

The Homogeneous Forcing of Mercury Oxidation to provide Low-Cost Capture

Final Report

Start Date: July 1, 2003
End Date: June 30, 2007

Authors: JOHN C. KRAMLICH AND LINDA CASTIGLONE

Issued April 2009

DOE Grant No. DE-FG26-03NT41808

*Department of Mechanical Engineering
University of Washington
Box 352600
Seattle, Washington 98195-2600*

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract

Trace amounts of mercury are found in all coals. During combustion, or during thermal treatment in advanced coal processes, this mercury is vaporized and can be released to the atmosphere with the ultimate combustion products. This has been a cause for concern for a number of years, and has resulted in a determination by the EPA to regulate and control these emissions. Present technology does not, however, provide inexpensive ways to capture or remove mercury.

Mercury that exits the furnace in the oxidized form (HgCl_2) is known to much more easily captured in existing pollution control equipment (e.g., wet scrubbers for SO_2), principally due to its high solubility in water. Work funded by DOE has helped understand the chemical kinetic processes that lead to mercury oxidation in furnaces. The scenario is as follows. In the flame the mercury is quantitatively vaporized as elemental mercury. Also, the chlorine in the fuel is released as HCl . The direct reaction $\text{Hg}+\text{HCl}$ is, however, far too slow to be of practical consequence in oxidation. The high temperature region does supports a small concentration of atomic chlorine. As the gases cool (either in the furnace convective passes, in the quench prior to cold gas cleanup, or within a sample probe), the decay in Cl atom is constrained by the slowness of the principal recombination reaction, $\text{Cl}+\text{Cl}+\text{M} \rightarrow \text{Cl}_2+\text{M}$. This allows chlorine atom to hold a temporary, local superequilibrium concentration. Once the gases drop below about 550°C, the mercury equilibrium shifts to favor HgCl_2 over Hg , and this superequilibrium chlorine atom promotes oxidation via the fast reactions $\text{Hg}+\text{Cl}+\text{M} \rightarrow \text{HgCl}+\text{M}$, $\text{HgCl}+\text{Cl}+\text{M} \rightarrow \text{HgCl}_2+\text{M}$, and $\text{HgCl}+\text{Cl}_2 \rightarrow \text{HgCl}_2+\text{Cl}$. Thus, the high temperature region provides the Cl needed for the reaction, while the quench region allows the Cl to persist and oxidize the mercury in the absence of decomposition reactions that would destroy the HgCl_2 .

Promoting mercury oxidation is one means of getting moderate-efficiency, "free" mercury capture when wet gas cleanup systems are already in place. The chemical kinetic model we developed to describe the oxidation process suggests that in fuel lean gases, the introduction of trace amounts of H_2 within the quench region leads to higher Cl concentrations via chain branching. The amount of additive, and the temperature at the addition point are critical.

We investigated this process in a high-temperature quartz flow reactor. The results do indicate a substantial amount of promotion of oxidation with the introduction of relatively small amounts of hydrogen at around 1000 K (~100 ppm relative to the furnace gas).

In practical systems the source of this hydrogen is likely to be a small natural gas steam reformer. This would also produce CO , so co-injection of CO was also tested. The CO did not provide any additional promotion, and in some cases led to a reduction in oxidation. We also examined the influence of NO and SO_2 on the promotion process. We did not see any influence under the conditions examined.

The present results were for a 0.5 s, isothermal plug flow environment. The next step should be to determine the appropriate injection point for the hydrogen and the performance under realistic temperature quench conditions. This could be accomplished first by chemical kinetic modeling, and then by tunnel flow experiment.

Table of Contents

Disclaimer	ii
Abstract	iii
1.0 Introduction	1
2.0 Review of Mercury Behavior in Combustion Systems	2
2.1 Mercury Sources and Impact	2
2.2 Coal Fired Power Plants and Atmospheric Mercury	5
2.3 Mercury Measurement Techniques	9
2.4 Regulation of Mercury Emissions	10
2.5 Mercury Removal in Pollution Control Devices	11
3.0 Known Mercury Oxidation Characteristics	20
3.1 Overview	20
3.2 Homogeneous Mercury Oxidation by Chlorine Species	21
3.3 Heterogeneous Mercury Behavior	33
3.4 Objectives	34
4.0 Experimental and Numerical Approach and Procedures	35
4.1 Experimental Apparatus and Procedures	35
4.1.1 Overview	35
4.1.2 Gas Supply System and Flow Panel	35
4.1.3 Clamshell heater and Quartz Reactor	38
4.1.4 Continuous Ultraviolet Analysis	38
4.1.5 Mercury Flow Clean-Up	43
4.1.6 Experimental Procedures	43
4.1.7 Data Analysis Techniques	44
4.2 Chemical Kinetic Analysis Methodology	44
4.2.1 Introduction	44
4.2.2 CHEMKIN	45
5.0 Results and Discussion	47
6.0 Conclusions	54
7.0 References and Bibliography	55

1.0 Introduction

Exposure to mercury is detrimental to the good health and well being of living organisms. Quantification and qualification of mercury, its sources, effects and mitigation was legislated for the first time by the Clean Air Act of 1990. Subsequent legislation specified the requirements of the United States government and provided funding for this and other mercury mitigation and control programs. In March of 2005, the U.S. Environmental Protection Agency (EPA) announced the details of proposed coal fired power plant mercury emissions regulation. While litigation has changed the regulatory pathway and made the final outcome uncertain, the eventual regulation poses a challenge to the electric power industry, as inexpensive solutions are not available for elementary mercury removal.

Coal fired power plants emit mercury in both the elemental and divalent (oxidized) forms. Oxidized mercury, or mercury chloride ($HgCl_2$), is soluble in water and therefore easily scrubbed from coal exhaust streams with existing wet scrubber technology. The fraction of total mercury emitted in the oxidized state from a particular plant is dependent on the chlorine content of the coal and on other less well-defined parameters. This reaction relationship provides a possible method that, properly exploited, could provide mercury control for minimal capital and operating cost. However, the reaction mechanisms are less well understood for mercury and chlorine than for most other pollutants.

In support of this, a program to define and evaluate the chemical kinetics within the coal combustion exhaust gas stream was undertaken. Specifically, the reaction mechanisms of Mercury with chlorine, hydrogen and carbon monoxide in the presence of nitrogen, water, oxygen and water were investigated. Experiments were conducted at ambient pressure over a range of temperatures from 922 to 1200 K. The concentration of elemental mercury was measured, with the amount of mercury oxidized as the difference between the known input mercury level and that measured. This approach allowed for the determination of the effect of hydrogen, carbon monoxide, or any combination of these species on the oxidation of mercury by chlorine. The results of the mercury experiments were compared with a chemical kinetics model.

2.0 Review of Mercury Behavior in Combustion Systems

Exposure to low levels of mercury was not identified as being hazardous to human health until the last quarter of the twentieth century. Historically, mercury has been used on a large scale in gold refining, in the chlor-alkali industry, and in other small-scale applications, *i.e.*, in thermometers, and to amalgamate dental fillings. Implication in tragic industrial poisoning incidents in Japan during the 1950's and Iraq in 1971 raised consciousness about the dangers of mercury exposure (Weiss, 1993). An effort to quantify atmospheric mercury levels, determine various sources and modes of contamination, and find safe exposure levels has been undertaken on a multi-national scale over the last twenty years. This section describes the sources of and issues regarding atmospheric mercury and the generation of such in coal combustion.

2.1 Mercury Sources and Impact

Mercury is a known Hazardous Air Pollutant (HAP) whose sources are both natural and anthropomorphic. Natural sources include geothermal venting, evaporation, vegetation release, wildfires and soil out-gassing. Anthropomorphic sources include the chlor-alkali industry, gold refining, smelters, cement production, sewage sludge incineration, municipal waste incinerators and fossil fuel combustion (Guijarro *et al.*, 1998). Coal combustion is a major point source for mercury pollution.

Mercury experiences a global flux where mercury cycles into and out of the atmosphere. This transient mercury reservoir contains mercury in three valence states: elemental (Hg^0), divalent or inorganic mercury salts (Hg_2Cl_2 , HgCl_2 , Hg^+ , and Hg^{+2}), and organic mercury or organic mercurials (methylmercury and phenylmercury) (Agency for Toxic Substances and Disease Registry, 2004). The latter is predominantly in the form of the methylmercury or CH_3Hg . Most natural sources put forth elemental mercury, while anthropomorphic sources put forth both elemental and divalent forms of mercury. Direct global anthropomorphic mercury emissions are estimated to have increased over fifty percent since pre-industrial times (Bergen *et al.*, 1999). Atmospheric elemental mercury has a half-life of six to twenty-four months thus allowing for long range transport in the atmosphere. Elemental mercury is considered inert due to its relative insolubility in water contributing to global transport mechanisms (Fthenakis *et al.*, 1995; Carpi, 1997; Bergen *et al.*, 1999). Often, deposited mercury in both elemental and oxidized forms is re-emitted back into the atmosphere as a gas, or associated with dust and other particulate matter, providing an additional source term for the total global reservoir flux (Bergen *et al.*, 1999; Environmental Protection Agency, 2003).

The chemical reaction pathways in the atmosphere are complex and not well understood. In the atmosphere, mercury is slowly oxidized by O_3 , H_2O_2 and the OH and NO_3 radicals in cloud water as well as bromine and chlorine complexes and radicals such as HCl and Cl_2 (Lin and Pehkonen, 1999; Gabriel *et al.*, 2003). These forms of mercury, as well as mercury oxidized in rain water, fog and clouds (Seigneur *et al.*, 1996) are more rapidly deposited through precipitation than elemental mercury, and dry deposition is found in all

cases. Only 5-8% of the mercury is deposited locally (within 50 km) while the remainder is a global reservoir contribution (Saroff and Lipfert, 1995). The slow processes of atmospheric oxidation, dry deposition, and re-emission lead directly to the long half-life and wide dispersal of atmospheric elemental mercury. Divalent, or oxidized mercury, is soluble in water and washed out of the atmosphere in rain water within five to fourteen days, with the amount deposited decreasing with distance from the source (Carpi, 1997; Bergen *et al.*, 1999). This dispersal pattern seems to justify the need for a regional approach to local mercury deposition as well as a global one (Seigneur *et al.*, 1996; Gabriel *et al.*, 2003). Mercury deposition was found to be dependent on the season, weather and wind conditions, and was found to be highly correlated with wind speed and direction (Cote *et al.*, 2000; Meij, 2001; Hohl *et al.*, 2004).

The DOE Energy Information Agency projects that in the year 2025, at least fifty percent of electricity generation will be from coal-combustion validating the fuel as a mainstay of power generation in the U.S. (Lewandowski *et al.*, 2004). Future increased use of coal combustion for energy in developing countries where emissions are generally unregulated threatens to increase the already large global reservoir of mercury, and this is currently of great concern. Table 2.1 tabulates the emissions from each continent (Levin, 2002). The fact that global as well as local considerations should be taken into account in future investigations has been discussed in public forums and is popular (Henry, 2005).

Mercury input from all terrestrial sources has been estimated at 7700 T/yr (Levin, 2002). Mercury input to the atmosphere from all anthropogenic sources has been estimated to be 5500 tons total into the global reservoir (Environmental Protection Agency, 2003) and, of that, one hundred fifty five tons are attributed to the U.S. (Pai *et al.*, 2000; Levin, 2002;

Source Continent	Emissions (U.S. Tons/yr)
North America	226.0
Central & South America	194.2
Europe	560.3
Asia	1231.5
Africa	271.3
Oceania	53.2
Total	2536.5

Table 2.1 Global Anthropogenic Emissions of Global Mercury by Continent (Levin, 2002).

Environmental Protection Agency, 2003). Of this amount, eighty seven percent is associated with combustion sources, while twenty seven percent, or eighty nine tons per year, is estimated to be associated with industrial coal combustion (Porcella *et al.*, 1996). Electric utilities alone put forth about 45 tons per year (Shea, 2004). This makes the U.S.

contribution to the total global mercury flux from coal combustion to be approximately 0.91%.

On the other end of the global atmospheric mercury cycle, sixty-two percent of mercury deposition in the U.S. is from air emissions (Whipple and Von Berg, 1996). It is estimated that approximately fifty two tons, or one third of the U.S. anthropomorphic emissions are deposited within the lower forty eight states, with an additional thirty five tons depositing from the global reservoir. Higher humidity geographic regions experience higher mercury deposition rates than that found in dry regions. Mercury hot spots from atmospheric deposition are predicted to occur in the northeastern United States, the southern Great Lakes, the Ohio River Valley, and scattered areas in the south. The highest levels of mercury deposition in the U.S. are predicted to be in the southeastern states (Environmental Protection Agency, 2003).

Mercury exposure is fatal to living organisms at high levels. A 1971 mercury poisoning incident involving methylmercury treated grain in Iraq serves as the baseline against which all other mercury exposures are compared as this incident has provided the only relatively complete set of quantitative data available regarding the health effects of mercury exposure (Lipfert and Saroff, 1996). Additional methylmercury exposure data have been obtained from high-exposure industrial water contamination in Japan as noted above. Extrapolation of the effects of the short-term, high-dose cases like Iraq to a maximum safe dosage level for long term exposure in humans is unreliable. Additional case studies in the Seychelle and Faroe Islands are being conducted to further quantify methylmercury exposure risk assessment (Whipple *et al.*, 1996; Brown, 1999; Environmental Protection Agency, 2003; Lipfert *et al.*, 2005). However it is of concern that these data are yet insufficient for a complete quantification of low-level mercury exposure (Davis, 1997; Lipfert *et al.*, 2005).

Although mercury in the elemental and divalent forms is easily eliminated from the body, methylmercury is a bio-accumulator. However, high exposures to inhaled elemental mercury do not cause death. Mercury exposure through inhalation will cause chest pain, lung damage, digestive failure, kidney failure, central nervous system damage and cause neurotoxicity in a developing fetus. Effects on the brain may include anxiety, memory problems, insomnia, anorexia, irritability, shyness, tremors, emotional labiality, changes in vision and/or hearing, and cognitive and motor dysfunction (Agency for Toxic Substances and Disease Registry, 2004). Additionally, it has been put forth that even a slight exposure could mean an across the board decrease in I.Q. for entire societies (Weiss, 1993).

Mercury enters the food chain in the aquatic environment when oxidized mercury is converted to methylmercury by bacteria. Moving up the aquatic food web, increasing levels of methylmercury are found. Methylmercury enters the human food chain through fish consumption leading to bioaccumulation. The effect of anthropomorphic mercury sources on methylmercury levels in aquatic life is not well defined (Seigneur *et al.*, 1996). Fish, bird and mammal populations exposed to mercury have been found to experience impaired growth and development, reproductive failure and brain

abnormalities. Since humans are at the top of the food web, consumption of contaminated meat is the major pathway to exposure and it therefore has been important to gain an understanding to this pathway (Environmental Protection Agency, 2003). It has been recommended by EPA that all pregnant women, women of childbearing age, nursing mothers and young children should avoid certain types of fish that are high in mercury (Environmental Protection Agency Mercury Rule, 2005).

Since the mercury contribution to the global reservoir from coal combustion is less than one percent, it has been argued that coal combustion generated mercury does not contribute significantly to methylmercury contamination of sea life. However, fresh water fish are more likely to be contaminated by mercury from coal combustion exhaust due to the mercury deposition patterns noted above. Thus mitigation of coal combustion mercury is anticipated to reduce methylmercury levels in fresh water fish. However the degree of such reduction has generated conflicting results (Environmental Protection Agency, 2003; Lipfert *et al.*, 2005).

An assessment of the ecological effect of mercury deposition has also been conducted. The study marked a long-term assessment of the complex environment within which we live in regions local to a pulp mill or power plant under consideration. The transport, accumulation and circulation of mercury were investigated in detail. Although no radical changes in the forest were noted, the soil geochemical characteristics had changed along with an increase in soil ph. Detrimental changes in the trees within the study area were also noted (Beim *et al.*, 1993). More recent studies have revealed that mercury concentrations found in the tissues of various species of wildlife equate to that found to cause adverse health effects in controlled experiments, and that some wild populations are actually experiencing adverse health effects specifically due to airborne mercury (Environmental Protection Agency, 2003). The EPA is currently unable to quantify health risks in populations surrounding coal-combustion emission sources (Shea, 2004).

2.2 Coal Fired Power Plants and Atmospheric Mercury

Coal contains trace element species of alumina, antimony, cadmium, iron, magnesium, titanium, cadmium, cobalt, chromium, copper, manganese, molybdenum, nickel, lead, vanadium, selenium, and mercury (Bush *et al.*, 1995). Mercury is of particular interest because it vaporizes easily in the combustion process and as it continues out of the stack into the environment, remaining in the vapor phase (Meij, 1991; Benson *et al.*, 1996; Vann Bush *et al.*, 1995). Measurements indicate that five to ninety percent of the mercury contained in the coal is exhausted out the stack (Jones, 1994). Mercury is present in flue gas at concentrations ranging from two to ten parts per billion (Senior *et al.*, 2000; Lissianski *et al.*, 2001). Conventional air pollution control devices are ineffective at removing elemental mercury from a coal combustion exhaust stream (Hargis and Pennline, 1997; Devito and Rosenhoover, 1999).

The presence of mercury in coal was discovered early and subsequently associated with mineral matter having the heaviest gravity fraction (Cavallaro *et al.*, 1978). Mercury has been associated with the minerals pyrite (FeS_2) and cinnabar (HgS) (Akers and Dospey,

1993; Luttrell *et al.*, 2000). Mineral matter itself causes fouling and corrosion within furnaces and removing it is very beneficial. Mercury exists in raw coal in low concentrations which average 0.1 ppmw. Pre-combustion coal conditioning has been explored as a technique for mineral and mercury removal from processed coal. Physically cleaning (washing) of coal was implemented for such and it was found that an average of thirty seven percent of the mercury was removed (Jones *et al.*, 1994, Devito *et al.*, 1994). As much as fifty percent has been removed using advanced cleaning methods (Luttrell *et al.*, 2000). Unfortunately, coal washing is not practiced at all coal combustion facilities (Davis, 1997) and advanced multi-step coal cleaning methodologies are likely to be effective on an industrial scale. Results have indicated that removal efficiencies of other trace elements and their associated minerals to be seventy-five to eighty-five percent. By comparison, coal washing removes considerably less mercury than other species suggesting that mercury in coal is associated with the organic fraction to a greater degree than the other trace element species described above. Feed coal pulverization has also been shown to mitigate trace element contamination (Luttrell *et al.*, 2000). Coal preheating has also been suggested for a pre-combustion coal conditioning technique. This process could vaporize up to seventy-five percent of the mercury for removal before the reaching the combustor (Bland *et al.*, 2004).

Raw coal has a mercury content that varies from one region to another, within a mine itself and also from one delivered load to another (Reij, 1991; Davis, 1997; Meij, 2002). Table 2.2 lists mercury concentrations found in raw coal from the U.S. and various other regions (Carpi, 1997; Meij, 2002). The high variation in mercury and halogen species like chlorine within coal has made it impossible to specifically quantify mercury emissions or speciation from any single combustion source. Thus quantification of total and speciated mercury emissions from coal based power generation is highly uncertain. The EPA is seeking additional information regarding this (Senior *et al.*, 1998). On a mass basis nearly thirty percent of the coal used in the U.S. is subbituminous, the remainder being bituminous (Brown *et al.*, 1999). Table 2.3 provides a summary of full-scale data on coal and its relationship with mercury.

Geographic Location	Mercury Concentration (µg/g)	
	(Carp, 1997)	(Meij, 2002)
Australia	0.03-0.25	0.08
Columbian	0.04	0.06
China	-	0.15
Egypt	-	0.10
Germany (Ruhr area)	-	0.16
Indonesia	-	0.04
New Zealand	-	0.05
Norway (Spitsbergen)	-	0.14
Polish	0.14-1.78	0.35
Russia (Kuzbass)	-	0.06
South Africa	-	0.09
Venezuela	-	0.08
Netherlands imported average	-	0.11
Eastern U.S.	0.09-0.51	0.14
Appalachian	0.24	-
Interior Eastern Coal	0.14	-
Illinois Basin	0.21	-
New Jersey	0.12-0.28	-

Table 2.2. Raw Coal Mercury Concentrations by Region

The relative amount of mercury and chlorine in raw coal has a profound effect on the mercury speciation in the flue gas of a coal-combustion facility. Additionally, mercury oxidation characteristics of different coals also seem to be due to characteristic differences in coal content of iron, sulfur, and calcium (Pavlish *et al.*, 2003). Bituminous coal has a greater amount of chlorine than subbituminous coal. As illustrated in Table 2.3, analysis of coal within the U.S. shows that although mercury is more abundant in

Coal Rank	Bituminous			Sub-bituminous	Lignite	Totals	
Region	Appalachian	Interior	Western	Western	Fort Union	Gulf Coast	
# Samples	19530	3763	1471	7989	424	623	33800
Average ICR Coal Analysis, Dry Basis							
Hg (ppm)	0.126	0.09	0.049	0.068	0.09	0.119	
Cl (ppm)	948	1348	215	124	139	221	
S (%)	1.67	2.45	0.57	0.48	1.15	1.39	
Ash (%)	11.7	10.4	10.5	7.9	13.4	23.6	
Btu/lb	13275	13001	12614	11917	10585	9646	
Other Coal Related Information							
Ca (ppm)	2700	6100	7000	14000	32000	33000	
Fe (ppm)	16000	23000	4200	10000	12000	20000	
Moisture (% ar)	2.5	6.6	4.2	19.4	37.6	34	
Heat Rate (Btu/kWh)	10002	10067	10047	10276	10805	10769	
Coal Production for Utility Use							
Tons ar (x1E6)	342	67	75	336	23	57	900
Dry Coal (Tons x 1E6)	333	63	72	271	14	37	790
Mercury in Utility Coal							
Mercury (ton)	42.1	5.4	3.5	18.4	1.3	4.5	75.1
lb Hg Emission /TBtu	9.5	6.6	3.9	5.7	8.3	12.5	
lb Hg Emissions /GWH	0.0951	0.07	0.039	0.0584	0.09	0.134	

Table 2.3. A Summary of ICR Data on Mercury in Utility Coal by Region and Coal Rank (Pavlish *et al.*, 2003).

Appalachian bituminous coal than western subbituminous coal, more mercury is removed burning the bituminous coal due to its higher chlorine content. It has been suggested that only coals with excessive amounts of chlorine provide reasonable mercury oxidation efficiencies. The excess chlorine in bituminous coal is correlated with a greater degree of flue gas speciation in the direction of oxidized mercury due to its higher chlorine content, although extents of mercury oxidation have not been found to be proportional only to fuel bound chlorine levels (Fujiwara *et al.*, 2002). Since conventional coal cleaning technologies are unable to capture elemental mercury, and oxidized mercury is captured with various efficiencies, it is critical to investigate the speciation of mercury at all stages of the flue gas conditioning system (Senior, *et al.*, 1997). Overall mercury speciation has been found to be dependent on both the flue gas temperature and coal chlorine content of the coal (Senior and Afonso, 2001).

Coal combustion emissions contain speciated mixtures of mercury where forty to eighty percent of the mercury emissions are in the oxidized state when eastern bituminous coal is burned; while only ten to twenty percent of the mercury emissions are oxidized for the burning of lignite and western subbituminous coals (Reynolds, 2004). Mixing bituminous and subbituminous coals have been suggested as a method to increase fuel chlorine concentration and improve mercury collection efficiency by shifting the balance of flue mercury to the oxidized state (Lissianski *et al.*, 2003; Sjostrom *et al.*, 2004).

Unfortunately, coal mixing increases the variability of mercury emissions directly causing unquantified mercury concentration variations in the flue gas that detrimentally impacts the ability for APCDs to perform consistently with regard to mercury removal (Fujiwara *et al.*, 2002). Blending of a small amount of high iron bituminous coal with subbituminous coal was found to increase mercury oxidation to levels up to ninety five percent (Gale *et al.*, 2003).

2.3 Mercury Measurement Techniques

Speciation defines the range of physiochemical forms that collectively compose the total. Accurate speciation of mercury, in coal fired power plant exhaust has been elusive in the past (Moskowitz, *et al.*, 1994; Rizeq *et al.*, 1994; Galbreath and Zygarlicki, 1996; Schlager *et al.*, 1995; Senior *et al.*, 1997; Senior *et al.*, 1998). Many methods to quantify speciation have been evaluated. Although it was determined that EPA Method 29 would capture all mercury physiochemical forms, it was not appropriate for use to determine accurate speciation (Laudel *et al.*, 1994). Additional mercury speciation methods investigated include iodated activated carbon traps, soda-lime traps, and various impinger solutions including potassium chloride, potassium carbonate, and hydrogen chloride (Chow and Connor, 1993).

