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Rotary kiln incineration of hazardous wastes: pilot-scale studies at Louisiana State University

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ROTARY KILN INCINERATION OF HAZARDOUS WASTES: PILOT-SCALE STUDIES AT LOUISIANA STATE UNIVERSITY

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Interdepartmental Program in
Engineering Science

by
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B.Sc., Acadia University, 1948
B.E., McGill University, 1950
M.S., Louisiana State University, 1971
December 2003

DEDICATION

To Eleanor, my wife and best friend. Thank you for your love, understanding and encouragement.

To our children, who are the delight of their father and mother:

Eleanor Joan Bloxham and her husband, Robert Bloxham;
John Sutherland Earle and his wife, Dana Sapatoru;
Robert Leonard Earle and his wife, Sri Susilowati.

To my brother and sisters, who have contributed so much to my life:

Leonard Hadley Earle and his wife, Charlotte Earle;
Barbara Hunter and her husband, Eugene Hunter;
Brooke Sheldon and her late husband, George Sheldon.

To my parents, who were the best of examples for their children:

Leonard Hadley Earle
Elsie Sutherland Earle

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GLOSSARY

AFTERBURNER	Secondary combustion furnace (SOC)
APCD	Air Pollution Control Device
AWFCO	Automatic Waste Feed Cutoff
BACT	Best Available Control Technology
BAGHOUSE	Fabric filter used to remove particulates from combustion gases
BOD	Biological Oxygen Demand
CAA	Clean Air Act
CEMS	Continuous Emission Monitoring System: Gas sampling and analytical equipment to monitor stack gases.
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
COD	Chemical Oxygen Demand
CFR	Code of Federal Regulations
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CWA	Clean Water Act
DAQ	Data Acquisition System
DEQ	Louisiana Department of Environmental Quality
DRE	Destruction and Removal Efficiency
EPA	United States Environmental Protection Agency
FUEL NOx	NOx produced by oxidation of nitrogen in fuel.

FR	Federal Register
HAP	Hazardous Air Pollutants
LEAN	Louisiana Environmental Action Network
LSU	Louisiana State University
MACT	Maximum Achievable Control Technology
MSDS	Material Safety Data Sheets
NOx	Nitrogen Oxides
PAH	Polynuclear Aromatic Hydrocarbon
PIC	Product of Incomplete Combustion
PLC	Programmable Logic Controller
POC	Primary Oxidation Chamber (Rotary Kiln)
POHC	Principal Organic Hazardous Constituent
RCRA	Resource Conservation and Recovery Act
RKI	Rotary Kiln Incinerator
SOC	Secondary Oxidation Chamber (Afterburner)
SOx	Sulfur Oxides
THC	Total Hydrocarbons
THERMAL NOx	NOx produced by oxidation of nitrogen in combustion air.
VOC	Volatile Organic Compound
VOST	Volatile Organic Sampling Train
UOD	Unsatisfied Oxygen Demand

ABSTRACT

Studies of incineration of surrogates for hazardous wastes are conducted in the pilot-scale rotary kiln incinerator (RKI) at Louisiana State University (LSU) in Baton Rouge, Louisiana. The purpose of the research is to investigate methods of treating and destroying hazardous wastes in a cost-effective and environmentally sound way. The objective is to provide process data that will contribute to increased knowledge for RKI design and operation. The LSU facility is a College of Engineering Combustion Laboratory that is unique in its large size as a university laboratory. It is equipped with individual instruments for analysis of O_2, CO, CO_2, HCl, SOx and NOx and a mass spectrometer to continuously monitor products of combustion for rigorous evaluation of efficiencies of operation.

Experiments conducted to investigate parameters and variables affecting the design and operation of the kiln substantiate mathematical treatment of material and energy balances. These investigations add new and useful data to be used in design of rotary kilns, a major objective of this research.

One of the principal contributions of this dissertation relates to the effects of batch feeding on instability of the combustion process. Surges in temperature, pressure, and their effects on products of incomplete combustion are discussed.

Other activities of the combustion laboratory are described: Incineration of still bottoms to recover byproduct potash produced by the Audubon Sugar Institute; burning of synthetic fireplace logs; study of incinerator stack gases; and determination of rates of fugitive emissions from flanges and valves.

Economics of operation and maintenance of the facility are calculated, tabulated, and related to contract charges for combustion studies on behalf of industrial clients. Future prospects for the laboratory as a research and teaching facility are discussed.

CHAPTER 1 INTRODUCTION

1.1 Overall Topic

1.1.1 Research Subject

The purpose of the research described here is to contribute to the understanding of methods for treating and destroying hazardous waste in cost effective and environmentally sound ways. The objective is to provide process data that will contribute to increased knowledge for rotary kiln incinerator (RKI) design and operation. Current understanding of all of the phenomena that govern RKI performance is far from complete. This lack of knowledge of the process leads to over-design, which is not economical. Of greater consequence is that inadequate equipment design or operation can lead to noxious gas emissions and/or incomplete destruction of waste material. In spite of a history of frequent public opposition to rotary kiln incinerators, these workhorses of the waste disposal industry continue to offer a solution to the problem of pollution of the land. If design can be improved, there is hope that with care in selection of sites, public hostility will be reduced. It is the goal of this research to add to the basic information needed for RKI design, and thus to contribute to the solution of waste disposal problems.

The overt reasons for objection to incineration given by the general population are odors and smoke. These are obvious discharges resulting from incomplete combustion and/or imperfect removal of undesirable chemicals and particulates from the effluent gases. Health hazards due to known or unknown chemicals in the gases are a hidden danger. In the usual case, landfill disposal of the ash, almost entirely free of organic material, does not cause objections. Water discharge can be treated to remove objectionable substances, and unless mishandled, is ordinarily not a matter of primary concern. Carbon dioxide discharged from electrical power plants, petroleum refineries and other manufacturing plants far exceeds the output from incinerators, and since carbon dioxide is invisible, odorless, and not a health hazard at low concentrations, it is not normally high on the list of arguments against combustion of waste. It is, however, a greenhouse gas and is a matter of great concern as a source of global warming. Water vapor in the gaseous discharge of kilns amounts to 20 to 50 percent of the total volume. On being contacted by air, that is, upon leaving a stack, some of the water vapor condenses, resulting in a harmless, although telltale plume. If the carbon dioxide and steam were not accompanied by odorous and smoky constituents of the gas, they would no more be criticized than the white clouds that emanate from petroleum processing plants. Elimination of the odors, smoke and noxious chemicals would greatly increase the acceptance of rotary kiln incinerators.

The problem under study here is the nature of the processes taking place in the kiln and not the cleanup of the effluent gases in the downstream pollution control equipment, although the latter is equally important and essential to the viability of all incineration. What happens in the kiln? In this dissertation, the essential variables and parameters in kiln operation are examined and interpreted in the light of empirical data. Mass and energy balances from pilot plant operation provide a basis for further research. Future revisions and improvements for the Louisiana State University (LSU) RKI are proposed.

1.1.2 Hazardous Waste Incineration-Background

The material abundance of modern life in the United States, in the form of food, clothing, and shelter is the product of an agricultural and industrial complex, which pours forth a cornucopia of substances and articles that nourish, sustain and enrich us. Manufacturing plants consume enormous quantities of raw materials and convert them to useful products. There are often, however, unwanted by-products. Among these are gas emissions, let loose into the atmosphere, examples of which are carbon monoxide, nitrogen and sulfur oxides, and many very powerful poisons such as dioxins and furans. There are contaminated water discharges. In addition, great quantities of liquid and solid wastes are produced. The subject of this dissertation is the disposal of these liquids and solids by incineration in rotary kilns.

In the middle of the twentieth century, before the federal government started regulating the discharge of waste materials, the usual practice of the generators of chemical and other hazardous wastes was to get rid of them in the least expensive way possible, often with insufficient regard for contamination of air, water, or land. The popular notion had always been that landfills, rivers, oceans and the atmosphere were large enough reservoirs to absorb the wastes without substantial damage to the environment. More recently, education of the public, promoted by environmentalists who were armed with university research that demonstrated the dangers of pollution, resulted in government legislation and expenditure to attempt correction of the problems. Commercial interests consistently opposed the government regulations, which forced them to spend money to dispose of effluents and often placed them at a competitive disadvantage.

Today, it is a widely held opinion that laws such as the Resource Recovery and Conservation Act (RCRA) and other air, water, and land pollution control laws are necessary controls. These laws are administered by the United States Environmental Protection Agency (EPA). In addition to the federal agency, each of the fifty state governments has the equivalent of an EPA, charged with local control of waste disposal.

1.1.3 Elements of Rotary Kiln Incineration

The RKI is a chemical reactor especially designed to burn solids, usually wastes that contaminate adsorbents (such as fuller's earth soaked with crude oil from an oil spill, or soil contaminated by liquids or solids in a landfill). Liquid wastes may also be treated either by direct feed to burners or in drums (plastic, fiber or steel). Although rotary kilns are not specifically designed to burn gases, they are used for that purpose in chemical manufacturing plants where advantage can be taken of pollution control equipment associated with a rotary kiln burning other waste.

The incineration of waste materials in a rotary kiln is an extremely complex process involving physical movement of solids, liquids, and gases, in addition to chemical reactions.

The primary oxidation chamber, (POC), is a steel cylinder, lined with refractory brick. The kiln rotates so that the particles of the solid wastes that are fed to it are agitated and tumbled repeatedly as they move through the inclined cylinder. The objective in mixing the solids is to expose surfaces of the waste material to heat from auxiliary burner flames, heat from flames of burning solids, flames from burning organic material (that which is to be destroyed), and to radiant heat from the walls of the kiln as well as heat conducted from the walls of the kiln. The heating results in desorption and evaporation of volatile compounds. The organic material undergoes chemical decomposition by heat and reaction with the oxygen-rich atmosphere of the kiln. Since mixing is not perfect, combustion in the rotary kiln is often incomplete, and carbon monoxide and other products of incomplete combustion (PICs) are substantial components of the product gases. The combustion is completed in a secondary oxidation chamber, (SOC), also called the afterburner. Auxiliary fuel and additional air are used to increase the reaction temperature.

Originally, rotary kiln process incinerators were designed for lime processing. The first to patent a rotary kiln was Frederick Ransom, in 1885 (LaGrega, Buckingham and Evans 1994). Today, rotary kilns are used in the production of lime, Portland and other cements, lightweight aggregate and solids that require very high heat for calcining. Hazardous wastes are often used as fuel in these kilns. The heating value of the waste and payments by the waste generator for disposal are attractive incentives for cement kiln operators. As a consequence, they are in a position to compete with commercial operators of RKIs. Of course, the very-difficult-to-treat wastes are left to the RKI operators.

Rotary equipment is also employed in drying operations, where water or other solvents are desorbed and evaporated from solids by using lower temperatures than in an RKI.

1.2 Rotary Kiln Research at LSU

1.2.1 Combustion Research

A long history of combustion research at LSU that led to investigation of the fundamentals of rotary kiln design was initiated by Mr. Gerry Daigre of Dow Chemical Company. Dr. T. W. Lester, then Chairman of the Mechanical Engineering Department at LSU, was an early Principal Investigator. A research program was planned including in-situ measurements from an industrial-scale kiln, laboratory-scale desorption characterization and kiln-simulator studies, and incinerator modeling efforts. Partial funding was supplied by the EPA through a grant to the Hazardous Waste Research Center directed by Dr. L. J. Thibodeaux (Cundy et al. 1989a).

The first experiments used Dow's industrial-scale rotary kiln incinerator. Pure chemicals, surrogates for hazardous wastes, were injected into the kiln and the effects on temperatures, flows, and destruction of the feed material were measured. The data provided new and useful information about the combustion process. Use of a full size kiln, however, involved scheduling and cost constraints.

The construction of a combustion laboratory with a pilot-scale rotary kiln incinerator was proposed to overcome these difficulties, to provide data at another level for use in scaling studies, and as a teaching facility for the university. Funding was provided in two grants from the Louisiana State Board of Regents, under the

Industrial Ties Program, from the Louisiana Educational Quality Support Fund. Additional monies were donated by the LSU Office of Research, LSU Mechanical and Chemical Engineering Departments, the College of Engineering, and Mr. Ken Hall of Dow Chemical Company.

1.2.2 Donations of Equipment and Enhancements

In the first grant award by the Board of Regents, they recommended that industry support be sought for donations of equipment. A major donation was made by Consertherm Division of Enercon Inc., Elyria, Ohio, a manufacturer of incinerators. Upon dismantling a facility that had been used to demonstrate the suitability of rotary kiln incineration for potential customers, Consertherm donated a complete RKI pilot plant. The equipment included three screw feeders, two combustors, a boiler, pollution control equipment, an ash conveyor, interconnecting ductwork and piping, electrical and instrumentation. This major contribution made possible a larger, more complete combustion laboratory than originally envisioned.

Additional donations of money, material, manpower, engineering, and technical assistance were used for reassembly, renovation and revision of the pilot plant. The principal donors were:

- Albemarle Corporation
- Ciba Geigy
- Doran Iron & Copper Works
- Dow Chemical Company
- Nalco Chemical Company

- Praxair
- Rollins Environmental Services

1.2.3 Components of the Combustion Laboratory

Figure 1.1 is a schematic flow diagram that shows the main elements of the pilot plant. Mercier (1995), in his M. S. thesis gives complete descriptions of the RKI's main components, namely:

1. The BATCH FEEDER is a water-cooled, pneumatically-driven ram with an 8" diameter by 20" long compartment for injecting containers of waste. The unit was designed and built as an LSU senior mechanical engineering project. Mounted on a steel platform, on wheels, the unit has a working mechanism made of 316 stainless steel. It is bolted to the face of the kiln. Each injection involves manual loading of a waste container, and manual initiation of an automatically-controlled cycle. During the cycle a sliding gate opens, a pneumatically-operated ram pushes the container of waste into the kiln, the ram retracts, and the gate closes. Also available at the kiln are three hydraulically-driven, screw feeders for continuous solid feeds to the kiln.

2. The ROTARY KILN, the primary oxidation chamber, (POC), is a refractory-brick-lined, horizontal, steel drum, mounted on rollers. The inside diameter is 31" and the length is 90". The kiln is rotated by a ½ horsepower, reversible, direct current motor, with variable speed drive. The rotating drum is positioned between a front face and the afterburner, both of which are stationary. To prevent leakage of gases to the atmosphere, the kiln operates at a slight vacuum. The vacuum is produced by an induced draft fan that draws the combustion gases through the whole system and

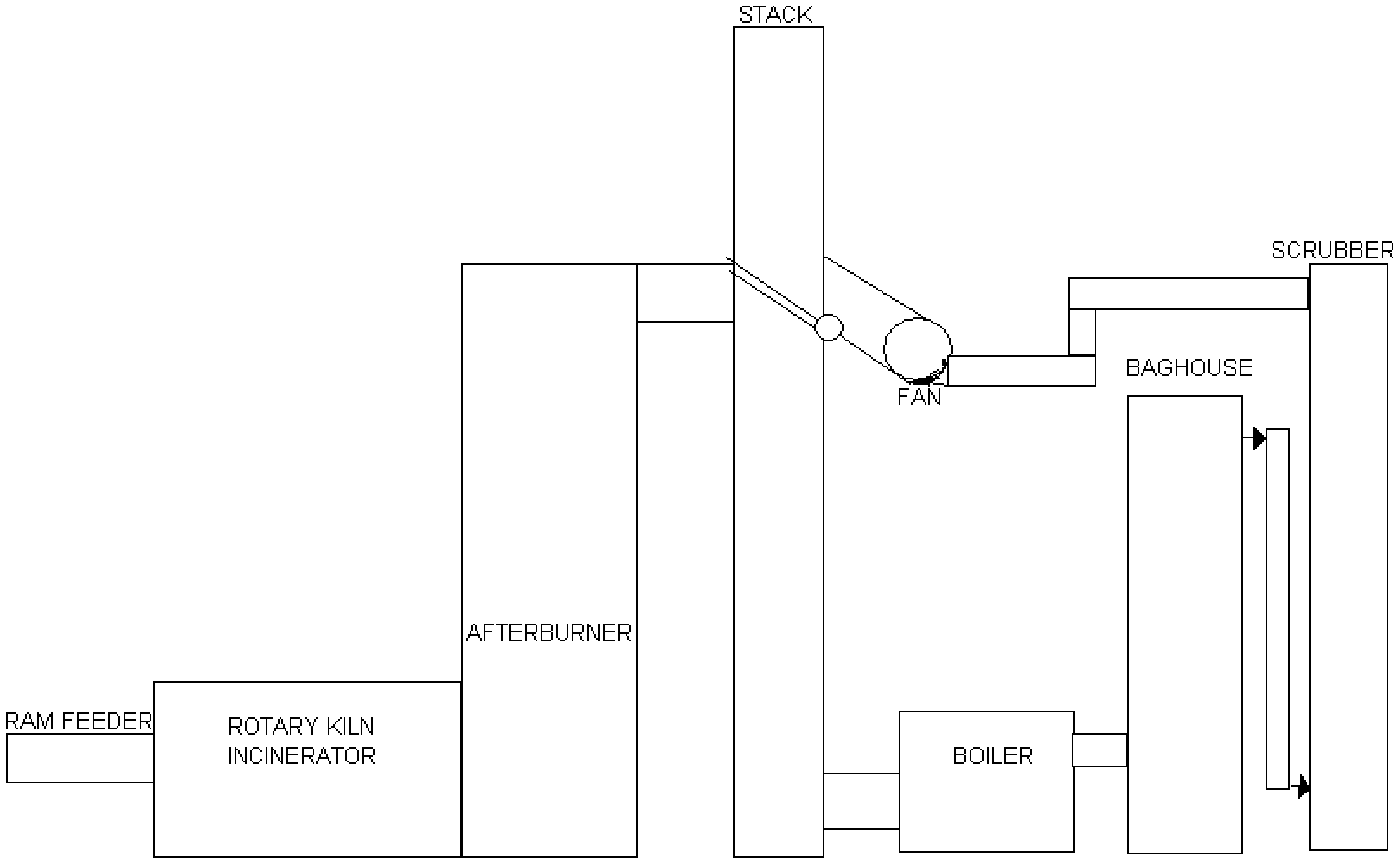


Figure 1.1 Rotary Kiln Incinerator

discharges to the exhaust stack. The rotating surfaces of the kiln are sealed at the front and afterburner stationary surfaces with seals fabricated from thin, flexible segments of stainless steel sheet metal. The front face has a water-cooled jacket.

A 1.2 MM Btu/hr natural gas burner provides heat to bring the interior of the kiln to operating temperature at startup, and to supplement the heat of combustion of the waste if the latter is insufficient to maintain operating temperature. Primary air is mixed with the natural gas fuel in the burner and secondary air can be supplied through a damper in the front of the kiln.

Solids move as a segment along the lower part of the kiln, and are discharged at the end of the kiln, free of volatile matter, into a chute that empties under water in a pit. The gases evolved in the kiln flow to a secondary oxidation chamber, the afterburner, where combustion is completed.

3. The AFTERBURNER, a secondary oxidation chamber, (SOC), is a refractory-brick-lined, vertical, steel, stationary furnace, attached to, and supporting the rotating kiln. A 1.2 MM Btu/hr auxiliary burner heats the incoming gases from the kiln to the normal operating temperature (1800^{o}F). The unit is capable of operating continuously at a temperature of 2200^{o}F. The gases flowing from the kiln pass through the flame of the burner. Secondary air is added by leakage from the seals of the rotary kiln. Additional secondary air can be added by manually adjusting the damper in an air inlet, if sufficient air is not being supplied by the burner. High CO or hydrocarbon levels in the effluent gases, as measured in the stack gas monitoring system, are indications that additional combustion air is required

4. The BOILER (waste heat boiler) is a Scotch marine fire-tube boiler that generates 10-psig steam in cooling the hot gases from the afterburner. The gases enter the tubes at 1800^oF and are cooled to about 275^oF. The cooling is necessary to prevent damage to Nomex filter bags in the next stage. Water feed to the boiler, on the shell side, is deaerated, steam preheated, Baton Rouge city water. Limit switches for high steam pressure and low water level protect the boiler in the event of misoperation. The 10-psig steam generated in the boiler is discharged to the atmosphere. In a full-size plant a very large amount of steam would be generated and would be used as an energy source.

In the ductwork between the boiler and the baghouse there is a damper and an air inlet. The damper is operated automatically, in response to afterburner outlet temperature. The air inlet is opened when the gases exiting the boiler approach the design limits for the filter bags. This allows inflow of cool air, diluting and cooling the combustion gas stream.

5. The BAGHOUSE is a filter containing 25 Nomex bags with a total area of 250 square feet. When particulate matter (soot) builds a cake on the filter bags, differential pressure builds up. In an automatic cycle, based on this differential pressure buildup, plant air is used to blow back the cake. The soot then falls into a hopper at the bottom of the baghouse.

6. The SCRUBBER is a packed tower in which the gases exiting the baghouse flow countercurrent to a weak caustic solution to remove acids or residual particulates. The scrubber system consists of the tower, a recirculation pump, a discharge pump, a

caustic mix tank with agitator, a caustic feed pump, and a wastewater holding tank. The acidity of the contact liquid is monitored by a pH probe in the scrubber bottom. Caustic is added automatically from the mix tank when the pH falls below 7.0, upon signal from the central controls.

7. The INDUCED DRAFT FAN draws the combustion gas from the scrubber and all of the upstream equipment, maintaining vacuum so that gases cannot leak from the upstream components. The fan is constructed of 316 stainless steel and is driven by a 7.5 horsepower, 3500 rpm, motor. The fan discharges the gases to the stack.

8. The exhaust STACK has an internal diameter of 10 inches, is 30 feet tall, and is lined with refractory gunite. The stack is equipped with a damper that in normal operation directs the combustion gases from the afterburner so that they are pulled through the boiler, baghouse and scrubber. If there is a process fault, such as an electrical failure or low boiler water level, the damper is operated automatically to change the flow from the afterburner directly to the stack. In such an emergency, the gases exit the facility without benefit of cleaning or cooling.

A sample of the combustion gas exiting the stack is drawn continuously through electrically heat-traced tubing to a battery of gas analyzers. Continuous records are kept of oxygen, carbon monoxide, carbon dioxide, total hydrocarbons, hydrochloric acid, sulfur oxides, nitrogen oxides and any other substances of interest in a particular experiment. Details of the continuous emission monitoring system of the exhaust gases are covered in Section 1.5.

1.3 Location and Regulation

1.3.1 Location

The RKI is a pilot-scale facility. Its size falls between that of a full-scale commercial incinerator and a typical bench-scale laboratory unit. It occupies an area of about one acre, including 1500 square feet of process area in an open steel structure, and numerous small buildings used as control room, analytical instrument housing and storage. When operating, the heat and carbon dioxide generated in the pilot plant amounts to approximately that which would be evolved from twenty houses or a small apartment building. Because of the size of the equipment, the steam, the stack discharge, and noise of the induced draft fan, it was necessary to locate the RKI away from the center of the main campus. A suitable university space was found at the edge of the campus, nearby the LSU Petroleum Engineering Well Facility and the LSU Hazardous Waste Collection and Storage Building.

1.3.2 Advisory Boards

Two Advisory Boards were formed to assist in establishing the RKI, to focus the research on industry-related problems, and to secure the cooperation of the local community. The Industrial Advisory Board was organized first and consisted of representatives from Ciba Geigy, Consertherm, Dow Chemical, Louisiana Department of Environmental Quality (DEQ), LSU, Praxair, and Rollins Environmental Services. At the suggestion of the Industrial Advisory Board, a Citizens' Advisory Board was formed. It consisted of five local persons known to be active in advocating public involvement in environmental regulation.

On the recommendation of the Citizens' Advisory Board, the project was described at a meeting of the Louisiana Environmental Action Network (LEAN). This was followed by a public presentation to further inform the local community. The public presentation was also a required part of obtaining a necessary permit from DEQ to operate the facility.

1.3.3 Louisiana Department of Environmental Quality

LSU's RKI was classified by the United States Environmental Protection Agency as a facility engaged in "treatability studies". Thus, it required, from the Louisiana DEQ, an Administrative Order, a Small Source Air Quality Permit, and a Water Discharge Permit.

The DEQ Administrative Order details the overall regulation of the RKI. Included were provisions for testing and inspection of equipment, notification of DEQ prior to conducting treatability studies, and monitoring and recording basic operating conditions. In addition, there were specific requirements with respect to safety protection of operating personnel, a contingency plan for emergencies, both written to minimize health hazards or environmental disturbances. The Order also required a closure plan for final disposal of the processing equipment at the end of its authorized use.

The Small Source Air Quality Permit was issued by the DEQ's Air Quality Division. The Permit required that during treatability studies the following be recorded:

- Kiln pressure

- Stack Opacity
- Baghouse maintenance
- Equipment Inspections
- Natural gas flow to kiln and afterburner
- Kiln and afterburner temperatures
- Feed material composition and rates
- Bag filter temperature
- Scrubber water acidity (pH)
- CO and O_2 -concentration in the stack gas, corrected to 7% O_2

The permit places limits on stack effluents, operating conditions, the total annual quantities of surrogate that may be treated, and the total allowable annual operating time. The entire system must be operated under vacuum to prevent fugitive emissions.

Particulate emissions are limited to a maximum of 0.04 grains per dry standard cubic foot (0.1 grams per cubic meter), at 7% O_2. Maximum CO in the stack gas is limited to 100 parts per million by volume.

Minimum oxygen content in the stack gas must be 2% (dry basis). The oxygen analyzer is mounted at the stack and analyzes the moisture-containing (wet) combustion gases. DEQ regulations require reporting on a dry basis, so it is necessary to calculate the adjustment from wet to dry basis.

When operating with feeds, in addition to natural gas, that is, when processing surrogates, a minimum temperature of 1600^0F must be maintained in the afterburner.

HCl emissions are limited to 4 pounds per hour, or emission controls that eliminate 99% of HCl produced must be in operation. The scrubber water acidity must be continuously monitored and maintained above a minimum pH of 7.0.

The facility must operate with 99% destruction and removal efficiency (DRE) of hydrocarbon feeds.

$$DRE = 100\% \times (W_{in} - W_{out}) / W_{in}$$

W_{in} = mass feed rate of POHC (Principal Organic Hazardous Constituent) to the incinerator

W_{out} = mass flow rate of POHC leaving the system (Code of Federal Regulations 1986).

The Engineering Division of DEQ issued a Water Discharge Permit for the RKI. Cooling water from the jacket at the front of the kiln and boiler blowdown are the only permitted discharges from the facility. When the scrubber is in use, its waste water must be collected and then trucked to the LSU or Baton Rouge sewer systems for treatment, or it must be evaporated in the pilot plant. The concern for water quality stems from discharge to an intermittent-flowing stream that empties into Bayou Fountaine, which then flows into Bayou Manchac. These drainage canals contain aquatic life, such as crawfish, minnows and other fish, frogs, turtles, and nutria.

The permit required that samples of water discharged from the RKI be analyzed by an independent laboratory and that reports be submitted to DEQ and Regional EPA offices on a quarterly schedule.

1.4 Control Scheme

Vital to the operation of an RKI is a control method that provides for safe operation of the plant within its process and regulatory specifications. A research facility has numerous additional requirements for measurement and control of process variables and parameters essential to evaluation of the process.

The following material is primarily derived from Vassiliou (1996) who describes the controls supplied by Consertherm and the subsequent additions and improvements made in consultation with Dr. Armando Corripio.

With the RKI equipment, Consertherm donated a Square D programmable logic controller (PLC). The memory of the PLC contained the control program that Consertherm used for their RKI operation. Between the time of decommissioning in Connecticut and construction in Baton Rouge, the control program was lost due to battery failure of the backup memory module. Consertherm had provided a tape backup of the control logic, but Square D could offer only expensive software and hardware solutions to the problems of program downloading and graphical processor emulation. There was also a notable discontinuity in the support for their PLC product line, possibly due to the recent acquisition of Square D by Schneider Electric SA.

To solve the dilemma, Rollins Environmental Services donated an Allen Bradley programmable logic controller with communication hardware and software; and Entergy Corporation donated a computer to be dedicated exclusively to the PLC. The presently configured control program in the Allen Bradley memory module reflects the current RKI requirements and extensive alterations due to the differences in the Allen Bradley and Square D architectures. The conversion and revision required a very thorough study of the control elements and verification of hundreds of panelboard and field wiring connections.

The PLC provides for semiautomatic operation of the RKI. Natural gas flow control and kiln drum revolution speed are, however, not included in the PLC scheme.

Natural gas flow to the kiln and afterburner auxiliary burners is measured by positive displacement meters and displayed on the main panelboard; flow is adjusted manually by means of a proportional-integral controller. With this manner of operation, constant attention to the control of temperatures is required of operators. Future automatic controls will include steady state as well as startup and shutdown gas regulation. Prior to startup, the gas flow valves are set at a beginning rate. No gas can flow, however, until the PLC is activated and a five-minute automatic purge, described below, is completed.

The kiln is rotated by a direct current motor. Adjustment of the speed on starting and stopping is manually controlled so that the operator can be assured that current surges do not overload the direct current motor. In a preliminary step of the startup procedure, kiln rotation controls are set at the desired rate, and kiln rotation is started.

The PLC, by means of limit switches, energizes or de-energizes pumps as required, and also operates alarms or shuts down equipment at the onset of unsafe or undesirable conditions. Among the most important of these functions is to shut down the entire process if the afterburner temperature is excessive or if the boiler water level is low. In such cases, the stack damper opens and the combustion gases are discharged directly to the stack without cooling in the boiler, filtration in the baghouse, or neutralization in the scrubber.

To prevent accidental ignition of a flammable gas mixture that might remain from previous operations, the kiln, afterburner and downstream equipment are purged at the start of a run. On startup (pulling the start button), the following sequential actions are automatic:

- The stack damper is closed, so that flow is directed through the boiler, baghouse, scrubber, fan and stack.
- The induced draft fan is activated.
- A five-minute period follows in which, with the fan drawing air through the kiln and all of the upstream equipment, the equipment is purged of any possibly explosive gases.
- The auxiliary burner of the afterburner is lighted.
- The activation of that burner is confirmed by a flame sensor.
- Upon confirmation that the auxiliary burner of the afterburner is lighted, the kiln auxiliary burner is lighted also. The burner lighting sequence assures that any unburned gases generated in the kiln will be subjected to high heat in the afterburner.

At that point, the operator gradually increases the gas flows to heat the kiln and afterburner to operating temperatures. Slow heating (150 Fahrenheit degrees per hour) is required so that the brick liners of the two combustors will not be damaged by rapid rise in temperature. At the end of a run, the gas flows are also slowly lowered so that the brick cools slowly, and is not overstressed.

1.5 Continuous Emission Monitoring System

A Continuous Emission Monitoring System (CEMS) has been designed and installed in the LSU RKI. The material in this discussion primarily follows a thesis by Muthukrishnan (1997) in which there is a full description of the design, installation, calibration and operation of the gas measurement system for the pilot plant. Direct measurements are made on a continuous basis of the concentrations of gases of interest exiting the stack. In addition to individual analyzers for O_2, CO, CO_2, total hydrocarbons (THC), HCl, NO_x, and SO_x, the CEMS is equipped with a mass spectrometer. The latter provides the capability of detecting and quantifying a wide range of compounds (Wada 2000).

