MERCURY EMISSION CONTROL FOR COAL FIRED POWER PLANTS

USING COAL AND BIOMASS

A Thesis

by

UDAYASARATHY ARCOT VIJAYASARATHY

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2007

Major Subject: Mechanical Engineering

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Approved by:

Chair of Committee, Kalyan Annamalai
Committee Members, Jerald Caton
                   Adonios Karpetis
Head of Department, Dennis O' Neal

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ABSTRACT

Mercury Emission Control for Coal Fired Power Plants

Using Coal and Biomass. (December 2007)

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Mercury is a leading concern among the air toxic metals addressed in the 1990 Clean Air Act Amendments (CAAA) because of its volatility, persistence, and bioaccumulation as methylmercury in the environment and its neurological health impacts. The Environmental Protection Agency (EPA) reports for 2001 shows that total mercury emissions from all sources in USA is about 145 tons per annum, of which coal fired power plants contribute around 33% of it, about 48 tons per annum. Unlike other trace metals that are emitted in particulate form, mercury is released in vapor phase in elemental (Hg^0) or oxidized (Hg^{2+}, mainly $HgCl_2$) form. To date, there is no post combustion treatment which can effectively capture elemental mercury vapor, but the oxidized form of mercury can be captured in traditional emission control devices such as wet flue gas defulrization (WFGD) units, since oxidized mercury ($HgCl_2$) is soluble in water.

The chlorine concentration present during coal combustion plays a major role in mercury oxidation, which is evident from the fact that plants burning coal having high chlorine content have less elemental mercury emissions. A novel method of co-firing blends of low chlorine content coal with high chlorine content cattle manure/biomass was

used in order to study its effect on mercury oxidation. For Texas Lignite and Wyoming coal the concentrations of chlorine are 139 ppm and 309 ppm on dry ash free basis, while for Low Ash Partially Composted Dairy Biomass it is 2,691 ppm.

Co-firing experiments were performed in a 100,000 BTU/hr (29.3 kW$_t$) Boiler Burner facility located in the Coal and Biomass Energy laboratory (CBEL); coal and biomass blends in proportions of 80:20, 90:10, 95:5 and 100:0 were investigated as fuels. The percentage reduction of Hg with 95:5, 90:10 and 80:20 blends were measured to be 28-50%, 42-62% and 71-75% respectively. Though cattle biomass serves as an additive to coal, to increase the chlorine concentration, it leads to higher ash loading. Low Ash and High Ash Partially Composted Dairy Biomass have 164% and 962% more ash than Wyoming coal respectively. As the fraction of cattle biomass in blend increases in proportion, ash loading problems increase simultaneously. An optimum blend ratio is arrived and suggested as 90:10 blend with good reduction in mercury emissions without any compromise on ash loading.

DEDICATION

To My Parents, Sister and Niece

ACKNOWLEDGEMENTS

NOMENCLATURE

Hg	Mercury
Hg^0	Elemental Mercury
Hg^T	Total Mercury
Hg^{2+}	Oxidized Mercury
Hg_P	Particulate Mercury
$HgCl_2$	Mercuric chloride
HCl	Hydrogen chloride
Sep. Sol.	Separated Solids
HA	High Ash
PC	Partially Composted
DB	Dairy Biomass
TXL	Texas Lignite Coal
WYC	Wyoming Subbituminous Coal
HHV	Higher Heating Value
DAF	Dry Ash Free
CVAA	Cold Vapor Atomic Absorption
NO_x	Nitrogen Oxides
SO_x	Sulfur Oxides
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
FGD	Flue Gas Desulfurization
EPA	Environmental Protection Agency
DOE	Department of Energy
TCEQ	Texas Commission on Environmental Quality

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1   INTRODUCTION

The drive for clean air has caused an increasing concern for control of toxic emissions from coal combustion systems namely NO_x, Hg, SO_x, particulate matter, etc. In particular, the metal emission mercury has been targeted for control; due to its unique characteristics such as high volatility, bio-accumulation and other toxic properties which could result in adverse health effects in human ecology. Exposure to elemental mercury may lead to lung injury, and nervous system failure. High exposures to inorganic mercury may cause memory loss, skin rashes, muscle weakness, etc. [1]

Mercury is emitted from a wide variety of natural and man-made sources. Alkali and metal processing, incineration of coal, medical and other waste, mining of gold and mercury are major contributors of anthropogenic sources, while natural sources of atmospheric mercury include volcanoes, thermal springs, geologic deposits of mercury, and volatilization from the ocean. Both these natural and human activities release elemental mercury vapor (Hg^0) into the atmosphere. Once in the atmosphere, mercury is widely disseminated and can circulate for upto a year, accounting for its wide-spread distribution. The elemental mercury vapor can then undergo a photochemical oxidation to become inorganic mercury that can combine with water vapors and travel back to the Earth's surface as rain. This 'mercury-water' is deposited in soils and bodies of water. Once in soil, the mercury accumulates until a physical event causes it to be released again. In water, inorganic mercury can be converted into insoluble mercury sulfide which settles out of the water and into the sediment, or it can be converted by bacteria that process sulfate into methylmercury.

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This document follows the style of *Combustion and Flame*.

The conversion of inorganic mercury to methylmercury is important for two reasons:

- Methylmercury is much more toxic than inorganic mercury.

- Organisms require a long time to eliminate methylmercury, which leads to bioaccumulation.

The methylmercury-processing bacteria may be consumed by the next higher organism up the food chain, or the bacteria may release the methylmercury into the water where it can adsorb (stick) to plankton, which can also be consumed by the next higher organism up the food chain. This pattern continues as small fish/organisms get eaten by progressively bigger and bigger fish until the fish are finally eaten by humans or other animals. Alternatively, both elemental mercury and organic (methyl) mercury can vaporize and re-enter the atmosphere and cycle through the environment. Hence mercury is a multimedia pollutant that is emitted, deposited, and reemitted on both a local and global scale in both terrestrial and marine environments. This entire mercury cycle is depicted in figure 1.1.

Owing to toxicity of mercury and its emission control problem from coal fired utilities contributing almost one-third of the total mercury emissions, EPA has shown its concern by releasing Clean Air Mercury Rule (CAMR) on March 15, 2005, which establishes standards of performance limiting mercury emissions from new and existing coal power plant and introduce a strict cap to reduce nationwide utility emissions of mercury in two distinct phases. The first phase cap is 38 tons and emissions will be reduced by taking advantage of "co-benefit" reductions – that is, mercury reductions achieved by reducing sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions under Clean Air Interstate Rule (CAIR). In the second phase, due in 2018, coal-fired power

plants will be subject to a second cap, which will reduce emissions to 15 tons upon full implementation.
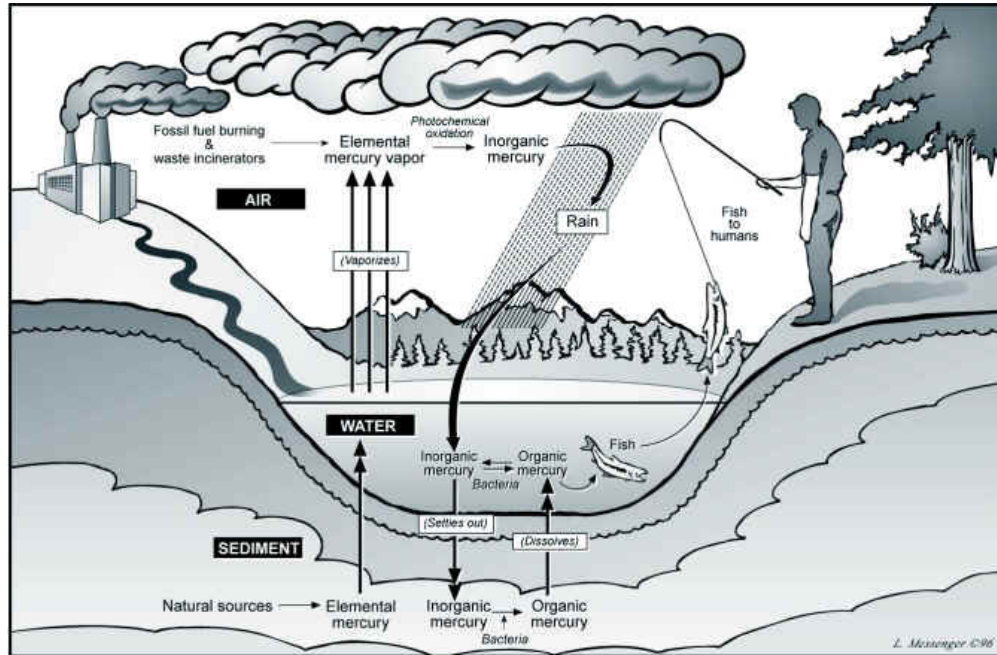
Figure 1.1 Mercury cycle [2]

The modes of occurrence of an element in coal can affect the way the element behaves during coal combustion. Because of the low concentrations of mercury and its volatility, it is particularly difficult to determine the modes of mercury occurrence in coal. US Geological Survey (USGS) research indicates that much of the mercury in coal is associated with pyrite, which generally forms after the coal is compacted. Other forms of mercury that have been reported in coal are organically bound, elemental, and in sulfide and selenide minerals.

Pulverized coal combustion is the most commonly used method in coal-fired power plants. Figure 1.2 shows a schematic of a typical coal fired power plant. The coal is ground (pulverized) to a fine powder, so that less than 2% is +300 μm and 70-75% is

below 75 μm, for a bituminous coal. The powdered coal is then blown into a combustion chamber of a boiler, where it is burned at temperatures around 1,400ºC. Surrounding the walls of the boiler room are pipes filled with high pressure water. Because of the intense heat, the water vaporizes into superheated high-pressure steam. The steam passes through a turbine (which is similar to a large propeller) connected to a generator. The incoming steam causes the turbine to rotate at high speeds, creating a magnetic field inside wound wire coils in the generator. This pushes an electric current through the wire coils out of the power plant through transmission lines. After the steam passes through the turbine chamber, it is cooled down in cooling towers and it again becomes part of the water/steam cycle. During the combustion of coal, products as a result of combustions result (CO_2, SO_2, NO_x, ash, slag, gypsum). Initially, the nitrogen oxides contained in the flue gas are reduced to harmless N_2, CO_2 and H_2O either in a SCR or SNCR kind of NO_x removal device. Subsequently, the flue gas is made dust free where particulate matter is removed in an electrostatic precipitator (ESP) or fabric filter (FF), and finally to remove SO_2 from stack gas, the flue is passed through a wet flue gas desulphurization (WFGD) unit where SO_2 dissolves in water when water is sprayed over it. The ash removed from the steam generator and the electro filter can be used in the construction industry, e.g. cement making.

Mercury may be controlled to limited success using existing control technologies, for instance, many power plants have existing mercury capture as co-benefit of air pollution control technologies for NOx, SOx and particulate matter. This includes capture of oxidized mercury in WFGD units. Use of selective catalytic reduction (SCR) units used for NOx control enhances oxidation of elemental mercury (Hg^0) to its soluble ionic form Hg^{2+} resulting in removal at WFGD system. Alternative technologies which emerged

recently include use of activated carbon injection (ACI) and advanced sorbents to capture mercury from flue gases at the fabric filters used to collect ash.
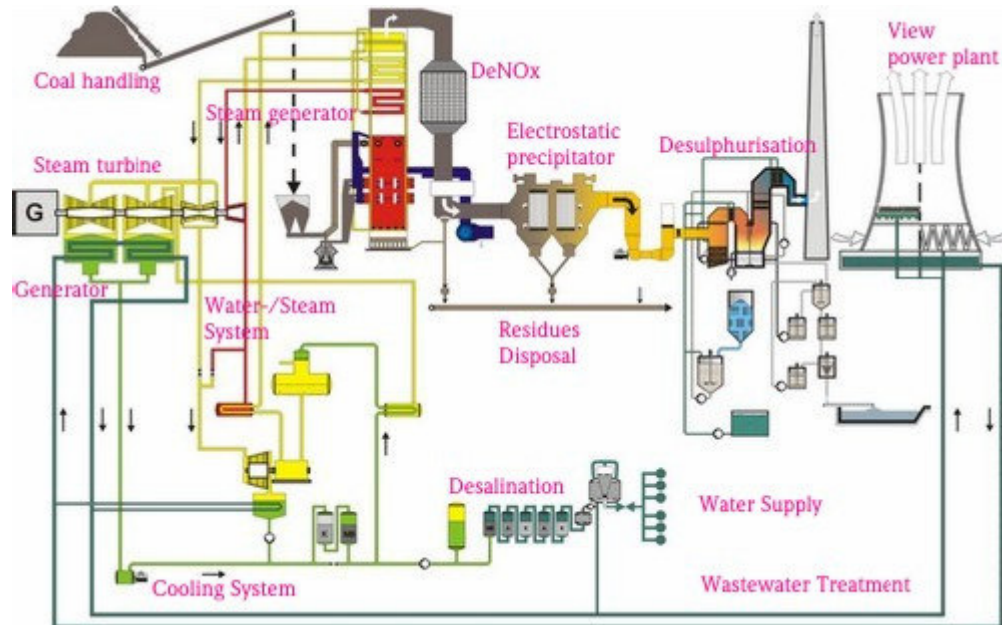
Figure 1.2 Layout of a coal fired power plant [3]

The current research concerns with the control of mercury emissions from coal fired power plants by adding small amounts of high chlorine content animal waste to increases mercury oxidation and hence its capture.

2   LITERATURE REVIEW

The literature review presents an overview of mercury emissions, its health effects, control technologies present and an insight to cattle biomass.

2.1   *Mercury Emissions*

While Mercury is one of the most useful of the heavy metals found in our daily lives, it is also one of the most deadly. The calculated atmospheric lifetime of elemental mercury is computed as the inverse of the net removal rate of mercury based on global measurements of deposition, balanced against the sum of sources (anthropogenic, terrestrial and oceanic). There is wide range of estimated of amount of mercury present in the atmosphere. Based upon the recent findings several researchers report that the amount of mercury in the atmosphere at any time may be in the range of 6000 to 7000 tons (Nriagu and Pacyna 1988; Nriagu 1989; Fitzgerald 1986; Lindquist el al 1994; Mason et al., 1996; Lamborg et al., 2002) [4]. Table 2.1 provides global totals as estimated by various authors. As can be seen, these estimates of overall global burden of mercury vary widely.

Table 2.1 Estimates of total release of mercury to the global environment [4]

Process	Lindquist *et al.* 1984	Nriagu & Pacyna 1988,Nriagu 1989	Fitzgerald 1986	Lindquist *et al.* 1991	Mason *et al.*, 1994	Pirrone *et al.*, 1996	Lamborg *et al.*, 2002
Anthropogenic releases	2000-10,000	3560 (910-6200)	2000	4500 (3000-6000)	5550 *1	2200	3000 *2
Natural releases	<15,000	2500 (100-4900)	3000-4000	3000 (2000-9000)	1650	2700	1400
Total present releases	2000-<25,000	6060 (1010-11,100)	5000-6000	7500 (5000-15,000)	7200	4900	4400

The mercury emitted from the power plants is not harmful; however, in the natural environment the mercury can go through a series of chemical transformations that convert the mercury to a highly toxic form that is concentrated in fish and birds. Of 158 tons of mercury being emitted by anthropogenic sources annually, coal fired power plants contribute about 33%, taking the largest share. Table 2.2 shows the source of mercury from various anthropogenic sources and their corresponding contribution in the US. Mercury is a natural constituent of coal and generally associated with pyrite (iron sulfide), commonly secondary arsenic-bearing pyrite, or is present in clay and the organics, or in coal with low iron content (pyrite) it occurs as a selinide [5]. The reported average mercury concentrations of 0.087 μg/g (ranging from 0.03–0.25μg/g) in Australian coal, 0.22 μg/g (ranging from 0.09–0.51 μg/g) in eastern U.S. coal, 0.04 μg/g in Colombian coal and 0.72 μg/g (ranging from 0.14–1.78 μg/g) in Polish coal [6]. The average mercury concentrations of 0.070 μg/g in bituminous coal, 0.027 μg/g in sub-bituminous coal and 0.118 μg/g in lignite coal [6]. It was estimated that typically 0.24 μg/g of mercury occurs in Appalachian coals, 0.14 μg/g in Interior Eastern coals and 0.21 μg/g in Illinois Basin coals [7]. Table 2.3 shows mercury values in selected U.S. coal areas from the U.S. Geological Survey Coal Quality (COALQUAL) database [8]. This is the way that mercury data are presented in most publications. This may be misleading because, in order to obtain similar energy outputs, more low-rank coal has to be burned than a higher-ranked coal. This can result in a net mobilization of more total mercury to the environment. A better way to compare mercury data for coal is on an equal energy basis. Table 2.4 shows mercury on equal energy basis, mean values for samples in selected U.S. coal areas [5]. Figure 2.1 shows the map, generated from the U.S. Geological Survey COALQUAL database compiled on mercury loading over the United

States atmosphere [9]. It clearly shows that mercury loading over the Texas region is very high compared to others. Out of the top ten power plants which contribute to mercury pollution, five are present in Texas.

Table 2.2 Sources of mercury in US [www.iit.edu/~ipro356s05/bg_sources.html]

Sources	Tons/yr	% Total
Utility boilers	52	32.8%
Municipal waste incenerators	29.6	18.7%
Commercial/industrial boilers	28.4	17.9%
Medical waste incenerators	16	10.1%
Hazardous waste incenerators	7.1	4.4%
General lab use	1.1	0.7%
Others	23.9	15.4%

Table 2.3 Mercury values in selected U.S. coal areas from the COALQUAL database [5]

	mean (ppm)	maximum (ppm)	number of samples
Appalachian	0.2	2.9	4,399
Eastern interior	0.1	0.4	301
Fort Union	0.13	1.2	300
Green River	0.09	1	418
Gulf Coast	0.22	0.6	29
Hams Fork	0.09	1	142
Pennsylvania anthracite	0.18	1.3	52
Powder River	0.1	1.4	616
Raton Mesa	0.09	0.5	40
San Juan River	0.08	0.9	194
Southwest Utah	0.1	0.5	42
Uinta	0.08	0.6	271
Western interior	0.18	1.6	311
Wind River	0.18	0.8	42

Table 2.4 Mercury on equal energy basis, mean values for samples in selected U.S. coal areas [5]

	mercury (pounds / 10^{12} BTU)	mean (ppm)
Appalachian	15.4	0.2
Eastern interior	8.2	0.1
Fort Union	21.8	0.13
Green River	6.6	0.09
Gulf Coast	36.4	0.22
Hams Fork	4.8	0.09
Pennsylvania anthracite	15.4	0.18
Powder River	12.6	0.1
Raton Mesa	6.6	0.09
San Juan River	7.7	0.08
Southwest Utah	11	0.1
Uinta	7.3	0.08
Western interior	16.1	0.18
Wind River	18.7	0.18
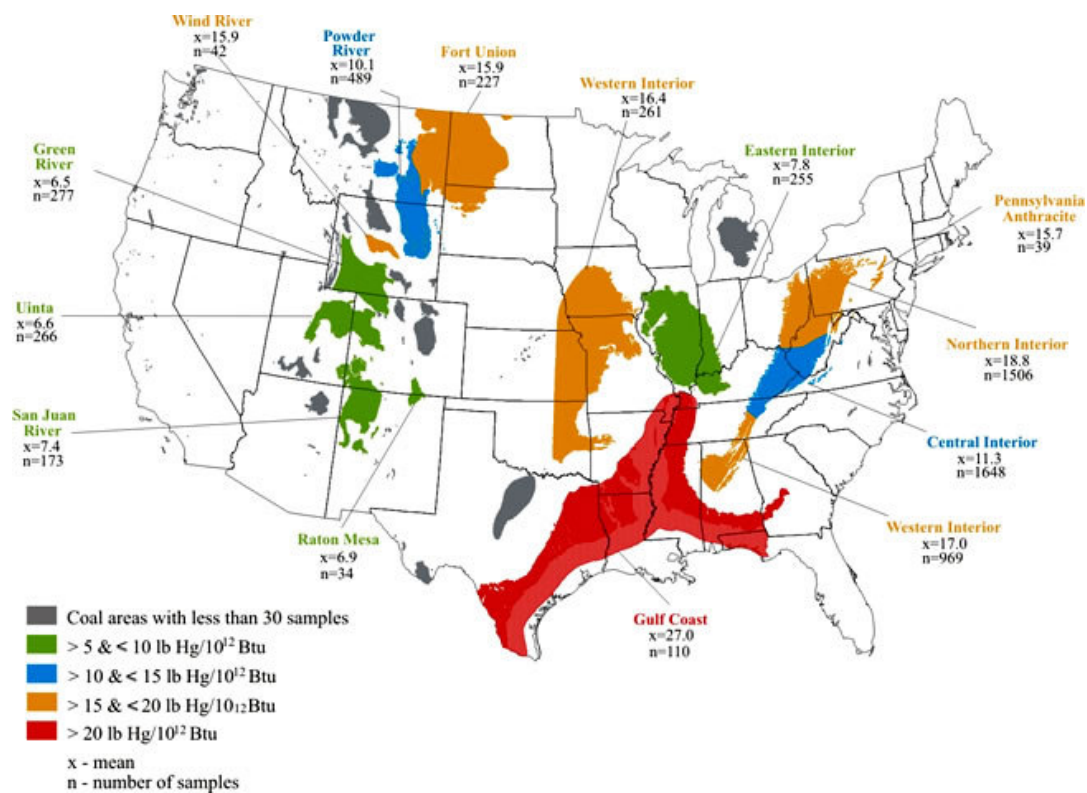
Figure 2.1 Mercury loadings (in pounds of Mercury per 10^{12} British thermal units (lbs Hg/10^{12} Btu)) [9]

2.2   *Elemental Mercury Properties*

Mercury also called quick silver is a chemical element in the periodic table that has

the symbol Hg and atomic number 80. Table 2.5 presents the properties of Hg.

