline and soybean seed trial burns. The production of volatile organic compounds is more dependent on system design and control than the type of fuel used. The trial fuels utilized were not found to greatly affect the quantity of emission produced.
11. The cement plant was successful in implementing alternative fuels to produce a consistent, high-quality product that increased cement performance while reducing the environmental footprint of the plant. The utilization of construction and demolition waste, woodchips and soybean seeds proved to be viable replacements for traditional fuels. The future use of these fuels depends on local availability, associated costs, and compatibility with a facility's production process.

12. Downdraft gasification has been explored as a means to extract chemical energy from poultry litter while limiting the throughput of potentially deleterious components with regards to use in firing a cement kiln. Flue gas recirculation allowed the reduction of the gasifier secondary air oxygen concentration by 40-45%, yielding an approximately 100˚C depression in average temperature. Results have shown that the clinkering is temperature independent, at least within the controllable temperature range. Limestone also had only a slight effect on the fusion when used to coat the pellets. However, limestone addition did display some promise in regards to chlorine capture, as ash analyses showed chlorine concentrations of more than four times greater in the limestone infused ash as compared to raw poultry litter. Experiments were conducted to explore the effectiveness of mixing limestone with raw poultry litter, the object being to coat more surface area and have a more even mixture. These resulted in the most consistent experiments with no ash clinkering.
13. The following recommendations are made toward implementing gasification of poultry litter as a cement kiln fuel supplement. Using a downdraft gasifier, it is necessary to dilute raw poultry litter to 35-40% and add 6.5% limestone/dry litter weight to prevent clinker formation and consistent syngas production. Contaminant retention appeared to be independent of limestone percentage, so addition of ~6.5% limestone/dry litter weight is the recommended ratio to limit the use of unnecessary extra additive while providing a factor of safety against clinkering issues. Conservative contaminant retention percentages to expect when using the methods in this report are: 89% chlorine retention, 94% potassium and sodium retention, and 100% phosphorus retention. Cooling and filtering the syngas at 60-100˚C appears to be necessary in capturing the maximum amount of contaminants.
14. A reliable, but convenient, sampling procedure was developed to estimate the combustion quality of broiler litter that is the best compromise between convenience and reliability. Variation in broiler litter samples from various farms was surprisingly low, with age of stack being the most important factor. It is concluded that 8 broiler litter samples be drawn from about 24-inches deep in the stack to obtain a reliable estimate of the mean of all composition components in the broiler litter sources evaluated, and this number is likely to be appropriate for most stacks.
15. The main issue with many of the potential alternative fuels is high moisture content. To mitigate this issue at the plant appropriate processes will need to be developed that may include dewatering, grinding, drying, storage, and blending to mitigate moisture issues. However, all the identified alternative fuels have potential competitive uses and many of them are being explored for commercial energy generation schemes, as direct fire for turbine boilers, in gasification systems, or as raw material sources for biodiesel. As

energy cost increase there will be an increasing competitive demand for these materials. Mitigating this effect is the cost of transporting many of the lower density materials to energy production facilities. As energy cost increase, transportation cost increase. As a result cement kilns located nearer to the source of the alternative fuel supply may have an advantage in the use of these alternative fuels.

14.2 RECOMMENDATIONS FOR FUTURE RESEARCH

Based on the work document in this report, the following conclusions can be drawn:

1. Continued development of a burn simulator to include effluent gas analysis is recommended. Further improvement of visualization quality and inclusion of shape correction for the image processing and analysis are needed.
2. A model needs to be developed to apply the temperature distributions from the burn simulator to estimations of combustion rates for various fuel types in conditions that mimic those in a cement plant.
3. A major factor limiting the effectiveness of this study was the fairly low substitution rate of the alternative fuels. Coal accounted for 70 to 90 percent of the total energy consumed during production. The alternative fuels tested during this study contributed only 5 to 16 percent of the total energy used during the pyroprocess. Changes in cement chemistry could not be solely attributed to the alternative fuels. This was due to observed cement physical changes paralleling significant fluctuations in kiln feed or coal chemical compositions. Increasing the substitution rate would allow the trial fuel's effects to be more pronounced and thus provide a better understanding of the interactions that occur between a utilized fuel and the performance of the portland cement. If the minimum substitution rates were increased, as well as implementing a variable feed approach similar to the woodchip trial performed in this study, an optimum replacement rate could be established.
4. Although a thorough sampling plan was developed for each burn, determining the effects of the alternative fuels on the cement chemistry and performance proved a difficult task. If the sampling plan was expanded to include enough samples of kiln feed, coal, and cement kiln dust to perform statistical analysis, a greater understanding of the consistency of these process inputs throughout a trial burn could be achieved. Increasing the number of specimens tested could also limit the number of inconsistent results between testing agencies. A sampling plan, however, is often limited by available funding, personnel, and time.
5. There were several trends that could not be explained regarding the emissions produced during the trial burns. Oxygen levels should be measured within the kiln. Knowing the

oxygen level present in the pyroprocess, which significantly effects the emissions formed, could be beneficial in order to explain the fluctuations observed in the NO_x, SO_2, and CO emissions.

6. Before implementing poultry litter gasification, further research should be performed. The high pressure drop across the gasifier when using raw poultry litter should be examined and methods of alleviating this explored. One suggestion is making poultry litter and limestone pellets, pre-mixed in the correct ratio. Other methods of gasification should be explored to compare their effectiveness in capturing contaminants as well as ease and consistency of operation using poultry litter. Design of a specialized gasifier around the high ash content, easily-clinkering poultry litter feedstock could be explored. Ways of increasing the percentage of poultry litter fed into the gasifier while maintaining stable performance should be explored. A study measuring the concentration of contaminants in the syngas itself could be performed to close in the mass balance and verify retention of contaminants in the char. The degree to which the syngas needs to be cooled and filtered to remove the maximum amount of contaminants should be examined.

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APPENDICES

APPENDIX A

CONTAMINANT MASS BALANCE SPREADSHEETS

Table A-23: Ash contents of the input feedstocks

Ash Content (% wt), dry basis			
Charcoal	Poultry Litter	Woodchips	Lime
5.64	19.63	0.28	56.31

Table A-24: Analyses of feedstocks used in mass balances and oxide to element % mass conversion factor. Limestone total $\neq$100% b/c CaO and MgO are calculated from carbonate percentages (seen in Table 5-4)

Oxide to Element Conversion	Input Ash analyses [% mass, ash basis]				Limestone [% mass, dry basis]
	Oxide	Poultry Litter	Woodchips	Charcoal	
0.467	SiO2	25.96	13.99	6.51	1.60
0.529	Al2O3	2.87	2.99	0.43	0.51
0.699	Fe2O3	1.47	6.55	0.97	0.59
0.715	CaO	28.29	35.50	78.06	43.41
0.603	MgO	4.65	11.95	2.15	7.18
0.742	Na2O	3.33	1.78	0.90	0.01
0.830	K2O	11.31	12.50	5.16	0.17
0.599	TiO2	0.07	0.00	0.00	0.05
0.436	P2O5	15.83	5.81	1.07	0.05
	BaO	0.00	0.47	0.43	0.01
	MnO2	0.23	3.73	2.04	0.06
0.401	SO3	3.52	4.39	1.91	0.16
	SrO	0.03	0.16	0.29	0.07
	Cl	3.13	0.22	0.07	0.00
	TOTAL	100.71	100.04	100.00	53.87
	Cl (Dry Basis)	0.502	0.003	0.022	0.000