Currently, mercury measurement techniques that do provide accurate speciation are cumbersome, expensive, time consuming, and prohibit real time data acquisition. Most methods listed above utilize wet chemistry in the form of solution impinger trains that collect mercury species. The solutions must subsequently be analyzed to determine total mercury collected, and mercury concentration is then calculated based on known flow rates. EPA approved methods include the EPA Method 29, Ontario-Hydro Method (OH),

Acetate Buffer, Tris Buffer and EPA 101A methods. Mercury Speciation Absorption (MESA), solid sorbent collection (Laudel *et al.*, 1996; McManus *et al.*, 1997; McManus *et al.*, 1998), and cold vapor-absorption atomic spectroscopy have also been evaluated (Otero Ray *et al.*, 2003). Although it was found to under-represent elemental mercury (Evans and Nevitt, 1997), the OH method was found to be the most accurate of the methods evaluated (Laudel *et al.*, 1998; Laudel 1999).

Drawbacks to the OH method include great complexity, high expense, and vulnerability to human error. For these reasons and the lack of real-time feedback, real-time mercury detectors have been under development and evaluation (Sjostrom *et al.*, 1997; Heidt *et al.*, 1998; Boylan, 2003; Dunn, *et al.*, 2003; Fisher *et al.*, 2004; Meischen *et al.*, 2004). Temperature and pressure issues, as well as complex and varying flue-gas compositions have provided challenges in development of commercial real-time mercury and chloride monitors. EPA method 7473 provides an atomic absorption technique that uses a partial mass balance analysis to determine mercury speciation with a short (five minute) turn-around time (Boylan *et al.*, 2003). The major source of interference in flue gas is H_2O , especially for spectroscopic methods (Boylan *et al.*, 2003; Buttermore *et al.*, 1995). Sorbent trap (Johnsen *et al.*, 2003), catalytic based (Fisher *et al.*, 2004), and x-ray (Johnsen *et al.*, 2003) measurement techniques are under development.

2.4 Regulation of Mercury Emissions

The U.S. Federal Government, as well as some individual states (Hagen and Weilert, 2001), have been in the process of regulating mercury emissions from anthropomorphic sources, in particular, coal-fired power plants. The Clean Air Act was enacted in 1963. It exempted utilities from emission controls. The Clean Air Act Amendment of 1977 directly addressed power plant emissions. At the time it was enacted, the 1977 amendment exempted existing power plants, although it did require new and modified plants to install current state-of-the-art pollution control equipment under the New Source Review (NSR) provision. The amendment was not specific enough and allowed for open interpretation, undermining the original purpose of the legislation (Smith, 2004) .

The 1990 Clean Air Act (CAA) amendment was the first legislation in the U.S. to address air toxics specifically. This legislation introduced sweeping changes to the Clean Air Act of 1963 including its subsequent amendments (the 1977 amendment being among them). Title III of the amendment deals specifically with one hundred eighty nine hazardous air pollutants (HAPs). This particular segment of the legislation required the Environmental Protection Agency (EPA) to quantify sources of HAPs and the amounts emitted. The EPA was also required to publish a schedule for the regulation of said HAPs at their sources once that source is determined. It also required the regulation of major sources like the petrochemical and smelting industries, as well as small sources like gas stations, printers and dry cleaners (Cooper and Alley, 2002).

The laws were written generally so to allow government regulatory agencies to do the research and analysis required to formulate specific regulations. Two types of standards were written: Ambient Air Quality Standards (AAQSSs) and Source Performance

Standards (SPSs). AAQSSs dealt with concentrations of pollutants in the outdoor atmosphere and were written in units of ppm or $\mu\text{g}/\text{m}^3$. SPSs applied to specific source emissions and were written in units of g/min or kg of pollutant per metric ton of product. In addition, the National New Source Performance Standards (NNSPSs) were written for specific pollutants from specific sources and apply only to new sources.

The National Emission Standards for Hazardous Air Pollutants (NESHAPs) were a separate category of standards. These applied specifically to emissions from point sources regarding HAPs. The NESHAPs applied to substances that may result “in an increase in serious irreversible, or incapacitating, reversible illness” and do not have AAQSSs. For mercury, as well as the other HAPs, the NESHAPs were very specific as to the sources and control methodology.

In 1999 the EPA put forth the Information Collection Request (ICR). This was designed to provide fundamental data for use by regulatory agencies in developing specific mercury control strategies. Part three of the ICR called for accurate determination of mercury speciation from coal-fired boilers. These data are available on the web at <http://www.epa.gov/ttn/atw/combust/utiltox/mercury.html>. Mercury Speciation data from eighty-three different boilers is available.

The maximum achievable control technology (MACT) regulations were put forth by the EPA during the last half of the 1990’s. They specifically address the HAPs from industrial and commercial combustion sources. On March 15, 2005, EPA issued the Clean Air Mercury Rule (CAMR) to permanently cap and reduce mercury emissions from coal-fired power plants. These regulations made the United States the first country in the world to regulate mercury emissions from utilities. This market-based cap-and-trade method was chosen over the MACT regulation approach and is very controversial (Pope, 2005). CAMR limits mercury emissions from both new and existing coal-fired power plants.

The Clean Air Rule (CAR), a cap-and-trade regulatory method was enacted at the same time as CAMR. These regulations require states to meet emission reduction requirements by either requiring power plants to participate in the cap-and-trade system, or to reduce emissions by any method of the state’s choosing. Methods of mercury control in pollution control devices are discussed in detail in Section 2.2. It should be noted that CAR is designed to work in concert with CAMR. On Feb. 8, 2008 the District of Columbia Circuit Court vacated the CAMR, citing inconsistencies with the Clean Air Act Amendments. On Feb. 6, 2009 the EPA indicated its intention of developing a new CAMR consistent with the Court’s finding. Regulatory changes continue as an understanding of mercury chemistry, emissions and health risks improves and will not achieve finality for some time to come (Farber *et al.*, 2004).

2.5 Mercury Removal in Pollution Control Devices

Very low concentrations of mercury are found in coal-combustion flue-gas emissions ranging from 5-20 $\mu\text{g}/\text{Nm}^3$ (Carey *et al.*, 1997; Pavlish *et al.*, 2003). A very low

concentration of mercury suspended within a large volume of flue gas implies mercury control methods are expensive on a cost per unit mercury captured. A preliminary estimate for costs of mercury removal from coal-fired power plants, on a national basis, is projected to run in the billions of dollars per year (Environmental Protection Agency, 2004). It has been demonstrated that the mercury concentration in the stack of any particular coal-combustion facility must be individually quantified for proper mercury emission analysis and control (Boylan *et al.*, 2003). The amount of mercury in a particular stack is a function of the complex nature of mercury chemistry and its marked dependence on coal composition, type, and mix, boiler design, combustion environment, operating conditions, heat transfer rate, existing air pollution control devices (APCDs) and operating practices.

Standard air pollution control devices are not designed to capture and retain mercury. Mercury, defined as a class III pollutant, remains vaporized in the boiler and through the exhaust system. Mercury speciation within the stack and plume has been investigated rigorously as described in Section 2.2. Since mercury emissions and speciation are found to vary widely, no single technological approach will be sufficient in all instances. Although a combination of APCDs may provide mercury removal efficiencies near ninety percent for some facilities, the same combination will not offer efficient mercury control for others (Pavlish *et al.*, 2003).

It is estimated that only forty percent of the mercury that enters a coal-fired combustion system is captured. The remainder exits the stack (Pavlish *et al.*, 2003). Sixty-five percent of utility power plants are equipped with only an ESP, ten percent are equipped with only a baghouse, and the remaining twenty-five percent are operated with both an ESP and FGD systems (Brown *et al.*, 1999). Various methods have been explored to find cost effective methods of mercury removal from coal-fired power plant exhaust. In some cases, standard air pollution control devices have been moderately effective by improving efficiencies with addition of sorbents or oxidizing agents. These treatment technologies are at varying levels of maturity, with some having proved successful and yet abandoned in the past, and others in the development phase. In all cases the efficiency of mercury collection is tied to the partitioning of mercury species: the greater the ratio of oxidized to elemental mercury, the higher the mercury collection efficiency. A short discussion of the effectiveness of standard air pollution control devices and some proposed modifications follows.

Various technologies have been investigated for the removal of mercury from coal-fired combustion exhaust streams in a number of categories: by coal rank, type of technology and type of control device. All mercury removal techniques must be evaluated against coal rank (bituminous, subbituminous and lignite,) the amount of mercury and chlorine in the coal (Liu *et al.*, 2001), and by type of modifications needed to effect sufficient mercury removal (*i.e.*, sorbent injection or use of catalysts). Traditional post combustion APCD types include electrostatic precipitation (ESP), fabric filter bag house(s), wet flue gas desulphurization (FGD) or 'wet scrubber', Selective Catalytic Reduction (SCR) and Selective Non-catalytic Reduction (SNCR) (Davis, 1997). Other mercury removal techniques investigated include photochemical oxidation (Granite and Pennline, 2002;

Pitoniak *et al.*, 2003; McLarnon *et al.*, 2004) and electro-catalytic oxidation (Helfritch and Feldman, 1999; McLarnon and Steen, 2003; Duncan, 2004, Peltier, 2004). Currently, the most mature technique for mercury removal is activated carbon injection (ACI) followed by particulate removal (Feeley and Carter, 2004; Renninger *et al.*, 2004), although others have varying degrees of commercial success. The traditional technologies, and retrofits under consideration are discussed below.

Electrostatic Precipitators and Fabric Filters

Fabric filter bag houses and dry electrostatic precipitation (ESP) are intended for removal of particulate matter. Fabric filtration bag houses separate particulate matter from dry exhaust utilizing passive filtration. The flue gases pass through a number of filters in parallel, removing particulate matter. A saturated metal like mercury that vaporizes in the combustion system will also nucleate or condensate on particulate ash that is subsequently collected in particulate control devices such as the ESP or bag house (Rizeq *et al.*, 1994). A standard ESP ionizes flue gas charging the entrained particles which migrating to collection plates. Mercury removal within ESPs is provided by fly ash agglomeration of mercury.

Fabric filter bag houses are more efficient at removing oxidized mercury from flue gas than ESP systems (Lissianski *et al.*, 2001), due to increased gas-surface interaction time on the fabric filter (Pavlish *et al.*, 2003). In both configurations, a structure is provided for particulate deposition, and this surface is cleaned at regular intervals. Fly ash has been determined to be a sink for elemental mercury species (Gustin and Ladwig, 2004), however mercury oxidized by chlorine has been found to be the predominant species found in fly ash (Benson *et al.*, 1996; McManus *et al.*, 1997; Dunham *et al.*, 2004). The amount of carbon in fly ash has been shown to vary widely. Variations in the amount of carbon contained in the fly ash contribute to this. Fly ash exhibits higher mercury collection efficiency when a higher carbon ratio is present (Lissianski *et al.*, 2001; Lissianski *et al.*, 2003). In general, both baghouses and ESPs were found to have little to no effect on removing vaporized elemental mercury emissions (Rizeq *et al.*, 1994). In some cases, ESPs have been shown to oxidize elemental mercury (Lissianski *et al.*, 2003).

Improvements in bag house and ESP performance in terms of mercury removal efficiency have been considered. Addition of chlorine to the flue gas upstream of a baghouse was shown to increase oxidized mercury levels at both the baghouse inlet and outlet (Gale *et al.*, 2003). Improved bag house filtration media are being investigated as a replacement for standard passive filtration media for a combination of mercury oxidation and active stoichiometric binding of oxidized mercury onto the bag surface (Durate *et al.*, 2003; Shi and Bayless, 2004). Placing fixed gold coated sorbent structures in the flow upstream of a baghouse allows mercury to amalgamate to the gold for removal without fly ash contamination is under evaluation (Sjostrom *et al.*, 2002; Ebner *et al.*, 2004). Acoustic treatment of flue gas has been found to improve small particulate capture and reduce the number of bag cleaning cycles (Meegan *et al.*, 2003). Use of a spray dryer in conjunction with a baghouse has been shown to remove oxidizing species from the flue gas, lowering

collection efficiencies of either a baghouse or and ESP to below twenty percent (Sjostrom *et al.*, 2004).

Wet ESP systems are used industrially to control pollutants such as sub-micron particles and droplets, acid mists, metals and mercury particles through direct contact with a liquid, usually water. Wet ESP systems have demonstrated mercury removal efficiencies of up to seventy-eight percent (Altman *et al.*, 2001). Under full scale conditions, a mercury collection of less than fifty percent has been associated with unmodified wet scrubbers in coal combustion flue gas (Sjostrom *et al.*, 2003). Another method of mercury removal, the plasma-enhanced wet ESP design, consists of injecting a reagent gas mix into the coronal discharge of a bank of electrodes located just upstream or within the ESP. Ionic reactions cause the flue gas mercury to be adsorbed by reagent droplets, creating aqueous mercuric ions that are collected and scrubbed in the wet ESP. This has demonstrated enhanced mercury collection performance over that of an unmodified wet ESP system (Montgomery *et al.*, 2003; Altman *et al.*, 2004).

Sorbent Technology

Methods of mercury removal enhancement using dry sorbent technology have been investigated in an attempt to improve mercury collection efficiencies. An excellent detailed review of the history of mercury emission reduction using dry sorbents and promoters is provided by Granite *et al.* (1998). Sorbent injection is a retrofit option for that has a potential for application in the seventy-five percent of coal-fired boilers in the U.S. not already equipped with FGD systems. Investigation of sorbents was initiated by the observation that different fly ashes demonstrated varying amount of mercury removal efficiency (Hall *et al.*, 1990; Norton *et al.*, 2000; Fujiwara, 2002). It was subsequently discovered that fly ash carbon content was the driving factor in mercury adsorption. This discovery has lead to a whole host of sorbent injection investigations.

Usually injected upstream of particulate control devices, spray dryers are the usual method of sorbent injection (Felsvang *et al.*, 2001). Variations in ash carbon content and ash partitioning have been demonstrated to cause wide fluctuations in mercury oxidation efficiency (Fujiwara *et al.*, 2002). Once dispersed throughout the flue gas, fly ash (Senior *et al.*, 1998), activated carbon, or other injected sorbents, provides a site where elemental and/or oxidized forms of mercury may be physioabsorbed onto the carbon of the particulates. This particulate matter is subsequently removed by ESP or bag houses (Liu *et al.*, 1998).

Methods of sorbent injection have been investigated. A comparison of fixed bed versus in-flight mercury adsorption by particulates showed in-flight to be the more effective method of mercury control (Clack *et al.*, 2003). Effective mercury removal through efficient injection turbulent mixing has been found to be the most advantageous mixing strategy as compared to increased residence times, or the isotropic turbulence of agitation (Clack *et al.*, 2003; Haddad, *et al.*, 2003). All sorbent performance is affected by flue gas composition and temperature. Since sorbent injection and mixing rely on mass transfer driven by the concentration gradient of mercury (Lee *et al.*, 2003), mass transfer

limitations enforce an upper limit to sorbent injection efficiency (Sjostrom *et al.*, 2002).

Dry sorbent technology is attractive as many power plants are already equipped with ESPs for removal of particulate matter (Miller *et al.*, 1998; Sjostrom *et al.*, 2002). Research in the field of mercury control utilizing sorbents has been undertaken with particular attention to *activated carbon injection* (ACI). A number of widely varying sorbent materials have been evaluated for mercury removal from flue gases with varying degrees of success. These include lime hydrate, zeolites (Morency *et al.*, 2000), kaolinite, manganese dioxide (Boren *et al.*, 2004), and limestone. A combination of lime and calcium based sorbents were also found to be effective (Ghorishi and Gullett, 1998; Felsvang *et al.*, 2001). Dry alkali and alkaline sorbents (Ghorishi and Gullett, 1998; Gullett *et al.*, 2000; Norton *et al.*, 2000,) along with oil based carbons, waste tire activated carbon (Lehmann *et al.*, 1998), hydrated limes and silicates (Singer *et al.*, 2001), pistachio nut shells (Rostam-Abadi *et al.*, 2001), carbon nanotubes, carbon based fixed structures (Dombrowski *et al.*, 2003; Sjostrom *et al.*, 2003), corn char, bamboo and carbon soot (Ley *et al.*, 2004) have also been investigated. Activated carbon has been found to be the most effective sorbent evaluated. Efforts in evaluation of alternative sorbent materials are focused on finding a sorbent that is more cost effective and efficient than ACI.

ACI was found to assist in elemental and oxidized mercury removal (Livengood *et al.*, 1995; Hassett and Eylands, 1999; Starns *et al.*, 2003). The general focus of sorbent research has focused on ACI. Mercury adsorption onto activated carbon is a function of carbon content (Serre *et al.*, 2000), surface area, pore size, gas temperature, humidity, mercury concentration and speciation and residence time (Babu *et al.*, 1994, Hassett and Eylands, 1999). Recent investigations indicate that mercury oxidation in coal derived flue gas is independent of residence time (Fujiwara *et al.*, 2002). The mechanism behind binding of mercury to activated carbon involves homogeneous surface reactions with surface functional groups (SFG). The SFG may include oxygenating organic species like chlorine or sulfur and/or oxygenating organic species (Ghorishi *et al.*, 2002). Enrichment of activated carbon with copper or iron oxide has also been shown to enhance mercury removal efficiency (Hall *et al.*, 1991; Lee *et al.*, 1998). There are a number of different activated carbon compounds being investigated, each demonstrating variable mercury collection efficiencies (Yan *et al.*, 2002; Yan *et al.*, 2003; Machalek *et al.*, 2004; Nelson *et al.*, 2004; Pavlish *et al.*, 2004). Staged carbon injection within an ESP has also been investigated with some success (Starns *et al.*, 2004).

ACI has drawbacks in that removal efficiency decreases with increasing temperature, large particle size and low mercury concentrations (Livengood *et al.*, 1995). ACI has been impregnated with various materials including iodine, chlorine, sulfur, sulfuric acid, potassium iodide or certain proprietary materials. This has been shown to improve mercury collection efficiencies through chemisorption (Guizarro *et al.*, 1998; Miller *et al.*, 1998; Mendioroz *et al.*, 1999; Hsu *et al.*, 2000; Li *et al.*, 2001; Ghorishi *et al.*, 2002; Biermann *et al.*, 2003; Rodriguez *et al.*, 2003; Sjostrom *et al.*, 2003; Sjostrom *et al.*, 2004).

Sorbents, although effective, are very expensive and pose disposal challenges. Several factors go into estimating the cost of using sorbents: power plant size, required removal efficiency of mercury, sorbent and sorbent disposal cost, installation/retrofitting costs, maintenance and operating costs (Meserole *et al.*, 2000). Large amounts of sorbent are required for full scale applications (Livengood *et al.*, 1996), estimates indicate as much as 100,000 pounds of activated carbon are needed to remove one pound of mercury (Helfritch and Feldman, 1999). Removal costs are expected to be as high as \$40 million per ton, as compared to \$5000 per ton of NO_x , significantly increasing solid waste disposal costs (DeVito and Rosenhoover, 1999; Mendelsohn and Livengood, 2000; Renninger *et al.*, 2004).

Strong variation in ACI removal efficiencies is most likely a function of the coal type (chlorine content). Mercury emissions from bituminous coals reach ninety percent, but only thirty percent of the mercury emissions from subbituminous or lignite coals are removed effectively by ACI (Durham, 2004). Current data indicate that, when using subbituminous coal, there can be an expected collection efficiency of twenty to thirty percent for an ESP. Plants equipped with a bag house demonstrate, on average, a fifty to sixty percent mercury removal rate using the same coal type. When combined in a single system, an ESP-bag house combination is able to remove almost ninety percent of the mercury in the flue-gas of a system burning subbituminous or lignite coal (Buttermore *et al.*, 1995). This requires higher injection rates of ACI as compared to that required for the same mercury removal efficiency burning bituminous coal (Pavlish *et al.*, 2003). It is suggested that improved collection efficiencies of smaller particles will increase mercury collection efficiency and a number of methods have been postulated (Brown *et al.*, 1999).

Combustor Optimization

Mercury control through combustor optimization such as coal reburn technology has been investigated as this staged combustion technique provides a high carbon ash that has been shown to be as effective as ACI at mercury removal (Li and Hwang, 1997; Lissianski *et al.*, 2001; Lissianski *et al.*, 2003; Lissianski *et al.*, 2004, Richardson *et al.*, 2004). A process has been patented whereby semi-combusted coal is injected just downstream of the boiler. This variation on ACI uses partially burned coal in a reburning type configuration to provide the carbon needed for mercury particulate capture at significantly less sorbent cost than ACI (Granite *et al.*, 2004). It has also been documented that injection of high iron ash will increase mercury oxidation (Gale *et al.*, 2003).

Wet Gas Desulphurization

Wet flue gas desulphurization (FGD) or ‘wet scrubber’ units exist in eighty-five percent of the FGD applications with the facilities in which they are installed representing twenty-five percent of the total (Peltier, 2002). Wet FGD systems provide SO_2 and SO_3 control through contact with a lime or limestone slurry in a spray tower. Lime is the more reactive of the two catalysts. Limestone converts sulfur compounds into calcium sulfate and calcium sulfite. FGD systems have been found to remove oxidized mercury but not

elemental mercury (Brown *et al.*, 1999). The general mechanism for removing oxidized mercury involves combining HgCl_2 and H_2S so they react in the gas phase producing HgS vapor which precipitates upon adsorption into the aqueous phase and becomes an insoluble solid (Renninger *et al.*, 2004). Conversion of elemental mercury to the oxidized form was found to be integral to wet scrubber mercury removal efficiency (Livengood *et al.*, 1996; Niksa and Fujiwara, 2004) implying that the amount of fuel bound chlorine is key to high scrubber efficiency (Yan *et al.*, 2003; Lewandowski *et al.*, 2004).

Using the nominal lime/limestone scrubber FGD, removal efficiencies have ranged from seven to forty-eight percent removal by fly ash, while the average mercury removal across the entire FGD system has ranged from forty-five to sixty-seven percent (Brown, *et al.*, 1999; DeVito and Rosenhoover, 1999). Wet scrubber efficiencies have been increased by increasing the gas/liquid area, or with the addition of oxidizing additives (Livengood *et al.*, 1995a; Livengood *et al.*, 1995b, Livengood and Mendelsohn, 2000; Livengood and Mendelsohn, 2001; Milobowski *et al.*, 2001). Unmodified lime spray dryer efficiency has been noted as thirty to fifty percent while addition of activated carbon can increase collection efficiencies to more than ninety percent (Gleiser and Felsvant, 1994; Serre *et al.*, 2000). Other researchers have reported variable mercury removal efficiencies for unmodified systems up to ninety-five percent, with that percentage dependent on the amount of oxidized mercury present (Chu and Porcella, 1995; Cooper and Alley, 2002). Catalysts have also been evaluated for use. Catalyst type, life cycle and regeneration cost is of great concern in this application (Richardson *et al.*, 2000; Blythe *et al.*, 2001; Blythe *et al.*, 2004).

The wide range of mercury removal efficiencies across FGD systems has lead researchers to consider mercury reduction reactions. Oxidized mercury reduction to elemental mercury across a scrubber has also been observed. Mechanistically it is believed that interaction of oxidized mercury with sulfur ions is the most likely reduction pathway (Brown *et al.*, 1999; Chang and Ghorishi, 2003; Blythe *et al.*, 2004). The solution chemistry of the liquid in the FGD determines mercury removal efficiency. The mechanism follows a path of oxidized mercury becoming ionized in solution and subsequently reacting with other dissolved elements in the slurry. These include cobalt, iron, manganese, nickel, sulfite (Blythe *et al.*, 2004), and tin. The sources of such are considered to be the entire scrubber system: the lime (or limestone), water, grinding medium and fly ash not collected in the ESP or baghouse (Renninger *et al.*, 2004). Aqueous sulfite and/or bisulfite species are also found to reduce oxidized mercury in FGD systems (Chang and Ghorishi, 2003).

