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

Quarterly Technical Progress Report

January 1 – March 31, 2006

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April 2006

Cooperative Agreement No. DE-FC26-03NT41840

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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 January 1, 2006 through March 31, 2006. Work was performed on the following activities. First, the fabrication and manufacture of the CFBC Facility were completed. The riser, primary cyclone and secondary cyclone of Circulating Fluidized Bed (CFB) Combustor have been erected. Second, the Mercury Control Workshop and the Grand Opening of Institute for Combustion Science and Environmental Technology (ICSET) were successfully held on February 22 and 23, 2006, respectively. Third, effects of hydrogen chlorine (HCl) and sulfur dioxide (SO₂) on mercury oxidation were studied in a drop tube reactor. The experimental results from this study are presented in this report. Finally, the proposed work for the next quarter is described in this report.

TABLE OF CONTENTS

DISCLAIMER	1
ABSTRACT	2
TABLE OF CONTENTS	3
LIST OF GRAPHS	4
LIST OF TABLES	5
1. EXECUTIVE SUMMARY	6
2. EXPERIMENTAL	6
2.1 Design and Manufacture of CFBC Facility	6
2.2 Grand Opening and Mercury Control Workshop.	8
2.2 Study on the Effects of Flue Gas Components on Mercury Oxidation . .	10
3. RESULTS AND DISCUSSION	11
3.1 Mercury Oxidation by HCl	11
3.2 Effect of SO ₂ on Mercury Oxidation	12
3.3 Thermodynamic Equilibrium Calculation	12
4. CONCLUSIONS	13
5. FUTURE WORK AND UPDATED PROJECT SCHEDULE	15
5.1 Future Work	15
5.2 Updated Project Schedule	15
ACRONYMS AND ABBREVIATIONS	16
REFERENCES	17

LIST OF GRAPHS

Figure 1.	Photographs of the CFB Combustor Installation	7
Figure 2.	Photographs from Grand opening of ICSET	9
Figure 3.	Photographs from Mercury Control Workshop	9
Figure 4.	Effect of HCl on Mercury Oxidation	11
Figure 5.	Effect of SO ₂ on Mercury Oxidation	12
Figure 6.	Thermodynamic Equilibrium Analysis for Mercury Oxidation. . .	14

LIST OF TABLES

Table 1	Test Matrix for Mercury Oxidation by HCl.	10
Table 2	Calculation Conditions for Thermodynamic Equilibrium Analysis.	14
Table 3	Updated Project Schedule	15

1. EXECUTIVE SUMMARY

Work was performed on the following activities this quarter (January 1, 2006 through March 31, 2006). First, 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 were completed. The main riser, primary cyclone and secondary cyclone sections of Circulating Fluidized Bed (CFB) Combustor have been erected in the CFBC Building. Second, the Mercury Control Workshop and the Grand Opening of Institute for Combustion Science and Environmental Technology (ICSET) were successfully held on February 22 and 23, 2006, respectively. Third, effects of flue gas components on mercury oxidation were investigated in a drop tube reactor. The present work focused on the effect of hydrogen chloride (HCl) and sulfur dioxide (SO₂). Finally, the work planned for the next quarter is introduced.

2 EXPERIMENTAL

2.1 Design and Manufacture of CFBC Facility

Fabrication and manufacture of the assembly and component parts of the CFBC Facility by Sterling Boiler & Mechanical Inc. of Evansville, Indiana were completed. Currently, the CFB Combustor is being installed in the CFBC Building. Figure 1 shows several photographs of the CFB Combustor installation.

During this period, the following progress was made on the design and erection of CFBC facility:

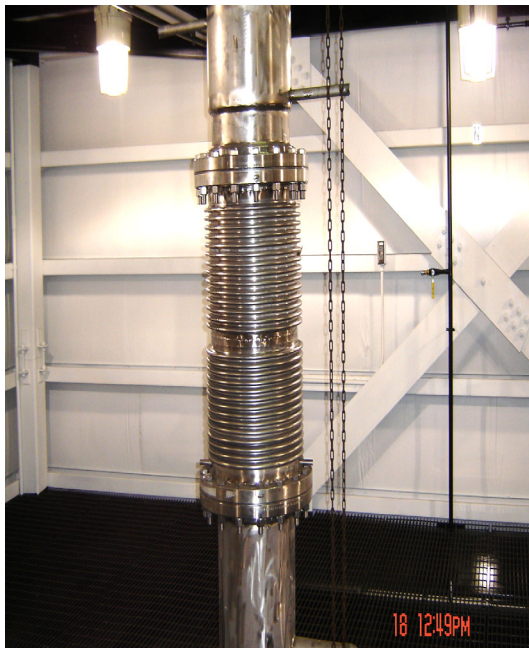
- a. The Main Riser, the Primary cyclone and Secondary Cyclone sections of CFB Combustor were installed.
- b. The services of a licensed professional engineer for the structural steel design were acquired via contract.
- c. The design plans for steel support structure, floor grating, and cargo lift system were produced.
- d. The steel support structure for the CFB Combustor components and floor grating in central portions of the Tower were installed.
- e. An Electrical Engineer for consultation on the design, specification, ordering of data acquisition and control hardware and software was hired. Job description for this position includes the development and application of software for effective operation



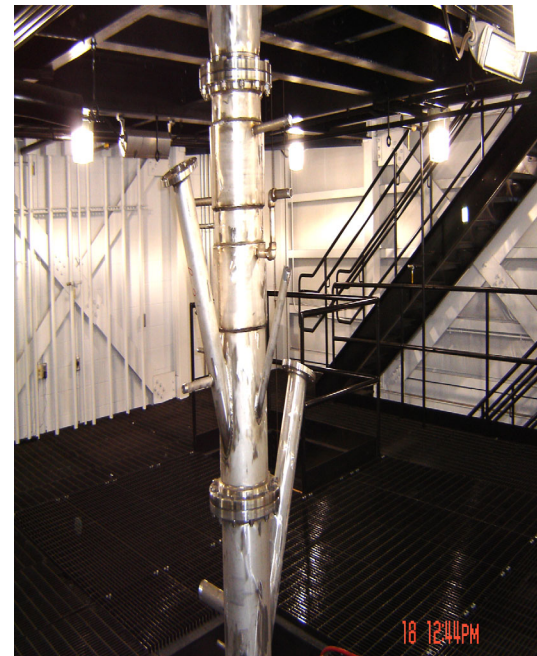
(a) Primary and secondary cyclones



(b) Riser on the third platform



(c) Thermal expansion on the riser



(d) Riser on the second platform

Figure 1 Photographs of the CFB Combustor Installation

and safe control of the CFB Combustor, as well as for the display and logging of acquired data and operating parameters.

- f. The advanced computer work station for product specification and order development purposes was purchased.
- g. The advanced computer work station for operating control, data acquisition and logging, as well as display of these data sets in CFBC Facility Control Room, including an uninterruptible power supply was purchased.
- h. Data acquisition and control interface hardware and interconnecting data signal cables were ordered.
- i. Load cells and summers for monitoring fuel/bed material bunker weights and feeding rates were purchased.
- j. Rotary air lock valves and their drives for fuel/bed material feeding were purchased.
- k. Eight thermal expansion joints for major components of CFBC Facility were purchased.
- l. Motors and drives for fuel/bed material input metering were ordered.
- m. Electrical utility throughout the tower to support anticipated emission monitoring instrumentation and process control equipment needs was upgraded.

2.2 Grand Opening and Mercury Control Workshop

The grand opening of ICSET was held at Western Kentucky University (WKU)'s Center for Research and Development on February 23, 2006. More than 200 people attended this ceremony including the President of WKU, a representative of U.S. Senator McConnell, and several representatives from industrial companies. During this ceremony, Commerce Secretary George Ward from State of Kentucky announced a collaboration to advance the cause of clean coal research in Kentucky and presented a check in the amount of \$352,999 from the Kentucky Office of Energy Policy to ICSET. Figure 2 shows several photographs from the grand opening ceremony.

A Mercury Control Workshop was also held on February 22 and 23. More than 60 people attended the workshop. The workshop demonstrated three different mercury measurement methods (Ontario Hydro method, Appendix K, and Continuous Emission Monitor) and several



(a)



(b)



(c)



(d)

Figure 2 Photographs from Grand Opening of ICSET



(a)



(b)

Figure 3 Photographs from Mercury Control Workshop

mercury control technologies (carbon-based mercury sorbents and non-carbon-based mercury sorbents). Figure 3 gives several photographs from the Mercury Control Workshop.