Table 2.5 Properties of Hg

Atomic Number	80
Atomic Symbol	Hg
Atomic Weight	200.61
Freezing Point	-38.87 °C (234.32 K)
Boiling Point	356.73 °C (629.88 K)
Density	13.546 g/mL (@ 20 °C)
Synonyms	Quicksilver, Hydrargyrum
beta=(1/v)dv/dT	0.181 x 1e-3 1/°C
Heat of fusion	2.7 cal/g
Heat of vaporization	65 cal/g
ln P in (kPa) = A - B/T, A = ln psat (TBP) + hfg/(RTBP); B= hfg/R	
R	0.04144 kJ/kg K
A, calculated	15.02
B, calculated	6562.171 K
Density	13.5462 g/cm3 @ 20 °C
Cpliq	0.03325 cal/g-K
Heat conductivity	0.0782, 0.083, 0.0947 W/cm-K @ 0 °C, 20 °C, 100 °C
Molecular dia	0.314 nm
Volume of Hg (T) = V*(1 + 1.82 x 10-4*t + 7.8 x 10-9*t^2), where t is in °C, and V is the volume at 0 °C	
viscosity	0.5123, 0.4022, 0.3543, 0.3208, 0.2777 poise @ 10 °C, 93.3, 149°, 204 °C, 316 °C
Its surface tension in air at 20 °C i	435.5 dyne/cm @ 20 °C

Mercury is a highly volatile metallic liquid having saturated vapor pressure of

0.00026 kPa (0.001950 torr) at room temperature of 25˚C (298.15 K). Antoine's vapor

pressure equation is given as:

$$\ln(P) = A + \frac{B}{T} \tag{2.1}$$

Where P is pressure in torr (mm of Hg), and T is temperature in K

From the data on vapor pressure at various temperatures [9], a linear plot of ln (P) and 1/T is plotted, from which constants of Antoine's vapor pressure equation is obtained as: A = 18.667, and B = -7443.47 K. Hence saturated vapor pressure for Hg at any temperature T K can be calculated from:

$$P = \exp\left(18.667 + \frac{7443.47}{T}\right) \tag{2.2}$$

2.3   Health Effects

Mercury is a naturally occurring heavy metal, classified as a toxic metal emitted both by natural and anthropogenic sources. It can exist in elemental, inorganic and organic forms. Elemental mercury though being a metal is highly volatile, especially at high temperatures like coal combustion or incinerators. They escape into the atmosphere without being captured in the any pollution control devices. Inorganic mercury may exist in mercuric or mercurous forms, which combines with other elements to form inorganic metal compounds or salts such as mercuric chloride, mercuric sulfide, mercuric oxide, mercuric selenide, etc. The inorganic mercury enters the atmosphere from mining of coal, coal combustion or during incineration of waste. Organic mercury can be formed from either elemental or inorganic compounds, and exist in various species such as methyl mercury, phenyl mercury, merthiolate, etc. In mercury contaminated soil or water, the micro-organisms can organify the mercury into methyl mercury, which concentrates in the food chain. The health effects of mercury are diverse and it may depend on the form of mercury encountered and severity and the length of exposure.

2.3.1 Elemental Mercury

Intoxication may occur in workers excessively exposed to mercury or to its compounds. The exposure may be due to mercury vapor, mist, dust, or fume, by inhalation, ingestion, or through skin. The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for mercury vapor is 100 microgram per cubic meter ($\mu g/m^3$) of air as a ceiling limit. Two general types of mercury intoxication exist, chronic and acute. Chronic mercury intoxication is caused by exposure to a low concentration of mercury over an extended period of time. Acute mercury intoxication is due to a greater exposure and is unrelated to time factors. Definite symptoms of chronic mercurialism may not appear until after six months of exposure, or longer. The symptoms are primarily of the nervous and digestive systems. The symptoms of overexposure to mercury may include such personality manifestations as: irritability, excitability, or excessive timidness. Other symptoms include: headaches, drowsiness or insomnia, and weakness. Many cases also include reports of sore mouths, excessive salivation, and perspiration. In mercury intoxication, a common symptom is a tremor which is aggravated by emotion or excitement [10].

2.3.2 Inorganic Mercury

Mercury can exist in inorganic salts such as mercurous chloride (Hg_2Cl_2), mercuric chloride ($HgCl_2$), mercuric sulphide (HgS), mercuric oxide (HgO) and many others. Of these $HgCl_2$ is the most toxic inorganic compound of mercury which is found in insecticides and rat poison. Exposure to inorganic mercury is mostly through ingestion. The most prominent effect is on kidneys, where mercury accumulates, leading to tubular necrosis. High exposures to inorganic mercury may also result in damage to the gastrointestinal tract, the nervous system. Symptoms of high exposures to inorganic

mercury include: skin rashes and dermatitis; mood swings; memory loss; mental disturbances; and muscle weakness [10].

2.3.3 Organic Mercury

Organic mercury is more toxic than inorganic mercury. Organic mercury compounds, also called organomercurials, are those containing covalent bonds between carbon and mercury. Examples are methylmercury, dimethylmercury and methylmercury chloride (methylmercuric chloride). The effects of organic mercury especially methylmercury are acute which include changes in vision, sensory disturbances in the arms and legs, cognitive disturbances, dermatitis, and muscle wasting. The developing nervous systems of the fetus and infants are considered to be susceptible to the effects of methyl mercury. Exposure of childbearing-aged women is of particular concern because of the potential adverse neurological effects of Hg in fetuses [10]. Outbreaks of methylmercury poisonings have made it clear that adults, children, and developing fetuses are at risk from ingestion exposure to methylmercury. During these poisoning outbreaks some mothers with no symptoms of nervous system damage gave birth to infants with severe disabilities, it became clear that the developing nervous system of the fetus may be more vulnerable to methylmercury than is the adult nervous system [11]. Table 2.6 shows the percentage of women with blood mercury concentration greater than 5.8 µg/L (this is an estimated level assumed to be with no appreciable harm).

Table 2.6 Percentage of women aged 16-49 years with blood mercury (Hg) levels ≥ 5.8µg/L, by race/ethnicity – National Health and Nutrition Examination Survey, United States, 1999-2002 [11]

Race/Ethnicity	No.	% with Hg levels ≥5.8 µg/L	(95% CI*)
Mexican American	1,106	1.70	(1.04–2.79)
White, non-Hispanic	1,377	5.77	(3.71–8.97)
Black, non-Hispanic	794	4.82	(2.55–9.11)
Total	3,637	5.66	(4.04–7.95)

∗ Confidence Interval

2.4   Mercury Behavior during Combustion

The chemical form of mercury in flue gas and its transformations during combustion dictates the mechanism of mercury capture. This is technically termed as mercury speciation. As discussed earlier mercury exists in three forms, viz.,

- Elemental mercury (Hg^0) – volatile metal which exist in gas phase at flue gas temperatures and is insoluble in water. It can not be captured by traditional pollution control devices such as particulate control units or flue gas desulphurization (FGD) units.

- Oxidized mercury (Hg^{2+}) – normally exist in gas phase, and can be captured by wet FGD type of units, since they are highly soluble in water.

- Mercury in particulate form (Hg_P) – exist in solid phase and can be easily captured at traditional particulate control devices such as electrostatic precipitator (ESP) or fabric filters (FF).

Mercury can exist in flue gas in any of these various forms with wide variations, and the speciation depends broadly on fuel type composition, combustor type and operating conditions, and pollution control devices present. In general, emissions of mercury from

coal combustion sources are approximately 20–50% elemental mercury (Hg^0) and 50–80% divalent mercury (Hg^{2+}), which may be predominantly $HgCl_2$, while particulate mercury constitutes less than 5% [3]. Experiments [12] conducted to study the fate and behavior mercury in power plants showed that 43% ($\pm 30\%$) of Hg present in the coal is found in the flue gases in vapor phase at the exit of pollution control devices, while the remaining 54% ($\pm 24\%$) was captured at wet FGD and ESP. With the presence of HCl, Hg^0 (partly) is converted into $HgCl_2$ at temperatures less than 500-800°C. According to the one of the test conducted it was found that 53% of the Hg presented in a water soluble form, mostly in the form of $HgCl_2$. However, it is still in the vapor phase due to the high temperature of flue gases (140-150°C).

Distribution of mercury species in coal combustion flue gases has been calculated using equilibrium calculations by Mojtahedi et al. [13] and Senior et al [14], which shows that all of the Hg exists in the form $HgCl_2$ below 450°C. And above 700°C, 99% of the Hg exist as gaseous Hg as shown in Fig. 2.2. The rest is in the form of HgO. Equilibrium is not attained in flue gas since the environment is highly transient and also due to fact that flue gas cools rapidly as heat is transferred from water to steam. Experiments conducted by Lindqvist et al. validates this proposition and confirmed that mercury exists in elemental form only at temperatures above 700°C [4].
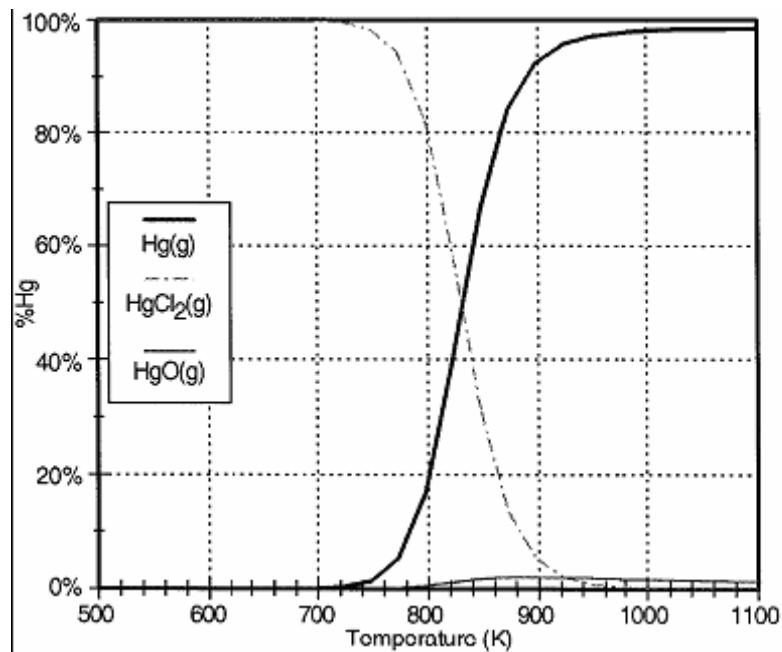
Figure 2.2 Equilibrium speciation of mercury in flue gas as a function of temperature [14]

Hall.B [15] said that the re-oxidation reaction is stated to occur rapidly at about 500°C and is described as:

$$2Hg(g) + 4HCl + O_2 \Leftrightarrow 2HgCl_2 \, (g,s) + 2H_2O \, (g)$$
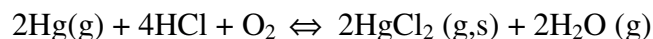
This occurs at temperatures between 400 to 700°C. Below 400°C, atomic chlorine is responsible for further Hg oxidation.

$$Hg + Cl_2 \rightarrow HgCl + Cl$$

$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$$
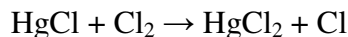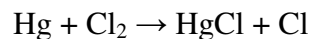
However, in case of flow reactor, where the temperature is very high at the upstream, stable HCl decomposes and supplies atomic chlorine which aids in formation of intermediate HgCl. As these species move downstream where temperature is lowered below 700°C, HgCl oxidizes further to form stable $HgCl_2$ which is favored at lower temperatures [16].

$$Hg + Cl \rightarrow HgCl$$

$$HgCl + HCl \rightarrow HgCl_2 + H$$

$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$$

$$HgCl + Cl \rightarrow HgCl_2$$
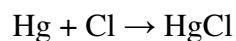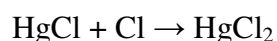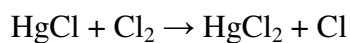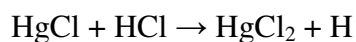
It can be said that for oxidation of Hg in presence of HCl, high temperatures is required to decompose HCl to produce atomic chlorine, and occurance of intermediate HgCl. While lower temperatures are required to further oxidize HgCl to $HgCl_2$.

Thus the extent of oxidation depends on the concentration of chlorine in flue gases. As shown in the Figure 2.3, the fraction of elemental Hg emission of coal-fired boilers decreases with increase in Cl content of coal [17]. The Cl content in Bituminous coals range from 200 to 2000 ppm (dry basis) while for low rank coals (sub-bituminous and lignite) it ranges from 20 to 200 ppm an order of magnitude lower. Thus the low rank Sub-bituminous and lignite coals reveal lower Hg capture (3-72 %) in co-benefit systems than higher rank bituminous coal (9-98 %) [7]. Hg removal plotted against coal chlorine content reveals increasing Hg capture with Cl due to $HgCl_2$ formation. As Cl is low in sub-bituminous and lignite coals, the Hg exists primarily as elemental Hg, which is difficult to capture.
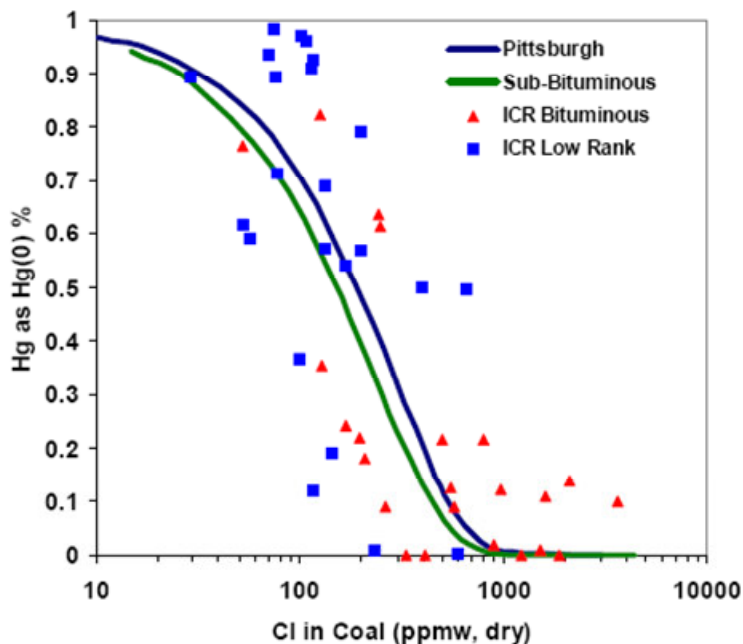
Figure 2.3 Effect of chlorine in coal with mercury emissions [17]

2.5   Mercury Control Technologies

Mercury is difficult to remove because it is present in vapor form since it is highly volatile. A variety of control approaches that address mercury during pre- and post-combustion can achieve reductions in mercury emissions from power generation facilities fueled by coal. Precombustion strategies essentially involve pollution prevention measures, such as fuel management by coal cleaning, or selection of lower mercury content fuels. These measures may achieve reductions in mercury concentrations in the fuel prior to the fuel entering the combustion zone. Post-combustion methodologies are generally absorption or conversion techniques focused on removal of one or more of the mercury species incorporated in the boiler exhaust stream. Many existing controls for gaseous and particulate pollutants can secondarily reduce mercury emissions through simultaneous "co-control" physical and chemical reactions.

2.5.1   Pre-combustion Mercury Control Techniques

Pre-combustion techniques for reducing mercury emissions are focused at lowering mercury concentrations prior to combustion. Pre-combustion approaches are principally fuel cleaning techniques, although fuel-switching or management strategies have also been investigated.

The cleaning techniques normally considered for pre-combustion control reductions are coal washing/cleaning with either an aqueous solution or with a magnetic medium as the separation medium. Other cleaning techniques, such as K-Fuel, have been developed that remove mercury through heat, although data for these non-aqueous cleaning approaches are limited.

Coal cleaning or washing is a physical technique that can remove coal contaminants that are bound with particulates or soils (commonly the pyritic fraction) associated with the coal. The degree of association of coal mercury with the mineral fraction has been estimated by several researchers as up to 50% of the total mercury content. Mercury that is bound organically to the carbon structure or absorbed onto internal carbon structures is little affected by cleaning. Mercury compounds associated with the particulate fraction (Hg^0 and Hg^{2+}) may be removed; however, a residual mineral content (from 8-15%) is typically retained in the cleaned coal. Cleaned coals also generally lose BTU content with a gain in moisture content. Toole-O'Neil et al. (1999) evaluated the tendency of coal cleaning to preferentially remove mercury. Of the 24 cases of coal cleaning cited, the average decrease in mercury concentration was 37% on an energy basis, ranging from 12% to 78% overall. On a mass basis, the average mercury reduction from coal cleaning was 30%, which indicates a coal cleaning factor of 0.70, a higher rate of mercury removal than that applied by EPA in 1997 (21%) (Brown et al. 1999).

In general, effective removal of coal contaminants may be enhanced when coals is finely ground and subjected to intense agitation. In practice, coal cleaning efficiencies vary considerably with multiple factors such as coal type, rank, ash content and mineral composition. Although these methods appear to reduce mercury, further post-combustion treatment must be performed to control remaining mercury. Some additional benefits of coal cleaning include a reduction in the sulfur content, which translates into lower $S0_2$ emissions, as well as reduced ash loading.

Coal cleaning is widely used on high rank coals in east such as bituminous and anthracite coals, to reduce ash and sulfur compounds. There is less experience with cleaning in lower rank western coals such as sub-bituminous and lignite.

Another pre-combustion technique considered is by strategically managing fuel used for combustion. Mercury emissions can be lowered for a distinct facility by selecting and burning fuels of lower mercury concentration. Within a given coal type, current data suggests that many deposits exhibit a high degree of variability in mercury content on a seam to seam basis. It is observed that the pyrite content in coal is high in the upper lithography, which increases the presence of higher mercury concentration in the upper seam of coal mines, since mercury is apparently attached to the pyrite fraction of the coal. The ability to selectively mine lower mercury concentration seams has not been demonstrated repetitively, nor have the business economics been quantified to encourage such mining efforts. While shifting coal types could impact mercury emissions, the economic and physical impacts of differing fuel types onto generation capabilities and the boiler and fuel handling complex are likely to exceed costs associated with direct controls.

2.5.2 Post-combustion Mercury Control Techniques

Mercury capture in existing emissions control equipment offers a cost effective mercury control option for coal-fired power plants. The incidental capture of mercury from coal-fired power plants varies significantly depending on the existing emissions control configuration and type of coal being burned. In post-combustion technique, there are three basic methods of flue gas treatment to capture mercury: first, capture of particulate-bound mercury in particulate matter (PM) control devices; second, adsorption of elemental and oxidized mercury onto sorbents for subsequent capture in PM control devices, and; third, removal of soluble oxidized mercury in wet scrubbers (including processes to convert elemental to oxidized mercury for subsequent capture in wet scrubbers).

Mercury speciation along the convective flue gas path determines the mode of mercury capture using these traditional pollution control devices. Figure 2.4 shows the various species of mercury present in the flue gas at different stages of a typical plant layout.
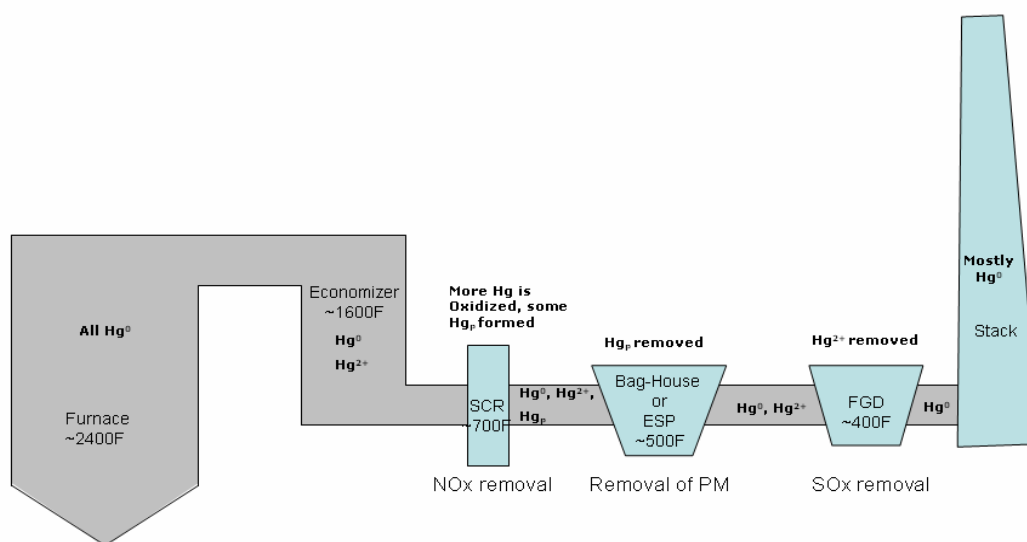
Figure 2.4 Mercury in flue gas path [18]

More than 20 percent of coal-fired utility boiler capacity in the United States uses wet FGD systems to control SO_2 emissions. Wet FGD systems remove gaseous SO_2 from flue gas by absorption. For SO_2 absorption, gaseous SO_2 is contacted with a caustic slurry, typically water and limestone or water and lime. Gaseous compounds of Hg^{2+} are generally water-soluble and can absorb in the aqueous slurry of a wet FGD system. However, gaseous Hg^0 is insoluble in water and therefore does not absorb in such slurries. When gaseous compounds of Hg^{2+} are absorbed in the liquid slurry of a wet FGD system, the dissolved species are believed to react with dissolved sulfides from the flue gas, such as H_2S, to form mercuric sulfide (HgS); the HgS precipitates from the liquid solution as sludge. The capture of Hg in units equipped with wet FGD scrubbers is dependent on the relative amount of Hg^{2+} in the inlet flue gas and on the PM control technology used. ICR data reflected that average Hg captures ranged from 29 percent for one ESP plus FGD unit burning subbituminous coal to 98 percent in a fabric filter (FF) plus wet flue gas desulfurization (WFGD) unit burning bituminous coal [19]. The high Hg capture in the FF plus WFGD unit was attributed to increased oxidization and capture of Hg in the FF followed by capture of any remaining Hg^{2+} in the wet scrubber.