Table A-3: Spreadsheet for 4.24% limestone/dry litter from 5/24/2010

** Denotes average value used for conveyor fall-through losses

Moisture Content (wet basis)				
	Charcoal	Warm up chips	Poultry Litter	Mix/After PL Chips
tin	13.5	13.7	13.7	13.5
wet	120.8	145.1	134.8	131.2
dry	114.7	128.7	119.9	115.2
moisture %	5.68	12.48	12.30	13.59

	Input [lbs], 2.6 lbs Limestone				
		wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	43.10	43.10	40.65	2.29
	Warm up Chips	30.30	30.30	26.52	0.07
PL MIX	**PL**	70	60.99	53.49	10.50
	Chips	130	123.64	106.83	0.30
	lime	2.60	2.27	2.27	1.28
	After PL Chips	200	188.09	162.52	0.46
	total	476.00	448.39	392.28	**14.90**
	Lime/Litter percentage	3.71%	3.71%	4.24%	

Elements IN [lbs]					
P	K	**Cl**	Na	Ca	
0.011	0.098	**0.009**	0.0153	1.2791	Charcoal
0.002	0.008	**0.001**	0.0010	0.0188	Warm up Chips
0.725	0.986	**0.269**	0.2594	2.1232	**PL**
0.008	0.031	**0.003**	0.0039	0.0759	**Chips**
0.000	0.003	**0.000**	0.0002	0.7029	**lime**
0.012	0.047	**0.005**	0.0060	0.1154	After PL Chips
0.758	1.173	**0.286**	0.286	4.315	***total***
0.032	0.187	**0.018**	0.026	2.192	***total (non PL)***
95.75%	84.02%	**93.76%**	90.76%	49.20%	*ratio from PL/total*

	Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
	Sorted PL+Lime	1.10	Mix Chips	3.20	3.16
	Sorted Mix Chips	3.20	PL	1.06	7.95
**	*Fall-through Chips/PL/Lime*	11.40	Lime	0.04	0.30
	Sorted 200 lbs	7.05	***total***	4.30	11.40
**	*Fall-through 200 lbs*	4.86	After PL Chips	7.05	4.86

	Output [lbs]			
		Recovered	**Dry**	**Actual Ash**
Gasifier	**Woodchips char**	5.90	5.90	0.15
	PL Ash	1.10	1.10	1.08
	Rest of Gasifier	18.50	18.46	8.46
	Below Grate	4.65	4.64	2.18
	HEX	0.95	0.94	0.54
	Filter	1.40	1.37	0.61
	total	32.50	32.40	**13.03**
			Ash Percent diff:	12.55%

Elements OUT [lbs]							
P	K	**Cl**	Na	Ca	Si	S	
0.0037	0.0153	**0.0003**	0.0019	0.0374	0.0096	0.0026	**Woodchips char**
0.0694	0.0803	**0.0009**	0.0211	0.3007	0.1087	0.0131	**PL ash**
0.4696	0.6753	**0.0582**	0.1558	2.1335	1.0418	0.0664	**Rest of Gasifier**
0.1131	0.1734	**0.0294**	0.0405	0.6402	0.2296	0.0158	Below Grate
0.0255	0.0420	**0.0530**	0.0065	0.1922	0.0121	0.0119	HEX
0.0282	0.0627	**0.0616**	0.0091	0.1900	0.0109	0.0239	Filter
0.7096	1.0490	**0.2034**	0.2349	3.4940	1.4128	0.1337	***total***
93.7%	89.4%	**71.0%**	82.2%	81.0%	**Ratio OUT/IN**		
				19.03%	% Difference		
115.7%	110.4%	**87.7%**	101.5%	100%	Norm. to Ca		

Output Ash Analyses																
		Oxide to Element Multiplier	0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%)	Na2O (%	K2O (%)	TiO2 (%	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
PL 5/24	0.00	1.6	21.49	2.61	1.35	38.88	5.58	2.63	8.94	0.12	14.68	0.05	0.51	3.02	0.06	0.08
Rest of Gasifier 5/24	0.20	54.17	26.34	3.26	1.44	35.28	5.59	2.48	9.61	0.08	12.72	0.06	0.58	1.96	0.06	0.69
Below Grate 5/24	0.32	53.05	22.57	2.56	1.42	41.16	4.54	2.51	9.60	0.07	11.91	0.09	0.62	1.81	0.08	1.35
HEX 5/24	1.39	41.88	4.75	1.62	1.35	49.39	6.78	1.62	9.29	0.00	10.72	0.20	1.12	5.47	0.13	9.74
Filter 5/24	2.47	55.01	3.80	1.29	1.76	43.28	5.97	1.99	12.30	0.00	10.53	0.20	1.25	9.72	0.14	10.02
Woodchip Char		97.50														

Table A-4: Spreadsheet for 6.49% limestone/dry litter from 5/17/2010

** Denotes average value used for conveyor fall-through losses

Moisture Content (wet basis)	Charcoal	Warm up chips	Poultry Litter	Mix/After PL Chips
tin	13.7	13.7	13.5	13.5
wet	107.0	127.5	140.4	135.6
dry	100.6	111.2	125.3	118.7
moisture %	6.86	14.32	11.90	13.84

	Input [lbs], 4 lbs Limestone	wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	47.55	47.55	44.29	2.50
	Warm up Chips	46.85	46.85	40.14	0.11
PL MIX	**PL**	70	61.26	53.97	10.59
	Chips	130	123.84	106.70	0.30
	lime	4.00	3.50	3.50	1.97
	After PL Chips	200	187.59	161.63	0.45
	total	498.40	470.59	410.22	**15.93**
	Lime/Litter percentage	5.71%	5.71%	6.49%	

Elements IN [lbs] P	K	Cl	Na	Ca	
0.012	0.107	**0.010**	0.0167	1.3936	Charcoal
0.003	0.012	**0.001**	0.0015	0.0285	Warm up Chips
0.732	0.995	**0.271**	0.2617	2.1422	**PL**
0.008	0.031	**0.003**	0.0039	0.0758	**Chips**
0.001	0.005	**0.000**	0.0003	1.0860	**lime**
0.011	0.047	**0.005**	0.0060	0.1148	After PL Chips
0.766	1.196	**0.290**	0.290	4.841	***total***
0.034	0.202	**0.019**	0.028	2.699	***total (non PL)***
95.52%	83.15%	**93.43%**	90.23%	44.25%	*ratio from PL/total*

	Sorted/Fall-through	[lbs]		Sorted	Fall-through
	Sorted PL+Lime	1.00	Mix Chips	3.00	3.16
	Sorted Mix Chips	3.00	PL	0.95	7.80
**	*Fall-through Chips/PL/Lime*	11.40	Lime	0.05	0.45
	Sorted 200 lbs	7.55	***total***	4.00	11.40
**	*Fall-through 200 lbs*	4.86	After PL Chips	7.55	4.86

	Output [lbs]	Recovered	Dry	Actual Ash
Gasifier	**Woodchips char**	3.45	3.45	0.09
	PL Ash	1.00	1.00	1.00
	Rest of Gasifier	19.50	19.45	10.35
	Below Grate	6.10	6.10	2.93
	HEX	1.40	1.38	0.87
	Filter	1.60	1.54	0.66
	total	33.05	32.92	**15.90**
			Ash Percent diff:	0.15%

