**Establishment of an Environmental Control Technology Laboratory
with a Circulating Fluidized-Bed Combustion System**

Quarterly Technical Progress Report

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ABSTRACT

This report is to present the progress made on the project “Establishment of an Environmental Control Technology Laboratory (ECTL) with a Circulating Fluidized-Bed Combustion (CFBC) System” during the period July 1, 2005 through September 30, 2005. The following tasks have been completed. First, the construction of the Circulating Fluidized-Bed (CFB) Combustor Building was completed. The experimental facilities have been moved into the CFB Combustor Building. Second, the fabrication and manufacture of the CFBC Facility is in the final stage and is expected to be completed before November 30, 2005. Third, the drop tube reactor has been remodeled and installed to meet the specific requirements for the investigation of the effects of flue gas composition on mercury oxidation. This study will start in the next quarter. Fourth, the effect of sulfur dioxide on molecular chlorine via the Deacon reaction was investigated. The experimental results from this study are presented in this report. Finally, the proposed work for the next quarter is described in this report.

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1. EXECUTIVE SUMMARY

The following tasks have been completed this quarter (July 1, 2005 through September 30, 2005). First, construction of the Circulating Fluidized Bed (CFB) Combustor Building was completed. The experimental facilities were moved into the CFBC building. Second, fabricating and manufacturing of the assembly and component parts of the Circulating Fluidized Bed Combustion (CFBC) Facility by Sterling Boiler & Mechanical Inc. of Evansville, Indiana are in progress. In view of the remaining design and fabrication work to be done, the erection phase is expected to be completed near the end of December 2005. Third, a drop tube reactor has been set up and integrated with a conversion module and a Semi-continuous Emission Monitor (SCEM) for mercury in order to make some fundamental investigations of effects of flue gas composition on mercury oxidation in the next quarter. Fourth, the effect of sulfur dioxide on molecular chlorine via the Deacon reaction was investigated. It was found that sulfur dioxide could be used to suppress the formation of molecular chlorine via the Deacon reaction. Finally, the work planned for the next quarter is introduced.

2. EXPERIMENTAL

2.1 Construction of CFB Combustor Building

The construction of the CFB Combustor Building has been completed. A heater for warming the CFB Combustor Building was installed. The painting, internal arrangement and paving of the outside area of the CFB Combustor Building was finished. Experimental facilities have been moved into the CFB Combustor Building and located on the ground floor. These experimental facilities include the laboratory-scale simulated fluidized-bed combustor, the multi-phase flow reactor, and several flue gas analyzers. The installation of a laboratory-scale unit for generating activated carbon using chicken waste is nearly completed. Figure 1 shows several photographs of the completed CFB Combustor Building.

2.2 Design and Manufacture of CFBC Facility

Currently, the component parts of the CFBC Facility are being fabricated by Sterling Boiler & Mechanical Inc. Figure 2 shows photographs of the component parts of CFBC Facility.

A licensed Professional Engineer has been retained by the Institute for Combustion Science and Environmental Technology to assist in the design and construction of several mechanical

considerations relating to the integration of the CFBC into the building structure, as well as fabrication and erection of the CFB Combustor.

Platforms of CFB Combustor Building

Ground floor of CFB Combustor Building

Figure 1 Photographs of the CFB Combustor Building

During this period, the following progress has been made on the design and modification of the CFBC Facility:

- a. Support framing for three supply bunkers, one ash bunker, and a hoist to facilitate component and analyzer equipment transport to elevated floor levels was designed.
- b. Anti-twist and anti-lateral deflection supports were incorporated in the overall CFB Combustor support structure design.
- c. The main riser, downcomer, and dual cyclone support framing to fill the 12 ½' x 14 ½' open area that is to be occupied by the CFB Combustor was designed.

