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

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Abstract

Oxidized mercury formed in combustors (*e.g.*, HgCl_2) is much more easily captured in existing pollution control equipment (*e.g.*, wet scrubbers for SO_2) than elemental mercury. This is principally due to the high solubility of the oxidized form in water. Work over the last several years in our laboratory and elsewhere has identified the general outlines of the homogeneous chemistry of oxidation. The goal of the work reported here is to make use of this knowledge of the oxidation mechanism to devise simple and inexpensive ways to promote the oxidation. The hypothesis is that simple fuels such as hydrogen or CO can promote oxidation via the free radicals they generate during their decomposition. These free radicals then promote the formation of Cl from HCl via reactions such as $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$. The Cl (and Cl_2 derived from Cl recombination) are considered the principal oxidizing species. In our studies, mercury vapor is exposed to HCl under isothermal conditions in a gas containing N_2 , O_2 , and H_2O . The experiments systematically explore the influence of reaction temperature, HCl concentration, and H_2O concentration. These baseline conditions are then perturbed by the addition of varying amounts of H_2 , CO, and H_2/CO added jointly. The following report presents the results of a literature review associated with the dissertation of the student supported by the program. This outlines the state-of-the-art in mercury behavior. It then describes the experimental facilities and the results of tests involving the promotion of the oxidation reaction by H_2 , CO, and H_2/CO combinations. These results indicate a substantial enhancement of oxidation under isothermal conditions at 900-1000 K, while the additives inhibit oxidation at 1200 K. The next step is to determine whether the existing chemical kinetic models of mercury oxidation are capable of reproducing this behavior. These models can then be used to extrapolate the findings to non-isothermal conditions typical of boiler environments. This would provide guidance on where to inject the oxidation promoters in a practical boiler, and how much promoter is required.

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Introduction

The EPA has recently released proposed mercury regulations for the nation's coal-fired electric generation plants. These regulations focus initially on moderate levels of emission reduction and they include an emissions trading option. The regulations thus provide a potential niche for technologies that deliver a moderate amount of control at a very low cost as opposed to high efficiency, but very high cost technologies (*e.g.*, activated carbon spray drying). Our research focuses on the fact that mercury emissions are partitioned into (1) elemental mercury, and (2) bivalent mercury (usually assumed to be HgCl_2). Bivalent mercury is water-soluble and is removed to a reasonable level of efficiency by aqueous back-end pollution control systems. Thus, the limestone slurry SO_2 scrubbers present in many plants can also remove much of the oxidized portion of the mercury emission at no additional cost.

This approach works best if the mercury can be forced to the oxidized state. Until a few years ago the mechanism governing the oxidation of mercury in coal combustion systems was unknown, so devising a way to promote the oxidation was not possible. Work in our laboratory and elsewhere has uncovered the broad outline of how mercury is homogeneously oxidized, and makes it possible to propose measures to promote oxidation. Here we will briefly review the oxidation mechanism (Sliger *et al*, 2000), and then discuss the proposed approach for promoting oxidation.

The community generally accepts that during combustion the mercury contained in coal is quantitatively released to the gas phase as elemental mercury, the favored equilibrium product at flame temperatures. At the same time, the coal chlorine is converted mostly to HCl. The direct reaction of $\text{Hg} + \text{HCl}$ is hindered by too large of an energy barrier to be of consequence under normal combustion conditions. A fraction of the HCl does, however, disassociate to produce atomic chlorine (Cl), which is capable of reacting with Hg. The reaction:

is believed to proceed near the collisional limit. At high temperatures, however, reverse reactions destroying the HgCl are fast and no appreciable HgCl concentration appears.

As the gases cool, the Cl begins to recombine via:

This reaction is relatively slow, and appears to allow a significant amount of Cl to persist into relatively low temperature environments. Under these conditions the oxidation reaction noted above will proceed. In addition, reactions involving the Cl_2 generated by the recombination reaction will also proceed.