Catalysts

Investigations into the combined use of wet scrubbers combined with ultrasonic injection of liquid sorbents or catalysts have also been pursued. These experimental investigations focused upon transformation of vaporized elemental mercury into the liquid form. Although partitioning was not investigated, it is probable that nearly one hundred percent elemental mercury removal was achieved through oxidation. These bench scale tests require additional investigation for determination of large scale practicality (Martin *et al.*,

1999; Mendelsohn and Livengood, 1999; Livengood and Mendelsohn, 2000). Use of chlorine or chloric acid solutions held promise in the laboratory (Mendelsohn and Livengood, 1999; Roy and Rochelle, 2001), however attempts at injecting vaporized chloride or chloric acid directly into the flue gas at full-scale caused significant corrosion in the boiler and air pre-heater plugging (Mendelsohn and Livengood, 1999; Peltier, 2003; Richardson *et al.*, 2003). Use of solid catalytic oxidation to enhance mercury removal efficiency in FGD systems has also been investigated. The catalyst is suspended in the flow stream on extruded pellets or wash coated honeycomb supports with the latter showing a higher collection efficiency (Blythe, *et al.*, 2001).

Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR)

The Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR) methods for NO_x control affect the flue gas mercury speciation and, when installed upstream of a FGD, are believed to improve FGD mercury removal through enhanced mercury oxidation. These SCR and SNCR processes utilize urea or ammonia in a reduction reaction with NO_x to form water and elemental nitrogen. The titanium and vanadium oxides used as catalysts in SCR promote mercury oxidation (Richardson *et al.*, 2002; Lee *et al.*, 2004; Richardson *et al.*, 2003). Mercury is found to oxidize across these systems with the presence of HCl (Lee *et al.*, 2003; Renninger, 2004). Systems with longer residence time had better oxidative results (Lee *et al.*, 2003; Renninger *et al.*, 2004). Additional research has shown NO_x as a promoter of mercury oxidation and SO_2 and H_2O as key factors in oxidized mercury reduction in the presence of fly ash (Lee *et al.*, 2000). Both the SCR and SNCR have limitations, either in terms of mercury removal efficiency, operating and maintenance cost, installation difficulties and flue gas contamination (Ferrell and Ellison, 2004). Laboratory data indicate a larger oxidation fraction than what has been measured at full scale. Results indicate a reduction in mercury oxidation efficiency only when burning bituminous coals. Additional testing is required to quantitatively evaluate SCR and SNCR mercury oxidation efficiencies (Pavlish *et al.*, 2003).

Multiple APCD Systems

In general, mercury is under controlled in most coal-combustion systems. Reconfiguration to systems with multiple APCDs, especially wet scrubbers, is inevitable for very high efficiency mercury removal (Lewandowski *et al.*, 2004). The cost associated with these upgrades, especially multiple APCDs, is expected to be high. Plants burning bituminous coals and equipped with wet scrubbers are expected to incur the lowest cost burden for mercury removal. The highest costs are expected from these plants burning subbituminous coals or lignite coals. Cost and performance estimates for full scale deployment of the technologies described above are currently preliminary and will become more accurate as the various technologies mature (Srivastava *et al.*, 2004).

Summary

In summary, physical coal cleaning mechanisms currently in use may remove between zero and sixty percent of the mercury in raw coal. Mercury removal across ESPs averaged four percent for hot side ESPs and twenty seven percent for cold side ESPs. Fabric filter mercury removal is more efficient than ESP systems removing an average of fifty eight percent. Addition of ACI to a plant has resulted in mercury removal efficiencies between twenty five and ninety five percent. FGD systems are installed on twenty five percent of the coal-fired utility boilers and remove up to ninety percent of oxidized mercury, leaving elemental mercury levels untouched. A fluidized bed combustor in combination with baghouse has demonstrated an average mercury removal efficiency of eighty six percent which is attributed to high carbon fly ash. SCR and SNCR technologies oxidize mercury but are yet to be adequately quantified. High mercury removal efficiencies may be achieved in one facility while implementation of the same configuration on another will produce completely different mercury removal efficiencies (Pavlish *et al.*, 2003).

Mercury oxidation is a key contributor to high mercury collection efficiencies that are desirable in today's regulatory market. Mercury oxidation by chlorine has been determined to be a significant promoter of mercury removal in APCDs, with coal chlorine content often driving the market value of certain coals. Sufficient chlorine is needed in the flue gas to drive the mercury speciation toward oxidized mercury for high efficiency mercury removal in all APCDs discussed. Mercury oxidation characteristics for both homogeneous and heterogeneous mechanisms are discussed below.

3.0 Known Mercury Oxidation Characteristics

3.1 Overview

Mercury chlorination by homogeneous gas phase reactions is considered to be an important mercury oxidation mechanism in coal combustion flue gas. Other homogenous mercury oxidation reaction pathways also exist, but are considered minor contributors. The species involved in these reactions include oxygen, nitrogen dioxide and nitrogen oxide (Pavlish *et al.*, 2003). Heterogeneous reactions involving mercury oxidation have been documented primarily involving surfaces and fly ash. Understanding the chemical kinetics and rate controlling mechanisms with regard to mercury and chlorine in the coal combustion system and is critical in understanding and controlling mercury emissions from coal-combustion sources (Brown *et al.*, 1999; Seeker and Hickerson, 1994; Mendelsohn and Livengood, 2000; Livengood *et al.*, 2003).

Coal combustion flue gases always contain nitrogen, oxygen, water, carbon dioxide, carbon monoxide and oxides of nitrogen. Typical raw gas constituents are listed in Table 3.1. Other constituents may include ammonia, chlorine, hydrogen chloride, hydrogen sulfide and sulfur dioxide, the amount of which is primarily dependent on the fuel composition. Mercury species are present in flue gas in widely varying amounts due to the wide dissimilarity of coal combustion processes and fuel types in each application making it a challenge to measure and predict. The speciation of mercury within the coal-combustion flue gas is dependent on many physical variables. This implies that conditioning of either the combustion process or flue gas itself may alter the mercury speciation within the flue gas making it more favorable for removal in standard air pollution control devices. For these reasons, a shift toward oxidized mercury fraction in the flue gas would increase mercury removal efficiency. Partial oxidation of mercury (approximately forty to eighty percent) has been observed when sufficient amounts of chlorine species are present in the coal (Livengood and Mendelsohn, 1997).

Species	Concentration
O ₂ (%)	4-10
CO ₂ (%)	10-16
CO (ppm)	10-100
NO (ppm)	100-1000
NO ₂ (ppm)	5-50
SO ₂ (ppm)	100-2000
HCl (ppm)	1-100
NH ₃ (ppm)	5
N ₂ O (ppm)	5-200
Hg (μg/m ³)	1-5

Table 3.1: Coal Combustion Flue Gas Constituent Concentrations (Hall *et al.*, 1991).

A goal of achieving cost effective methods of mercury oxidation in flue gas has motivated a number of investigations into the homogeneous and heterogeneous oxidation processes of mercury. Historically, homogeneous reactions have been believed to be the dominant mechanism for mercury oxidation. More recent work has implicated heterogeneous reactions to be as important as a pathway for mercury oxidation as both homogeneous and heterogeneous mercury oxidation pathways have both been observed experimentally (Fujiwara *et al.*, 2002). Experts have listed gas and solid phase reactions as well as elemental mercury, chlorine and hydrochloric acid mechanisms as priorities in gaining a better understanding of mercury oxidation phenomena in coal combustion flue gas (Livengood *et al.*, 2003).

Equilibrium and elementary reaction kinetics in current models do not adequately describe gas phase mercury reactions in coal-combustion flue gas (Lu *et al.*, 2004). Ongoing computer modeling efforts include optimization of the chemical kinetic mechanisms for both homogeneous and heterogeneous pathways, and the anchoring of said mechanisms to experimental data. Development of a comprehensive model for mercury oxidation would reduce the costs associated with development and implementation of flue gas cleaning systems specifically targeted at mercury collection and removal. This development effort has included collection of empirical data regarding mercury oxidation in bench, pilot and full-scale configurations and chemical kinetic models of both homogeneous and heterogeneous reactions representative of the empirical data. The history and current state of the art of mercury oxidation understanding, and the pertinent experimental and analytical databases from the literature are discussed.

3.2 Homogeneous Mercury Oxidation by Chlorine Species

The Basis for Oxidation Mechanism Development

Mercury possesses a very low vaporization temperature, thus being completely in the vapor state during the coal combustion process. Thus if no other chemical reactions take place, only elemental mercury will be present in the flue gas. This is not the case in actual practice. In the flue gas, elemental mercury is dominant at temperatures over 675 K (Rizeq *et al.*, 1994). As the flue gas makes its way through the exhaust system, through the air pollution control devices, and up the stack some portion of the elemental mercury will oxidize. Oxidized mercury has been found to only exist in coal-combustion exhaust when chlorine is present and mercury is readily oxidized by chlorine (Hall *et al.*, 1991; Sliger and Kramlich; 2000; Lee *et al.*, 2004). Oxidized mercury in coal-combustion flue gas has been shown to be almost exclusively HgCl_2 (Galbreath and Zygarlicki, 1998).

Raw coal contains trace amounts of chlorine as shown in Table 2.3. Chlorine is present in amounts significant enough to cause up to ninety percent oxidation. Elemental mercury will also be oxidized in the presence of hydrogen chloride (Hall *et al.*, 1991; Livengood and Mendelsohn, 1998). Although homogenous gas phase reactions have historically been considered the dominant mechanism, there is some disagreement (Fujiwara *et al.*, 2002).

Data comparisons

Field data indicate significant variation in the amount of mercury oxidized upstream of air pollution control devices (Brown, 1999), however a rough correlation has been made between chlorine present in the coal and amount of oxidation present as shown in Figure 3.1. The data scatter has been attributed to many factors some of which include boiler design, fuel make-up, ash properties, flue gas conditioning, and the number and type of APCDs, all of which are considered significant factors in determining the amount of oxidation that will occur. Additionally, mercury oxidation rates are known to be affected

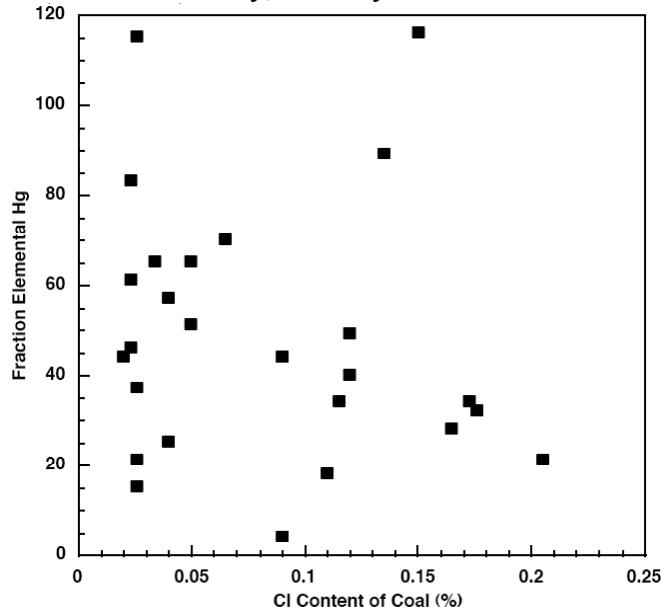


Figure 3.1: Influence of Coal Chlorine Content on the Oxidation State of Mercury Upstream of Flue Gas Cleaning Equipment From Hall *et al.*, 1991 (Kramlich and Sliger, 2000).

by the atomic chlorine concentration and gas cooling or quench rate (Widmer *et al.*, 1998; Kramlich and Sliger, 2000,) but may be dependent on the complete time and temperature history of the flue gas for homogeneous gas phase reactions (Wang *et al.*, 2003), however this has been disputed (Fujiwara *et al.*, 2002).

The mercury oxidation rate is independent of the coal mercury content as the concentration of chlorine in the flue gas is at super-equilibrium levels relative to that of mercury, and reactions with mercury do nothing to alter their overall concentration. Other flue gas reactions determine the overall concentrations of all constituents relative to the oxidation of mercury (Senior *et al.*, 2000).

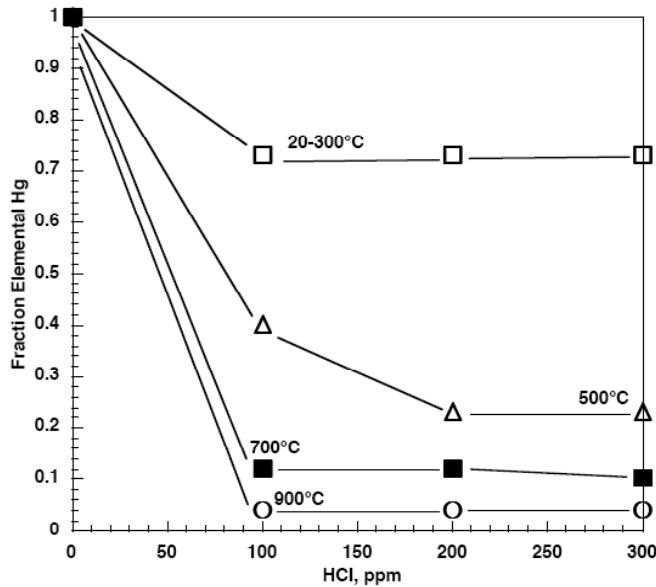


Figure 3.2: Data Showing the Oxidation of Mercury by HCl at Various Temperatures (Hall *et al.*, 1991).

Species other than chlorine or hydrogen chloride that are found in flue gas also affect the oxidation of mercury. Oxygen was found to be a weak oxidant of mercury (Niksa *et al.*, 2001). Water vapor, sulfur dioxide (Widmer *et al.*, 1998, Kramlich and Sliger, 2000) and carbon dioxide were found to inhibit mercury oxidation. Sulfur Dioxide does not react with mercury directly but was found to retard the mercury oxidation process with chlorine. Nitrogen dioxide and is found to also be a mercury oxidant, but to a much lesser degree than chlorine species (Hall *et al.*, 1991). Nitrogen oxide can either promote or inhibit mercury oxidation. This is a function of concentration. When nitrogen oxide is present in the flue gas, extents of mercury oxidation increase under conditions of rapid quenching, and when absent the extents of oxidation of mercury diminish (Niksa *et al.*, 2001).

Figure 3.2 illustrates the increasing oxidation rate of mercury by hydrogen chloride with increasing temperature. The data reported in Figure 3.3 agree that chlorine is a more efficient oxidizer of mercury than hydrogen chloride, and increasing chlorine species concentration increases mercury oxidation (Widmer *et al.*, 1998; Galbreath *et al.*, 1998, Lee *et al.*, 1998; Kramlich and Sliger, 2000). It is also depicted that mercury oxidation increases with increasing temperature. Non-isothermal mercury oxidation efficiencies included in Table 3.6 show conflicting results over widely varied conditions and are depicted in Figure 3.2 (Hall *et al.*, 1991; Mamani-Paco and Helble, 2000).

Global oxidation of mercury with primary oxidants chlorine and hydrogen chloride does occur and the reactions are generally homogeneous in nature. Molecular chlorine is more effective than hydrogen chloride as shown in both Tables 3.5 and 3.6. The reactions with hydrogen chloride are applicable in this as the chlorine that is released from coal combustion, operating in fuel-lean conditions, will appear as hydrogen chloride.

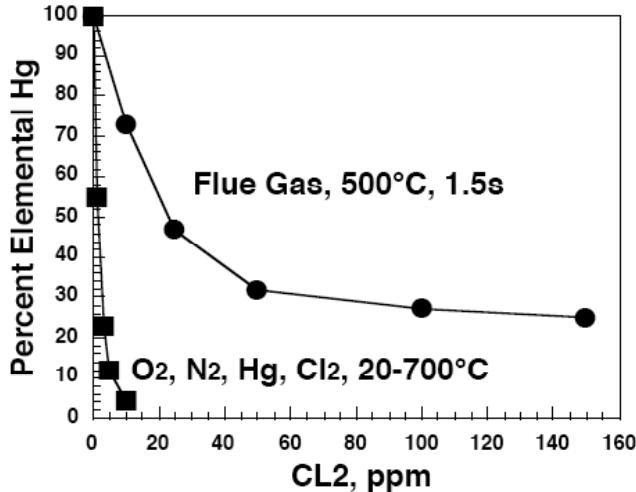


Figure 3.3: The influence of Cl_2 Concentration on Mercury Oxidation Characteristics (Hall *et al.*, 1991).

Both isothermal and non-isothermal experiments investigating mercury transformation kinetics have been conducted by a number of researchers. The isothermal mercury oxidation experiments are summarized in Table 3.5, while the non-isothermal tests are presented in Table 3.6. The isothermal experiments (Sliger *et al.*, 2000; Lee *et al.*, 1998; Gaspar *et al.*, 1997; Hall *et al.*, 1991; Widmer *et al.*, 1998) presented in Table 3.5 cover a range of variables: mercury concentration, temperature, residence time, quench rate and oxidizing species, as well as the concentration variation for mercury and chlorine species. The non-isothermal experiments in Table 3.6 (Hall *et al.*, 1990; Hall *et al.*, 1991; Galbreath and Zygarlicki, 1998; Mamani-Paco and Helble, 2000,) show mercury oxidation efficiencies to vary widely from none to one hundred percent conversion for all cases described. General conclusions may still be reached from the data: increasing chlorine content, whether from hydrogen chloride or chlorine, causes increased oxidation.

It should be noted that all of the experiments currently being discussed used mercury concentrations in excess of what is found in full scale testing of coal combustion flue gas.

Coal chlorine is released primarily as hydrogen chloride during the coal combustion process. Data comparisons for mercury oxidation with hydrogen chloride are presented graphically in Figures 3.4 and 3.5 for different test programs. Details of each test configuration are presented in Table 3.7. All test performed utilized mercury concentrations greater than that found in coal combustion flue gas. The former presents data from test configurations with different carrier gas species present but shows a general trend in that increased mercury oxidation is realized from increased hydrogen chloride concentration. Data shown in Figure 3.5 indicate a trend of increasing mercury oxidation with increasing temperature. Major variations between experimental data are attributed to differences in experimental gas constituents and test conditions and may be explained by insight gained from chemical kinetic modeling (Kramlich and Sliger, 2000; Niksa, *et al.*, 2001; Senior *et al.*, 2002). The gas constituents for the experiments of Figure 3.5 are tabulated in Table 3.8.

	Sliger and Kramlich, 2000	Lee <i>et al.</i> , 1998	Gaspar <i>et al.</i> , 1997	Hall <i>et al.</i> , 1991	Widmer <i>et al.</i> , 1998			
Gas Species	-	-	-	-	-			
	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂			
	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O			
	O ₂	O ₂	O ₂	O ₂	O ₂			
	N ₂	N ₂	N ₂	N ₂	N ₂			
	HCl	HCl	HCl	HCl	HCl			
	-	-	-	Cl ₂	-			
	-	SO ₂	-	SO ₂	-			
	-	-	-	H ₂ S	-			
	-	-	-	NH ₃	-			
Mercury Concentration (μg/m ³)	53 137	400	3000	100	370 ppb			
Oxidizing Species Concentration (ppm)	HCl 10-100	HCl 50,100, 200	Cl ₂ 11- 50	HCl 300 3000	HCl 100- 300	Cl ₂ 2-10	HCl 300-3000	
Temperature (K)	1333-1344	423-1027	696-1149	293-1173	693-1153			
Particulate Loading	No	No	No	No	No			
Residence Time (s)	1.4	2	0.7	2.8, -0.7	1			
Mercury Oxidation (%)	0-75	HCl 27	Cl ₂ 100	HCl (300) 20-80	HCl 30- 95	Cl ₂ 50- 95	HCl (3000) 40-98	HCl 20-98
Combustion Source	Natural Gas	Simulated	Simulated	Simulated	Simulated	Simulated		
Cooling Rate (K/s)	5600	Undefined	Undefined	Undefined	Undefined	Undefined		

Table 3.5: Isothermal Mercury Oxidation Experimental Comparison (Mamani-Paco and Helble, 2000).

	Galbreath and Zyglicki, 1998	Hall <i>et al.</i> , 1991		Hall <i>et al.</i> , 1990		Mamani-Paco and Helble, 2000				
Gas Species	CO	CO		CO		CO				
	CO ₂	CO ₂		CO ₂		CO ₂				
	-	H ₂ O		H ₂ O		H ₂ O				
	O ₂	O ₂		O ₂		O ₂				
	-	N ₂		N ₂		N ₂				
	HCl	HCl		HCl		HCl				
	-	Cl ₂		-		-				
	SO _x	-		-		-				
	-	-		-		-				
	-	-		-		-				
Mercury Concentration(μg/m ³)	10	140		150	50					
Oxidizing Species Concentration (ppm)	HCl 10-100	HCl 11,1 50	Cl ₂ 11-150	HCl 250	HCl 100- 500	Cl ₂ 50- 500	HCl+CL ₂ 150+50			
Temperature (K)	473	773		>773	563, 693, 793					
Residence Time (s)	2.5	1.5		0.8	1.4, 3.6, 6.2, 9.0					
Particulate Loading	Y/N	No		ACI	No					
Mercury Oxidation (%)	10 ppm HCl	100 ppm HCl	HCl	Cl ₂	HCl	O ₂	HCl	HCl+CL ₂		
	0-50	70-80	62	70	70	20-30	2	10		
Combustion Source	SB Coal		Propane		Propane		Methane			
Cooling Rate (K/s)	420		200-300		Undefined		40-400			

Table 3.6: Non-Isothermal Mercury Oxidation Experimental Comparison (Mamani-Paco and Helble, 2000).

Name	Experiment	Comments on Experimental Data	References
Ghorishi	Flow tube, HCl, no water, 2% O ₂	Oxidation is much lower than Hall's data (no water). O ₂ is low (2%) compared to Hall (10%).	S. B. Ghorishi, <i>et al.</i> , 1998; J.R. Edwards, <i>et al.</i> , 2001.
Hall	Flow tube, HCl, no water, 10% O ₂ , effect of temperature, $\tau = 1\text{s}$	High oxidation (>50%) for all temperatures except 573 K.	B. Hall, <i>et al.</i> , 1991.
Sliger (1)	Flow tube, effect of water and HCl, 11% O ₂ $\tau = 1\text{s}$	Oxidation consistent with Hall (no water)=> nearly complete at ~1200 K. Water inhibits oxidation.	R.N. Sliger, <i>et al.</i> , 2000; R.N. Sliger, Ph.D. Thesis, University of Washington.
Sliger (2)	Nat. gas flame, HCl added after flame, high cooling rate, 25 ppm NO, $\tau = 0.5\text{s}$	Experimental data: Lower oxidation observed in tunnel furnace than in quartz furnace. Why? -Higher O ₂ in quartz furnace -25 ppm NO in tunnel furnace -wall effects in quartz furnace - radicals from flame	R.N. Sliger, <i>et al.</i> , 2000; R.N. Sliger, Ph.D. Thesis, University of Washington.
UConn	CH ₄ flame, HCl or Cl ₂ added after flame; low cooling rate, ~100 ppm NO	Conversion ($\phi = 0.9$) lower than Sliger ($\phi \sim 0.8$); effect of O ₂ or cooling rate?	Qiu, <i>et al.</i> , 2003
Widmer	Flow tube, high HCl, 10% O ₂ , effect of initial temperature, $\tau = 1\text{s}$	300 ppm results consistent with Sliger at 8% O ₂ . High oxidation at temperatures <900 K	J.A. Gaspar, <i>et al.</i> , 1997; J.R. Edwards, <i>et al.</i> , 2001.

Table 3.7: A Comparison of Test Conditions for Quartz Flow Reactor Data (Lighty *et al.*, 2004).