Component Parts of Riser

Component Parts of Loopseal

Component Parts of Cyclone

Component Parts of Downcomer

Figure 2. Photographs of Component Parts of the CFBC Facility

Simultaneously, a Sterling Boiler and Mechanical manager in charge of the project erection phase made a site visit to review the logistics and available resources. Material handling equipment such as a personnel lift and forklift have been purchased to facilitate the erection of the CFB Combustor, as well as future reconfiguration activities that may be required to support new research initiatives. Erection of the CFB Combustor is expected to be completed near the end of December 2005.

2.3 Set-up of the Laboratory-scale Drop Tube Reactor

A laboratory-scale drop tube reactor has been remodeled and installed to investigate the effects of combustion flue gas composition on the oxidation of elemental mercury. Figure 3 shows the schematic of the laboratory-scale drop tube reactor. The dimensions of this reactor are listed in Table 1. The tubular reactor is a 4 feet long 2 inch inside diameter (I.D.) stainless steel pipe. To protect the stainless steel pipe and eliminate the scraps generated by the metal tube due to oxidization at high temperature, a 1.575 inch I.D. ceramic pipe is inserted into this stainless steel pipe. The drop tube reactor can be heated to a temperature of 2200°F with two electric furnaces. A thermocouple inserted into the reactor is used to monitor the internal temperature. A two-channel temperature controller is utilized to control the furnaces to maintain the desired temperature. A powder screw feeder at the top of the reactor is used to feed solid particles such as ash and catalyst into the reactor.

Table 1. Dimensions of the Laboratory-scale Drop Tube Reactor

Stainless Steel Pipe I.D. (inch)	Ceramic Pipe I.D. (inch)	Total Length (inch)	Length of Heating Section (inch)
2	1.575	48	43

In order to measure the gaseous mercury and its speciation in the flue gas exiting from the reactor, the following steps have been taken. First, a mini stainless steel cyclone, which has a high separation efficiency, was fixed at the outlet of the reactor. The cyclone can separate the fly ash and catalyst from the simulated flue gas stream. Therefore, the accumulation of fly ash and catalyst in the gas sampling line can be abated. The fly ash and catalyst collected by the solid collection vessel and captured by the cyclone will be analyzed for mercury. Second, a stainless

steel filter was installed at the outlet of cyclone. The fine particles of the fly ash and catalyst, which cannot be separated from the flue gas through the cyclone, can be removed through the filter before the flue gas enters the analyzer. Third, a mercury source was combined with this reactor to supply a known concentration of mercury (elemental). A conversion module and mercury Semi-continuous Emission Monitor (SCEM) were integrated with the drop tube reactor. In the next quarter, tests for the effects of combustion flue gas composition on the oxidation of elemental mercury will be conducted on this unit.

Figure 3 Schematic of the Modified Drop Tube Reactor

2.4 Experimental Study on the Effect of Sulfur Dioxide (SO₂) on the Formation of Chlorine (Cl₂) via the Deacon Reaction

2.4.1 Background on the Effect of SO₂ on the Formation of Cl₂ through the Deacon Reaction

One of the major issues challenging environmental management and pollution control is the disposal of an ever-increasing amount of municipal solid waste (MSW). Incineration is an important waste-to-energy technology used for the disposal of MSW. However, the development of such facilities has slowed significantly in recent years, due to apprehension over possible emissions of hazardous chlorinated organics, especially the harmful polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)^{1,2}. Molecular chlorine is a key intermediate in the formation of PCDDs and PCDFs. Theoretically, the emission of chlorinated organics can be effectively inhibited if the molecular chlorine yield is reduced. The Deacon reaction was proposed as a mechanism for the formation of molecular chlorine during the combustion of MSW:

Some researchers^{3,4} have suggested that co-firing high sulfur coal with MSW may reduce the emission of toxic chlorinated organics through the reaction between SO₂ and Cl₂:

The objective of this study is to examine the possible effect of sulfur species on the formation of molecular chlorine via the Deacon reaction and to determine the optimum sulfur to chlorine ratio to prevent the emissions of chlorinated organic materials.