More than 10 percent of the U.S. coal-fired utility boiler capacity uses spray dryer absorber (SDA) systems to control SO_2 emissions. An SDA system operates by the same principle as a wet FGD system using a lime scrubbing agent, except that the flue gas is mixed with a fine mist of lime slurry instead of a bulk liquid (as in wet scrubbing). The SO_2 is absorbed in the slurry and reacts with the hydrated lime reagent to form solid calcium sulfite and calcium sulfate. Hg^{2+} may also be absorbed. Sorbent particles containing SO_2 and Hg are captured in the downstream PM control device (either an ESP or FF). If the PM control device is a FF, there is the potential for additional capture of

gaseous Hg^0 as the flue gas passes through the bag filter cake composed of fly ash and dried slurry particles. ICR data reflected that units equipped with SDA scrubbers (SDA/ESP or SDA/FF systems) exhibited average Hg captures ranging from 98 percent for units burning bituminous coals to 24 percent for units burning subbituminous coal [4].

There has been increasing number of generators installing selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) systems to reduce NOx emissions. SCR devices for reduction of NOx emissions have long been expected to enhance mercury capture by particulate collection devices and SO_2 scrubbers through increased oxidation of mercury. Conversion of more of the elemental mercury to Hg^{2+} would increase the potential removal in a wet FGD, but is not expected to significantly increase removal by precipitators and fabric filters.

The catalyst in SCR system provides sites for mercury oxidation, and the effect of oxidation of elemental mercury by SCR catalyst may be affected by the following:

- The space velocity of the catalyst;

- The temperature of the reaction;

- The concentration of ammonia;

- The age of the catalyst; and

- The concentration of chlorine in the gas stream.

Confounding issues that surround SCR usage in quantifying the degree of oxidation are that when SCR is in place, increase of both unburned carbon (LOI in ash, due to low NOx burner applications) and of excess ammonia (ammonia slip) are both generally present. The increase in unburned carbon may function as a synthetic "activated carbon" that results in direct "carbon" capture of both Hg^0 and Hg^{2+} species. Un-reacted ammonia (slip) is adsorbed onto particulate surfaces and may also enhance sulfur mercury

reactions, again with the result being that Hg_P bound onto ash particulates is subjected to more effective removal by particulate control devices. A negative aspect impacting SCR usage is that de-activation, or poisoning, of catalytic function of SCR has been reported associated with lignite coals.

Summary of post combustion type of mercury emission control devices are presented in table 2.7 which shows varying effectiveness percentage of mercury capture. The effectiveness of mercury capture is particular to a specific plant operation, hence wide variation is observed over different configurations of plant layout and also type of coal burnt in the reactor.

Table 2.7 Average mercury capture by existing post-combustion control configurations used for PC-fired boilers [20]

Post-combustion Control Strategy	Post-combustion Emission Control Device Configuration	Average Mercury Capture by Control Configuration		
		Coal Burned in Pulverized-coal-fired Boiler Unit		
		Bituminous Coal	Subbituminous Coal	Lignite
PM Control Only	CS-ESP	36 %	3%	0 %
	HS-ESP	9 %	6 %	not tested
	FF	90 %	72 %	not tested
	PS	not tested	9 %	not tested
PM Control and Spray Dryer Adsorber	SDA+CS-ESP	not tested	35 %	not tested
	SDA+FF	98 %	24 %	0 %
	SDA+FF+SCR	98 %	not tested	not tested
PM Control and Wet FGD System[a]	PS+FGD	12 %	0 %	33%
	CS-ESP+FGD	75 %	29 %	44 %
	HS-ESP+FGD	49 %	29 %	not tested
	FF+FGD	98 %	not tested	not tested

CS-ESP = cold-side electrostatic precipitator   (a) Estimated capture across both control devices
HS-ESP = hot-side electrostatic precipitator
FF = fabric filter
PS = particle scrubber
SDA = spray dryer absorber system

2.5.3   Emerging Technology for Mercury Control

Post combustion mercury control options are relatively expensive to implement. One reason for the expense is that large flue gas volumes must be treated to capture very small amount of mercury; typical mercury concentrations in untreated flue gas are in the range of few $\mu g/m^3$. One of the dry control technologies that are emerging for mercury emissions reduction is the use of activated carbon injection (ACI). ACI is used upstream of a particulate control device, and under most conditions, if the carbon achieves good contact with the gaseous mercury for a sufficient amount of time, it will adsorb the mercury, both elemental and oxidized forms of mercury. The resulting mercury-laden carbon could then be collected by the downstream particulate control. The amount of mercury adsorbed is dependant upon the mercury adsorption capacity of the activated carbon and the mass transfer characteristics of the system, where the mercury removal will increase with increasing sorbent capacity up to the mass transfer limit of the system.

The capacity of activated carbons can be affected by flue gas composition and temperature depending on the mercury species present. For elemental mercury, lack of halides such as chloride/chlorine in the flue gas can reduce the carbon capacity significantly. This happens since the elemental mercury adsorbed on the carbon inhibits further adsorbtion, while the effect of oxidized mercury is not significant. A temperature effect can be seen when conditions exist where the carbon capacities may decrease below the threshold levels, such as where high levels of oxidized mercury exist and the temperature is significantly greater than 300°F (150°C) [4].

2.6   Cattle Biomass

There is considerable concern regarding the potential global environmental impact of fossil fuels used for power generation. By increasing the fraction of renewable energy in

the national energy supply, some of the impact can be mitigated. Co-firing biomass with coal in traditional coal-fired boilers or using biomass as a reburn fuel in advanced coal-fired boiler configurations represent two options for combined renewable and fossil energy utilization. To add to the above, it can also be considered the best solution to combat the challenging waste disposal problem, with 110 million tons of dry animal manure produced annually in the United States. National Agricultural Statistics Service (NASS) reports that cattle in US grew from 98.2 million in 1990 to 971 million in 2006. With an estimate of each animal fed leaving approximately one ton collectable cattle manure in 5 months containing 35% moisture and 65% solids (combustibles+ash), the bio-waste can contribute to surface or ground water contamination and air pollution problems with the release of CH_4 (a greenhouse gas), NH_3, H_2S, amides, volatile organic acids, mercaptans, esters, and other compounds [21].

The sole source biomass as fuel for combustion application have limitations primarily due to highly variable properties (high ash, high moisture, salt composition, etc.) of manure and the associated flame stability problems. By blending biomass with coal and firing it in existing boiler burners the problems can be eliminated since cattle manure can be readily combusted in the presence of high heating value coal. It is known from previous works of Annamalai et al. on co-firing cattle biomass with coal that, it has great potential in reducing fossil fuel based CO_2, reduction in NO_x, reduction in fuel costs since biomass is cheaper than coal, and minimization of soil, water, and air pollution.

Apart from the above, cattle biomass has very high amount of chlorine content compared to coal with relatively good heating value. For instance, low ash partially composted dairy biomass contains 88% higher chlorine content compared to Wyoming subbituminous coal, while its heating value is almost 70% as that of the coal on an as

received basis. This gives a potential use for blending coal with biomass and co-firing it in existing boilers to increase the chlorine content in the fuel, and hence achieve higher mercury oxidation and hence its capture to reduce elemental mercury emissions.

Recent research activities of reburning cattle biomass with coal [22] have shown remarkable results of reducing NOx emissions by almost 90%. Simulation studies conducted previously by Puchakayala [23], predicted very effective mercury oxidation when coal is fired with biomass. He showed that presence of high chlorine concentration in flue gases substantially reduces elemental mercury emissions. Figure 2.5 shows results of blending feedlot biomass with coal in proportions of 10:90 and 20:80, by which 65-80% of mercury was converted to mercuric chloride, while for pure coal only 9% mercury was oxidized.
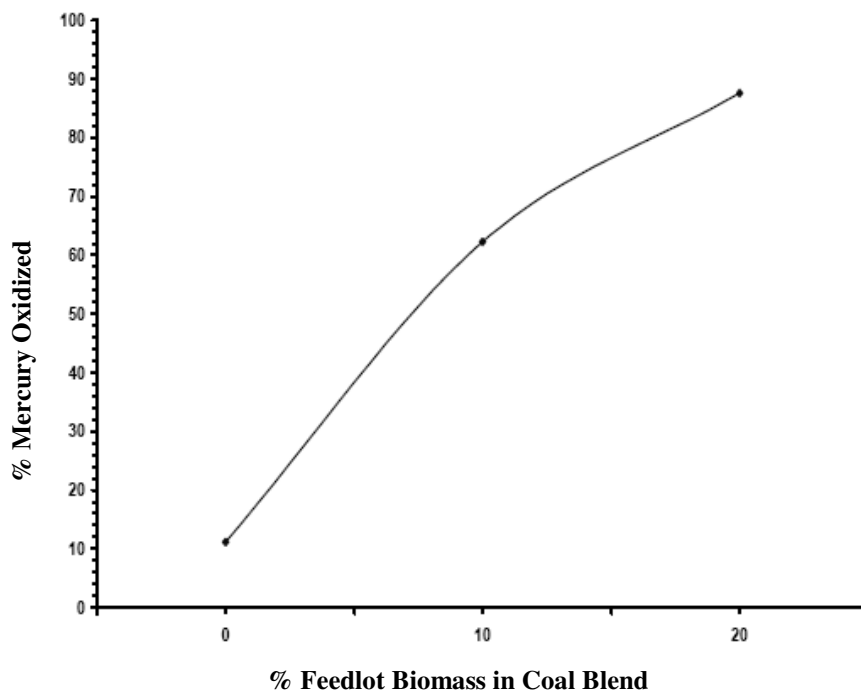
Figure 2.5 Effect of blending coal with biomass on mercury oxidation [23]

It is apparent from the review that no previous work has been performed to study the effect of co-firing coal and biomass blends on mercury emission. The current work deals with the study of mercury emission rates with various proportions of coal and biomass blends, more specifically with dairy biomass.

3   OBJECTIVES

The proposed research implements a novel method of co-firing coal with cattle manure/biomass which helps in oxidization of elemental mercury into its soluble ionic compound, mainly mercuric chloride ($HgCl_2$) which can be captured using traditional pollution control devices. Specifically dairy manure or dairy biomass will be used as co-fired fuel with coal in this study to investigate levels of elemental mercury reduction and to determine operating conditions for optimum mercury reduction.

Survey data from Information Collection Request (ICR) shows that high rank coals such as bituminous coal have large chlorine content, while low rank coals such as sub-bituminous or lignite coal have lower percentages of chlorine. This goes to highlight that there may be less amount of chlorine species during combustion of low rank coals, which results in lower oxidation of mercury, and hence cause pollution threat. This research draws interest from two aspects, firstly, it makes use of energy potential from waste, cattle manure which would be blended with coal to add to the heating value of the blended fuel and act as an oxidizing agent to aid mercury capture; secondly, it addresses the waste disposal problems in cattle farms.

The tasks that follow the current objectives are listed below:

1.) Obtain proximate and ultimate analysis of coal and Dairy Biomass (DB) used as fuels, including Hg and Cl contents

2.) Condition flue gases for mercury measurement

3.) Setup a wet chemistry system to measure both elemental and total mercury content in the flue gas

4.) Conduct parametric studies on

    a. Equivalence ratio

    b. Different fuels

    c. Different blend ratio of fuels

5.) Obtain temperature and mercury profiles along the reactor for limited cases

6.) Obtain results for elemental and oxidized mercury in gas phase

7.) Deduce the emission in terms of g/GJ (on heat basis) by developing relations for flue gas volume per GJ

8.) Suggest optimum operating conditions for maximum reduction of mercury emissions

4   EXPERIMENTAL FACILITY AND PROCEDURE

In order to validate reduction in mercury emission, co-firing experiments were conducted on a 100,000 BTU/hr small scale coal fired boiler burner at the Coal and Biomass Energy Laboratory, Texas A&M University. This section briefly describes the facilities used and modifications made to report the results.

4.1   *Proximate and Ultimate Analysis*

Proximate and ultimate analyses were conducted to determine the basic fuel properties, mercury and chlorine content of each type of fuel used. The analyses done by Hazen Inc., Golden, CO, a commercial testing laboratory, reported ash, moisture, volatile matter and fixed carbon fractions in the fuel and also the constituent elements in the fuel, such as carbon, hydrogen, nitrogen, oxygen and sulfur. The analysis report is available in the results section of this document.

4.2   *Boiler Burner Facility*

The furnace consisting of a 15.24 cm (6 in) diameter, 182.88 cm (6 ft) long downward fired combustor, is made with a steel frame containing a two inch layer of insulation and a two inch section of refractory (Dimensions are shown in Figure 4.1 and 4.2). The top section of the furnace is the main burner which has a swirl burner (or injector) and a quarl section. The swirl injector consists of a swirler and a nozzle. The swirling jet of the primary air is generated by the swirler and mixed with the primary fuel and air from the injection nozzle. The quarl is a diffusing section molded with the top section of the refractory which aids to stabilize the recirculation zone. A swirl number of 0.69 to 0.82 and quarl half angle of 24^0 are used for the burner operation. Appendix A shows the derivation on swirl number and a brief description of quarl.

Along the walls of the furnace are several gas sampling ports and temperature measurements ports. There are also three wall temperature measurement locations. K type thermocouples were used to make temperature measurements and were displayed on LabView software on a personal computer. Water jets at the near bottom are used to cool the hot exhaust gasses before they enter the exhaust system. Solid fuel is fed using commercial Acrison feeder system, where fuel is carried to the furnace by carrier air (also called primary air) through an eductor. Shop air at 101.3 kPa (14.6 psig) is used for primary air supply through two Dwyer VFA-9 flowmeters. Secondary air is supplied to the furnace by an air compressor and controlled by Dwyer RMC flow meter, an electronic air flow meter. The furnace is operated at slight negative pressure to ensure flames are within the furnace and no exhaust gas leaks to the laboratory. A vacuum of 0.25 cm (0.1 inch) is achieved through an exhaust fan and a damper on the exhaust line.

A portable commercial GreenLine 8000 flue gas analyzer is used to measure different gas species such as CO, CO_2, O_2, NO_x, SO_x and C_xH_y. It employs two methods for measurements; electrochemical (EC) sensors to make CO, CO_2, NO_x, SO_2 and O_2 measurements and non-dispersive infrared (NDIR) sensors to make CO, CO_2, C_xH_y measurements. Mercury Instrument VM 3000 is used to measure mercury species in the flue gas using cold vapor atomic absorption (CVAA) principle. The schematic of the experimental layout is shown in figure 4.3.
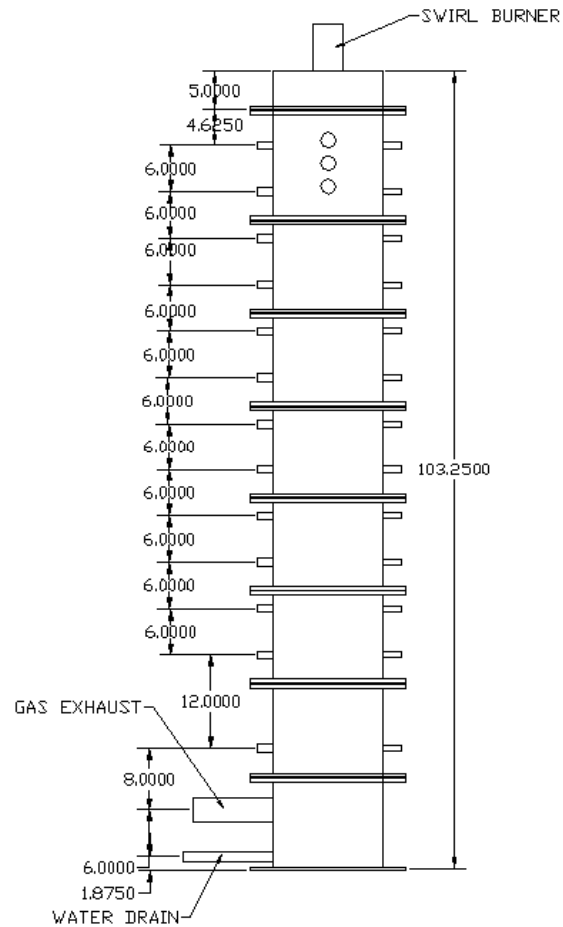
Figure 4.1 Dimensions of the furnace
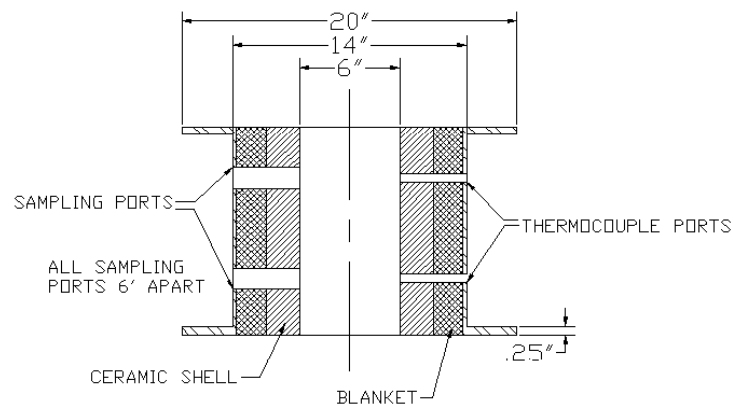
Figure 4.2 Vertical section of the boiler
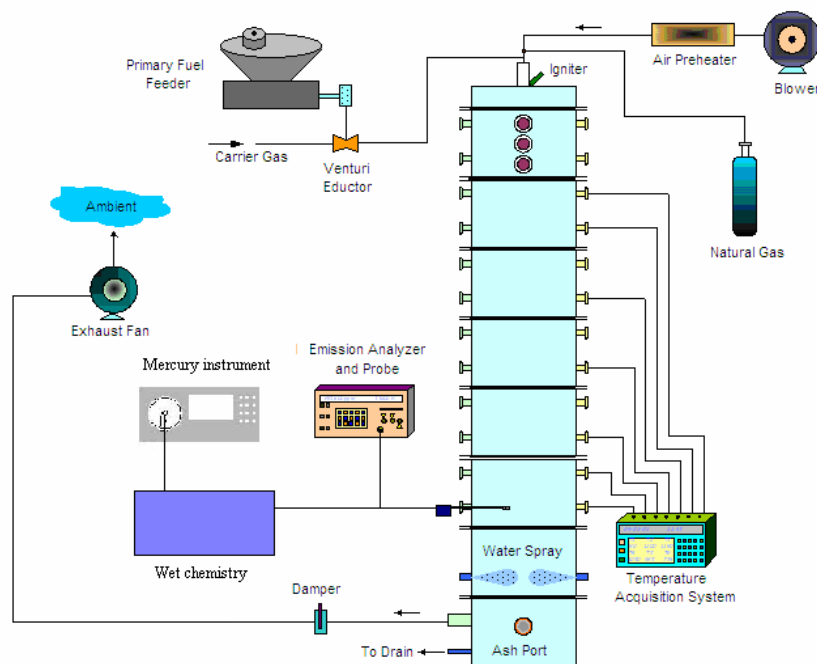
Figure 4.3 Schematic layout of the furnace and accessories

4.3   Mercury Measurement and Wet Chemistry System

Mercury measurement technologies in flue gas have been speculated and have been listed as a challenge due to its very low concentration (less than $10\mu g/m^3$ or 1.2 ppb), and also the inherent complications in reading oxidized mercury. At Coal and Biomass Energy Laboratory (CBEL), Texas A&M University, mercury measurement is done using VM3000, Mercury Instrument which adopts CVAA principle. The CVAA method determines the mercury concentration in the gas by measuring the attenuation of the light produced by a mercury vapor lamp as it passes through a cell that contains the sample gas. The mercury atoms in the cell absorb UV light at their characteristic wavelength of 253.7 nm. The measurement principle is discussed in appendix G. Other flue gas constituents such as SO_2 absorb light across a wide spectrum including the 243.7

wavelength, thus acting as an interferant. Water vapor and particulate are also broadband absorbers that must be dealt with in CVAA measurement [24].

Mercury is present in three different forms in flue gas, viz., elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate mercury (Hg^P). Particulate form of mercury in flue gases of utility boilers or any coal combustion process is in the range of 3% to 8%, which is considered negligible. Moreover, particulate mercury can be easily trapped in conventional ash removal devices such as baghouse or ESP, and hence does not create any potential toxic emission threat. Since the intention in this research is to convert as much elemental mercury into oxidized form, it is essential to measure both the elemental and oxidized mercury concentration in the flue gas, which would enable us compare results with the relation of each fuel used to effective mercury oxidation and hence evaluate its efficiency in mercury capture.

