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Research and Development

FUNDAMENTALS OF MERCURY
SPECIATION AND CONTROL
IN COAL-FIRED BOILERS

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Prepared by

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FOREWORD

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E. Timothy Oppelt, Director
National Risk Management Research Laboratory

EPA REVIEW NOTICE

Fundamentals of Mercury Speciation and Control in Coal-Fired Boilers

Prepared By:

S. Behrooz Ghorishi

ARCADIS Geraghty & Miller, Inc.
4915 Prospectus Drive
P.O. Box 13109
Research Triangle Park, NC 27709

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EPA Work Assignment Manager:

Chun Wai Lee

Air Pollution Prevention and Control Division
National Risk Management Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Prepared for:
U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

ABSTRACT

Understanding the transformation of mercury species in coal combustion flue gases is of interest to both those responsible for developing control technologies and those responsible for setting regulations on mercury emissions. Mercury speciation in simulated coal combustion flue gases was investigated. The effects of coal fly ash and flue gas parameters on the oxidation of elemental mercury (Hg^0) in the presence of hydrogen chloride (HCl), in a simulated post-combustion region, and in the baghouse portion of air pollution control systems (APCS) were studied. Gas-phase studies indicated that the in-flight post-combustion oxidation of Hg^0 in the presence of HCl is very slow and proceeds at measurable rates only at high temperatures (>700°C) and high HCl concentrations (>200 ppm). The presence of sulfur dioxide (SO_2) and water vapor in the simulated flue gas significantly inhibited the gas-phase oxidation of Hg^0 in the presence of HCl. On the other hand, a preliminary investigation indicated that gas-phase reaction of Hg^0 with chlorine (Cl_2) is fast. At 40°C and in the presence of 50 ppmv Cl_2, 100% of the input Hg^0 was oxidized in the gas-phase within 2 seconds of residence time. These results indicate that Cl_2 is a much more active chlorinating agent than HCl. The effects of coal fly ash components and compositions were investigated using a fixed-bed of model or simulated fly ashes. The primary focus was on evaluating the catalytic Hg^0 oxidation activity of major mineral constituents of coal fly ashes: alumina (Al_2O_3), silica (SiO_2), iron (III) oxide (Fe_2O_3), copper (II) oxide (CuO), and calcium oxide (CaO). Copper and iron oxides were the only two components that exhibited significant catalytic activity toward a surface-mediated oxidation of Hg^0. The observed catalytic activities were hypothesized to be effected through the formation of a chlorinating agent (most probably Cl_2) from gas-phase HCl on the surface of metal oxides (the Deacon process reaction). Copper was a much more active catalyst than iron, and its catalytic activity was less influenced by the presence of oxidation inhibitors (SO_2 and water vapor) in the simulated flue gas. The presence of small quantities of CuO (0.1% wt) in the model fly ash caused a 95% oxidation of Hg^0 in the temperature range of 150-250°C. The same extent of Hg^0 oxidation was obtained by adding 14% (wt) Fe_2O_3 to the model fly ash.

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1. INTRODUCTION

Title III of the 1990 Clean Air Act Amendments (CAAA) requires the U.S. Environmental Protection Agency (EPA) to submit a study to Congress on 189 hazardous air pollutants (HAPs) from industrial sources. This study will include an emission and risk (to public health) assessment of the HAPs. Among the 189 HAPs, mercury has drawn special attention due to its increased levels in the environment and its bioaccumulation in the food chain [1,2]. An EPA report to Congress cites the largest emitters of mercury as coal-fired utilities, medical waste incinerators (MWIs), municipal waste combustors (MWCs), chloro-alkali plants, copper and lead smelters, and cement kilns [3]. These sources are estimated to account for over 90% of the anthropogenic mercury emissions in the U.S. Utility boilers account for nearly 25% of the total anthropogenic emissions of which more than 90% are attributable to coal-fired utility boilers.

Mercury, a trace constituent of coal [4], is readily volatilized during coal combustion [5]. Mercury is the most volatile species among various trace metals, and major portions of it can pass through an existing air pollution control system (APCS) unless it is adsorbed onto particulate matter (PM) and collected or removed by PM control devices [5]. Several methods of controlling mercury emissions are either in commercial use or development for MWCs and MWIs [6]. Dry sorbent injection (DSI) of activated carbon followed by fabric filtration (FF) has shown consistently high (>90%) mercury removal in MWC applications. Spray drying (SD) followed by FF and electrostatic precipitators (ESPs) followed by 2 stage acid gas wet scrubbers (WS) have also been found to remove substantial (60-90%) amounts of mercury in MWCs. However, these technologies have not been as successful in removing mercury from coal-fired flue gases [7].