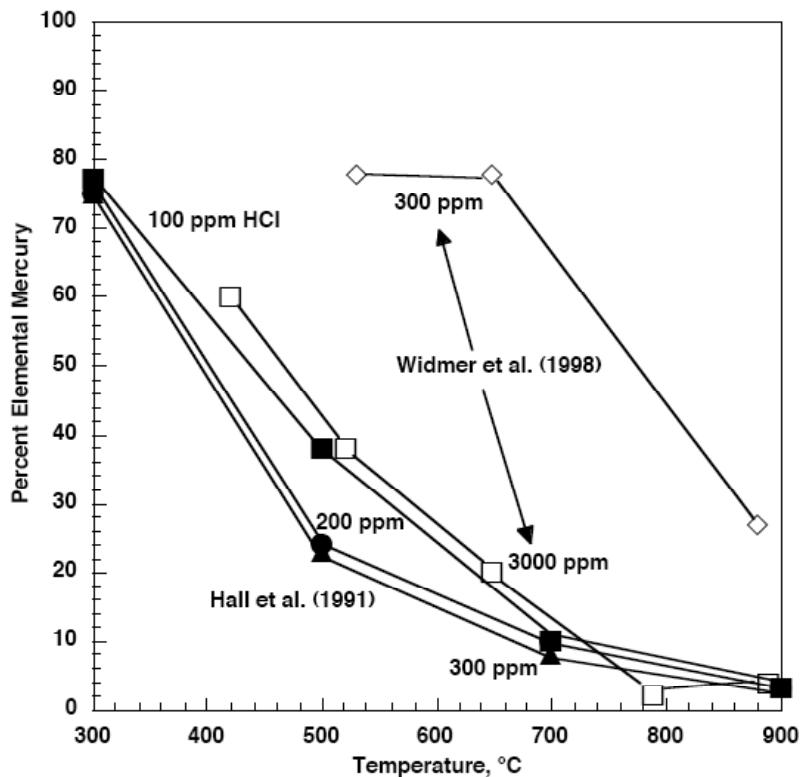


Figure 3.4: Comparison of Mercury Oxidation by HCl under Flue Gas Environments, CO_2 and H_2O -Free Artificial Atmospheres and Simulated Flue Gas (Sliger *et al.*, 2000).

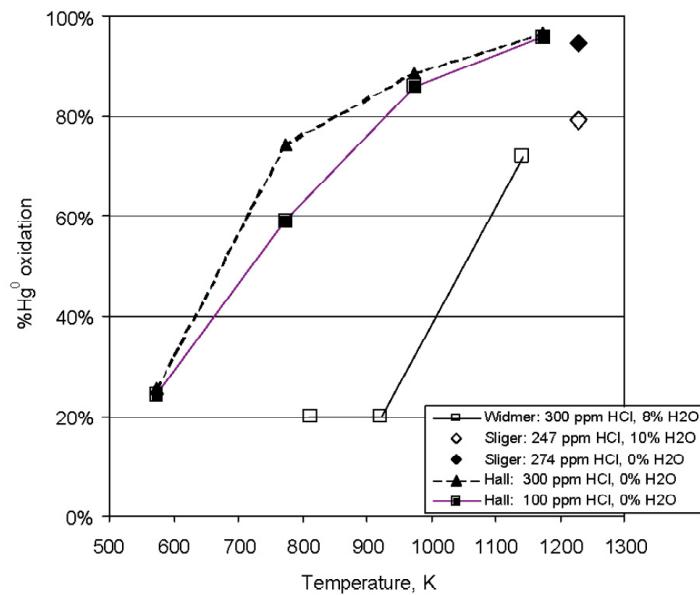


Figure 3.5: Comparison of Laboratory Scale Quartz Reactor Data (Lighty *et al.*, 2004).

	Ghorishi	Hall	Sliger	Widmer
N ₂ vol %	93.0%	90.0%	Balance	72.0%
O ₂ vol %	2.0%	10.0%	11.0%	10.0%
CO ₂ vol %	5.0%	0.0%	0.0%	10.0%
H ₂ O vol %	0.0%, 50-200	0.0% 100-300	0-14% 39, 274	8.0% 300,3000
Hg ppm	0.04	0.12	0.10	0.37
Cl/Hg ratio	1250-5000	800-2500	390-2700	800-8000

Table 3.8: A Comparison of Gas Constituents found in Quartz Reactor Tests (Lighty *et al.*, 2004)

Conflicting with most homogenous experimental results, laboratory tests using a stoichiometric flame with no particulate matter or fly ash resulted in no appreciable mercury oxidation by chlorine at temperatures below 773 K. This implies that any oxidation that is observed at low temperatures may be caused by gas-solid surface reactions. Further, these results indicated that mercury concentrations in flue gas may be insufficient for significant mercury oxidation to occur by homogeneous reactions alone and that additional research is needed to separate the homogeneous and heterogeneous reaction paths (Mamani-Paco and Helble, 2000).

Equilibrium

Under equilibrium conditions, decreasing temperatures below 673 K causes a shift from elemental mercury to a predominance of oxidized mercury in the form of HgCl₂.

Equilibrium calculations for mercury and hydrogen chloride at various temperatures and hydrogen chloride concentrations are provided in Figure 3.6 illustrating that as the gas temperature decreases, the equilibrium concentration of mercuric chloride (HgCl₂) increases (Hall *et al.*, 1991; Widmer *et al.*, 1998). When hydrogen chloride concentration is varied from fifty to five hundred pars per million, the 50% equilibrium conversion point, or cross over temperature, shifts upward from 798 K to 913 K. These trends are influenced by variation in mercury concentration, and are consistent with other reported data (Gullett, 1994, Rizeq *et al.*, 1994; Senior *et al.*, 2000). Over this temperature range chlorine will recombine to form Cl₂ and HCl and, depending on conditions, may exist as Cl₂ or Cl (Kramlich and Sliger, 2000). There is disagreement between the equilibrium results and collected reactor data where Cl₂ was found to react rapidly with mercury models leads to the conclusion that mercury chemistry is frozen at 825 K (Senior *et al.*, 2000). As the temperature decreases from that at the boiler exit to 1300 K, equilibrium models are applicable. At lower temperatures, the reaction rates drop exponentially until

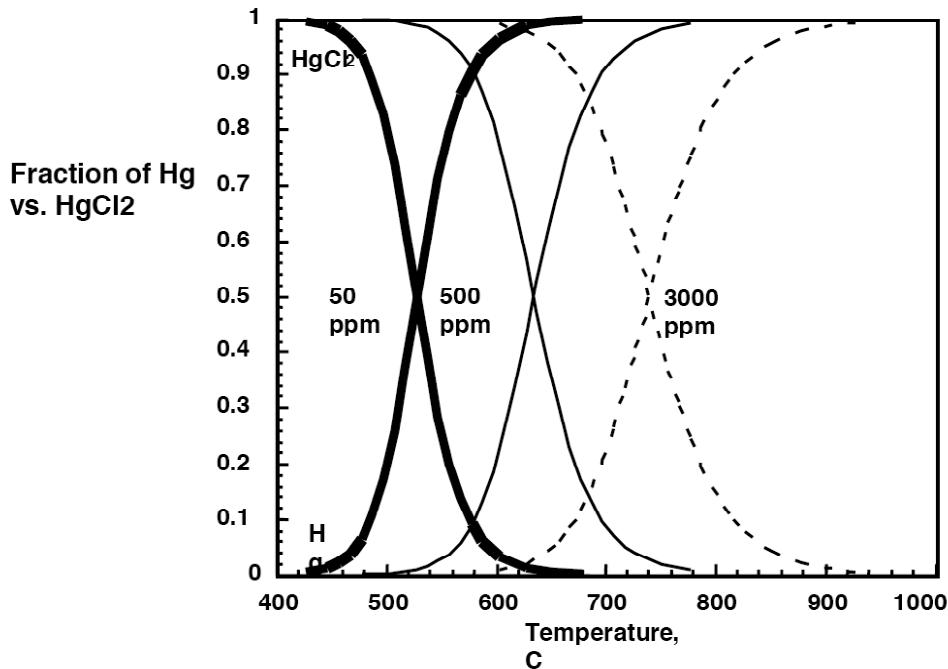


Figure 3.6: Equilibrium Mercury Oxidation Behavior as a Function of Temperature (Sliger *et al.*, 2000).

the reaction is frozen (Widmer *et al.*, 1998). Frozen equilibrium does not account for the effects of cooling rate on mercury oxidation mandating the use of chemical kinetic models that encompass major mercury reaction pathways for accurate mercury speciation predictions in the flue gases (Mamani-Paco *et al.*, 2000).

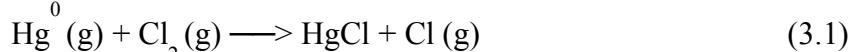
Comparison of the data in Tables 3.5, 3.6, and Figure 3.2 with the equilibrium model in Figure 3.6 indicated a conflict between equilibrium prediction and actual mercury measurements for mercury speciation. The implication is that overriding kinetic limitations exists. This disagreement with equilibrium calculations also implies that there is a chemical kinetic constraint on mercury oxidation under real world conditions. The mercury is believed to be speciated during the quenching of the flue-gas somewhere between the furnace exit and the stack (Senior *et al.*, 2000; Sliger and Kramlich, 2000; Livengood *et al.*, 2003; Lu *et al.*, 2004).

At high temperatures (above 400 °C) volatized mercury and hydrogen chloride both exist in an elemental vapor state. The use of equilibrium modeling at these temperatures has been shown to be invalid (Rizeq, *et al.*, 1994; Senior *et al.*, 1997; Brown *et al.*, 1999; Senior *et al.*, 2000; Sliger and Kramlich, 2000,) but provides insight into the chemical kinetic mechanism and initial estimates of mercury speciation. If speciation were equilibrium controlled, all flue gas mercury would be converted to mercury chloride in the presence of excess chlorine, which is contradictory to real conditions. Full-scale data report that between twenty and fifty percent of the mercury that leaves the stack is in the form of elemental mercury, even with adequate excess chlorine (Senior *et al.*, 2000).

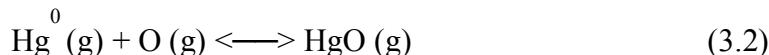
Chemical Kinetics

Comparisons of equilibrium modeling with bench-scale and field data indicate that chemical kinetic limitations are associated with mercury oxidation mechanisms in coal combustion flue gas. Chemical kinetic modeling provides a method to obtain mercury accurate speciation in this application. The mercury reaction set is yet still under development. The model, in particular the reaction mechanism and rate coefficients, has progressed over the years with recent developments in reaction rates improving accuracy of modeling over the entire range of temperatures found in coal combustion flue gas from the boiler to the stack exit. Each kinetic model was formed or modified to provide a better match to empirical data. Some models proved more accurate than others, but none to date provides a mechanistic tool for accurate analysis of mercury oxidation by chlorine under all flue gas conditions. Without a detailed discussion of the individual successes and failings of each set of combustion reactions, they are presented below. In this manner a more consistent explanation of additions and modifications to the overall mechanism and the logic behind each is presented. Subsequently a discussion of the results drawn from kinetic modeling efforts will be discussed.

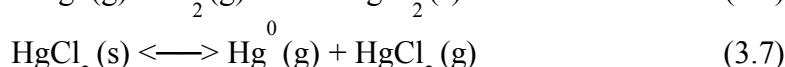
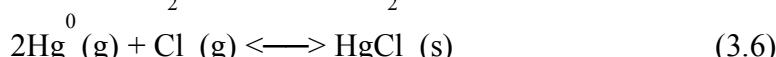
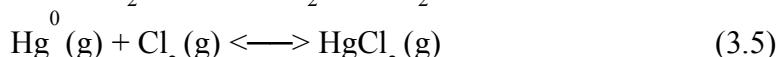
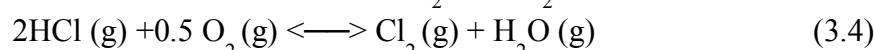
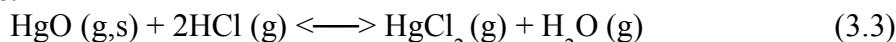
The historical foundation of mercury oxidation kinetics was the 1949 proposal of a one step mechanism for mercury oxidation by chlorine given by Equation 3.1. This pointed



to an intermediary step in the oxidation pathway of Hg^0 to HgCl_2 , requiring a reaction with either Cl or Cl_2 for full oxidation to HgCl_2 (Livengood *et al.*, 2002). Investigations by Hall into mercury reactions in flue gas began in earnest with the definition of a mechanism in 1990 for the oxidation of mercury by oxygen over the temperature range of 475-775 K by the reaction

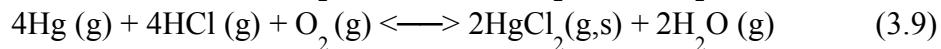
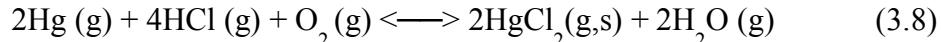


(Hall *et al.*, 1990). A general chemical kinetic reaction set for mercury oxidation was also proposed by Hall for chlorine formation from hydrogen chloride in 1991. The reaction set was empirically determined and is defined by equations 3.3 to 3.7. This was the first multi-step chemical kinetic mechanism for the oxidation of mercury by chlorine to be put forth in the literature.

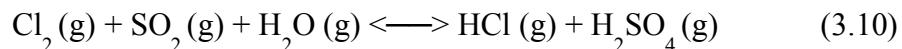


In addition, Hall proposed two possible overall reactions for mercury oxidation that were defined as Equations 3.8 and 3.9 (Hall *et al.*, 1991). Because the sum of Equations 3.2 and 3.3 yields Equation 3.8, below, a possible intermediate step is postulated to be the

formation of HgO as an intermediate species in the mercury oxidation mechanism. This formulation is not generally utilized in current overall mercury oxidation mechanisms (Livengood *et al.*, 2002).

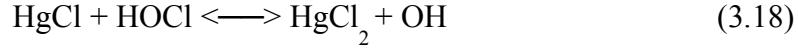
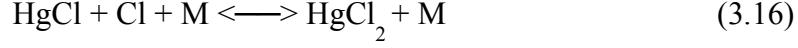
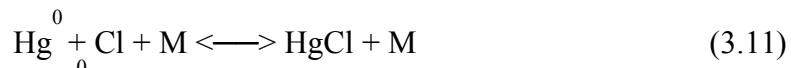


Mercury oxidation is inhibited by the presence of sulfur dioxide in flue gas. In 1999 a reaction was proposed by Ghorishi for this phenomena and put forth as



where the scavenging of Cl_2 by SO_2 is shown as the inhibiting mechanism (Ghorishi *et al.*, 1999).

An eight step reaction mechanism was put forth by Widmer in 2000 describing the formation of mercury chloride. The reaction set (2000a) includes Equations 3.11 to 3.18. Rate constants were estimated from the literature (Widmer *et al.*, 2000). Qualitative evaluation of these reactions has shown that fast oxidation of Hg occurs through the reaction in Equation 3.11.



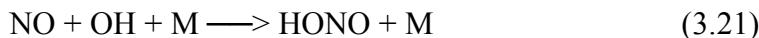
Modifications to the 2000 mechanism (2000b) were made by Sliger to improve accuracy. Equation 3.19, the reverse of equation 3.12, was added to the mechanism. However, it was determined that the abstraction path for production of mercury, equation 3.20, must also be considered, therefore providing a twelve step reaction mechanism (Sliger *et al.*, 2000).



Two mechanisms were developed independently in 2001. The first by Edwards (2001a) was developed to model bench-scale experimental data by Widmer and Ghorishi (Widmer *et al.*, 1998; Ghorishi, 1998) by reworking the 2000 reaction mechanism to include a total of sixty reactions involving 21 different species (Edwards *et al.*, 2001). The 2001 model was used as the baseline to which was added the reaction in equation 3.1 for mercury oxidation by oxygen. In addition to the mercury-chlorine reaction

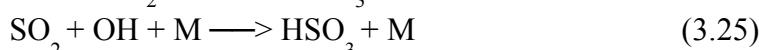
mechanism of 2000, and the mercury-oxygen reaction mechanism of 1990, a fourteen step mechanism for the production of chlorine and atomic chlorine from various chlorine containing species (Cl, Cl₂, ClO, HCl and HOCl). The set forms an 18 step reaction mechanism. To this was added a twenty five step hydrocarbon mechanism involving hydrogen, oxygen and carbon monoxide and a fourteen step mechanism for the carbonyl chloride (COCl) and formyl radical (CHO). This model was only shown to be accurate in the high temperature regime.

Niksa put forth the second 2001 mechanism, 2001b. This mechanism was based on the 2000a, eight-step mercury oxidation mechanism, with the addition of sub-mechanisms for coupling chlorine chemistry with the chemistry of nitrogen oxides, carbon monoxide oxidation and H/N/O. This mechanism was anchored against experimental data from Hall, Mamani-Paco, Sliger, and Widmer (Hall *et al.*, 1991; Mamani-Paco *et al.*, 2000; Sliger *et al.*, 2000; and Widmer *et al.*, 1998). Results indicate only high temperature data are modeled accurately and mercury oxidation predictions were over predicted by the model. This was attributed to the presence of nitrogen oxide and water and the postulated reaction given by the reaction



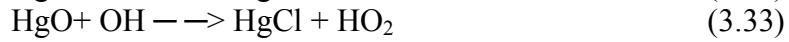
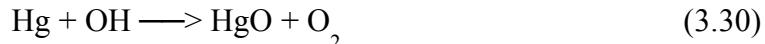
(Niksa *et al.*, 2001). The extremely complex nature of the effect of NO across the temperature range of interest was not apparent until the development of this particular chemical kinetic mechanism (Livengood *et al.*, 2002).

Enhancements to the overall reaction mechanism in 2003 by Qui added reactions for the additional species sulfur monoxide and sulfur monochloride as well as reactions for reduction of OH radicals and subsequent reduction in HOCl radicals. This is represented by the inclusion of the reactions in equations 3.22 through 3.26 in the mechanism. (Qiu *et al.*, 2003). These reactions provide additional paths for the generation of chlorine atoms.



A more fully evolved chemical kinetic reaction mechanism (2003) was also put forth by Xu in the year 2003. This mechanism consists of 107 reactions and 30 species, including a six step mechanism for reactions involving HgO (Xu *et al.*, 2003). The HgO mechanism is put forth in Equations 3.28 through 3.33.





3.3 Heterogeneous Mercury Behavior

At least three distinct ways have been suggested for heterogeneous behavior to influence the fate of mercury. These are:

- Interaction of mercury with coal ash.
- Capture of mercury by sorbents (discussed above).
- Promotion of catalytic Cl_2 generation followed by homogeneous mercury oxidation.

The intimate contact that occurs between coal ash and gaseous combustion products raises the issue of whether ash exerts a catalytic influence on oxidation. Early observations suggest that ash might catalytically promote oxidation (Laudal *et al.*, 1997; Karatza *et al.*, 1998). Testing on individual components in fly ash shows that Fe_2O_3 (Ghorishi *et al.*, 1999; Zhuang *et al.*, 2000) and CuO (Ghorishi *et al.*, 1999) can catalytically oxidize mercury in the presence of HCl . However, the presence of CaO tends to deactivate this process (Lee *et al.*, 2000). The powerful catalytic activity of CuO is suggested as one reason why mercury from waste incinerators (which typically contain much more copper in their ash) is so much more oxidized than that from coal combustion (Lee *et al.*, 2000). Some of the other major constituents in ash have been tested (TiO_2 , SiO_2 and Al_2O_3) and found to not be active under HCl (Zhuang *et al.*, 2000; Lee *et al.*, 2000). Recent testing of coal ashes indicate little activity (Norton *et al.*, 2000). Thus, the implication is that while some components of coal ash can promote oxidation under HCl , mixed minerals tend to deactivate this effect.

Ash constituents have been found to promote catalytic oxidation under NO_2 . Both SiO_2 and Al_2O_3 are active under these conditions (Ghorishi *et al.*, 1999). The NO_2 concentrations used in these studies (*e.g.*, 200 ppm) are, however, generally much higher than those found in practice.

The ability of activated carbon to absorb oxidized mercury is well known. Measurements have also shown that carbon in ash can absorb mercury (Hassett and Eylands, 1999). It has been suggested, however, that NO_2 can oxidize mercury off of carbon sorbents (Miller *et al.*, 1998). As mentioned above, a number of treatments for carbon surfaces have been investigated (iodine, sulfur, gold) as means of enhancing capture or promoting oxidation.

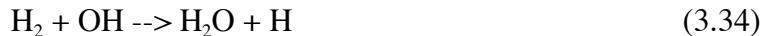
Another oxidation mechanism has been proposed by Senior *et al.* (1997). This is based on the homogeneous oxidation of mercury by Cl_2 . Here, Cl_2 is catalytically generated by the interaction of HCl with fly ash and char. Once formed, the Cl_2 rapidly reacts with the Hg , and the oxidized mercury is partially captured by the char. This idea originates from

mechanisms developed to explain the formation of chlorinated dibenzo-p-dioxins in downstream incineration equipment.

3.4 Objectives

The preceding discussion indicates that improved mercury oxidation results in better capture in existing air pollution control devices. The presence of chlorine enhances oxidation, but the simply adding chlorine to the combustion gases is not a particularly good means of improving capture. The approach proposed here is to improve the performance of existing chlorine as an oxidizer. The data and modeling indicates the availability of Cl-atom in the quench region as the principal barrier to mercury oxidation. Thus, the goal is to increase Cl-atom concentrations at or above the temperature where oxidation starts to occur.

In fuel-lean gases, the introduction of H_2 into the quench region is indicated as increasing OH concentrations via the chain branching sequence:



The OH in turn promotes $HCl + OH \rightarrow Cl + H_2O$. The chlorine atom is then available to force oxidation. The kinetics indicate that this process is sensitive to (1) the temperature within the quench region at which the H_2 is added and (2) the amount of H_2 used. In particular, injection of the H_2 at a higher temperature may tend to reduce Cl by forcing it towards equilibrium (this occurs via $H_2 + Cl \rightarrow HCl + H$). However, injection of H_2 at a lower temperature, and the use of relatively low amounts of H_2 , leads to a selective promotion of Cl concentrations (the reaction noted above, $H_2 + Cl$, slows due to its activation energy). The kinetics suggest that ~50 ppm of H_2 is appropriate. The goal of the work reported here is to experimentally test this hypothesis. The testing also examines the role of NO and SO_2 on any promotion observed.

4.0 Experimental and Numerical Approach and Procedures

4.1 Experimental Apparatus and Procedures

4.1.1 Overview

The main focus of this effort was to measure the amount of mercury oxidized under controlled conditions. The combustion process itself was sidestepped by supplying desired exhaust gas species that were subsequently both mixed and heated to temperature in the quartz reactor. The flow was then quenched to 350 F and the elemental mercury measured using a modified Buck mercury analyzer. Exhaust gasses were safely treated and exhausted to atmosphere. The complete apparatus used to create the flow path consisted of a mercury bubbler, gas supply system, flow panel, gas pre-mixing manifold, clamshell heater, quartz reactor, mercury detector, and impinger system. This system is shown diagrammatically in Figure 4.1 where heated lines are shown in red. Atmospheric pressure was obtained from the University of Washington Atmospheric Sciences web site <http://www.atmos.washington.edu>. A detailed discussion of the hardware configuration follows.

4.1.2 Gas Supply System and Flow Panel

Gas was stored and supplied to the flow panel using specialty mix gases stored in commercial gas storage bottles. All gasses were ultra high purity and were controlled with high precision regulators at 238 kPa. Hydrogen chloride, hydrogen and carbon monoxide gasses were supplied to the system at concentrations of 1500 ppm, balance ultra pure nitrogen. This allowed for introduction at the target concentration of 300 ppm for each of the three mixtures. The nitrogen and the carbon monoxide mix were filtered using activated charcoal filters to prevent reactor contamination. The gas was piped into the flow panel using tubing materials appropriate to the gas species in question. The flow panel both controlled and metered the gasses into manifolds for mixing and delivery to the reactor. Flow circuits were designed to minimized flow circuit volume to reduce species sequestration and to shorten purge and equilibration times. Each gas flow circuit was independent and consisted of an upstream two or three way valve, precision ball valve, flowmeter, pressure gage, and manifold valve. This system allowed for redundant safety and precision flow control. Atmospheric temperature was measured at the flow panel for each data point. A schematic of the flow panel is presented in Figure 4.2. Nitrogen purges were included in reactive gas circuits for both preservation of the equipment and safety. Reactive gas circuit purge was accomplished using gaseous nitrogen introduced through the three way valve located just upstream of the flow metering device.