Specific conditions of the Small Source Permit stipulate that the RKI comply with the following emission and equipment standards:

1. Stack O_2 concentrations shall be maintained above 2% by volume on a dry basis.
2. Stack CO concentration shall be maintained at 100 ppmv (parts per million by volume) or less based on a 60-minute rolling average, corrected to 7% O_2 (dry).
3. Particulate concentration in stack gas shall not exceed 0.04 grains per dry SCF (standard cubic foot), corrected to 7% O_2 (dry).

4. Continuous analyzers shall be installed, maintained and calibrated to provide a continuous record of O_2 and CO concentrations in the stack.

The Administrative Order, moreover, requires that the continuous monitoring include continuously sampling the regulated parameters and evaluating the response at least once every 15 seconds and computing and recording the average values once every 60 seconds.

There are two categories of CEMS: Extractive and In-situ. Extractive systems convey a sample of gas from a stack to analyzers, usually located at some distance and housed in a sheltered environment for protection of instruments and personnel from the weather. In this category two designs are used: Fully extractive and Dilution Extractive.

A fully extractive design includes a sample probe, filters, sample tubing which is heated to keep the sample at a temperature above its dew point, a cooler, or other device to remove water vapor and thereby to provide a sample of dry gas, analytical equipment for continuous monitoring, and recording apparatus.

In dilution extractive systems clean, dry, instrument air (often 50 to 250 times the sample volume) is added to the sample at or near the sample probe. The dilution air acts to reduce the water vapor concentration in the gas, which might otherwise condense, and in liquid form dissolve water-soluble components of the gas. Sample handling is simplified since it is unnecessary to heat the transport tubing to prevent condensation. The large amount of dilution, however, greatly reduces the concentration of gases of interest and thus the accuracy of the analyses. Coal-fired boilers, pulp and paper mills, sugar refineries and other plants with large amounts of particulates are typical installations that use dilution extractive systems.

Insitu systems monitor the sample at the source and except for filtering to remove particulates do not require conditioning and do not involve transport. The analytical results are on a wet basis. Since the regulations specify dry basis, calculations to convert to dry basis are necessary to determine compliance with DEQ requirements.

The RKI CEMS has an insitu oxygen analyzer and a fully extractive system for the other analyzers and the mass spectrometer. The LSU installation includes a silicon carbide sample probe which was purchased with the oxygen analyzer, a filter, a zirconium oxide oxygen analyzer, electrically-heated stainless steel tubing for transporting the wet sample, a vacuum pump, a Nafion dryer to remove water vapor, a conditioned (dry) sample header, analyzers for CO, CO_2, HCl, NOx and SOx, and a mass spectrometer. The tubing is heat-traced to maintain the temperature above the dew point, since the stack gas at 170°F is saturated with water (40% by volume). A dry sample is required for the analyzers and mass spectrometer. The Nafion dryer is used to remove the water.

Nafion is a copolymer of Teflon and perfluoro 3-6-dioxa-4-methyl-7-octene sulfonic acid (Dupont, Inc.). The sulfonic acid group has a high degree of water of hydration and can absorb up to 13 molecules of water per sulfonic group in the copolymer. Nafion is highly selective to water and removes the water from the sample in the gas phase without affecting the other components. The dryer consists of a bundle of 200 Nafion tubes (.03 inch od x .023 inch id) by 15 inches long in a heat exchanger-like configuration. The wet gas, moving through the inside of the tubes, loses water to the Nafion and dry gas is discharged to the sample header. A purge of instrument air flows on the outside of the tubes, removing water from the Nafion.

The output signals from the analyzers are transmitted to the Data Acquisition System, where they are digitized, displayed on the computer monitor and recorded every 30 seconds. The mass spectrometer has a separate data acquisition system and computer. A future improvement would be increased computer hardware and software so that data from the mass spectrometer can be transmitted to the main data base with the aim of integrating on-line information with process control.

The requirements of the Small Source Permit were met in tests conducted while burning natural gas. These tests were conducted specifically to qualify the in-situ oxygen analyzer, the fully extractive sample system and the analyzer for CO. The permit specifies only visual inspection for opacity (by a trained observer). In the recommendations for future improvements, the installation of a laser back-scattering or other opacity meter is included.

1.6 Data Acquisition System (DAQ)

1.6.1 Labview

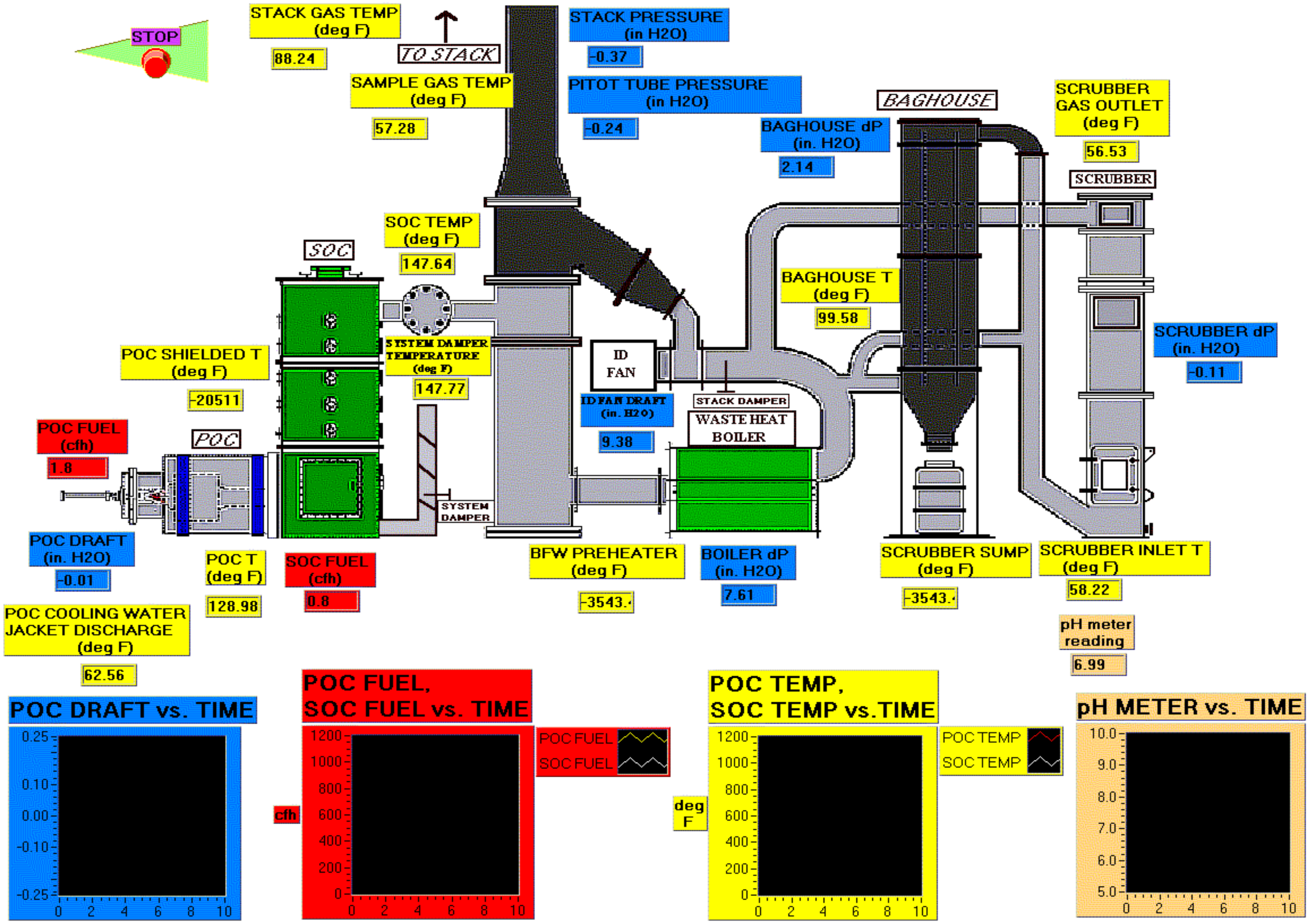
Absolutely essential to RKI research is a good data acquisition, display and recording system, not only for adjusting operating conditions during experimental runs, but also for retrieval of data for subsequent analysis. A computer-operated National Instruments, Inc. (Labview) software program was adapted to the needs of the RKI, and together with signal-conditioning modules (also from National Instruments), was installed in the RKI. The basis for much of the following writing on this subject is due to Prawiro (1999), who in consultation with Dr. Armando Corripio, designed the system, which continuously collects, displays and records process data.

Process data such as temperatures, pressures, flow rates and analyses of gases, must be continuously displayed and recorded at short time intervals for efficient and safe operation of the facility, to provide data for analysis (research), and to satisfy regulatory requirements.

1.6.2 Flowsheet Display

Before the advent of electronic computers, manufacturing plants were equipped with large panelboards on which process data were displayed and recorded in individual instruments. Consertherm supplied such a panel with the RKI. The current system, however, is up-to-date and includes computer monitor screen display of the process data in a flowsheet form, computer software with spreadsheet and graphical programs, hardware with signal conditioning and input/output boards, and DAQ software.

Computer capacity was an important consideration in designing the DAQ as the data collected for analysis requires a large amount of space. Display of process data in flowsheet form required a large computer monitor screen. The National Instruments' Labview program provided strong technical support, easy interface with other programs such as Microsoft Excel, and was user-friendly. Figure 1.2 is the computer screen display for the process. All of the most important temperatures,



STACK GAS TEMP (deg F) 88.24

SAMPLE GAS TEMP (deg F) 57.28

STACK PRESSURE (in H2O) -0.37

PITOT TUBE PRESSURE (in H2O) -0.24

BAGHOUSE dP (in. H2O) 2.14

SCRUBBER GAS OUTLET (deg F) 56.53

SOC TEMP (deg F) 147.64

BAGHOUSE T (deg F) 99.58

SYSTEM DAMPER TEMPERATURE (deg F) 147.77

POC SHIELDED T (deg F) -20511

SCRUBBER dP (in. H2O) -0.11

ID FAN DRAFT (in. H2O) 9.38

POC FUEL (cfh) 1.8

POC DRAFT (in. H2O) -0.01

POC T (deg F) 128.98

SOC FUEL (cfh) 0.8

BFW PREHEATER (deg F) -3543.

BOILER dP (in. H2O) 7.61

SCRUBBER SUMP (deg F) -3543.

SCRUBBER INLET T (deg F) 58.22

pH meter reading 6.99

POC COOLING WATER JACKET DISCHARGE (deg F) 62.56

Figure 1.2 Computer Flowsheet Display

pressures and flow rates are shown on this screen and are simultaneously recorded in an Excel program.

Although the instrumentation and ladder logic supplied with the RKI by Consertherm served very well for that company's determinations of waste incinerability, advances in control systems and the more elaborate instrumentation necessary in a teaching and research facility require automatic process control. Looking to the future, as a first step, the ladder logic would be transferred to the DAQ computer, and it would then be the basis for automatic control of RKI operation.

Figure 1.3 is a second, auxiliary display on which the O_2, CO, CO_2, HCl, THC, NOx and SOx readings are shown as they are relayed from the individual analytical instruments.

1.6.3 Recording

The mass spectrometer data logging system is not compatible with the DAQ in that language differences prevent transmission of mass spectrometer data to the DAQ. Correction of this deficiency is a much-to-be-desired improvement, both for data analysis and for a future digitized, automatic control system.

A 54-second time interval between recordings of individual data points leads to an incomplete log, and the missing data are often vital to establishing maxima, minima, or trends. Considerable effort was made to shorten the time interval. Program size was first thought to be the source of the problem. The program was shortened, without avail (Wight 1999). Additional RAM was added to the DAQ computer, again without success. A program that converted the DAQ program into an executable file

Figure 1.3 Computer Analytical Data Display

did not improve the cycling time. The difficulty was finally traced to the DAQ hardware, where noise-filter frequency can be adjusted. Unfortunately, there are only two available settings for the low pass filter, 4 Hz or 4 kHz. At 4 Hz more signal noise is eliminated, but a waiting time of one second is required while the signal settles down (National Instruments 1995). With so many channels to monitor, the length of time between recordings necessarily increases. At 4 kHz, the system has a faster scan rate but the signal is excessively noisy.

The solution to the problem is in digital filtering, which is provided in a Labview Professional Development package. In Chapter 6 of this dissertation, acquisition of this enhancement is recommended.

Complete details are available in the M. S. thesis “The Design of a Data Acquisition (DAQ) System for a Rotary Kiln Incinerator” (Prawiro 1997).

When the kiln is in operation, the data being recorded cannot be accessed for analysis. Thus, it is necessary to wait until the end of a run to fully analyze the data. Addition of Dynamic Data Exchange, a Labview programming change would solve this problem. Such a change is listed in Chapter 6.

CHAPTER 2 LITERATURE REVIEW

This literature survey is a review of previous research directed at understanding the basic processes of rotary kiln incineration. In the first section, suggestions for possible improvements are sought in studies of similar equipment (cement kilns, rotary driers), as well as RKIs. The second section covers investigations by LSU researchers that expanded knowledge about actual internal conditions in full-size industrial kilns. The third part of this chapter deals with numerous pilot plant studies, mostly conducted by the University of Utah and by the EPA. The final section of this chapter covers research about kiln operations that relate to the areas of concern of the public discussed in Chapter 1.

The results of studies at the LSU pilot-scale RKI are the subjects of Chapters 3, 4, 5, and 6. Chapter 3 is based on routine pilot plant data used to calculate material and heat balances. These basic presentations are based on the overall reliability of data collected during operation of the RKI. Batch trials are the subject of Chapter 4, which emphasizes the similarity of operation between pilot-scale and full-scale RKIs. Incinerability of still bottoms and recovery of byproduct potash are described in the first section of Chapter 5. Also part of Chapter 5, although not RKI research, the analytical equipment at the laboratory was used to evaluate emissions from synthetic firelogs made of wood refuse and soybean wax. Stack emission tests were conducted using a remote-sensing, portable, optical gas detector. Chapter 6 covers recommendations, fee calculations and a discussion of future prospects. Chapter 7 summarizes conclusions.

2.1 Studies of Cement Kilns, Rotary Dryers, and RKIs

The rotary kiln incinerator is also called a primary oxidation chamber; since in the incineration process, organic wastes are evaporated and oxidized when exposed to high temperatures and oxygen in air. It might also be referred to as a desorber; since the primary duty of the device is to separate contaminants from the solids, thus making the solids inert. Another classification for an RKI would be mixer. Mixing is not an easy operation, even for liquids or gases. The resort to movement of the container, that is, rotation of the kiln, is indicative of the difficulty of mixing solids. It is necessary to tumble, agitate and vibrate the solid particles so that the surfaces are exposed to heat. The RKI is also properly called a chemical reactor; since it is equipment in which chemical reactions take place. Incineration, then, is a unit process, a term used by early chemical engineers in calling attention to chemical engineering as: Chemical Engineering = Unit Processes (Chemical Changes) + Unit Operations (Physical Changes). This definition was used by Shreve (1945), and it is noteworthy that in his list of 25 unit processes, Combustion is first and Oxidation is second. It is also interesting that Shreve defines combustion as “completed oxidation”.

The basis for design of rotary kiln incinerators has evolved from experience with cement kilns, lime kilns, and similar equipment. In these process vessels, solids undergo mixing and heating to high temperatures for a multitude of purposes such as driving off water of hydration or carbon dioxide, oxidation or reduction, production of alumina or recovery of metals from ores, and so on. In addition, much useful background information comes from design of rotary dryers, which usually operate at much lower temperatures than RKIs. Another source of knowledge is industrial furnace and boiler performance. Combustion research has made great contributions to this practical material. The complexity of RKI systems, however, has been a roadblock to finding the controlling mechanisms of mass and energy transfer peculiar to the specialized processing functions of these waste burners. At present, an RKI is designed with much engineering company in-house information and with rules-of-thumb and experience of the manufacturer included.

The information from cement kiln and rotary dryer research is almost entirely related to specific processes where generalizations based on fundamental physical and chemical processes are hidden in empirical data. The emphasis is on the essential, available data that relate design details such as size of equipment or energy quantities to production rates.

Toward the end of the nineteenth century, when the first rotary cement kilns were built, they were 18 inches in diameter and 15 feet long (Peray and Waddell 1972). Sizes now range up to 18 feet in diameter and 600 feet long. Feed preparation is a major concern in the manufacture of cement. Diverse ingredients such as limestone, sand, shale, and clay must be weighed and blended, sometimes wetted and/or pelletized, and fed at a constant rate to the kiln. Flow of solids and gases may be countercurrent or cocurrent. There are four process zones in the kiln: dehydration, calcination, clinkerizing and cooling. Cement kilns operate with about 5 percent excess air, so that oxygen content of the flue gases is between 0.7 and 1.5 percent. The temperatures and reactions are shown in Table 2.1.

Table 2.1 Cement Kiln Temperatures and Reactions

Temperature (^{o}F)	Reaction
212	Evaporation of free water
930+	Evaporation of combined water from the clay
1480+	Evolution of CO_2 from limestone ($CaCO_3$), start of calcination
1470-1650	Formation of dicalcium silicate ($2CaO.SiO_2$)
2000-2200	Formation of tricalcium aluminate ($3CaO.Al_2O_3$), and tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$)
2300-2650	Formation of tricalcium silicate ($3CaO.SiO_2$), with progressive disappearance of free lime (CaO)

Peray provides valuable explanations of methods of raw material preparation and explains adjusting material feed rates, air rates, fuel rates, and rotation speeds while maintaining temperature control at the several required levels. His book is a training manual for operators, teaching operating and maintenance procedures, and the basics of automatic control. It also has an extensive section on handling emergencies.

Cement kilns frequently use hazardous wastes as fuel, since many chemical wastes have heat content of the order of 10,000 Btu per pound (Santoleri, Reynolds and Theodore 2000). Flow of solids is usually countercurrent to the combustion gases which heat the solid material. More efficient heat transfer is obtained in this manner. Typical kiln data are given as:

Gas temperature in the burning zone: 4000 °F;

Clinker temperature in the burning zone: 2700 °F;

Gas residence time: 10 seconds;

Solids residence time: 2-3 hours.

The temperature of the zone of injection, and the residence time at temperature, are critical to destruction of waste. If it is liquid, the waste can be blended with the regular fuel, or it can be injected separately into the burner flame.

Solids may not be fed at the cold end of the kiln with the incoming cold raw material where volatile organic compounds would contaminate the exiting gases, and they may not be fed at the hot end where they could produce reducing conditions, which adversely affect cement quality. In the latter case, cement would have lower strength, stability, setup time, and color. In the reducing atmosphere, tetra calcium aluminoferrite does not form, the Fe_2O_3 being reduced to FeO, producing a lower strength, quick-setting cement.

Solids in drums are introduced to kilns in the calcining zone with a hatch in the rotating kiln wall, but the amount must be carefully regulated so that oxygen is not depleted, causing a reducing atmosphere. Another method of feeding hazardous waste is by injecting it in containers using an air cannon, which propels the waste containers into the calcining zone.

Lightweight aggregate is made from clay, shale or slate, and is a component of building materials. When combined with cement it produces a lightweight concrete used either as thermal insulation or for structural purposes. The hazardous waste usually fed to lightweight aggregate kilns is normally injected as the only fuel.

Calcination of minerals or other substances, often involves drying, reheating, and subsequent cooling (Bauer 1954). Heat is absorbed in dissociation of the mineral and in this endothermic process, particle size and density are of prime importance. “A calcining particle acts somewhat like a sponge with heat being conducted from the surface inward. Heat is absorbed by the dissociation front which slowly sinks toward the particle center." Inside this front the material has not yet been brought to dissociation temperature and pressure. When dissociation is completed, the endothermic process is concluded and the particle temperature rises. Often the calcining occurs at two temperature levels (250 °F and 450 °F, for gypsum or 1000 °F and 2500 °F for bauxite).

Bauer lists factors that influence efficiency of heat utilization as kiln geometry, material loads, flame lengths and shape, flow pattern of secondary air entering the kiln, and location and direction of fuel and air streams with respect to kiln axis.

The bed of material being treated can be subjected to a reducing atmosphere by positioning the fuel burner near the bottom of the kiln, pointed up and introducing secondary air above it. On the other hand, an oxidizing atmosphere will be in contact with the bed if the burner is positioned high and pointed low, with the secondary air admitted at the bottom of the kiln.

Bauer states "stratification of gases in a rotary kiln is much more pronounced than commonly realized." While this condition may be wasteful of fuel (unburned combustibles flowing downstream from the combustion zone), the lack of perfect mixing may prevent temperatures from rising too high for most calcining operations.

Although usually operated at much lower temperatures than RKIs, rotary dryers are also rotating, cylindrical, solids mixers. Drying is defined as a process in which bound and/or unbound volatile substances are removed from solids (Yliniemi

1999). Her thesis explores heat transfer to the solids and to the volatile matter, and mass transfer of the volatile matter, as a liquid or as a vapor within the solid pores, and as a vapor from the surface. For dryers, operating at lower temperatures than RKIs, heat transfer is mostly by convection, which is much more important than conduction or radiation heat transfer. Yliniemi points out that although evaporation from the surface is essential to drying, knowledge of the phenomena that take place inside the solid is of assistance in design. Consideration is given to the following three modes of transport of volatiles in the pores of a solid: 1. Movement resulting from a concentration difference of the volatiles in liquid form; 2. With only liquid existing in the pores of the solid, flow is due to liquid-solid attraction (capillary action); 3. Movement of volatiles in the pores is in the vapor phase.

Evolution of adsorbed compounds, related to movement in the pores, is a subject that receives special attention in chemical engineering as it deals directly with processes in which solid catalysts are used to promote chemical reactions, and packing made from porous pellets that are used in distillation and absorption columns. It is of great interest to petroleum producers who are concerned with underground movement of water and petroleum.

A dynamic model, based on heat transfer (by convection, conduction is not included), and mass transfer was developed by Yliniemi. The dryer is a distributed parameter system, with moisture and temperature both functions of distance and time:

$$\frac{\partial Xi(l,t)}{\partial t} = Vi(t)\frac{\partial Xi(l,t)}{\partial l} = fi(Xi,l,t) = -Rw$$

Xi = moisture in solids phase, kg H_2O/kg solids

Vi = linear velocity of solids phase, meter/second

l = axial distance, meter

t = time, second

Rw=drying rate, (kg H_2O/kg solids)/second

The distributed model was described as complex, and it was therefore simplified to a lumped parameter model in which the partial derivative of the length is replaced by the length of the drum, resulting in:

$$\frac{dXs,out}{dt}+Vs\frac{(Xs,out-Xs,in)}{L}=-Rw$$

Xs = solids moisture, kg H_2O/kg solids

The rotary dryer model developed in Yliniemi's thesis accounted for:

1. Solids particle size and shape, density, and solvent content;
2. Diameter and length of drum;
3. Operating conditions, including temperature and flow rate of feed, temperature and flow rate of heating gases, and slope and rotation rate of the drum.

The model applied only to the particular pilot plant kiln considered by Yliniemi in that it includes values of parameters determined experimentally in that kiln as well as some found in literature on the subject of drying. The researchers cited are Duchesne, Thibault and Babin (1997), and Sharples, Glikin and Warne (1964).

Recent innovations in the field of drying were reviewed (Kudra and Mujumdar 2002). Their early paragraphs could be written for RKI's simply by substituting rotary kiln incinerator for dryer. The fact is, drying technology and RKI technology are primitive when compared with many processes and operations that have received the concentrated attention of the chemical process industry. In this book, Kudra and Mujumdar placed emphasis on intensification of drying rates and multistaging of convective dryers.

In discussing intensification, focus is on impinging flow configuration as opposed to parallel flow configuration when removing surface moisture. Gas-solid suspensions provide higher heat transfer rates than single-phase flow. The heat transfer rate is two to three times higher for impinging gas–particle flows than for gas flow alone. Recirculation of fines in spray drying often results in better drying rates. These comments should be seriously considered when proposing new processing methods in rotary kiln incineration.

For rotary dryers, only two innovations are described. The first is pulse drying. Pulse combustion has been proposed for waste incineration but the momentary high pressure, and the consequent possibility of escape of hazardous vapors, is a problem. The second idea is a new configuration of baffles. In the case of an RKI, the high temperatures preclude the use of elaborate baffles.

In 1980, Eastman Kodak Company initiated a destruction and removal efficiency (DRE) and carbon monoxide emissions program for an RKI. In a subsequently published parametric study, the parameters for these tests were reported as temperature of the kiln, air flow, flow of waste materials (including composition and method of feeding), processing time, and kiln rotation rate (Wood 1987). It was stated that the highest increments of DRE are obtained at high temperatures and at considerable cost in processing time. Flame zone processing contributed significantly to successful incineration. Regulating air flow and kiln rotation rate was recommended as a method for coping with variations in heat of combustion of waste. It was claimed that the tests indicate that limits on CO emissions assured proper operation of a kiln.

A trial burn was conducted at the Cincinnati Metropolitan Sewer District hazardous waste incinerator (Gorman and Ananth 1984). The two combustors in the system consisted of an RKI with a rating of 55 million kJ/hr (15,000 kW, 52 million Btu/hr) and a cyclone furnace with a rating of 65 kW. Both were connected to a single combustion chamber that acted as an afterburner, providing additional residence time at 1800^{o}F.for the exit gases from the two furnaces. Two wastes, one classified as pesticide-containing material, the other as a high-chlorine content waste, were separately fed in two series of tests. The first waste contained chloroform, carbon tetrachloride, tetrachloroethylene, hexachloroethane, hexachlorobenzene, and hexachlorocyclopentadiene. The second contained trichloroethane, tetrachloroethane, bromodichloromethane, pentachloroethane, hexachloroethane, and dichlorobenzene. Temperatures of 1650 ^{o}F, 2000 ^{o}F and 2400 ^{o}F and residence times of the gases in the ranges of 1.5 to 2.2 seconds and 3.3 to 3.7 seconds were used in the first series of tests with the pesticide-containing waste. Six runs were made in this first series. In the second series, the temperatures were the same but only three runs at 3.3 to 3.7 seconds of residence time were performed. Compositions and flow rates of input waste feed, auxiliary heating oil, scrubber water, and all effluents, including ash and discharges from all pollution control devices and the stack were recorded.

A 99.99 percent DRE was achieved by the incinerators for all of the wastes except in the case of bromodichloromethane when fired at 1650°F. A demister malfunction was attributed to be the cause of failure to meet the maximum particulate requirement of no more than 180 milligrams per dry standard cubic meter (0.08 grains per standard cubic foot). It was concluded that three replicate tests must be performed for a trial burn. Selection of principal organic hazardous compounds (POHCs), the substance on which DRE was calculated, should consider concentration in the waste, since experience indicated that at least 100 ppm in the waste would be needed to be assured of detection in the stack gas when sampled for two hours.

The Kodak program and other early kiln evaluations provide valuable guidance for RKI design without, however, examining the details of the processing operation. The actual exploration of conditions inside a kiln in full operation, undertaken at LSU in cooperation with Dow Chemical Company and Ciba Geigy Corporation, is the subject of the next section.

2.2 LSU Program of Rotary Kiln Research

As discussed in Chapter 1, a major part of the LSU experimental program undertaken by Lester, Sterling and Cundy, directed toward better understanding of rotary kiln incinerator performance, involved experiments using Dow Chemical Company's kiln. For the first time experiments with a full-size industrial kiln were designed to determine governing principles of RKI design and operation. In the report on the first tests, the overall goals of the program were described as: "developing a rudimentary understanding of, and a predictive capability for rotary kiln and afterburner performance as influenced by basic design and operational parameters" (Cundy et al. 1989a).

The Dow rotary kiln has an internal diameter of 3.2 meters and a length of 10.7 meters. It is equipped with three burners and has a design capability of 17,270 kW (60 million Btu/hr), with an outlet temperature of 800°C. Two swizzle nozzles are installed on the inlet end of the kiln to provide turbulence air. The combustion gases exit to a transition section and then to an afterburner with a design capability of 7030 kW (24 million Btu/hr), with an outlet temperature of 1000°C. Residence time of the gases in the afterburner is 2 seconds minimum.

No solids were fed in the first trials in the Dow kiln, but liquid carbon tetrachloride was injected as a surrogate for waste. Water-cooled probes were used to sample gases and to make temperature measurements at the kiln exit and afterburner.

A fuel-rich combustion zone would result from measured input air and fuel. However, in-leakage of air at kiln seals, and at the hydraulic ram pack feed inlet, raised oxygen levels to between 8-12 percent in the stack gas. A lack of complete mixing was detected in the gases exiting the rotating kiln as evidenced by low temperature and high oxygen content of gases in the lower region of the kiln. Addition of turbulence air gave added confirmation that the gases in the kiln were not well mixed. It was concluded that single-point measurements in the kiln could not be relied upon to define DREs for hazardous waste. It was also stated that the results of the experiments should not be taken to apply generally to other rotary kilns. At this point, a start had been made in delving into the undefined and unknown conditions in a kiln.

A second set of experiments, also with liquid carbon tetrachloride as surrogate, confirmed the vertical-plane non-uniformities in composition and temperature in the exit of the kiln (Cundy et al. 1989b). As pointed out in the notes on the first experiments, the kiln is equipped with two air inlet nozzles to supply swirling turbulence air. Turbulence air increases the mixing of gases in the kiln, but it also, overall, reduces temperatures. In consequence, oxidation of the waste in the kiln is less complete than when operating without turbulence air. This condition adds to the duty of the afterburner, where complete oxidation must be achieved. The complexity of the process demonstrated the need for correct fluid flow and heat transfer models as preliminary steps in progress toward the final goal of predictive capability.

In the third set of experiments in the Dow kiln, again with liquid carbon tetrachloride as surrogate, the non-uniformities observed previously were confirmed and were shown to persist beyond the transition section and into the afterburner (Cundy et al.1989c). Satisfactory DREs were achieved in the afterburner at all times in spite of incomplete oxidation in the kiln.

The first three sets of experiments were conducted during steady state operation of the kiln, that is, feed rates, air rates, and other variances held steady during sampling periods (Sterling and Montestruc 1989). Mass flow, heat transfer, and chemical reactions continued apace, but the time-averaged rates were essentially constant. In this steady flow, the interior of the kiln was characterized by roaring, luminous flames and violent (turbulent) mixing of air, feed and combustion gases.

Essentially, however, conditions were stable, as measured by pressure, temperature and gas composition at various locations.

Feed to RKIs is often in batch form using fiber drums containing liquids or liquids adsorbed on solids or any type of combustible material. On entering the kiln, the drum is heated rapidly, causing its walls to weaken and disintegrate. The contents are then spilled onto the red-hot surfaces of the kiln. When a drum bursts, all semblance of order seems to be lost. Visibility is partially or totally obscured by clouds of soot and other products of incomplete combustion (PICs). Obtaining meaningful data in this situation is a daunting task.

Batch feeding of toluene in the Dow kiln was conducted in the fourth of the experiments (Cundy et al.1989d), (Lester et al.1990). The LSU researchers recorded the evolution of toluene and the transients in gas compositions and temperatures. The repeatability of measurements of temperatures and gas compositions was demonstrated. Each pack of toluene produced two substantial soot clouds. The intermittent release of hydrocarbons that produced the soot clouds was interpreted as resulting from the combined effects of bed motion, container breakup, and heat transfer.