The instrument is limited to read only elemental mercury, and not the total mercury. There are several ways to condition the flue gas to read both elemental and total mercury. To list them, they are Wet Chemistry method, Dry Sorbent method and Thermocatalytic converter. The Dry Sorbent method and Thermocatalytic converter are highly expensive methods, hence Wet Chemistry based flue gas conditioning is used for this research. The U.S. Environmental Protection Agency (EPA) Methods 101A and 29, and the Ontario Hydro method have been validated for measuring total mercury emissions from coal-fired boilers by wet chemistry method, though the Ontario Hydro method has become a standard for mercury speciation measurements in coal combustion flue gas. However, these wet-chemistry methods are difficult to perform, costly, time-consuming, and labor-intensive.

Several on-line analyzers have been developed primarily for measuring mercury emissions. University of Utah previously devised one such method based on modified Ontario-Hydro method, which was adapted, constructed and used in this study. In this system the sample gas is pulled in two streams directly from sampling port of the existing 100,000 BTU/hr small scale boiler into a set of conditioning impingers. One stream is bubbled through 10% stannous chloride ($SnCl_2$) solution to reduce oxidized mercury species to elemental mercury. The stream then contacts a solution of 10% sodium hydroxide (NaOH, caustic solution) to remove acid gases. This stream represents the total mercury concentration in the reactor.

The second stream is first treated with 10% potassium chloride (KCl) solution to remove oxidized mercury species and then is also treated in 10% caustic solution for acid gas removal. This stream is representative of the elemental mercury concentration in the reactor. Oxidized mercury species is calculated as the difference between total and elemental mercury concentrations. Water is removed from the sample gas by a chiller and then each stream is intermittently sent to the analyzer by a valve box connected to the analyzer [25]. By doing this, the flue gas temperature was reduced to nearly room temperature which was required for measurement as suggested by the manufacturer. The complete circuit of mercury wetted path is made through Tygon R3603 tubing which has low mercury memory. To ensure the reagents' active reaction in the impingers with flue gas, fresh chemicals are replenished into the system and spent chemicals are removed using two different 4 channel peristaltic pumps. The schematic of the wet chemistry system is shown in figure 4.4.

A quick silver inertial separation (QSIS) filter manufactured by Apogee Scientific Inc., was originally planned to be used in the flue gas conditioning system to negate the

effects of particulate matter, which could cause unpredictable speciation between elemental and oxidized mercury. After the construction of filtration system it was realized that it would not be suitable for the application such as this study owing to relatively smaller size of boiler used. Moreover, since mercury bound particulate matter constitutes only 3 to 8% of the total mercury, and its extremely small concentration, the filtration system was deployed.
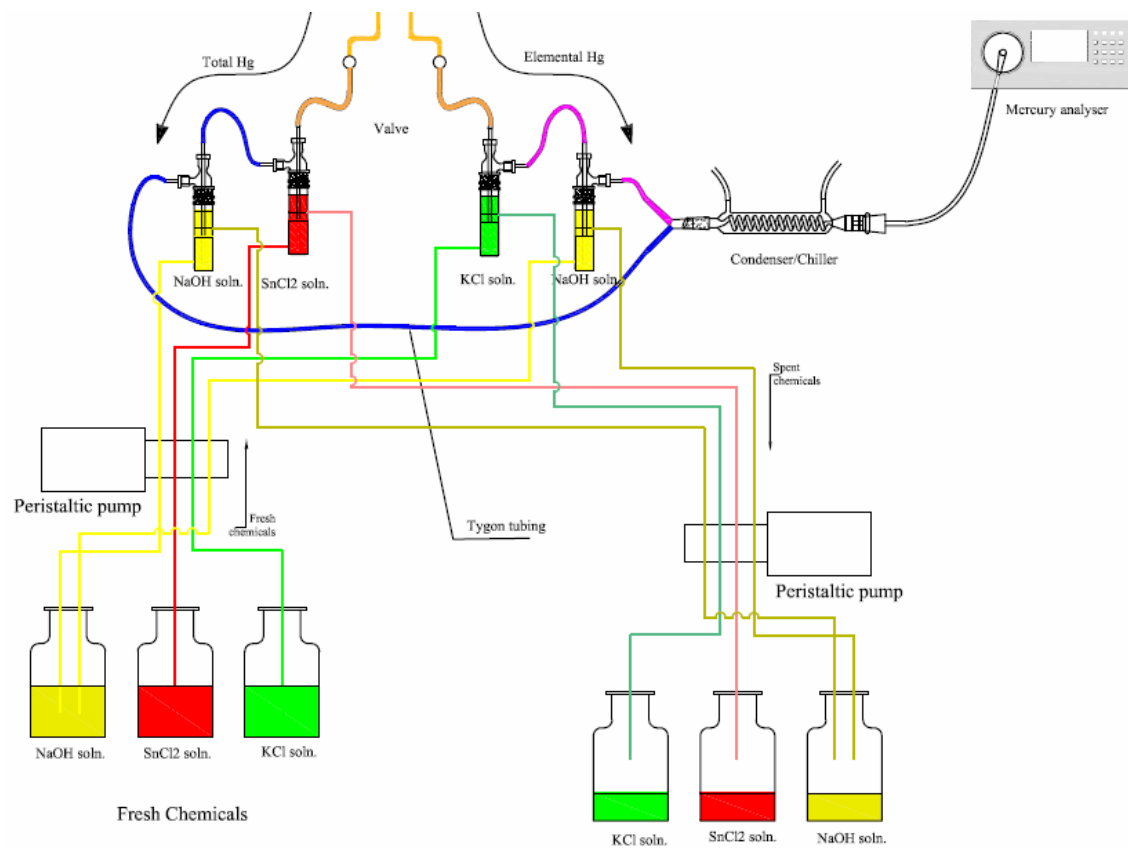
Figure 4.4 Wet chemistry based flue gas conditioning system

4.4   Procedure

Conducting experiments during coal and fuel blend combustion followed three distinct steps: preparation phase, firing phase and measurement phase. In preparation

phase, the furnace is preheated to a temperature of about 2000 F by burning natural gas only at near stoichiometric condition with air being supplied from secondary air supply channel. This process of preheating takes about 3 to 4 hours until steady state is attained. In the meantime, the fuel feeder is loaded with required solid fuel, and feed rate is calibrated manually by measuring mass of fuel flow in specific amount of time (normally in 1 minute). Once steady state is attained, the second phase of firing solid fuel can begin. The natural gas supply is turned off and feeder motor is started to feed solid fuel which is carried by carrier air (also called primary air) to the furnace. Air flow rates are adjusted by varying the secondary air flow rate, the means by which desired equivalence ratios are achieved (from lean to rich combustion). Once steady state is attained (which takes roughly 10 minutes), measurement phase begins, when sampling probe is plugged into the sampling port to make measurements of flue gas species using GreenLine analyzer. Once these readings are taken, mercury measurements are made using VM3000 analyzer and wet chemistry system. This measurement step is followed for every equivalence ratio. Finally on completing the set of experiments at the end of the day, fuel supply is turned off and the furnace is allowed to cool down. Detailed step by step procedure is described in Appendix B, the operating parameters for each case is listed in Appendix C, and sample calculation of air flow rates is given in Appendix D.

5   RESULTS AND DISCUSSION

This section reports the fuels used during experiments, their proximate and ultimate analysis results, base case mercury measurements, results of mercury measurement from each case conducted, discussion of extent of mercury oxidation under different operating conditions, and other observations.

5.1   Fuels Used

Fuels used during experiments were Texas Lignite Coal (TXL), Wyoming Subbituminous Coal (WYC), Seperated Solids Partially Composted Dairy Biomass (Sep. Sol. PC-DB), High Ash Partially Composted Dairy Biomass (HA PC-DB), and their blends. Dairy Biomass (DB) fuels used for this study, Separated Solids Partially Composted Dairy Biomass (Sep. Sol. PC-DB) and High Ash Partially Composted Dairy Biomass (HA PC-DB), were supplied by Texas Agricultural Experiment Station, Amarillo, TX. Prior to shipping, the DB fuels sourced from dairy farm in Comanche County, TX were composted partially (half the complete composting time) for 45 days involving successive wetting and turning cycles and then placed in a green house to facilitate drying. Once the DB were dried to >10%, bulk samples were processed with a hammer mill and the Vortec impact mill to grind them to particle size convenient to burn in the existing 100,000 BTU/hr facility at Texas A&M University, College Station.

The blends of fuels fired were mixed on weight basis, in following proportion:

- 95:5 – Coal:Biomass
- 90:10 – Coal:Biomass
- 80:20 – Coal:Biomass

Overall, 13 different fuel blends were fired (all combinations of fuels and ratios as stated above, except 80:20 – TXL:HA PC-DB).

5.2 Proximate and Ultimate Analysis

The fuels used for experimentation were tested for their combustible properties and elemental constituents. 3 individual samples of each fuel were prepared and sent to Hazen Research Inc., Golden, CO for analysis. The analysis results were used to as input to an EXCEL program to extract useful combustion related properties of the fuels and are made available as TAMU Fuel Data Bank. A web page (http://www1.mengr.tamu.edu/REL/TAMU%20FDB.htm) for TAMU Fuel Data Bank has been created and all useful data for fuels are stored and updated. The average of three samples for each fuel used for this study is reported in table 5.1 (complete analysis report available in Appendix E).

Table 5.1 Proximate and ultimate analysis of fuels used

Fuel Source	Texas Lignite and Wyoming Powder River Basin Coal provided by TXU Energy, Dallas		Dairy Farm in Comanche County, Texas	
Reference	[26]		[27]	
Ananlysis Lab	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO
Sample ID	TXL 113-115	PRB 116-118	128-130	131-133
Date of sampling	10/10/2005	10/10/2005	5/15/2006	5/15/2006
Date of analysis	11/29/2005	11/29/2005	10/23/2006	10/23/2006
Ash	11.46	5.64	14.93	59.91
Dry Loss (% Moisture)	38.34	32.88	25.26	12.21
FC	25.41	32.99	12.95	3.85
VM	24.79	28.49	46.86	24.04
Carbon, C	37.18	46.52	35.21	18.04
Hydrogen, H	2.12	2.73	3.71	1.45
Nitrogen, N	0.68	0.66	1.93	1.15
Oxygen, O (diff)	9.61	11.29	18.60	7.07
Sulfur, S	0.61	0.27	0.43	0.19
HHV (kJ/kg)	14,287	18,193	12,844	4,312
Chlorine, Cl %, (ppm)	0.007 (70 ppm)	0.019 (190 ppm)	0.161 (1610 ppm)	0.398 (3980 ppm)
Mercury, Hg g/kg (ppb)	0.00013 (130 ppb)	0.00007 (70ppb)	0.00004 (40 ppb)	0.00003 (30 ppb)

Table 5.2 shows few of the derived properties extracted from the analysis results which aid us compare the ash, chlorine and mercury content or loading with different fuels on as received and dry ash free (DAF) basis.

Table 5.2 Few derived properties of fuels

	Txlig-3 samples	Wy Coal-3 samples	DB-Sep solids-PC-2006	DB-HA-PC
HHV (kJ/kg)	14286.82	18193.02	12844.17	4312.40
HHV, Boie Equation (kJ/kg)	14582.32	18347.96	14799.12	7336.17
HHV, DAF (kJ/kg)	28459.80	29593.38	21473.37	15466.57
Chlorine, Cl % (ppm)	0.007 (70 ppm)	0.019 (190 ppm)	0.161 (1610 ppm)	0.398 (3980 ppm)
Cl DAF % (ppm)	0.0139 (139 ppm)	0.0309 (309 ppm)	0.2691 (2691 ppm)	1.4274 (14274 ppm)
Cl, g/GJ	4.899620184	10.44356385	125.3486795	922.9190957
Mercury, Hg g/kg (ppb)	0.00013 (130 ppb)	0.00007 (70 ppb)	0.00004 (40 ppb)	0.00003 (30 ppb)
Hg DAF g/kg (ppb)	0.000258 (258 ppb)	0.0001138 (113.8 ppb)	0.0000668 (66.8 ppb)	0.0001075 (107.5 ppb)
Hg, g/GJ	0.009099295	0.003847629	0.003114253	0.006956677
Ash Loading (kg/GJ)	8.02371134	3.10008948	11.62050617	138.9199528

It can be seen that WYC has twice as much Cl content as that of TXL on heat basis, while its Hg content is three times lower than that of TXL, which means WYC produces lesser mercury emissions compared to TXL. It can also be seen that DB has much higher chlorine content (1610 ppm to 3980 ppm), which is 14 to 39% higher compared to coal (70 ppm to 190 ppm), while its heating value ranges from 23 to 70% to that of the coal. When DB is blended with coal in different proportions, it tends to increase the chlorine and ash content in the coal based fuel, but decreases the heating value. Figure 5.1 depicts the same graphically.

Table 5.3 shows the heating value, chlorine content, mercury content and ash loading for each type of blend used for the study.

Figure 5.2 shows the variation of estimated chlorine content and change in heating value of the fuel blend compared to pure 100% coal.
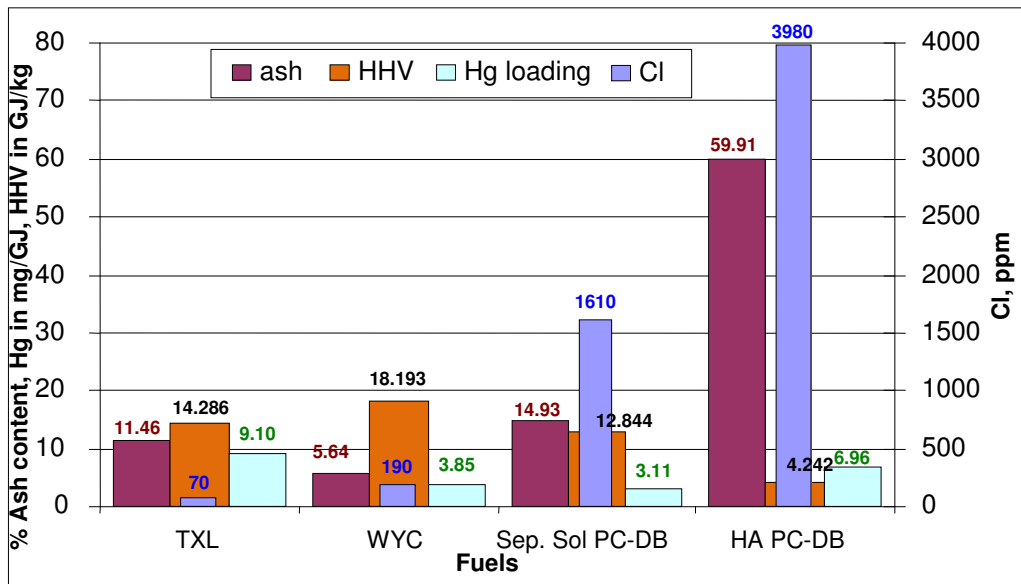
Figure 5.1 Derived properties of fuels in graphical form

Table 5.3 Properties of various blends used for the study

Blend	Fuels	HHV (kJ/kg)	Chlorine content		Mercury content		Ash % (as received)	Ash loading (kg/GJ)
			ppm	g/GJ	ppb	g/GJ		
100	TXL	14286	70	4.8999	130	0.0091	11.46	8.02
95-5	TXL-Sep Sol PC-DB	14213.9	147	10.3420	125.5	0.0088	11.6335	8.18
90-10	TXL-Sep Sol PC-DB	14141.8	224	15.8396	121	0.0086	11.807	8.35
80-20	TXL-Sep Sol PC-DB	13997.6	378	27.0046	112	0.0080	12.154	8.68
95-5	TXL-HA PC-DB	13783.8	265.5	19.2617	125	0.0091	13.8825	10.07
90-10	TXL-HA PC-DB	13281.6	461	34.7097	120	0.0090	16.305	12.28
80-20	TXL-HA PC-DB	12277.2	852	69.3969	110	0.0090	21.15	17.23
100	WYC	18193	190	10.4436	70	0.0038	5.64	3.10
95-5	WYC-Sep Sol PC-DB	17925.55	261	14.5602	68.5	0.0038	6.1045	3.41
90-10	WYC-Sep Sol PC-DB	17658.1	332	18.8016	67	0.0038	6.569	3.72
80-20	WYC-Sep Sol PC-DB	17123.2	474	27.6817	64	0.0037	7.498	4.38
95-5	WYC-HA PC-DB	17495.45	379.5	21.6914	68	0.0039	8.3535	4.77
90-10	WYC-HA PC-DB	16797.9	569	33.8733	66	0.0039	11.067	6.59
80-20	WYC-HA PC-DB	15402.8	948	61.5473	62	0.0040	16.494	10.71
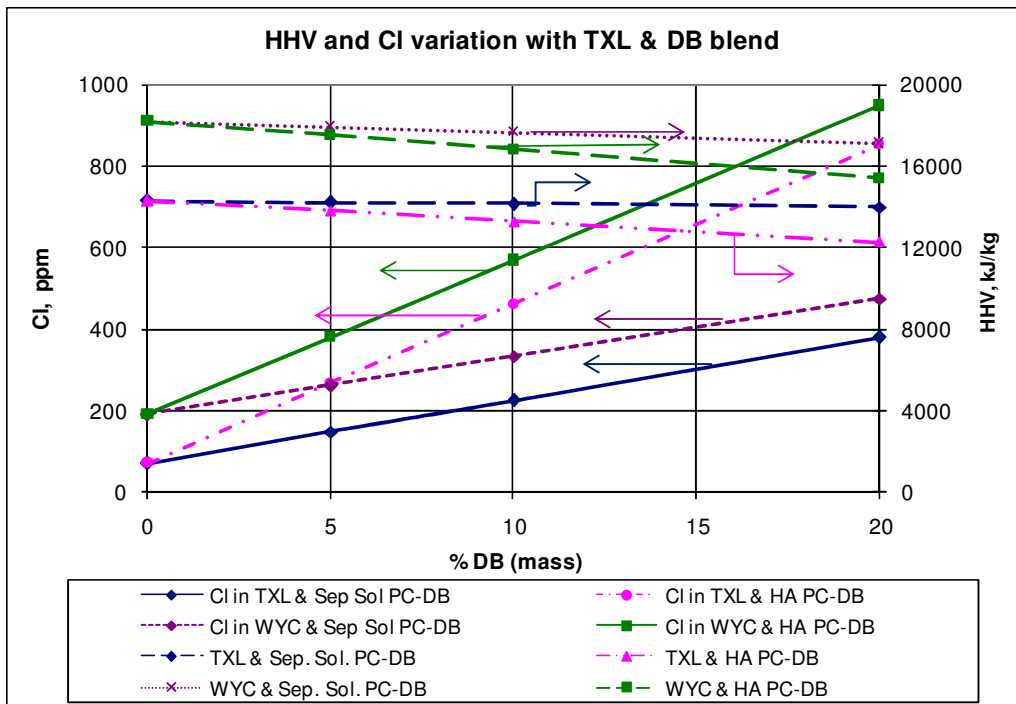
Figure 5.2 Variation of Cl and heating values for different blends
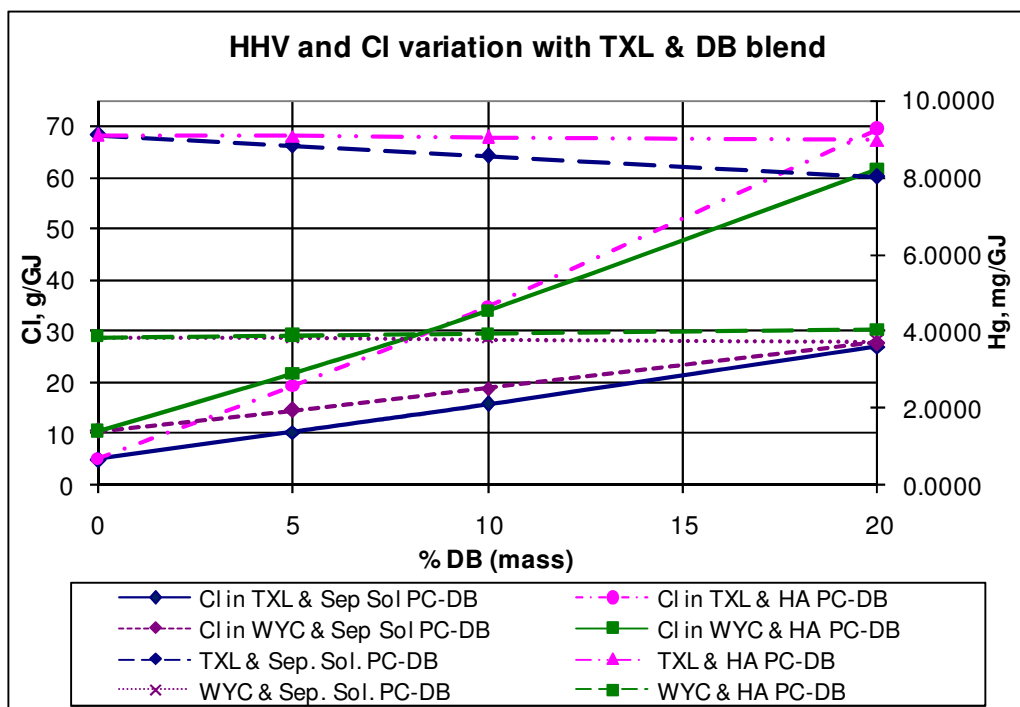
Figure 5.3 Variation of Cl and mercury for different blends

It is seen that as the blending proportion of DB increases in the fuel, heating value decreases while the chlorine content increases in the blend. The heating value of the blend shows much steeper decrease when blended with high ash PC-DB compared to low ash PC-DB, due to the lower heating value of the high ash fuel contributed mainly by higher percentage of ash content. Decreasing the blended fuel's heating value leads to increase in firing fuel feed rate, which in turn increases ash loading. Thus the ash loading cumulatively increases faster with high ash blends at higher proportions of DB.

