REDUCTION OF INHERENT MERCURY EMISSIONS IN PC COMBUSTION

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Abstract

Mercury emission compliance presents one of the major potential challenges raised by the 1990 Clean Air Act Amendments. Simple ways of controlling emissions have not been identified. The variability in the field data suggest that inherent mercury emissions may be reduced if the source of this inherent capture can be identified and controlled. The key mechanisms appear to involve the oxidation of mercury to Hg^{++} , generally producing the more reactive HgCl_2 , followed by its capture by certain components of the fly ash or char, or in the air pollution control equipment. This research focuses on identifying the rate-limiting steps associated with the oxidation step.

Work in this reporting period focused on testing of the kinetic mechanism reported in the previous semiannual report, and the interpretation of data (both ours and literature). This model yields good qualitative agreement with the data and indicates that mercury oxidation occurs during the thermal quench of the combustion gases. The model also suggests that atomic chlorine is the key oxidizing species. The oxidation is limited to a temperature window between 700-400°C that is defined by the overlap of (1) a region of significant superequilibrium Cl concentration, and (2) a region where oxidized mercury is favored by equilibrium. Above 700°C reverse reactions effectively limit oxidized mercury concentrations. Below 400°C, atomic chlorine concentrations are too low to support further oxidation. The implication of these results are that homogeneous oxidation is governed primarily by (1) HCl concentration, (2) quench rate, and (3) background gas composition.

Work conducted under the present grant has been the subject of one journal paper that was accepted for publication during the reporting period (Sliger *et al.*, 1999).

Introduction

The possible imposition of mercury emission regulations presents a serious challenge to the coal-fired utility industry and to the waste incineration industry. Field studies show that coal fired plants emit anywhere from 5% to 95% of the mercury contained in their coal. The reasons for this variability are poorly understood, but appear to involve the oxidation state of the mercury, the properties of the mineral matter associated with the coal, and the type of existing air pollution control equipment installed on the furnace. In particular, oxidized mercury (almost exclusively as HgCl_2) is known to show higher retention in the furnace and air pollution control equipment, a property attributed to its water solubility and its higher reactivity relative to elemental mercury. Thus, oxidation is a critical step that tends to reduce stack emissions. The factors that govern the oxidation of mercury in furnaces are, however, not known. The identification of the mechanisms that are active in

promoting oxidation is the first step in devising means of controlling the oxidation and capture process.

The literature clearly shows that homogeneous oxidation pathways exist (Hall *et al.*, 1991; Widmer *et al.*, 1998). In addition, heterogeneous processes are also considered to be important contributors in some regimes, either via promoting direct oxidation or by catalytically generating reactants for homogeneous oxidation (Senior *et al.*, 1997). In any case, an *accurate homogeneous oxidation mechanism* is needed as a component in any overall model of the fate of mercury in practical combustion. The work reported here focuses on this goal.

Overview of Mercury Oxidation Chemistry

Mercury is of sufficiently high volatility that it is presumed to completely vaporize in the flame irrespective of its original form. At flame temperatures, equilibrium indicates mercury will exist in the elemental state. As temperatures fall, the favored equilibrium product shifts to HgCl_2 , with cross-over temperatures ranging from 530 to 740°C, depending on the background HCl concentration. Thus, mercury oxidation would appear to be a low-temperature process.

In fuel-lean flames, the predominant form of chlorine is as HCl, so the examination of HCl as an oxidant has been an important component in oxidation studies. The global reaction of $\text{Hg} + \text{HCl}$ has been studied in flow reactor experiments (Hall *et al.*, 1991; Widmer *et al.*, 1998). The results show that mercury oxidation increases with temperature, at least to 900°C. This is in apparent contradiction to the equilibrium results, which indicate that at these temperatures elemental mercury is the exclusive form. To understand these results, we need to examine the elementary reactions involved. (A detailed discussion is presented in Semiannual Report No. 7.)

The elementary reaction $\text{Hg} + \text{HCl}$ is hindered by a very high energy barrier due to the stability of HCl, and cannot be considered as an important path under practical conditions. This, coupled with the appearance of oxidation at higher temperatures, suggests that the elementary oxidation process occurs via a decomposition intermediate of HCl. The appearance of this intermediate would be promoted by higher temperatures. One such intermediate is chlorine atom. The rate of the reaction:

has been reported in the literature. This low energy barrier reaction proceeds at room temperature at a rate near the collision limit, and its rate constant shows little apparent temperature dependence.

The subsequent oxidation of HgCl to HgCl_2 could occur via several paths, including:

Although an abstraction path must be considered for the latter reaction:

Another pathway is the direct oxidation of Hg by Cl_2 :

The rate of this reaction has been measured in flow reactor studies (Hall *et al.*, 1991) and found to proceed at room temperature. As mentioned above, the difficulty is the manufacture of enough Cl_2 to promote the reaction.

We have examined Reaction 2 in detail in the preceding Semiannual Report, and have concluded that it is too slow to contribute to the second oxidation step. Reaction 3 cannot contribute at high temperature due to the low concentration of Cl_2 under these conditions. Reaction 4 has, however, essentially no energy barrier and is expected to proceed at near the collision limit. Thus, the scenario indicated by this analysis suggests that replicating chlorine atom behavior is the key to modeling high-temperature mercury oxidation chemistry.