Elements OUT [lbs] P	K	Cl	Na	Ca	Si	S	
0.0022	0.0090	**0.0002**	0.0011	0.0221	0.0057	0.0015	**Woodchips char**
0.0511	0.0719	**0.0017**	0.0178	0.2494	0.1340	0.0099	**PL ash**
0.5247	0.7827	**0.0889**	0.1908	2.9060	1.1173	0.0703	**Rest of Gasifier**
0.1480	0.2117	**0.0520**	0.0584	0.9829	0.2335	0.0251	Below Grate
0.0363	0.0594	**0.0817**	0.0110	0.3265	0.0171	0.0191	HEX
0.0260	0.0632	**0.0654**	0.0095	0.2236	0.0121	0.0205	Filter
0.7882	1.1978	**0.2899**	0.2887	4.7106	1.5198	0.1465	***total***
102.9%	100.1%	**100.0%**	99.5%	97.3%	**Ratio OUT/IN**		
				2.69%	% Difference		
105.7%	102.9%	**102.7%**	102.3%	100%	Norm. to Ca		

Output Ash Analyses																
Oxide to Element Multiplier			0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%)	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
PL Ash 5/17	0.00	0.06	28.69	3.87	1.48	34.92	4.96	2.40	8.67	0.10	11.71	0.07	0.45	2.48	0.06	0.17
Rest of Gasifier 5/17	0.25	46.77	23.09	3.39	1.74	39.27	6.02	2.48	9.11	0.07	11.61	0.09	0.70	1.70	0.07	0.86
Below Gasifier 5/17	0.07	51.98	17.07	2.14	1.57	46.98	4.80	2.69	8.71	0.05	11.58	0.13	0.66	2.14	0.10	1.78
HEX 5/17	1.24	36.92	4.20	1.46	1.61	52.38	6.63	1.70	8.20	0.00	9.52	0.23	1.20	5.47	0.15	9.37
Filter 5/17	3.93	56.83	3.91	1.19	2.86	47.15	5.23	1.93	11.47	0.00	8.99	0.29	1.43	7.72	0.17	9.86
Woodchip Char		97.48														

Table A-5: Spreadsheet for 8.95% limestone/dry litter from 5/19/2010

** Denotes average value used for conveyor fall-through losses

Moisture Content (wet basis)	Charcoal	Warm up chips	Poultry Litter	Mix/After PL Chips
tin	13.5	13.7	13.7	13.5
wet	130.1	151.0	98.9	126.7
dry	123.2	130.6	87.1	111.1
moisture %	5.92	14.86	13.85	13.78

	Input [lbs], 5.4 lbs Limestone	wet	wet - (Sorted + Fall-through)	dry	Theoretical Ash
	Charcoal	44.00	44.00	41.40	2.33
	Warm up Chips	41.75	41.75	35.55	0.10
PL MIX	**PL**	70	60.96	52.51	10.31
	Chips	130	123.54	106.52	0.30
	lime	5.40	4.70	4.70	2.65
	After PL Chips	200	189.59	163.46	0.46
	total	491.15	464.54	404.14	**16.15**
	Lime/Litter percentage	7.71%	7.71%	8.95%	

Elements IN [lbs]	P	K	Cl	Na	Ca
Charcoal	0.011	0.100	**0.009**	0.0156	1.3026
Warm up Chips	0.003	0.010	**0.001**	0.0013	0.0252
PL	0.712	0.968	**0.264**	0.2546	2.0845
Chips	0.008	0.031	**0.003**	0.0039	0.0757
lime	0.001	0.007	**0.000**	0.0003	1.4589
After PL Chips	0.012	0.047	**0.005**	0.0060	0.1161
total	0.746	1.163	**0.282**	0.282	5.063
total (non PL)	0.034	0.195	**0.018**	0.027	2.978
ratio from PL/total	95.50%	83.20%	**93.50%**	90.34%	41.17%

	Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
	Sorted PL+Lime	1.50	Mix Chips	3.30	3.16
	Sorted Mix Chips	3.30	PL	1.39	7.65
**	*Fall-through Chips/PL/Lime*	11.40	Lime	0.11	0.59
	Sorted 200 lbs	5.55	***total***	4.80	11.40
**	*Fall-through 200 lbs*	4.86	After PL Chips	5.55	4.86

	Output [lbs]	**Recovered**	**Dry**	**Actual Ash**
Gasifier	**Woodchips char**	9.20	9.20	0.11
	PL Ash	0.65	0.65	0.63
	Rest of Gasifier	18.00	17.90	9.53
	Below Grate	5.90	5.87	2.93
	HEX	1.30	1.29	0.83
	Filter	1.75	1.70	0.87
	total	36.80	36.60	**14.90**
		Ash Percent diff:		7.75%

Elements OUT [lbs]	P	K	Cl	Na	Ca	Si	S
Woodchips char	0.0027	0.0111	**0.0002**	0.0014	0.0271	0.0070	0.0019
PL ash	0.0364	0.0448	**0.0007**	0.0112	0.1905	0.0543	0.0087
Rest of Gasifier	0.4611	0.7247	**0.0819**	0.1673	2.8780	0.9146	0.0707
Below Grate	0.1584	0.2014	**0.0378**	0.0630	0.9346	0.2574	0.0218
HEX	0.0391	0.0482	**0.0559**	0.0098	0.3145	0.0193	0.0172
Filter	0.0400	0.0825	**0.0818**	0.0135	0.2798	0.0154	0.0314
total	0.7377	1.1128	**0.2584**	0.2662	4.6244	1.2679	0.1517
Ratio OUT/IN	98.9%	95.7%	**91.7%**	94.5%	91.3%		
% Difference					8.66%		
Norm. to Ca	108.3%	104.7%	**100.4%**	103.4%	100%		

Output Ash Analyses															
		Oxide to Element Multiplier	0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%)	Na2O (%	K2O (%)	TiO2 (%	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
PL 5/19	0.00	3.08	18.43	2.77	1.46	42.31	6.53	2.39	8.57	0.06	13.23	0.06	0.55	3.45	0.06	0.12
Rest of Gasifier 5/19	0.57	46.73	20.52	2.84	1.28	42.24	7.16	2.37	9.16	0.06	11.08	0.08	0.65	1.85	0.07	0.86
Below Gasifier 5/19	0.51	50.16	18.82	2.39	1.28	44.70	5.46	2.90	8.29	0.03	12.41	0.11	0.65	1.86	0.08	1.29
HEX 5/19	0.98	35.63	4.99	1.66	1.27	53.10	7.96	1.60	7.01	0.00	10.80	0.14	0.96	5.17	0.12	6.75
Filter 5/19	2.87	48.80	3.78	1.27	2.05	44.99	5.90	2.09	11.43	0.00	10.54	0.23	1.30	9.01	0.14	9.40
Woodchip Char		98.84														

Table A-6: Spreadsheet for 4.31% limestone/dry litter from 6/3/2010

Moisture Content (wet basis)				
	Charcoal	Warm up chips	Poultry Litter	ix/After PL Chips
tin	13.5	13.7	13.5	13.7
wet	182.8	145.3	163.2	165.9
dry	174.1	133.1	142.4	144.3
moisture %	5.14	9.27	13.89	14.19