2.3 Study on Effects of Flue Gas Components on Mercury Oxidation

2.3.1 Introduction

It has been generally accepted that mercury chlorination, the reaction of elemental mercury (Hg^0) with hydrogen chloride (HCl) or chlorine (Cl_2) to form mercuric chloride (HgCl_2), is the dominant mercury transformation mechanism in coal combustion flue gas^{1,2,3}. Chlorine is evolved from coal combustion primarily as HCl . A very small portion is transformed to Cl_2 via the Deacon reaction⁴ in the post-combustion environment. In addition to HCl and Cl_2 , other components of combustion flue gas also influence mercury oxidation, such as sulfur dioxide (SO_2) and nitrous oxide (NO_x) et al.

In the previous report, effect of Cl_2 on mercury oxidation has been studied. The present work focused on the factors of HCl and SO_2 .

2.3.2 Experimental set-up and Experimental conditions

The experiments were conducted in a laboratory-scale drop tube reactor. The mercury measuring system used in this study is the Semi-continuous Emission Monitor (SCEM) system from PS analytical. The detailed description can be found in the previous report.

Table 1 Test Matrix for Mercury Oxidation by HCl

Run No.	Gas composition				Reactor temperature °C
	HCl (ppm)	SO_2 (ppm)	O_2 (ppm)	N_2	
1A	25	0	5	Balance	200
1B	25	0	5	Balance	350
1C	25	0	5	Balance	500
2A	200	0	5	Balance	200
2B	200	0	5	Balance	350
2C	200	0	5	Balance	500
3A	30	0	5	Balance	350
3B	30	500	5	Balance	350
3C	30	1000	5	Balance	350
3D	30	2000	5	Balance	350

In this study, 28,000 ng/m³ elemental mercury and various concentrations of HCl and SO₂ were injected into a simple gas mixture of 5% oxygen(O₂) and 95% nitrogen(N₂) by volume under different reactor temperatures. The test matrix is shown in Table 1. The temperature at gas sampling port is about 200°C.

3. RESULTS AND DISCUSSION

3.1 Mercury Oxidation by HCl

Figure 4 presents the results of mercury oxidation by HCl in the drop tube reactor. It was found that the maximum oxidation of elemental mercury occurred at the temperature of about 350 °C under given experimental conditions in this study. With an increase in HCl concentration, the oxidization of elemental mercury increased. The maximum conversion rate was 36% at 25 ppm HCl and 57% at 200ppm HCl.