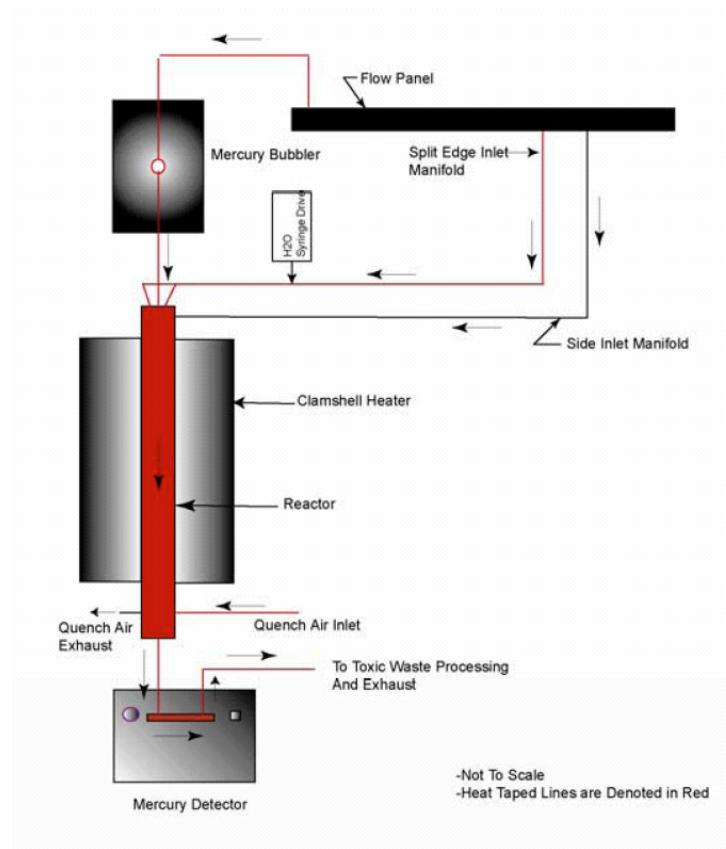


Figure 4.1 Schematic of experimental apparatus.

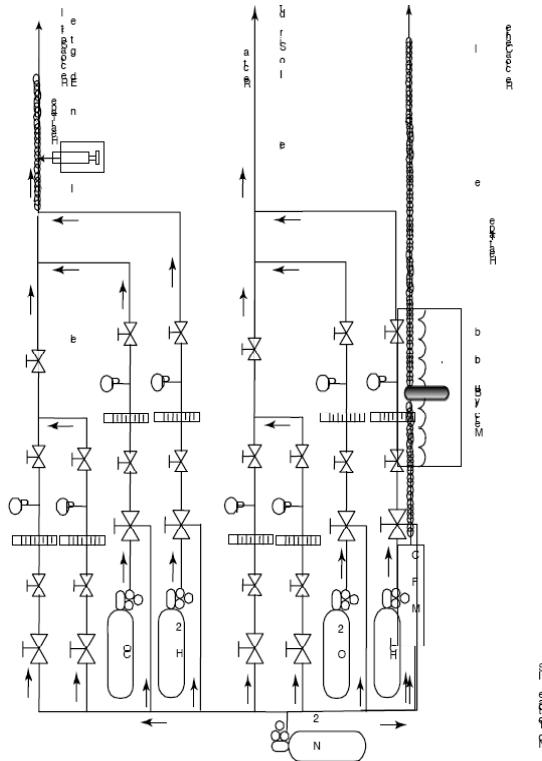


Figure 2.2: Schematic of Flow panel and Manifold System.

Figure 4.2: Schematic of Flow panel and Manifold System.

Premixing was achieved using the gas supply manifolding system, as well as the mixing region located in the reactor. Nitrogen was always used as the carrier gas for subsequently added minority species. Figure 4.2 shows the manifolding structure and grouping of gases. All manifold tubing and fittings were stainless steel wherever possible.

Vaporized mercury was provided to the reactor by saturating gaseous nitrogen that was put in contact with liquid mercury at a temperature specified to achieve the defined mercury concentration. The mercury vaporization system, or mercury bubbler, was constructed by immersing a sealed, mercury filled impinger in a heated distilled water bath. The bath was electrically heated and underwent constant mixing to keep the bath temperature constant. The distilled water bath and mercury impinger, along with impinger support hardware and a thermocouple, were covered with glass to minimize evaporation and to help provide a more constant bath temperature. Figure 4.2 shows bubbler position within the flow system. A Matheson mass flow controller provided accurate flow control for the flow through the bubbler. All surfaces which came into contact with mercury were made of quartz glass to mitigate mercury sequestration. The circuit was constructed of discreet sections of glass tubing two inches long and 0.25 inch diameter. These sections were clamped together. This design gave flexibility to the glass line which would have otherwise been rigid and subject to breakage. Heat tape was used

to maintain the incoming bubbler nitrogen at close to the same temperature as the water bath. Both the water bath and line temperatures were monitored for small variations that would affect the calculated mercury concentration.

Water vapor was supplied to the reactor using a syringe drive, a 50 ml gas-tight syringe with a luer lock fitting. The syringe drive was positioned just upstream of the reactor and was designed to provide water vapor at a flow rate varying from 0.001 ml/min to 10 ml/min. The syringe drive allowed for accurate and variable water injection into a preheated mix of gasses chosen for each run. The water supply line temperature was maintained as close to 394 K as possible using heat tape. Figure 4.2 illustrates the relative position of the syringe drive in the flow circuit.

4.1.3 Clamshell heater and Quartz Reactor

The premixed gasses from the two manifolds are combined in the quartz reactor, which is suspended within a cylindrical clamshell oven. Figure 4.3 presents the quartz reactor. It is designed to provide three distinct zones. The first allows for combining and preheating the premixed gas from the manifold system containing nitrogen, hydrogen, carbon monoxide and water. The reactor flow path turns the flow in two 180° turns while exposing it to temperature, subsequently introducing it to zone 2, a central mixing/reaction chamber. The second premixed line containing nitrogen, oxygen and hydrogen chloride is split at the entrance to the reactor, only to be recombined with the mercury stream within the preheat zone of the reactor at the entrance to zone 2. This mix is then injected into the central mixing chamber through a 0.5 mm choked nozzle providing a turbulent mixing condition. At this point the mercury is combined with a mix of HCl and a combination of H₂ and/or CO, beginning the reaction zone. Previous calculations indicate that mixing occurs within the first 5.6 cm of zone 2, the length of which is 20.3 cm. The last zone of the reactor is the quench region. This portion of the reactor protrudes out the back of the clamshell furnace and is kept at 464 K with preheated gasses manifolded in a way similar to that found in zone 1. A detailed scale drawing of the quartz flow reactor is given in Figure 4.3. The flow schematic is shown in Figure 4.4. Figure 4.5 shows a photograph of the system.

4.1.4 Continuous Ultraviolet Analysis

A modified Buck 400A mercury analyzer was used for continuous mercury monitoring of the flow stream. The Buck Analyzer measures only elemental mercury using ultraviolet optical absorption system and has a sensitivity of 0.01 micrograms of mercury. An absorption cell is suspended between an ultraviolet light source and a UV sensitive photo cell. Only light at 253.7 nm is absorbed by the mercury passing through the cell. The change in energy transmitted to the photo cell is detected, thus the amount of elemental mercury detected is directly related to the amount of light at 253.7 nm which reaches the detector, or percent transmittance. The relationship between mercury concentration in the absorption cell and percent transmittance of the detector are related by Beer's law:

$$I = I_0 \exp(-kcl) \quad (4.1)$$

where:

I = emergent beam intensity

I_0 = Incident beam intensity

k = constant of proportionality

c = Mercury concentration (mole/m³)

l = optical tube length

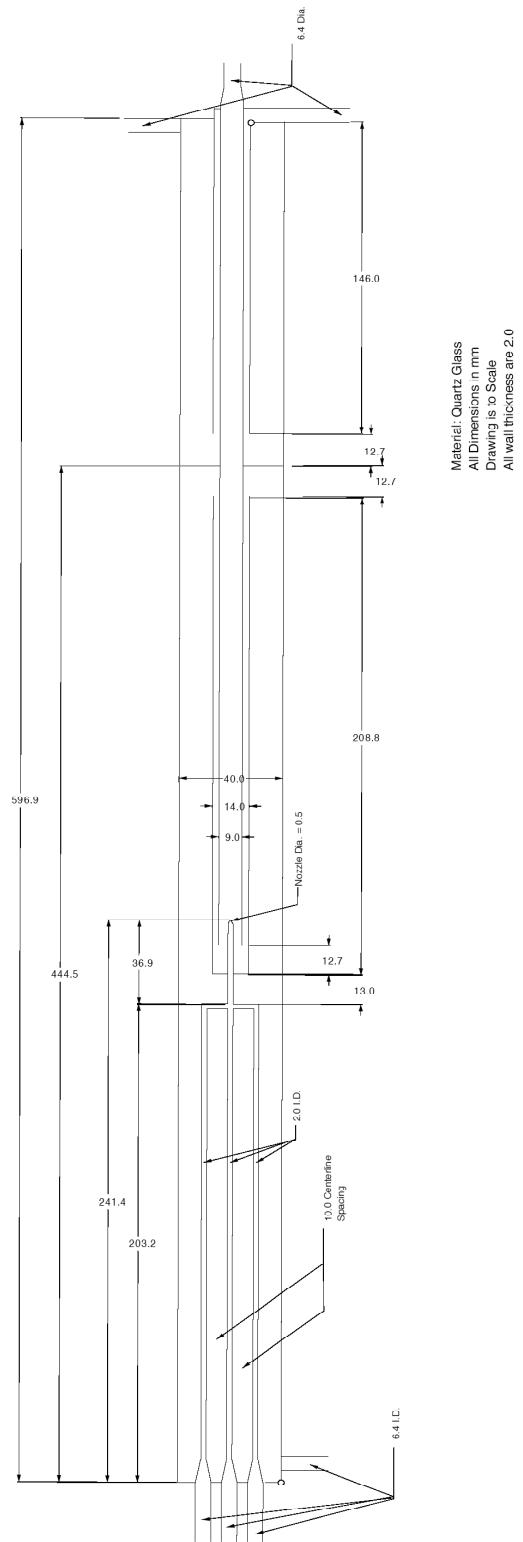


Figure 4.3. Quartz Flow Reactor Scale Drawing.

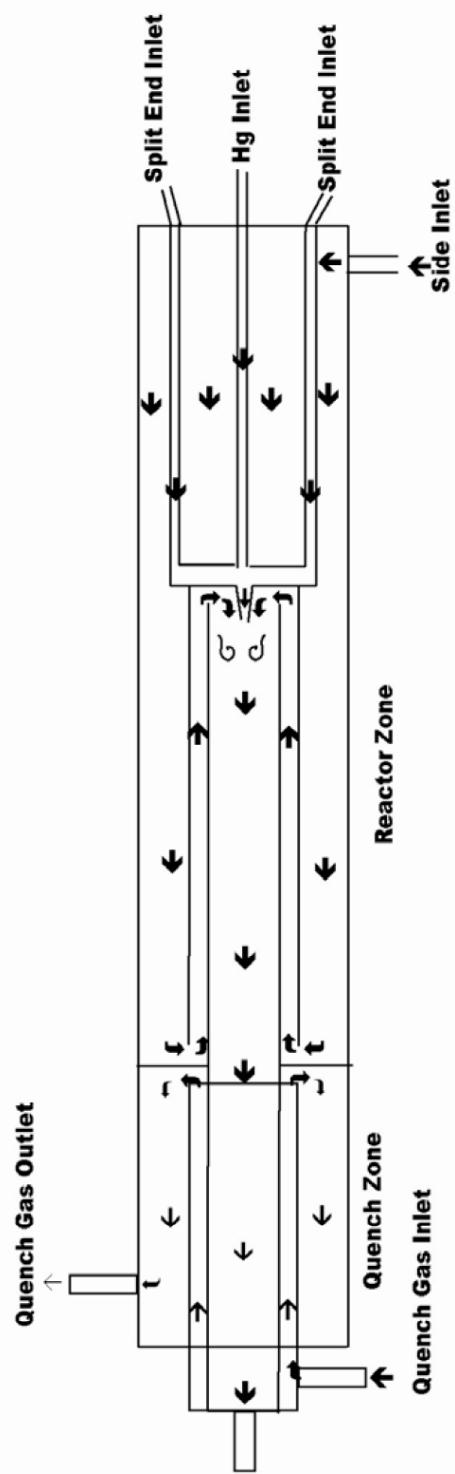


Figure 4.4: Quartz Flow Reactor Flow Schematic.

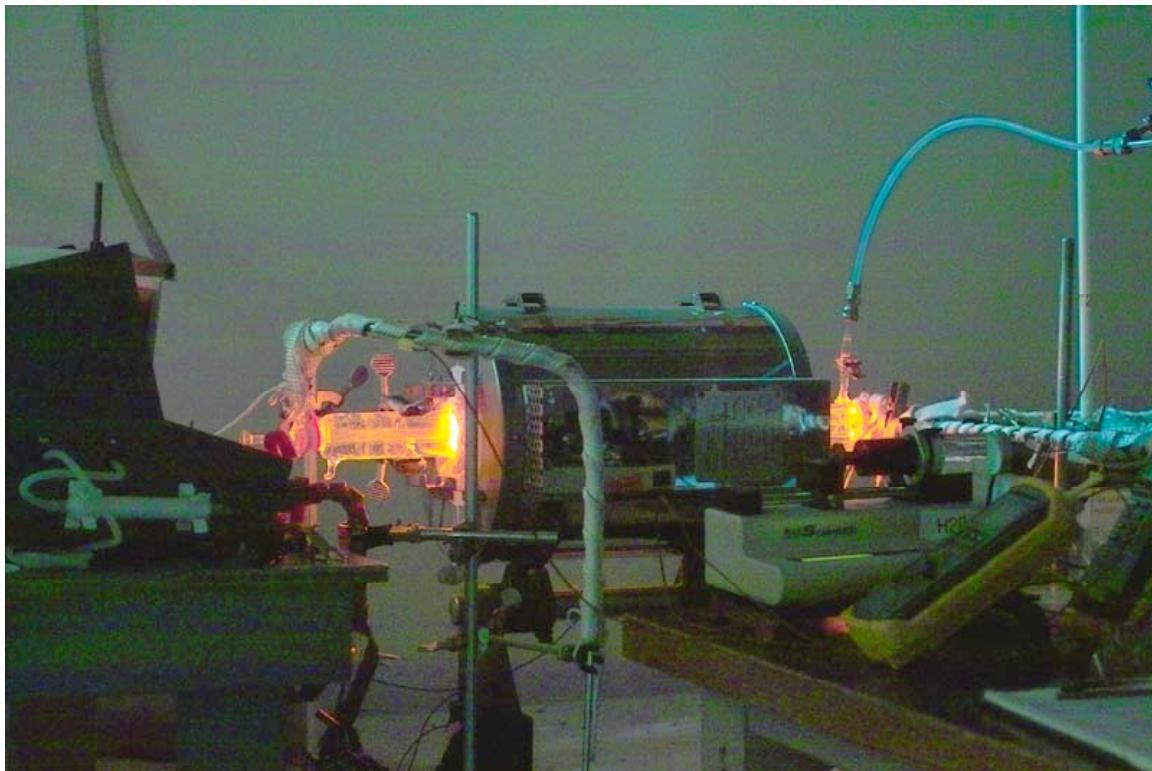


Figure 4.5. Quartz flow reactor.

Modifications to the analyzer were extensive for this particular application. The detector was designed to operate on discreet samples drawn in with a pump at a flow rate of 1950 sccm, while in this test program, a continuous flow of 300 sccm at atmospheric pressure must be monitored during each test series. The flow pump was bypassed to allow for these considerations. The detector cell was plumbed directly into the flow path immediately downstream of the reactor quench region. This helped to minimize sequestration regions in the flow system. The absorption cell was heated to 400 K to eliminate water condensation from the flow stream onto the absorption cell surfaces, as this causes a known detector interference problem. Because of heating of the absorption cell, and subsequent heating of the Buck analyzer, additional exterior cooling in the form of a small fan blowing on the back of the instrument, was added. In addition, the cavity in which the detector is positioned was vented to atmosphere. A shop air purge was retrofitted within the detector cell cavity to provide a constant amount of atmospheric water vapor variation of which was found to adversely affect the phototube detector. Even this small amount of water vapor was found to profoundly interfere with light transmittance at the operational frequency causing data to be unstable. A strip chart recorder was added to determine data trends.

Calibrations were conducted at the beginning and end of each test run. Analyzer calibration was conducted by introduction of a various known elemental mercury concentrations and developing a polynomial curve fit for the data. Baseline shift readily occurs in this instrument and was rectified by depriving the system of mercury and re-zeroing the Buck analyzer across the span of the instrument.

4.1.5 Mercury Flow Clean-Up

Cleaning of the mercury contaminated gasses was required before venting to atmosphere. Once the mercury laden stream was analyzed, the flow was ducted to an impinger containing a mixture of nitric acid and potassium permanganate, mixed per EPA method 29. Maintained in an ice bath, the impinger scrubbed all elemental and oxidized mercury out of the gas stream before it was exhausted to atmosphere. Impinger liquid was appropriately disposed and replaced of at the end of each set of tests.

4.1.6 Experimental Procedures

The data acquisition process in this experiment required long reactor equilibration times and very delicate adjustments to the equipment. The presence of nitrogen was maintained in the flow circuit at all times. Time to reactor equilibration from a cold start to full operational capacity was five to seven days. Complete reactor purge was found to take approximately 48 hours. Data point equilibration times varied and were longest when hydrogen was involved, varying from ten minutes per data point for a calibration, to four hours for an acid calibration, to six hours when hydrogen was used. It is believed that the mechanism behind these phenomena is both chemical and aerodynamic. Molecular sequestration occurred in a number of geometric spaces throughout the flow system, and was most likely also sequestered within the stainless steel of the supply manifolds. In addition, the internal flow structure of the reactor favored creation of recirculation zones. At very low concentrations, often on the order of 25 ppm, these recirculation zones also allowed for trapping of key molecules. These phenomena drove the very long equilibration periods experienced. Once these lag times were defined, the accuracy and repeatability of the experiment were assured.

Each test required a procedural check list including verification of the flow streams for pressure and flow rate, maintaining flow conditioning water and ice baths and calibrating the equipment. The mercury bubbler provided vaporized mercury at a known concentration and was located just upstream of the reactor. The temperature of the water bath and the heated glass line were recorded. This stream was then introduced to a flow mix of nitrogen, oxygen and water vapor input at the farthest point upstream in the manifold, followed by hydrogen chloride and subsequently hydrogen and/or carbon monoxide. Each introduction was followed by the appropriate equilibration period for the reactor. Data was taken both by hand and by using a strip chart recorder for detector measurements. For each stream the line pressure and flow rates were documented. Temperatures of the water line, mercury bubbler and bubbler supply line, reactor, quench gas, and detector were documented as well as atmospheric temperature and pressure. Data sheets were generated on a custom basis for each test using an Excel spreadsheet and manufacturer supplied flow calibration curves for each flowmeter. A strip chart recorder was used to monitor trend of the percent transmittance, and to ensure that instrument drift was monitored, detected and corrected.

This experimental configuration exhibited complex behaviors which limited the way a test series could be conducted. Equilibration times for adding species were found to an

order of magnitude less than that found in subtracting species. Increasing temperatures required, again, less equilibration time than decreasing temperatures. And finally, it was found that when changing species mix it perturbed the system less to subtract nitrogen first and then to add additional or new gas species. Therefore all test series were conducted by increasing oxidizing species rather than decreasing them, and by subtracting neutral species before adding oxidizing species. Further, temperature surveys were conducted starting from 922 K increasing to 1200 K. Violation of these rules caused unstable reactor operation and inconsistent data in all cases.

4.1.7 Data Analysis Techniques

Data was analyzed using Excel spreadsheets to which hand recorded data was transferred and subsequently manipulated. In the case of the measured flow rates, the data was converted from the raw form, in terms of percent full scale, into units of sccm. This was then converted into units appropriate for the species or mixture being metered. The amount of elemental mercury input to the gas stream was determined by calculating the amount of mercury produced by the mercury bubbler based upon the relationship between partial pressure, the mercury-nitrogen interface temperature, and vapor mole fraction. The calculated mole fraction of the mercury input was then converted using total flow rate to reflect an overall mercury concentration. This value was then “assigned” to a percent transmittance based on the detector readout. At this time only nitrogen, oxygen and water vapor are combined with vaporized elemental mercury. This data is then fitted with a polynomial curve fit providing the calibration curve for the Buck mercury analyzer for a particular test series.

During that portion of the test program where mercury is oxidized in the reactor, the amount of elemental mercury input is at a fixed flow rate and variations in input elemental mercury concentration occur only due to temperature variations in the mercury bubbler water bath temperature. When oxidation occurs, the elemental mercury that was converted to the oxidized form is no longer visible to the detector, and thus the difference between the known input level and the measured output mercury concentration is the amount of oxidized mercury in the flow stream. Variations in oxidized mercury as a function of temperature and relative concentrations of oxidizing species are calculated. All concentration data were plotted as a function of time and/or temperature as appropriate. Additional temperature data recorded include: atmospheric, water line, quench supply line, detector flow circuit from the reactor through the Buck 400a. Line pressures downstream of each flow meter were recorded as well.

4.2 Chemical Kinetic Analysis Methodology

4.2.1 Introduction

Understanding the chemical kinetic mechanism underlying the observed phenomena is the key factor in the understanding of possible applications for cleaning mercury laden combustion exhaust. CHEMKIN is a computer code that provides an empirically based analytical tool to represent the molecular interactions that occur in the heated reactor. It is

the modeling of the breaking of chemical bonds and reformation into new species that CHEMKIN allows for. Although empirical results indicate strong homogeneous oxidation of mercury, the effect of hydrogen and carbon monoxide has not been formally characterized. Thus a chemical kinetic mechanism was developed in parallel with the experimental portion of this effort.

4.2.2 CHEMKIN

The original CHEMKIN model was developed by Sandia National laboratories, and is now owned and supported by Reaction Design inc. CHEMKIN 4.1 (Kee *et al.*, 2004) was used in this modeling effort. Providing a graphical interface, and graphical post processing capability, CHEMKIN 4.1 supplies many reactor model components of which only the input, mixer and plug flow reactor modules were utilized. The most important part of the model was to provide an accurate chemistry set for the analysis. The chemistry set used provided reaction rate coefficients as defined by the modified Arrhenius rate expression:

$$k = AT^\beta \exp(-E_A/RT) \quad (4.2)$$

where:
 A = kinetic pre-exponential A factor
 β = activation energy
 E_A = pre-exponential constant
 $(-E_A/RT)$ = Boltzman factor

The kinetic pre-exponential A factor takes into account the steric factor and collision frequency, excluding concentrations. A derivation of this relationship may be found in any combustion text, and is not included here. The chemistry set data are available from the literature or from detailed estimates. Detailed geometric and flow data were input to set the boundary conditions of the model. In this investigation values representing actual flow conditions were input to match the model to the experimental conditions as closely as possible. A detailed discussion of the reactor model follows.

The plug flow reactor (PFR) model provides and idealized flow system that is tubular in form, assuming steady state operation. This idealized model of reduced dimensionality assumes no mixing in the axial direction and complete mixing in the transverse direction. This allows the achievable reactant conversion to be maximized. The assumption of no transverse gradients implies the absence of mass-transfer limitations and also contributes to maximized reactor performance. The use of first order ordinary differential equations (ODE), and the lack of transport property calculations, makes the PFR model in CHEMKIN computationally efficient as well.

The CHEMKIN model provides a number of options regarding the reactor energy balance: constrained temperature, adiabatic reactor, specified heat loss and specified heat transfer coefficient. The constrained temperature option allows for either isothermal modeling, or for a construction that allows the axial temperature distribution to be specified. In this case the energy equation is not solved. In the adiabatic reactor option, heat transfer is zero and the energy equation is solved. The specified heat loss option can

be either a constant heat flux or a defined axial heat flux profile. Last, the specified heat-transfer coefficient option allows the heat transfer coefficient to be a function of axial distance, but it is defined in terms of the ambient temperature and the overall heat transfer coefficient.

The CHEMKIN graphical user interface is an interactive canvas upon which the model is spread out allowing for input and output in user defined units. A modular flow charting system is used to build the model in terms of module choice, connections and boundary condition input. The chemistry and thermochemical data sets are pre-processed before the model is run. This provides a method to separate the chemistry processing from the model itself for more efficient troubleshooting and processing.

5.0 Results and Discussion

The first series of tests are designed to establish the baseline that is used throughout the remainder of the testing. These involved establishing the baseline oxidation characteristics as a function of reaction temperature and HCl concentration. The experimental conditions included a 0.5 s isothermal residence time at three temperatures (922, 978, 1200 K, or 1200, 1300, 1700°F). The O₂ concentration was 4% (volume), the H₂O was 5 ppm, and the elemental mercury was 1020 µg/m³. The HCl concentration was varied from 0-500 ppm. The balance of the reactants was N₂.

Figure 5.1 shows the results. As usual, no oxidation was measured in the absence of HCl. Oxidation increased with temperature, with essentially quantitative oxidation occurring at the highest temperature. For 922 and 978 K, the amount of oxidation reached an asymptotic level after a certain HCl concentration (250 ppm HCl at 922 K, 50 ppm at 978 K), and further increases in HCl did not improve oxidation.