These excursions or transients in temperature and composition of kiln gases, termed “puffs” by incinerator operators, are accompanied by pressure increases. A possible consequence is overpressure of the kiln with potential damage to the brick lining or the shell, leakage of hazardous materials to the surroundings and, in the extreme, injury to personnel. In the usual case, however, the most serious effect of a puff is the incomplete oxidation of the organic material, both the kiln and the afterburner being overloaded. Products of incomplete combustion are then likely to be discharged to the atmosphere.

Environmental Protection Agency researchers have given considerable attention to minimization of these transient puffs. Some of their publications are presented in Section 2.3.

Xylene/sorbent packs were used for a further study of exit conditions in the Dow kiln (Cundy et al.1991a). Oxygen, carbon dioxide, carbon monoxide, total hydrocarbons and temperatures were continuously recorded from two locations near the exit of the kiln while batch loading single plastic packs approximately every ten minutes. Operation was at two rotation rates and with/without turbulent air. The two sampling locations were the same as in the earlier experiments with continuous carbon tetrachloride injection. Two separate days of operation were required to access the two locations. It was shown that excursions in kiln conditions correlate well with bursting behavior (macro-scale motion) and not the micro-motion associated with homogeneous bed slumping. It was acknowledged that the integrated evolution characteristics of field and pilot scale matched well.

The same field data from the Dow kiln and pilot scale data from the University of Utah demonstrate that integrated analysis may be used to smooth the data and that indeed they are comparable (Lester et al. 1991). Analysis of the flow data would have been more straightforward if it were not for the previously reported gradients in composition and temperature in the upper and lower parts of the kiln. The solution adopted was to treat the total molar flow as “a superposition of two well-mixed plug flows”. Weighting factors based on CO_2 in the upper and lower streams were used to apportion the flows. Another method of apportionment of the total flow was use of temperature-weighting factors. The CO_2 and temperature-weighting factors were shown to give much the same results. Very good agreement (CO_2 balance closure) was obtained for operation without turbulence air; with turbulence air there was less success for unknown reasons, although it was suggested that the flow pattern might have altered on introduction of turbulence air. In that case, the two-point measurement provided by the probing may not have been representative of the flow.

Comparing pilot scale data and field scale data revealed that less than adequate carbon balances in the field data and the differences in containment for the packs caused problems. The waste surrogate was inserted in the pilot simulator without a container, whereas the containers used for the field scale were plastic drums with metal rings securing the covers. The plastic drums did not disintegrate until the end of thirty seconds in the kiln. To make the data comparable, the beginning and end of the time periods were each truncated by adoption of an “evolution interval.” By considering the middle 80% of contaminant evolution, the problems were eliminated.

In previous studies (Henein, Brimacombe and Watkinson 1983a, 1983b), bed motion was correlated with fill fraction and a modified Froude number defined as:

$Fr' = Fr(D/d_p)^{**0.5}$

$Fr = \omega^2 D/2g$

D = kiln diameter (m)

g = gravitational acceleration (9.81 m/s^2)

d_p = mean sorbent particle diameter (cm)

The modified Froude number consists of two dimensionless factors: the ratio of centrifugal force to gravitational force exerted on the bed of solids, and the ratio of the kiln diameter to the mean sorbent particle diameter.

Returning to the experiments in the Dow kiln (Lester et al. 1991), modified Froude numbers were used to compare evolution intervals and bed temperatures. Both field-scale and pilot-scale data were plotted at 4.2 cm bed depth and various kiln rotation speeds.

In an overview of the LSU program, a systems approach to incinerator performance analysis and a progress report were presented (Sterling et al. 1990). Data were from the Dow kiln operating with continuous injection or with packs of carbon tetrachloride, toluene, dichloromethane and xylene. Kiln rotation was added as a variation in the experiments with packs, and as before, turbulence air was a variable, on or off. “A remarkable degree of reproducibility from pack to pack was obtained.”

Evolution rates of dichloromethane in the Dow kiln, based on carbon and energy balances, were reported (Cook et al.1992). This analysis confirmed the calculation procedures used previously (Lester et al. 1991) but with the same reconciliation problem operating with turbulence air. Additionally, data such as the effects of rotation rate were provided. This information was very useful in modeling kiln operation and in giving direction to further research.

An investigation of incineration of batch-loaded toluene/sorbent packs in the Dow kiln was presented (Leger et al.1993b and 1993d). Mass balances were determined and evolution rates of toluene were calculated. Rotation rates were varied and operation was with and without turbulence air. Cumulative evolution curves were generated and were stated to be readily fitted to the expression:

$$N\ (C_7\ H_8)\ (t) \ = \ 1\text{-}e^{-t/\tau}$$

N is the normalized evolution rate of toluene. The exponential time constant, τ, represents the time for toluene evolution.

In the LSU program, the first numerical model of RKI operation was presented (Leger et al. 1993c). The 3-dimensional model was based on firing of natural gas only; no waste was fed. The continuity and momentum conservation equations were solved. The kinetic energy of turbulence and its dissipation rate were predicted and then used to solve for Reynold's stresses. Kinetics of methane combustion were included and heat of combustion was incorporated in energy calculations. Radiant heat transfer was not included in this model because of lack of wall temperature data. The Dow kiln was used to provide geometry for the model. In the model, it was divided into 12,240 control volumes, each with dimensions of .21 x .21 x .38 meters. Solution parameters were:

Pressure

X, Y, Z velocities (Cartesian coordinates are used)

Turbulence kinetic energy

Turbulence kinetic energy dissipation

Enthalpies of gases

N_2, O_2, CH_4, CO_2, H_2O concentrations

Plots of vector velocity components and gas temperatures at cross-sections of the kiln were presented, as well as comparisons with experimental data for O_2, CO_2 and temperature. Insight into the processes in the kiln was gained through parametric studies and interpretation of model vs. experimental results. Additional details are available (Leger 1992).

Combustion gas velocities and temperatures in the exit of the Dow kiln were measured using a water-cooled probe (Jakway et al.1995). Tests were made using auxiliary natural gas burners only. Results confirmed that velocities as well as temperatures are highly stratified and that some reverse flow occurs in the kiln. Mass balance calculations provided a check on the experimental data. Additionally, results from the Leger numerical model, described above, compared favorably with these experimental data.

A bi-directional velocity probe was used in a Ciba-Geigy Corporation rotary kiln incinerator to obtain temperature and velocity data (Patton 1995). Vertical stratification in temperature and velocity measurements was similar to the data from the Dow kiln. It was found that the highest temperatures and velocities were at the top of the kiln, indicating that this was the active combustion zone. Such a condition results from the central location of the burner and the natural buoyancy of the hot gases.

Suppression of transient oxygen demand was studied in experiments in the Ciba-Geigy Corporation rotary kiln (Candler 1995). The investigation had the objective of seeking a method of feeding that would reduce puff formation. Four feed modes were used:

1. Combustible powder (waste herbicide) only, in drums;
2. Feed was the same as 1, but the kiln had a bed of sand;
3. Feed was the same as 1, except that a layer of sand was placed in the drum with the powder;
4. Feed was the same as 1, except sand was mixed with the powder in the drum.

The latter two showed a 20% reduction in the peak value of oxygen consumption. Therefore, either could be a potential solution to the problem of feed trip, automatic waste feed cutoff (AWFCO), when the oxygen level was below the regulatory requirement. The cost of special packaging, however, was considered prohibitive.

Alternative solutions were discussed, including:

1. Mixing waste of high heat of combustion with waste of lower Btu content or inert material in a bulk mixing operation prior to drumming. The cost of such a procedure was also considered prohibitive.
2. Operating at lowest possible temperatures. With high waste feed rates, auxiliary gas rates are already at a minimum.
3. Operating at minimum rotating speeds. Some rotation is necessary.
4. Using compartmented containers. Cost would be prohibitive, as for the sand mixing.

A second-generation, 3-dimensional, numerical model, based on LSU's background in combustion research and steady state operation of the Dow kiln, was presented (Jakway et al. 1996). This model included radiation and soot in the heat transfer analysis. An arrangement of 9,826 control volumes in Cartesian coordinates accounted for the cylindrical shape of the kiln and included the rectangular transition zone at the kiln exit. Soot, CO_2, and H_2O in the natural gas flames were taken to be responsible for radiant heat generation. A Damkohler number, chemical reaction rate/ diffusion rate, was evaluated to show that the rate of mixing of gases in the kiln is much slower than reaction. Mixing, therefore, controls the rate of processing. Verification of the validity of the model was based on comparison with experimental data, and sensitivity studies.

2.3 Pilot Plant Investigations

A team of researchers at the University of Utah cooperated with LSU in rotary kiln incinerator research (Lighty et al.1989). A pilot scale (61 cm inside diameter) rotary kiln simulator was constructed to study the essential duty of a kiln, desorption of the organic contaminant from the solid carrier. A feature of the kiln was that the RKI process was simulated, not by movement of solids through the kiln, but by movement of the auxiliary gas flame. This kiln had a burner capacity of 73 kW (250,000 Btu/hr). Performance tests showed that the kiln accurately duplicated RKI processing at full scale.

A classification of the distribution of contaminants was presented (Lighty et al.1989). The volatile substances were classified as "(1) adsorbed onto the internal pore structure of the particles, (2) adsorbed onto the external surface of the particles within a bed, or (3) liquid phase within a bed.” This breakdown simplified the complexity of investigating the processes taking place in a rotary kiln environment by first exploring fundamental transfer phenomena within particles and then within the bulk of solids in the kiln.

In the tests at the University of Utah, in an apparatus constructed for the experiments, combustion gases were passed through 1.3 cm thick beds of porous material contaminated with adsorbed volatile organics. Desorption rates were measured. Movement of volatiles through pores of a particle to the bulk environment were taken to represent desorption from single particles, and thus as intraparticle transfer. Using a different apparatus, beds of particles 5.1 and 7.6 cm thick were heated by a hot surface at the bottom of the beds while a gas purge was passed over the top surfaces. The rate of evolution of volatiles, in this case, was controlled by interparticle transfer, the movement of volatiles between the particles. In experiments with the Utah RKI simulator, the rates of desorption more nearly matched the intraparticle than the interparticle mass transfer rates. Thus, it was concluded that the mixing action of the rotary device reduces the interparticle mass transfer resistance. LSU researchers (Lester et al. 1991) arrived at the same conclusion, that is, intraparticle transfer is controlling. Further research at the University of Utah, with p-xylene as volatile matter and a clay-like soil as adsorbent, was reported (Lighty et al.1990). It was indicated that the result of thermal treatment, that is the amount of contaminant remaining adsorbed on the solid, depends on the final temperature of the solid particles, and thus on the extent to which they are agitated and tumbled to expose them to the heat sources. It was concluded, in this report, that intraparticle mass transfer was not controlling and that particle surface concentration is directly related to gas-phase concentration. Calculations of Knudsen and molecular diffusivities suggest that internal diffusion processes exceed overall evolution rates by several orders of magnitude. Based on gas phase/adsorbed phase equilibrium, a mass transfer/desorption model was presented. Freundlich isotherms at four temperatures were constructed for p-xylene and the clay soil used in these experiments. Good agreement with the model and experimental results was demonstrated. The research carried out at the University of Utah contributed greatly to the models that were subsequently developed at LSU.

The University of Utah RKI simulator was used to investigate bed mixing and heat transfer in a batch-loaded kiln (Leger et al. 1992a). Time constants for bulk heating and mixing were developed from the results of the experiments. Mixing was shown to be important to initial heating of batches. These studies, at 360^0C, did not consider the radiation present in high temperature incineration.

One of the LSU models was for heat transfer in rotary desorbers (Cook 1993). The heat transfer process between the rotating wall of a desorber and the bed of solids was an important feature of the model. Radiant and convective heating were also included in the calculations. Energy balances were used to predict temperatures in a kiln. In experiments performed with the Utah kiln, with water as the volatile matter to wet the solids, particle size, initial moisture content of solids, and rotation rate were varied. Cook describes the solids mixing process in a kiln as “slipping, slumping, rolling or cascading,” depending on the nature of the solids and the rate of revolution. Dynamic angle of repose was discussed. The model predicted, with good accuracy, the progress of water evaporation and the progressive temperatures in the process.

The U. S. Environmental Protection Agency (EPA) also constructed a 73 kW rotary kiln incinerator with the same method of simulation as used at the University of Utah, movement of the burner flame rather than movement of the solids (Linak 1987a). The source of the unusual design is not mentioned in the description of either of the kilns. The EPA kiln was used in this study to investigate transient puffs generated when the kiln was fed batches of plastic rods. Mass and surface area of charge, type of plastic and temperature of operation were independent variables in these tests. Since this particular kiln could be operated without an outlet burner, (the afterburner in a full-size kiln installation), it was possible to follow puff generation from total hydrocarbon measurements in the stack. It was recognized in the report that proper design of the afterburner is critical in handling transient puffs. Increasing kiln temperature actually increased instantaneous puff intensity due to accelerated volatilization rates, even although the total emission of PICs decreased.

An investigation of puff generation in the pilot plant, with liquids adsorbed on corncobs as feed, was reported (Linak 1987b). The parameters in the study were liquid mass, liquid composition, kiln temperature, and kiln rotation speed. The total magnitude and instantaneous intensity of the pollutant puffs leaving the kiln were measured. The liquids were toluene, methylene chloride, carbon tetrachloride and No.

5 fuel oil. Puff intensity was increased with increased mass loading. Increased kiln rotation rates also increased the magnitude of puffs. It was shown that puffs contained toxic secondary combustion products, and that “chlorinated PIC compounds were more likely to be formed when mixtures of dissimilar materials such as toluene and carbon tetrachloride were burned, than when carbon tetrachloride was burned alone.” Toluene was described as a known soot precursor. This fact was also reported in the LSU/Dow experimental results. No single online measurement sufficed to detect all excursions. In most cases, volatile hydrocarbons in the exit gas of the kiln gave an adequate indication of problems. Filter residue (particulate matter, soot) was a superior indicator for toluene. For carbon tetrachloride, CO concentration appeared to be a better indicator.

A subsequent presentation on the same subject (Linak et al.1987c) added that future work could be directed at improvement of the performance of the kiln as an oxidizer. It was pointed out that operating at high temperatures and with good contacting of wastes and heat sources may not be the sought-after solution, since those are the conditions that exacerbate the puffs.

A theoretical model of puff generation from toluene/sorbent packs was presented (Wendt and Linak 1988). The model based toluene evolution on vapor pressure of the contaminant and surface area of the carrier solids. The solids were assumed to fragment with each revolution of the kiln. The model was stated to show promise as a first step in modeling puffs and ranking wastes.

Oxygen enrichment of the flow to the auxiliary burner of the 73 kW EPA RKI simulator was used in experiments to evaluate its effects on puff generation (Linak et al. 1988). Once again, toluene adsorbed on corncob sorbent was used as the waste surrogate. The increase in temperature caused by the oxygen enrichment was detrimental in controlling transient puffs. Moreover, it was stated, oxygen may increase NOx emissions, that also may be especially high with nitrogen-containing wastes. Consideration was given to operating at lower temperatures in the kiln and using oxygen in the afterburner.

Practical methods for minimization of transient puffs were the subject of a report (Lemieux et al. 1990). A model was developed, based on the assumption that the rate of waste evolution is controlling in puff generation, and not the rate at which the evolved gases mix with oxygen-laden kiln gases. Note that in the Jakway model, cited above, with only natural gas burning in a kiln, mixing controls the process, being much slower than reaction. Building on the model of Wendt and Linak, the kiln process was analyzed in two parts: 1. The effect of varying temperature on heat transfer and therefore evolution rate, and 2. The effect of varying kiln rotation speed on breakup of solids, and therefore exposure of surfaces to heat.

Three sets of experiments were considered:

1. Puff magnitude was measured without O_2 addition. Data were from Linak (1987b).
2. Similar, except steady O_2 addition. Data were from Wendt and Linak (1988).

3. Similar, except with pulsed O_2 addition.

For the first test set it was found that the data can be correlated with the following expression:

$$\text{Puff magnitude} = \exp[a + b(\text{rpm}) + c(\text{mass})T + d(T) + e(\text{mass})]$$

Where a, b, c, d and e are constants and T is the kiln temperature.

For the second set, the raw data were adjusted to account for dilution effects, then correlated with:

$$\text{Puff magnitude} = a' + b'(T) + c'(Po_2) + d'(T^2) + e'(Po_2)(T) + f'(Po_2)^2 + g'(F)$$

where a', b' c', d', e', f' and g' are constants, F is flue gas flow rate and Po_2 is the partial pressure of oxygen.

For the third set, the raw data were also adjusted for dilution effects and correlated to a simple linear model in terms of Po_2 and T.

Experiments with EPA-designed, innovative packaging were recounted (Lemieux et al. 1992). As a potential solution for the problem of puff generation that occurs when RKIs are fed in batches, compartmented containers of several different designs were fed to EPA's 73 kW RKI simulator. Segmented cylinders, concentric cylinders and combinations were tried. A theoretical kiln waste release model was developed. The model accurately predicted the smaller transient puffs produced with slower release of waste.

A dimensionless indicator of puff magnitude, Unsatisfied Oxygen Demand (UOD), was developed using time-integrated measurements of carbon monoxide, total hydrocarbons and soot.

$UOD = (XthcMthcWthc + XcoMcoWco + XpMpWp) / (XwasteMwasteWwaste)$. The symbols Xthc, Xco, Xp and Xwaste represent the mass fractions of carbon in total hydrocarbons, carbon monoxide, particulates (soot and non-volatile organics), and waste. Mthc, Mco, and Mp represent the mass emissions of each species, and Mwaste represents the mass of waste fed over the measurement period. Wthc, Wco, Wp, and Wwaste are weighting factors that account for the stoichiometric oxygen demand of each species, so that the UOD represents unburned carbon-containing matter. The UOD was considered an indicator of the relative degree of poor combustion during the time that measurements were made.

An examination was made of potential operating parameters to minimize emissions during rotary kiln emergency safety vent openings (Lemieux et al. (1994). This research was by a joint task force of EPA and Occupational Safety and Health Administration (OSHA) personnel. EPA regulations require that feed to RKIs be cut off automatically when permit regulations of amount of emissions are exceeded or when an emergency such as electrical or water failure occurs. This requirement, AWFCO, takes care of feed not yet fed to the kiln, but it does not address the problem of incompletely treated material in the kiln when the emergency arises.

In the experimental work, charges of 50% toluene and 50% carbon tetrachloride on corncob sorbent were fed in batches to the EPA RKI simulator. Independent variables in the tests were kiln rotation speed, air flow to the kiln, and the presence or absence of a simulated flare. Dependent variables were peak HCl concentration, puff magnitude, and selected organic compounds. Mechanical problems limited the downturn in kiln rotation speed to 0.44 rpm. Air flow could not be lowered as much as desired because of in-leakage and kiln design which would not permit operating with a vacuum of more than 20” of water. HCl in the effluent was shown to be lower with low air flow and with low or no kiln rotation. Puff magnitude was found to be lower with low air flow, and lower with low, but non-zero kiln rpm, but not at zero or high rpm.

It was observed that kiln emissions of PICs (upstream of the afterburner) were about the same during emergency vent openings as they were in normal operation. This was said to result from the higher oxygen levels in the kiln following the vent opening. It was concluded that an in-stack flare, lighted during a safety vent opening, would dramatically reduce organic emissions.

A model of the effect of waste and sorbent properties was proposed based on the primary importance of waste boiling point and waste oxygen requirements (Lemieux et al.1995). This theoretical model incorporated a vaporization/surface renewal approach and predicted puff magnitude. It was concluded, based on the results, that waste boiling point and waste oxygen requirement, are better predictors of puffs, than waste heat of combustion, which is now the usual method of limiting containerized waste feed rates. Resin sorbents are superior in controlling puffs when compared with the corncob and sawdust sorbents used for the model evaluations. It was stated that resins appear to bind solvents in a way that results in burning of the solvent with the solid resin, and that substantial vaporization is not the controlling process. The model, therefore, is not applicable to resin sorbents. In cases where the sorbent is burned, that is, where there is very little ash, the process is quite different than when the ash is a major constituent.

2.4 RKI Operating Parameters

The following were listed as advantages of the RKI in treatment of hazardous waste (Brunner 1996):

1. Able to incinerate a wide variety of waste streams (solids, slurries, sludges, liquids, gases) and several at the same time (Brunner does not mention that the only reason for the unusual shape, compared with other furnaces, and for rotating the cylinder, is to agitate the solid waste, and thus expose the particles to heat and oxygen-bearing gases);
2. Minimal waste preprocessing required, compared with other incinerators;
3. Existing techniques (slagging) for direct disposal of waste in metal drums;
4. Availability of many types of feed mechanisms (ram feeder, screw, gravity feed, direct injection of liquids, sludges, etc.);
5. Easy control of residence time of solid waste and ash in the kiln;
6. High turbulence of the solids and effective contact with air within the kiln. LSU researchers found, however, that considerable stratification in temperature and composition of the gases existed at the exit of the Dow Chemical Company kiln (Cundy et al.1989a).

Disadvantages listed by Brunner are:

1. Relatively high particulate carryover to the gas stream because of turbulence of the waste stream;

2. A separate afterburner is required for the complete destruction of volatiles;
3. Little or no ability to control conditions along the kiln length in a conventional kiln;
4. Relatively high amount of excess air, nominally 100 to 150 percent of stoichiometric;
5. Effective seal is difficult to maintain;
6. A significant amount of heat is lost in the ash discharge;
7. Operation in a slagging mode to process inorganic wastes or metal drums increases kiln maintenance requirements.

Included in Brunner's enumeration of variations in kiln design are parallel flow or counterflow, slagging or nonslagging, and refractory or bare wall. Counterflow is suggested for wastes that have very high moisture content because the steam vapors could snuff out an auxiliary flame. Operation in slagging mode is appropriate for high temperatures that are required to melt drums or to treat some wastes. Bare walls, that is, without refractory brick lining, are suitable for low temperature operation such as in soil remediation. The conventional kiln has a parallel flow system, is nonslagging, and has refractory-lined walls.

2.5 Gaseous Emissions

2.5.1. Nitrogen Oxides

Nitrogen oxide (NO), and nitrogen dioxide (NO_2) are the chief oxides of nitrogen generated in combustion with air; together they are called NOx. Nitrous oxide (N_2O, laughing gas) and nitrogen tetroxide (N_2O_4) are also produced in combustion with air but in much smaller amounts than NO and NO_2. Nitrogen in combustion air and chemically bound nitrogen in waste or auxiliary fuel are the sources of NOx. Usually the nitrogen in waste or fuel is minor.

There are three principal mechanisms for NOx formation: thermal, prompt and fuel (Baukal 2000).

Thermal NOx, formed in the high temperature reaction of oxygen with nitrogen in atmospheric air, is generated by a mechanism first proposed as follows (Zeldovich 1946):

$$\begin{aligned}&O + N_2 \leftrightarrow NO + N\\&N + O_2 \leftrightarrow NO + O\\&N + OH \leftrightarrow NO + H\end{aligned}$$

Temperature is more important than oxygen concentration in the formation of thermal NO_x, and the best practical means of controlling NO is to reduce the combustion gas temperature and to a lesser extent, the oxygen concentration (Glassman 1996). Conversion to NO is minimal below 2000°F and peaks at about 25% excess air Baukal 2000). It is apparent that operating below 2000°F, and with high excess air, as is normal with RKI's, is appropriate. Baukal also considered air preheat and fuel preheat effects on NOx production. Both increase flame temperature and therefore NOx generation. Preheat is important to thermal efficiency in boiler and process furnace operation, but is not a part of usual RKI operation. In cement kilns, high temperature operation is a necessity, and air preheat is essential to fuel economy. Consequently, the cement kiln operator is at a disadvantage in NOx control.

Prompt NOx is a product of secondary mechanisms for NOx formation, by reaction of oxygen, nitrogen and hydrocarbon radicals. These reactions occur in the flame and in the burned gases and are a source of NOx in lower temperature combustion processes. Prompt NOx sources are identified by Glassman (1996):

1. Non-equilibrium O and OH concentrations in the reaction zone and burned gas, which accelerate the rate of formation;
2. Production of HCN as a precursor to CN, NCO and HNCO which lead to N, NH, and NH_2, all of which lead to NO.
3. The reactions:

$$O + N_2 + M \longrightarrow N_2O + M$$

$$N_2O + O \longrightarrow NO + NO$$

These reactions are most important at high excess air, at low temperature and when total NO formation rate is low.

NOx from fuel-bound or waste-bound nitrogen is the result of oxidation of nitrogen in the fuel with HCN as an important intermediate and by tortuous and similar routes to those shown above for prompt NOx.

Injecting water (or steam) into the flame is one method used to reduce flame temperature and thus to reduce NOx formation. Glassman suggests that O radical concentration is also reduced by the "scavenging reaction": $H_2O + O \longrightarrow 2OH$

2.5.2 Sulfur Oxides

The oxides of sulfur are referred to as SO_x. Combustion of waste or fuels containing sulfur compounds has SO_2 as the major sulfur product but SO_3 is usually present as a small percent of SO_2 (Glassman 1996). At low temperatures H_2SO_4 may be present, but above 500°C, H_2SO_4 dissociates into sulfur trioxide and water. Hydrogen sulfide, organic sulfides, organic disulfides and organic thiols may also be present in trace amounts in the kiln outlet. Removal of the sulfur compounds takes place in the downstream air pollution control equipment. Scrubbing with weak caustic solution effectively removes most of the sulfur compounds.

Incomplete removal, allowing escape of even trace quantities of H_2S and mercaptans, can result in odor problems and adverse public relations.

2.5.3 Particulates

The main source of particulates in the kiln exit is in heat-generated soot. A large part originates as an early product of the evolution of volatile organic compounds from the waste material. Upon first encountering the high heat of the kiln, the feed undergoes either “pure or oxidative pyrolysis” (Glassman 1996). For nonaromatic material, the precursors undergo cyclization to form an aromatic ring, which then add alkyl groups and develop into a polynuclear aromatic hydrocarbon (PAH).

These structures can be the nucleus for a soot particle that is not destroyed in the kiln, or, indeed, in the afterburner flame.

The same process occurs in the auxiliary fuel flame and it is beneficial in that soot particles are the main source of radiant heat that is important to heat transfer to the waste and to kiln walls. Much of this soot is subsequently consumed in the kiln flame or in the afterburner.

The air pollution control equipment removes soot with filters (bag houses), electrostatic precipitators (wet or dry) or scrubbers.

In the process, however, soot particles can offer beginning sites for the formation of carbon-hydrogen-oxygen-halogen compounds. Examples are the over 200 dioxin/furan compounds (dioxin = polychlorinated dibenzo-p-dioxin (PCDD) and furan = polychlorinated dibenzo-furan (PCDF). These have been classified as extremely toxic chemicals. It is common experience that a Bunsen flame will smoke until the air is adjusted. In the same way an acetylene flame will smoke when it is first lighted. These phenomena, resulting from lack of oxygen properly mixed with fuel, that is, a fuel-rich flame, indicate that superior performance, less sooting, can be obtained with careful adjustment of primary air to burners.

Another factor is mixing of combustion air with volatile matter as it is evolved from the waste. Addition of extra air, in the form of turbulence air, as employed in the Dow kiln, is a partial solution to the problem of soot generation.

The foregoing review is intended to illustrate that although much is known about hazardous waste combustion in rotary kiln incinerators, much remains to be learned. It is important that the learning continue so that this process be will be improved and made acceptable to all concerned. In the chapters that follow, some of the LSU pilot plant research is described, new data are recorded, and the usefulness of the pilot plant as a research and teaching facility is demonstrated.

CHAPTER 3 MASS AND ENERGY

Basic operations of the LSU RKI pilot plant are presented in this chapter. In the first of the following sections, kiln characteristics are discussed. The heating and oxidation of hazardous waste materials are described and background is provided for mass and material balance presentations. The chapter's main research content covers time constants derived from POC gas rate changes.

3.1 Kiln Characteristics

As discussed in the preceding chapter, the primary objective of RKI processing is to heat the material in order to drive off the volatile fraction. With excess oxygen, oxidation is begun in the kiln and is completed in the afterburner. The essential accomplishment in the kiln, however, is the removal of organics, leaving a 'clean' ash. Since residual amounts of hazardous materials in the ash could be dissolved by groundwater and then escape to the environment, ash must be sampled, analyzed, and recycled if necessary. The ash, usually of much smaller volume than the original waste, can then be disposed of in a landfill. It continues to be classified as hazardous waste (40 CFR 265.300-316). Figure 3.1 is a diagram showing major features of the kiln and afterburner.

The required heat input comes from two sources, which are the auxiliary burners and the heat of combustion of the waste. Auxiliary burners are required to bring the kiln to operating temperature before feeding hazardous waste. If wastes were fed at low kiln temperatures, incomplete removal of organics from ash would result. The vapors evolved at low temperatures would be less completely oxidized

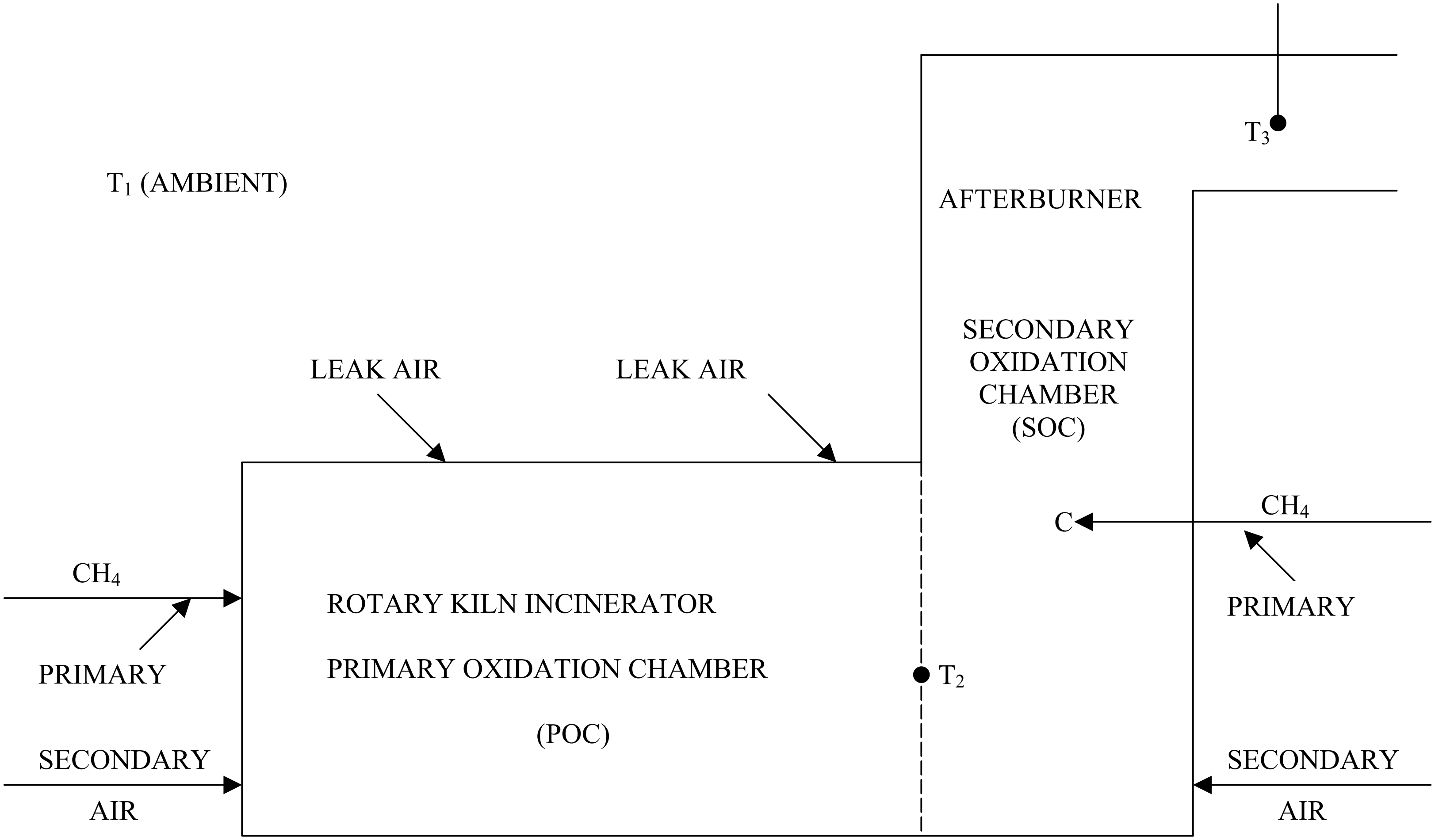


Figure 3.1 Kiln and Afterburner

than in normal operation, when temperatures are high, and in consequence the afterburner would be overloaded. A second function of an auxiliary burner or burners is to supplement the heat provided by the waste. Depending on its chemical makeup and the amount of inert material, a waste may have a low heat of combustion. It may also have very high moisture content. In either of these cases, supplementary heat must be provided to maintain the temperature required for complete removal of moisture and volatile matter.