	Input [lbs], 2.6 lbs Limestone				
		wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	45.55	45.55	43.21	2.44
	Warm up Chips	61.90	61.90	56.16	0.16
PL MIX	**PL**	70	60.62	52.20	10.25
	Mix Chips	130	123.73	106.17	0.30
	Lime	2.60	2.25	2.25	1.27
	After PL Chips	200	186.00	159.60	0.45
	total	510.05	480.05	419.59	**14.85**
	Lime/Litter percentage	3.71%	3.71%	4.31%	

Elements IN [lbs]					
P	K	Cl	Na	Ca	
0.011	0.104	**0.010**	0.0163	1.3596	Charcoal
0.004	0.016	**0.002**	0.0021	0.0399	Warm up Chips
0.708	0.962	**0.262**	0.2531	2.0719	**PL**
0.008	0.031	**0.003**	0.0039	0.0754	**Chips**
0.000	0.003	**0.000**	0.0002	0.6986	**lime**
0.011	0.046	**0.005**	0.0059	0.1134	After PL Chips
0.743	1.163	**0.281**	0.281	4.359	***total***
0.035	0.201	**0.019**	0.028	2.287	***total (non PL)***
95.33%	82.70%	**93.17%**	89.94%	47.53%	*ratio from PL/total*

Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
Sorted PL+Lime	2.70	Mix Chips	3.25	3.02
Sorted Mix Chips	3.25	PL	2.60	6.78
Fall-through Chips/PL/Lime	10.05	Lime	0.10	0.25
Sorted 200 lbs	9.35	***total***	5.95	10.05
Fall-through 200 lbs	4.65	After PL Chips	9.35	4.65

	Output [lbs]			
		Recovered	**Dry**	**Actual Ash**
Gasifi	**Woodchips char**	7.35	7.35	0.74
	Gasifier	18.55	17.88	11.81
	After Grate	6.80	6.68	3.45
	total	32.70		**16.00**
			Ash Percent diff:	-7.74%

Elements OUT [lbs]					
P	K	Cl	Na	Ca	
0.0186	0.0763	**0.0016**	0.0097	0.1865	**Woodchips char**
0.7243	0.9185	**0.0706**	0.2454	3.5036	**Gasifier**
0.1809	0.1745	**0.2160**	0.0594	1.2071	After Grate
0.9238	1.1693	0.2882	0.3144	4.8972	***total***
124.41%	100.52%	**102.47%**	111.72%	112.35%	**Ratio OUT/IN**
				-12.35%	% Difference
110.7%	89.5%	91.2%	99.4%	100%	Norm. to Ca

Output Ash Analyses																
	Oxide to Element Multiplier		0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%)	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
Gasifier 6/3	3.59	33.94	19.40	2.44	1.21	41.49	5.79	2.80	9.36	0.04	14.05	0.03	0.44	2.39	0.11	0.60
After Grate 6/3	1.74	48.33	12.71	1.68	1.28	48.92	5.27	2.32	6.09	0.02	12.00	0.06	0.55	4.09	0.16	6.26

Table A-7: Spreadsheet for 6.69% limestone/dry litter from 5/26/2010

** Denotes average value used for conveyor fall-through losses

Moisture Content (wet basis)	Charcoal	Warm up chips	Poultry Litter	ix/After PL Chips
tin	13.7	13.7	13.5	13.5
wet	115.1	121.3	146.5	157.0
dry	110.1	116.5	127.1	136.9
moisture %	4.93	4.46	14.59	14.01

	Input [lbs], 4 lbs Limestone	wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	36.25	36.25	34.46	1.94
	Warm up Chips	39.00	39.00	37.26	0.10
PL MIX	**PL**	70	61.35	52.40	10.29
	Mix Chips	130	124.64	107.18	0.30
	lime	4.00	3.51	3.51	1.97
	After PL Chips	200	186.99	160.80	0.45
	total	479.25	451.74	395.61	**15.06**
	Lime/Litter percentage	5.71%	5.71%	6.69%	

Elements IN [lbs]	P	K	Cl	Na	Ca
Charcoal	0.009	0.083	**0.008**	0.0130	1.0844
Warm up Chips	0.003	0.011	**0.001**	0.0014	0.0265
PL	0.711	0.966	**0.263**	0.2541	2.0801
Chips	0.008	0.031	**0.003**	0.0040	0.0761
lime	0.001	0.005	**0.000**	0.0003	1.0877
After PL Chips	0.011	0.047	**0.005**	0.0059	0.1142
total	0.742	1.143	**0.280**	0.279	4.469
total (non PL)	0.031	0.177	**0.017**	0.025	2.389
ratio from PL/total	95.76%	84.52%	**94.01%**	91.20%	46.54%

	Sorted/Fall-through	**[lbs]**		**Sorted**	**Fall-through**
	Sorted PL+Lime	0.90	Mixed Chips	2.20	3.16
	Sorted mix Chips	2.20	PL	0.85	7.80
**	*all-through Chips/PL/Lime*	11.40	Lime	0.05	0.45
	Sorted 200 lbs	8.15	***total***	3.10	11.40
**	*Fall-through 200 lbs*	4.86	After PL Chips	8.15	4.86

	Output [lbs]	Recovered	Dry	Actual Ash
Gasifi	**Woodchips char**	6.75	6.75	0.36
	Gasifier	19.25	19.21	12.09
	After Grate	5.55	5.48	2.67
	total	31.55		**15.12**
			Ash Percent diff:	-0.41%

Elements OUT [lbs]	P	K	Cl	Na	Ca
Woodchips char	0.0092	0.0376	**0.0008**	0.0048	0.0920
Gasifier	0.6713	0.8964	**0.0676**	0.2515	3.4076
After Grate	0.1546	0.0906	**0.1609**	0.0427	0.9180
total	0.8352	1.0246	0.2293	0.2990	4.4175
Ratio OUT/IN	112.53%	89.66%	**81.94%**	107.31%	98.85%
% Difference					1.15%
Norm. to Ca	113.8%	90.7%	82.9%	108.6%	100%

Output Ash Analyses																
	Oxide to Element Multiplier		0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basi	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	MgO (%	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	BaO (%)	MnO2 (%)	SO3 (%)	SrO (%)	Cl (%)
Gasifier 5/26	0.22	37.08	21.74	3.13	1.58	39.45	6.36	2.81	8.93	0.09	12.73	0.09	0.63	1.98	0.06	0.56
After Grate 5/26	1.26	51.21	12.05	1.97	1.61	48.04	6.07	2.15	4.08	0.06	13.25	0.14	0.88	4.96	0.10	6.02
Woodchip Char		94.63														

Table A-8: Spreadsheet for 8.92% limestone/dry litter from 6/1/2010

Moisture Content (wet basis)				
	Charcoal	Warm up chips	Poultry Litter	Mix/After PL Chips
tin	13.5	13.7	13.7	13.5
wet	132.5	144.2	116.4	144.2
dry	125.1	131.3	102.5	129.6
moisture %	6.22	9.89	13.53	11.17

	Input [lbs], 5.4 lbs Limestone				
		wet	wet - (Sorted + Fall through)	dry	Theoretical Ash
	Charcoal	37.10	37.10	34.79	1.96
	Warm up Chips	35.10	35.10	31.63	0.09
PL MIX	**PL**	70	59.85	51.75	10.16
	Mix Chips	130	123.29	109.51	0.31
	Lime	5.40	4.62	4.62	2.60
	After PL Chips	200	186.50	165.67	0.46
	total	477.60	446.45	397.97	**15.58**
	Lime/Litter percentage	7.71%	7.71%	8.92%	