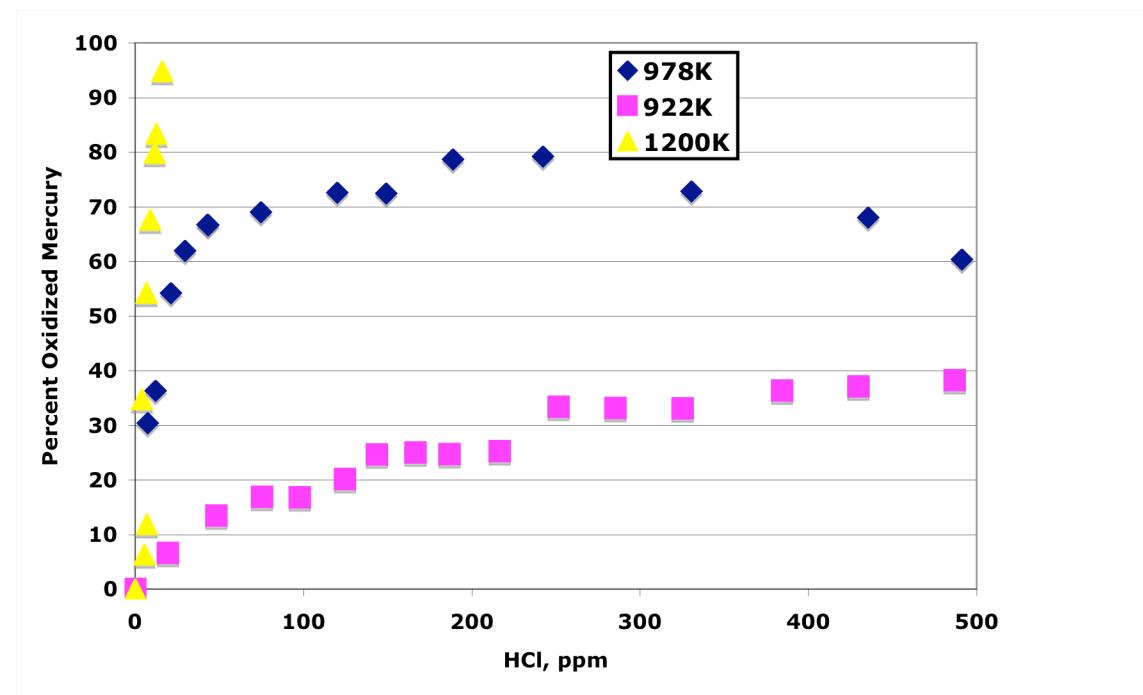


Figure 5.1. Percent elemental mercury oxidized as a function of HCl concentration and reactor temperature.

The very high oxidation fractions at the highest temperatures were investigated with the chemical kinetic model. The results indicate that the equilibrium Cl-atom concentrations are approximately 20x higher in dry gas compared with the same gas with 10% water. Large amounts of water promote the reaction:



Thus, the oxidation in nearly dry gas tend to be much more complete than oxidation under the corresponding conditions with realistic amounts of water.

This has helped resolve one of the inconsistencies in the literature data. Figure 3.5 shows that for essentially identical conditions, the Hall *et al.* data exhibit significantly higher reactivity. The Hall data were dry, and this is the potential reason.

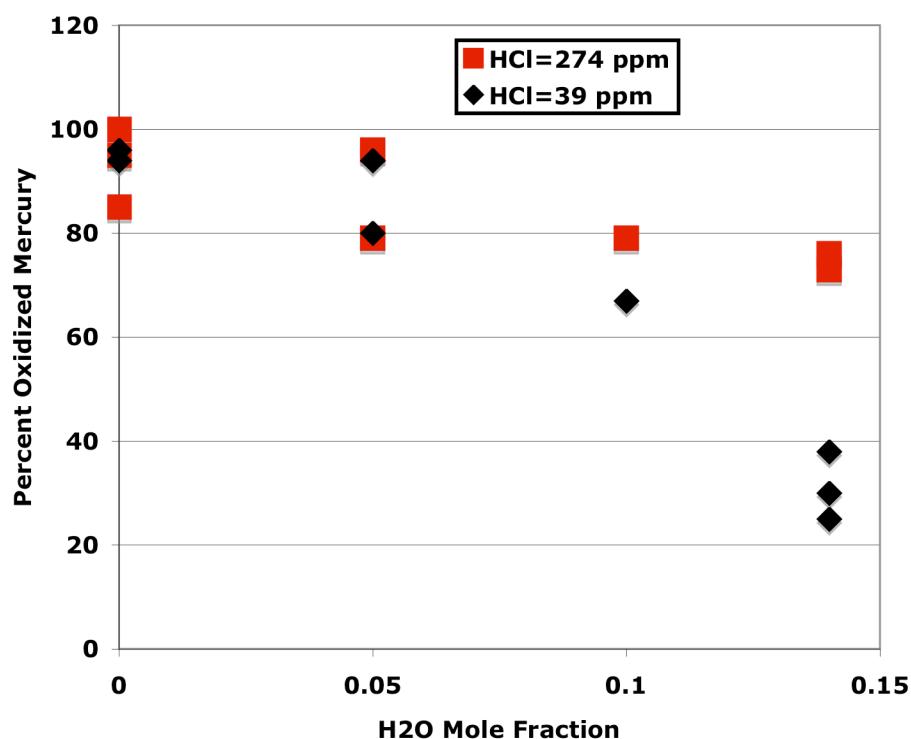
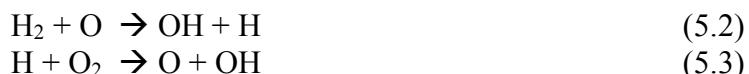


Figure 5.2. Influence of water vapor on the oxidation of mercury.

The present reactor was used to test this hypothesis. The experiment was run under the conditions of Figure 5.1 at 1200 K with variable water vapor at two HCl concentrations. The results are shown in Figure 5.2. In all cases, the presence of the water reduced the amount of mercury oxidation. In particular, the more realistic 39 ppm HCl case showed a drop from almost 100% oxidation at dry conditions to around 30% oxidation at a realistic 14% water vapor. This suggests the importance of using the appropriate background composition during testing.

Hydrogen is hypothesized to promote oxidation due to the following mechanism. The addition of H₂ at an appropriate temperature results in the initiation of a slow oxidation reaction sequence:



The excess OH generated then provides Cl-atom via:



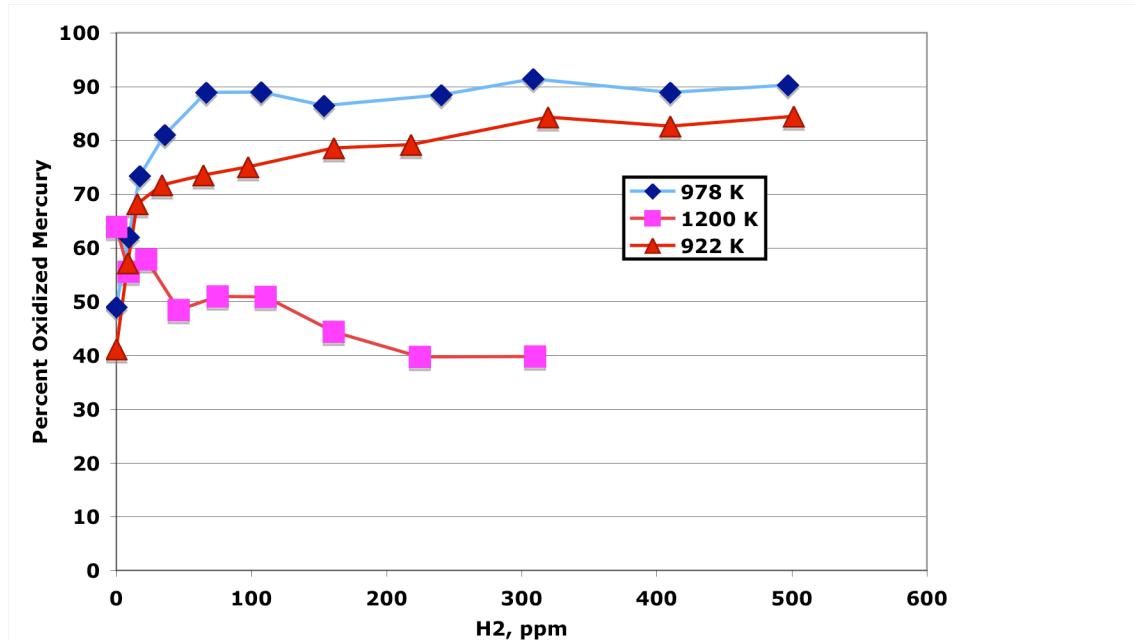


Figure 5.3. Promotion of mercury oxidation by the addition of hydrogen at three temperatures.

The Cl-atom then oxidizes mercury.

The first two tasks are to determine if promotion takes place, and to find under what conditions it is most favored. Clearly, addition of hydrogen at high temperatures will result in OH production under conditions where mercury oxidation is not favored. By the time the gas has cooled to the mercury oxidation window, the OH and Cl will have relaxed back towards their equilibrium values. Addition at too cold of a temperature results in little hydrogen reaction, leaving no promotion.

Figure 5.3 shows data taken under the following conditions. The reactor residence time was 0.5 s isothermal. The oxygen concentration was 4%, and the water vapor was 14% by volume. The HCl concentration was 330 ppm, and the initial elemental mercury was 930 $\mu\text{g}/\text{m}^3$. Under these conditions, the lowest temperature oxidation (922 K) was improved from 40% to 80%. The 978 K oxidation was improved from 49% to 90%, while the 1200 K data went from 64% with no H₂ to 40 percent. In all cases essentially all the promotion (or demotion) effect took place by the time 50-100 ppm of H₂ were added to the experiment.

Application of the chemical kinetic model to the results suggested that at the higher temperatures, the more vigorous chemical reaction was promoting a reverse reaction in which Cl is stripped off of HgCl and HgCl₂:



This appears to illustrate the balance between providing some OH to promote Cl formation and oxidation, while not providing so many radicals that the HgCl reverts back

to Hg.

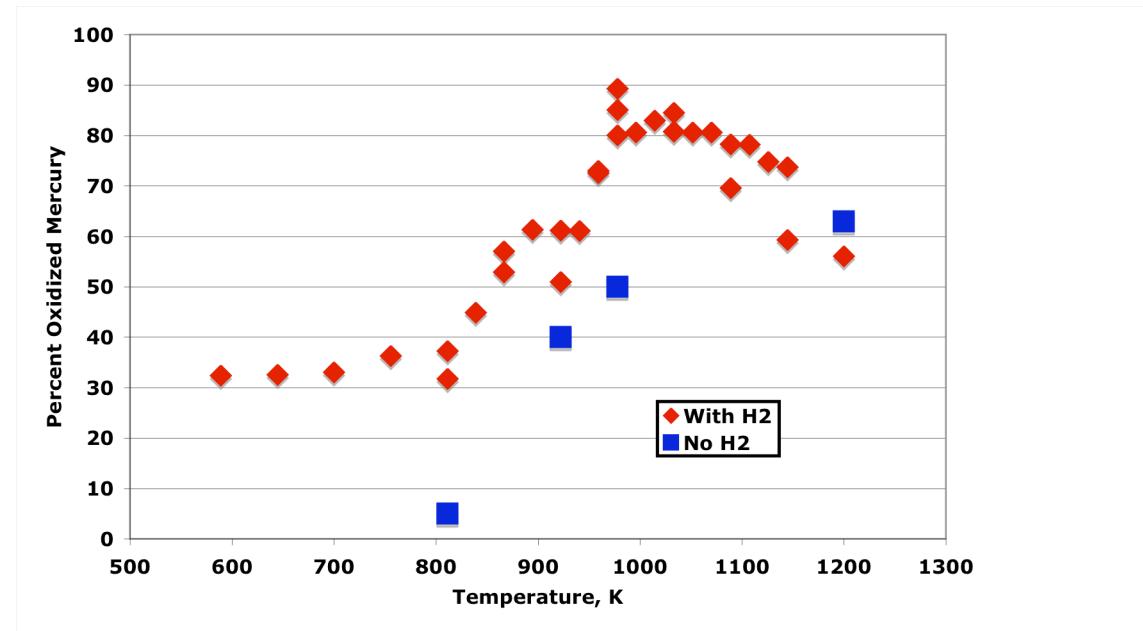


Figure 5.4. Influence of H₂ addition on mercury oxidation.

The importance of establishing the temperature window led to an extensive test series examining this parameter. The results shown in Figure 5.4 were obtained under the following conditions: 4% O₂, 14% H₂O, 410 ppm H₂, 440 ppm HCl, 0.5 s reactor isothermal residence time, 950 $\mu\text{g}/\text{m}^3$ initial elemental mercury.

The results suggest a significant promotion in the 800-1100 K window. Below 800 K a steady 30% oxidized fraction is observed while no oxidation takes place in the absence of H₂. As these temperatures are too cold for homogeneous H₂ oxidation, it may suggest a catalytic H₂ activation process taking place on the reactor wall. We have not addressed this point further at present.

Application of the chemical kinetic model results in an interpretation similar to that noted in the discussion of Figure 5.3. Within an appropriate temperature window, the H₂ reacts in a sequence that generates excess OH, which generates Cl atom via reaction 5.4. The subsequent reaction with Hg proceeds at near the collisional limit. At the higher temperatures, the reaction of the H₂ proceeds in an environment where radical reactions are fast and the radicals are as likely to scavenge HgCl into Hg as to promote additional Cl formation.

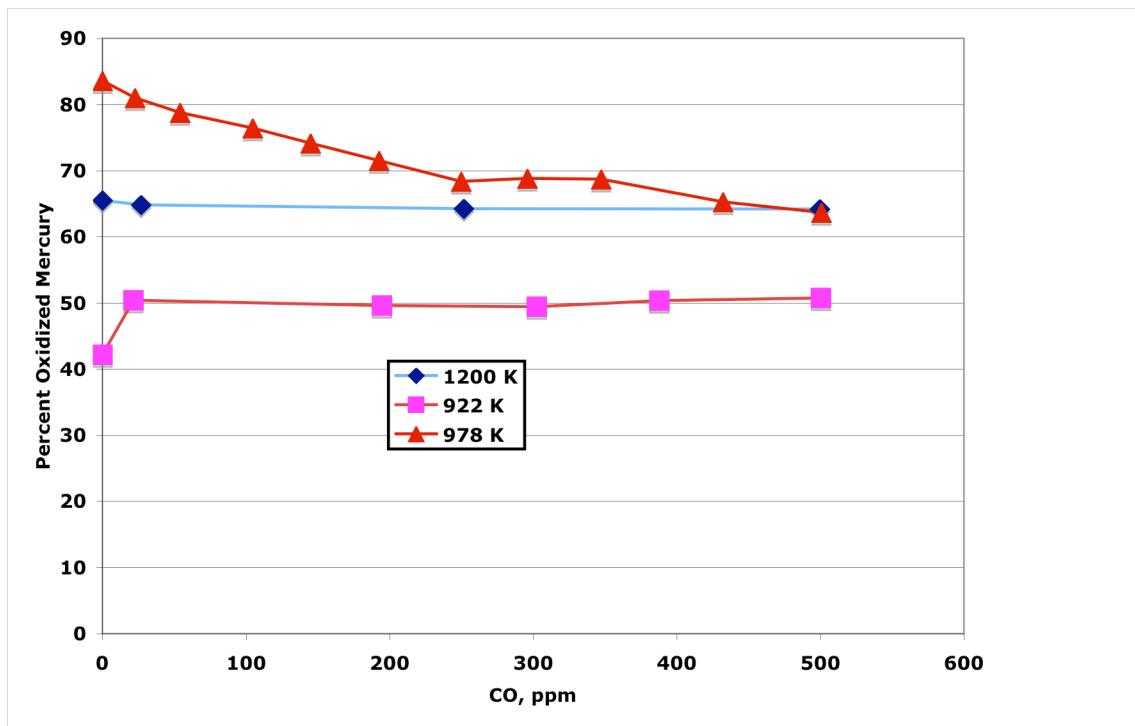


Figure 5.5. Influence of CO addition on mercury oxidation.

In a power plant the likely source of H₂ for injection as a promoter is via steam reforming of natural gas. The raw product will contain significant concentrations of H₂O, CO₂ and CO in addition to the H₂. The CO is potentially reactive, and one question would be whether it could act as an additional promoter, and inert, or a deactivation agent.

The data shown in Figure 5.5 were generated to test this. The conditions were: 4% O₂, 14% H₂O, 120 ppm H₂, 25 ppm HCl, 0.5 s reactor isothermal residence time, 950 $\mu\text{g}/\text{m}^3$ initial elemental mercury. The results indicate that the CO had no effect at the highest temperature, only a moderate effect at the lowest temperature, and it reduced oxidation at 978 K. The chemical kinetic model indicated that at the higher temperature, the radical reactions were fast enough from the H₂ reaction that the additional fuel provided by the CO had little effect. Note that in the data the addition of hydrogen beyond 50-100 ppm had little effect, and at the higher temperature the CO essentially behaved as if it were excess hydrogen.

At the lowest temperature the CO appeared to not react in the model, thus yielding essentially no effect on the mercury oxidation. At 978 K the model suggests the following scenario. The CO of course is a more difficult species to oxidize than hydrogen, generally requiring a higher temperature. Introduction of CO into a reacting hydrogen system at such a low temperature causes the CO to become a radical absorber rather than a net radical generator. This results in a general lowering of OH concentrations, leading to a reduction in mercury oxidation. Thus, the presence of CO in reformer product gas may be detriment to oxidation.

The presence of NO in combustion products could possibly influence the promotion of

oxidation by H₂. The suspected pathway is via the shuttle reaction between NO and NO₂:



This could potentially act as a sink for free radicals.

Previous tests under H₂ promotion were rerun to briefly test this. The conditions were the same as those of Figure 5.4 at 922, 978, and 1200 K, but with 200 ppm NO added to the system. The results shown in Figure 5.6 do not indicate any significant change in the oxidation over the promoted case.

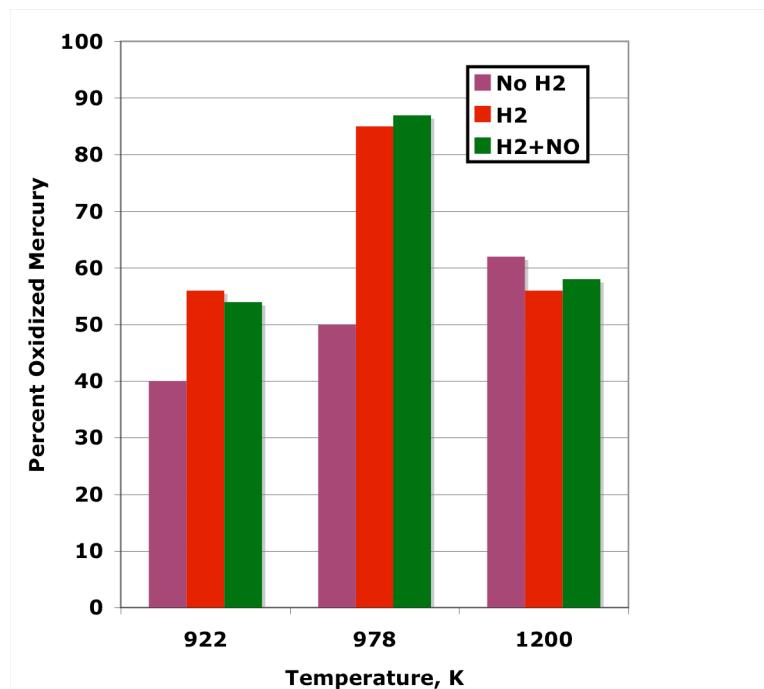


Figure 5.6. Influence of 200 ppm NO on the promoted oxidation of Hg.

The chemical kinetic model was used to examine these trends. The results suggest that at these temperatures, insufficient HO₂ radicals are generated to provide a sufficient pool to drive NO oxidation. Thus, the model predicts that NO will act essentially as an inert under these conditions, something that the data suggest. The alternate pathway for oxidation suggested by reaction 3.31 (NO₂ + Hg → HgO + NO) does not appear to be active here due to the low NO₂ concentration.

The same experiment was repeated with 500 ppm SO₂. The hypothesis again was that the shuttle reaction between SO₂ and SO₃. The results are shown in Figure 5.7. The results indicate no change in the degree of oxidation relative to the promoted baseline, and a slight reduction in oxidation at 1200 K. We did not include the sulfur reactions in the chemical kinetic model due to their uncertainty, so for the present we do not have a chemical kinetic interpretation of these results.

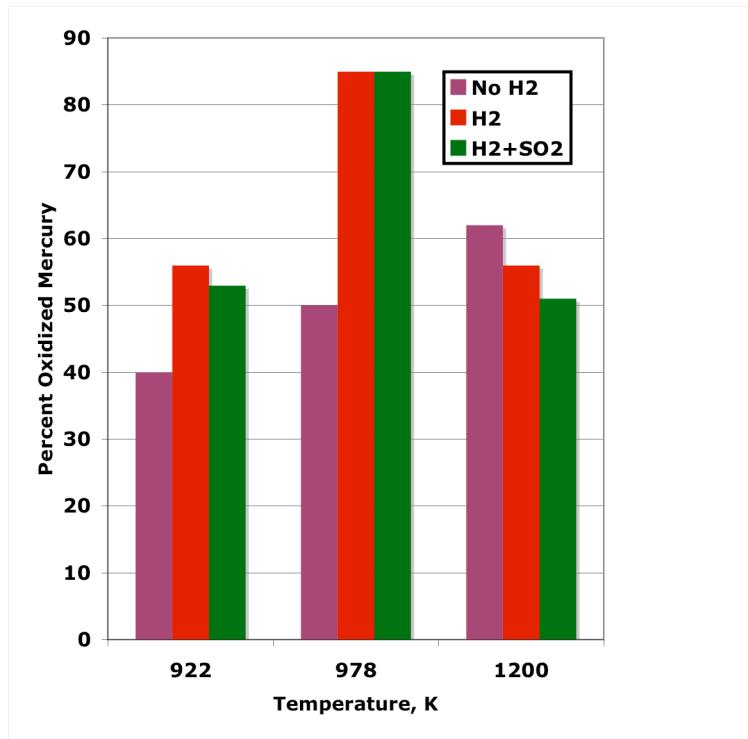


Figure 5.7. Influence of 500 ppm SO₂ on the promoted oxidation of Hg.

Our original statement of work included a task looking at the oxidation of Hg by Cl₂ injection. Due to materials incompatibilities in the present experimental system, it turned out to be impossible to include Cl₂ with the reagents. This task was of relatively minor importance to the overall objectives, so it was not pursued further as to do so would have involved a relatively expensive modification of the reactor and flow system.

6.0 Conclusions

The work presented here addresses the issue of mercury removal from the flue gas streams at coal-fired power plants. Flue gas mercury is present generally as either elemental vapor or bivalent HgCl_2 . The latter can be removed by wet FGD systems, so promoting the oxidation of the mercury is one means of improving capture. Should the eventual regulations allow a niche for systems that provide moderate capture levels, then the promotion of oxidation followed by FGD capture could be a feasible process. The feasibility hinges on technically being able to accomplish the promotion of oxidation in a way that keeps costs low.

The homogeneous oxidation of mercury is generally thought to proceed via reactions between Hg and Cl and/or Cl_2 . Since the predominant chlorine form in flue gas is HCl , some means of generating the more reactive Cl or Cl_2 species is needed. Previous research suggests that the flame zone provides some. The hypothesis explored in the present research is that the introduction of relatively small amounts of H_2 at economizer temperatures could result in a burst in OH radical, followed by conversion of HCl to Cl via $\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}$. Cl_2 is formed via recombination of Cl . This added Cl at lower temperatures then promotes Hg oxidation via $\text{Hg} + \text{Cl} \rightarrow \text{HgCl}$ and $\text{HgCl} + \text{Cl} \rightarrow \text{HgCl}_2$.

Isothermal testing indicated that the oxidation reaction was promoted by relatively small amount of H_2 (<100 ppm) in the temperature range of 800-1100 K. This suggests that injection of these small amounts of H_2 , possibly in the economizer region, could give an additional boost of oxidation. Chemical kinetic modeling suggests that injecting too hot results in additional radicals, but that they have more time to relax towards equilibrium before optimal mercury oxidation temperatures are reached.