The primary reason suspected for the observed differences in mercury capture between waste and coal combustors is the differences in the mercury species present in waste incineration and coal combustion flue gases. Thus, an important scientific issue that needs to be addressed is the chemical form of mercury in combustion system flue gases. A significantly lower mercury concentration in coal combustion flue gas compared to that in MWCs may also be an important contributing factor to the observed different mercury capture behavior between the two combustion systems. Previous EPA studies have shown the relative ease of controlling oxidized

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mercury (specifically mercuric chloride, $HgCl_2$) as opposed to elemental mercury (Hg^0) [8,9]. Hall et al. [10] showed that in a simulated MWC mercury is mainly found as ionic mercury (Hg^{2+}) in flue gas. They postulated that $HgCl_2$ is the most favorable mercuric species due to thermochemical equilibrium calculations in the presence of relatively high hydrogen chloride (HCl) concentrations in MWC flue gas. On the other hand, due to the low HCl concentration, Hg^0 is believed to be the prevailing form of mercury in emissions from coal combustion processes [11]. However, recent pilot-scale coal combustion test results have indicated that combustion of certain types of coal (Blacksville, a bituminous coal from Pittsburgh No. 8 seam) can lead to a flue gas mercury species profile dominated by Hg^{2+} (most probably $HgCl_2$)[12].

Most researchers agree that mercury in coal vaporizes completely in the combustion zone of a boiler and leaves this zone in the form of Hg^0 in the gas phase. Some oxidation of Hg^0 may occur as the flue gas cools. At the economizer exit, where the flue gas typically enters the APCS, mercury can be found as Hg^0 or Hg^{2+}. Predicting emissions of mercury species has been a problem since the transformation of Hg^0 in the post-combustion region is not well understood. A detailed review on the state of knowledge on mercury speciation in coal-fired processes has been performed by Senior et al. [13]. Their review and another investigation [14] concluded that the assumption of gas-phase equilibrium for mercury species in coal-fired flue gases is not valid, and major reaction pathways for mercury oxidation in coal combustion flue gas need to be investigated. These investigations should include fly-ash-mediated surface reactions as well as gas-phase reactions. Senior et al. [13] posed two important questions that should be the focus of the on-going and future research:

1- What is the rate of oxidation of Hg^0 in the post-combustion flue gas? Answering this question would lead to prediction of gas-phase mercury speciation at the inlet and outlet of the APCS.

2- What properties (or which components) of coal fly ash affect the oxidation of Hg^0? In other words, what are the processes through which fly ash components mediate or catalyze the transformation of gaseous Hg^0 to its oxidized forms?

Thus, the objective of the Phase I (Phase II is discussed in the Future Research Section) of this research project was to conduct bench-scale studies to identify and characterize the role of flue

gas parameters (temperature and composition) and fly ash properties on the speciation of mercury. The focus of the study was on the oxidation of Hg^0. The extent of Hg^0 oxidation was determined by comparing the measured inlet and outlet Hg^0 concentrations across the oxidation reactor (cf. Experimental Procedure). These measurements provided information on the conversion of Hg^0 to its oxidized inorganic compounds. No speculation was made as to the nature of these compounds, since current analytical methods are not capable of distinguishing between different oxidized mercury species. The inorganic mercury compounds that are considered important in combustion processes are $HgS(s)$, $HgO(s,g)$, $HgCl_2(s,g)$, $Hg_2Cl_2(s)$, and $HgSO_4(s)$ [15]. As mentioned earlier, thermochemical equilibrium calculations have shown that, in the presence of sufficiently high HCl, $HgCl_2$ is the most favorable oxidized species. Since throughout this study HCl was present in large excess (mole ratio of $HCl/Hg^0 > 1250$), $HgCl_2$ may be the dominant mercury compound formed during oxidation reactions of Hg^0.

The chlorine in combustion flue gases is primarily in the form of HCl at the APCS operating temperatures. Throughout most of this study, the oxidation of Hg^0 was investigated while HCl was present in the simulated flue gas. Oxidation of Hg^0 was studied under two different test programs: (1) homogeneous gas-phase tests and (2) heterogeneous gas-solid tests. In the gas-phase tests, the effects of flue gas temperature and HCl concentration on the oxidation of Hg^0 were investigated. This test project was designed to simulate and study potential gas-phase oxidation of Hg^0 in the post-combustion regions of coal combustion processes. This oxidation (if any) may occur downstream of the combustion chamber at temperatures favoring equilibrium concentrations of HCl and Hg^{2+}. A preliminary investigation was also conducted to study gas-phase oxidation of Hg^0 in the presence of Cl_2.