The heat supplied to the kiln from the heat of combustion of the waste may vary widely. For example, a drum of pure wax would supply heat at 15,000 to 20,000 Btu per pound. A mixture of clay and crude oil (2 to 3% organics) would produce, in the burning of the hydrocarbons, about 500 Btu per pound. If that mixture also contained 10% water, the available heat would be reduced by 100 Btu per pound of mixture required to boil off the water. At 50 percent moisture, the auxiliary burners would necessarily carry the whole load, and be required to supply the heat to evaporate the water and the waste. These numbers show in a general way that auxiliary heating requirements depend very much on the nature of the waste.

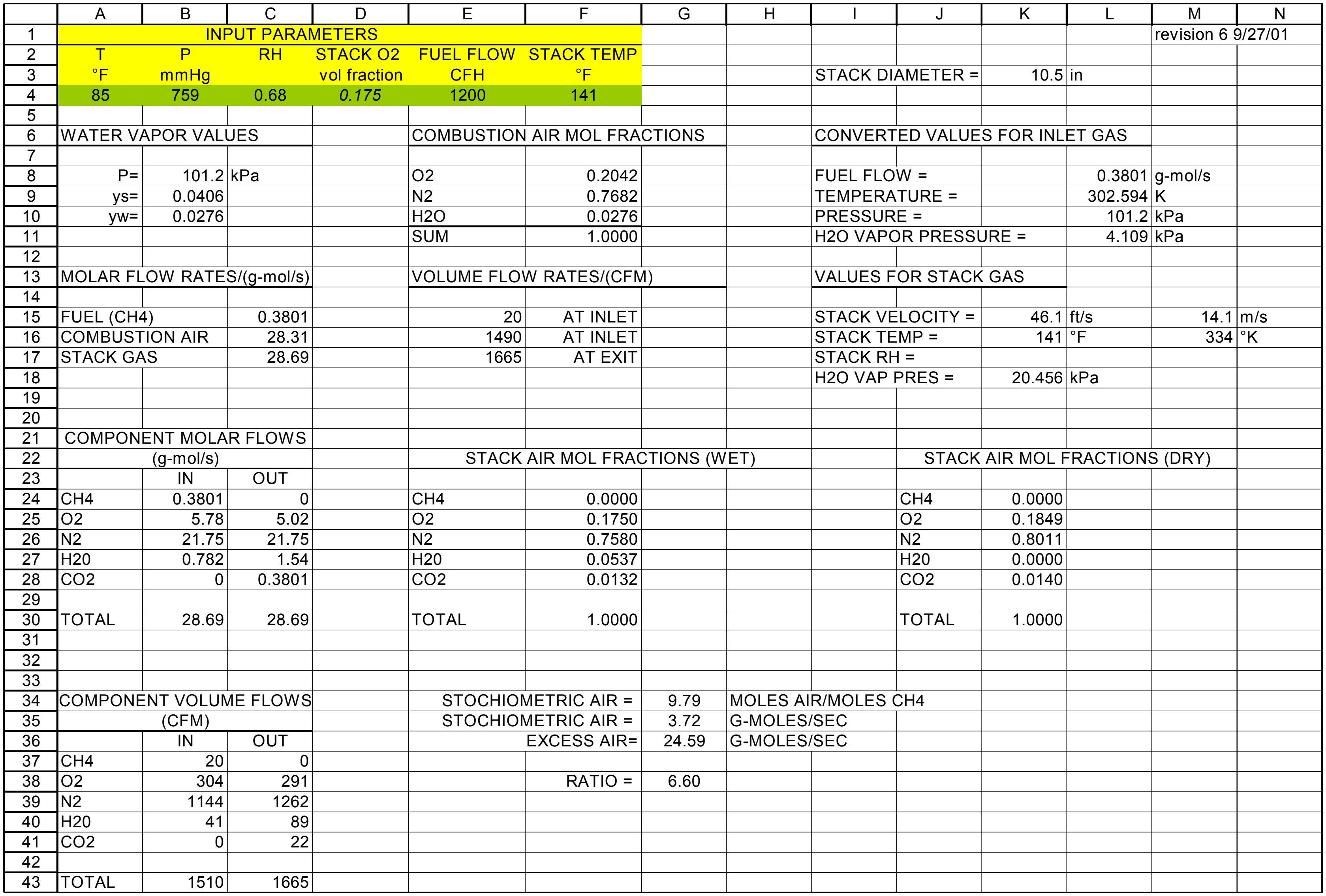
Important variables in rotary kiln operation, therefore, are waste characteristics, feed rate, auxiliary fuel rate, temperatures in the kiln, and the total amount of air entering the kiln. The total air includes primary, secondary and leak air. Primary air is drawn in by natural gas flames assisted by blowers. Secondary air is added if necessary, usually drawn in by the vacuum of the kiln. Leak air enters at loading hatches, kiln seals, and flanged connections of the ductwork and the air pollution control equipment. The total air affects the temperatures in the kiln because air in excess of that required for complete oxidation must be heated along with the products of combustion. Direct measurement of the total amount of air entering the system is nearly impossible because, with the kiln operating at a slight vacuum, the leak sources mentioned above, especially the very large diameter seals on the rotating cylinder, are a major source of air infiltration. This problem is common to all rotary kilns. Every kiln manufacturer has his own seal design, and seals are as important to kilns as they are to pumps or high pressure processing vessels. Knowing the composition of the exit gas, however, permits back-calculation of the total amount of air entering the kiln.

3.2 Mass and Energy Balances

Mass balances for the LSU RKI involve back-calculation of the total amount of air fed to the kiln plus leak air. With a known fuel input rate, it is possible to relate input of fuel to output of carbon dioxide. With known oxygen content of the stack gas, the rate of air input may be calculated. These calculations are based on complete oxidation to carbon dioxide and water of all organic matter fed to the kiln (Rester 1997).

Figure 3.2, on the next page, is a sample calculation of the material balance.

Energy balances are more complex and incorporate calculation of heat transfer coefficients in estimating heat losses. Moreover, the full array of temperatures is not known and must be approximated. Table 3.1 is a breakdown of a heat balance by category.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	INPUT PARAMETERS												revision 6 9/27/01	
2	T	P	RH	STACK O2	FUEL FLOW	STACK TEMP								
3	°F	mmHg		vol fraction	CFH	°F			STACK DIAMETER =		10.5	in		
4	85	759	0.68	*0.175*	1200	141								
5														
6	WATER VAPOR VALUES				COMBUSTION AIR MOL FRACTIONS				CONVERTED VALUES FOR INLET GAS					
7														
8	P=	101.2	kPa		O2	0.2042			FUEL FLOW =			0.3801	g-mol/s	
9	ys=	0.0406			N2	0.7682			TEMPERATURE =			302.594	K	
10	yw=	0.0276			H2O	0.0276			PRESSURE =			101.2	kPa	
11					SUM	1.0000			H2O VAPOR PRESSURE =			4.109	kPa	
12														
13	MOLAR FLOW RATES/(g-mol/s)				VOLUME FLOW RATES/(CFM)				VALUES FOR STACK GAS					
14														
15	FUEL (CH4)		0.3801		20	AT INLET			STACK VELOCITY =	46.1	ft/s		14.1	m/s
16	COMBUSTION AIR		28.31		1490	AT INLET			STACK TEMP =	141	°F		334	°K
17	STACK GAS		28.69		1665	AT EXIT			STACK RH =					
18									H2O VAP PRES =	20.456	kPa			
19														
20														
21	COMPONENT MOLAR FLOWS													
22		(g-mol/s)			STACK AIR MOL FRACTIONS (WET)					STACK AIR MOL FRACTIONS (DRY)				
23		IN	OUT											
24	CH4	0.3801	0		CH4	0.0000				CH4	0.0000			
25	O2	5.78	5.02		O2	0.1750				O2	0.1849			
26	N2	21.75	21.75		N2	0.7580				N2	0.8011			
27	H20	0.782	1.54		H20	0.0537				H20	0.0000			
28	CO2	0	0.3801		CO2	0.0132				CO2	0.0140			
29														
30	TOTAL	28.69	28.69		TOTAL	1.0000				TOTAL	1.0000			
31														
32														
33														
34	COMPONENT VOLUME FLOWS					STOCHIOMETRIC AIR =	9.79	MOLES AIR/MOLES CH4						
35		(CFM)				STOCHIOMETRIC AIR =	3.72	G-MOLES/SEC						
36		IN	OUT			EXCESS AIR=	24.59	G-MOLES/SEC						
37	CH4	20	0											
38	O2	304	291			RATIO =	6.60							
39	N2	1144	1262											
40	H20	41	89											
41	CO2	0	22											
42														
43	TOTAL	1510	1665											

Figure 3.2 Sample Calculation of Material Balance

Table 3.1 Heat Balance Categories

	Btu/hr
Heat Input: methane combustion, lhv=960 Btu/scf	1,170,000
Heat Output:	
POC Cooling Water, 10%	112,000
Kiln and Afterburner Shell Losses, 9%	105,000
Steam Generation, 48%	560,000
Combustion Gases (Stack), 28%	330,000
Total accounted for, 95%	1,107,000

The 95% closure is considered reasonable, based as it is on the uncertain heat transfer coefficients and estimated temperatures.

3.3 Time Constants

The interactions of the auxiliary fuel, air flow, and the temperatures in the kiln and afterburner, are central to the following discussion.

Changes in POC gas flow rate have a greater effect on SOC temperature than changes in SOC gas flow rate. This is a consequence of difference in design of the burners. The POC burner has a fuel to air ratio of 1 to 30 (200 percent excess air) whereas the SOC burner has a fuel to air ratio of 1 to 10 (about stoichiometric). The difference in air ratios results in the POC gas rate being more effective in temperature control of both the kiln and the afterburner. Normally, therefore, SOC gas rate is held steady, and change is by adjusting POC gas flow rate. When waste feed is added to the kiln, the heat content of the waste permits a cutback in the POC gas flow rate. Adding a waste of high heating value can cause a rapid increase in kiln temperature. Because automatic waste feed cut-off, (AWFCO), at high temperature causes a shutdown in production, it is important to have guidance as to the effect of changes in POC gas flow rate. “POC gas flow rate is the only variable that can directly manipulate the POC temperature (other than closely controlling the feed rate)” (Rester 1997).

The POC temperature is measured by a bare, ungrounded thermocouple located at the center of the cylindrical kiln, at the exit end. The thermocouple is exposed to convective heat transfer from the combustion gases and radiant heat transfer from six sources. Those six sources are the combustion gases, the luminosity of the POC and SOC burner flames, the red-hot kiln walls, and the red-hot and white-hot afterburner walls. Parts of the afterburner walls reach a white-hot condition because the SOC burner flame impinges on them. The POC thermocouple is in direct line of sight with each of these radiant sources. At the entrance of the kiln, temperatures are lower, resulting in a very complex distribution of compositions and temperatures.

SOC temperature is determined by measuring the temperature of the combustion gases in the ductwork immediately downstream of the afterburner with a thermocouple shielded by a thermowell. This thermowell does not have line of sight with any of the radiant heat sources in the kiln or afterburner but it does receive radiant heating from the walls of the 18-inch inside diameter, refractory-lined ductwork that is the exit conduit for the combustion gases.

The three numerical models developed at LSU (Leger (1992), Cook (1993) and Jakway (1996)) are reviewed in Chapter 2 and the content of those models bears on the data presented here.

Leger did not include radiant heat transfer in his model. Cook's desorber model operated at relatively low temperatures where radiant effects were secondary, although his submodel included wall, bed and gas as radiant heat sources. Jakway includes radiant energy in each zone of his model and includes the effect of soot, carbon dioxide and water. Jakway takes flame luminosity into account.

For the LSU pilot-scale RKI, the gases in the kiln are exposed to radiant energy from the afterburner flame and the red-hot and white-hot refractory walls of the afterburner. These are not considered in the models by Leger and Jakway, based as they are on Dow kiln geometry, or by Cook, whose desorber model was based on the University of Utah simulator.

The unknowns and variability of gas composition and temperature in the kiln greatly increase the difficulties of understanding kiln processes. Jakway, for example, assumes that soot is consumed at 1/3 of the length of the kiln, in a kiln where flame length extends to 2/3 of the length of the kiln. In the LSU pilot kiln the POC burner flame often extends to the full length of the kiln and in fact, the flame is usually yellow (luminous) for its complete length.

In seeking "appropriate models of the multitudes of interacting phenomena in the kiln", Sterling and Montestruc (1989) point out that study of the continuous time records of measured variables in the kiln should lead to identification of "a set of parameters that are reliable and reproducible characterizations of the process for a given set of operating conditions."

A full model of the kiln would include the heat generated by combustion and the interaction of all of the heat transfer sources. It is suggested that since a complete tabulation of temperatures is not available (everywhere in the combustion gases and on every surface and in the flames), a start can be made by evaluating the overall heating effects. It may then be possible to separate convection heating from radiant effects. Responses to changes in heat input provide a means to determine time constants for each effect, giving some insight to the processes.

The need for effective and efficient temperature control requires knowledge of the effect of changing the POC gas rate on the steady state temperatures of both the POC and SOC (Rester 1997). In early runs of the LSU RKI, using only natural gas in the auxiliary burners, step changes were made in POC gas rates to determine the magnitude of temperature changes and the response times, that is, the times required to reach new steady states. Data were collected continuously at 20-second intervals from the time of a step change in gas flow rate to a new steady temperature. In plotting the data for the first ten minutes, when rates of change were large, the points were 20 seconds apart, but at later, slower rates, three data points were averaged together.

The step change in gas flow is the input to the process. The total change in temperature represents the process output. The amount of time required for the process to reach a new steady state is referred to as the response time.

A first-order exponential or decay function represents the response to a step change where the response is the result of a single process. In this simple case, the reaction is the same for a step-up or a step-down.

$$T = T_0 + \Delta T\,(1 - e^{-t/\tau})$$

T is the temperature at any time t;

T_0 is the initial temperature;

ΔT is the total temperature change accomplished to reach a new steady state;

t = time, minutes

τ = system time constant, in units of time, indicative of the speed of response of the process.

At the end of one time constant ($t = \tau$), 63.2 percent of the total temperature change will have been accomplished.

$$T = T_0 + \Delta T\,(1 - e^{-1}) = T_0 + \Delta T\,(0.632)$$

After five time constants, 99.3 percent of the total temperature change will have been accomplished.

$$T = T_0 + \Delta T\,(1 - e^{-5}) = T_0 + \Delta T\,(0.993)$$

No simple response is to be expected for a kiln thermocouple, exposed to six sources of radiant heating that vary with the geometry of the two furnaces, and bathed in a turbulent flow of gases that are not spatially uniform in composition or temperature. Fortunately, however, superposition of solutions allows treatment of simultaneous linear processes as additive.

It was found that two decay functions provide a better fit for the data of the kiln than a single decay function (Rester 1997).

$$T = T_0 + \Delta T[(\%\ \mathrm{Fast})(1 - e^{-t/\tau_{POC-1}}) + (1 - (\%\ \mathrm{Fast})(1 - e^{-t/\tau_{POC-2}})]$$

%Fast represents the fraction of the total response that is due to a fast effect.

Table 3.2 gives results for step up tests. In the four trials for step up in POC gas rate, the data were averaged to determine the %Fast, τ_1, and τ_2.

Table 3.2 POC Gas Flow Rate Increases, (Step Up), and Time Constants

Trial No.	Run No.	Initial CH_4 Rate Ft^3/hr	Step Change Ft^3/hr	Initial Temperature °F	ΔT F°	τ_1 Min.	τ_2 Min.	% Fast
1	2	460	200	1530	185	0.84	87.2	47.5
2	2	360	100	1610	290	0.92	45.9	42.2
3	3	430	190	1550	90	1.71	77.3	43.2
4	3	500	220	1630	170	1.71	88.7	37.5
Average						1.3	75	43
Std. Dev.						0.5	20	4

Figure 3.3 is a plot of dimensionless temperature change vs. time constants, which shows fast and slow effects and their sum for step-up in POC gas flow rate. The effects of differences in the initial temperatures and size of the step changes in the experiments are minimized by making the temperature change non-dimensional.

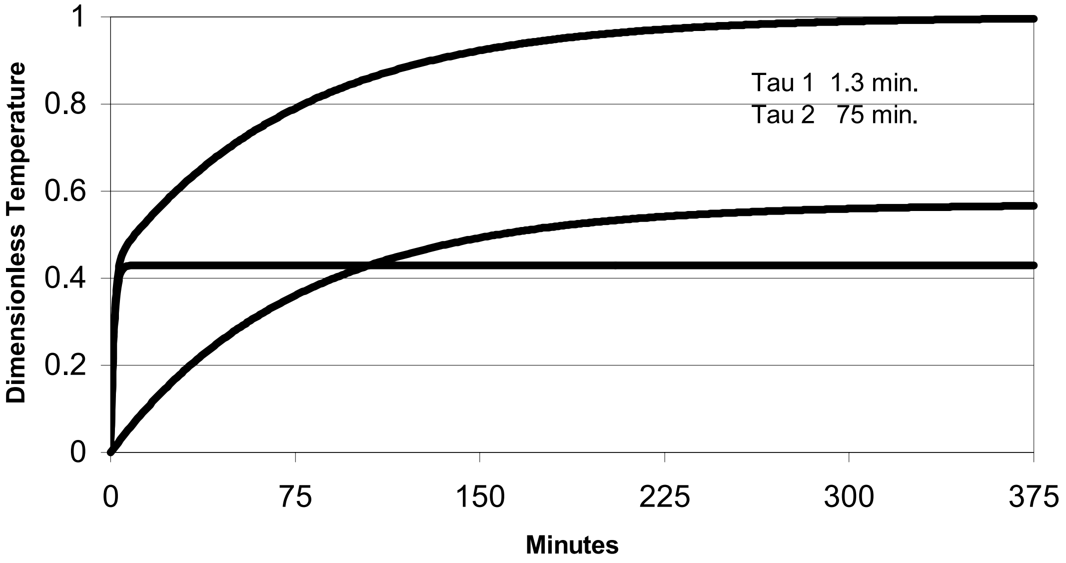


Figure 3.3 POC Time Constants – Step Up

For the kiln burner, an increase in gas flow rate produces a very rapid increase in flame temperature and in the temperature of the combustion gases (including excess air). This is principally due to greater heat input, but also because the fuel to air ratio becomes richer. The amount of primary air increases, but not proportionately. This is because the inlet blower has a constant speed. The fast response by the thermocouple is due to the increase in convection heating.

The response time for a bare, ungrounded, type K thermocouple is about 1.3 minutes (Omega 1995). Increasing the gas flow produces an immediate increase in flame and combustion gas temperatures; thus, it appears that the fast time constant is due mostly to the response of the thermocouple. 63.2% of the effect is realized in 1.3 minutes (Rester 1997).

The radiant heating effect is proportional to the fourth power of the temperature and to the emissivity of the sources. When gas rate is increased, the increase in wall temperature does not take immediate effect, and the full force of radiant heating on the thermocouple is not transmitted from the walls until they reach a new steady temperature. Radiant heating, however, amounts to 57 percent of the total. Before the full effect is realized, the heat capacity of the refractory walls must be satisfied.

The principal contributors to the radiation from flames are CO_2, H_2O, and soot (Jakway 1995). These substances radiate heat at numerous frequencies, in all directions, and at various distances to the walls of the kiln. Part of the energy is absorbed and part is reflected. That which is absorbed raises the temperature of the absorbing substance. The reflected part then is transmitted to another part of the walls, or to the gas molecules from whence it came, and to every object in line of sight. After numerous transmissions, absorptions, and reflections, all at the speed of light, the temperatures of all of the sources are changed. The changes due to radiation act, of course, on the thermocouple, and are the cause of the slow part of the response.

The absorptivity, α, of a substance is a measure of the fraction of radiation received that is absorbed. (α = heat absorbed by a surface / heat transmitted to the surface). For an ideal, black body, $\alpha = 1$. The emissivity of a substance is the measure of the ratio of radiation emitted to that emitted by a black body at the same temperature. (ε = radiant energy emitted by a substance / radiant energy emitted by a black body at the same temperature). For an ideal, black body, $\varepsilon = 1$. Kirchhoff's law applies when, at a given temperature, radiation from and to a surface is in equilibrium, ($\varepsilon = \alpha$) (Bird, Stewart and Lightfoot 1960).

The Stefan-Boltzmann law relates energy radiated from a black body to temperature of the body. Radiated heat, Btu/(hr·ft^2) = ($\sigma * T^4$). σ is the Stefan-Boltzmann constant = 0.1712 Btu/(hr·ft^2·^{o}R^4).

Geometry of the system comes into play in that the angle of emission and the angle of incidence of the radiation and the distance between the two bodies must be taken into account.

Table 3.3 and Figure 3.4 give results of step-down tests. Here the fast response is shown to be about the same as the fast response for the step-up. The radiant heat loss, however, has a time constant that is about one-half the value in the step-up results, 43 minutes vs. 75 minutes.

Table 3.3 POC Gas Flow Decreases, (Step Down), and Time Constants

Trial No.	Run No.	Initial CH_4 Rate Ft^3/hr	Step Change Ft^3/hr	Initial Temperature °F	ΔT F°	τ_1 Min.	τ_2 Min.	% Fast
5	2	475	105	1840	-65	0.92	33.7	49.2
6	2	660	185	1900	-70	0.88	36.0	44.2
7	2	650	175	1670	-90	0.84	37.5	46.3
8	3	610	180	1825	-155	2.00	45.2	53.8
9	3	800	230	1915	-115	1.50	40.3	55.1
10	3	670	170	1825	-200	1.58	62.9	36.2
Average						1.3	43	47
Std. Dev.						0.5	11	7

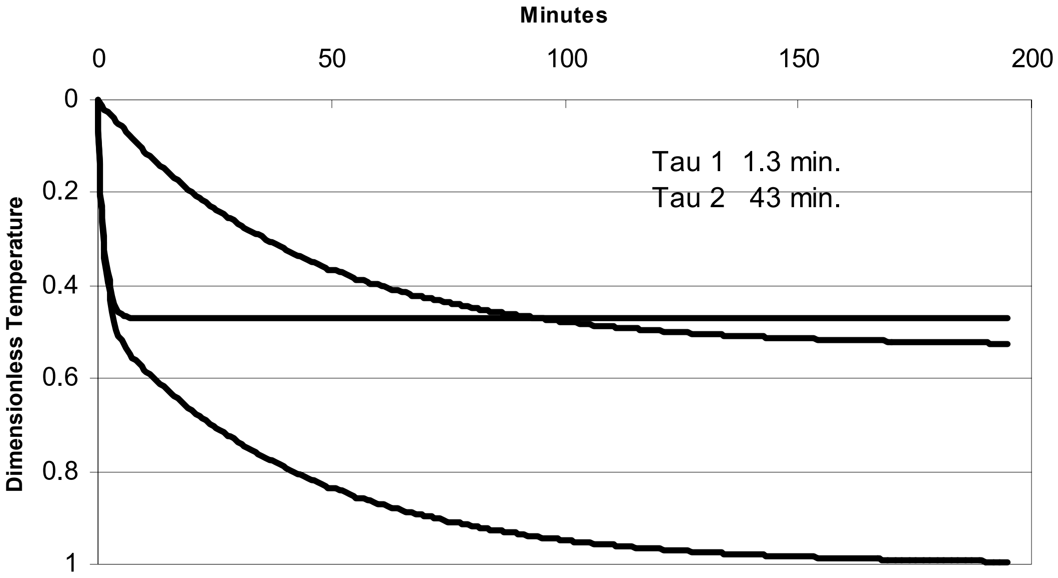


Figure 3.4 POC Time Constants – Step Down

The radiant heating effect is proportional to the fourth power of the temperature and the emissivity of the sources. When gas rate is increased, the increase in wall temperature and other sources of radiation do not take immediate effect and the full force of radiant heating is not transmitted from the walls until they reach a new steady state. When the gas flow rate is decreased, the fast response reflects the rapid decrease in flame and gas temperatures. Radiating at high temperature, the walls lose temperature more rapidly than it was gained when increasing.

Table 3.4 and Figure 3.5 record response of the SOC temperature for step-up of input. The SOC thermocouple is shielded by a thermowell, and its fast step-up time constant is about four times as long as for the POC fast time constant (5.6/1.3). The validity of the temperature of the gas was checked to determine if the thermowell were cooled by contact with the external wall of the piping. The temperature at the end of the well (that registered by the thermocouple) is given by (Bird, Stewart and Lightfoot 1960):

$$(T(\text{indicated}) - T(\text{actual})) / (T(\text{wall}) - T(\text{actual})) = 1 / \cosh((hL^2/kB)^{**.5})$$

where T(indicated) is the thermocouple indicated temperature, 1800°F;

T(actual) is the corrected temperature for the combustion gases, the unknown;

T(wall) is the temperature of the outside wall of the piping, 350°F;

h is a heat transfer coefficient estimated at 120 Btu/(hr(ft^2)°F);

k is the thermal conductivity of stainless steel thermowell = 60 Btu/(hr(ft)°F);

B is the thickness of the thermowell wall = 0.1 inch

L is the length of insertion of the thermowell = 1 foot

$$(1800 - T(\text{actual}))/(350-T(\text{actual})) = 1/\cosh[(120*1/(60*(0.1/12))^{**.5})]$$

$$=1/\cosh 15$$

$$=1/(3\text{x}10^6)$$

$$1800 - T(\text{actual}) = (350 - T(\text{actual}))/(3 \text{ x } 10^6)$$

Thus, the temperature correction is indicated to be much less than one °F.

Table 3.4 SOC Time Constants – Step Up

Trial No.	Run No.	Initial CH_4 Rate Ft^3/hr	Step Change Ft^3/hr	Initial Temperature °F	ΔT F°	τ_1 min.	τ_2 min.	% Fast
1	2	460	200	1690	65	5.0	97.3	13.5
2	2	360	100	1730	150	3.1	30.2	20.0
3	3	430	190	1725	35	5.6	48.9	35.1
4	3	500	220	1760	170	8.7	111.1	25.9
Average						5.6	72	24
Std. Dev.						2.3	39	9

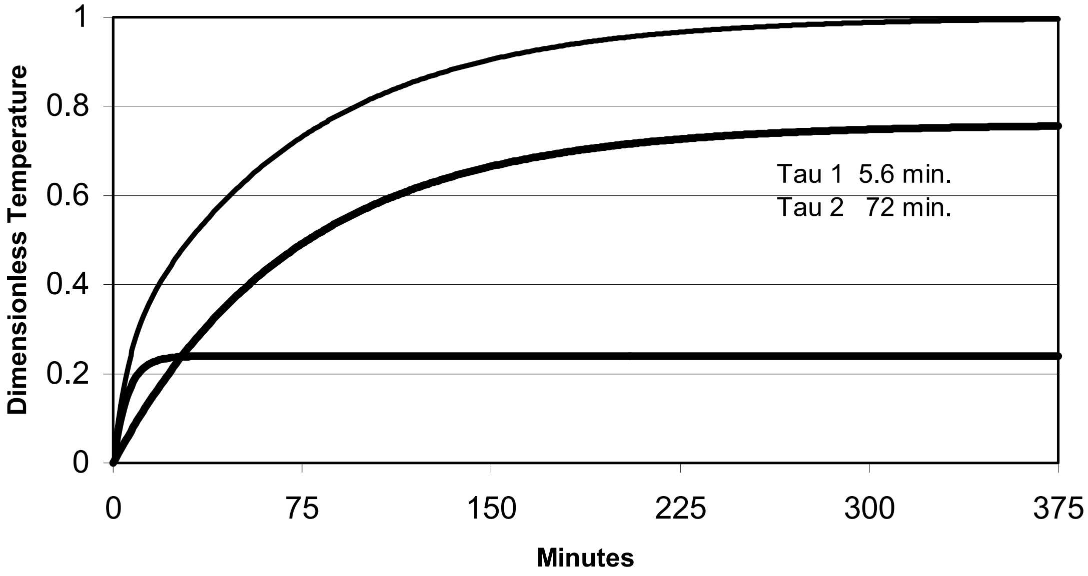


Figure 3.5 SOC Time Constants – Step Up

Results for the SOC time constants upon stepping down are shown below.

The decrease in the time for the second SOC constant, upon stepping down, is seen to be similar to its POC counterpart. Here the only sources of radiation are the refractory of the ductwork and the combustion gases, and yet the result is similar.