5.3   *Base Case Mercury*

Mercury measurements made when 100% coal fired is reported in this section and is termed base case with which other blend ratios will be compared to judge the reduction in mercury emissions. In all cases, total and elemental mercury were measured but mercury in particulate form was not measured. Figure 5.3 shows the variation of elemental and total mercury at various equivalence ratios for TXL and WYC. For all cases, the error band lies at $\pm$ 0.1µg/m^3 which is the least count or the resolution of the mercury instrument specified by the manufacturer. The elemental mercury for TXL and WYC is 0.8 and 0.7 µg/m^3 at stoichiometry, and it fluctuates to a maximum of 1.2µg/m^3 for TXL. It is interesting to note that total mercury for TXL is higher than that for WYC, which means the oxidized fraction of mercury is greater for TXL than that for WYC, which is evident from the figure 5.4. This may be predominantly due to presence of higher ash content in the fuel which provides greater site and chance for mercury oxidation. It can be observed that during lean combustion (lower equivalence ratio) there is mercury variation seen more obviously with total mercury concentration, while at stoichiometry and richer conditions, there is not much variation. This may be attributed from the fact that at richer conditions there is presence of unburnt carbon which adsorbs and re-emits mercury at a

fairly stable rate, while during lean combustion, the excess air burns unburnt carbon present on the refractory walls and causes release of more mercury.
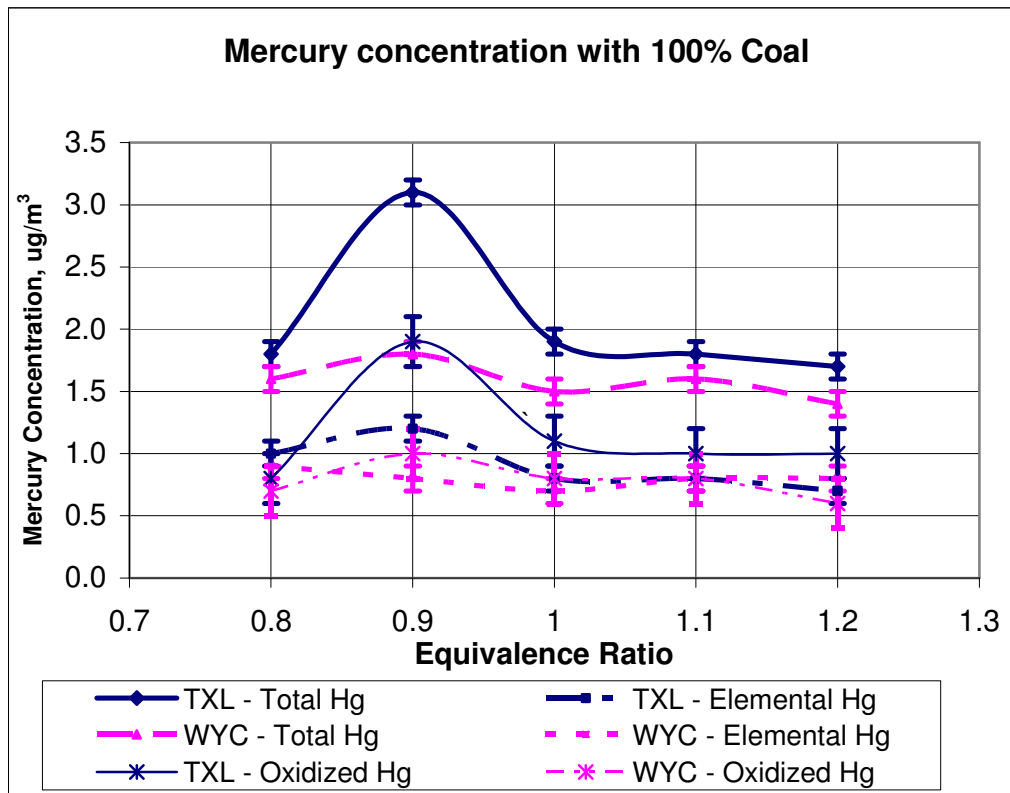
Figure 5.4 Base case results on elemental and oxidized mercury for coal

5.4   Blending TXL with DB

In order to validate the hypothesis that blending of coal with DB can reduce Hg emission, experiments were performed by blending TXL with DB. The blending causes increased chlorine content in the fuels which aids mercury oxidation and hence reduce emission of elemental mercury. Figures 5.5 and 5.6 show the variation of elemental mercury for TXL with different blends of DB at various equivalence ratios. As chlorine content in the blend increases with increase in DB proportion (figure 5.2), there is

increased chance of more available chlorine species at combustion temperatures. This increase in chlorine species react with mercury as temperature drops down along the furnace and forms stable and soluble mercuric chloride ($HgCl_2$), and fewer elemental Hg is emitted.

Compared to pure TXL, ash loading increases slightly on blending with DB; however Cl content increases by 2 to 5.5 times on blending with Sep. Sol. PC-DB, and 4 to 7 times on blending with HA PC-DB (Table 5.3); while Hg content in the blended fuel decreases marginally. Hence there is more available chlorine species in the blend in contrast to lower Hg input from the fuel, which is responsible for higher Hg oxidation and lower emission of elemental Hg. Reduction of elemental mercury emissions at higher equivalence ratios is due to a combination of Hg oxidation due to chlorine species and also due to unburnt combustibles in the furnace present either directly attached to the walls of the furnace or unburnt fraction present in the ash which captures a part of Hg and also aids in providing increased sites for oxidation of Hg.

The case of 80-20 blend of TXL and HA PC-DB is not reported, since heavy ash loading clogged the sampling ports making measurements not possible. It is also evident from table 5.3 that 80-20 blend of TXL and HA PC-DB has more than twice the amount of ash loading compared to 100% TXL, hence it can also be deduced that this fuel blend is not suitable for any practical purposes due to heavy ash loading.
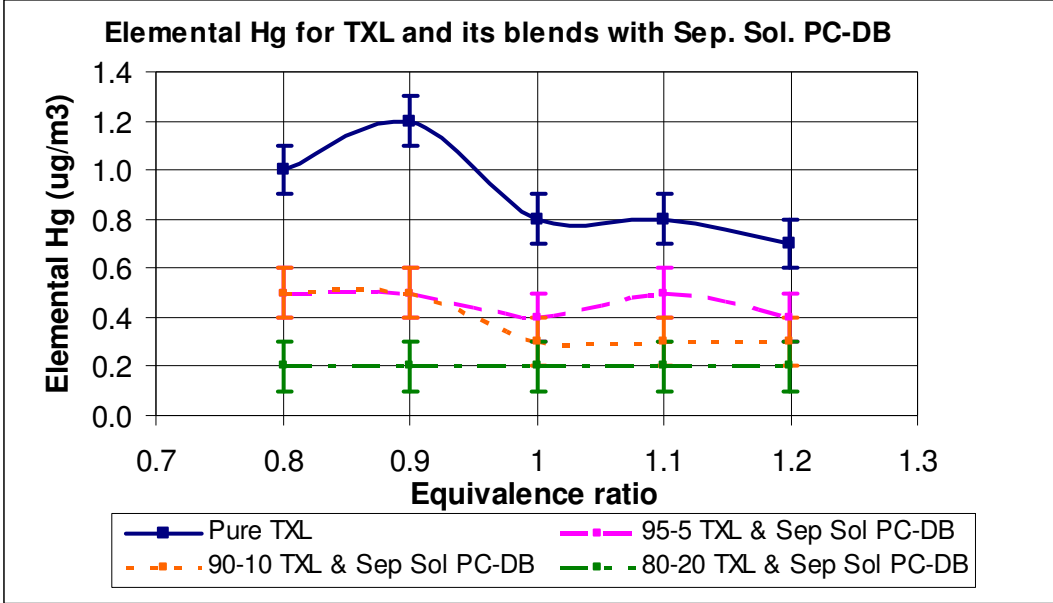
Figure 5.5 Elemental Hg for TXL and its blends with Sep. Sol. PC-DB
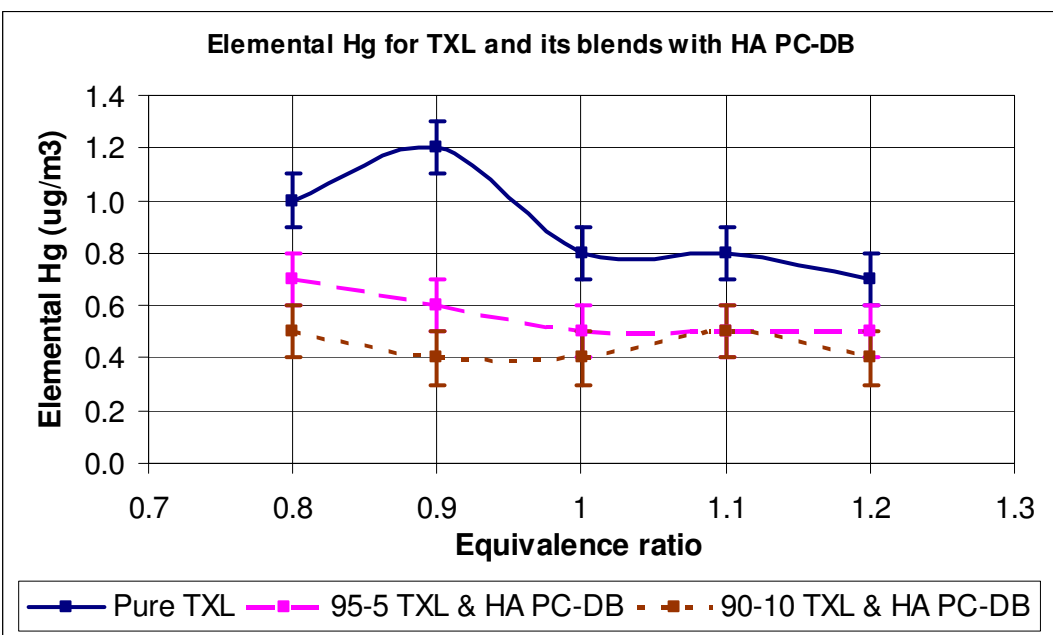
Figure 5.6 Elemental Hg for TXL and its blends with HA PC-DB

5.5   *Blending WYC with DB*

When WYC is blended with DB, similar reduction in elemental mercury occurs due to increase in chlorine content in the fuel. Figures 5.7 and 5.8 show the variation of elemental mercury for WYC when mixed with DB at different ratios and various equivalence ratios.

As opposed to TXL, there is no obvious peak in total mercury measurements for WYC. This may be due to lower ash loading of WYC, which is almost one-third that of TXL. However, as equivalence ratio increases (combustion goes from lean to stoichiometry stage), the elemental mercury emissions decrease primarily due to presence of higher unburnt combustibles on refractory walls or ash creating sites for increased oxidation. But the total and elemental mercury emissions for WYC remains fairly at a lower range due to decreased Hg loading (one-third as that of TXL on heat basis) and increased chlorine content (almost double as that of TXL on heat basis).

Similar to TXL and its blends with DB, WYC also shows decreased elemental mercury emissions with increase in DB proportion to the blend. Some perturbations are observed with change in equivalence ratio which may be the contribution of ash loading emanated from burning coal. The behavior of ash to adsorb and re-emit mercury is not consistent with temperature or flue gas composition, hence the fluctuations. This is more obvious when observed with the results from burning blends of HA DB.

From figures 5.5 to 5.8, a very obvious trend can be easily observed, which is, as DB ratio in the blend increases, the elemental mercury concentration falls. And also seen is that, for 80-20 blend of any coal with any DB, the elemental mercury is at its least value $(0.2\mu g/m^3)$. This level of mercury concentration is very low and near the resolution of the mercury measuring instrument. It can be deduced that at 80-20 blend of coal and DB,

there is more than sufficient chlorine in the blend to almost completely oxidize all elemental mercury to oxidized mercury during or immediately after combustion.
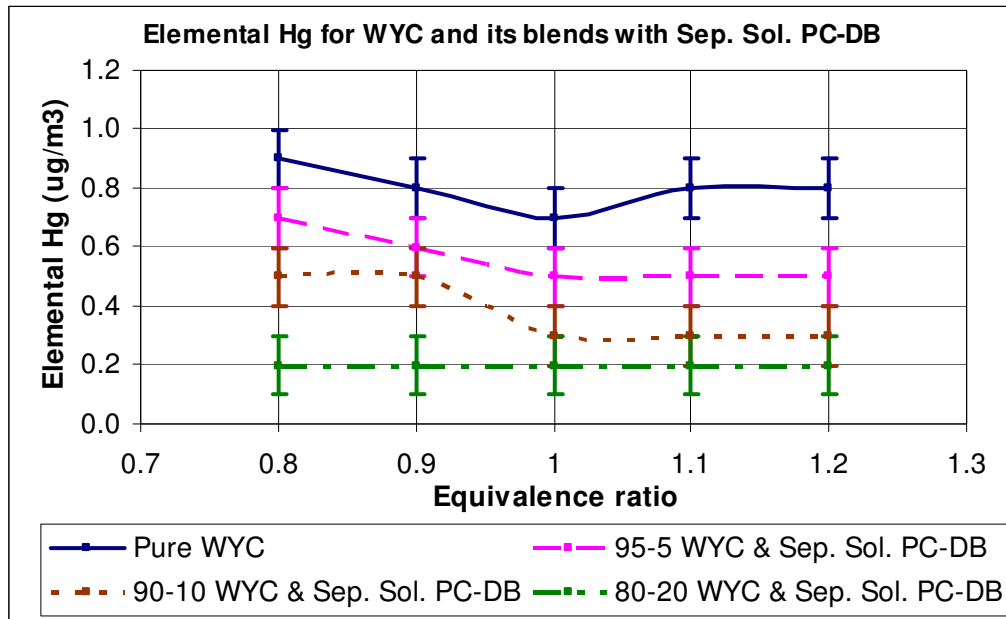
Figure 5.7 Elemental Hg for WYC and its blends with Sep. Sol. PC-DB
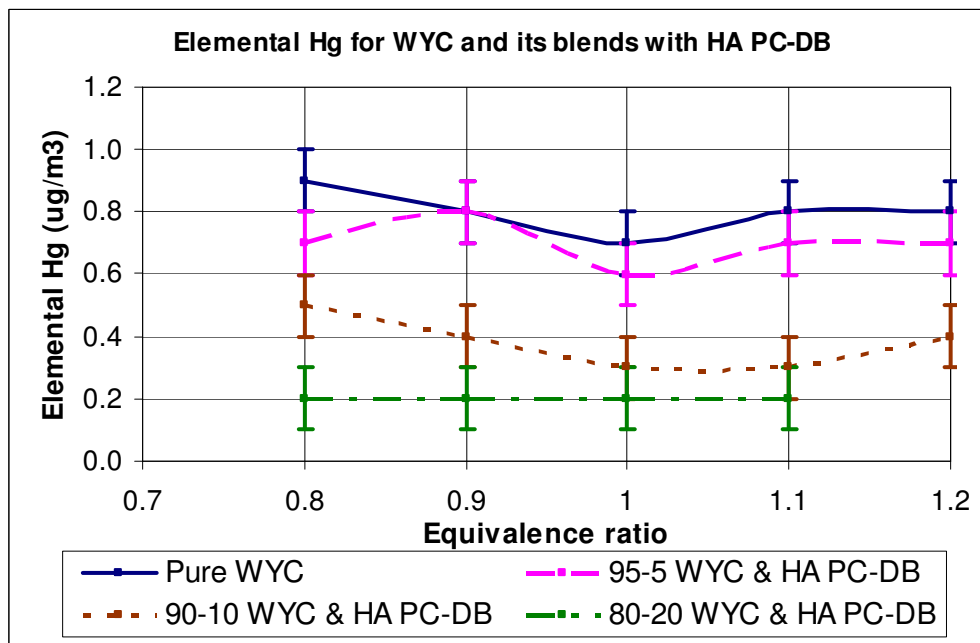
Figure 5.8 Elemental Hg for WYC and its blends with HA PC-DB

5.6   *Effect of Blend Ratios*

As discussed in the previous section, increasing fractions of DB in blended mixtures of coal and DB, increases the chlorine content which causes increased mercury oxidation, hence reduction in elemental mercury. This result is presented in figure 5.9. It can be observed that elemental mercury is least for 80-20 blend of coal and DB, and though elemental mercury concentration falls rapidly from pure coal firing to 90-10 coal and DB blend, beyond 90-10 blend until 80-20 blend the change is not very much.

The reduction in elemental mercury concentration due to blending of DB to coal could occur for two reasons, the first being presence of more chlorine species in the fuel blend which causes increased mercury oxidation and hence reduction in elemental mercury, and secondly due to reduced mercury input during firing. DB has very low mercury content compared to coal; hence in 80-20 coal and DB blend, the mercury input from coal is reduced by 20% which may yield reduced mercury emissions. To understand this fact, a plot of mercury emitted on energy basis (mg/GJ) is presented in figure 5.10, which shows not much significant change from the trend as discussed on mercury concentration levels with blend ratios. The estimation of Hg in mg/GJ requires an estimation of flue gas volume by empirical method at STP in m^3/GJ from input rates of fuel and air. The derivation of mercury emissions in mg/GJ and a sample calculation is shown in appendix F.
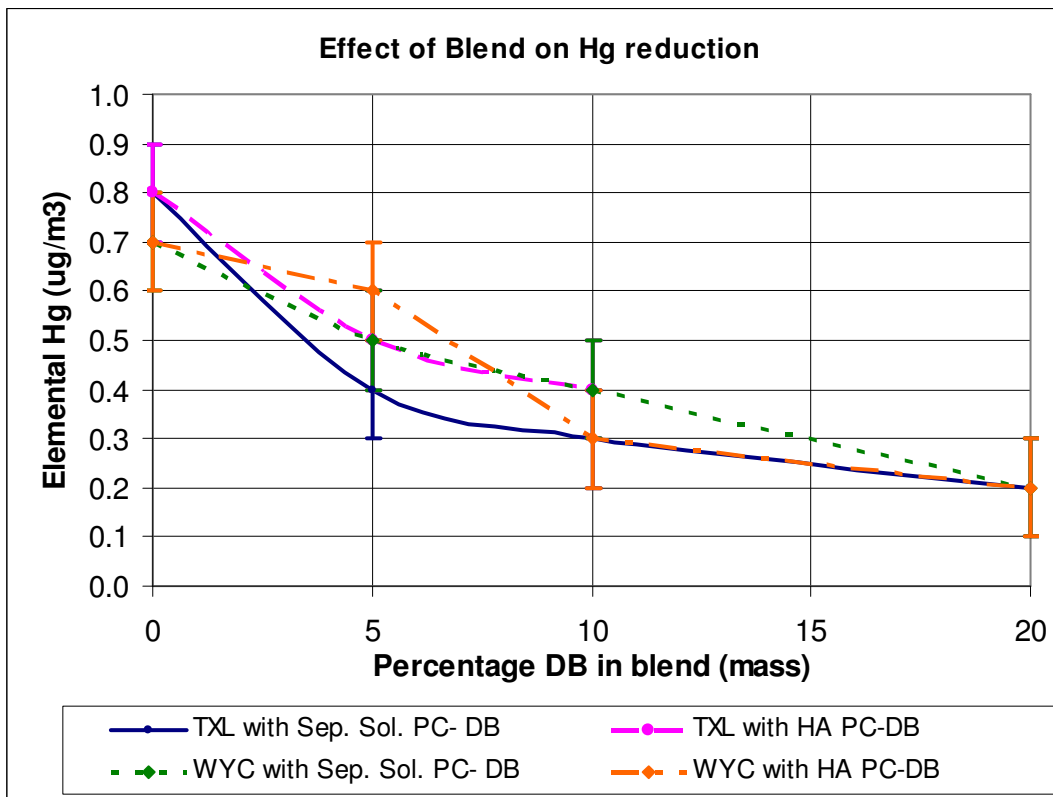
***Figure 5.9 Effect on elemental mercury (µg/m³) when blending DB with coal on flue gas
concentration basis***

Figure 5.11 shows the effect of oxidized mercury variation on mg/GJ basis with varying proportion of DB in fuel blend. It can be seen that oxidized mercury increases with increase in mass proportion of Sep. Sol. PC-DB with coal in the blend, which is due to increased Cl species in the fuel with increase in DB. For blending of HA PC-DB with coal, it is observed that oxidized Hg decreases with increasing DB proportion by mass upto 10%. This can be explained as it causes increased ash loading during combustion which may capture Hg species by adsorption.