Thus, the general idea is that:

- The high temperature environment provides the reactive chlorine species needed for oxidation, but no net oxidation occurs here due to fast reverse reactions that convert HgCl and HgCl₂ back to Hg.
- The reactive chlorine species survive the thermal quench of the flame gases (which occurs either in a probe or due to heat extraction in the furnace).
- At lower temperatures the reactive chlorine species oxidize the Hg, and the reverse decomposition reactions are negligible.

These mechanistic ideas have undergone continued refinement over the last five years. First, the role of NO as a mercury oxidation deactivator has been attributed to the loss of OH (which is important for converting HCl to Cl) via (Niksa *et al.*, 2001, Livengood *et al.*, 2002):

Additional reactions have been proposed by which sulfur species can generate chlorine atoms (Qiu *et al.*, 2003). Also, although direct formation of HgO in the absence of chlorine is not indicated, reactions that generate HgO through chlorine intermediates have been suggested (Xu *et al.*, 2003). For example:

Given this overall scenario, how would one enhance the conversion of elemental Hg to the water-soluble oxidized form needed to take advantage of capture by existing wet pollution control equipment? Since the conversion of HCl to Cl is primarily via:

one approach is to enhance free radical concentrations in the post-flame region. Our approach is to introduce small amounts of species such as H₂ or CO at appropriate locations in the post flame gases. The oxidation of these species generate superequilibrium free radical concentrations that can promote Cl formation in the down stream region, where it can be effectively used in increasing Hg oxidation. In a practical system, the source of the H₂ or CO would be from a small on-line natural gas reformer.

The goals of the research presented here are to answer the following questions:

- Will this approach work?
- Assuming it will, how much agent should be injected, and what is the optimum injection temperature?
- Is H₂ versus CO the preferred agent, or does a mixture of the two provide the best results?
- Can the results be accurately described by chemical kinetic models?

- If so, can these models be used to accurately extrapolate the results to practical, non-isothermal systems (*i.e.*, where should the agent be injected, and how much should be injected to achieve best results under typical boiler time/temperature histories)?

Literature Review on Homogeneous Chemistry

This section presents a literature review on the homogeneous mercury oxidation problem. This is based on a portion of the dissertation being drafted by Linda Castiglione, the Ph.D. student being supported by the present grant.

Mercury chlorination by homogeneous gas phase reactions is considered an important mercury oxidation mechanism in coal combustion flue gas. Homogeneous mercury oxidation reaction pathways involving other species exist, but are considered to have a lesser effect on the overall oxidation rate. The species involved in these reactions include oxygen, nitrogen dioxide and nitrogen oxide (Pavlish *et al.*, 2004). Heterogeneous reactions involving mercury oxidation have been documented primarily involving surfaces and fly ash, as well as SCR catalysts. 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.*, 2002).

The amount of mercury emitted, and the oxidation state of the mercury vary widely from plant to plant. While the oxidation state correlates roughly with the coal chlorine content, a number of other factors are thought to influence oxidation, *e.g.*, mineral matter composition, coal burnout, and the presence of pollution control equipment. When sufficient amounts of chlorine species are present in the coal, wet pollution control equipment has been noted to reduce overall mercury emissions (Livengood and Mendelsohn, 1997).

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.*, 2002). 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 the 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 here.

The Basis for Oxidation Mechanism Development Mercury possesses a very low vaporization temperature being completely in the vaporized 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 system, 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 *et al.* 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.) 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 *et al.*, 1999), however a rough correlation has been made between chlorine present in the coal and amount of oxidation present. 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 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, 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).

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 and Helble 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 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 and Helble 2001). 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 show conflicting results over widely varied conditions (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. 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.

Both isothermal and non-isothermal experiments investigating mercury transformation kinetics have been conducted by a number of researchers. The isothermal experiments (Sliger *et al.*, 2000; Lee *et al.*, 1998; Gaspar *et al.*, 1997; Hall *et al.*, 1991; Widmer *et al.*, 1998) 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 (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 from a wide variety of sources indicate that oxidation increases for both increasing reaction temperature and increasing HCl concentrations. 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 and Afonso, 2001).