Table 3.5 SOC Time Constants – Step Down

Trial No.	Run No.	Initial CH_4 Rate Ft^3/hr	Step Change Ft^3/hr	Initial Temperature °F	ΔT F°	τ_1 min.	τ_2 min.	% Fast
5	2	475	105	1835	-40	1.7	28.0	9.7
6	2	660	185	1935	-80	4.1	38.5	29.6
7	2	650	175	1785	-45	1.6	34.1	10.1
8	3	610	180	1840	-115	0.4	42.2	7.6
9	3	800	230	1900	-70	2.6	26.9	15.3
10	3	670	170	1835	-100	4.9	79.1	13.4
Average						2.6	41	14
Std. Dev.						1.7	19	8

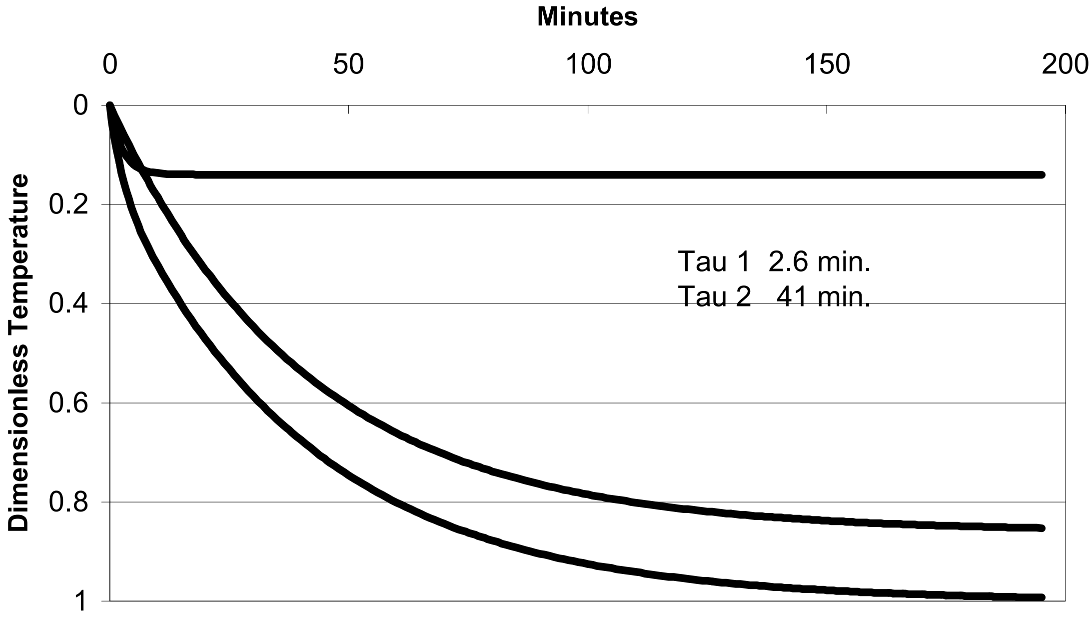


Figure 3.6 SOC Time Constants – Step Down

Table 3.6 is a recap of Tables 3.2, 3.3, 3.4, and 3.5 for easier comparison.

Table 3.6 Time Constants Summary

Step	POC τ_1 minutes	POC τ_2 minutes	%Fast	SOC τ_1 minutes	SOC τ_2 minutes	%Fast
Up	1.3	75	43%	5.6	72	24%
Down	1.3	43	47%	2.6	41	14%

These time constants provide valuable guidance to operators in predicting the effect on both combustion chambers of changes in gas flow rates. In the M. S. thesis, "Development of Process Characterization and Operating Procedures for the L.S.U. Rotary Kiln Incinerator," more details of these experiments are presented (Rester 1997).

CHAPTER 4 BATCH TRIALS

4.1 Batch Feeding

Waste materials can be fed to RKIs continuously or in batches. When fed in batches, the waste is packaged in drums that may contain solids, or liquids, or liquids adsorbed on solids. This chapter describes pilot plant experiments undertaken to demonstrate the capabilities of the LSU RKI as a research laboratory, capable of duplicating waste processing as practiced at full scale (Wight 1999).

In Chapter 2, batch feeding in the Dow and Ciba-Geigy kilns and in RKI simulators was reviewed to set the background for descriptions of experiments in the LSU kiln for similar trials of batch feeding where transient puffs are of importance. It will be recalled that although several models were developed and several methods of puff suppression were suggested, no solution was offered that would prevent the first puff. After that first puff, cutting auxiliary gas rate and/or reducing feed rate were the only practical alternatives.

The kiln operator, of course, has the waste analysis as a guide. On occasion, however, an analytical error or mistake in drum filling can result in a charge that temporarily exceeds the capacity of the kiln. Moreover, charging a kiln at its maximum rate, the point of most economical operation, often results in excessive loading. Thus, operation outside normal and desirable conditions can happen, and it is necessary to understand the process so as to reduce its deleterious effects when possible. It should be remembered, however, that satisfactory DREs have been achieved in all of the tests performed so far in the full-size and pilot-size kilns, due to completion of oxidation in afterburners.

4.2 Experiments

4.2.1 Objectives

The first experimental trials of the LSU RKI in which surrogates for waste material were burned had the following objectives:

1. To demonstrate that system responses are consistent, that is, the combustion gas compositions and combustion gas temperatures are repetitive and stable;
2. To show that system responses are comparable to the responses recorded in a full-size kiln, to give confirmation that data from this pilot plant may be used for scale-up;
3. To explore safe operating conditions of the kiln, afterburner, and downstream air pollution control equipment.

4.2.2 Procedure

Two surrogates for hydrocarbon wastes, toluene and xylene, were used in these tests. They were chosen so that the experiments could be related to earlier tests in the Dow kiln where toluene and xylene were the feed materials (Lester et al. 1990, Cundy et al. 1991, Leger et al. 1993, Jakway et al. 1995).

In the Dow trials, the same amount of VOC was fed in each pack. The fiber packs weighed 3.2 kg. and each contained 22.7 kg. of montmorillite granules as adsorbent for 18.9 liters of solvent.

To arrive at the appropriate loading for the pilot RKI, scaling down was calculated in two ways. The first method was based on burner heat duty for each of the kilns. The second method compared the volumes of the two combustion chambers.

The burners' capacities were 1.2 million Btu/hr for the LSU kiln and 8.5 million Btu/hr for the Dow RKI. This ratio of 1 to 7 indicated a feed to the pilot RKI of 2.7 liters per pack.

The volumes of the combustion chambers were 40 ft^3 for the LSU kiln and 3000 ft^3 for the Dow RKI. The resulting ratio of 1 to 75 indicated a suitable feed for the LSU kiln of 0.252 liters per pack. This quantity translates to 2.37 gram moles of toluene and 2.06 gram moles of xylene.

It was assumed that the burner for the LSU kiln was oversized when compared with the Dow burner and thus it was judged prudent to use the volume ratio calculation. Moreover, proceeding with caution, batches were made up at 50%, 75%, 100%, 110% and 125% of the calculated amounts. Four of each of these five sizes were made up for toluene and xylene, making a total of 40 samples. One-pint, wax-coated milk cartons were filled with montmorillite granules as adsorbent material (Eagle-Picher Industries "Floor Dry Celatom"). Good thermal stability and high porosity are characteristics of the main constituent, 100% calcined diatomaceous earth. The product material safety data sheet (MSDS) states that celatom does not decompose thermally. In tests the celatom was found to be capable of adsorbing more than its own weight of toluene or xylene. Each carton was filled with one-half pound of Celatom.

The solvents were added to the cartons, which were then sealed by melting the wax of the carton on a hot plate.

The kiln was started up and, after reaching target values of kiln and afterburner temperatures (1500 °F, and 1700 °F), conditions were held steady for four hours.

A bed of solids was then built up in the kiln by feeding inert packs, pint milk cartons filled with Celatom, but without VOC. Packs were fed at five-minute intervals until the bed was of such a depth that it would slide down the wall of the kiln. At that point, the bed was about four inches deep at the front of the kiln.

Forty inert packs, a total of 20 pounds of Celatom, were required to build the bed. Typically, in about one second after insertion the walls of a pack started to scorch. Two seconds later it would burst into flames, which lasted about thirty seconds. At the end of that time, all of the paper carton had burned.

The bed, as viewed from the afterburner end, was in the lower right quadrant of the kiln. As the kiln rotated, the bed would ride up and then slide back.

The kiln rotation rate was set at its maximum rate (0.19 rpm), about one half of the average of slow and fast rotation rates of the Dow kiln (0.1 and 0.25 rpm) during similar tests. The Dow kiln diameter, however, is four times that of the LSU RKI. Consequently, at its slow speed, the Dow kiln's peripheral speed was twice that of the LSU kiln. At the fast rotation rate for the Dow kiln, its peripheral speed was five times that of the pilot kiln.

In the Dow kiln, the bed motion when processing toluene exhibited a slipping movement, that is, the bed would slide back down after riding up. In the Dow tests with xylene, a slumping motion of the bed was observed. After riding up with the rotation of the kiln, the granular material of the bed would roll back, which resulted in a new bed being formed. In these pilot kiln tests, a sliding motion of the bed was observed for both toluene and xylene.

Two hours after the first of the packs with inert material were fed to the kiln, some of the ash reached the ash hopper. After three hours, there was a continual discharge.

Before beginning to feed waste surrogates, the stack sample line was purged, and each of the analyzers was calibrated.

The toluene packs were first to be fed, starting with those containing the smallest amount of solvent and continuing through the twenty packs. Packs were fed at 10-minute intervals. The packaging reacted in the same way as for the inert packs.

When the packs with solvent were scorched and burned, however, the VOC was released and it burst into flame, generating a puff. Starting with the light packs, the first puffs were not so intense. The kiln was not fully obscured by the puff and no black smoke was produced. As the amount of toluene (or xylene) was increased, the puffs increased in intensity, obscuring the kiln interior with black smoke for about five seconds. The soot traveled rapidly to the afterburner. The kiln atmosphere then became clear until the bed slid down again, exposing fresh solvent to the heat from conduction, convection and radiation. A second, less intense puff was then created. Although smaller than the first puff, the smoke from the second puff partly obscured the front of the kiln (Wight 1999). Without flaring up again the residual material continued to burn for five minutes. All of the flames had died out before the next pack was fed, ten minutes later.

All of the packs exhibited this two-puff behavior and the toluene and xylene burned with no visible differences (Wight 1999).

The soot in the kiln revealed a stagnation zone near the front of the kiln. After the first puff, most of the soot was swept out to the afterburner, but a small amount remained near the front of the kiln. This soot gradually mixed with the other combustion products, and was dispersed with them. It was completely removed before insertion of the next pack.

A calibration check of the gas analyzers was performed in the period between injection of toluene packs and xylene packs and again at the end of the experiment. This provided assurance that calibration had been maintained and that instrument readings had not drifted from their original settings.

At steady state, all of the natural gas flow to the POC and the SOC was burned to CO_2, as evidenced by very low carbon monoxide and total hydrocarbon readings. The CO_2 record shows that the steady flow of CO_2 amounted to 2.4 percent of the stack gas (dry basis) before the start of toluene pack insertions. At that time the POC and SOC temperatures were 1520 °F and 1720 °F, respectively. At the end of the toluene part of the experiment, the steady state CO_2 percentage remained at 2.4 percent. POC and SOC temperatures were then 1530 °F and 1760 °F, respectively.

At the end of the xylene packs, the steady state CO_2 percentage was 2.42 percent. The POC and SOC temperatures were 1525 °F and 1770 °F, respectively.

4.2.3 Results

A record of CO_2 concentration versus time as the toluene packs were processed is exhibited in Figure 4.1. The repetitive nature of the rapid rise in CO_2 and the shape of the responses correspond to data obtained with the Dow kiln when burning toluene packs with a slipping bed motion (Leger at al. 1993 b and 1993 d).

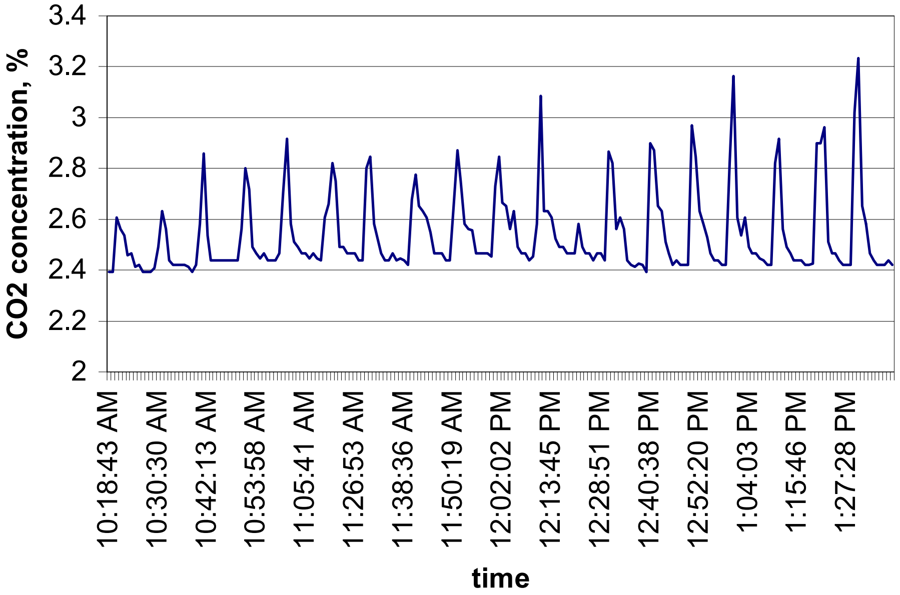


Figure 4.1 Toluene Evolution (CO_2 concentration vs. time)

The two spikes, or puffs, are apparent for many of the packs; the second puff is usually of about one half the magnitude of the first and in many cases it appears as a shoulder at this scale. Scale magnitudes are important features of graphical presentation, and this plot with a short time scale emphasizes the rapid rise in evolution rate as reflected in CO_2 percentages.

Figure 4.2 presents similar data for xylene packs. As stated earlier, no difference was noted in the behavior of the packs with xylene. Here, again, the second spikes and shoulders show up in the chart.

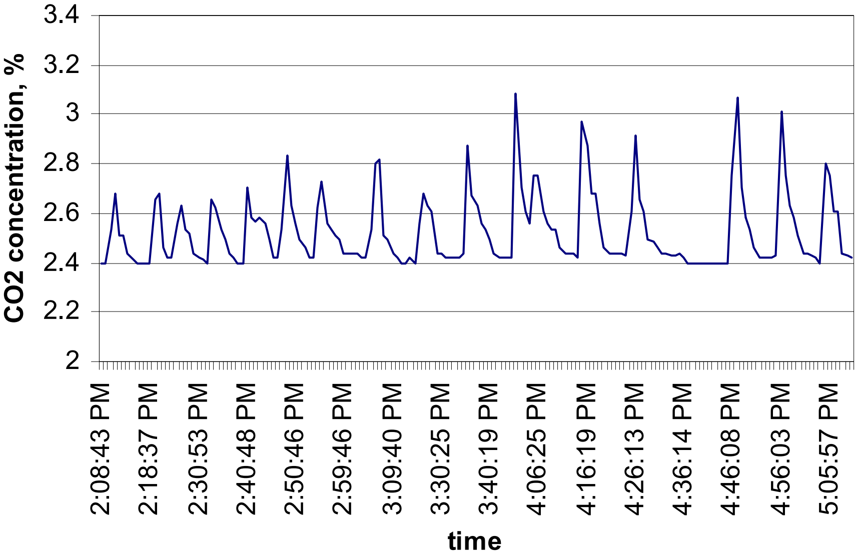


Figure 4.2 Xylene Evolution (CO_2 concentration vs. time)

As examples of the effect of the time scale, Figures 4.3 and 4.4 present CO_2 concentration vs. time for typical, single toluene and xylene packs. Stretching the time scale provides a better look at the dynamics. It also reveals that sampling every 54 seconds results in missing many maxima, minima and trends as was discussed in Chapter 1.

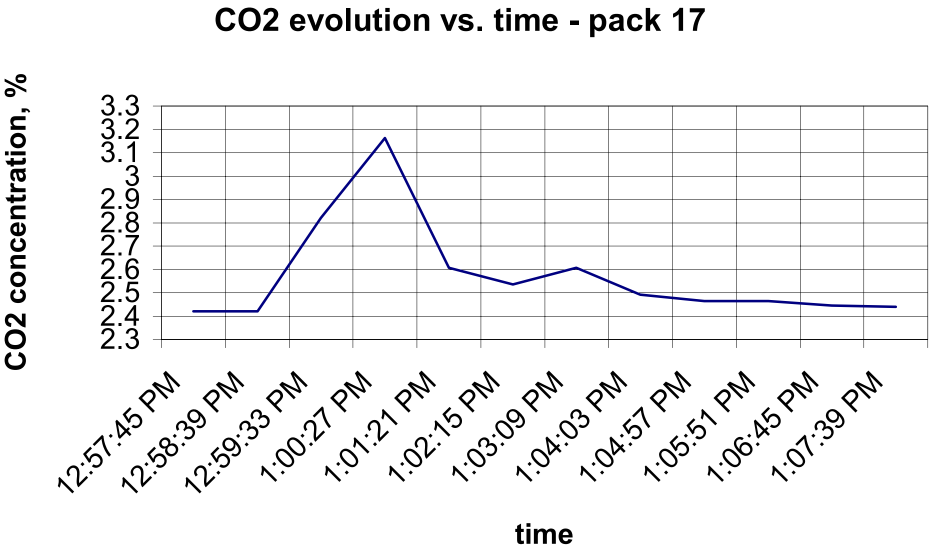


Figure 4.3 Toluene Evolution from a Single Pack

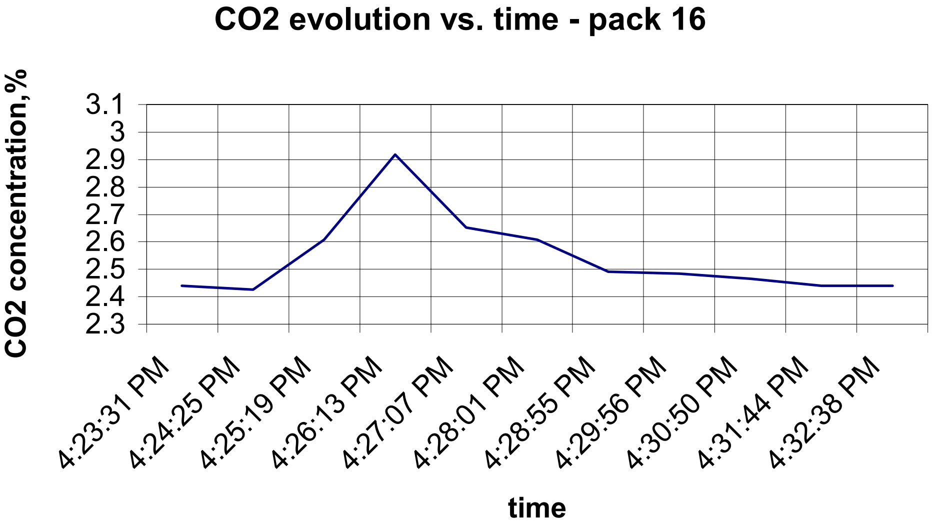


Figure 4.4 Xylene Evolution from a Single Pack

A complete set of these expanded plots is provided in Appendix A.

The slipping bed witnessed in these experiments in the pilot kiln occurred with both toluene and xylene. In the Dow tests, the reason for the difference (slumping for xylene and slipping for toluene) was judged a possible consequence of a change in the smoothness of the walls of the kiln (Leger et al. 1993d). The slipping was hypothesized to be a superior bed characteristic for wastes with low volatility and low heat of combustion, since in slipping bed motion, the new waste is not buried in the older, burned out waste. For volatile wastes, and those with high heats of combustion, the mixing of new material with the old, thus shielding the new material for a time from the heat of the flames, was considered an advantage.

The role of the cloud of soot in intermittent blocking off radiant heat to the batch of waste was recognized by LSU researchers (Lester et al. 1990). They discussed the possibility that maximum evolution rates would occur when the bed slumping behavior and the periodic exposure to radiant heating were of the same frequency, each reinforcing the other's effect.

The average total amount of CO_2 produced from packs of each size is illustrated in Figure 4.5 for the toluene packs and in Figure 4.6 for the xylene packs.

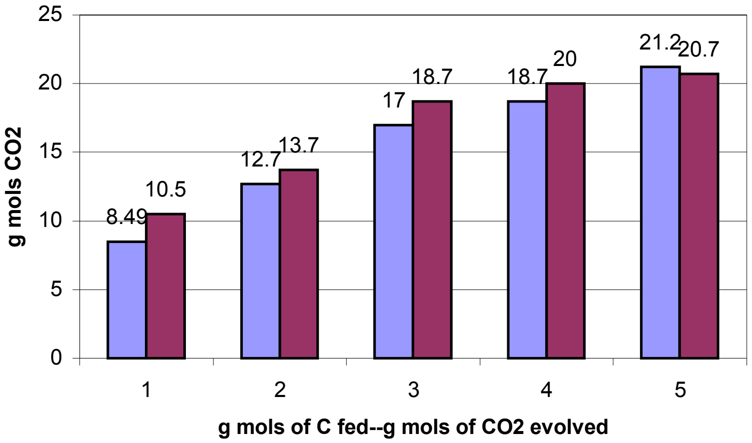


Figure 4.5 Toluene Evolution

These two charts are presented to demonstrate that pilot plant data recorded for this experiment were consistent, and reasonably accurate.

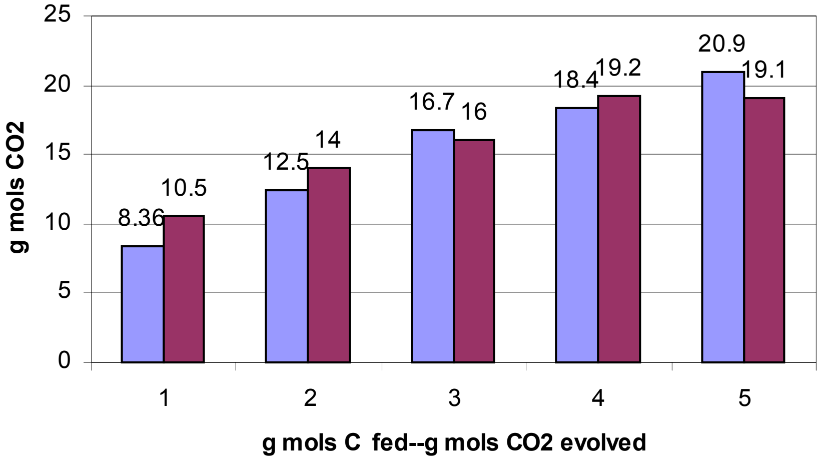


Figure 4.6 Xylene Evolution

Two possible sources of error in the results should be recognized:

1. Measurement of amount of toluene or xylene added to each pack; and
2. The 54-second timing of the recording of the data by the DAQ system that cuts off some of the peaks.

Before the experiment, the CO_2 analyzer had been replaced. An adjustment of the signal to the DAQ system was required, but was overlooked. The resultant errors in the recorded data remain, but have been noted in the log book, and have been corrected in subsequent publications (Wight 1999).

It was reported (Leger et al. 1993d) that data from eight packs of toluene processed in the Dow kiln were used to evaluate a time constant for toluene evolution. Oxygen concentration at the afterburner, and at the stack, and CO_2 concentration at the afterburner were all used in the calculations. The time constant was determined by fitting the data to:

$$\mathrm{N}(C_7H_8)(t) = 1 - e^{-t/\tau}$$

N is the normalized evolution rate of toluene. The average of 24 determinations was 141 seconds with a standard deviation of 23 seconds.

Using the CO_2 data recorded for the middle-sized toluene packs in this set of experiments and the above formula (applied to the smaller packs) an average time constant of 133 seconds was determined.

For the middle-sized xylene packs, the formula used was:

$$\mathrm{N}(C_8H_{10})(t) = 1 - e^{-t/\tau}$$

N is the normalized evolution rate of xylene. For xylene the time constant was determined to be 127 seconds.

Additional information is contained in the M. S. thesis by Robert Wight, "Qualitative Analysis of the Combustion of Toluene and Xylene in a Pilot Scale Rotary Kiln Incinerator" (Wight 1999).

CHAPTER 5 OTHER RESEARCH TOPICS

5.1 Still Bottoms Processing

As part of a program to study co-production of ethanol and glycerol from sugar cane molasses, the Audubon Sugar Institute, under the direction of Dr. Willem Kampen, investigated the recovery of a byproduct by incineration of still bottoms (Munene 2000).

Objectives of the incineration tests were to determine:

1. The suitability of rotary kiln incineration for disposal of still bottoms; and
2. The amount and quality of potash that could be recovered from the ash.

Molasses can be fermented to produce ethyl alcohol with a small amount of glycerol. Adjustment of several fermentation parameters and use of suitable yeast greatly increases the yield of glycerol. Glycerol is a more valuable product than ethanol, and co-production of ethanol and glycerol from sugar cane molasses has been recommended (Munene 2000).

For the tests described here, a normal fermentation of molasses was conducted. The product was distilled to recover alcohol. The still bottoms were combined with more molasses and still bottoms from other fermentations, and a second fermentation was carried out with altered conditions and different yeast.

The product of this final fermentation was distilled to recover glycerol and ethanol. The final stillage was evaporated to 66% solids. The solids consisted of sugars, proteins, fats and ash. The heat of combustion was reported to be 4000 Btu per lb.

The RKI was operated with a POC temperature of 1600 °F and an SOC temperature of 1840 °F. Empty, one-quart milk cartons were first fed to the kiln, 25 of them, five every ten minutes to obtain carton ash samples as a basis.

One-quart cartons were then filled three quarters full of stillage. Cartons were fed singly at intervals of six minutes, followed by two cartons at a time every ten minutes, and then three cartons at a time every fifteen minutes. A total of 78 cartons, three-quarters full, containing 60 liters of stillage were fed.

At the end of the run, the refractory surfaces of the kiln were found to be coated with ash. It had been molten and then solidified on the walls. In addition, considerable solid ash in lumps up to four inches in diameter, gravel and dust were found in the kiln and in the ash pit. Only a very small amount of flyash was recovered from the baghouse.

Ash production was 150 lbs per ton of molasses. The ash formed small clinkers in the kiln (up to four inches in diameter). A portion of the ash was ground into a powder (<0.5 mm). Analysis indicated that the ash consisted of 25% potassium, 7% silicon, and about 2% each of sodium, aluminum, and iron. Hot water dissolved five percent of the potassium, and the solution had a pH of 13.7. Cold water dissolved seven percent of the potassium and the pH of the solution was 11.1. Nonetheless, with its high potassium content, the ash can be considered as a potential fertilizer, worth almost $80 per ton (Munene 2000).

The incineration of the still bottoms successfully removed the organic matter, thus meeting the first of the objectives of the experiment. It would not be difficult to feed the stillage as a liquid, which would be an easier process than packaging in cartons or drums. Moreover, a simpler furnace than a rotary kiln might be appropriate for the liquid feed, which could be readily pumped and atomized.

In her M. S. thesis, “Co-production of Glycerol and.Ethanol from Blackstrap Molasses,” Munene gives a comprehensive treatment to the fermentation of molasses, recovery of glycerol and ethanol, capital costs of competing process plants, as well as a description of the incineration part of the project.

5.2 Firelogs

Research sponsored by the LSU School of Forestry, Wildlife and Fisheries was conducted to evaluate the burning characteristics of synthetic firelogs (Houston, 1999). The project was directed by Dr. Ramsey Smith and Dr. C. F. de Hoop.

With natural firewood and with purchased firelogs, the latter made with petroleum-based binders, soot deposits in ductwork and chimneys are a fire hazard and a cleaning problem. The purposes of the research were to develop a firelog that would be a cleaner-burning log than is commercially available and to provide a use for wood waste (sawdust and wood milling waste).

Wood refuse and a soybean-based wax were used to produce LSU firelogs for testing. Sample firelogs with the following wax contents were manufactured: 25%, 33%, 50% and 60%. The wood material contained approximately 13% moisture.

For burning comparison tests, five varieties of commercial firelogs and oak firewood were purchased. Figure 5.1 is a photograph of the Residential Fireplace Simulator that was set up nearby the RKI. The firebox and stack were commercial

Figure 5.1 Fireplace

units. A digital scale was set below the firebox to provide continuous measurements of the weight of a log as burning progressed. A turbine meter was installed near the top of the stack to supply combustion gas velocity (and thus volumetric flow) measurements.

The combustion gas was continuously sampled, and drawn through heated, ¼″ stainless steel tubing to an oxygen analyzer. Dual filters were installed in the line to remove particulates. The sample was then piped to the continuous emissions monitoring system used for the kiln. CO and total hydrocarbons were measured with the individual analytical instruments and CO_2 was measured using the mass spectrometer.

The LSU-produced synthetic firelogs produced less carbon monoxide and less PICs as measured by THC (total hydrocarbons) than oak logs or petroleum-based firelogs.

The amount of CO_2, CO, and Total Hydrocarbons (THC) evolved from the various firelogs is summarized in Table 5.1.

Table 5.1 Combustion Gases Evolved from Firelogs

	Lb moles per Lb of firelog		
	$CO_2 \times 10^2$	$CO \times 10^3$	$THC \times 10^4$
AMERICA'S CHOICE	5.36	0.752	4.25
DURAFLAME	4.57	1.09	2.64
GOLDFLAME	5.26	1.10	3.46
HEARTHSIDE	4.18	0.996	2.39
TOPCREST	4.71	0.652	4.63
OAK	4.27	1.57	2.62
LSU 25% WAX	3.61	0.967	1.37
LSU 33% WAX	3.69	0.844	1.68
LSU 50% WAX	4.03	0.554	1.44
LSU 60% WAX	5.45	1.01	0.122

Figure 5.2 is a typical set of graphs of analytical data recorded during the burning of one of the commercial firelogs, America's Choice. (Note the CO_2-O_2 mirror image).

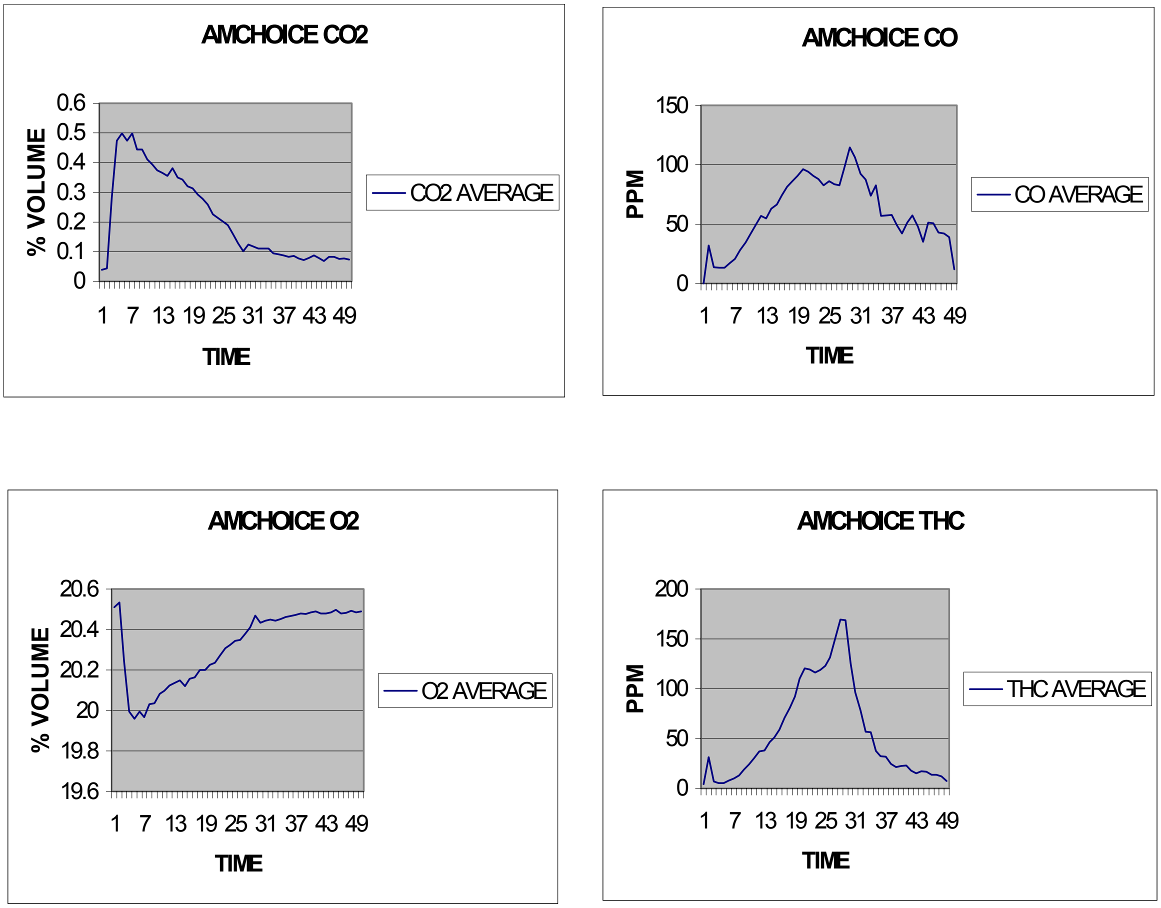


Figure 5.2 Firelog Analytical Data

The wrappers on the commercial firelogs had printed instructions that the fireplace doors be left open. Gusts of wind, on some days, caused spikes in the data. Differences in sizes (lengths and diameters) of the logs resulted in differences in the burn times, and in the relative amount of surface exposed to flames and air. The number of logs included in each test was varied to try to maintain the same weight.