Figure 5.12 shows the effect of elemental mercury with amount of chlorine in the fuel. As DB in fuel blend increases, the chlorine content increases linearly which increases oxidation of mercury and hence reduce elemental mercury concentration.
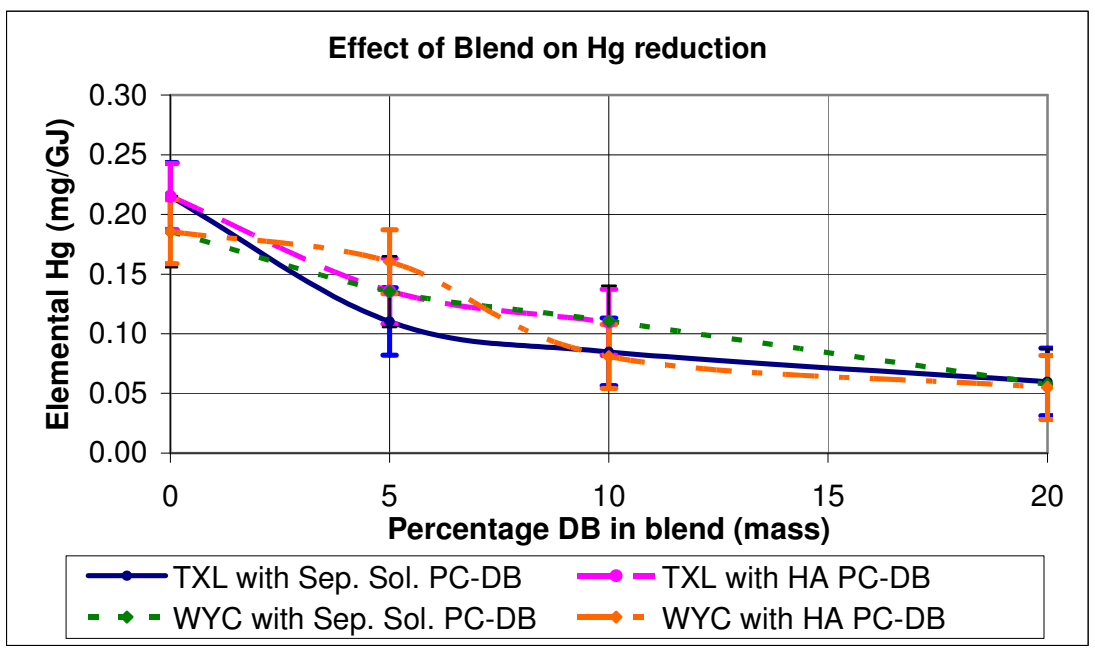
Figure 5.10 Effect on elemental mercury emitted (mg/GJ) when blending DB with coal on energy basis
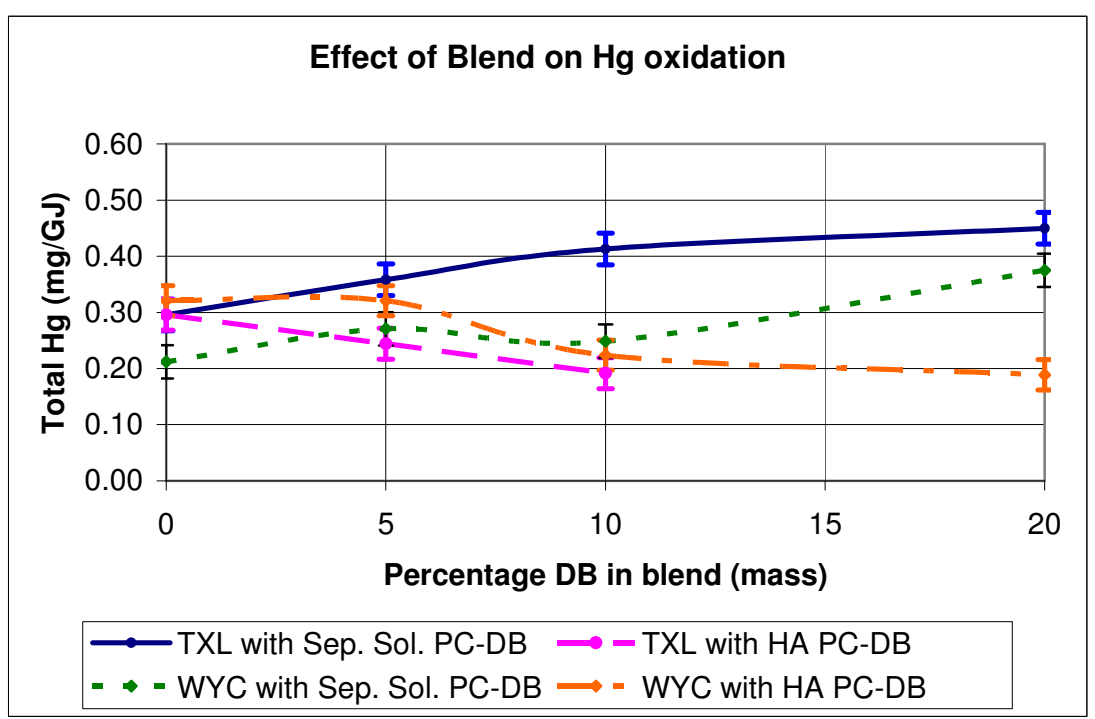
Figure 5.11 Effect on oxidized mercury emitted (mg/GJ) when blending DB with coal on energy basis
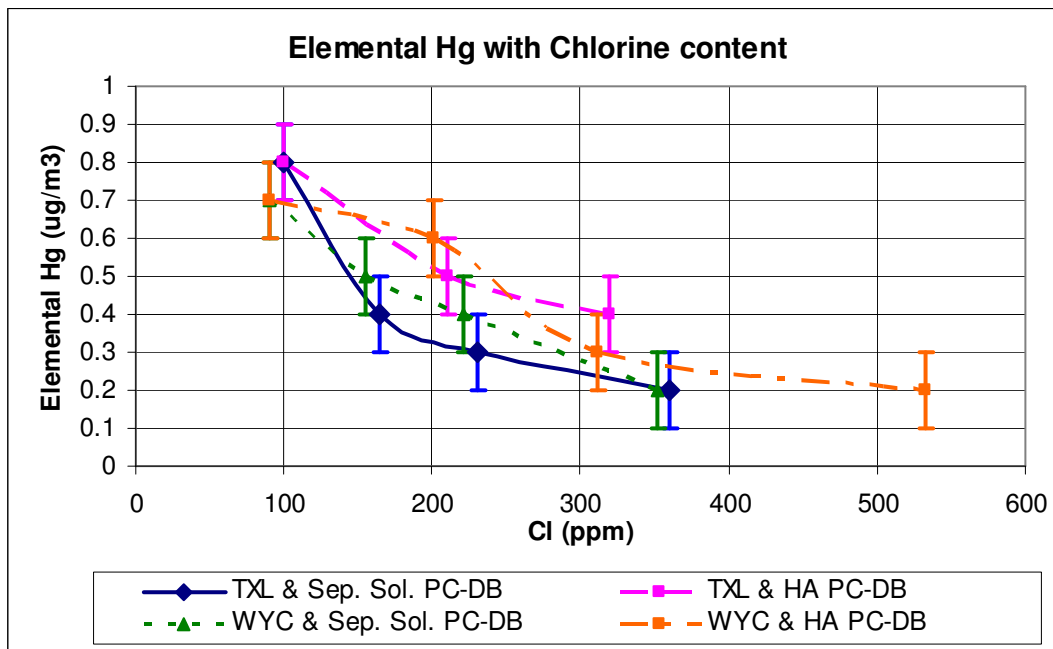
Figure 5.12 Effect on elemental mercury with chlorine content in fuel

5.7   Effect of NOx on Mercury

It is stated that NO_x inhibits mercury oxidation [18]. As equivalence ratio increases, NO_x emissions decrease due to decreased O_2 availability during rich combustion, and also observed is that elemental mercury emissions is reduced due to increased unburnt fraction. Figure 5.13 shows the variation of elemental mercury with NO_x for selected fuels at various equivalence ratios. It can be seen that as NO_x increases, the emission on elemental mercury increases slightly, or in other words oxidation of mercury is retarded marginally. It has to be noted that NO_x increases as equivalence ratios decreases, i.e., higher NO_x is produced at lean combustion and lower NO_x at rich condition. It can not be stated for sure whether it is the absence of NO_x increases mercury oxidation or the higher unburnt fraction of carbon at rich combustion scenarios aid mercury oxidation.

Qualitatively it may be the contribution of both the facts, hence the trend of mercury variation with varying NO_x can not be affirmed.
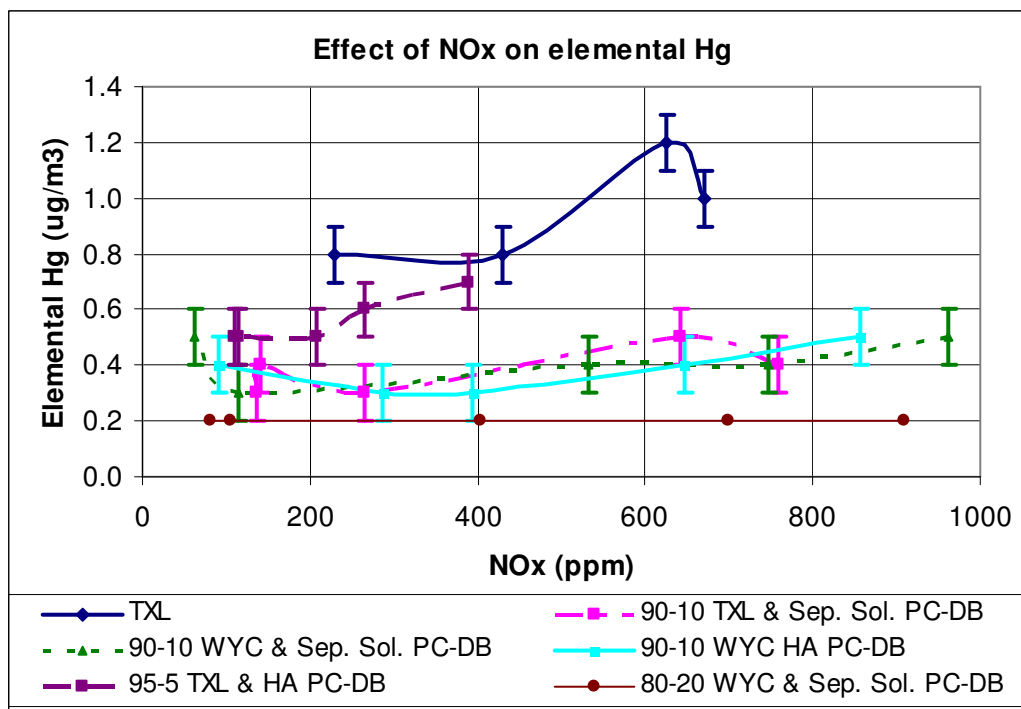
Figure 5.13 Effect of NOx on elemental mercury

5.8   Other Observations

Mercury speciation depends on lot of factors such as presence of ash, ash constituents, refractory type used in boiler, unburnt carbon during combustion and several others which is yet to be investigated and reasoned. The factors though found to play a role, due to unpredictable behavior of mercury in presence of innumerous factors, it still remains a mystery.

During one particular day of co-firing experiment, 4 different blends of WYC and high ash PC-DB were tested within period of 6 hours. Experiments were started with 95-5 blend of WYC and HA PC-DB, increased to 90-10 after 168 minutes, 80-20 after 300

minutes and 100% pure WYC after 380 minutes successively at times shown in table 5.4. Also for each blend tested, equivalence ratios were varied. The purpose of the experiment is to check whether chlorinated ash deposition on the refractor walls by the blends of high ash content fuel would cause decrease in elemental mercury emission when pure coal is fired. The summary of results of elemental mercury with respect to time is reported in table 5.4 and same is represented graphically in figure 5.14. It is seen that with change of fuel from 95-5 WYC and HA PC-DB blend to 80-20 blend there is significant reduction in elemental mercury from 0.8 $\mu g/m^3$ to 0.2 $\mu g/m^3$ as expected, which is assumed to be largely due to presence of chlorine and hence mercury oxidation. The experiment was followed by next fuel, which was 100% pure WYC, for which mercury measured was around 0.4 $\mu g/m^3$. However, when the reactor is cleaned and WYC is fired first mercury emission measured 0.8 $\mu g/m^3$ (figure 5.4). This difference in measured value of elemental Hg on 100% pure WYC on this stated day, shown in table 5.4, may be due to firing of high ash fuels during previous cases which might have deposited ash and unburnt carbon richly impregnated with chlorine species adsorbed on the refractory walls of the furnace which has the possibility to capture elemental mercury on its surface and re-emit at a later

Table 5.4 Mercury measurements with time

	Equivalence ratio	Time	Total Hg	Elemental Hg
95:5 WYC-HA PC-DB Duration : 62 mins	1	10:32	1.8	0.6
	0.9	10:44	1.7	0.8
	0.8	10:58	2.0	0.7
	1.1	11:18	1.3	0.7
	1.2	11:34	1.3	0.7
90:10 WYC-HA PC-DB Duration : 52 mins	1	13:20	1.0	0.3
	0.9	13:32	1.1	0.4
	0.8	13:44	0.9	0.5
	1.1	13:56	1.3	0.3
	1.2	14:12	1.2	0.4
80:20 WYC-HA PC-DB Duration : 46 mins	1	15:02	1.5	0.2
	0.9	15:15	1.0	0.2
	0.8	15:25	1.3	0.2
	1.1	15:48	1.3	0.2
100% WYC Duration : 20 mins	0.9	16:22	1.5	0.3
	1	16:30	1.3	0.4
	1.2	16:42	1.4	0.4
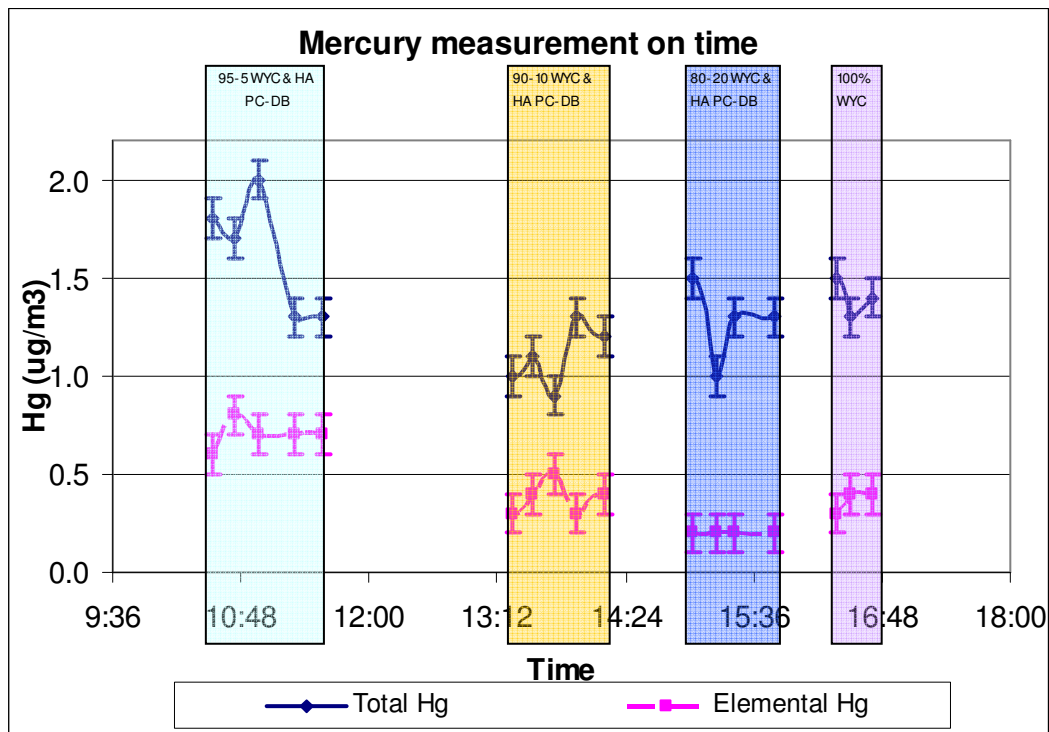
Figure 5.14 Elemental mercury measured during 6 hours time for 4 different fuels

The relevant pilot scale tests performed by SRI revealed that the interpretation of data on Hg with short duration experiments is uncertain.

5.9 Validation of Simulation

Simulation studies on isolated particle combustion in flue gases conducted previously by Puchakayala et al. [23], predicted effective mercury oxidation when coal is fired with biomass. He showed that presence of high chlorine concentration in flue gases substantially reduces elemental mercury emissions. Figure 5.15 shows results of blending feedlot biomass with coal in proportions of 10:90 and 20:80, by which 65-80% of mercury was converted to mercuric chloride, while for pure coal only 9% mercury was oxidized. Experimental results shown in figure 5.16 shows that 88% of mercury is

oxidized when 20:80 blend is used and 50% of mercury exists in oxidized form when pure coal is fired. Lower oxidation percentage with WYC is due to reduced mercury concentration since WYC already contains higher amount of chlorine compared to TXL. Though the range of oxidation percentages vary, the trend followed is the same, i.e., mercury oxidation increases with increase in biomass in the fuel blend.
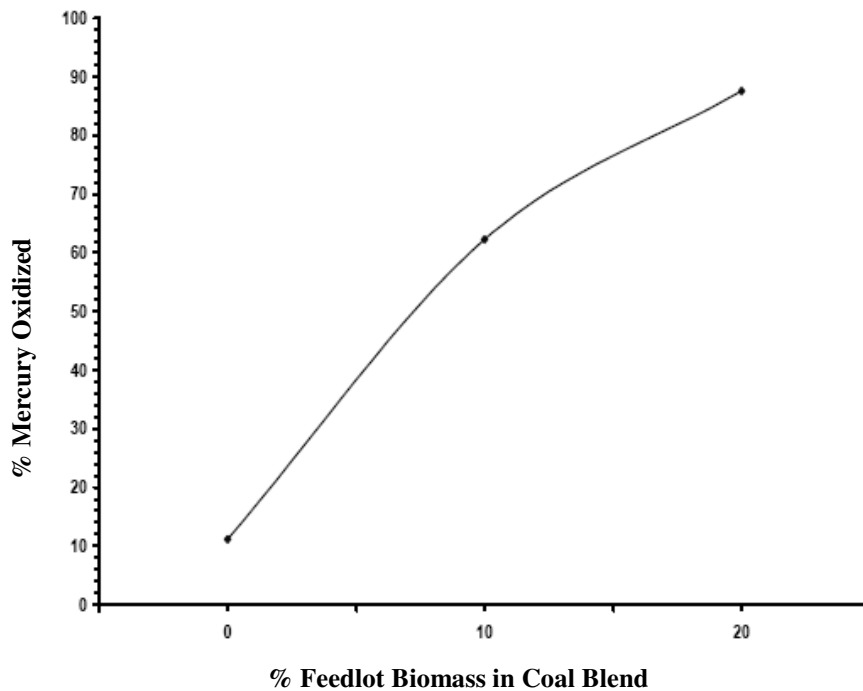
Figure 5.15 Effect of blending coal with biomass on mercury oxidation [23]
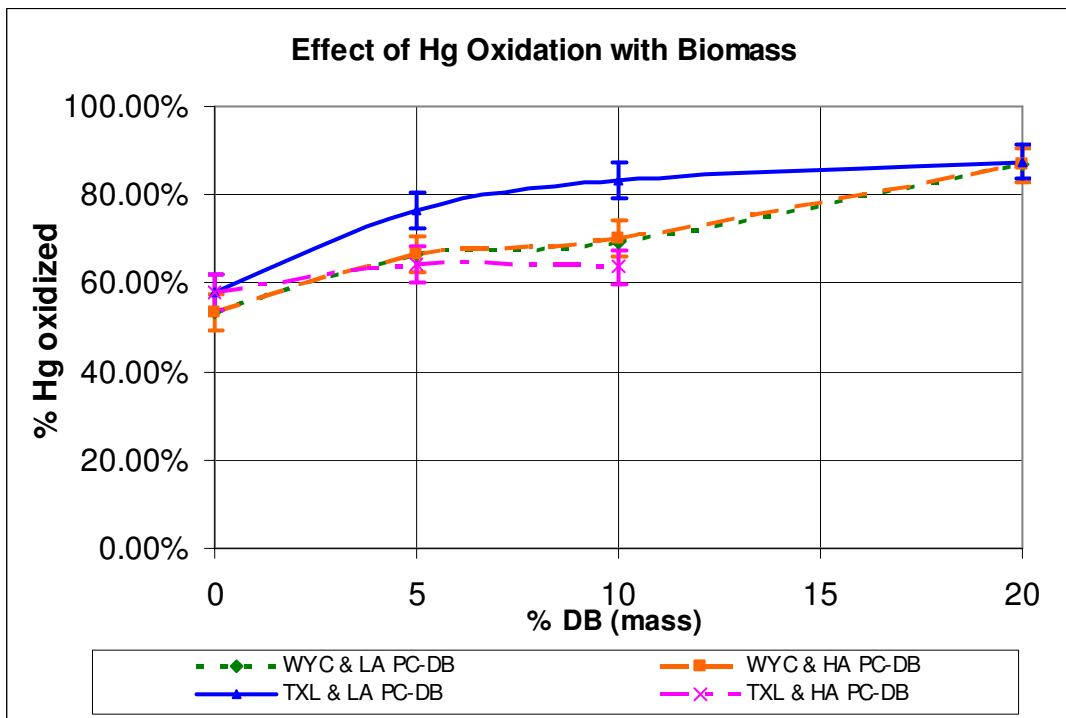
Figure 5.16 Experimental results of mercury oxidation with DB

6   SUMMARY AND CONCLUSIONS

After conducting the study of mercury reduction using dairy biomass blends in coal, it was determined that increase in biomass to coal-biomass blends aids in mercury oxidation. To summarize,

1. Elemental Hg reduces by 75% from pure TXL to 80:20 blend of TXL:LA PC-DB, when oxidized Hg is as high as 88%

2. Elemental Hg reduces by 72% from pure WYC to 80:20 blend of WYC:LA PC-DB, when oxidized Hg is as high as 87%

3. Increasing biomass causes increased ash loading, which is evident from the following:

    (i)   80:20 blend of TXL: Sep. Sol. PC-DB increases ash by 6% to pure TXL

    (ii)   80:20 blend of TXL: HA PC-DB increases ash by 85% to pure TXL

    (iii)   80:20 blend of WYC: Sep. Sol. PC-DB increases ash by 33% to pure WYC

    (iv)   80:20 blend of WYC: HA PC-DB increases ash by 192% to pure WYC

4. The optimum fuel blend would be coal and Sep. Sol. PC-DB in a blend ratio of 90:10 on mass basis without much compromise on ash while achieving good mercury reduction, which is evident from the following:

    (i)   62% reduction in Hg^0 for TXL with Sep. Sol. PC-DB

    (ii)   50% reduction in Hg^0 for TXL with HA PC-DB

    (iii)   42% reduction in Hg^0 for WYC with Sep. Sol. PC-DB

    (iv)   57% reduction in Hg^0 for WYC with HA PC-DB

5. Equivalence ratio does not have a great effect on mercury oxidation during combustion at stoichiometric or richer conditions.