Conflicting with most homogeneous 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 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 HgCl_2 . Equilibrium calculations for mercury and hydrogen chloride at various temperatures and hydrogen chloride concentrations are provided in Figure 1 illustrating that as the gas temperature decreases, the equilibrium concentration of mercuric chloride (HgCl_2) increases (Hall *et al.*, 1991; Widmer *et al.*, 1998.) When hydrogen chloride concentration is varied from fifty to five hundred parts 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.*,

Figure 1. Equilibrium oxidation predictions.

1994; Senior *et al.*, 2000.) There is disagreement between the equilibrium results and collected reactor data where Cl_2 was found to react rapidly with mercury, which 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 rapidly until 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 and Helble 2000). Comparison of the data reported above with the equilibrium model in Figure 1 indicates a conflict between equilibrium prediction and actual mercury measurements for mercury speciation. Specifically, in the experiments, high temperature favors oxidation, while equilibrium suggests that low temperatures favor the oxidized form. 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 speciation is believed to be set 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.*, 2002; Lu *et al.*, 2004.)

At high temperatures (above 400°C) mercury and hydrogen chloride both exist in a 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 controlled by equilibrium, all flue gas mercury would be converted to mercuric chloride in the presence of excess chlorine, which is contradictory to observation. 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 accurate speciation in this application. The mercury reaction set is still not completely defined. The reaction mechanism and rate coefficients have 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. Each kinetic model was formed or modified to provide a better match to experimental data. Some models proved more accurate than others, but none to date provides a complete mechanistic tool for accurate analysis of mercury oxidation by chlorine under all flue gas conditions.

The historical foundation of mercury oxidation kinetics was the 1949 proposal of a one step mechanism for mercury oxidation by chlorine:

This implies an intermediary step in the oxidation pathway of Hg 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 (Hall *et al.*, 1990) into mercury reactions in flue gas began in earnest with the definition of a mechanism for the oxidation of mercury by oxygen over the temperature range of 475-775 K by the reaction:

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 the following reactions. 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 an additional possible overall reaction for mercury oxidation that is listed below (Hall *et al.*, 1991.) This global reaction is thought to include the formation of HgO as an intermediate species in the mercury oxidation mechanism. This mechanism 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 (Ghorishi *et al.*, 1999) for this phenomena and put forth as

where the scavenging of Cl_2 by SO_2 is suggested as an inhibiting mechanism

An eight step reaction mechanism was put forth by Widmer *et al.* (2000) describing the formation of mercury chloride. In the reaction set listed below, the rate constants were estimated from the literature Qualitative evaluation of these reactions has shown that fast oxidation of Hg occurs through the first reaction.

Modifications to the 2000 mechanism (2000b) were made by Sliger *et al.* (2000) to improve accuracy. Specific rates were added for the following two reactions to accurately capture the branching ratio between the addition and abstraction reactions.

Two mechanisms were developed independently in 2001. The first by Edwards *et al.* (2001) was developed to model bench-scale experimental data by Widmer and Ghorishi (Widmer *et al.*, 1998; Ghorishi and Gullett, 1998) by reworking the previous 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 $\text{Hg} + \text{O} \rightarrow \text{HgO}$ listed above. 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 was included (Cl , Cl_2 , ClO , HCl and HOCl .) The set forms an 18 step reaction mechanism that is included in Appendix A of this document with reaction rate constants. 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 *et al.* (2001) 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 reactions. 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

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 *et al.* (2003) 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 following reactions in the mechanism. 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 *et al.* (2003) in the year 2003. This mechanism consists of 107 reactions and 30 species, including a six step mechanism for reactions involving HgO. The HgO portion of mechanism is put forth below.

These mechanisms form the basis by which we will both interpret our data and extrapolate our results to non-isothermal systems.

Experimental

The experiments are performed in a quartz flow reactor system. This provides an approximately 0.5 second isothermal reaction environment where the temperature can be varied from ambient to

1700 K. Figure 2 shows the clamshell oven that contains the quartz flow reactor. The various reagent gases (N_2 , O_2 , HCl , H_2 , CO) are metered (see Figure 3) and introduced in separate quartz preheat channels. Figure 4 shows a cross-section of the reactor itself. The system provides four isolated preheat channels. Three of the channels are premixed just upstream of a 0.5 mm nozzle. The fourth stream flows around the outside, and it contains most of the flow (O_2 and the N_2 not used for Hg and H_2O transport). Water is metered as a liquid via a syringe drive, and is converted to vapor by an electric vaporizer before being mixed with the gases. Mercury vapor is generated by passing N_2 through a bubbler/saturator that contains liquid Hg in a constant temperature bath. This vapor stream is then diluted.