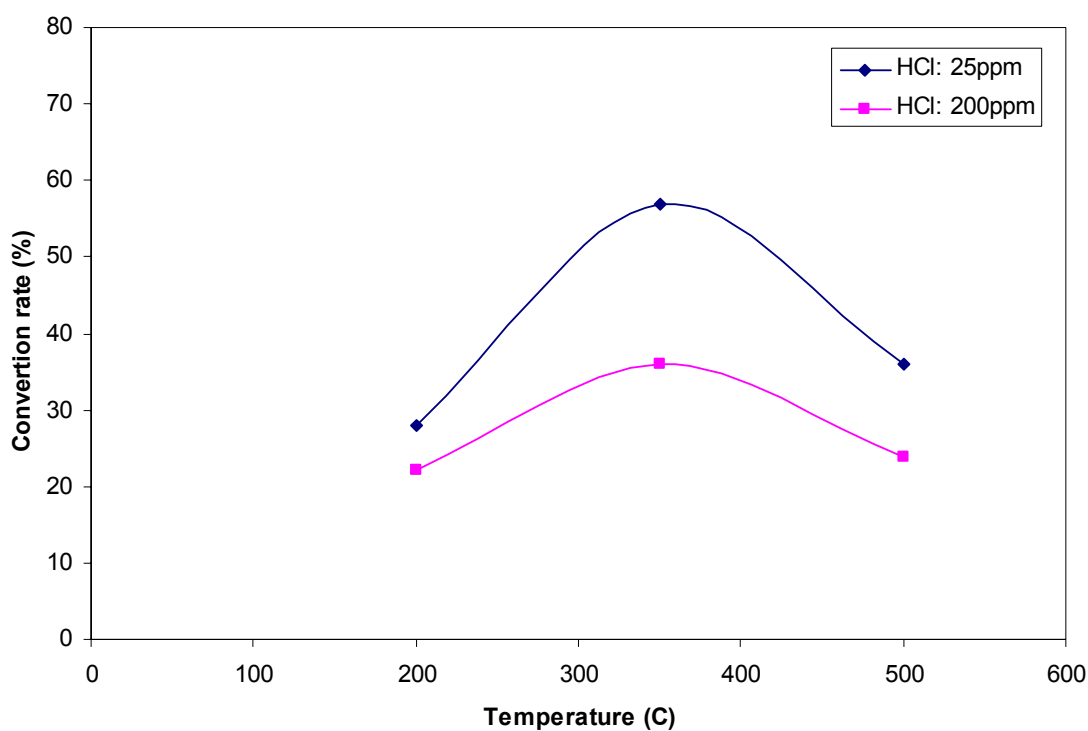


Figure 4 Effect of HCl on Mercury Oxidation

Also, the kinetic and thermodynamic aspects of mercury oxidation by HCl were found to act at the same time as shown in Figure 4. At lower temperatures, the kinetic aspect dominated the reaction. With increasing temperature, the conversion rate of elemental mercury increased.

When the temperature exceeded 350 °C, thermodynamics gradually played an important role in this reaction, due to the rate in which mercury oxidation decreased with increasing temperature. Thus, the conversion rate is high around 350 °C. Further investigation needs to be conducted to support this conclusion.

3.2 Effect of SO₂ on Mercury Oxidation

Figure 5 shows effect of SO₂ on mercury oxidation. Although SO₂ does not react directly with mercury, the presence of SO₂ in the gas was found to reduce the amount of elemental mercury oxidized by HCl as shown in Figure 5. The oxidation of elemental mercury was found to decrease with an increase in SO₂ concentration. When the SO₂ concentration in the gas increased from 0 to 2000ppm, the conversion rate of elemental mercury decreased from 33.6% to 22%.

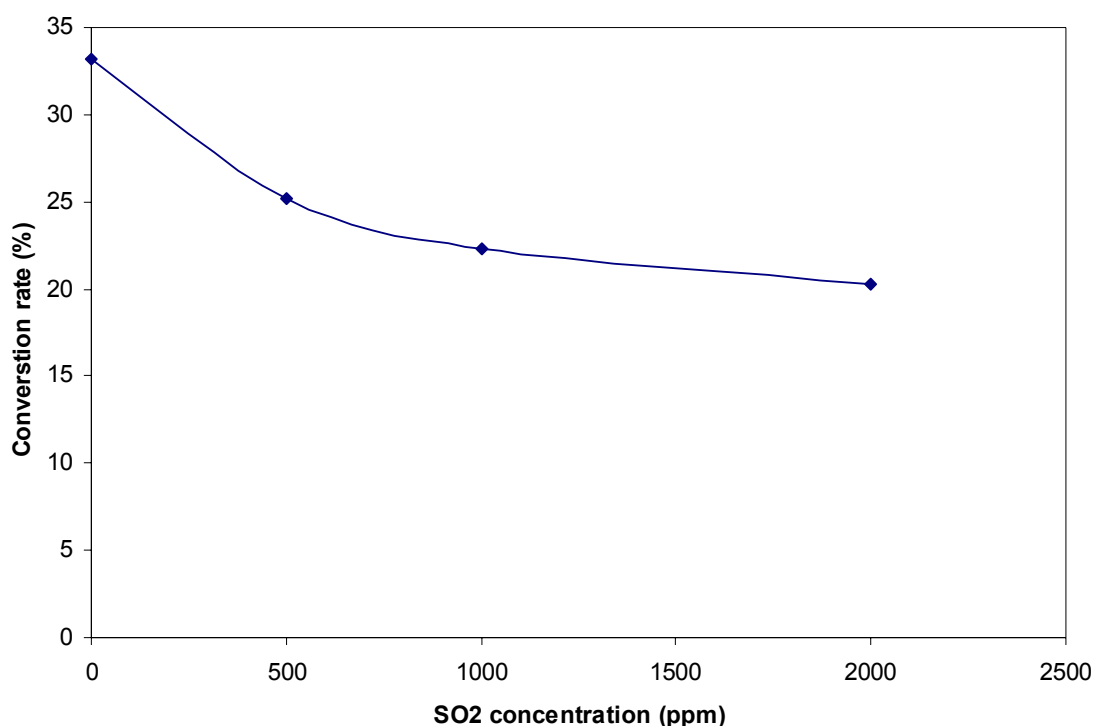


Figure 5 Effect of SO₂ on mercury oxidation

3.3 Thermodynamic Equilibrium Calculation

In this study, the so-called F*A*CT software package was used to simulate the mercury oxidation in real coal combustion system. The thermodynamic database employed in the

F*A*CT software package is based on JANAF Thermo-Chemical Tables and it includes about 5000 species and compounds including mercury and bromine. Table 2 shows the calculation conditions. Figure 6 shows the simulation results.