6. Effect of NOx on mercury oxidation can not be said conclusively.

7. Ash plays a role in aiding mercury oxidation which is evident from low elemental Hg in 100% WYC seen immediately after burning 80-20 WYC high ash blend.

7   FUTURE IMPROVEMENTS AND RESEARCH

In order to better understand certain aspects of the conducted research and to verify the results obtained, several additional research areas are presented:

1. Make measurements using more accurate mercury measuring equipment, like the use of thermo-catalytic converter for conditioning flue gas

2. Make measurements on longer period of time (to ensure steady state)

3. Account for mercury in particulate form: ash analysis

4. Study the effect of mercury oxidation on particle size and ash content

5. Make measurements of mercury species along the axial length of the furnace, to understand the speciation with temperature drop or completion of combustion

6. Use dedicated calibration kit for accurate calibration of the mercury instrument

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APPENDIX A

Derivation of Swirl Number and Quarl Angle

A.1   Derivation of swirl number

The swirl injector consists of a swirler and a nozzle. The swirling jet of the primary air is usually generated by the swirler with hub to accommodate the fuel injection nozzle. The photograph of the swirl injector of the primary fuel and air is shown in Figure 3.2. The swirling jet has a significant effect on flame characteristics and combustion performances. A higher swirl number leads higher angular-to-linear momentum, and it sets up a recirculation zone in the near burner region, which helps the flame stabilization by mixing the hot flue gas stream with the incoming fuel [28]. As the swirl number is increased, the length of recirculation zone is progressively increased with a small change in width and pushes the flame towards the burner [29].
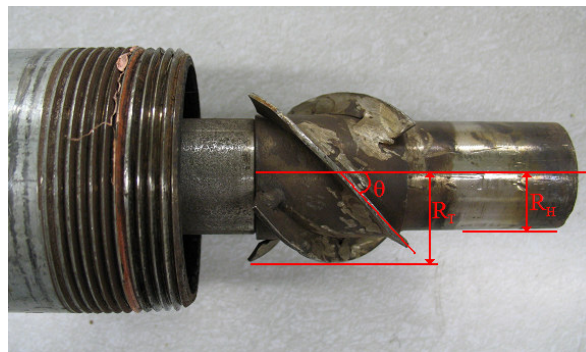
Figure A.1Photograph of the swirl generator

For an axial swirl generator, the calculation of the swirl number is explained in Reference [30] and the swirl number is defined as

$$S = \frac{2}{3}\left(\frac{1-\alpha^3}{1-\alpha^2}\right)\tan\theta \qquad\qquad (A.1)$$

where

$$\alpha = \frac{R_H}{R_T} \qquad\qquad (A.2)$$

α is a radius ratio, θ is a blade angle, R_H is a hub radius, and R_T is a tube radius. The swirl number of the fuel injector in the current boiler facility was calculated from 0.69 to 0.82 depending on the blade angle as listed in Table A.1. Since the blade was handmade, the blade angle was not accurate; raging 40 to 45º. Installing the swirl injector made the lower NO_x emission from the fuel combustions.

Table A.1 Swirl number of the swirl generator of the fuel injector

Blade angle, θ	40º ~ 45º
Hub radius, R_H	12.7 mm (0.5 in)
Tube radius, R_T	20.6 mm (1.620 in)
Swirl number, S	0.69 ~ 0.82

A.2 Quarl angle

The quarl is important in the creation and stabilization of the recirculation zone during combustion. The quarl is a diffuser that helps to stabilize the recirculation zone. With a properly shaped quarl, it is possible to form a recirculation zone at swirl numbers less than 0.6. The quarl is a diffuser that stabilizes the flow as it exits the burner nozzle and creates an area of lower pressure at the top of the furnace that strengthens the recirculation zone. The quarl half angle for this furnace is 24° and L/D of 1.8 [30, 31].

APPENDIX B

Step by Step Procedure for Conducting Experiments

Procedure for conducting co-firing experiment followed:

1. Determine all operating conditions.

      a. main burner air requirements

      b. natural gas requirements (for pre-heating)

2. Turn on temperature data acquisition system.

3. Turn on exhaust fans.

4. Turn on Primary Air to approximately 50 % of the total required airflow.

5. Turn on cooling water and cooling water sump. The cooling water flow should be around 3 gpm.

6. Start the propane torch and allow to heat furnace to 300 °F.

7. Turn on the main burner at 60% natural gas flow rate. (a fuel rich flame is more stable than a lean flame).

8. Look in view ports to ensure flame is present.

9. Allow the furnace to run for approximately one hour with propane torches lit.

10. Remove propane torch.

11. Increase the natural gas flow to 100% of total heat input (flow rate of 42.6 slpm)

12. Increase the primary air to 100% (stoichiometric combustion for natural gas)

13. Allow furnace to heat for two or three more hours (until steady state – flat temperature profile).

14. While preheating, calibrate the volumetric feeder system for the fuel being used.

15. Shut the natural gas supply and turn on the feeder motor and carrier (motive) air to desired level (air goes through venturi).

16. Set the secondary air flow to achieve stoichiometric combustion of fuel fired.

17. Allow furnace to reach steady state for 30 minutes.

18. Take measurements of flue gases using GreenLine gas analyzer.

19. Switch to wet chemistry conditioning system and measure mercury species using VM 3000.

20. To change equivalence ratio, set the desired air flow rate and follow steps 16 to 19.

21. At the end of experiments for the day turn off primary air, stop feeder and unplug all analyzers.

22. Let the burner cool with the secondary air on. Once the furnace cools to 200 °F, secondary air, cooling water, and exhaust fans can be turned off.

APPENDIX C

Operating Parameters for Experiments

Table C.1 Operating parameters for TXL and its blends with DB

	Equivalence Ratio	Fuel Flow Rate		Required Air		Primary Air				Secondary Air (SLPM)
		lbs/hr	g/min	SCFH	SLPM	Motive	Aspirated	Total (SCFH)	Total (SLPM)	
Texas Lignite	0.8	16.278	123.060	1220.76	576.14	100	80	180	84.95	490
	0.9	16.278	123.060	1085.12	512.12	100	80	180	84.95	428
	1	16.278	123.060	976.61	460.91	100	80	180	84.95	376
	1.1	16.278	123.060	887.83	419.01	100	80	180	84.95	334
	1.2	16.278	123.060	813.84	384.09	100	80	180	84.95	312
95-5 TXL SepSol PC-DB	0.8	16.360	123.680	1253.82	591.74	100	80	180	84.95	506
	0.9	16.360	123.680	1114.51	525.99	100	80	180	84.95	441
	1	16.360	123.680	1003.05	473.39	100	80	180	84.95	388
	1.1	16.360	123.680	911.87	430.35	100	80	180	84.95	345
	1.2	16.360	123.680	835.88	394.49	100	80	180	84.95	309
90-10 TXL SepSol PC-DB	0.8	16.445	124.320	1287.21	607.50	110	100	210	99.11	508
	0.9	16.445	124.320	1144.19	540.00	110	100	210	99.11	440
	1	16.445	124.320	1029.77	486.00	110	100	210	99.11	386
	1.1	16.445	124.320	936.15	441.82	110	100	210	99.11	343
	1.2	16.445	124.320	858.14	405.00	110	100	210	99.11	305
80-20 TXL SepSol PC-DB	0.8	16.614	125.600	1355.03	639.50	110	100	210	99.11	540
	0.9	16.614	125.600	1204.47	568.45	110	100	210	99.11	469
	1	16.614	125.600	1084.02	511.60	110	100	210	99.11	412
	1.1	16.614	125.600	985.48	465.09	110	100	210	99.11	366
	1.2	16.614	125.600	903.35	426.34	110	100	210	99.11	327
95-5 TXL HA PC-DB	0.8	16.867	127.510	1232.85	581.84	110	100	210	99.11	483
	0.9	16.867	127.510	1095.86	517.19	110	100	210	99.11	419
	1	16.867	127.510	986.28	465.47	110	100	210	99.11	367
	1.1	16.867	127.510	896.62	423.16	110	100	210	99.11	325
	1.2	16.867	127.510	821.90	387.89	110	100	210	99.11	288
90-10 TXL HA PC-DB	0.8	17.500	132.300	1250.06	589.96	110	100	210	99.11	491
	0.9	17.500	132.300	1111.16	524.41	110	100	210	99.11	426
	1	17.500	132.300	1000.05	471.97	110	100	210	99.11	373
	1.1	17.500	132.300	909.13	429.06	110	100	210	99.11	330
	1.2	17.500	132.300	833.37	393.31	110	100	210	99.11	294

Table C.2 Operating parameters for WYC and its blends with DB

	Equivalence Ratio	Fuel Flow Rate		Required Air		Primary Air				Secondary Air (SLPM)
		lbs/hr	g/min	SCFH	SLPM	Motive	Aspirated	Total (SCFH)	Total (SLPM)	
Wyoming Coal	0.8	12.783	96.640	1124.30	530.61	110	100	210	99.11	479
	0.9	12.783	96.640	1072.75	506.28	110	100	210	99.11	421
	1	12.783	96.640	965.47	455.65	110	100	210	99.11	370
	1.1	12.783	96.640	877.70	414.23	110	100	210	99.11	329
	1.2	12.783	96.640	832.87	393.07	110	100	210	99.11	292
95-5 WYC SepSol PC-DB	0.8	12.974	98.080	1233.55	582.17	110	100	210	99.11	483
	0.9	12.974	98.080	1096.50	517.49	110	100	210	99.11	419
	1	12.974	98.080	986.84	465.74	110	100	210	99.11	366
	1.1	12.974	98.080	897.13	423.40	110	100	210	99.11	324
	1.2	12.974	98.080	822.37	388.12	110	100	210	99.11	289
90-10 WYC SepSol PC-DB	0.8	13.171	99.570	1261.07	595.16	110	100	210	99.11	497
	0.9	13.171	99.570	1120.95	529.03	110	100	210	99.11	430
	1	13.171	99.570	1008.86	476.13	110	100	210	99.11	377
	1.1	13.171	99.570	917.14	432.84	110	100	210	99.11	334
	1.2	13.171	99.570	840.71	396.77	110	100	210	99.11	298
80-20 WYC SepSol PC-DB	0.8	13.582	102.680	1318.69	622.35	110	100	210	99.11	524
	0.9	13.582	102.680	1172.17	553.20	110	100	210	99.11	455
	1	13.582	102.680	1054.95	497.88	110	100	210	99.11	399
	1.1	13.582	102.680	959.05	452.62	110	100	210	99.11	354
	1.2	13.582	102.680	879.13	414.90	110	100	210	99.11	316
95-5 WYC HA PC-DB	0.8	13.290	100.470	1261.95	595.57	110	100	210	99.11	497
	0.9	13.290	100.470	1121.73	529.40	110	100	210	99.11	431
	1	13.290	100.470	1009.56	476.46	110	100	210	99.11	378
	1.1	13.290	100.470	917.78	433.14	110	100	210	99.11	334
	1.2	13.290	100.470	841.30	397.05	110	100	210	99.11	298
90-10 WYC HA PC-DB	0.8	13.839	104.620	1277.18	602.76	110	100	210	99.11	504
	0.9	13.839	104.620	1135.27	535.79	110	100	210	99.11	437
	1	13.839	104.620	1021.74	482.21	110	100	210	99.11	384
	1.1	13.839	104.620	928.86	438.37	110	100	210	99.11	340
	1.2	13.839	104.620	851.45	401.84	110	100	210	99.11	303
80-20 WYC HA PC-DB	0.8	15.085	114.040	1250.84	590.33	110	100	210	99.11	491
	0.9	15.085	114.040	1111.86	524.74	110	100	210	99.11	426
	1	15.085	114.040	1000.67	472.26	110	100	210	99.11	374

APPENDIX D

Sample Calculations for Feed Rate and Air Flow Rates

D.1   Fuel Feed Rate

$$Fuel\ feed\ rate = \frac{Heat\ required,\ kJ/s}{HHV,\ kJ/kg} \times \frac{1000\ g/kg}{1/60\ \min/s} = \frac{29.3 \times 60 \times 1000}{HHV}\ g/\min \quad (D.1)$$

For TXL, HHV = 14,289 kJ/kg, hence,

$$Fuel\ feed\ rate = \frac{29.3 \times 60 \times 1000}{14,289} = 123.06\ g/\min\ or\ 7.384\ kg/hr$$

D.2   Air Flow

Emperical formula for TXL (as is) from Proximate and Ultimate analysis is

$$C_{3.095}H_{2.106}N_{0.0485}O_{0.6004}S_{0.01892} \tag{D.2}$$

On DAF basis, it is:

$$C_{6.167}H_{4.196}N_{0.0967}O_{1.196}S_{0.0376} \tag{D.3}$$

Combustion chemical equation is given by:
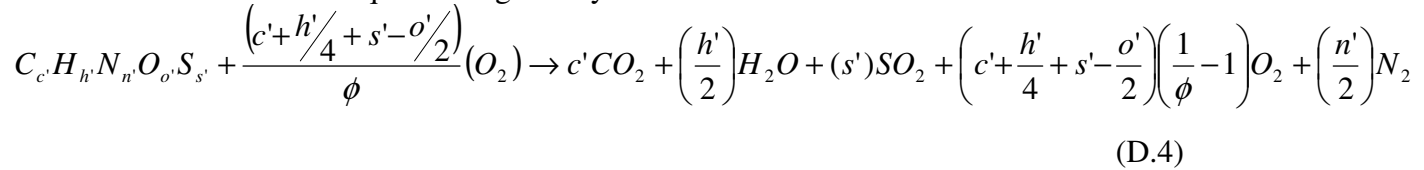
$$C_{c'}H_{h'}N_{n'}O_{o'}S_{s'} + \frac{\left(c' + h'/4 + s' - o'/2\right)}{\phi}(O_2) \rightarrow c'CO_2 + \left(\frac{h'}{2}\right)H_2O + (s')SO_2 + \left(c' + \frac{h'}{4} + s' - \frac{o'}{2}\right)\left(\frac{1}{\phi} - 1\right)O_2 + \left(\frac{n'}{2}\right)N_2$$

$$\tag{D.4}$$

Where Φ is equivalence ratio

For Stoichiometric combustion in pure O_2, calculate the number of product moles

$CO_2 = c' = 6.167$

$H_2O = h'/2 = 2.098$

$SO_2 = s' = 0.0376$

$N_2 = n'/2 = 0.04835$

Oxygen required for combustion $= \left(c' + \frac{h'}{4} + s' - \frac{o'}{2}\right)\left(\frac{1}{\phi} - 1\right) = 6.6557$ kmoles O_2/kmole DAF fuel

$$\tag{D.5}$$

Air required = 3.76 X 6.6557 = 31.681 kmoles air/kmole DAF fuel

Air required in kg/kg DAF fuel $= \dfrac{31.681\ kmoles\ air/kmoles\ DAF\ fuel}{MW_{DAF,fuel}\ kg\ DAF\ fuel/kmoles\ DAF\ fuel} \times 28.97\ kg\ air/kmoles\ air$

(D.6)

$MW_{DAF,fuel}$ = 100 kg/kmoles DAF fuel

Stoichiometric air required = 9.178 kg air/kg DAF fuel

For Φ = 0.9 (slightly lean),

Air required = $\dfrac{Stoichiometric\ air,\ kg\ /\ kg\ DAF\ fuel}{\phi} = \dfrac{9.178\ kg\ air\ /\ kg\ DAF\ fuel}{0.9}$

(D.7)

Air required = 10.197 kg air/kg DAF fuel

Actual air required = $Air\ required\ for\ DAF\ fuel,\ kg\ air\ /\ kg\ DAF\ fuel \times \dfrac{(100 - M - A)}{100}$

(D.8)

M = moisture = 38.337%, and A = ash = 11.463%

Actual air required = $10.197\ kg\ air\ /\ kg\ DAF\ fuel \times \dfrac{(100 - 38.337 - 11.463)}{100}$ = 5.1193 kg air/kg fuel

Air flow rate in kg/hr = $Air\ flow\ rate,\ kg\ air\ /\ kg\ fuel \times fuel\ flow\ rate,\ kg\ fuel\ /\ hr$

(D.9)

Air flow rate in kg/hr = $5.1193\ kg\ air\ /\ kg\ fuel \times 7.384\ kg\ fuel\ /\ hr$ = 37.79 kg air/hr

Air density = 1.23 kg/m^3

Air flow rate in m^3/hr = $\dfrac{37.79\ kg\ air\ /\ hr}{1.23\ kg\ air\ /\ m^3\ air}$ = $30.73\ m^3\ /\ hr$

Air flow rate in SCFH = $30.73\ m^3\ /\ hr \times 35.314\ ft^3\ /\ m^3 = 1085.123\ SCFH$

Air flow rate in slpm = $\dfrac{37.79\ kg\ air\ /\ hr}{1.23\ kg\ air\ /\ m^3\ air}$ = $30.73\ m^3\ /\ hr \times 1000\ l\ /\ m^3 \times \dfrac{1}{60}\ hr\ /\ min$

= $512.16\ l\ /\ min$

APPENDIX E

Table E.1 Proximate and ultimate analysis for 3 samples of Sep. Sol. PC-DB

	DB-Sep solids-PC-2006 (3 samples)				
Fuel Source	Mx 7 Dairy in Comanche County, Texas				
Reference	Preliminary Interpretation of Data from Proximate, Ultimate and Ash Analysis, by John M. Sweeten & Kevin Heflin. Results of June 7, 2006 Samples Taken from Feedlot and Dairy Biomass BioFuel Feedstocks at TAES/USDA-ARS, Bushland, TX. Oct 23, 2003				
Ananlysis Lab	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	
Sample ID	128	129	130	128-130 (Mean)	128-130 (Std. Dev.)
Date of sampling	5/15/2006	5/15/2006	5/15/2006	5/15/2006	5/15/2006
Date of analysis	10/23/2006	10/23/2006	10/23/2006	10/23/2006	10/23/2006
Ash	14.39	14.09	16.09	14.86	1.08
Dry Loss (% Moisture)	23.73	34.45	17.61	25.26	8.52
FC	13.06	10.87	15.08	13.00	2.11
VM	48.82	40.59	51.22	46.88	5.58
Carbon, C	36.63	30.48	38.52	35.21	4.20
Hydrogen, H	3.86	3.22	4.06	3.71	0.44
Nitrogen, N	1.93	1.72	2.14	1.93	0.21
Oxygen, O (diff)	19.02	15.67	21.10	18.60	2.74
Sulfur, S	0.44	0.37	0.48	0.43	0.06
HHV (kJ/kg)	13,307	11,179	14,047	12,844	1,489
Chlorine, Cl	0.14	0.12	0.16	0.14	0.02
Mercury, Hg					

ASH PROPERTIES
Ash Elemental Analysis (%):
(Ash was calcined @ 1100 deg. F (600 deg. C) prior to analysis)

	128	129	130	8-130 (Composite)%	
Silicon, SiO2	31.43	30.68	31.97	31.36	0.65
Aluminum, Al2O3	2.83	2.79	3.05	2.89	0.14
Titanium, TiO2	0.21	0.17	0.21	0.20	0.02
Iron, Fe2O3	1.55	1.75	1.56	1.62	0.11
Calcium, CaO	26.3	26.4	26.5	26.40	0.10
Magnesium, MgO	7.51	7.51	7.38	7.47	0.08
Sodium, Na2O	2.22	2.27	2.28	2.26	0.03
Potassium, K2O	6.95	6.89	6.87	6.90	0.04
Phosphorus, P2O5	6	5.98	6.04	6.01	0.03
Sulfur, SO3	4.76	5.4	4	4.72	0.70
Chlorine, Cl	1.02	0.96	0.78	0.92	0.12
Carbon dioxide, CO2	11.6	9.88	7	9.49	2.32
Total ash analysis	102.38	100.68	97.64	96.45	

Metals in Ash, equal-weight-composite, mg/kg

	128	129	130		
Arsenic	3.39	4.05	3.48	3.64	0.36
Barium	1260	1040	1180	1160.00	111.36
Cadmium	5.9	6	6.5	6.13	0.32
Chromium	60	80	60	66.67	11.55
Lead	26	25	22	24.33	2.08
Mercury	0.02	0.01	0.02	0.02	0.01
Selenium	4	6	4	4.67	1.15
Silver	<2	<2	<2	<2	0.00
Total metals in ash	1359.31	1161.06	1276	1265.46	99.54

Table E.2 Proximate and ultimate analysis for 3 samples of HA PC-DB

	DB-HA-PC (3 samples)				
Fuel Source	**Mx 7 Dairy in Comanche County, Texas**				
Reference	**Preliminary Interpretation of Data from Proximate, Ultimate and Ash Analysis, by John M. Sweeten & Kevin Heflin. Results of June 7, 2006 Samples Taken from Feedlot and Dairy Biomass BioFuel Feedstocks at TAES/USDA-ARS, Bushland, TX. Oct 23, 2003**				
Ananlysis Lab	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	
Sample ID	**131**	**132**	**133**	**131-133 (Mean)**	**131-133 (Std. Dev.)**
Date of sampling	**5/15/2006**	**5/15/2006**	**5/15/2006**	**5/15/2006**	**5/15/2006**
Date of analysis	**10/23/2006**	**10/23/2006**	**10/23/2006**	**10/23/2006**	**10/23/2006**
Ash	61.79	61.70	56.18	59.89	3.21
Dry Loss (% Moisture)	9.95	8.43	18.24	12.21	5.28
FC	4.66	5.14	1.95	3.92	1.72
VM	23.60	24.73	23.63	23.99	0.64
Carbon, C	18.58	19.22	16.33	18.04	1.52
Hydrogen, H	1.53	1.57	1.26	1.45	0.17
Nitrogen, N	1.15	1.20	1.10	1.15	0.05
Oxygen, O (diff)	6.85	7.64	6.72	7.07	0.50
Sulfur, S	0.15	0.24	0.17	0.19	0.05
HHV (kJ/kg)	4,340	4,605	3,989	4,312	309
Chlorine, Cl	0.23	0.24	0.22	0.23	0.01
Mercury, Hg					