Elements IN [lbs]					
P	K	**Cl**	Na	Ca	
0.009	0.084	**0.008**	0.0131	1.0948	Charcoal
0.002	0.009	**0.001**	0.0012	0.0225	Warm up Chips
0.702	0.954	**0.260**	0.2509	2.0541	**PL**
0.008	0.032	**0.003**	0.0040	0.0778	**Chips**
0.001	0.007	**0.000**	0.0003	1.4324	**lime**
0.012	0.048	**0.005**	0.0061	0.1177	After PL Chips
0.734	1.133	**0.277**	0.276	4.799	***total***
0.032	0.180	**0.017**	0.025	2.745	***total (non PL)***
95.65%	84.14%	**93.89%**	91.01%	42.80%	*ratio from PL/total*

Sorted/Fall-through	[lbs]		Sorted	Fall-through
Sorted PL+Lime	1.50	Mix Chips	3.40	3.32
Sorted Mix Chips	3.40	PL	1.39	8.76
Fall-through Chips/PL/Lime	12.75	Lime	0.11	0.68
Sorted 200 lbs	8.40	*total*	4.90	12.75
Fall-through 200 lbs	5.10	After PL Chips	8.40	5.10

	Output [lbs]			
		Recovered	Dry	Actual Ash
Gasifi	**Woodchips char**	7.45	7.45	0.46
	Gasifier	18.15	18.09	8.22
	After Grate	6.25	6.19	2.95
	total	31.85		**11.63**
			Percent diff:	25.36%

Elements OUT [lbs]					
P	K	**Cl**	Na	Ca	
0.0116	0.0475	**0.0010**	0.0060	0.1162	**Woodchips char**
0.4398	0.7383	**0.0755**	0.1349	2.4171	**Gasifier**
0.1504	0.2482	**0.1642**	0.0494	0.9486	After Grate
0.6017	1.0341	0.2407	0.1903	3.4820	***total***
82.01%	91.23%	**87.01%**	69.04%	72.55%	**Ratio OUT/IN**
				27.45%	% Difference
113.0%	125.7%	119.9%	95.2%	100%	Norm. to Ca

Output Ash Analyses																
		Oxide to Element Multiplier	0.467	0.529	0.699	0.715	0.603	0.742	0.830	0.599	0.436			0.401		
	Moist (% As Rec)	LOI (% Dry Basis)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	BaO (%)	MnO_2 (%)	SO_3 (%)	SrO (%)	Cl (%)
Gasifier 6/1	0.35	54.56	17.64	3.43	1.57	41.15	6.75	2.21	10.82	0.08	12.26	0.11	0.69	2.52	0.08	0.92
After Grate 6/1	0.93	52.32	12.56	2.11	1.58	44.96	5.82	2.25	10.13	0.02	11.67	0.11	0.78	3.61	0.10	5.56
Woodchip Char		93.85														

APPENDIX B

SAMPLE CALCULATIONS

To calculate the input mass of K from poultry litter in the 6.49% limestone experiment in Table A-4:

$$m_{K_{litter,IN}} = \left(m_{litter,wet} - m_{litter,sorted} - m_{litter,fall\ thru}\right) \cdot \left(1 - \frac{Moisture\ \%_{litter}}{100}\right) \cdot \left(\frac{\%\ Ash_{litter}}{100}\right) \cdot \left(\frac{K_2O\ \%_{litter}}{100}\right) \cdot \left(\frac{\%\ K}{K_2O\%_{litter}}\right) \qquad \text{Equation B. 1}$$

$$= (70.00\ lbs - 0.95\ lbs - 7.80\ lbs) \cdot \left(1 - \frac{11.90\%}{100}\right) \cdot \left(\frac{19.63\%}{100}\right) \cdot \left(\frac{11.31\%}{100}\right) \cdot (0.830)$$

$$m_{K_{litter,IN}} = 0.995\ lbs$$

Similarly, the amount of K from each biomass input can be determined. The mass of K from each source can then simply be summed to get total K put in the gasifier.

To calculate the mass of K recovered from the char Below the Grate:

$$m_{K_{Below\ Grate,OUT}} = \left(m_{Below\ Grate,wet}\right) \cdot \left(1 - \frac{Moisture\ \%_{Below\ Grate}}{100}\right) \cdot \left(1 - \frac{\%\ LOI_{Below\ Grate}}{100}\right) \cdot \left(\frac{K_2O\ \%_{Below\ Grate}}{100}\right) \cdot \left(\frac{\%\ K}{K_2O\%_{Below\ Grate}}\right) \qquad \text{Equation B. 2}$$

$$= (6.10\ lbs) \cdot \left(1 - \frac{0.07\%}{100}\right) \cdot \left(1 - \frac{51.98\%}{100}\right) \cdot \left(\frac{8.71\%}{100}\right) \cdot (0.830)$$

$$m_{K_{Below\ Grate,OUT}} = 0.2117\ lbs$$

Similarly, the amount of K from each location can be determined. The mass of K from each location can then simply be summed to get total K recovered.

To find the amount of poultry litter in the mixture of fines collected from below the conveyor in Table A-4:

$$m_{litter,fall-thru} = \left[m_{fall-thru,mix} - \left(\frac{m_{chips,fall-thru}}{200.00\ lbs\ chips}\right) \cdot (130.00\ lbs\ mixed\ chips)\right] \cdot \left(\frac{m_{litter,wet}}{m_{litter,wet} + m_{limestone}}\right) \qquad \text{Equation B. 3}$$

$$= \left[11.40\ lbs - \left(\frac{4.86\ lbs}{200.00\ lbs\ chips}\right) \cdot (130.00\ lbs\ mixed\ chips)\right] \cdot \left(\frac{70.00\ lbs}{70.00\ lbs + 4.00\ lbs}\right)$$

$$m_{litter,fall-thru} = 7.80\ lbs$$

APPENDIX C

UNCERTAINTY ANALYSIS

Uncertainty associated with measured quantities is presented in this appendix, however the largest sources of uncertainty in the experiments are unquantifiable and derive from mixing and sampling of char and biomass as well as unknown losses. The uncertainty of various measuring devices is shown in Table C-1.

Table C-1: Uncertainty of instruments used

Device	Units	Uncertainty
Thermocouples	˚C	±2.2˚C
CAI Nova Analyzer	% Volume	CO: ±0.6% CO_2: ±0.6% CH_4: ±0.3% O_2: ±0.5%
HiTech K1550 Analyzer	% Volume	H_2: ±2%
Ohaus CD-11 Digital Scale	lbs	±0.05 lbs

The uncertainty estimates from the ash, moisture, and elemental analyses are shown in Table C-2.