It is recommended that for future tests, larger synthetic logs, comparable to the commercial logs in size, be provided for the tests. The synthetic logs should have a paper wrapper, as do the commercial logs, for easier lighting. The research summary given here is more completely reported in the M. S. thesis, “The Development of a Firelog with Improved Air Emissions” (Houston 1999). Another of the researchers gives further details (Wight 1999).

5.3 Combustion Safety and Incinerator Emissions Testing

Testing of incinerator stack emissions was conducted at the RKI as one phase in the evaluation of the capabilities of a remote-sensing, portable, optical gas detector. The version of the instrument tested was adapted for remote sensing and characterization of stack gas emissions. The objective in the stack emission trials was to determine if the Image Multi-Spectral Sensing Spectrometer (IMSS) was capable of making accurate measurements of common stack emissions at EPA-regulated concentration levels. The instrument was originally developed by Pacific Advanced Technology, Inc. for the U.S. Department of Defense. The military planned to use it for detection of such targets as battlefield chemicals, and exhaust from guided missiles.

The device, acting in the same way as a photographic camera, records spectrographic emissions of target gases. The design has the advantage that no background target has to be set up. A background target is necessary in FTIR (Fourier Transform Infrared) imaging, another method of detecting distant gas emissions. For the purpose of monitoring air pollutants, such a non-intrusive device as the IMSS could have many uses.

For this experiment, methane and propane were chosen as the tracer gases to be injected in the system, in such quantities that the stack gases would contain 1,000 to 10,000 ppmv.

The IMSS camera was set up 200 feet from the stack. The kiln was started up, burning natural gas.

Input to the process, prior to introduction of test gases, methane and propane is shown in Table 5.2.

Table 5.2 Natural Gas and Air Flow

	gm mol/sec	ft^3/hr
Natural gas	0.37	1136
Air	9.96	30600
Total	10.33	31736

For stoichiometric proportions, based on one mole of methane, the overall combustion reaction may be written:

$$CH_4 + 2O_2 + 0.14H_2O + 7.52N_2 \rightarrow CO_2 + 2.14H_2O + 7.52N_2$$

Thus, the stoichiometric requirement is 9.66 moles of moist air per mole of fuel. In the reaction, there is no change in the total number of moles. Water included on the left side of the equation is humidity in air.

As mentioned previously, the kiln operates with very high excess air. For the actual conditions, the air rate was 26.89 moles of moist air per mole of fuel, which amounts to 175 percent excess air. The gas flow from the stack under these conditions amounted to 600 ft^3/min. (36000 ft^3/hr.). The amounts of tracer organics, at 1,000 to 10,000 ppmv translated to 0.1% to 1% of the stack gas, and thus were 36 to 360 ft^3/hr.

The maximum flow volume of tracer gas was 25 percent of the amount of natural gas fed to the burners. Propane has a heat of combustion that is 2½ times that of methane. The propane tracer, at maximum flow, therefore, contributed enough fuel to equal more than 60% of the burner usage.

The two hydrocarbons were a potential hazard if not treated with caution. An explosion of the hydrocarbons could result in damage to equipment and be a threat to people. With such serious potential consequences if the gases were not treated with care, a review of combustion processes was in order.

The character of the combustion process depends strongly on whether fuel and oxygen are mixed before initiation of the chemical reactions, and on fluid flow (Linan and Williams 1996).

When fuel and oxygen are premixed the resultant flow may be turbulent (as in a spark-ignited gasoline engine), or laminar (as in a Bunsen flame or a flat flame). When the two reactants are not premixed, the flames produced are designated diffusion flames. Examples of turbulent, diffusion flames are Diesel engines and H_2/O_2 rocket motors. Wood fires and candles exemplify laminar diffusion flames (Warnatz, Maas and Dibble 1996).

Flammability limits for gas mixtures are often listed as explosion limits. “Explosion” is a general term referring to a chemical reaction accompanied by rapid heat release and/or pressure buildup (Glassman 1996). It is common practice to use the terms flame, combustion wave and deflagration, although a detonation is another class of combustion wave. A deflagration is a subsonic wave. A detonation is a supersonic shock wave. Both are sustained by chemical reaction. Mixtures that propagate a burning zone or combustion wave are considered to be within the flammability limits of the gas.

Flammability limits for methane in air at 26 degrees C. and one atmosphere pressure are 5 to 15 volume percent (Zebatakis 1965). For the same conditions of temperature and pressure, the flammability limits of propane are 2.1 to 9.5 volume percent. Moderate changes in pressure do not ordinarily affect the limits of flammability of paraffins in air.

Temperature is another matter.

Table 5.3 Temperatures of the Combustion Gas in RKI Process Equipment

Rotary kiln	900°C.
Afterburner	1000°C.
Boiler (Tube side)	1000°C. to 150°C.
Baghouse	150°C. to 120°C.
Stack	80°C.

For hydrocarbons the lower limit of flammability decreases 8 percent on the average for every 100 Centigrade degrees elevation of temperature (Zebatakis 1965). On this basis, lower limits for the test gases in the pilot plant equipment would be:

Table 5.4 Lower Limits for Tracer Gas Concentrations

	Methane, %	Propane, %
Rotary kiln	1.5	0.6
Afterburner	1.0	0.5
Boiler (Tube side)	1.0	0.5
Baghouse	4.5	1.9
Stack	4.6	1.9

Zebatakis recommends a safety factor of ½ to ¾ in using the flammability limits. In the presence of the very hot gases in the kiln, afterburner or boiler the hydrocarbons would be consumed. It was thus concluded that the safest place to add these two hydrocarbons would be in the stack.

It was also necessary to consider the concentrations resulting when pure hydrocarbon is released into a stack gas that is 3.6% CO_2, 12.8% O_2, 8.6% H_2O and 75% N_2. The lower flammability limits, adjusted for temperature as given above, are for hydrocarbons in air, which is considerably richer in oxygen than the stack gas. This fact would seem to provide additional protection. However, as the hydrocarbon mixes with the stack gas, its concentration moves, for example, from 100% to 1% or .1%, passing through the flammable mixture zone.

To assure that the gases to be introduced to the stack were rapidly and thoroughly mixed, they were fed to a sparger, located well upstream (below, in elevation) of the stack sampling point. The gas was piped to the top of the stack, and it was fed in a pipe down to the sparger.

Natural gas, which was used as the methane hydrocarbon, was available at 5 ounces per square inch pressure gauge. This is equivalent to 0.3 lbs/in^2 gauge or 776 mmHg absolute. Such a low positive pressure was a matter of concern. Testing of the system to assure adequate flow and dispersion was done using argon. In the design, pressure drop in a 3/4 –inch diameter, 75-foot long hose to the top of the stack, the sparger inlet pipe, elbows and valves plus the outlet holes in the sparger was calculated using physical models and software programs included in Guidelines for

Chemical Process Quantitative Risk Analysis (Center for Chemical Process Safety 2000).

Natural gas flow was controlled without difficulty and concentrations from 0.1 to 1 percent were emitted from the stack. The IMSS detector, set up about 200 feet away, was used to record spectral images of the escaping gases. Unfortunately, little success was experienced with methane. In laboratory tests by Pacific Advanced Technology in California, difficulty with methane had been attributed to interference of water at methane absorption wave lengths. The stack emissions tested were about eight percent water.

Propane flow from liquefied gas bottles was more difficult to control. As the propane evaporated, frost gathered on the metal surface of the gas bottle. Spraying the bottle with water was first tried as a method of warming the container, and it was then immersed in a water bath. Although the use of a water bath was not entirely satisfactory, flows of the desired range of concentrations were obtained. Concentrations of the stack exit gases were measured with the mass spectrometer and the readings were checked with a gas chromatograph. The portable gas chromatograph was loaned for the experiment by Dr. Edward Overton of the LSU Department of Environmental Studies.

The only images obtained by the IMSS were for 0.31% and 0.71% propane. In this case, the images showed the presence of propane tracer gas. Further examination for spectra distortions caused by atmospheric interference and instrument variation was suggested (Harlow and Sterling 2002).

5.4 Fugitive Emissions

The stack emissions discussed in the last section are, in general, known, and measurable sources of gaseous discharges to the atmosphere. The leaks of materials from piping and equipment in chemical plants, petroleum refineries and manufacturing plants of all kinds are categorized as fugitive emissions. The leaks are so-called because they are unintentional and occur mainly because of deficiencies in design, operation and maintenance. Pump and compressor seals, valves, flanges, screwed tubing and pipe fittings, instruments, pressure relief devices or any equipment containing organic or inorganic compounds can be sources of fugitive emissions.

EPA regulations require data collection and analysis in process facilities where volatile organic compounds (VOCs) or total organic compounds (TOCs) or other regulated materials are stored, transported, or processed.

Four methods of estimating equipment leak emissions are part of the regulations (U.S. EPA 1995). All of the methods involve an equipment count.

Method 1 applies average emission factors to arrive at Composite Total Emissions. Different factors are used for synthetic organic chemical manufacturers, petroleum refineries, marketing terminals and oil and gas production facilities.

The other three methods use screening data collected by using a portable monitoring instrument to sample the atmosphere in the immediate location of equipment (such as at every pump seal). Screening values are measures of concentration of leaking compounds, reported in ppmv.

Method 2, formerly known as the leak/no-leak approach, uses 10,000 ppmv as the leak definition. As for method 1, a complete set of emission rates in kg/hr are stipulated for various types of leak sources, in this case rates are given for ≥ 10,000 ppmv and < 10,000 ppmv.

Method 3, the EPA correlation approach, establishes a default zero (minimum) leak rate when no leakage is actually detected. For actual screening values there are correlations that make it possible to calculate leak rates in kg/hr for any detector analysis, Graphs are presented for leak rates up to 1,000,000 ppmv (EPA 1995). Provision is also made for instrument readings that are "pegged out" at 10,000 ppmv and 100,000 ppmv.

Method 4 involves logging emissions as well as obtaining screening values to set up leak rate correlations that are specific to the equipment being tested. The extra effort may be useful in proving that for a specific process unit (very well maintained, for example) does not leak as much as EPA correlations would specify.

The continual testing and record-keeping is a task imposed on industry by the EPA to ensure reduction of fugitive emissions.

The imaging spectrometer (IMSS) described in Section 5.3 was also proposed as a detector for fugitive emissions. A flanged 3″ valve was set up as shown in Figure 5.3, as a leak source. By loosening bolts on the flanges and at different times on the bonnet of the valve, measuring gas flow with rotameters as shown, it is possible to calculate leak rates. At the same time, an approved EPA instrument can be used to determine concentrations of gases at the contrived leak spots. The test equipment has

Figure 5.3 Fugitive Emissions Testing Apparatus

been set up, but Pacific Advanced Technology decided to conduct tests in California, and do not presently plan to bring the IMSS to Baton Rouge.

Although the original plan was not followed, the potential for a valuable contribution to fugitive emission testing exists with equipment as it has been constructed. The data from tests could be of great use in evaluating EPA correlation factors.

CHAPTER 6 SUMMARY

This chapter starts with a section containing recommendations for modifications and improvements. Fees for operation of the RKI on behalf of industrial clients form the basis for the next section, 6.2. The dissertation concludes, in Section 6.3, with some forward-looking statements about prospects for the future.

6.1. Recommendations

Each student, upon completing his/her research at the RKI has prepared a list of recommendations for repairs, maintenance, and improvements. Many of the suggestions have been acted upon; some remain to be implemented; and the list continues to grow.

a. Vassiliou (1996) proposed the installation of “Stack Sample Bypass-Valves and Sample Cooling Unit.” The CEMS draws a gas sample from the stack. Under normal operating conditions, the gas is warmed to slightly above its dewpoint. In an emergency, such as an electrical failure, the stack damper automatically opens, and hot combustion gas from the afterburner exits directly to the stack. In such cases the stack gas, and therefore the sample gas, drawn to the analyzers by a vacuum pump, can reach 2000 °F. The Nafion sample dryer and the analytical instruments are not constructed to withstand very high temperatures.

It would not be satisfactory to merely shut off the flow to the analytical instruments, since DEQ regulations require continuous analysis as long as there is effluent from the stack. Moreover, study of the effluents following an upset could be a part of research. Vassiliou suggested construction of an automatic bypass and cooling unit for the hot gases. This suggestion has been repeated by others, with sketches of various valve arrangements and cooling units (Muthukrisnan 1997, Rester 1997). The design, probably following the Vassiliou model, needs to be finalized, and the installation completed.

b. Additional Temperature and Pressure Sensors, Transmitters, and Flow Metering Devices were suggested. The original plant was constructed principally as a demonstration facility for determining the incinerability of waste materials. Much more is required of a combustion research laboratory. Even after the addition of many measuring devices, new analytical sample points, temperature and pressure sensors are needed and will be required as each new experiment is designed. For example, an additional complete sample extraction system with a duplicate CEMS has been proposed. Such a system would sample gases at the kiln exit, downstream of the afterburner and at the outlet of each of the air pollution control devices. At present, the following items are on hand to start installation:

1. A high temperature sample probe, a duplicate of the one now in use in the stack.
2. A Johnson Yokogawa Corporation Oxygen Analyzer.
3. Insulated, ¼”, 316 stainless steel tubing with electrical heat tracing. The electrical tracing regulates the sample temperature so that the temperature does not fall below the dewpoint.
4. A temperature controller for the electrical tracing listed above.
5. A Nafion Dryer to remove water from the sample, plus a spare.

6. A carbon monoxide analyzer.
7. Sample nozzles at the kiln exit and afterburner exit.

The above list constitutes perhaps half of the material required for a complete, new CEMS system with multiple sampling points.

As a minimum, one new cooler would be needed. The kiln exit sample will be at about 1600 °F., and the afterburner exit sample will be at about 1800 °F. Two such coolers for samples extracted from these locations are required to be designed and built unless sampling were switched from one sample point to another.

Another mass spectrometer, a gas chromatograph, or individual analytical instruments would be essential for a more than minimal additional system.

> In addition, improved sample probes need to be designed and fabricated. Probe design involves considerations of fluid dynamics, temperature, cooling methods, and strength of materials. Designing and testing a number of configurations would be a challenging and worthwhile project.

c. A Stack Damper Proximity Switch was recommended for the pneumatic cylinder that operates the damper. The signal from the switch could actuate the stack sample bypass recommended above (Vassiliou 1996). The ladder logic of the PLC could be altered to achieve the same objective.

d. Load indicators for all motors would provide performance monitors and would signal need for maintenance.

e. Control Strategy Upgrades should include decoupling of natural gas flow controllers. The natural gas flow controllers are fed from a common source. Looking forward to automatic control of the process, provision should be made in the control system to prevent interaction of the gas flow control loops. Unless they are decoupled, by automatically switching one of them to manual operation when there are wide swings in demand, the complete control system could become unstable (Vassiliou 1996).

f. A complete, distributed control system should be designed and installed so that the facility will be instrumented in an up-to-date manner, to increase stability of operations, and to teach students about automatic control. As a teaching facility, the presently installed control equipment is far from optimal. There are some advantages in manual control in learning a process, of course, but the pilot plant should be updated to the latest technology. Such an upgrade would enhance the facility's attractiveness to students but also to faculty and industrial clients.

g. Shielded thermocouples have been recommended to overcome the radiant heating effect of luminous flames, soot and kiln walls. Rester (1997) suggested three designs for open wells that would shield thermocouples from radiation while permitting them to be contacted by the combustion gases.

h. Frequent failures of the flame sensing devices (Fireye®) of the kiln and afterburner burners have been experienced since the start of operations. One of the interlocking safety features prevents the kiln burner from firing, unless the afterburner burner is firing. This is a precautionary measure, so that the kiln cannot be burning waste unless the afterburner is activated to complete combustion of any gases generated. Failure of the SOC Fireye® to shut off its signal, when its burner was shut down has resulted, on a number of occasions, in the POC burner continuing to operate. These devices need to be replaced to assure reliability and safety.

i. In Chapter 4, it was noted that the kiln burner was judged to be oversized for the volume of the kiln. Its flame extends the entire length of the kiln. The flame from the burner for the afterburner, at maximum gas flow, impinges on the refractory of the afterburner wall, indicating that it, also, is oversized. Replacement of these two burners and the two flame sensing devices would be a useful project.

j. At the same time, it would be advantageous to provide upper and lower inlet ports for two kiln burners. Then, if designed to be directed vertically and horizontally (articulated), the effects of flame positioning could be studied. With the capability provided by articulated burners, an attack could be made on the stratification of temperature, composition and flow detected in the Dow experiments. Another enhancement would be nozzles for the introduction of swirling, turbulence air.

k. Muthukrisnan (1997) discusses the need for automatic, continuous measurement and recording of relative humidity of air input to the process and of the humidity of the stack gases. At present, it is necessary to determine the relative humidity and to manually input the data in material balance calculations. The measurement and recording should be automated.

l. The stack gas oxygen analyzer analyzes the wet stack gas, and the wet analysis is displayed and recorded by the DAQ. The DEQ’s Small Source Permit for the LSU RKI requires that stack oxygen concentrations be maintained above two percent on a dry basis. With the installation of automated recording of humidity of the stack gases, DAQ calculation, display and recording of dry O_2 concentrations would be possible.

m. Currently, the DAQ displays and records the concentration of carbon monoxide on a dry basis. The DEQ Small Source Permit, however, regulates the amount of CO at 100 ppmv corrected to seven percent oxygen.

$$\mathrm{CO(corrected)} = \frac{\mathrm{CO}_{\mathrm{actual}} \times 14}{21 - \%\mathrm{O}_2\mathrm{dry}}$$

With the O_2 dry concentration available, as in the previously suggested modification, the corrected CO concentration could be displayed and recorded by the DAQ (Muthukrisnan 1997).

n. An uninterruptible power supply (UPS) was recommended to prevent loss of control in electrical storms when outages of minor duration affect computers controlling the process (PLC) and data acquisition (DAQ) (Rester 1997).

o. Development of a research program aimed at the puff problem is an urgent priority. Steam quenching needs to be investigated as a method of regulating excursions of PICs.

p. Improvements for continuous emission monitoring systems are continually sought by the EPA. Equipment manufacturers seek certification of new instruments. Regulated companies are wary of new, more stringent requirements for pollution control. All of these parties are potential participants in a major project with the objective of certifying mass spectrometers and similar instruments.

Future experiments will take the direction indicated by research interests of faculty and students and by the availability of funding. The pilot plant is so constructed that almost any medium-sized combustion project could be undertaken. Flexibility to adapt to client needs is illustrated in the projects undertaken so far and others that have been proposed.

In the next section, 6.2, some aspects of the funding topic are discussed. Section 6.3 relates to status and future prospects for rotary kiln incineration at LSU.

6.2. Fees for Operation of the RKI

The primary objective of the LSU RKI Laboratory is to conduct combustion research, with emphasis on rotary kiln incineration. Industrial clients seeking research assistance are intended to be the main source of support for the operations of the facility. Potential clients could be manufacturers wishing to test new products, such as a burner or a filter. Other examples are companies that need incinerability information for a proposed new waste stream, or evaluation of combustion conditions to reduce generation of pollutants.

For cost and operation purposes, projects fall into two main categories. Minor projects involve short runs of the kiln and very few modifications of equipment or procedure. Major projects encompass any extended undertaking. Examples of the latter would be a week or more of operation or installation of a new equipment item as part of the investigation.

For contractual purposes, projects are also divided into a small and a large category. There are differences in the requirements of the LSU Office of Sponsored Research, the regulator of all research programs funded by industrial clients. For example, where total project costs are less than $10,000, overhead charges on salaries and services are not charged to the project. For major projects, the overhead burden is a very considerable cost, and it must be borne by the sponsor of the project.

Exemption from the overhead cost makes it possible to hold costs down where there is a minor expenditure of university resources. In instances where only a minimum run is required there is no attempt to recover annual costs of depreciation and maintenance. A three-day run is the practical minimum, considering heating up, performing tests, and cooling down. Often, however, such a beginning is a first step in a longer-range program of research.

Table 6.1 is a sample of a minor project cost estimate.

Table 6.1 Project Budget

1. Salaries		
Undergraduate assistants (100 hours)		$1,000
2. Travel		0
3. Equipment		0
4. Supplies		
i Calibration Gases	2,000	
ii Supplies (piping, instruments)	4,000	6,000
5. Operating Services (internal)		400
6. Professional Service Fees (external)		1,600
Total Direct Costs		9,000
Total Cost		$9,000

Often the client’s cost is larger than the amount of the contract with LSU. For instance, a recent proposal, in addition to a three-day run of the kiln, involved employing a contractor to take samples using an EPA-approved volatile organic sampling train (VOST). The estimate for the sampling was five to six thousand dollars. The contractor recommended that sample analysis be done by an independent laboratory at an estimated cost of $12,000. In another case, an equipment manufacturer required that stack gas at a temperature of 800°F be supplied for their proposed tests. Cleaning the gases includes cooling before they enter the baghouse and scrubber. This project would require a heat exchanger to reheat the gases, at a cost of four to five thousand dollars.

Fees for major research programs must necessarily absorb all of the relevant costs of operation including salaries for faculty and other supervision, all other direct and indirect costs, and allowances for annual maintenance and depreciation. In addition, some contribution to future improvement of the facility is expected in any undertaking.

To arrive at suitable charges, estimates have been made of projected reimbursable costs. The estimates are based on 84 days per year of operation of the kiln, which would amount to twelve seven-day trials.

A senior researcher and a technician are listed as full-time personnel to plan and execute experiments. Operating labor is provided by part-time undergraduate student trainees. The rate for student wages is for billable hours, somewhat higher than their normal rate, but a bargain for an industrial customer. Utilities are natural gas, electricity and cooling water. The other direct cost items, supplies, tools and maintenance, are allowances based on history.

Depreciation is a 15-year, straight line, write-off of the present investment. Fifteen years was chosen as an average useful life for the equipment and auxiliaries in this service. Some of the equipment is in need of replacement soon (the baghouse and the burners for the kiln and afterburner).

The added ten percent for improvements, which was mentioned previously, is needed soon for upgrading the process control system and adding to the sampling points for combustion gas analysis.

Table 6.2 is a sample estimate that lists the relevant costs. The total can be divided by the expected operating (kiln firing) days for the year. In that case, the calculated rate is $3,000 per day.

Thus, a 3-day run would have a price of $9,000, which indicates that our under-$10,000 budget would recover actual costs. It is important to have this low-cost option available, since in many cases potential clients want a first, quick look at feasibility. Moreover, valuable relationships can be established in such projects.

Table 6.2 Annual Costs

Personnel:		
Research Supervisor	$45,000	
Technician	35,000	
Students		
Two × 20 hours/week × $10/hour	20,000	
Subtotal Salaries		100,000
Utilities	15,000	
Supplies	7,000	
Tools	2,000	
Instrument Maintenance	8,000	
Shop Maintenance	6,000	38,000
Total Direct Costs		138,000
Indirect Costs (47%)		65,000
Depreciation		33,000
Improvements 10% of above		24,000
Total Annual Cost		$260,000

Note, however, that there is no provision in the estimates for compensation of faculty or graduate students, if they are involved, as they are likely to be. These items probably should be calculated separately for each project since the amount of time could vary widely.

Since the kiln operates around the clock, it has been standard practice to work twelve-hour shifts. Such a schedule works well for short runs. It might be necessary to increase personnel temporarily for lengthy trials.

6.3 Future Prospects

The prospects for an industry-supported RKI laboratory at LSU are encouraging, based on accomplishments to date, and hopeful, based on capabilities and the need for fundamental research.

The achievements, so far, are the design, construction, startup, and satisfactory operation of a unique combustion laboratory centered on a mid-sized rotary kiln incinerator. The continuous emission monitoring system is equal or superior to any available at an industrial or at a research facility engaged in rotary kiln incineration.

Up to the present time, eight students have earned Master of Science degrees, and one person of a Ph.D. degree, based on research at the LSU RKI. Approximately three dozen undergraduates have benefited from instruction and projects that related to engineering aspects of operation and maintenance of the kiln equipment. A number of them have obtained employment, upon graduating, in positions where their kiln experience has been an asset. The effectiveness of the facility as a teaching laboratory has thus been demonstrated.

The experiments that have been conducted thus far have added to the knowledge base for incineration, reinforcing the value of research at the pilot scale, and pointing the way to further research.

Smoke and odor are the obvious indications of less than satisfactory operation of a rotary kiln incinerator. Even more important, however, than these disagreeable discharges, is the hidden danger of poisoning of the atmosphere from incinerator effluents. Methods for control of NO_X, SO_X, particulates, carbon monoxide, and poisons such as dioxins, must be investigated. The problems will not go away without dedicated research.

Government participation in implementing long-term solutions to waste disposal is held by many to be heavy-handed. It may be argued, however, that there would be little or no pollution control without government interference. It is only necessary to recall atmospheric conditions in Pittsburgh or London, fifty years ago and compare with today's situation to realize that change was necessary. Lack of government control results in current atmospheric conditions in Eastern Europe and Asia that are comparable to our own situation only a few years ago. The solution is continued research.

It has been suggested that training of incinerator operators offers a potential for improvement of performance. Incinerator operators are now required by regulations to be trained. The American Society of Mechanical Engineers offers a certification course directed to incinerator operators. The course consists of two parts, Provisional Certification and Operator Certification. Instruction of 100 to 150 hours and a written test, are required in the first phase. Operator Certification in the second phase involves site-specific training and an oral examination. Certificates are valid for five years.

There is no doubt that training is as necessary and valuable for incinerator operators as for boiler operators. Boiler operators are required by law to be qualified and certified to operate boilers operating at or above 15 psig. Note, however, there is no such legal requirement for certification of operators of high pressure equipment in chemical plants, paper mills, petroleum refineries, and the like. Formal training for incinerator and chemical plant operators may be a future use for facilities similar to the LSU RKI. A neighboring facility, The Petroleum Engineering Research and Technology Transfer Laboratory, currently offers training programs for petroleum production personnel.

The Louisiana State University Rotary Kiln Incinerator is equipped and prepared to engage in a wide variety of research and teaching projects. The research effort will be undertaken somewhere, and LSU is an obvious candidate for the work.

CHAPTER 7 CONCLUSIONS

In the following discussion, a number of important conclusions resulting from the research in the LSU RKI are summarized, and it is concluded that the pilot plant has demonstrated its value as a research and teaching laboratory.

7.1 Rotary Kiln Incineration

7.1.1 Time Constants

The time constants presented in Chapter 3 demonstrate the complexity of convection and radiant heat transfer in the kiln. Their relative importance is indicated in the responses to step-ups and step-downs in POC gas flow rates. It will be recalled that the convection or fast, time constant for the POC was 1.3 minutes, whether stepping up or stepping down. For the radiant effect, the time constant was 75 minutes in stepping up and 43 minutes in stepping down. The data show that the radiant heat gain is slower than the heat loss, which occurs at a higher temperature. This is an expected result. What is valuable, new information is the magnitude of the difference in the particular situation with six sources of radiant energy (the two flames, the combustion gases, the red-hot walls of the kiln and afterburner, and the white-hot wall of the afterburner).

The corresponding data for the SOC temperature in the same experiments demonstrate that, whereas exposure to the flame affected the Fast time constant in the POC determinations, such was not the case for the SOC, where the temperature measurement was made at a location beyond the direct influence of the flame. With respect to the radiant effect, the SOC thermocouple has only one source, the walls of the ductwork. The time constant attributed to radiant effect, however, shows approximately the same decrease as for the POC counterpart. This time constant was 72 minutes for stepping up and 41 minutes for stepping down, almost exactly the same as for the POC. It also is notable that in stepping up, the Fast effect for the SOC is about one quarter of the total, whereas it is nearly half of the total for the POC. In stepping down the fast effect for the SOC amounts to 14% whereas it is practically unchanged as a percent of the total for the POC.

7.1.2 Consistency of Data

The material and energy balances presented in Chapter 3 are based on routine operations of the pilot plant. They illustrate the reproducibility of the process data in the incineration experiments.

One objective of the batch trials described in Chapter 4 was to demonstrate that pilot plant system responses were repetitive and stable. The results obtained in these experiments illustrate the consistency and reliability of the data. Attention is drawn to CO_2 evolution data charted in Figures 4.5 and 4.6.

7.1.3 Similarity of Pilot-Scale and Full-Scale Responses

Another goal of the batch trials was to show that process characteristics were comparable to those of full-size industrial kilns, and thus to determine the suitability of pilot plant data for scale-up calculations. Recordings of CO_2 concentration in the stack gas, as indicators of VOC evolution in the kiln, produce remarkably similar profiles to those obtained in the full-size Dow kiln. A two-puff response can be clearly identified at both scales. Although pack sizes for the pilot kiln, based on burner ratio, were 1/75th the size of those in the larger kiln, the time constants for evolution of VOC are comparable.

Table 7.1 Time Constants for Evolution of VOCs

Feed Volume and Material	Time Constant
18.9-liter toluene packs in Dow kiln	141 seconds
0.252-liter toluene packs in LSU RKI1	133 seconds
0.252-liter xylene packs in LSU RKI1	127 seconds

These data appear to indicate that temperature is the controlling factor, not the size of the pack or the volume of the kiln. On the other hand, the indication may be that burner ratio was a remarkably good basis for the pack-size ratio.

7.1.4 Incinerability of Still Bottoms

Still bottoms processing was undertaken to determine the incinerability of the distillation residue and to assess the possibility of recovering the potash byproduct. The organic matter was successfully volatilized and oxidized. Ash production was 150 lbs. per ton, and the ash contained 25% potassium. It was concluded from the apparent pumpability of the still bottoms that a rotary kiln would not be necessary to incinerate the material, but that a conventional, stationery furnace with a liquid feed would be more appropriate.