Figure 2. Quartz flow reactor system and clamshell oven.

Figure 3. Manifold flow panel.

The details of the process are as follows. The reactor 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 H_2 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 gases manifolded in a way similar to that found in zone 1.

A modified Buck 400A mercury analyzer is 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

Figure 4. Schematic cross-section of the quartz flow reactor.

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:

$$I = I_0 e^{-kcl} \quad (1)$$

where:

- I = emergent beam intensity
- I_0 = Incident beam intensity
- k = constant of proportionality
- c = Mercury concentration (mole/m³)
- l = optical tube length

Modifications to the analyzer are extensive for this particular application. The detector is designed to operate on discrete 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 is bypassed to allow for these considerations. The detector cell is plumbed directly into the flow path immediately downstream of the reactor quench region. This helps minimize sequestration regions in the flow system. The absorption cell is 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 is added. In addition, the cavity in which the detector is positioned is vented to atmosphere. A shop air purge is retrofitted within the detector cell cavity to provide a constant amount of atmospheric water vapor variation of which is found to adversely affect the phototube detector. Even this small amount of water vapor is found to profoundly interfere with light transmittance at the operational frequency causing data to be unstable. A strip chart recorder is added to determine data trends.

Calibrations are conducted at the beginning and end of each test run. Analyzer calibration is 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 are rectified by depriving the system of mercury and re-zeroing the Buck analyzer across the span of the instrument.

Cleaning of the mercury contaminated gasses is required before venting to atmosphere. Once the mercury laden stream is analyzed, the flow is 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 scrubs all elemental and oxidized mercury out of the gas stream before it was exhausted to atmosphere. Impinger liquid is appropriately disposed and replaced of at the end of each set of tests.

The data acquisition process in this experiment requires long reactor equilibration times and very delicate adjustments to the equipment. The presence of nitrogen is maintained in the flow circuit at all times. Time to reactor equilibration from a cold start to full operational capacity is five to seven days. Complete reactor purge is found to take approximately 48 hours. Data point equilibration times varied and are longest when hydrogen is involved, varying from ten minutes

per data point for a calibration, to four hours for an acid calibration, to six hours when hydrogen is used. It is believed that the mechanism behind these phenomena involve both chemical and transport processes. Molecular sequestration occurred in a number of geometric spaces throughout the flow system, and is 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 are defined, the accuracy and repeatability of the experiment are assured.

Each test requires 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 provides vaporized mercury at a known concentration and is located just upstream of the reactor. The temperature of the water bath and the heated glass line are recorded. This stream is 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 is followed by the appropriate equilibration period for the reactor. Data are taken both by hand and by using a strip chart recorder for detector measurements. For each stream the line pressure and flow rates are documented. Temperatures of the water line, mercury bubbler and bubbler supply line, reactor, quench gas, and detector are documented as well as atmospheric temperature and pressure. Data sheets are 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 is used to monitor the trend of the percent transmittance, and to ensure that instrument drift was monitored, detected and corrected.

This experimental configuration exhibit complex behaviors which limit the way test series are conducted. Equilibration times for adding species are found to an order of magnitude less than that found in subtracting species. Increasing temperatures require, 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 are conducted by increasing oxidizing species rather than decreasing them, and by subtracting neutral species before adding oxidizing species. Further, temperature surveys are conducted starting from 922 K increasing to 1200 K. Violation of these rules caused unstable reactor operation and inconsistent data in all cases.