Table C-2: Uncertainty of biomass and char analyses, units are % mass. Oxide and Cl are on an Ash basis

Parameter	Uncertainty
Moisture, as received	±0.1%
Ash, dry basis	±0.1%
Na_2O	y = 0.0024x + 0.0205
MgO	y = 0.0035x + 0.0291
Al_2O_3	y = 0.0026x + 0.0849
SiO_2	y = 0.0028x + 0.1343
P_2O_5	y = 0.0158x + 0.0056
SO_3	y = 0.0145x + 0.0821
K_2O	y = 0.0101x + 0.0104
CaO	y = 0.0056x + 0.0759
TiO_2	y = 0.0155x + 0.0364
MnO_2	y = 0.01x + 0.0046
Fe_2O_3	y = 0.0104x + 0.0234
SrO	y = 0.0556x + 0.0015
BaO	y = 0.0087x + 0.004
Cl	y = 0.028x + 0.02

Because uncertainty propagation through to the calculated retention percentage is dependent on the particular elemental oxide and its concentration, a general equation will be formulated and example result calculated. The general form of the propagated uncertainty equation, as denoted by Beckwith, 1990 for a function $f(x_1, x_2 \ldots x_n)$ is (Beckwith, et al., 1990):

$$U_f = \pm\sqrt{\left(U_{x_1}\frac{\partial f}{\partial x_1}\right)^2 + \left(U_{x_2}\frac{\partial f}{\partial x_2}\right)^2 + \cdots + \left(U_{x_n}\frac{\partial f}{\partial x_n}\right)^2} \qquad \text{Equation C.1}$$

For the actual weight of feedstock *i* put into the gasifier (m_i), the measure weight ($m_{wet,i}$) minus the weight of the sorted feedstock ($m_{sorted,i}$) and conveyor loss weight ($m_{loss,i}$) is:

$$m_i = m_{wet,i} - m_{sorted,i} - m_{loss,i} \qquad \text{Equation C.2}$$

$$U_{m_i} = \pm\sqrt{\left(U_{m_{wet,i}}\frac{\partial m_i}{\partial m_{wet,i}}\right)^2 + \left(U_{m_{sorted,i}}\frac{\partial m_i}{\partial m_{sorted,i}}\right)^2 + \left(U_{m_{loss,i}}\frac{\partial m_i}{\partial m_{loss,i}}\right)^2} \qquad \text{Equation C.3}$$

$$= \pm\sqrt{\left(U_{m_{wet,i}}(1)\right)^2 + \left(U_{m_{sorted,i}}(-1)\right)^2 + \left(U_{m_{loss,i}}(-1)\right)^2} \qquad \text{Equation C.4}$$

Using the uncertainty of the electronic scale (±0.05 lbs) for each measured weight:

$$U_{m_i} = \pm 0.0866 \qquad \text{Equation C.5}$$

The total mass calculated for each element *E*, from each feedstock *i* put into the gasifier is then:

$$m_{E_{i,IN}} = m_i \cdot \left(\frac{Dry\,\%_i}{100}\right) \cdot \left(\frac{\%\,Ash_i}{100}\right) \cdot \left(\frac{E_xO_y\%_i}{100}\right) \cdot \left(\frac{\%\,E}{E_xO_y\%_i}\right) \qquad \text{Equation C. 6}$$

**Note: $Dry\,\%_i = (100 - \%\,Moisture_i)$

**Note: Oxide to Element Conversion factor $\left(\frac{\%\,E}{E_xO_y\%_i}\right)$ is from Equation 4.4, and is a constant

Uncertainty of $m_{E_{i,IN}}$ is:

$$U_{m_{E_{i,IN}}} = \pm\sqrt{\left(U_{m_i}\frac{\partial m_{E_{i,IN}}}{\partial m_i}\right)^2 + \left(U_{Dry\,\%_i}\frac{\partial m_{E_{i,IN}}}{\partial Dry\,\%_i}\right)^2 + \left(U_{\%\,Ash_i}\frac{\partial m_{E_{i,IN}}}{\partial\%\,Ash_i}\right)^2 + \left(U_{E_xO_y\%_i}\frac{\partial m_{E_{i,IN}}}{\partial E_xO_y\%_i}\right)^2}$$

Equation C.7

$$= \pm\sqrt{\left(U_{m_i}\frac{m_{E_{i,IN}}}{m_i}\right)^2 + \left(U_{Dry\,\%_i}\frac{m_{E_{i,IN}}}{Dry\,\%_i}\right)^2 + \left(U_{\%\,Ash_i}\frac{m_{E_{i,IN}}}{\%\,Ash_i}\right)^2 + \left(U_{E_xO_y\%_i}\frac{m_{E_{i,IN}}}{E_xO_y\%_i}\right)^2} \qquad \text{Equation C.8}$$

$$= \pm m_{E_{i,IN}} \sqrt{\left(\frac{U_{m_i}}{m_i}\right)^2 + \left(\frac{U_{Dry\,\%_i}}{Dry\,\%_i}\right)^2 + \left(\frac{U_{\%\,Ash_i}}{\%\,Ash_i}\right)^2 + \left(\frac{U_{E_xO_y\%_i}}{E_xO_y\%_i}\right)^2}$$ Equation C.9

It becomes apparent at this point, the dependence of uncertainty on the specific element and feedstock of interest. The equations for $U_{E_xO_y\%_i}$were given in Table C-2. The uncertainty of Moisture % and % Ash can be found in the same table, and $U_{m_i}$was found in Equation C.5.

$$U_{m_{E_{i,IN}}} = \pm m_{E_{i,IN}} \sqrt{\left(\frac{(0.0866\ lbs)}{m_i}\right)^2 + \left(\frac{(0.1\%)}{Dry\,\%_i}\right)^2 + \left(\frac{(0.1\%)}{\%\,Ash_i}\right)^2 + \left(\frac{(m(E_xO_y\%_i)+b\,\%)}{E_xO_y\%_i}\right)^2}$$ Equation C.10

From here, values will be used from the K in poultry litter data of the 6.43% limestone experiment in Table A-4. This will represent a general value of uncertainty.

From Table A-4: m_{litter}=61.26 lbs, $Dry\ \%_{litter}$= (100-11.90) = 88.1%, $m_{K_{litter,IN}}$=0.995 lbs

From Table A-1: $\%\ Ash_{litter}$= 19.63%

From Table A-2: $K_2O\%_{litter}$ = 11.31%

From Table C-2: $U_{K_2O\%_{litter}}$ = 0.0101($K_2O\%_{litter}$) + 0.0104 = ±0.125

$$U_{m_{K_{litter,IN}}} = \pm 0.01221$$ Equation C.11

Repeating Equation C.10 for the rest of the sources of K:

$$U_{m_{K_{Charcoal,IN}}} = \pm 0.00231$$

$$U_{m_{K_{warm\ up\ chips,IN}}} = \pm 0.00417$$

$$U_{m_{K_{mix\ chips,IN}}} = \pm 0.01108$$

$$U_{m_{K_{limestone,IN}}} = \pm 0.000373$$

$$U_{m_{K_{after\ litter\ chips,IN}}} = \pm 0.01678$$

Using a similar approach as Equations C.2-C.4, the uncertainty for total K input (found to be 1.196 lbs) is:

$$U_{m_{K_{Total,IN}}} = \pm 0.02400$$ Equation C.12

Similarly, the uncertainty for the total K recovered in the char is:

$$U_{m_{K_{Total,OUT}}} = \pm 0.01078 \qquad \text{Equation C.13}$$

Therefore, uncertainty of the ratio $\frac{m_{K_{Total,OUT}}}{m_{K_{Total,IN}}}$, presented as “retention percent K” is:

$$U_{retention\,\%\,K} = \pm(retention\;\%\;K)\sqrt{\left(\frac{U_{OUT}}{m_{K_{Total,OUT}}}\right)^2 + \left(\frac{U_{IN}}{m_{K_{Total,IN}}}\right)^2} \qquad \text{Equation C.14}$$

$$\boxed{U_{retention\,\%\,K} = \pm 2.201\%}$$

Uncertainties for other retention percentages can be found similarly.