The most likely source of the H_2 in practice would be a small steam reformer operating on a natural gas feedstock. Unless this is followed by a water gas shift system, the product gas of this reformer would also contain CO . Thus, one question was whether the CO would act as an additional promoter. Testing indicated that the CO was generally inert. In the most strongly promoted H_2 condition, the CO did reduce oxidation somewhat. Testing with 200 ppm NO and 500 ppm SO_2 did not show any change in performance.

The next steps are:

1. Use the chemical kinetic model to identify appropriate injection temperatures and H_2 concentrations for realistic quench environments.
2. Perform tunnel furnace tests on H_2 injection under realistic, non-isothermal environments.

7.0 References and Bibliography

Agency For Toxic Substances and Disease Registry (ATSDR), 'Toxicological Profile for Mercury", U.S. Department of Health and Human Services, Public Health Service, CAS # 7439-97-6, <http://atsdr.cec.gov/MHMI/mmg46.html>, March 2004.

Akers, D. and R. Dospeoy, "Overview of the Use of Coal Cleaning to Reduce Air Toxics", *Minerals and Metallurgical Processing*, Volume 10, Number3, August 1993.

Altman, R., Buckley, W. and I. Ray, "Wet Electrostatic Precipitation Demonstrating Multiple Pollutant Control in Industrial applications Holds Promise for Coal-Fired Utility Emission Reduction of Acid Mist, PM2.5, and Mercury", *The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control*, Chicago, Ill, August 2001.

Altman, R., Battleson, D., Montgometry, J., Buckley, W., Ray, I., Altshuler, B. and J Reynolds, "Pilot Scale Test Results on Plasma-Enhanced Electrostatic Precipitation Technology for Mercury Removal", *Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium*, Paper No. 121, Washington D.C., August 2004.

Babu, M., Licata A., and L. P. Nethe, *Proceedings: EPA Mutipollutant Sorbent Reactivity Workshop*, pp. 202-223, Triangle Park, NC, July 1994.

Beim, A. M., Grosheva, E. I. and B. K. Pavlov, "Complex Ecological Assessment of the Influence of Pulp Mill and Power Plant Emissions on the Environment", Managing Hazardous Air Pollutants: State of the Art, Cow and Connor, EPRI-TR-101890, pp. 235-236, 1993.

Benson, S.A., Erickson, T.A., Zygarlicke, C.J., O'Keef, C. A., Katrinak, K. A., Allen, S. E., Hassett, D. J., Hauseman and N. T. Holcombe, "Trace Metal Transformations in Gasification", 1996 Advanced Coal- Fired Power Systems Review Meeting, Morgantown, WVA, July 1996.

Bergan, T., Gallardo, L., and N. Rodhe, "Mercury in the Global Troposphere: a Three Dimensional Model Study", *Atmospheric Environment*, Volume 33, pp. 1575-1585, 1999.

Biermann, J., Voogt, N., Sorooshian, A., Wendt, J. O. L., Merritt, R and T. K. Gale, "In-Flight Capture of Elemental and Oxidized Mercury in Coal Combustion Flue Gases by a Novel Mineral Sorbent Between 320 and 1540°F (160-840°C)", *Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium*, Washington, D. C., May 2003.

Bland, A., Sellakumar, K., Guffey, F., Walling, G., Steen, D. and E. Klunder, "A Novel Approach to Mercury Control by Pre-Combustion, Thermal Treatment of Low Rank Coals-Project Update", 97th Annual Conference of the Air and Waste Management Association, Indianapolis, IN, June 2004.

Bloom, N. S., "Mercury Speciation in Flue Gas: Overcoming Analytical Difficulties", Managing Hazardous Air Pollutants: State of the Art, pp. 148-160, CRC Press, 1993.

Blythe, G., Machalek, t., Marsh, B., Miller, S., Richardson, C., Richardson, M. and K.

Searcy, "Enhanced Control of Mercury by Wet Flue Gas Desulphurization Systems Final Report, Phase II", EPRI, Palo Alto, CA, and U. S. Department of Energy, National Energy Technology Laboratory, Pittsburgh PA, June 2001.

Blythe, G., Richardson, C. F. and R. G. Rhudy, "Catalytic Oxidation of Mercury in Flue Gas for Enhanced Removal in Wet FGD Systems", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Blythe, G., Richardson, C. F., Lani, B. W., Rhudy, R. G., Strohfus, M., Riveland, G. and L. Loritz, "Pilot Testing of Oxidation Catalysts for Enhanced Mercury Control by Wet FGD", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 36, Washington D.C., August 2004.

Blythe, G., DeBerry, D., Marsh, B., Paradis, J., Range, J. and R. Rhudy, "Bench-Scale Evaluation of the Fate of Mercury in Wet FGD Systems", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 59, Washington D.C., August 2004.

Boren, R. M., Hammel, C. F., Harris, L. E. and M. R. Bleckinger, "Pilot Test Results from EnviroScrub Technologies Multi-Pollutant Pahlman Process™ Technology for NO_x, SO₂, and Mercury", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 59, Washington D.C., August 2004.

Boylan, H. M., Cain, R. D. and H. M. Kingston, "A new Method to Assess Mercury Emissions: A Study of Three Coal-Fired Electric-Generating Power Station Configurations", J. Air & Waste Manage. Assoc., Volume 53, pp 1318-1325, 2003.

Brown, T. D., Smith, D. N., Hargis, R. A. and W. J. O'Doud, "Mercury Measurement and its Control: What We Know, Have Learned, and Need to Further Investigate", Journal of the Air and Waste Management Association, Volume 49, pp 628-640, 1999.

Buttermore, W. H., Norton, G. A., Chriswell, C. D., Eckels, D. E. and R. E. Peters, "Development of Mercury and Chloride Monitors for Coal Gasifiers", Advanced Coal-Fired Power Systems 1995 Review Meeting, CONF-9506162-37, Morgantown, West Virginia, June 1995.

Carey, T. R., Hargrove, O. W. Jr., Richardson, C. F., Chang, R. and Meserole, F. B., "Factors Affecting Mercury Control in Utility Flue Gas Using Sorbent Injection", 90th Annual Conference of the Air and Waste Management Association, 97-WA72A.05, Toronto, Ontario, Canada, June 1997.

Carpi, A., "Mercury From Combustion Sources: "A Review of the Chemical Species Emitted and Their Transport in the Atmosphere", Water, Soil and Air Pollution, 98:241-254, 1997.

Cavallaro, J. A., Gibbon, G. A. and A. W. Deurbrouk, "A Washibility and Analytical Evaluation of Potential Pollution from Trace Elements in Coal", EPA-600/7-78-038, March 1978.

Chang, J. C. S. and S. B. Ghorishi, "Simulation and Evaluation of Elemental Mercury Concentration Increase in Flue Gas across a Wet Scrubber", Environ. Sci.

Technol., Volume 37, pp 5763-5766, 2003.

Chang, J. C. S. and S. B. Ghorishi, "Why does Flue Gas Elemental Mercury Concentration Increase Across a Wet Scrubber?", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Chu, P. and D.B. Porcella, "Mercury Stack Emissions from U.S. Electricity Power Plants", Journal of Water, Air and Soil Pollution, Volume 80, pp. 135-144, 1995.

Clack, H. L., Narasimhan, U. and S. D. Serre, "Direct Comparison of fixed Bed and In-th Flight Trace Gas Adsorption for Mercury Control", 96th Annual Meeting of the Air and Waste Management Association, Paper No. 69606, San Diego, CA, June 2003.

Clack, H. L., Narasimhan, U. and S. D. Serre, "The Relative Importance of Turbulent Mixing on the Adsorption of Mercury within a Gas-Sorbent Suspension", Air and Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Cooper, C. D. and F. C. Alley, Air Pollution Control, A Design Approach, ISBN 1-57766-218-0, 2002.

Cote, C. M., Baldauf, R. W., Carter, R.E., Marotz, G.A. and D. L. Lane, " Mercury Deposition Levels Surrounding Two Different Hazardous Burning Facilities", 93rd Annual Conference of the Air and Waste Management Association, Salt Lake City, UT, June 2000.

Davis, S. E., "Mercury Emissions and Coal-Fired Power Plants: Understanding the Problems and Identifying Solutions", 90th Annual Conference of the Air and Waste Management Association, 97-TA121.06, Toronto, Ontario, Canada, June 1997.

Devito, M., Rosendale, L., Conrad, V. and B. Jackson, "Trace Elements in Coals and their Emissions", Proceedings of the American Power Conference, Vol. 56-1:438, 1994.

DeVito, M. S. and W. A. Rosenhoover, "Flue Gas Hg Measurements from Coal-Fired Boilers Equipped with Wet Scrubbers", 92nd Annual Conference of the Air and Waste Management Association, 99-33, St. Louis, MI, June 1999.

Dombrowski, K. D., Machalek, T., Richardson, C. F., Chang, R. and M. Rostam-Abadi, "Recent Developments in EPRI's Novel Mercury Sorbent Development Program", Air and Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Duncan, J., "A Tale of Two Processes", Power, Volume 158, Issue 8, pp 50-53, October 1994.

Dunham, G. E., DeWall, R. A. and C. L. Senior, "Fixed Bed Studies of the Interactions Between Mercury and Coal Combustion Fly Ashes", Air & Waste Management Association's 90th Annual Meeting & Exhibition, 97-WA72A.08, Toronto, Canada, June 1997.

Dunn, J. E. Jr., Kinder, K. K., Calicago, J. A. III, Davis, W. T., Geisler, T. J., Allen, M. W., Kelly, T J. and S. J. Priebe, "Evaluation of Mercury Continuous Emission Monitors at the U.S. DOE TSCA Incinerator", 96th Annual Meeting of the Air and

Waste Management Association, Paper No. 70249, San Diego, CA, June 2003.

Durante, V. A., Stark, S., Gebert, R., Xu, Z., Bucher, R., Keeney, R. and B. Ghorishi, "A Novel Technology to Immobilize Mercury from Flue Gases", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Durham, M., "Sorbent Injection Making Progress", Power, Volume 158, Issue 8, pp 54-59, October 1994.

Ebner, T., Ley, T., Slye, R., Fisher, K., Chang, R., Richardson, C., Machalek, T., Aljoe, W., Strohfus, M., and S. Sjostrom, "Large Scale Demonstration of the MERCAP™ Technology for Mercury Control", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 78, Washington D.C., August 2004.

Edwards, J. R., Srivastava, R. K. and J. D. Kilgroe, "A Study of Gas-Phase Mercury Speciation Using Detailed Chemical Kinetics", J. Air & Waste Manage. Assoc., Volume 51, pp 869-877, 2001.

Environmental Protection Agency, "Mercury Study Report to Congress: Overview", <http://www.epa.gov/oar/mercover.html>, March, 2003.

Environmental Protection Agency Mercury Rule, <http://www.epa.gov/cleanair2004/>, March 2005.

Evans, A. P. and K. D. Nevitt, "Mercury Speciation Measurements on a 10MWe Coal Fired Boiler Simulator", 90th Annual Conference of the Air and Waste Management Association, Toronto, Ontario, Canada, June 1997.

Farber, P. S., Snell, K. and T. P. Krause, "New Source Review Changes, Multi-Pollutant Legislation, and Resource Initiatives Affecting Power Plants", 97th Annual Conference of the Air and Waste Management Association, Indianapolis, IN, June 2004.

Felsvang, V., Maly, P., Ho, L., Zamansky, V., England, G. and R. Seeker, "Multi-Pollutant Control for Boilers Firing Low-Rank Coals", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Ferrell, R. J. and W. E. Ellison, "Emerging Technologies for Simultaneous Removal of SOX, NOX, and Mercury in Scrubber-Type FGD Systems", 97th Annual Conference of the Air and Waste Management Association, Indianapolis, IN, June 2004.

Fisher, K., McLaren, S., Ley, T. and R. Slye, "Evaluations of Real-Time Monitoring of Mercury in Coal Combustion Flue Gas", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Poster No. 76, Washington D.C., August 2004.

Frandsen, F., Dam-Johansen, K. and P. Rasmussen, "Trace Elements from Combustion and Gasification of coal-An Equilibrium Approach, Progress in Energy and Combustion Science, Volume 20, Issue 2, pp 115-138, 1994.

Fthenakis, V. M., F. Lipfert, P. Moskowitz and L. Saroff, "An Assessment of Mercury Emissions and Health Risks from a Coal Fired Power Plant", Journal of Hazardous Materials, Volume 44: pp. 209-215, 1995.

Fujiwara, N., Fujita, Y., Tomura, K., Moritomi, H., Tuji, T., Takatsu, S. and S. Niksa,

“Mercury Transformations in the Exhausts from Lab-Scale Coal Flames”, Fuel, Volume 81, pp 2045-2052, 2002.

Gabriel, M., Williamson, D. and S. Brooks, “Special Topics on the Relationship Between the Transport of Mercury Through the Watershed and Atmospheric deposition”, 96th Annual Meeting of the Air and Waste Management Association, Paper No. 69690, San Diego, CA, June 2003.

Galbreath, K. C. and C. J. Zygarlike, “Mercury Speciation in Coal Combustion and Gasification Flue Gasses”, Environmental Science and Technology, Volume 30: Number 8, pp 2421-2426, 1996.

Galbreath, K. C. and C. J. Zygarlike, “Mercury Transformations in Coal Combustion Flue Gas”, Proceedings of the Conference on Air Quality: Mercury, Trace Elements and Particulate Matter, M Lean, VA, December 1998.

Gale, T. K., Merritt, R. L., Cushing, K. M. and G. R. Offen, “Mercury Speciation as a Function of Flue Gas Chlorine Content and Composition in a 1 MW Semi-Industrial Scale Coal-Fired Facility”, Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Gaspar, J. A., Widmer, N. C., Cole, J. A. and W. R. Seeker, “Proceedings of the International Conference on Incineration and Thermal Treatment Technologies-1997, pp 661-665, 1997.

Gaspar, J. A., Widmer, N. C., Cole, J. A. and W. R. Seeker, “Proceedings of the International Conference on Incineration and Thermal Treatment Technologies-1998, pp 565-568, 1998.

Ghorishi, B. and B. K. Gullett, “Sorption of Mercury Species by Activated Carbons and Calcium Based Sorbents: Effect of Temperature, Mercury Concentration and Acid Gasses” Waste Management and Research, Volume 16, Number 6, pp 582-593, 1998.

Ghorishi, B. S., Lee, W. C., and Kilgroe, J. D., “Mercury Speciation in combustion Systems: Studies with Simulated Flue gases and Model Fly Ashes”, 92nd Annual Conference of the Air and Waste Management Association, St. Louis, MO (1999).

Ghorishi, S. B., Keeney, R. M., Serre, S. D., Gullett, B. K. and W. S. Jozewicz, “Development of a Cl-impregnated Activated Carbon for Entrained-Flow Capture of Elemental Mercury”, Environ. Sci. Technol., Volume 36, pp 4454-4459, 2002.

Gleiser, R. and K. Felsvang, “Mercury Emission Reduction using Activated Carbon with Spray Dryer Flue Gas Desulphurization”, Proceedings of the American Power Conference, Volume 56, pp 452-457, 1994.

Glesman, S.H., Sjostrom, S., Dene, C. and E. Prestbo, “Mercury Flue Gas Measurements: Understanding Draft EPA Method 324 and Validation Results”, Air and Waste Management Association’s Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 106, Washington D.C., August 2004.

Granite, E. J., Pennline, H. W. and R. A. Hayes, “Sorbents for Mercury Removal From Flue Gas”, DOE/FETC/TR-98-01, January 1998.

Granite, E. J. and H. W. Pennline, “Photochemical Removal of Mercury from Flue Gas”, Ind. Eng. Chem. Res., Volume 41, pp 5470-5476, 2002.

Granite, E. J., Pennline, H. W., O’Dowd, W. J., Freeman, M. C. and R. Hargis, “The Thief Process for Mercury Removal from Flue Gas”, Air and Waste Management

Association's Combined Power Plant Air Pollution Control Mega Symposium, Washington D.C., August 2004.

Guijarro, M. I., Mendioroz, S. and V. Munoz, "Effect of Morphology of Sulfurized Materials in the Retention of Mercury from Gas Streams", *Ind. Eng. Chem. Res.*, Volume 37, PP 1088-1094, 1998.

Gullett, B. K., "Sorbent Injection for Dioxin/Furan Prevention and Mercury Control", Mutipollutant Sorbent Reactivity Workshop, Research Triangle Park, North Carolina, July 1994.

Gullett, B. K., Ghorishi, B., Keeney, R. and F. E. Huggins, "Mercuric Chloride Capture by Alkaline Sorbents", 93rd Annual Conference of the Air and Waste Management Association, Paper Number 259, Salt Lake City, UT, June 2000.

Gustin, M. S. and K. Ladwig, "An Assessment of the Significance of Mercury Release from Coal Fly Ash", *J. Air & Waste Manage. Assoc.*, Volume 54, pp 320-330, 2004.

Haddad, E., Ralston, J., Green, G. and S. Castagnero, "Full-Scale Evaluation of a Multi-Pollutant Reduction Technology: SO₂, Hg and NO_x", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Hagan, M. A. and C. V. Weilert, "Getting a Head Start: Local and State Programs", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Hall, B., Lindqvist, O., and E. Ljungström, E., "Mercury Chemistry in Simulated Flue Gases Related to Waste Incineration Conditions", *Environ. Sci. Technol.*, Volume 24, pp 108-111, 1990.

Hall, B., Schlager, P. and O. Lindqvist, "Chemical Reactions of Mercury in Combustion Flue Gases", *Water, Soil and Air Pollution*, Volume 56, pp 3-14, 1991.

Hargis, R. A. and H. W. Pennline, "Trace Element Distribution and Mercury Speciation in a Pilot-Scale Coal Combustor Burning Blacksville Coal", 90th Annual Conference of the Air and Waste Management Association, 97-WP72B.04, Toronto, Ontario, Canada, June 1997.

Hassett, D. J., and K. E. Eylands, "Mercury Capture on Coal Combustion Fly Ash", *Fuel*, Volume 78, pp 243-248, 1999.

Heidt, M. K., Laudel, D. L., Brown, T. D., and B. R. Nott, "Evaluation of Continuous Monitors for Mercury Measurements in Pilot Scale Tests", 91st Annual Meeting & Exhibition, 98-WP79A.04, San Diego, CA, June 1998.

Helfritch, D. J. and P. L. Feldman, "Flue Gas Mercury Control by Means of Corona Discharge", 92rd Annual Conference of the Air and Waste Management Association, Paper Number 99-157, St. Louis, MO, June 1999.

Henry, C., "Handling Coal's Comeback", *The Philadelphia Inquirer*, Section C: page 1, March 5, 2005.

Hohl, C. M., Carter, R. M., Guerra, S., Lane, D. D., Marotz, G. A. and R. W. Baldauf, "Investigation of Atmospheric Mercury Deposition Using Both Wet and Dry Deposition, and Soil Samples", 97th Annual Conference of the Air and Waste

Management Association, Paper Number 401, Indianapolis, IN, June 2004.

Hsu, H. C., Rostam-Abadi, M., Rood, M. J., Chen, S. and R. Chang, "Preparation of Sulfur impregnated Activated Carbon Fibers (ACFs) For Removal of Mercury Vapor From Simulated Coal-Combustion Flue Gases", 93rd Annual Conference of the Air and Waste Management Association, Paper Number 435, Salt Lake City, UT, June 2000.

Johnsen, B. E., Cooper, J. A., Fry, S. C. and M. P. Nakanishi, "Evaluation of a New Filter for Use in Multi-Metal and Mercury CEMs: Mercury Trapping Efficiency", 96th Annual Meeting of the Air and Waste Management Association, Paper No. 70080, San Diego, CA, June 2003.

Johnsen, B. E., Fry, S. C. and J. A. Cooper, "X-Ray Based Continuous Emissions Monitor for Mercury and Other Elements", 96th Annual Meeting of the Air and Waste Management Association, Paper No. 70082, San Diego, CA, June 2003.

Jones, C., Consensus On Air Toxics Eludes Industry To Date", Power, Volume 148, Issue 8, pp 50-59, October 1994.

Karatza, D., Lancia, A., and Musmarra, D., "Fly Ash Capture of Mercuric Chloride Vapors from Exhaust Combustion Gas", *Environ. Sci. Technol.* **32**, 3999-4004 (1998).

Kee, R. J., Rupley, F. M, Miller, J. A., Coltrin, M. E., Grcar, J. F., Meeks, E., Moffat, H. K., Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Stewart, W. E., Glarborg, P., Wang, C., Adigun, O., Houf, W. G., Chou, C. P., Miller, S. F., Ho, P. and D. J. Young, CHEMKIN Release 4.0.1, Reaction Design, Inc., San Diego, CA, 2004.

Kramlich, K.C. and R. N. Sliger, "Reduction of Inherent Mercury Emissions in PC Combustion Final Report", DOE Grant No. DE-FG22-95PC95216, August 2000.

Laudel, D. H., Heidt, M. K. and B. Nott, "Evaluation of Mercury Speciation by EPA (Draft) Method 29", 11th Annual Coal Preparation, Utilization and Environmental Control Contractors Conference, pp. 143-150, Pittsburgh, PA, July 1995.

Laudel, D. H., Heidt, M. K., Nott, B. and T. D. Brown, "Bench and Pilot-Scale Evaluation of Mercury Speciation Measurement Methods", First Joint Power and Fuel Systems Contractors Conference, Pittsburgh, PA, July 1996.

Laudal, D. L., Heidt, M. K., Galbreath, K. C., Nott, B. R., and Brown, T. D., "State of the Art: Mercury Speciation Measurement in Coal Combustion Systems", 90th Annual Conference of the Air and Waste Management Association, Toronto (June 1997).

Laudel, D. H., Brown, T. and B. Nott, "Effect of Flue Gas Constituents on Mercury Speciation", Proceedings of the Conference on Air Quality: Mercury, Trace Elements, and Particulate Matter", M Lean, VA, December 1998.

Laudel, D. L., "Field Validation of the Ontario Hydro Mercury Speciation Sampling Method at Site E-29", 99-EERC-07-02, July 1999.

Lee, C. W., Kilgroe, J. D. and S. B Ghorishi, "Mercury Control Research: Effects of Fly Ash and Flue Gas Parameters on Mercury Speciation", Proceedings of the 6th Annual Waste-to-Energy Conference, EPA/600/A98/075, pp 221-238, Miami Beach, FL, 1998.

Lee, C. W., Kilgroe, J. D. and S. B Ghorishi, "Speciation of Mercury in the Presence of Coal and Waste Combustion Fly Ashes", 93rd Annual Conference of the Air and Waste Management Association, Paper No. 167, Salt Lake City, UT, June 2000.

Lee, C. W., Srivastava, R. K., Ghorishi, S. B., Hastings, T. W. and F. M. Stevens, "Study of Speciation of Mercury under Simulated SCR NO_x Emission Control Conditions", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Lee, C. W., Srivastava, R. K., Ghorishi, S. B., Hastings, T. W. and F. M. Stevens, "Investigation of Selective Catalytic Reduction Impact on Mercury Speciation under Simulated NO_x Emission Control Conditions", J. Air & Waste Manage. Assoc., Volume 54, pp 1560-1566, 2004.

Lee, C. W., Srivastava, R. K., Ghorishi, S. B., Karwowski, J., Hastings, T. W. and J. Hirishi, "Effect of SCR Catalyst on Mercury Speciation", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 7, Washington D.C., August 2004.

Lee, J.-Y., Khang, S.-J. and T. C. Keener, "Mercury Removal from Flue Gas with Aerisols Generated by SO₃-NH₃ Reactions", 96th Annual Meeting of the Air and Waste Management Association, Paper No. 69342, San Diego, CA, June 2003.

Lehmann, C. M., B., Rostam-Adabi, M., Rood, M. J. and J. Sun, J. Energy Fuels, Volume 12, Number 6, pp 1095, 1998.

Levin, L., Mercury Inventory and Source Characterization: Emerging Data", 95th Annual Conference of the Air and Waste Management Association, Baltimore, MD, June 2002.

Lewandowski, D., Deluliis, N. and K. Lindsay, "Regulations Spur the Demand for Eastern Coal", Power, New York, Volume 148, pp 36-38, October, 2004.

Ley, T., Ebner, T., Fisher, K., Slye, R., Patton, R. and R. Chang, "Assessment of Low-Cost Novel Sorbents for Coal-Fired Power Plant Mercury Control", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 61, Washington D.C., August 2004.