2.4.2 Experimental Setup and Analysis Technique

Experiments were conducted in a quartz tube reactor system as shown in Figure 4. The reactor was mounted horizontally in an electrically heated furnace. In order to simulate conditions of an atmospheric Fluidized Bed Combustion (AFBC) system, the reactor was heated to 820 °C. Temperature is measured by a chromel-alumel thermocouple inserted in the lower part of the oven and displayed on a digital thermometer. The composition of the process gases can be adjusted using the calibrated Teflon flow meters before being introduced the reaction system. The gases are combined in a mixing chamber filled with glass beads before being introduced into the reactor.

The reaction products are swept into a cooled trap containing the selected absorbent, which is prepared by dissolving a carefully controlled amount of phenol into methylene chloride. Phenol was chosen as the sorbent for molecular chlorine since it traps Cl_2 very well and has little interaction with hydrochloric acid (HCl). Upon completion of the reaction, the solution is concentrated to 1ml and subjected to gas chromatography/mass spectrometry (GC/MS) analysis. A Shimadzu QP5000 system equipped with an NIST/EPA/NIH 62000 compound database was employed in this study.

Figure 4 Schematic of the tube reactor

2.4.3 Experimental Procedure

Different sulfur to chlorine ratios were tested in this study in order to examine the effect of SO_2 on the formation of chlorine through the Deacon reaction. The process gas consisted of HCl , SO_2 , air and nitrogen. The total gas flow rate was fixed at 180ml/min for the purpose of establishing comparable reaction conditions. The flow rate of HCl and air was set as 60ml/min in

each experiment and nitrogen was used as the balance gas. Various S/Cl ratios can be obtained by varying the flow rate of SO₂.

3 EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results from the experimental study to determine the effect of SO₂ on the formation of Cl₂ under different reaction conditions are shown in Figure 5. As shown in the Figure 5, the production of chlorine is high without SO₂ present in the reaction system. With an increase in the S/Cl ratio, the production of chlorine drops rapidly until the S/Cl ratio approaches the 2.5/1. After that, further increases in the ratio of S/Cl appear to have no effect on the production of molecular chlorine.

Figure 5 Effect of S/Cl Ratio on the Conversion Rate of HCl to Cl₂

In this study, the amount of HCl and air in the reaction system was fixed, and only the flow rate of SO₂ was changed in order to adjust the S/Cl ratio. It is reasonable to conclude that when the S/Cl ratio is about 2.5/1, the two reaction mechanisms are in equilibrium, and the Cl₂ generated from the Deacon reaction is completely depleted by the SO₂ present in the reaction system. Introducing more SO₂ into the system has no additional benefit since there is a limited supply of HCl.

With respect to the inhibiting mechanism of sulfur on the formation of Cl₂, the reaction between SO₂ and Cl₂ should be taken into account. Smith⁵ performed the equilibrium calculation

toward Reaction 2, according to the free energy and enthalpy data of the species involved in the reaction system. The result showed that the $\text{Cl}_2\text{-SO}_2$ reaction is strongly favored over the entire temperature range, and the amount of Cl_2 reacted was limited only by the available SO_2 . However, this homogeneous reaction is not measurable below a temperature of 800°C due to the kinetics of the reaction that may prevent observation of appreciable product until testing at a higher temperature. In a series of experiments conducted to examine the reaction between SO_2 and Cl_2 , Ragunathan and Gullet⁶ reported that HCl formation in the presence of SO_2 was consistent with Reaction 2, although the maximum conversion rate of molecular chlorine was less than the theoretical value of nearly 100% conversion.

Upon closer examination of the reaction system involved in this project, $\text{HCl-SO}_2\text{-O}_2$, the initial concentration of each gas, either O_2 or SO_2 is in excess compared to HCl . In the presence of SO_2 , Cl_2 generated from the Deacon reaction would be converted back to HCl . In the view of the Le Chatelier Principle, the reaction between SO_2 and Cl_2 will facilitate the production of Cl_2 via Reaction 1. On the other hand, the presence of a large amount of O_2 in the system may cause a negligible effect. Consequently, as illustrated in Figure 2, the production of molecular chlorine, which is monitored by the relative yield of chlorinated phenol, exhibits a linear relationship with the sulfur-to-chlorine ratio until the S/Cl ratio reaches 2.5/1. Such a dependency illustrates the occurrence of Reaction 2.