APPENDIX D

ADDITIONAL FIGURES

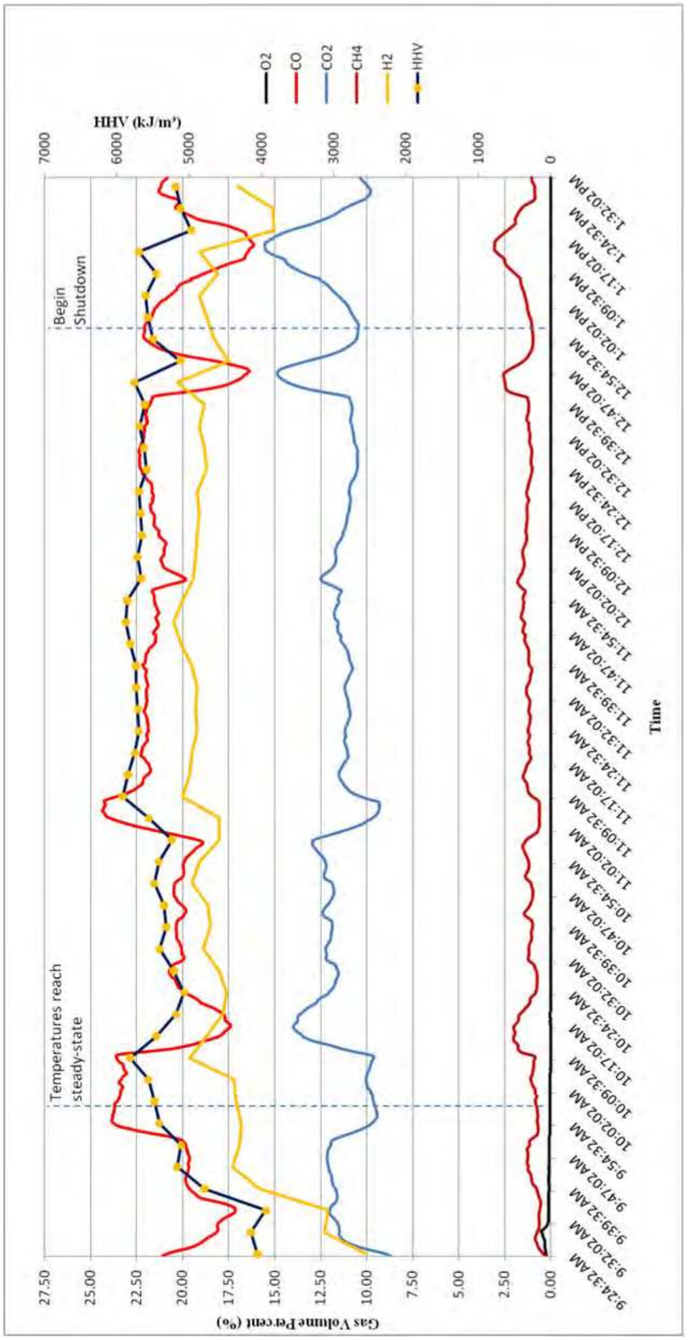

Figure D-43: Dry syngas composition vs. Time for a standard woodchip run, fluctuations in composition are typical, with an average HHV ~5.4 MJ/m³

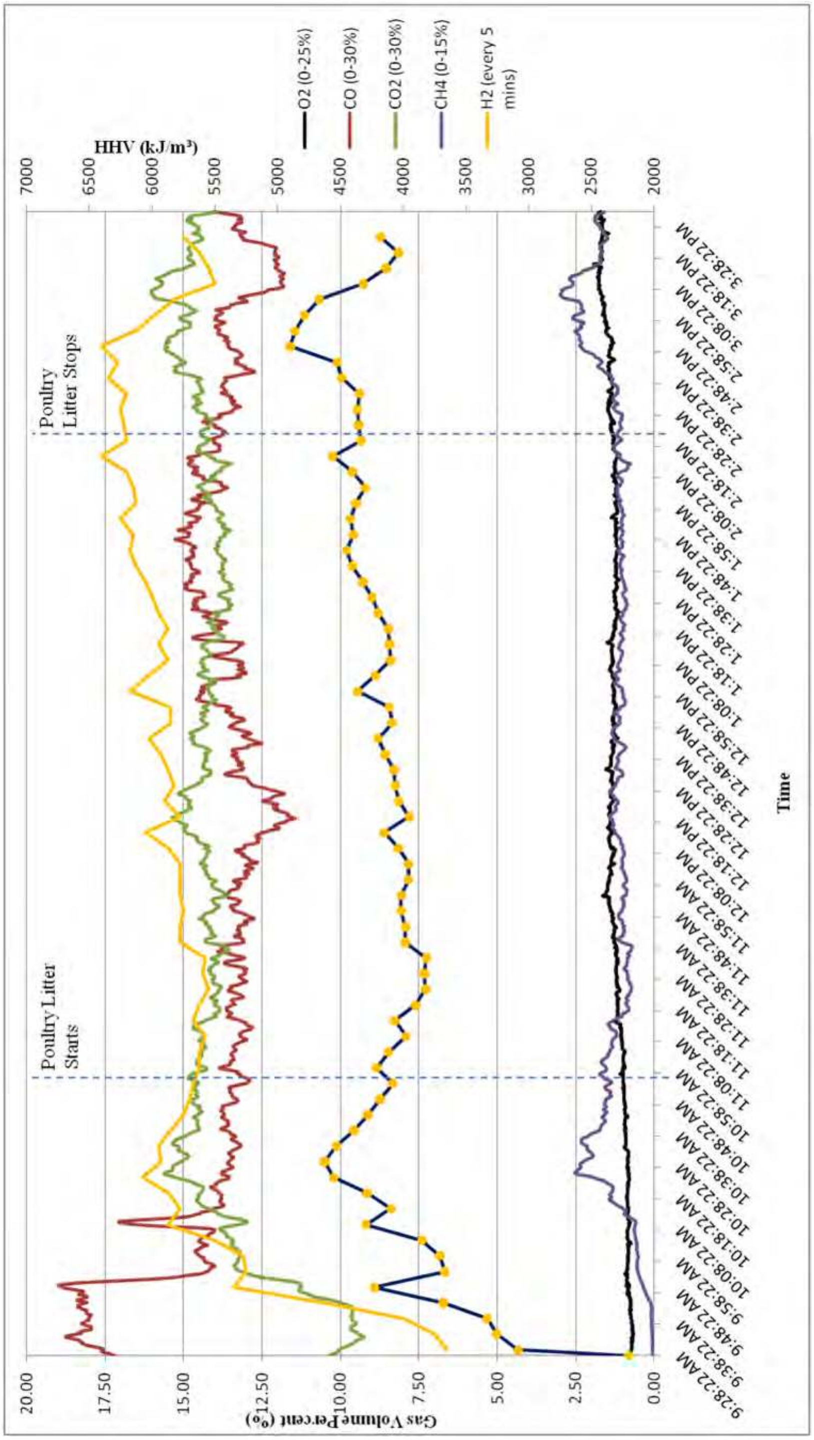

Figure D-44: Dry syngas composition vs. time during flue gas recirculation experiment (Section 10.1.2)