From Figure 6, it can be seen that more than 90% of the mercury was transformed into HgCl_2 when temperature was below 400 °C at the equilibrium status. Furthermore, elemental mercury was found to be the major mercury species when the temperature was above 700 °C at equilibrium status. This indicated that HgCl_2 is unstable and easily decomposed into elemental mercury at higher temperature. That explains why mercury oxidation by HCl decreased when the temperature increased above 400 °C.

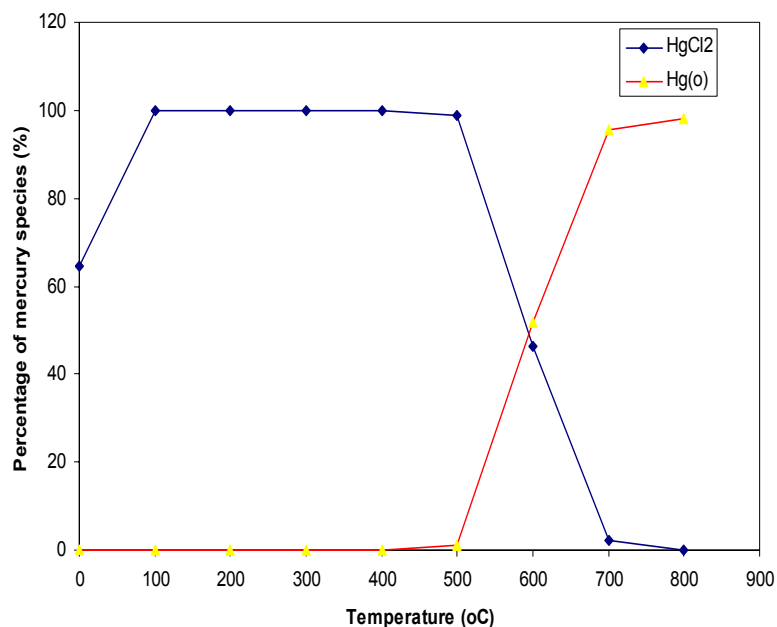
4. CONCLUSIONS

During this quarter, the following progress has been made:

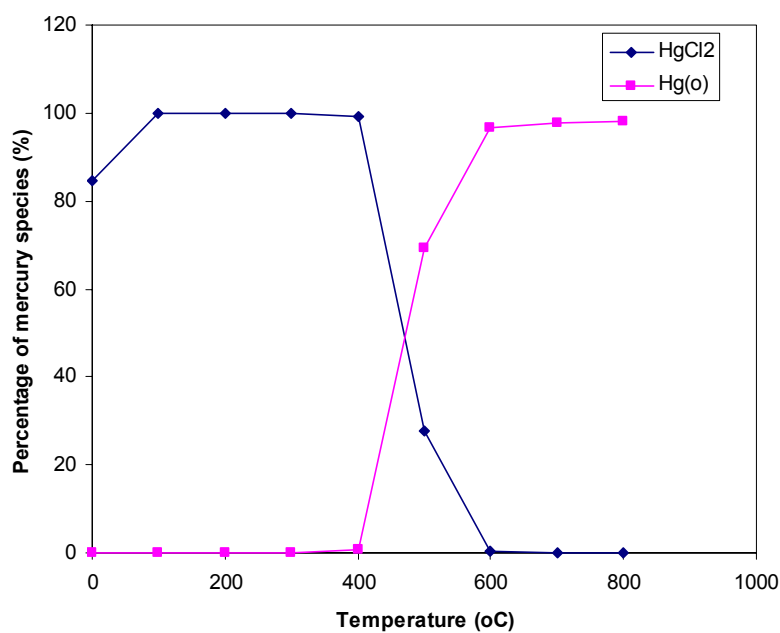
- ◆ Fabricating and manufacturing of the assembly and component parts of the CFBC Facility by Sterling Boiler & Mechanical Inc. of Evansville, Indiana was completed. The CFBC main riser, primary cyclone and secondary cyclone sections were erected.
- ◆ Design of process control and development of data acquisition system for CFBC Facility is in progress.
- ◆ The Grand opening of ICSET was successfully held at WKU's Center for Research and Development on February 23, 2006. A Mercury Control Workshop was also conducted on February 22-23, 2006.
- ◆ Mercury oxidation by HCl has been investigated in a drop tube reactor. The following conclusions were drawn from the experimental results:
 - The mercury oxidation by HCl did not monotonically increase with temperature. The maximum conversion rate appeared at the temperature of about 350 °C under the experimental conditions of this study. Mercury oxidation was found to increase with an increase in HCl concentration.
 - The presence of SO_2 inhibited mercury oxidation by HCl although SO_2 does not react directly with mercury. The mercury oxidation was found to decrease with increasing SO_2 concentration.