Li, Y. H., Serre, S. D., Lee, C. W. and B. K. Gullett, "Elemental Mercury Adsorption by Activated Carbon Treated with Sulfuric acid", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Li, Z. and J. Hwang, "Mercury Distribution in Fly Ash Components", Air & Waste Management Association's 90th Annual Meeting & Exhibition, 97-WP72B.05, Toronto, Canada, June 1997.

Lighty, J. S., Silcox, G., Senior, C. and J. Helble, "Fundamentals of Mercury Oxidation in Flue Gas, Technical Annual Report", DOE Report Number DE-FG26-03NT41797, August 2004.

Lin, C. J. and S.O. Pehkonen, "The Chemistry of Atmospheric Mercury: A Review", Atmospheric Environment, 33:2067-2079, 1999.

Lipfert, F. W. and L. Saroff, "Methylmercury Risk Assessment Issues", Managing Hazardous Air Pollutants: State of the Art, EPRI TR-101890, 237-248, 1993.

Lipfert, F., Morris, S., Sullivan, t., Moskowitz, P. and S. Renninger, "Methylmercury,

Fish Consumption, and the Precautionary Principle", J. Air & Waste Manage. Assoc., Volume 55, pp 388-398, April 2005.

Lissianski, V., Zamansky, V., Maly, P. Seeker, R., Folsom, B. and R. Koppang, "Novel Technology for Multiple Pollutant Control", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Lissianski, V., Maly, P., Lo, H., Zamansky, V. M., England, G. C. and W. R. Seeker, "Multi-Pollutant Control for Boilers Firing Low-Rank Coals", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Paper No. 8, Washington, D. C., May 2003.

Lissianski, V., Seeker, W. R., Lo, H., Maly, P., Zamansky, V. M. and G. C. England, "Combustion modifications Can Be Optimized for Mercury Control", 96th Annual Meeting of the Air and Waste Management Association, Paper No. 69315, San Diego, CA, June 2003.

Lissianski, V., Maly, P. and R. Seeker, "Combustion Staging-First Step in Reduction of Mercury Emissions", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 43, Washington D.C., August 2004.

Liu, K., Gao, Y., Kellie, S., Pan, W.-P., Riley, J. T., Ho, K. K. and A. K. Mehta, "A Study of Mercury Removal in FBC Systems Fired with High Chlorine Coals", Comb. Sci. and Tech., Volume 164, pp 145-162, 2001.

Liu, W., Vidić, R. D., and T. D. Brown, "Optimization of Sulfur Impregnation Protocol for fixed Bed Application of Activated Carbon-Based Sorbents for Gas-Phase Mercury Removal", Eviron. Sci. Technol., Volume 32, pp 531-538, 1998.

Livengood, C. D., Mendelsohn, M.H., Huang, H. S. and J. M. Wu, "Development of Mercury Control Techniques for Utility Boilers", 88th Annual Meeting of the Air and Waste Management Association, San Antonio, TX, June 1995a.

Livengood, C. D., Mendelsohn, M.H., Huang, H. S. and J. M. Wu, "Removal of Mercury From Coal-Combustion Flue-Gas" 12th Annual Pittsburgh Coal Conference, Pittsburgh, PA, September 1995b.

Livengood, C. D. and M. H. Mendelsohn, "Enhanced Control of Hg Emissions Through Modified Speciation", Air & Waste Management Association's 90th Annual Meeting & Exhibition, 97-WA72A.08, Toronto, Canada, June 1997.

Livengood, C. D. and M. H. Mendelsohn, "Process for combined Control of Mercury and Nitric Oxide", EPRI/DOE/EPA Combined Utility Air Pollutant Control Symposium, ANL/ES/CP-98498, Atlanta, GA, August 1999.

Livengood, C. D. and M. H. Mendelsohn, "A New Method for Oxidation of Gaseous, Elemental Mercury" Air & Waste Management Association's Mercury in the Environment Specialty Conference, ANL/ES/CP-98436, Minneapolis, MN, September 1999.

Livengood, C. D. and M. H. Mendelsohn, "Process for Combined Control of Mercury and Nitric Oxide", EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium, ANL/ES/CP-98498, Atlanta, GA, August 1999.

Livengood, C. D. and M. H. Mendelsohn, "A Process for Combined Control of Mercury

and Nitric Oxide", 94th Annual Conference of the Air and Waste Management Association, Paper No. 850, Orlando, FL, June 2001.

Livengood, C. D., Mendelsohn, M.H. and B. W. Lani, "Mercury Chemistry in Flue Gas, A Critical Review", 95th Annual Conference of the Air and Waste Management Association, Paper No. 451, Baltimore, MD, June 2002.

Lu, D. Y., Granatstein, D. L. and D. J. Rose, "Study of Mercury Speciation from Simulated Coal Gasification", Ind. Eng. Chem. Res., Volume 43, pp 5400-5404, 2004.

Luttell, G. H., Kohmuench, J. N. and R.-H. Yoon, "An Evaluation of Coal Preparation Technologies for Controlling Trace Element Emissions", Fuel Processing Technology, Volume 65-66, pp 407-422, 2000.

Machalek, T., Richardson, C., Dombrowski, K., Ley, T., Ebner, T., Fisher, K., Brickett, L., Chang, R., Strohfus, M., Smokey, S. and S. Sjostrom, "Full-Scale Activated Carbon Injection for Mercury Control in Flue Gas Derived From North Dakota Lignite", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 83, Washington D.C., August 2004.

Mamani-Paco and J. J. Helble, "Bench Scale Examination of Mercury Oxidation under Non-isothermal Conditions", 93rd Annual Conference of the Air and Waste Management Association, Salt Lake City, UT, June 2000.

Martin, K., Gonzalez, E., Zhou, C. Q., Livengood, C. D. and M. H. Mendelsohn, "Elemental Mercury Control Using a Wet Scrubber", 61st Annual Meeting of the American Power Conference, Chicago, IL, April 1999.

McLarnon, C. R. and D. Steen, "Combined SO₂, NO_X, PM and Hg Removal From Coal Fired Boilers", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

McLarnon, C. R., Granite, E. J. and H. W. Pennline, "Initial Testing of Photochemical Oxidation for Elemental Mercury Removal from Subbituminous Flue Gas Streams, Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 75, Washington D.C., August 2004.

McManus, T. J., Agabede, R. O., Bochan, A. J., Clements, J. L. and R. P. Khosah, "Comparative Evaluation of ATS Method 1, the Ontario Hydro Method and EPA Method 29 for Capture and Analysis of Mercury Species", Air & Waste Management Association's 90th Annual Meeting & Exhibition, 97-WA72A.08, Toronto, Canada, June 1997.

McManus, T. J., Agabede, R. O. and R. P. Khosah, "Conversion of Elemental Mercury to the Oxidized Form in A Fabric Filter Baghouse", Air & Waste Management Association's 91st Annual Meeting & Exhibition, 98-WP79A.07, San Diego, CA, June 1998.

Meegan, G. D., Peterson, C., Hawkins, T. Gant, J., Muston, B., Floyd, E. and C. Clark, "Enhancing Mercury Particulate Removal by Acoustic Flue Gas Conditioning", Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D.C., May 2003.

Meij, R., "Background Concentrations of Gaseous Mercury and Other Gaseous Trace Elements in the Netherlands and the Contribution of Coal-Fired Power Stations", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Meij, R, Vredenbregt, L. H. J. and H. te Winkel, "The Fate and Behavior of Mercury in Coal Fired Power Plants", J. Air & Waste Manage. Assoc., Volume 52, pp 912-917, 2002.

Meischen, S. J., Van Pelt, V. J., Zarate, E. A. and E. A. Stephens Jr., "Gas-Phase Mercury Reduction to Measure Total Mercury in the Flue Gas of a Coal-Fired Boiler", J. Air & Waste Manage. Assoc., Volume 54, pp 60-67, 2004.

Mendelsohn, M. H. and C. D. Livengood, "A New Method for Oxidation of Gaseous, Elemental Mercury", Air and Waste Management Association Mercury in the Environment Specialty Conference, ANL/ES/CP-98436, Minneapolis, MN, September 1999.

Mendelsohn, M. H. and C. D. Livengood, "Development of a Process for Combined Removal of Mercury and Nitric Oxides from Flue Gas", 17th Annual International Pittsburgh Coal Conference, ANL/ES/CP-101334, Pittsburgh, PA, September 2000.

Mendioroz, S., Guijarro, M. I., Bermejo, P. J., and B. Munoz, "Mercury Retrieval from Flue Gas by Monolithic Adsorbents Based on Sulfurized Sepiolite", Environ. Sci. Techno., Volume 33, pp 1697-1702, 1999.

Meserole, F. B., Richardson, C. F., Miller, S. D., Searcy, K. and R. Chang, "Estimating the Costs of Electric Utility Mercury Control Using Sorbent Injection", 93rd Annual Conference of the Air and Waste Management Association, Salt Lake City, UT, June 2000.

Miller, S.J., Dunham, G. E., Olson, E. S. and T. D. Brown, "Mercury Sorbent Development for Coal-Fired Boilers", Proceedings for the Conference on Air Quality: Mercury, Trace Elements and Particulate Matter, M'Lean, VA, December 1998.

Milobowski, M. G., Amrheim, G. T., Kudlac, G. A. and D. M. Yurchison, "Wet FGD Enhanced Mercury Control for Coal-Fired Utility Boilers", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Montgomery, J. L., Whitworth, C. G., Battleson, D. M., Ray, I., Buckley, W., Reynolds, J. and R. Altman, "Latest Developments of the Plasma-Enhanced Electrostatic Precipitator for Mercury Removal in Offgas", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Moskowitz, P. D., Saroff, L., Bolger, M., Cicmanec, J. and S. Durkee, DOE/FDA/EPA Workshop on Methylmercury and Human Health, No. 97233, Bethesda, MD, March 23, 1994.

Nelson, S., Landreth, R., Zhou, Q. Z. and J. Miller, "Accumulated Poer-Plant Mercury-Removal Experience with Brominated PAC Injection", Air and Waste

Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 95, Washington D.C., August 2004.

Niksa, S. and J. J. Helble, "Interpreting Laboratory Test Data on Homogeneous Mercury Oxidation in Coal-Derived Exhausts", EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Niksa, S. and N. Fujiwara, "The impact of Wet FGD Scrubbing on Hg Emissions From Coal-Fired Power Stations" Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 59, Washington D.C., August 2004.

Norton, G. A., Yang, H., Brown, R. C., Laudel, D. L., Dunham, G. E. and J. M. Okoh, "Effects of Fly Ash on Mercury Oxidation in Simulated Flue Gas Environments", 93rd Annual Conference of the Air and Waste Management Association, Salt Lake City, UT, June 2000.

Otero Rey, J. R., Lopez-Vilarino, J. M., Pineiro, J. M., Alonso-Rodriguez, E., Muniategui-Lorenzo, S., Lopez-Mahia, P. and D. Prada-Rodriguez, "As, Hg, and Se Flue Gas Sampling in a coal-Fired Power Plant and Their Fate during Coal Combustion", Environ. Sci. Tehnol., Volume 37, pp 5262-5267, 2003.

Pai, P., Nieme, D., and Powers, W., "A North American Inventory of Anthropogenic Mercury Emissions", 93rd Annual Conference of the Air and Waste Management Association, Paper No. 167, Salt Lake City, UT, June 2000.

Pavlish, J.H., Sondeal, E. A., Mann, M. D., Olson, E. S., Galbreath, K. C., Laudal, D. L. and S. A. Benson, "Status Review of Mercury Control Options for Coal-Fired Power Plants", Fuel Processing Technology, Volume 82, pp 89-165, 2003.

Pavlish, J. H., Holms, M. J., Galbreath, K. C., Zhuang, Y. and B. M. Pavlish, "Pilot Scale Investigation of Mercury Control Technologies for Utilities Burning Lignite Coal", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Pavlish, J. H., Holms, M. J. , Zhuang, Y., Galbreath, K. C., Benson, S. A. and B. M. Pavlish, "Pilot Scale Testing of Sorbent Injection and Fuel Additives for Mercury Control", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 108, Washington D.C., August 2004.

Peletier, R., "Mercury Removal Standards are Coming. Where's the Technology?", Power, New York, Volume 147, Issue 4, pp 40-52, May 2003.

Pflughhoeft-Hassett, D. F., Dockter, B. A., Eylands, K. E., Hassett, D. J., and J. H. Pavlish, "Impact of Mercury Emission Control Technologies on Conventional Coal-Combustion By-Product Management", 89th Annual Meeting of the Air and Waste Management Assoc., 96-RA1114.03, Nashville, TN, June 1996.

Pitoniak, E. R., Wu, C.-Y., Londeree, D., Mazyck, D. and K. Powers, "Oxidation of Vapor-Phase Mercury Using an Innovative Adsorption-Photocatalytic Oxidation System", 96th Annual Meeting of the Air and Waste Management Association, Paper No. 69582, San Diego, CA, June 2003.

Pope, C., "Bush Uses Rule Book to Roll Back Protections", Seattle Post-Intelligencer,

Section A, page 1, March 15, 2005.

Porcella, D. B., Chu, P., and M. A. Allen, "Continental Mercury Emissions to the Atmosphere: Relationship to the Global Mercury Cycle", 89th Annual Meeting of the Air and Waste Management Assoc., 96-RA154.02, Nashville, TN, June 1996.

Reij, R., "The Fate of Mercury in Coal Fired Power Plants and the Influence of Wet FGD", Water, Soil and Air Pollution, Volume 56, pp. 21-33, 1991.

Renninger, S.A., Farthing, G.A. Ghorishi, S. B., Teets, C., and J. A. Neureuter, "Effects of SCR Catalyst, Ammonia Injection and Sodium Hydrosulfide on the Speciation and Removal of Mercury within a Forced-Oxidized Limestone Scrubber", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 15, Washington D.C., August 2004.

Renninger, S.A., Farthing, G.A. Ghorishi, S. B., Teets, C., and J. A. Neureuter, "Using Wet FGD Systems to Absorb Mercury", Power, New York, Volume 148, Issue 8, pp 44-48, October 2004.

Richardson, C., Blythe, G., Rhudy, R. and T. Brown, "Enhanced Control of Mercury by Wet FGD Systems", 93rd Annual Conference of the Air and Waste Management Association, Paper Number 435, Salt Lake City, UT, June 2000.

Richardson, C., Machalek, T., Miller, S., Dene, C. and R. Chang, "Effect of NO_x Control Processes on Mercury Speciation in Utility Flue Gas", j. Air & Waste Manage. Assoc., Volume 52, pp 941-947, 2003.

Richardson, C., Machalek, T., Marsh, B., Miller, S., Richardson, M., Chang, R., Strohfus, M., Smokey, S., Hagley, T., Juip, G. and R. Rosvold, "Chemical Addition for Mercury Control in Flue Derived from Western Coals", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 63, Washington D.C., August 2004.

Richardson, C., Machalek, T., Coleman, G., Chang, R., Carpenter, T., Potter, S. and D. Styer, "Boiler Modifications for Integrated NOX and Mercury Removal from Flue Gas", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 79, Washington D.C., August 2004.

Reynolds, J., "Mercury Removal via Wet ESP", Power, New York, Volume 148, Issue 8, pp 54-58, October 2004.

Rizeq, R., Hansell, D. and W. Seeker, "Predictions of Metals Emissions and Partitioning in Coal -Fired Combustion Systems", Fuel Processing Technology, Volume 39, pp 219-236, 1994.

Rodriguez, S. J., Lee, T.-G., Hedrick, E., Biswas, P., "Iodine Room Temperature Sorbents for Mercury Capture in Combustion Environments", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Rostam-Abadi, M., Chen, S., Lizzio, A. A., His, H.-C., Lehmann, C. M. B., Rood, M., Chang, R., Richardson, C., Machalek, T and M. Richardson, Development of Low Cost Sorbents for Mercury Removal from Utility Flue Gas", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Roy, S. and G. T. Rochelle, "Chlorine Adsorption in Sulfite Systems: A Mechanism in Mercury Removal", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Saroff, L. and F. W. Lipfert, "A Systems Approach to Risk Assessment: Application to th Methylmercury from Coal Combustion", 20 International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, March 1995.

Schlager, R. J. Wilson, K. G. and A. D. Sappy, "Real-Time Analysis of Total Elemental and Total Speciated Mercury" 11 Annual Coal Preparation, Utilization and Environmental Control Contractors Conference, pp. 137-142, Pittsburgh, PA, July 1995.

Seeker, R. and J. D. Hickerson, "Session Two: Partitioning of Trace Elements in Power Plants", Fuel Processing Technology, Volume 39, pp 237-249, 1994.

Seigneur, C., Constantaninou, E., Pai, P., Mitchell, D. and P. Gillespie, "Regional Assessment Of Potential Health Risks Due to Mercury Atmospheric Deposition", 89 th Annual Meeting of the Air and Waste Management Assoc., Nashville, TN, 96-RA154.01, June 1996.

Senior, C.L., Boole, L. E., Huffman, G.P., Huggins G. P., Huggins, F. E., Shah, N., Sarofim, A., Olmez, I. and T. Zeng, "A Fundamental Study of Mercury Partitioning in Coal Fired Power Plant Flue Gas", Air & Waste Management Association's 90 th Annual Meeting & Exhibition, Toronto, Canada, June 1997.

Senior, C.L., Morency, J. L., Huffman, G.P., Huggins, F. E., Shah, N., Peterson, T., Shadman, F. and B. Wu, "Interactions Between Vapor-Phase Mercury and Coal Fly Ash Under Simulated Utility Power Plant Flue Gas Conditions", 91 st Annual Meeting & Exhibition, 98-RA79B.04, San Diego, CA, June 1998.

Senior, C.L., Boole, L. E., Huffman, G.P., Huggins G. P., Huggins, F. E., Shah, N., Sarofim, A., Olmez, I. and T. Zeng, "Toxic Substances from Coal Combustion-A Comprehensive Assessment", DE-AC22-95PC95101-11, December 1998.

Senior, C.L., Sarofim, A. F., Zeng, T., Helble, J. J. and R. Mamani-Paco, "Gas Phase Transformations of Mercury in Coal-Fired Power Plants", Fuel Processing Technology, Volume 63, pp 197-213, 2000.

Senoir, C. L. and R. F. Afonso, "Validation of Fundamentally Based Model for Mercury Emissions from Coal-Fired Power Plants Using ICR Data", 94 th Annual Conference of the Air and Waste Management Association, Paper No. 259, Orlando, FL, June 2001.

Serre, S. S., Gullett, B. K., and S. B. Ghorishi, "Elemental Capture by Activated Carbon in a Flow Reactor", 93 rd Annual Conference of the Air and Waste Management Association, Paper No. 261, Salt Lake City, UT, June 2000.

Shea, Q., "Mercury Control Requires Flexibility", Power, New York, Volume 148, Issue 8, pp 30-31, October 2004.

Shi, L. and D. J. Bayless, "Removal of Mercury from Flue Gas by Coated Fabric Filters", 97 th Annual Conference of the Air and Waste Management Association, Indianapolis, IN, June 2004.

Singer, C. F., Ghorishi, B. and C. B. Sedman, "Lime Based Multi-Pollutant Sorbants", The U.S. EPA-DOE-EPRI Combined Power Plant Air Pollution Control Symposium: The Mega Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects, and Control, Chicago, Ill, August 2001.

Sliger, R. C., Kramlich, J. C. and N. M. Marinov, "Development of an Elementary rd Homogeneous Mercury Oxidation Mechanism", 93 Annual Conference of the Air and Waste Management Association, Paper No. 261, Salt Lake City, UT, June 2000.

Sjostrom, S., Roberts, D. L., Anderson, D. L., Anderson, G., Sagan, F. and J. Smith, "Development and Field Testing of a Continuous, Real-Time, Speciating Mercury Analyzer", 90 th Annual Conference of the Air and Waste Management Association, 97-WA72A.06, Toronto, Ontario, Canada, June 1997.

Sjostrom, S., Ebner, T., Slye, R. and R. Chang, "MerCAP: A Novel Approach for Vapor-Phase Mercury Capture", 95 th Annual Conference of the Air and Waste Management Association, Baltimore, MD, June 2002.

Sjostrom, S., Ebner, T., Ley, T., Slye, R., Richardson, C., Machalek, T., Richardson, M., and R. Chang, "Assessing Sorbents for Mercury Control in Coal-Combustion Flue Gas", J. Air & Waste Manage. Assoc., Volume 52, pp 902-911, 2002.

Sjostrom, S., Chang, R., Hagley, T. Rudek, Skelton, J., Ebner, T. and Slye, R., "Full-Scale Evaluation of Mercury Control Across a Wet Scrubber", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Sjostrom, S., Chang, R., Strophus, M., Johnson, D., Hagley, D., Ebner, T., Slye, R., Richardson, C. and V. Belba, "Development and Demonstration of Mercury Control by Adsorption Process (MerCAPTM)", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Sjostrom, S., Starns, T., Amrhein, J., Bustard, J., Durham, M., Penrod, W., Linville, C., O'Palko, A. and R. Chang, "Full-Scale Evaluation of Mercury Control by Injecting Activated Carbon Upstream of a Spray Dryer and Fabric Filter" Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 71, Washington D.C., August 2004.

Smith, D. J., "The Emissions Squeeze: Environmental Regulations Getting Tighter", Power Engineering, Volume 108, Issue 4, pp 26-31, April 2004.

Srivastava, R. K., Staudt, J. E. and W. Jozewicz, "Preliminary Estimates of Performance and Cost of Mercury Emission Control Technology Applications on Electric Utility Boilers: An Update", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 59, Washington D.C., August 2004.

Starns, T., Bustard, J., Durham, M., Martin, C., Schlager, R., Sjostrom, S., Lindsey, C., Donnelly, B., Afonso, R., Chang, R. and S. Renninger, "Results of Activated Carbon Injection Upstream of Electrostatic Precipitators for Mercury Control", Air And Waste Management Association Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D. C., May 2003.

Starns, T., Amrhein, J., Martin, C., Sjostrom, S., Bullinger, C., Stockdill, D., Strofus, M.

and R. Chang, "Full Scale Evaluation of TOXECON II™ on a Lignite-Fired Boiler", Air and Waste Management Association's Combined Power Plant Air Pollution Control Mega Symposium, Paper No. 72, Washington D.C., August 2004.

Vann Bush, P., E. B. Dismuks and W. K. Fowler, "Characterizing Mercury Emissions From a Coal Fired Power Plant Utilizing a Venturi FGD System", DOE # AC22-93 PC 93254, pp.105-112, 1995.

Warnatz, J., Maas, U., and Dibble, R.W., Combustion, Springer Publishing Company, 67-71 (1996).

Widmer, N. C., Cole, J. A., Seeker, W. R. and J. A. Gaspar, "Practical Limitation of Mercury Speciation in Simulated Municipal Waste Incinerator Flue Gas", *Combust. Sci. Techno.*, Volume 134, pp 315-326, 1998.

Widmer, N. C., West, J. and J. A. Cole, "Thermochemical Study of Mercury Oxidation in Utility Boiler Flue Gases", 93rd Annual Conference of the Air and Waste Management Association, Paper No. 390, Salt Lake City, UT, June 2000.

Weiss, B., "Neurotoxic Risks of Methyl Mercury", Managing Hazardous Air Pollutants, State of the Art, EPRI TR-101890: 237-248, 1993.

Whipple, C. G. and R. Von Berg, "Analytical Issues in the Exposure Assessment of Mercury Emissions from Coal Fired Power Plants", 89th Annual Meeting of the Air and Waste Management Assoc., 96-RA154.03, Nashville, TN, June 1996.

Yan, R., Liang, D. T., Tsen, L., Wong, Y. P. and Y. K. Lee, "Adsorption of Mercury in Combustion Flue Gas by Activated Carbon", 95th Annual Conference of the Air and Waste Management Association, Baltimore, MD, June 2002.

Yan, R., Ng, Y. L., Liang, D. T. , Lim, C. S. and Y. Wang, "Bench Scale Experimental Study on the Effect of Flue Gas Composition on Mercury Removal by activated Carbon Adsorption", 96th Annual Meeting of the Air and Waste Management Association, Paper No. 69541, San Diego, CA, June 2003.

Zhuang, Y., Biswas, P., Quintan, M. E., Lee, T. G., Arar, E., "Kinetic Study of Adsorption and Transformation of Mercury on Fly Ash Particles in an Entrained Flow Reactor", 93rd Annual Conference of the Air and Waste Management Association, Paper No. 331, Salt Lake City, UT (June 2000).