7.2 Other Research Topics

The adaptability and versatility of the facility to accommodate a diverse range of projects is indicated by the following activities in which advantage was taken of existing equipment and/or analytic capability. With suitable modifications, almost any combustion experiment could be conducted on the large-size, remotely located property.

7.2.1 Firelogs

Synthetic fireplace logs were produced by the LSU School of Forestry, Wildlife and Fisheries for the purpose of developing a synthetic log that would be cleaner-burning than natural wood or currently-available petroleum-based logs. An additional goal was to develop a use for wood waste such as sawdust or wood shavings. Rated on the basis of the amount of total hydrocarbons in the chimney effluent, the LSU synthetic logs were shown to be cleaner than oak or commercial logs. In the amount of CO produced, the LSU logs were about the same as the others. The LSU log with 60% wax binder was superior to all of the others in the amount of heat released, as measured by CO_2 production per pound of firelog.

7.2.2 Stack Emissions

Tests of the capability of a remote-sensing, portable, optical gas detector were conducted to evaluate the Image Multi-Spectral (IMSS), an invention of Pacific Advanced Technology, Inc. Apparatus was designed to inject hydrocarbon gases into the stack of the RKI. Natural gas was successfully regulated and injected at various concentrations from one-tenth of one percent to one percent of the stack gas effluent. Difficulty was experienced with propane feeding from bottles. Evaporation of liquid propane cooled the bottle’s contents to below the boiling point, making the flow erratic. The IMSS was not successful in detecting the methane in natural gas. Pacific Advanced Technology considered it possible that spectral emissions from water vapor interfered with methane detection. The stack gases contained 8% water. Propane at 0.31% and 0.71% was detected.

7.2.3 Fugitive Emissions

In an example of research growing out of previous work, apparatus suitable for generation and measurement of fugitive emissions from flanges and valves was constructed to further evaluate the capabilities of the IMSS system. The equipment consisted of a gas source, a battery of rotameters to measure gas flow, a muffle furnace to heat the gas, 3” piping, and a 3”, 150# flanged valve. The tests were not carried out because Pacific Advanced Technology decided not to come to Baton Rouge, but to conduct tests in California. The test set-up in Baton Rouge was constructed to meet ASME specifications, and it is concluded that tests using an EPA-approved gas detector should be undertaken to provide new and valuable data.

7.3 Future Considerations

The pilot plant has demonstrated its value as a research and teaching facility as substantiated by the work of nine graduate students, (Eight M. S., and one PhD. thus far), whose research was conducted at the laboratory.

It is concluded that rotary kiln research will be required in the future. It will be done somewhere. The LSU RKI has the basic equipment needed to make important contributions to solution of vital pollution problems.

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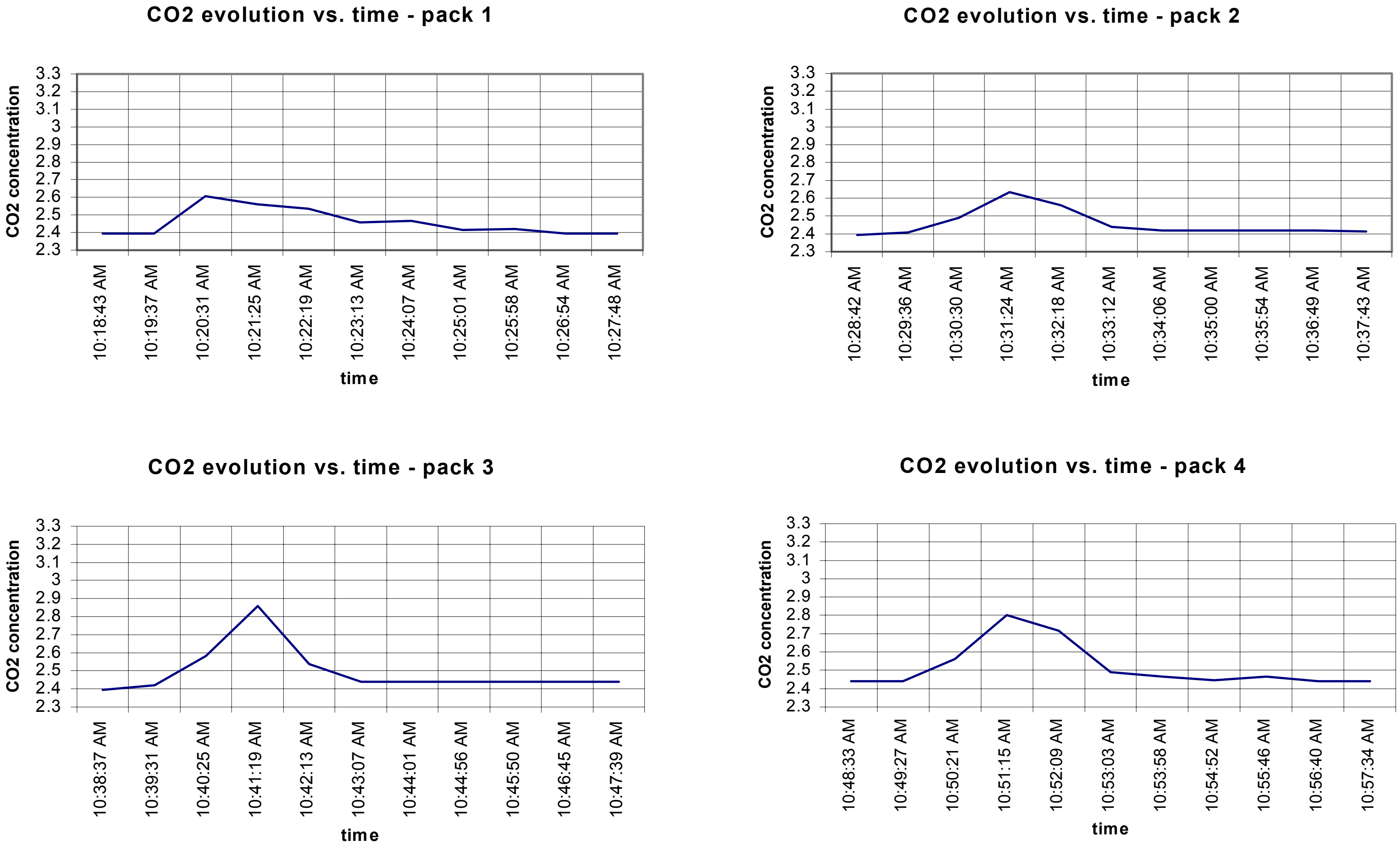
APPENDIX A: TOLUENE AND XYLENE CHARTS

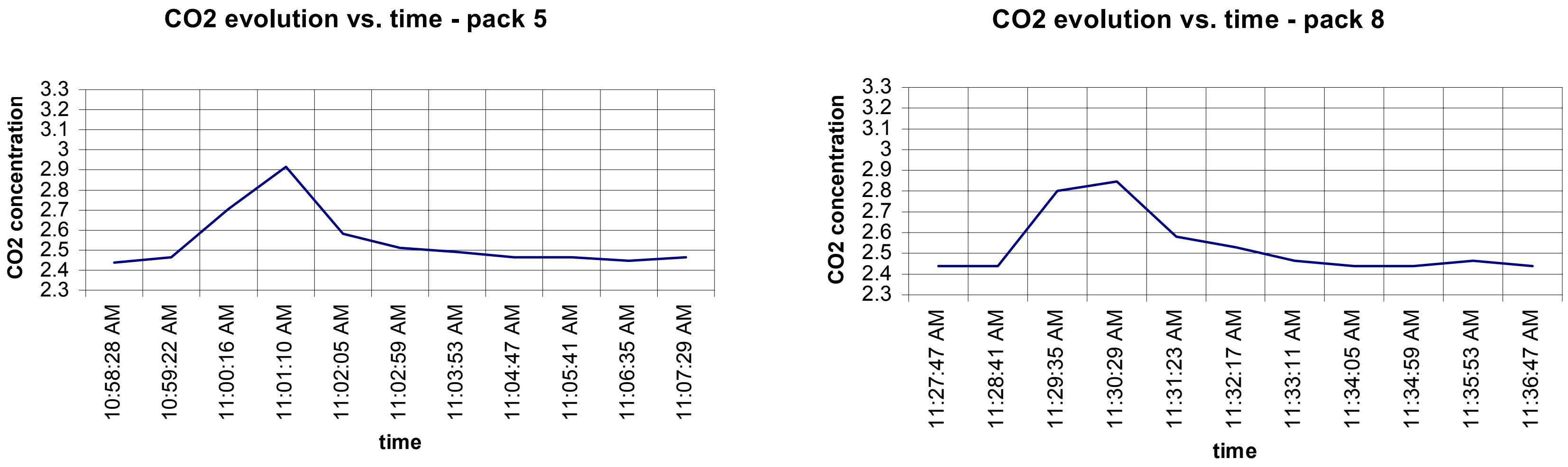

CO2 evolution vs. time - pack 1

CO2 evolution vs. time - pack 2

CO2 evolution vs. time - pack 3

CO2 evolution vs. time - pack 4

Figure A.1 Toluene – 1.19 gm moles per pack


CO2 evolution vs. time - pack 5

CO2 evolution vs. time - pack 8

Pack 6 and Pack 7 not recorded due to DAQ failure

Figure A.2 Toluene – 1.78 gm moles per pack

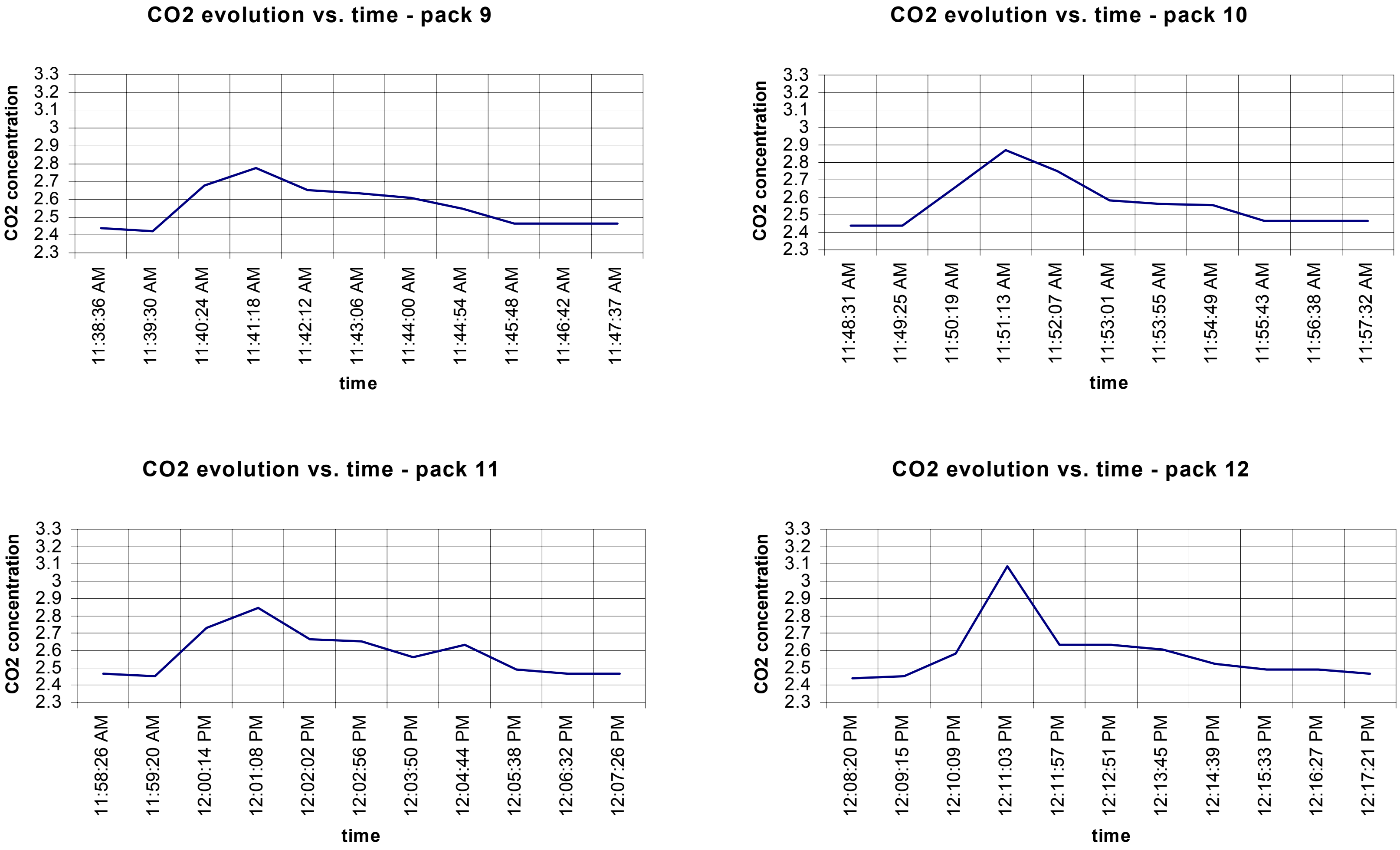
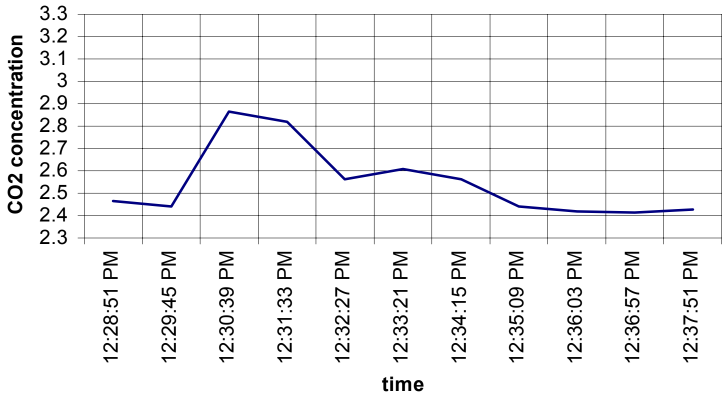


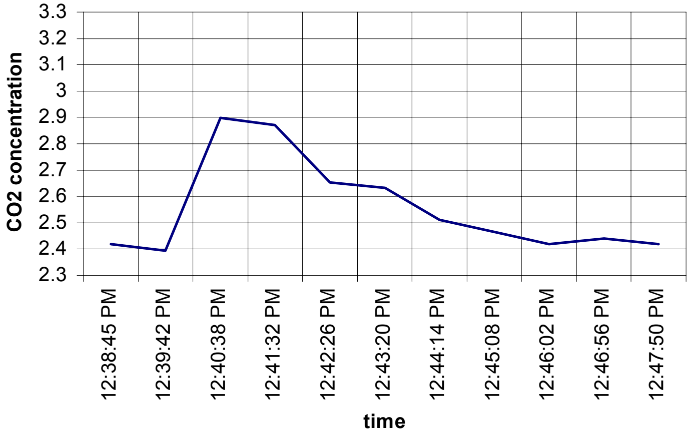
Figure A.3 Toluene – 2.37 gm moles per pack

Pack 13 not recorded due to DAQ failure

CO2 evolution vs. time - pack 14



CO2 evolution vs. time - pack 15



CO2 evolution vs. time - pack 16

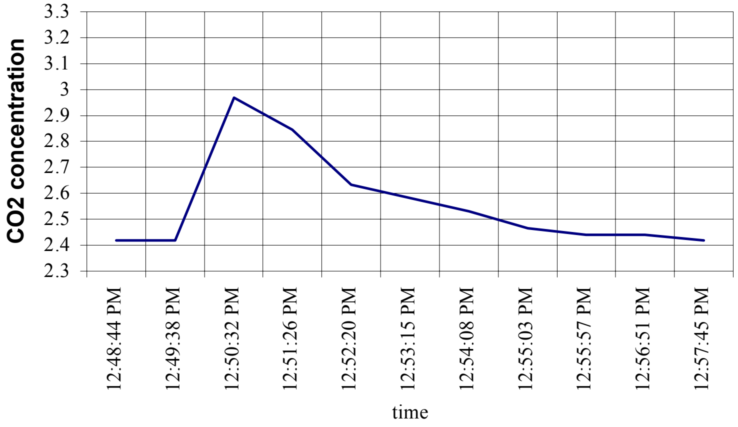


Figure A.4 Toluene – 2.61 gm moles per pack

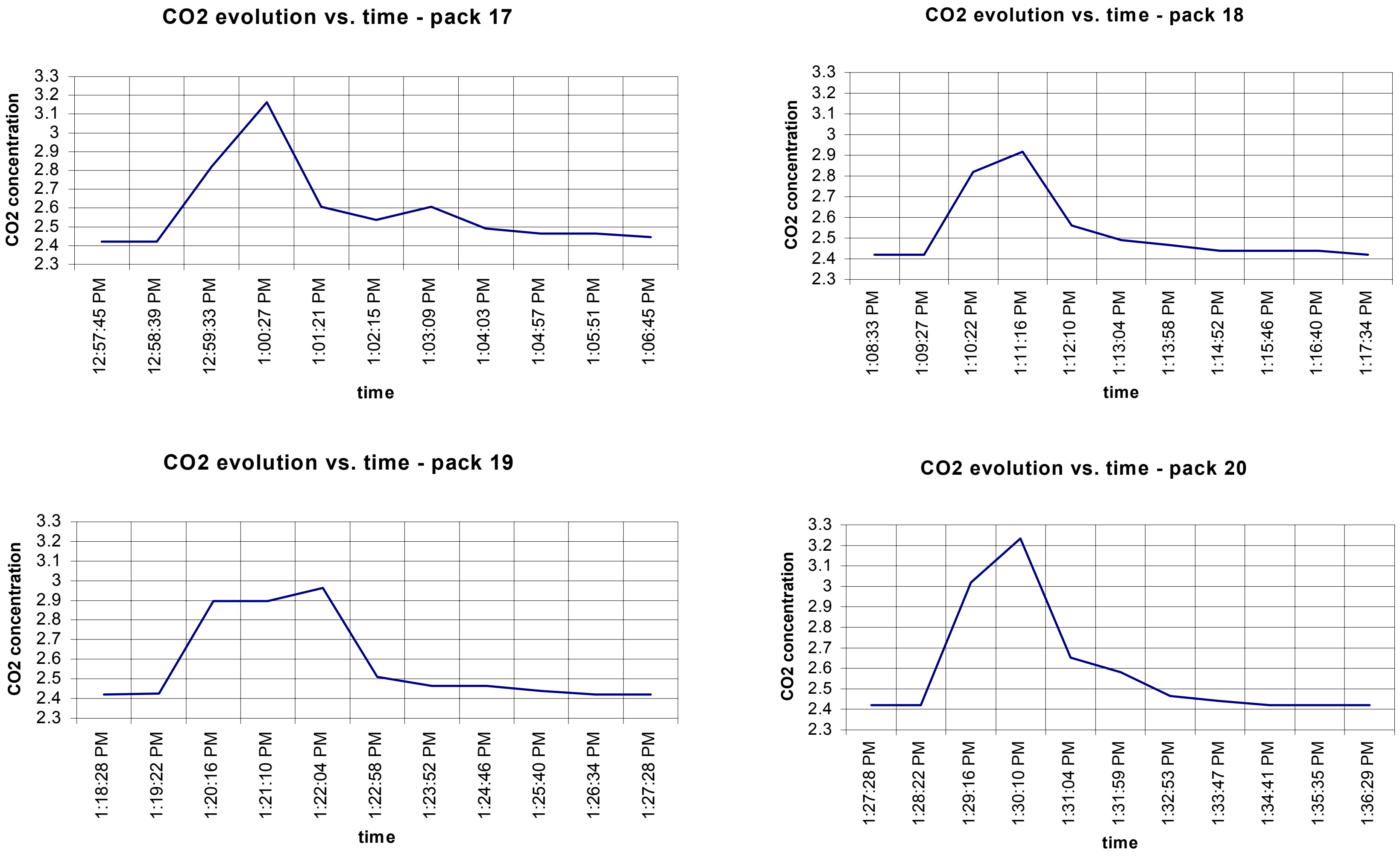
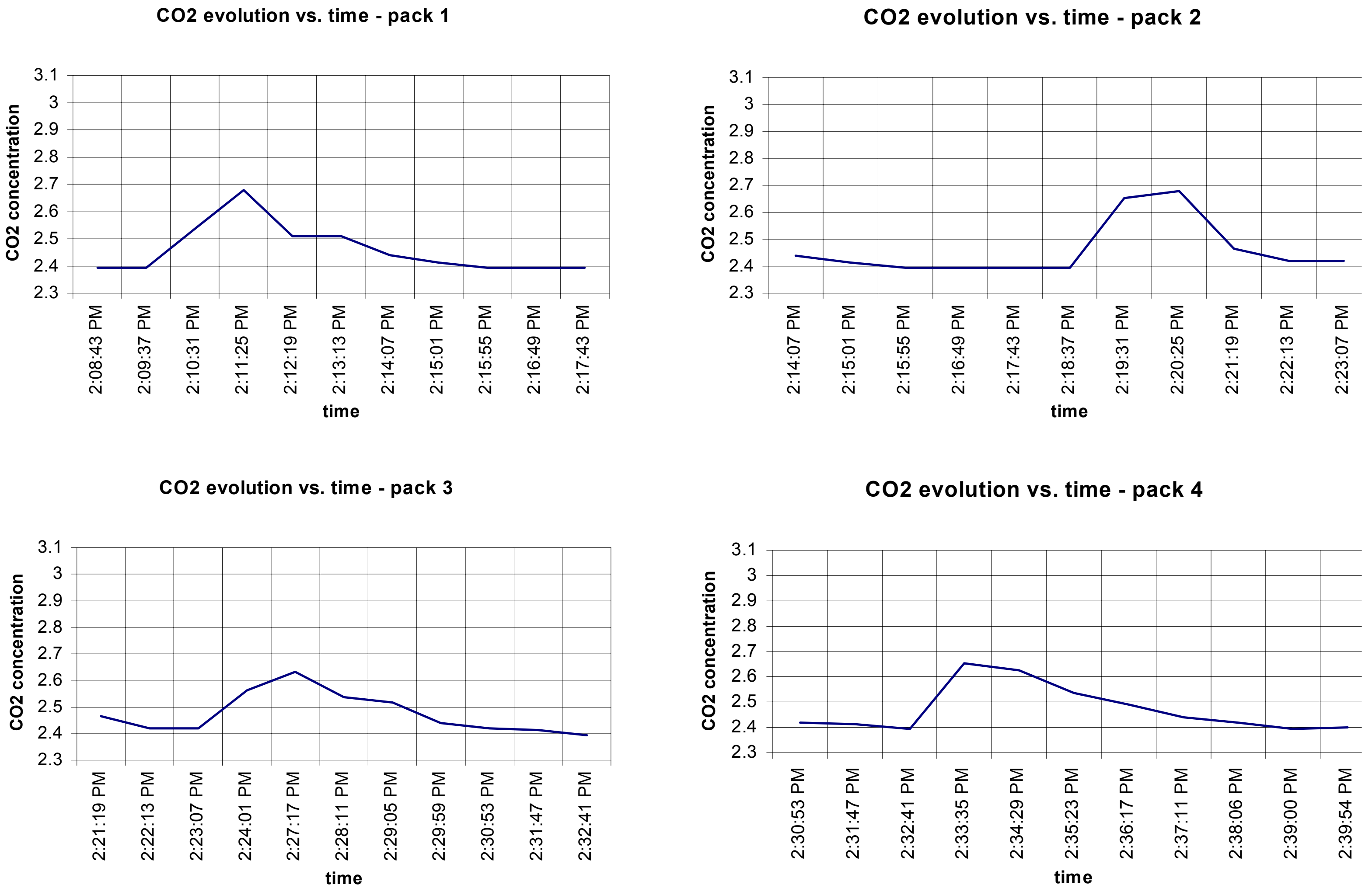


Figure A.5 Toluene –2.96 gm moles per pack

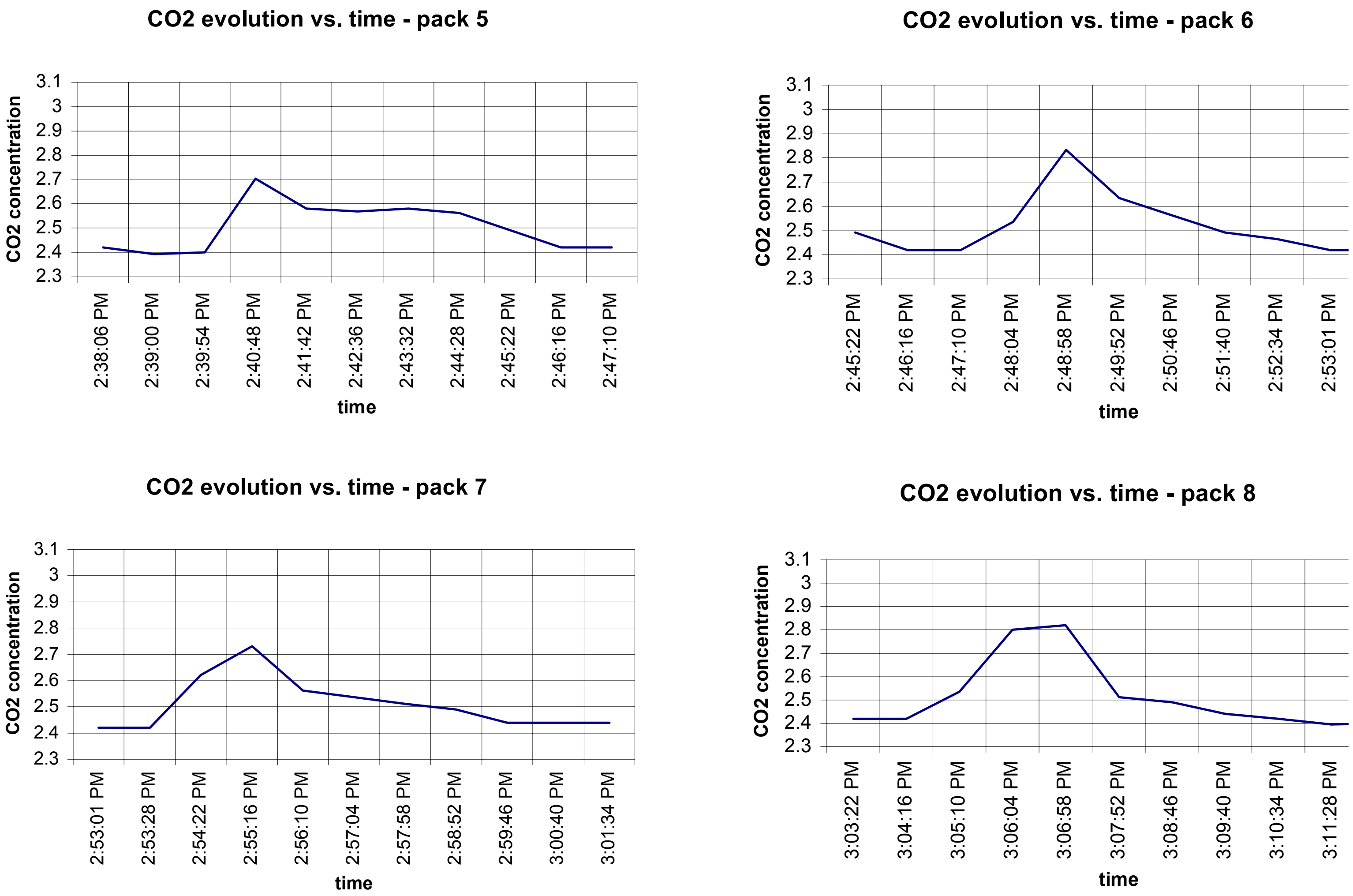

CO2 evolution vs. time - pack 1

CO2 evolution vs. time - pack 2

CO2 evolution vs. time - pack 3

CO2 evolution vs. time - pack 4

Figure A.6 Xylene – 1.03 gm moles per pack

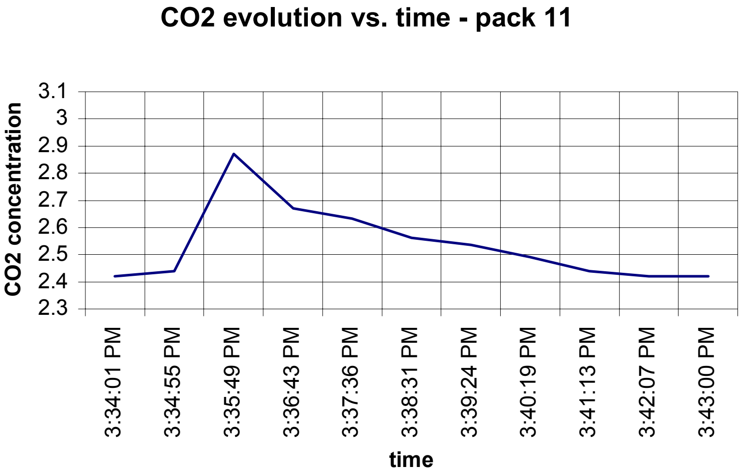

CO2 evolution vs. time - pack 5

CO2 evolution vs. time - pack 6

CO2 evolution vs. time - pack 7

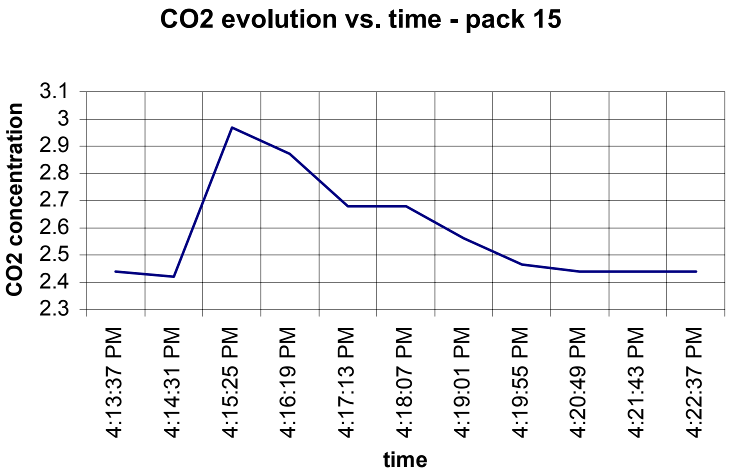
CO2 evolution vs. time - pack 8

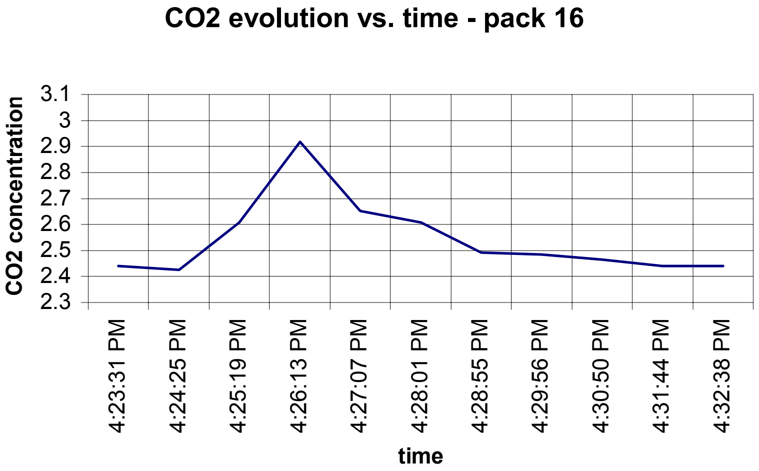
Figure A.7 Xylene – 1.55 gm moles per pack