Experimental Apparatus and Procedure

The experiment is a flow reactor system that uses a natural gas flame as the source of reactants; it has been described previously (Chenevert *et al.*, 1998). The system is down-fired on natural gas and air at a rate of 16.1 kW. During testing, a mercury acetate solution is atomized into the flame, where it decomposes and is reduced to elemental mercury. The flow channel narrows to 2.5 cm diameter, at which point HCl is injected and dispersed. Following injection, the reactor expands to a 20 cm diameter, which is held to the sample point. The reactor is insulated, and uses external heating to maintain a near isothermal temperature profile.

Two approaches are used to characterize mercury. The first is a simplification of EPA Method 29. In the present experiments a quartz probe is used without a filter since no particulate matter is present in the experiment. There is no SO_2 to act as an interfering species, and molecular chlorine are expected to be too low to cause an interference. In addition, a Buck Hg analyzer is available and will be used in the future to speed data taking. Since HCl flow to the experiment can be interrupted and reestablished at will, the difference between the Hg° signal with no HCl present (representing the total reactor mercury flow) and Hg° with HCl present (representing the unoxidized fraction) is used to generate accurate and fast oxidation data.

Preliminary Results and Discussion

Figure 1 shows data obtained at 922°C (analysis via Method 29). The general trend is consistent with the data of Hall *et al.* and Widmer *et al.* in that oxidation increases with increasing HCl. The Hall data for a comparable temperature are also shown on the plot. Note that these data show a much higher oxidation extent at essentially the same temperature and a shorter residence time.

The kinetic mechanism uses a $\text{H}_2/\text{O}_2/\text{CO}/\text{CO}_2$ reaction set from the literature (Warnatz *et al.*, 1996), along with the reactions involving Cl , Cl_2 , HCl , ClO , HOCl , from the NIST data base (NIST, 1999), and the Reactions 1-6 involving mercury noted above. The present experimental system is modeled as a plug-flow reactor at the measured temperature with the calculation starting at the chlorine injection point. Due to the potential for continued reaction within the sampling system during the cooling of the gases, the probe is treated as an extension of the plug-flow reactor, operating at a quench of ~ 5400 K/s to room temperature.

Figure 1. Comparison of data and kinetic model for the present data (922°C, 1.4 s) and literature (900°C, 0.7s).

The results of the calculation are shown in Figure 1. Analysis of the results indicates that the entire oxidation is due to $\text{Hg} + \text{Cl} \rightarrow \text{HgCl}$ and $\text{HgCl} + \text{Cl} \rightarrow \text{HgCl}_2$. Furthermore, the entire oxidation is taking place within the temperature quench environment provided by the sample probe. Time-resolved modeling shows the following scenario. At the inlet to the quench region, mercury is in its elemental equilibrium state. The shallow temperature decline in the furnace causes a decrease in equilibrium Cl, while kinetic constraints on recombination maintain the calculated Cl somewhat above the equilibrium value at the probe inlet. The rapid quench coupled with kinetic constraints on recombination cause the chlorine atom to hold a significant superequilibrium concentration. This, coupled with the slowing of the reverse of Reactions 1 and 4, leads to oxidation. The oxidation proceeds within a window between 700-400°C associated with the overlap of (1) superequilibrium Cl (for $T > 400^\circ\text{C}$), and (2) HgCl_2 as a favored equilibrium product (for $T < 700^\circ\text{C}$). Also note that this quench behavior must occur in any system since hot gases must cool to near room temperature before measurement, either in a furnace or in a probe. The quench rate does, however, influence the degree of conversion (Sliger *et al.*, 1999).

The model was also applied to the Hall *et al.* (1991) experiment, with the results shown in Figure 1. Note that since the 900°C reaction gases were necessarily quenched to room temperature before analysis, we included a quench at 5400 K/s in the model of these data. The much higher oxidation extent is due to the background composition used in the Hall experiment (10% O_2 , trace HCl, Hg, balance N_2). The near absence of H_2O leads to an approximately 30x increase in equilibrium Cl, causing the much more extensive oxidation.

Thus, the critical issues for study are (1) experiments that test the validity of the proposed model, and (2) development of improved detailed understanding of the important individual reaction rates.

Conclusions

A number of experiments, including the present data, suggest that mercury oxidation occurs at temperatures above the point where equilibrium predicts only elemental mercury will exist. Examination of possible elementary reactions indicates that only reactions with Cl are fast enough to account for the oxidation. Chemical kinetic modeling of the reaction environment, including the inevitable quench that must precede analysis (which occurs either in a probe or in the furnace), suggests that the oxidation occurs within a window between 700 and 400°C that is the result of the overlap of (1) a region of superequilibrium Cl concentration, and (2) a region where oxidized mercury is favored by equilibrium. The implication of these results are that homogeneous oxidation is governed primarily by (1) HCl concentration, (2) quench rate, and (3) background gas composition. The latter point is illustrated by the almost dry Hall data, where equilibrium Cl concentration are substantially elevated above those in the present experiment, resulting in much more oxidation. It also suggests that adding chlorine to improve oxidation will be most effective if the chlorine is exposed to a high-temperature environment, as observed in field data.

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