ASH PROPERTIES

Ash Elemental Analysis (%):
(Ash was calcined @ 1100 deg. F (600 deg. C) prior to analysis)

Silicon, SiO2	42.08	48.65	41.27	44.00	4.05
Aluminum, Al2O3	4.35	4.05	4.1	4.17	0.16
Titanium, TiO2	0.21	0.21	0.21	0.21	0.00
Iron, Fe2O3	1.46	1.41	1.44	1.44	0.03
Calcium, CaO	26.8	24	26.8	25.87	1.62
Magnesium, MgO	5.17	4.59	5.02	4.93	0.30
Sodium, Na2O	0.85	0.78	0.9	0.84	0.06
Potassium, K2O	3.63	3.38	3.67	3.56	0.16
Phosphorus, P2O5	2.02	2.87	2.08	2.32	0.47
Sulfur, SO3	0.79	0.98	0.64	0.80	0.17
Chlorine, Cl	0.49	0.46	0.53	0.49	0.04
Carbon dioxide, CO2	10.96	7.5	14.29	10.92	3.40
Total ash analysis	98.81	98.88	100.95	99.55	

Metals in Ash, equal-weight-composite, mg/kg

Arsenic	2.95	2.95	2.98	2.96	0.017320508
Barium	2370	2370	2620	2453.333333	144.3375673
Cadmium	6	6.3	5.4	5.9	0.458257569
Chromium	70	70	70	70	0
Lead	14	13	13	13.33333333	0.577350269
Mercury	0.02	0.02	0.2	0.08	0.103923048
Selenium	<2	<2	<2	<2	0
Silver	<2	<2	<2	<2	0
Total metals in ash	2462.97	2462.27	2711.58	2545.606667	143.7375491

Table E.3 Proximate and ultimate analysis for 3 samples of TXL

	Txlig-3 samples				
Fuel Source	TXU Energy, Dallas, TX				
Reference	Combustion-Fuel Properties of Manure or Compost from Paved vs. Un-paved				
Ananlysis Lab	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	
Sample ID	TXL 113	TXL 114	TXL 115	TXL 113-115 (mean)	TXL 113-115 (Std. Dev.)
Date of sampling	10/10/2005	10/10/2005	10/10/2005	10/10/2005	10/10/2005
Date of analysis	11/29/2005	11/29/2005	11/29/2005	11/29/2005	11/29/2005
Ash	11.39	12.00	11.00	11.46	0.50
Dry Loss (% Moisture)	38.68	38.32	38.01	38.34	0.34
FC	24.93	25.18	26.12	25.41	0.63
VM	25.00	24.50	24.87	24.79	0.26
Carbon, C	37.10	36.57	37.88	37.18	0.66
Hydrogen, H	2.21	2.09	2.07	2.12	0.08
Nitrogen, N	0.68	0.67	0.69	0.68	0.01
Oxygen, O (diff)	9.24	9.76	9.82	9.61	0.32
Sulfur, S	0.70	0.59	0.53	0.61	0.09
HHV (kJ/kg)	14179.30	14065.32	14623.56	14286.82	295.40

Chlorine, Cl				0.010	

Mercury, Hg				0.00017	

ASH PROPERTIES

Ash Elemental Analysis (%):
(Ash was calcined @ 1100 deg. F (600 deg. C) prior to analysis)

				TXL 113-115 (composite)%	
Silicon, SiO2				48.72	
Aluminum, Al2O3				16.04	
Titanium, TiO2				0.85	
Iron, Fe2O3				7.44	
Calcium, CaO				11.70	
Magnesium, MgO				1.93	
Sodium, Na2O				0.29	
Potassium, K2O				0.61	
Phosphorus, P2O5				0.10	
Sulfur, SO3				10.80	
Chlorine, Cl				<0.01	
Carbon dioxide, CO2				0.08	
Total ash analysis				98.56	

Metals in Ash, equal-weight-composite, mg/kg

Arsenic				24.7	
Barium				1590	
Cadmium				3.4	
Chromium				98	
Lead				47	
Mercury				0.01	
Selenium				<2	
Silver				<2	
Total metals in ash				1763.11	

Table E.4 Proximate and ultimate analysis for 3 samples of WYC

	Wy Coal-3 samples				
Fuel Source	TXU Energy, Dallas, TX				
Reference	Combustion-Fuel Properties of Manure or Compost from Paved vs. Un-paved				
Ananlysis Lab	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO	Hazen research inc., Golden, CO
Sample ID	PRB 116	PRB 117	PRB 118	PRB 116-118 (Mean)	PRB 116-118 (Std. Dev.)
Date of sampling	10/10/2005	10/10/2005	10/10/2005	10/10/2005	10/10/2005
Date of analysis	11/29/2005	11/29/2005	11/29/2005	11/29/2005	11/29/2005
Ash	4.50	8.08	4.34	5.64	2.11
Dry Loss (% Moisture)	32.78	32.59	33.28	32.88	0.36
FC	33.63	31.48	33.85	32.99	1.31
VM	29.09	27.85	28.53	28.49	0.62
Carbon, C	47.78	44.54	47.25	46.52	1.74
Hydrogen, H	2.76	2.65	2.78	2.73	0.07
Nitrogen, N	0.68	0.67	0.62	0.66	0.03
Oxygen, O (diff)	11.21	11.22	11.45	11.29	0.14
Sulfur, S	0.29	0.25	0.28	0.27	0.02
HHV (kJ/kg)	18724.30	17461.28	18403.31	18193.02	655.93
Chlorine, Cl				0.009	
Mercury, Hg				0.00014	

ASH PROPERTIES
Ash Elemental Analysis (%):
(Ash was calcined @ 1100 deg. F (600 deg. C) prior to analysis)

				PRB 116-118 (Composite)%	
Silicon, SiO2				31.73	
Aluminum, Al2O3				17.27	
Titanium, TiO2				1.35	
Iron, Fe2O3				4.61	
Calcium, CaO				22.2	
Magnesium, MgO				5.62	
Sodium, Na2O				1.43	
Potassium, K2O				0.67	
Phosphorus, P2O5				0.8	
Sulfur, SO3				10.4	
Chlorine, Cl				<0.01	
Carbon dioxide, CO2				0.37	
Total ash analysis				96.45	

Metals in Ash, equal-weight-composite, mg/kg

Arsenic				17.6	
Barium				6230	
Cadmium				5.2	
Chromium				110	
Lead				130	
Mercury				<.01	
Selenium				<2	
Silver				<2	
Total metals in ash				6492.8	

APPENDIX F

F.1 Estimation of mercury emissions in mg/GJ

On obtaining the mercury concentration in flue gases as $\mu g/m^3$ (as read from the instrument), we can calculate the emission rate in terms of mg/GJ by estimating the volume of flue gas emitted per GJ of the fuel and mercury mass present in that volume of flue gas.

Taking the example of TXL, for stoichiometric condition the mercury concentration was found to be:

$Hg^T = 1.9\ \mu g/m^3$

$Hg^0 = 0.8\ \mu g/m^3$

To calculate the volume of flue gas per GJ:

Emperical formula for TXL (as is) from Proximate and Ultimate analysis is

$$C_{3.095}H_{2.106}N_{0.0485}O_{0.6004}S_{0.01892} \tag{F.1}$$

On DAF basis, it is:

$$C_{6.167}H_{4.196}N_{0.0967}O_{1.196}S_{0.0376} \tag{F.2}$$

Combustion chemical equation is given by:

$$C_{c'}H_{h'}N_{n'}O_{o'}S_{s'} + \frac{\left(c' + h'/4 + s' - o'/2\right)}{\phi}(O_2 + 3.76N_2) \rightarrow c'CO_2 + \left(\frac{h'}{2}\right)H_2O + (s')SO_2 + \left[\frac{\left(c' + \frac{h'}{4} + s' - \frac{o'}{2}\right)}{\phi} \times 3.76 + \left(\frac{n'}{2}\right)\right]N_2 + \left(c' + \frac{h'}{4} + s' - \frac{o'}{2}\right)\left(\frac{1}{\phi} - 1\right)O_2$$

$$\tag{F.3}$$
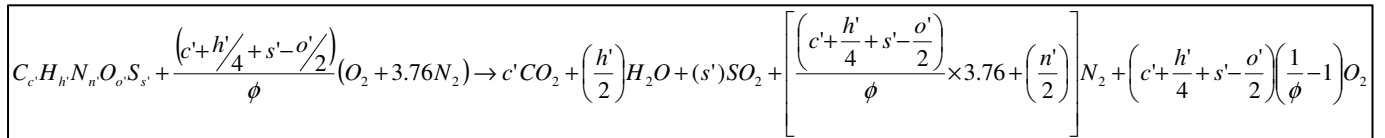
Where Φ is equivalence ratio

For Stoichiometric combustion in pure O_2, calculate the number of product moles for DAF fuel:

$CO_2 = c' = 6.167$

$H_2O = h'/2 = 2.098$

$SO_2 = s' = 0.0376$

$$O_2 = \left(c' + \frac{h'}{4} + s' - \frac{o'}{2}\right)\left(\frac{1}{\phi} - 1\right) = 0 \tag{F.4}$$

$$N_2 = \left[\frac{\left(c' + \dfrac{h'}{4} + s' - \dfrac{o'}{2}\right)}{\phi} \times 3.76 + \left(\frac{n'}{2}\right)\right] = 25.074 \tag{F.5}$$

Total no. of dry product moles = 31.27 kmoles of flue/kmole of DAF fuel

$$\Rightarrow \frac{31.27 \; kmoles \; of \; flue \, / \, kmole \; of \; DAF \; fuel}{MW_{DAF \; fuel}, kg \, / \, kmole \; of \; DAF \; fuel} = 0.3127 \; kmoles \; of \; flue \, / \, kg \; of \; DAF \; fuel$$

$$\tag{F.6}$$

Ash, A = 11.46 %

Moisture, M = 38.33 %

Total no. of product moles in kmoles/kg of as is fuel:

$$\Rightarrow 0.3127 \; kmoles \; of \; flue \, / \, kg \; of \; DAF \; fuel \times \frac{[100 - (M + A)] \; kg \; of \; DAF \; fuel}{100 \; kg \; of \; as \; is \; fuel} \tag{F.7}$$

$$\Rightarrow 0.15702 \; kmoles \, / \, kg \; of \; as \; is \; fuel$$

From appendix D, fuel feed rate is 123.05 g/min or 0.00205 kg/s

∴ Product moles in kmoles/s :

$$\Rightarrow 0.15702 \; kmoles \, / \, kg \; of \; as \; is \; fuel \times fuel \; feed \; rate, kg \; of \; as \; is \; fuel \, / \, s \tag{F.8}$$

$$\Rightarrow 0.15702 \; kmoles \, / \, kg \; of \; as \; is \; fuel \times 0.00205 \; kg \; of \; as \; is \; fuel \, / \, s$$
$$\Rightarrow 0.00032204 \; kmoles \, / \, s$$

Power of the boiler = 29.3 kW or 29.3 kJ/s

$$\text{Product moles in kmoles/GJ} = \frac{0.00032204 \; kmoles \, / \, s}{29.3 \; kJ \, / \, s} \times \frac{10^6 \; kJ}{1 \; GJ} = 10.988 \; kmoles \, / \, GJ$$

$$\tag{F.9}$$

We know that 1 kmole at SATP occupies a volume of 24.5 m^3

Hence product gases in m^3/GJ = 10.988 X 24.5 = 269.22 m^3/GJ

Mercury concentration in flue gas:

Total mercury in flue gas:

$Hg^T = 1.9$ µg/m^3

$$\Rightarrow 1.9 \; \mu g / m^3 \; of \; flue \; gas \times 269.22 \; m^3 \; of \; flue \; gas / GJ \times \frac{1 \; mg}{10^3 \; \mu g} = 0.51152 \; mg / GJ$$

(F.10)

Elemental mercury in flue gas:

$Hg^0 = 0.8$ µg/m^3

$$\Rightarrow 0.8 \; \mu g / m^3 \; of \; flue \; gas \times 269.22 \; m^3 \; of \; flue \; gas / GJ \times \frac{1 \; mg}{10^3 \; \mu g} = 0.21537 \; mg / GJ$$

(F.11)

F.2 Mercury conversion efficiency:

The mercury loading during combustion can be estimated once the concentration of

mercury in the fuel is known.

Mercury concentration in TXL fuel = 0.00013 g/kg

$$Mercury \; loading \; from \; fuel = \frac{Hg, \; g / kg \; in \; fuel}{HHV, \; kJ / kg \; of \; as \; is \; fuel} \times \frac{1000 \; mg}{1 \; g} \times \frac{1000 \; kJ}{1 \; GJ}$$ (F.12)

$$\Rightarrow \frac{0.00013 \; g / kg \; in \; fuel}{14289 \; kJ / kg \; of \; as \; is \; fuel} \times \frac{10^3 \; mg}{1 \; g} \times \frac{10^6 \; kJ}{1 \; GJ} = 9.098 \; mg / GJ$$

$$Total \; Hg \; conversion \; efficiency = \frac{Total \; Hg \; in \; flue \; gas, \; mg / GJ}{Hg \; input \; from \; fuel, \; mg / GJ} \times 100\%$$ (F.13)

$$\Rightarrow \frac{0.51152 \; mg / GJ}{9.098 \; mg / GJ} \times 100 = 5.62 \%$$

$$Elemental \; Hg \; conversion \; efficiency = \frac{Elemental \; Hg \; in \; flue \; gas, \; mg / GJ}{Hg \; input \; from \; fuel, \; mg / GJ} \times 100\%$$

(F.14)

$$\Rightarrow \frac{0.21537 \; mg / GJ}{9.098 \; mg / GJ} \times 100 = 2.37\%$$

APPENDIX G

Measuring Principle of VM 3000 Used for Mercury Measurement

The mercury concentration is measured in an optical cell made of fused silica. An inbuilt maintenance-free membrane pump continuously feeds the sample gas from sampling port to the optical cell where light absorption measurement takes place at a wavelength of 253.7 nm. Cold vapor atomic absoption (CVAA) spectroscopy is extremely sensitive for mercury determination and has been used successfully for many years.

The analyzer uses a high-frequency driven electrodeless Hg low pressure discharge lamp (EDL) as UV light source. It generates emission lines of an extremely narrow bandwidth which are congruent with the absorption lines of the Hg atoms. A reference beam feedback control method is used to ensure high stability of UV source. To prevent temperature drift both the lamp unit and the detectors are temperature-stabilized to be 25˚C with the use of heated optical cell. Schematic of measurement principle and components are shown in figure G.1.
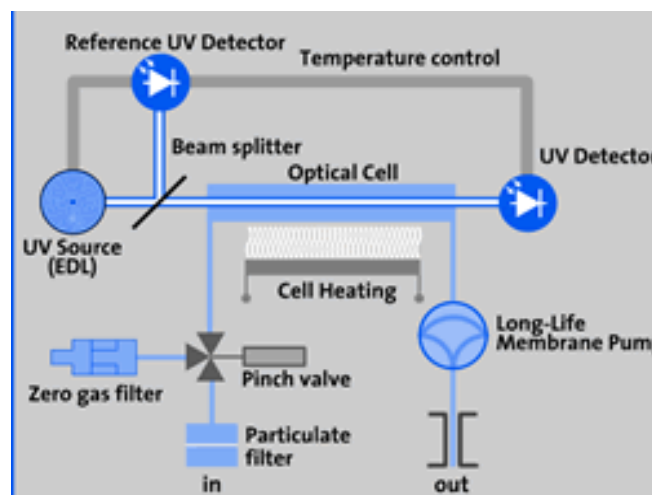

Figure G.1 Measurement principle of CVAA

The measurement sensitivity of the instrument is same as accuracy of the instrument which is stated as 0.1µg/m³. The instrument was calibrated by the manufacturers on 06/21/2006, with a warranty on calibration for two years.

Calibration validation

Attempts were made for calibrating the instrument before experimentation began. This employed mercury permeation source in form of mercury permeation tube. The permeation tube was enclosed in a tubular glass case which was wound around with heating tapes to maintain a specific permeation rate of mercury at a desired temperature. The entire setup was housed in an external casing packed with glass wool as insulating medium. Nitrogen gas from nitrogen cylinder source was used as carrier gas to carry the permeated mercury and also to dilute the concentration. The heating tapes were temperature controlled using a PID controller and a desired temperature was set at the controller. Thermocouples were inserted into the glass case to measure the inlet and outlet temperatures of carrier gas to from the case. Figure G.2 shows the schematic of the setup used for calibration.
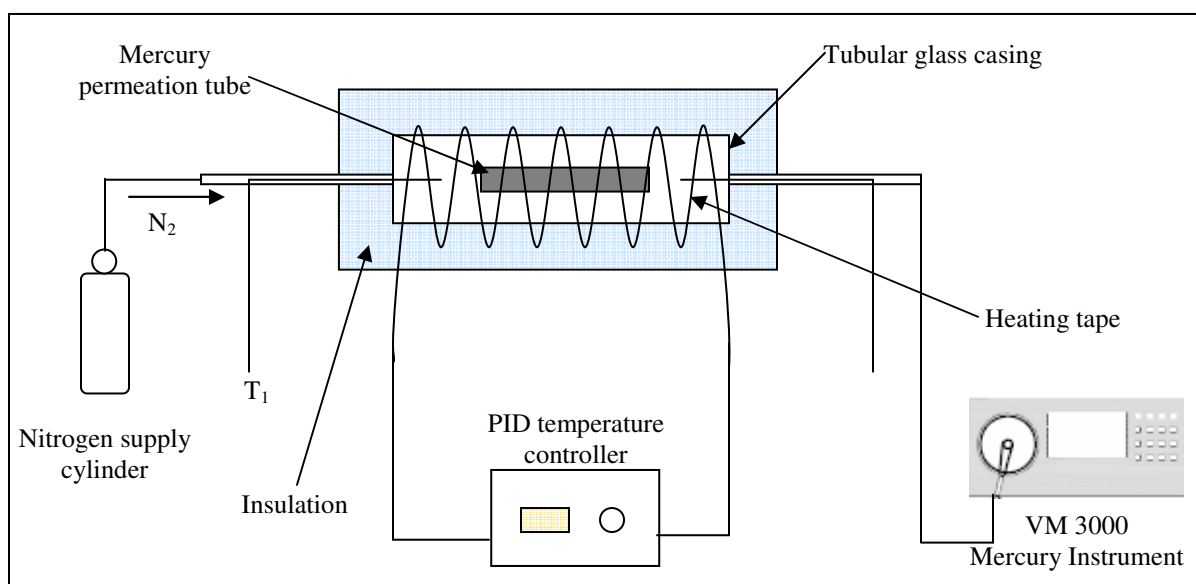

Figure G.2 Schematic setup of mercury calibration system

The permeation rate of the mercury permeation tube is given by the manufacturer as 1746.16 ng/min at 100°C, and a decrease of 10% of mercury permeation rate with every degree Celcius drop in temperature. From the above specification, the permeation rate for different temperatures was deduced.

During calibration, temperature of the tubular glass casing was set at 88°C using the PID controller. Flow rate of carrier nitrogen gas was set at a stable rate of 1.1 lpm. The thermocouples measured the temperatures at inlet and outlet and were recorded as 70°C and 70.2°C respectively. It is to be noted that the mercury permeation tube is at a higher temperature as that indicated by the inlet and outlet temperatures, since the temperatures are not measured within exact coincidence of heating tapes. It is found that the interior of the glass tube nearest to the permeation tube measured 88-89°C. Under such conditions, the mercury instrument read a value of 514 $\mu g/m^3$.

Permeation rate of mercury at 100°C = 1746.16 ng/min

Permeation rate of mercury calculated at 88°C = 493.167 ng/min

N_2 flow rate = 1.1 lpm = 0.0011 m^3/min

Hg concentration in the flow = $\dfrac{Hg\ permeation\ rate,\ ng\ /\ \min}{N_2\ flowrate,\ m^3\ /\ \min}$ (G.1)

$$\Rightarrow \frac{498.167\ ng\ /\ \min}{0.0011\ m^3\ /\ \min} = 44833.38\ ng\ /\ m^3 = 448.33\ \mu g\ /\ m^3$$

Similarly, permeation rate of mercury at 89°C = 547.96 ng/min

Hg concentration in the flow considering 89°C = 498.15 $\mu g/m^3$

Average of permeation of Hg at above two temperatures = 473.12 $\mu g/m^3$

Error = $\dfrac{(Actual\ Hg\ measurement\ recorded - Hg\ input\ from\ permeation tube)}{Hg\ input\ from\ permeation tube} \times 100\%$

(G.2)

$$\Rightarrow \frac{(514 - 473.12)\ \mu g\ /\ m^3}{473.12\ \mu g\ /\ m^3} \times 100\% = 8.6\ \%$$

Hence error in measurement is roughly 8.6 %.

VITA

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