Packs 8, 9, and 12 not recorded due to DAQ failure

Figure A.8 Xylene – 2.06 gm moles per pack



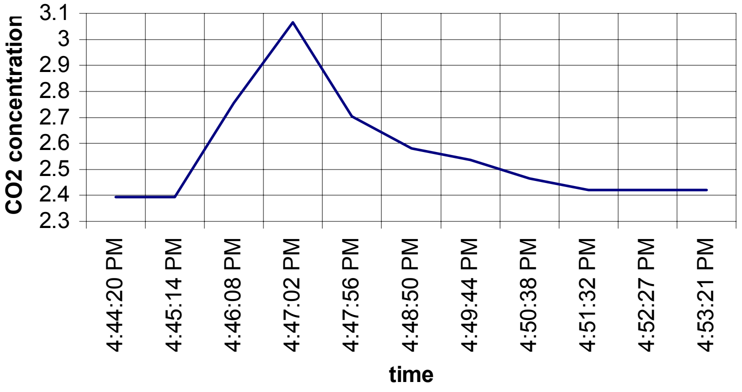


Pack 13 and Pack 14 not recorded due to DAQ failure

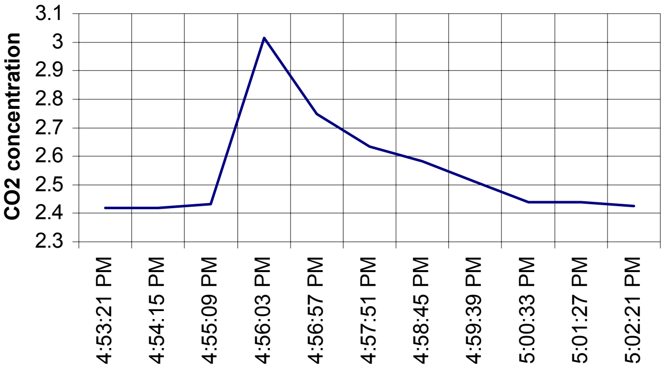
Figure A.9 Xylene – 2.27 gm moles per pack

Pack 17 not recorded due to DAQ failure

CO2 evolution vs. time - pack 18



CO2 evolution vs. time - pack 19



CO2 evolution vs. time - pack 20

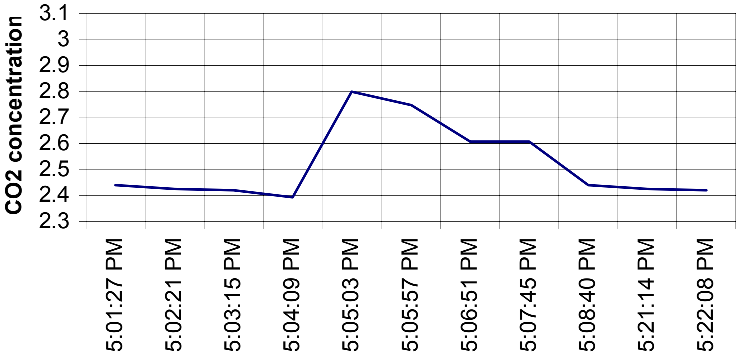


Figure A.10 Xylene – 2.58 gm moles per pack

APPENDIX B: PROCESS AND INSTRUMENT DIAGRAM

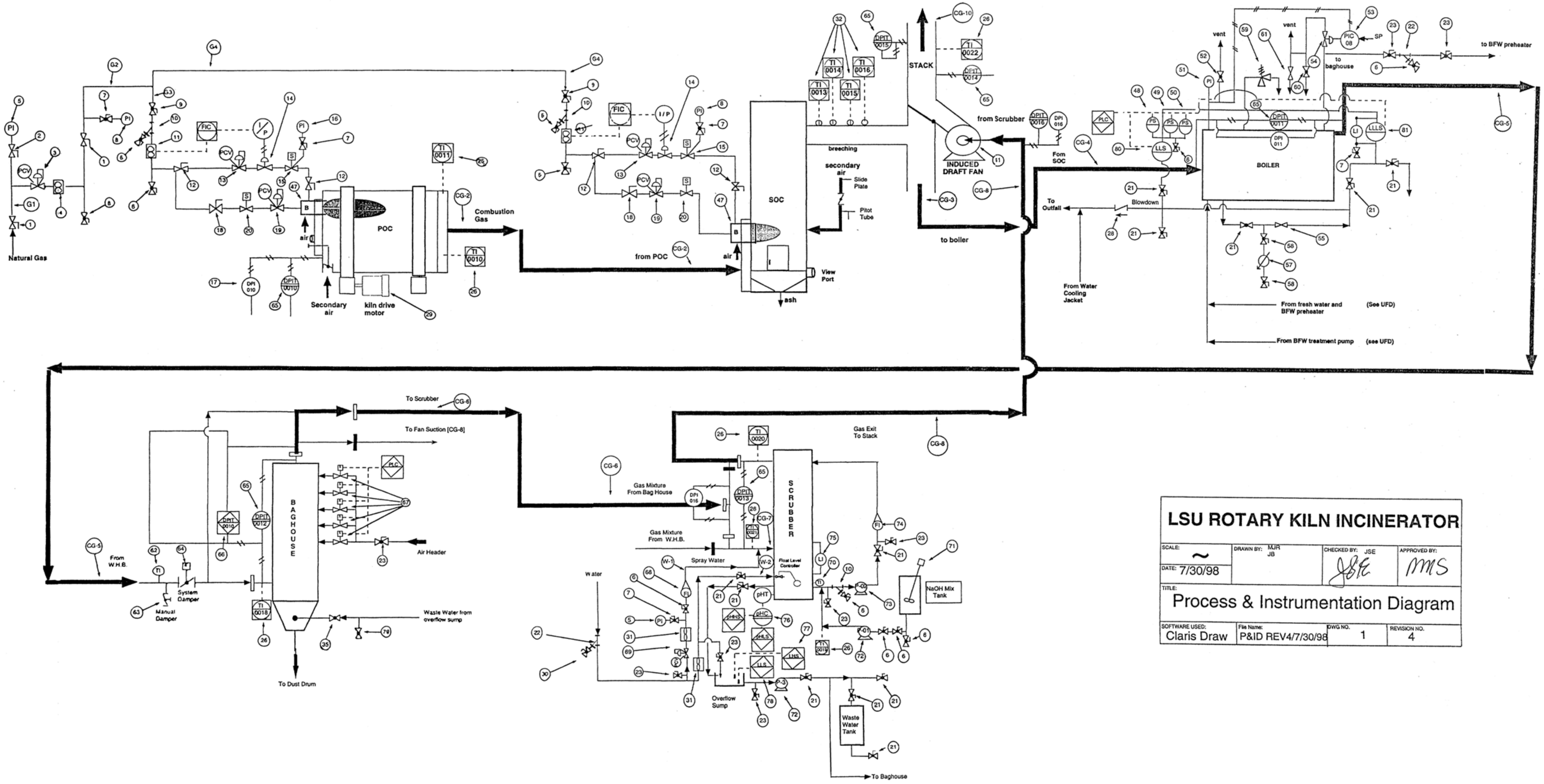


Figure B1. Piping and Instrumentation Diagram (P&ID) for the LSU Pilot-Scale Rotary Kiln Incinerator

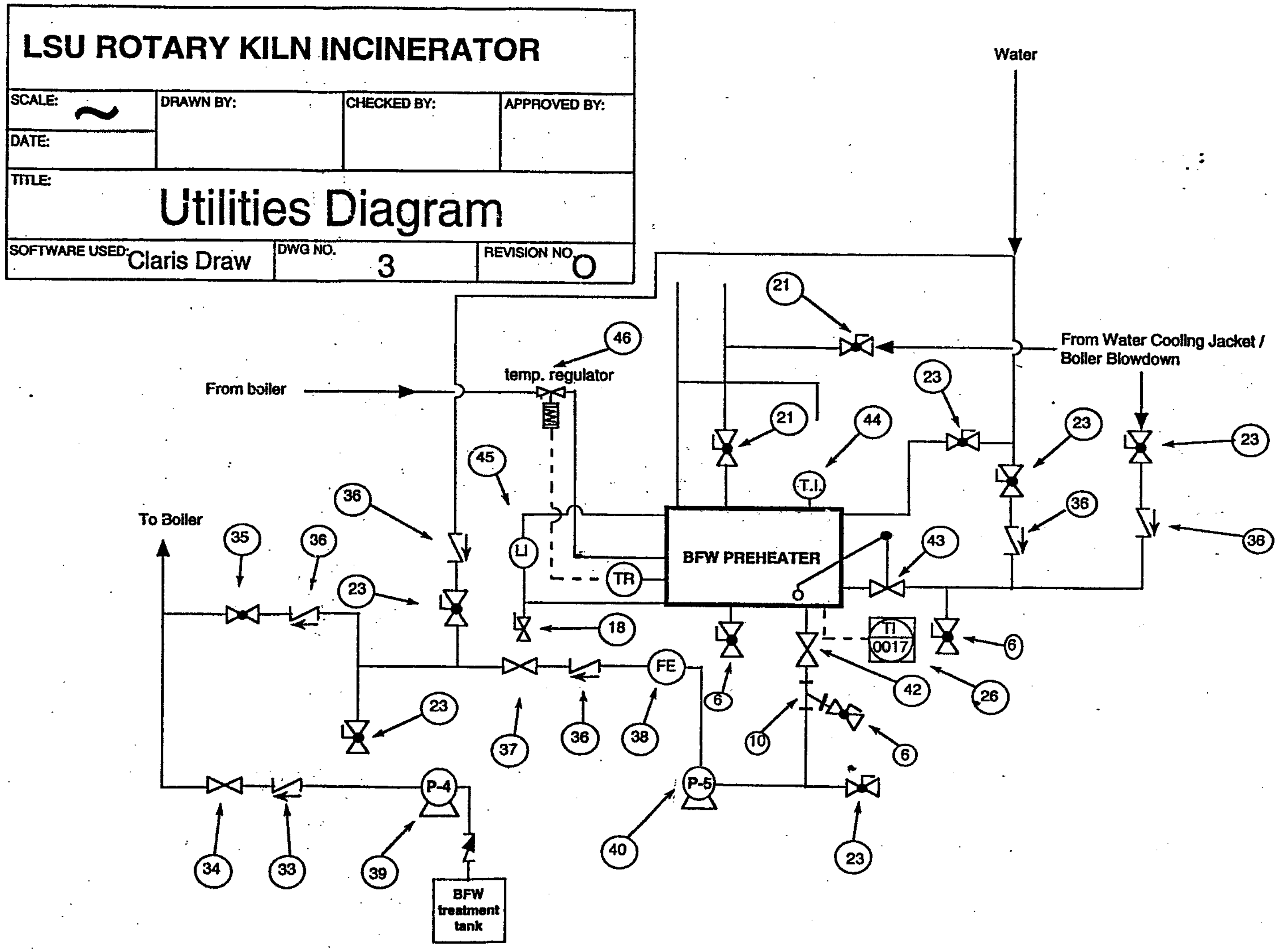


Figure B.2.1 Boiler Feed Water P&ID for LSU Pilot-Scale Rotary Kiln Incinerator

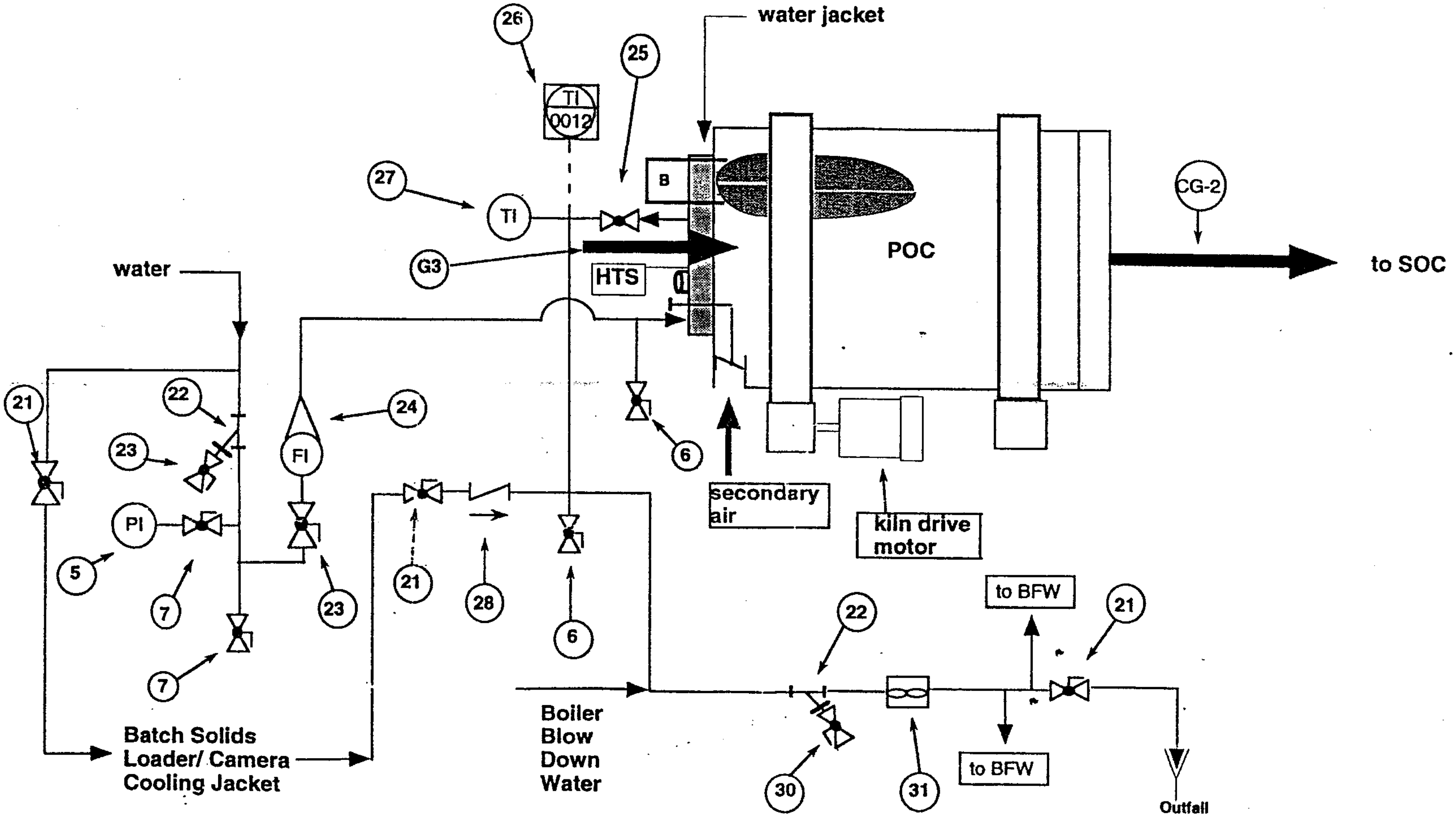


Figure B.2.2 Primary Oxidation Chamber Water P&ID for LSU Pilot-Scale Rotary Kiln Incinerator

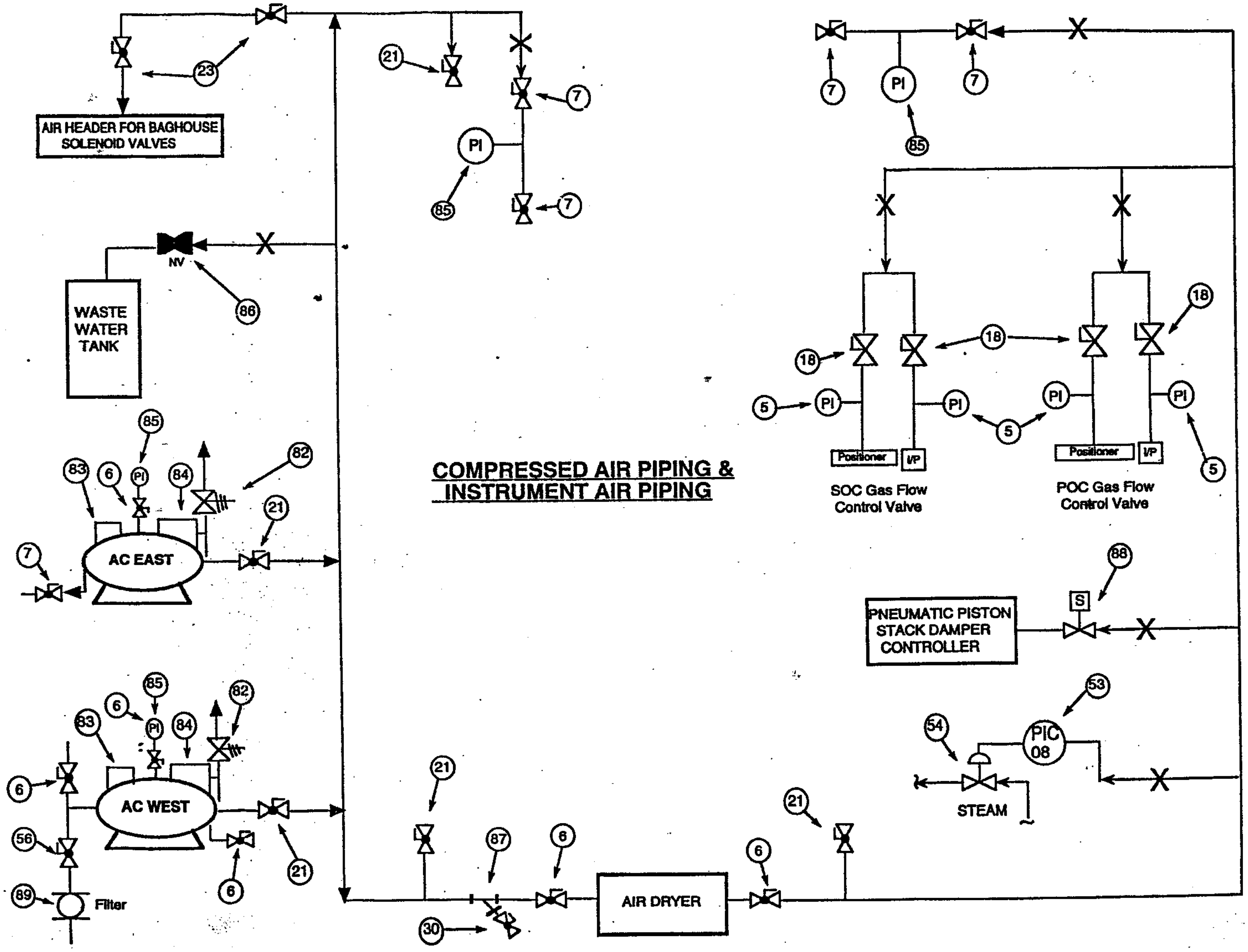


Figure B.2.3 Compressed Air and Instrument Air P&ID for LSU Pilot-Scale Rotary Kiln Incinerator

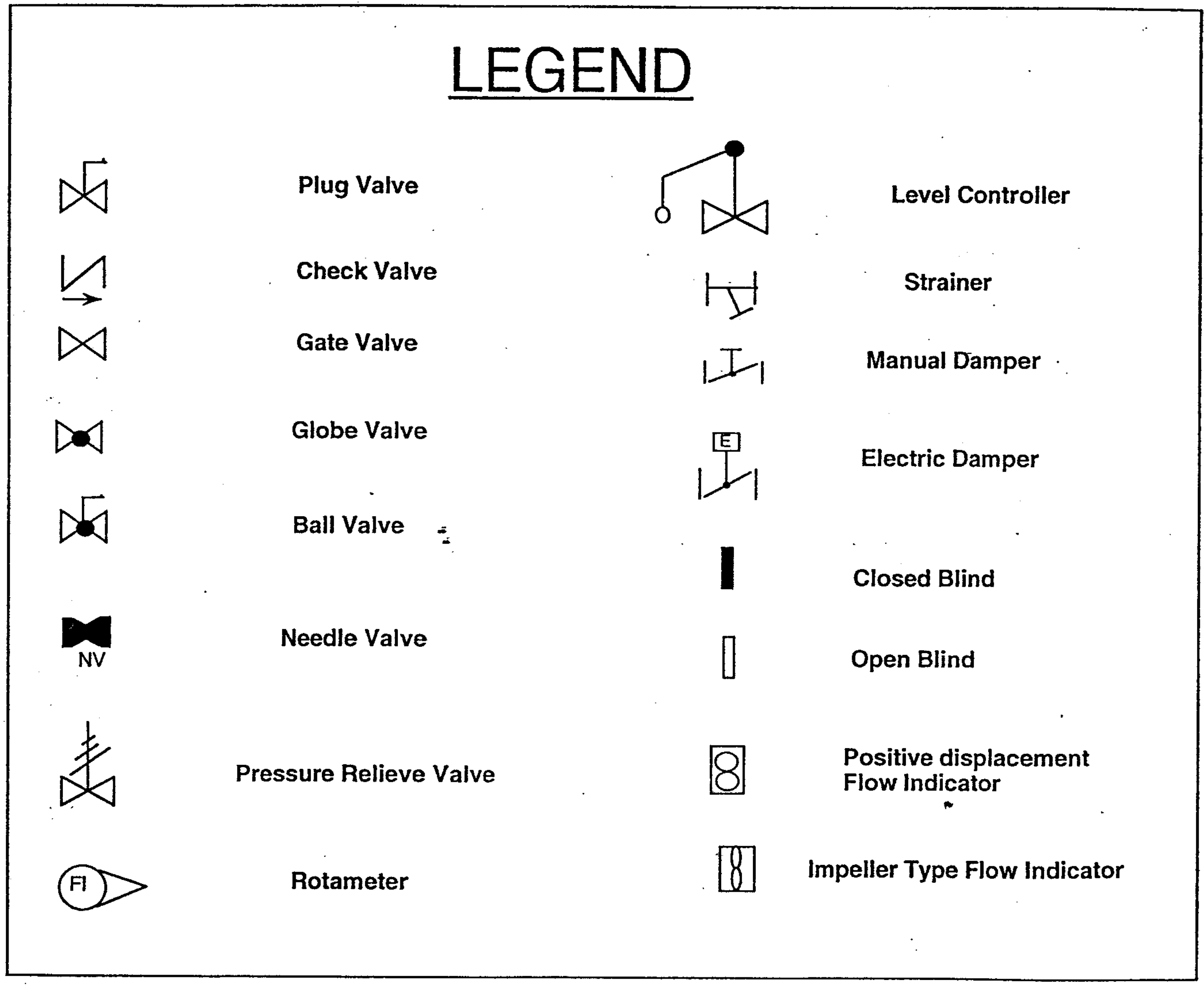


Figure B.2.4 P&ID Legend for Figures B.1 to B.2.3

P & I.D.

ITEM	DESCRIPTION	QUANTITY
G1	High Pressure Natural Gas Line	1
G2	Low Pressure Natural Gas Line	1
G3	POC Gas Line	1
G4	SOC Gas Line	1
CG-2	Combustion Gas Leaving POC	1
CG-4	Combustion Gas Leaving SOC	1
CG-5	Combustion Gas Leaving Boiler	1
CG-6	Combustion Gas Leaving Baghouse	1
CG-7	Combustion Gas Entering Scrubber	1
CG-8	Combustion Gas Leaving Scrubber	1
CG-9	Combustion Gas Leaving I.D. Fan	1
CG-10	Combustion Gas Leaving the Stack	1
1	2" Plug Valve	2
2	1" Plug Valve	1
3	Equimeter Pressure regulator Type IRV Spring 6"-14" Orifice 1/2"-10 degree	1
4	Equimeter Flow Indicator No. 3000 meter Capacity per hour = 3000 cuft @ 2" diff or 1450 cuft @ 1/2" diff Max Working P = 100 psi	1
5	USG P.I. (0-100 psi)	7
6	1/2" Ball Valve	23
7	1/4" Ball Valve	14
8	USG P.I. (0-20 oz/in^2)	2
9	1 1/2" Speedaire Ball Valve	2
10	1 1/2" Strainer	4
11	Dresser Roots Meter Model 175 Max P = 175 psig Max Q = 800 CFH B/M = 0500932-101	2
12	1 1/4" Plug Valve	4
13	1 1/4" Maxitrol Pressure Reducer Model RV60	2
14	1 1/4" SVF F.C.I. Valve Model H25 Type SR-2C	2
15	1 1/4" ITT Solenoid Valve Cat. No. K3A772 Gas psi Max= 1 1/2 Volts=120 Hz=60 Watts=14 Amps=260	2
16	USG P.I. (0-20 oz/in^2 or 0 - 35in H2O)	1

ITEM	DESCRIPTION	QUANTITY
17	Dwyer Manometer (0-1.0 in. H_2O)	1
18	1/4" Plug Valve	7
19	Maxitrol 1/4" Pressure Reducer Model R400S Max inlet P = 5 psig	2
20	Valve Volts=120 Amps = .115 PSI=150 CY=60	2
21	1" Ball Valve	21
22	3/4" Strainer	4
23	3/4" Ball Valve	18
24	Blue White Flowmeter Model F-45750LHE-12 (0-10 GPM or 0-40LPM)	1
25	1" Globe Valve	1
26	Omega K-Type Thermocouple	9
27	Tel-Tru Thermometer (50-300F)	1
28	1" Check Valve	2
29	Serial=K82MM5560 Ratio=1200 HP=.2 RPM=1730	1
30	3/8" Ball Valve	2
31	20 Size=3/4" Max Flow = 22 GPM Max P= 150 psi Max T=195 F	3
32	Thermocouple with protection head and thermowells	4
33	1/2" Check Valve	1
34	1/2" Gate Valve	1
35	3/4" Globe Valve	2
36	3/4" Check Valve	5
37	3/4" Gate Valve	1
38	3/4" Neptune Trident Meter Model MK 1333	1
39	Liquid Metronics Inc. Diaphragm Pump Model B111-91T Max Output CPD=38.5 Max P = 150 psi	1
40	Worthington Centrifugal Pump Model D520 IMP D = 8.6 Design P=75@ 100F IMP	1
41	Spencer Blowers Serial # = 400037 Cat. #=RB-254-FAN HP=5DP=10"H2O RPM=3500 Inlet T=500°F Inlet P=14.7 psia 1087 CFM	1
42	1 1/4" Gate Valve	1

ITEM	DESCRIPTION	QUANTITY
43	McDonnell Level Controller No. 21 Max Body P = 35 lbs Max Inlet P = 150 lbs	1
44	H.D. Terice Co. Thermometer (0-250 °F or 0-120 °C)	1
45	Sight Glass for the BFW	1
46	3/4" Spirax Sarco Temperature Controller Model 506 Δ P max=150 psi Tmax=500°F Cv=4.5	1
47	Barbe Manufacturing Co. Natural Gas Burner Model 1BS1200C Max Input=1200000 BTU/hr Min Input=500000 BTU/hr Volts=120 AC Cycles=60 Main Burner Gas Regulator set at 5-7" Overall Rating 12 Amps or less	2
48	Honeywell Pressuretrol Pressure Switch (PI-0019) Spare Unit Main (0-50 psi) ΔP (4-12 psi)	1
49	Honeywell Pressuretrol Pressure Switch (PI-0020) Alarm Unit Main (0-15 psi) ΔP (1-6 psi)	1
50	Honeywell Pressuretrol Pressure Switch (PI-0019) Shutoff Unit Main (0-50 psi) ΔP (4-12 psi)	1
51	Ashcrott P.I. (0-60 psi)	1
52	1/4" Globe Valve	1
53	Wizard Controller PIC-08 Type=4195KAR Input = 0-30 psi Output = 15-3 psi	1
54	2" Wizard Control Valve	1
55	1" Gate Valve	1
56	1" Flanged Glove Valve	2
57	1/4" Copper Tubing Cooling System	1
58	1/4" Ball Valve with tube fittings	1
59	2" Republic Relief Valve Set = 15 Date: 11-8-95 Job# 8004	1
60	2" Globe Valve	1
61	2" Gate Valve	1
62	Tel-Tru Thermometer (150-750 F)	1

ITEM	DESCRIPTION	QUANTITY
63	Manual Air Damper	1
64	Honeywell System Damper	1
65	Alphaline Pressure Transmitter Cal. -17 to -7 In. H_2O Output=4-20MA Supply=45 VDC MAX. Max W.P. 285psi	6
66	Photohelic ΔP Indicator (0-10 in. H2O) Max. P = 25 psig	1
67	Goyen Controls Solenoid Valve Model RCA6	5
68	Key Instruments Rotameter (6-60 GPH Water)	1
69	Watts Regulator Control Valve No.N35B 1/2 Model U Set STD. 50 Range 25-75 Max P= 400psi Max T=180 F	1
70	Tel-Tru Thermometer (50-500 °F)	1
71	Dayton Split Phase Motor With Stainless Empelor and Shaft Model 5K041 HP=1/8 RPM=1725 V=115/230 FLA=3.0/1.5 FR=D56Y Hz=60 PH=.1	1
72	Reliance Pump ID#T56H1019N ZJ Type=TPR FR=EA56C HP=1/4 RPM=1725	2
73	IwakiMagnet Pump Model MDH 25RV6 Head 36 ft Capacity 5GPM Speed 3450 RPM Motor 1/2 HP	1
74	F&P Co. Rotameter (0.1-12 CFM Water)	1
75	Pen Berthy Sight Glass Model N7A P=500 psi @ 100 F	1
76	pH Meter Type 47 Range(0-14)	1
77	(LHS) Scrubber Overflow tank level	1
78	(LLLS) Scrubber Overflow tank level	1
79	1/2" Globe Valve	1
80	Low Level Alarm McDonnell No. 150M Pump Control & Low Water Cut-off Max Boiler Pressure=150 lbs	1

ITEM	DESCRIPTION	QUANTITY
81	Low Level Interlock McDonnell No. 157 Pump Control & Low Water Cut-off and Alarm Max Boiler Pressure = 150 lbs	1
82	1/4" UV Spring Loaded Relieve Valve Model SH25 125 psi 99 SCFH	2
83	(East) General Electric Induction Motor Model 5KG324D23 (West) Fairbanks-Morse Induction Motor Type QZK	2
84	Air Pump Model 3Z493A	2
85	USG PI (0 - 200 psi)	4
86	3/4" Needle Valve	1
87	1" Strainer	1
88	SMC Solenoid Valve Model NVFS2106	1

APPENDIX C: PHOTOGRAPHS

Baghouse, Scrubber, Wastewater Tank, and Afterburner

Rotary Kiln Incinerator and Afterburner

Baghouse

Induced Draft Fan and Stack

Combustion Gas Analyzers

Mass Spectrometer

VITA

John Sutherland Earle was born in Massachusetts in 1925. Most of his early education was in Canada. After serving in the United States Navy in World War II, he was graduated in 1948 from Acadia University with a Bachelor of Science in chemistry. In 1950, he was graduated from McGill University with a Bachelor of Engineering in chemical engineering. During forty years engaged in engineering of chemical and petroleum plants, he worked in eight states of the United States and in Canada, South Africa, Scotland, and Chile. In 1971, he was graduated from Louisiana State University with a Master of Science in chemical engineering.

He is married to Eleanor Lee Earle, and has a daughter and two sons.