4 CONCLUSIONS

During this quarter, the following progress has been made:

- ◆ The construction of the CFB Combustor Building was completed and the experimental facilities were relocated in the CFB Combustor Building.
- ◆ Fabrication and manufacture of the assembly and component parts of the CFBC Facility are in the final stage. The preparations for project erection phase were completed. Erection is expected to be completed near the end of December 2005.
- ◆ A drop tube reactor was remodeled and will be utilized in a study to investigate the effects of combustion flue gas components on the oxidation of elemental mercury.
- ◆ The effect of SO_2 on the formation of Cl_2 via the Deacon reaction has been investigated in a quartz tube furnace. The following conclusions can be summarized from the experimental results:

- Sulfur dioxide is an effective inhibitor that can be used to suppress the formation of molecular chlorine via the Deacon reaction.
- As the sulfur-to-chlorine ratio in the fuel approaches 2.5/1, a dramatic decrease in chlorine production is observed.
- Sulfur enhancement of MSW by co-firing with coal followed by SO₂ emission controls may be the most practical strategy for minimizing the emission of chlorinated organics.

5. FUTURE WORK AND UPDATED PROJECT SCHEDULE

5.1 Future work

During the next quarter, work will focus on the following tasks:

- ◆ Continuously cooperate with Sterling Boiler & Mechanical, Inc. on manufacturing all parts of the CFBC Facility. The fabrication of the CFBC's component parts is in the final stage.
- ◆ Install the CFBC Facility in the CFB Combustor Building following the completion of fabrication of all parts of the CFBC Facility.
- ◆ Identify a contractor to design and install the process control and measurement system for the CFBC Facility.
- ◆ Continue to investigate conditions for oxidation of HCl to chlorine (Deacon Reaction) in the flue gas atmosphere.
- ◆ Investigate the effects of combustion flue gas composition on mercury oxidation in the modified drop tube reactor. Several types of fly ash with identified components from coals with different chlorine contents will be used as catalysts during the testing.

5.2 Updated Project Schedule

Based on the current status of the project, the updated schedule for the remainder of the project is shown in Table 2.

Table 2 Updated Project Schedule

Task	Updated Schedule
Grand opening of new Combustion Laboratory	December 8, 2005
Complete fabrication of all parts of CFBC Facility	Before November 30, 2005
Initiate erection of the CFBC Facility	November 28, 2005
Complete the installation of the CFBC Facility	December 30, 2005
Release the contract to a qualified vendor for design and installation of the process control and measurement system of the CFBC Facility	December 30, 2005
Complete tests to study the oxidation of hydrogen chloride to chlorine by the Deacon reaction. Complete tests for effects of flue gas composition on mercury oxidation on the modified drop tube furnace.	December 30, 2005
Complete the installation of the process control and measurement system of the CFBC facility. Based on the experimental data obtained from the laboratory-scale FBC facility, the investigation of the optimal conditions for co-firing waste materials with high sulfur coals will have been completed on the CFBC facility.	March 31, 2006
The effect of air staging, fuel feeding position, and limestone feeding on the gaseous emissions will have been studied on the CFBC facility.	June 30, 2006
The mercury emissions from co-firing of waste materials with high sulfur coal will have been investigated on the CFBC facility.	September 30, 2006

ACRONYMS AND ABBREVIATIONS

AFBC Atmosphere Fluidized-Bed Combustion

CFB Circulating Fluidized Bed

CFBC	Circulating Fluidized Bed Combustion
Cl	Chlorine
DOE	U.S. Department of Energy
ECTL	Environmental Control Technology Laboratory
FBC	Fluidized-Bed Combustion
ft	Feet
I.D.	Inside diameter
MSW	Municipal solid waste
S	Sulfur
SCEM	Semi-continuous Emission Monitor

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