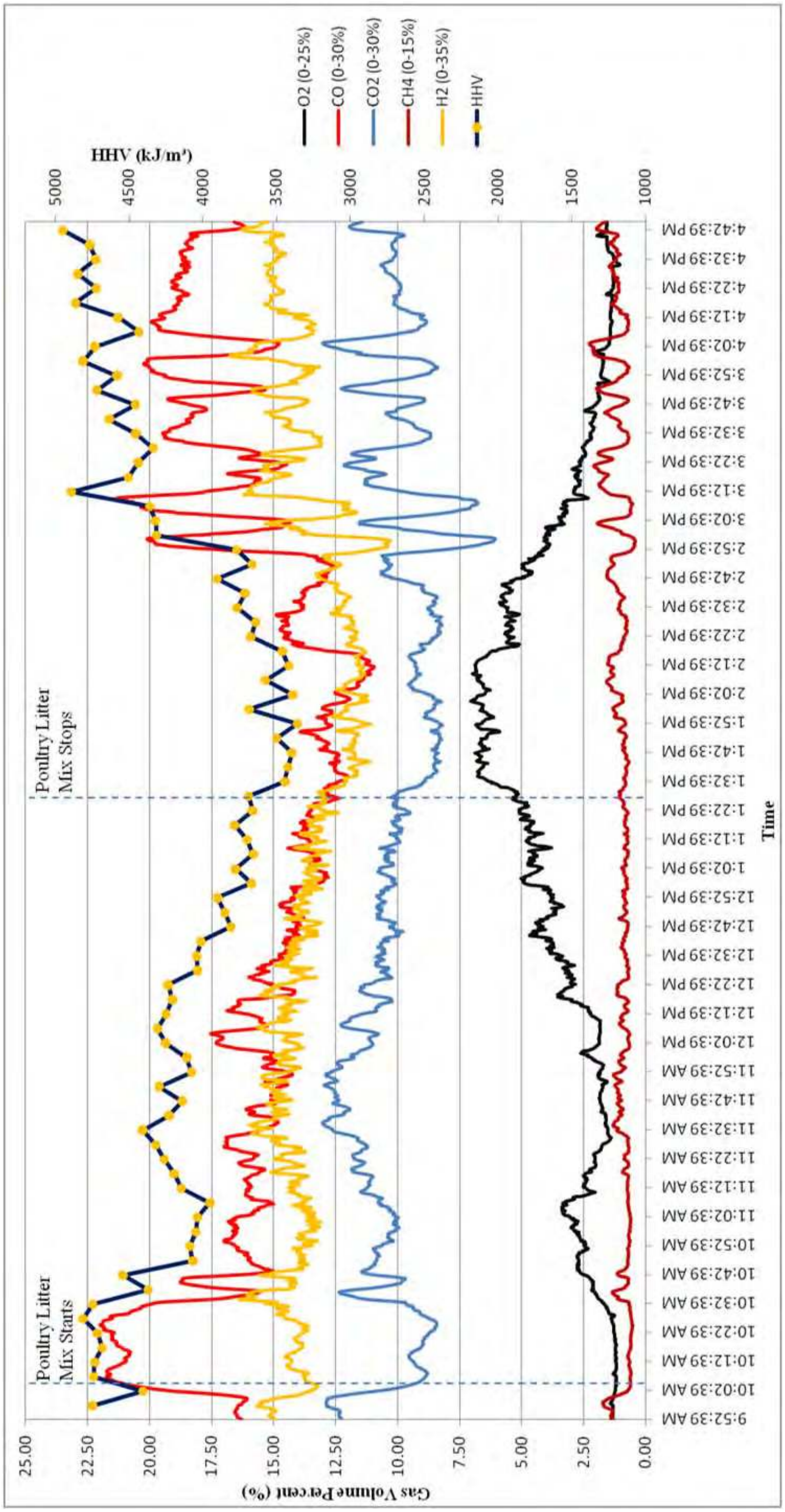

Figure D-45: Dry syngas composition vs. time during raw litter, 5% limestone, and 60:40 (woodchip:litter) experiment (Section 10.1.4)

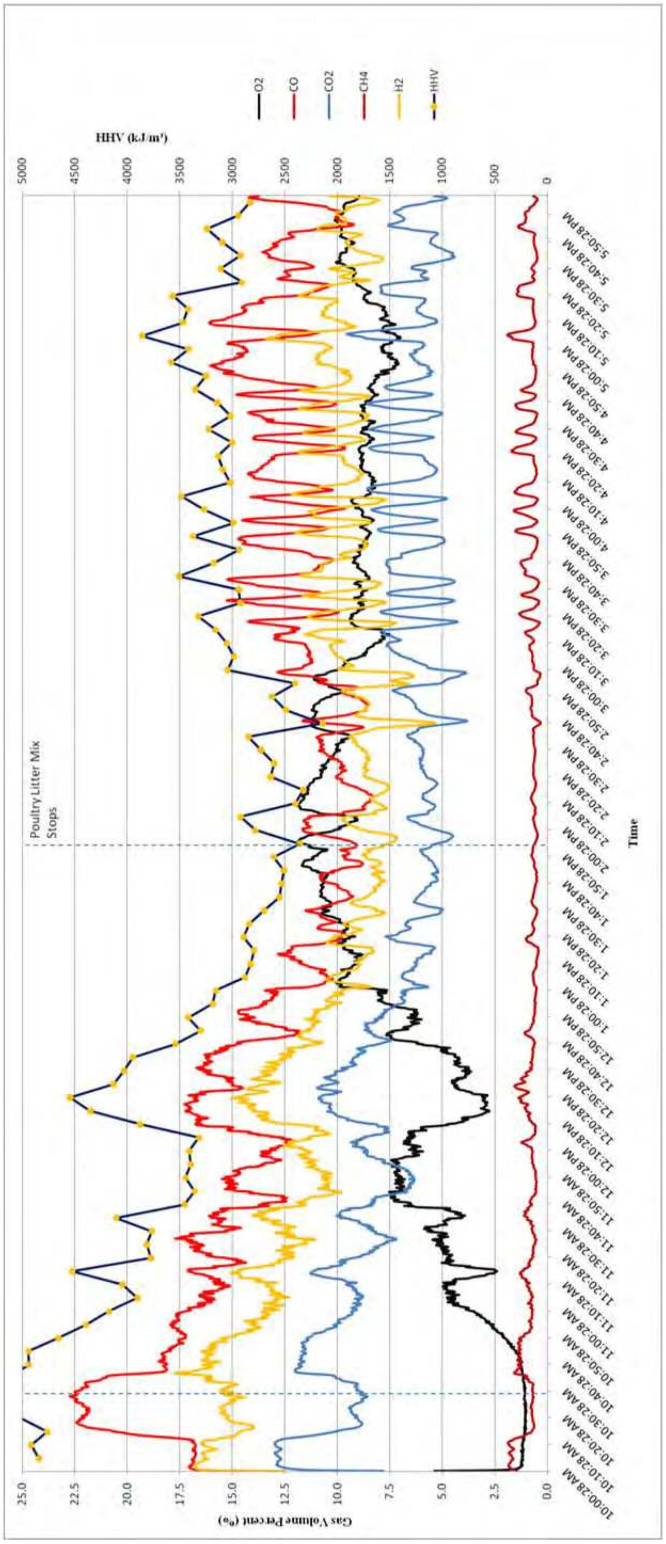

Figure D-46: Dry syngas composition vs. time during 8.95% Limestone/Dry Litter experiment. Very typical of all experiments in contaminant retention study (Section 10.2)