Results and Discussion

Our previous report addressed the role of water as an inhibitor for oxidation. A summary of these results is shown in Figure 5, which indicates that oxidation is essentially complete in dry gases. Under the low HCl loading, increasing the water vapor concentration to typical combustion values did indeed significantly deactivate the oxidation process. With the higher HCl loading, the deactivation was much less pronounced. Although detailed chemical kinetic modeling of these specific experiments has not been done, the results suggest that the higher HCl concentrations are capable of forcing a more significant Cl concentration in the face of the reverse reaction driven by water vapor. Thus, it is clear that water has a significant role in the

oxidation process, and it provides an explanation for the difference noted between the results of Hall *et al.* and others.

Figure 5. Influence of water vapor concentration on Hg oxidation.

Figure 6 shows baseline data on oxidation by HCl without any promoters. The conditions are identical to those of Figure 5 except the water concentration is 5 ppm. This shows many of the features that have been noted in earlier studies. First, there is no oxidation in the absence of HCl. Next, the oxidation is strongly promoted by higher temperatures. In our present understanding of the process, this occurs due to higher concentrations of Cl being generated at higher temperatures, leading to more oxidation during quench. Finally, we see that much of the oxidation occurs with the first increments of HCl addition, and only a little more oxidation noted with increasing HCl.

Figure 7 shows the effect of adding H₂ to the reaction mixture. The conditions are identical to those of Figure 3, but with HCl held constant at 330 ppm and the water concentration is increased to 5% (mole). Note that this generally results in a significant decrease in mercury oxidation when no H₂ is present. The figure shows that the addition of H₂ generally results in a substantial enhancement of mercury oxidation at the lower temperatures, and in fact actually reduces oxidation at the highest temperatures. Finally, note that the full benefit of H₂ injection is realized at fairly low concentrations. In this case, most of the promotion effect is achieved by the time 25-50 ppm of H₂ is injected.

Figure 6. Oxidation of mercury by HCl in the absence of promoters at three temperatures (K).

This interesting behavior led us to investigate the temperature dependence of the oxidation in more detail. This resulted in Figure 8 where the H_2 concentration was held constant at 100 ppm. The results indicate that the promotion is most pronounced for the 1200-1300 K reactor temperatures, while it is gone by 1700 K. Another interesting observation is that some oxidation appears to persist to fairly low temperatures in the presence of H_2 , while in its absence there is essentially no promotion.

We investigated CO as a promoter at varying concentrations and at each of the temperatures. The results indicated no change in the oxidation state.

Figure 7. Influence of H₂ on mercury oxidation.

Figure 8. Influence of temperature on mercury oxidation with and without H₂.

Figure 9. Influence of CO on mercury oxidation in the presence of H₂.

Finally, the co-injection of CO with H₂ was investigated. Figure 9 shows that there is a slight promotion effect when the CO is included at 1200 K, and none at 1700 K. At present we are working to fully quantify these preliminary results.

Conclusions

At the end of the second year of the program, we have perfected the experimental system and achieved repeatable results. We repeated a series of baseline results and have shown that the oxidation as a function of temperature and HCl is consistent with past measurements. We also demonstrated the effect of water on the oxidation process. This solves one of the outstanding questions from the data record: why the results of Hall *et al.* (1990, 1991) give so much more fractional oxidation than those of others who have used similar experimental conditions. In the case of Hall, the dry experiments lead to much higher oxidation. We systematically investigated the influence of added H₂ on oxidation in tests that varied temperature and the amount of H₂ added. The results indicate a significant increase in oxidation, particularly when the H₂ was injected at lower temperatures. At the highest temperature of 1200 K the H₂ reduced the amount of oxidation.

One important finding is that only fairly small amounts of H₂ are needed to provide the promotion. Much of the promotion effect was achieved with only 50 ppm of H₂ addition. If steam reforming of natural gas is used to generate the H₂, then the amount of natural gas needed by a utility boiler calculates to a quite small amount (a 600 MWe plant would require the order of 0.4 ft³/s of natural gas under these assumptions).

The next step is to determine whether the existing chemical kinetic models of mercury oxidation are capable of reproducing this behavior. These models can then be used to extrapolate the findings to non-isothermal conditions typical of boiler environments. This would provide guidance on where to inject the oxidation promoters in a practical boiler, and how much promoter is required.

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