Table 2 Calculation Conditions for Thermodynamic Equilibrium Calculation

Figure No.	N ₂	H ₂ O	O ₂	CO ₂	SO ₂	HCl	Hg
Figure 6(a)	0.80	0.07	0.06	0.13	1000E-6	150E-6	10 E-9
Figure 6(b)	0.80	0.07	0.06	0.13	500E-6	10E-6	10 E-9



(a)



(b)

Figure 6 Thermodynamic Equilibrium Analysis for Mercury Oxidation

5. FUTURE WORK AND UPDATED PROJECT SCHEDULE

5.1 Future work

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

- ◆ Continue installation of the CFBC Facility including downer, bunker, duct, loopseal, I.D. fan, and combustion air supply blowers et al.
- ◆ Design and install the process control and measurement system for CFBC Facility.
- ◆ Investigate Polycyclic Aromatic Hydrocarbons (PAHs) emission from co-firing of chicken waste with coal in a laboratory-scale fluidized bed combustor (FBC).
- ◆ Continue to investigate the effects of combustion flue gas components on mercury oxidation in the drop tube reactor.

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 3.

Table 3 Updated Project Schedule

Task	Updated Schedule
Complete the installation of the CFBC Facility	August 30, 2006
Complete the installation of the process control and measurement system of the CFBC facility.	August 30, 2006
Complete investigation of effects of combustion flue gas components on mercury oxidation in a drop tube reactor	June 30, 2006
Complete investigation of PAHs emission from co-firing of chicken waste with coal in a lab-scale fluidized bed combustor	September 30, 2006
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 be completed in the CFBC Facility.	November 30, 2006
The effect of air staging, fuel feeding position, and	February 15, 2007

limestone feeding on the gaseous emissions will be studied in the CFBC Facility.	
The mercury emissions from co-firing of waste materials with high sulfur coal will be investigated in the CFBC Facility.	April 30, 2007
Submit final report	September 15, 2007

ACRONYMS AND ABBREVIATIONS

CFB	Circulating Fluidized Bed
CFBC	Circulating Fluidized Bed Combustion
Cl ₂	Chlorine
Cl	Atomic chlorine
DOE	U.S. Department of Energy
ECTL	Environmental Control Technology Laboratory
FBC	Fluidized-Bed Combustor
HCl	Hydrogen chlorine
Hg	Mercury
Hg ⁰	Elemental mercury
Hg ²⁺	Oxidized mercury
HgCl ₂	Mercuric chloride
N ₂	Nitrogen
NO _x	Nitric oxide
PAHs	Polycyclic Aromatic Hydrocarbons
ppm	Parts per million
SCEM	Semi-continuous Emission Monitor
SO ₂	Sulfur dioxide
O ₂	Oxygen

REFERENCES

- [1] Constance L. Senior, Adel F. Sarofim, Taofang Zeng, Joseph J. Helble, Ruben Mamani-Paco. Gas phase transformations of mercury in coal-fired power plants. *Fuel Processing Technology*. 2000, 63:197~213.
- [2] Jun Wang, Janmes T. Cobb Jr. and William W. Elder. Study of mercury oxidation in the post-combustion zones of coal fired boilers. *Fuel Chemistry Division Preprints*. 2001, 46(2):712~713.
- [3] Kevin C. Galbreath and Christopher J. Zygarlicke. Mercury speciation in coal combustion and gasification flue gases. *Environmental Science and Technology*. 1996, 30(8):2421-2426.
- [4] H.Y. Pan, R.G. Minet, S.W. Benson, T.T. Tsotsis. Process for converting hydrogen chloride to chlorine. *Industrial Engineering Chemistry Research*. 1994, 33:2996~3003.