In a second program, heterogeneous, gas-solid phase tests were designed to simulate conditions in the baghouse portion of the APCS. In baghouses, the flue gas penetrates a fixed-bed of fly ash and other combustion residues at low temperatures (150-250 °C). Fly ash is a complex mixture of many minerals. The characterization of the structure of coal fly ash is the subject of on-going research [16]. The amount of information on this important subject is rather limited at this time. In this project, the effects of coal fly ash composition on the oxidation of Hg^0 (in the presence of HCl) were studied using model (simulated) fly ashes. Fly ash composition

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experiments were limited to studies on the effects of the inorganic constituents of coal fly ash. Model fly ashes were formulated by physically mixing oxides of silicon (Si), aluminum (Al), calcium (Ca), iron (Fe), and copper (Cu). These oxides are abundant in a variety of coal fly ashes [16], and they may be instrumental in promoting catalytic surface reactions involving Hg^0, HCl, and other flue gas components.

2.   EXPERIMENTAL PROCEDURE

A schematic of the experimental setup used to study the oxidation of Hg^0 is shown in Figure 1. Pure $Hg^0(l)$ in a permeation tube (VICI Metronics, Inc.) generated the desired Hg^0 vapor. The concentration of $Hg^0(g)$ was controlled by adjusting the water bath temperature. A detailed description for the calibration of the Hg^0 vapor generation system and its quality control checks have been reported elsewhere [8,9]. The Hg^0 vapor generated was carried into the manifold by a nitrogen (N_2) stream where it mixed with carbon dioxide (CO_2), oxygen (O_2), HCl, SO_2, and water vapor (H_2O) at a constant total system flowrate of 300 cm^3/min (at standard temperature of $25\,°C$ and pressure of 101.4 kPa). A three-way valve placed before the manifold (Figure 1) diverted the Hg^0-laden N_2 stream away from the manifold when desired. The first three-way valve placed ahead of the oxidation reactor was used to direct flow to or away from the reactor. The reactor inlet Hg^0 concentration was measured when the valve was turned to the by-pass mode. It should be noted that the oxidation reactor is made of quartz, and the connecting lines are made of Teflon. Prior quality control checks [8,9] showed that this system had no affinity for elemental mercury.

In the gas-phase tests, the oxidation reactor was empty and surrounded by a temperature-controlled furnace. The gas-phase residence time (in the reactor) was 2 seconds at $850\,°C$. In the heterogeneous gas-solid tests, the model fly ash to be studied (0.25g, bed length of approximately 2 cm) was placed in the oxidation reactor which was maintained at the desired bed temperature by a temperature-controlled heating tape. It should be noted that, in the presence of HCl, the heterogeneous tests were performed at a much lower temperature ($150-250\,°C$) compared to those for gas-phase tests.

At the beginning of each test, the concentration of Hg^0 vapor generated by the permeation

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tube (hereafter, inlet concentration, Hg_{in}) was registered by an on-line ultraviolet (UV) Hg^0 analyzer (Buck 400A, detection limit of 1 ppb Hg^0), while the oxidation reactor was in the by-pass mode. It is important to note that the UV analyzer does not respond to oxidized forms of mercury. During each test with the reactor on-line, the post-reaction or outlet Hg^0 vapor concentration (Hg_{out}) was measured continuously using the Hg^0 UV analyzer (experimental variability of ±5%). Considering the fact that mercury in the flue gas exists in either the elemental or oxidized form, the difference between the inlet and the outlet Hg^0 concentration was used to quantify the extent of oxidation of Hg^0 in the reactor as a function of experimental parameters. Percent oxidation was obtained as:

$$\% \text{ Oxidation} = 100*(Hg_{in}-Hg_{out})/Hg_{in}$$

Water vapor creates interferences in the UV Hg^0 analyzer. Prior to entering the Hg^0 analyzer, water vapor was removed from the simulated flue gases. A NAFION® gas sample dryer (Perma Pure, Inc.) was used to selectively remove water vapor from the effluent of the oxidation reactor. Repeated quality assurance checks have indicated that this system has no affinity toward adsorption of Hg^0 and acid gases present in the flue gas. The UV Hg^0 analyzer used in this study responded to SO_2 as well as Hg^0. For instance, a gas stream consisting of 500 ppm SO_2 and 40 ppb Hg^0 produces a SO_2/Hg^0 signal ratio of 1/12. Contributions from SO_2 were corrected by placing a SO_2 analyzer (UV, model 721AT2, Bovar Engineering, Inc.) on-line, downstream of the Hg^0 analyzer. The SO_2 analyzer is incapable of responding to mercury in the concentration range used in this study. By subtracting the SO_2 signal measured by the SO_2 analyzer from the total response of the Hg^0 analyzer, the outlet Hg^0 concentration was obtained.

3.   RESULTS AND DISCUSSION

3.1   Homogeneous Gas-Phase Oxidation of Hg^0

The gas-phase tests were designed to study the potential gas-phase oxidation of Hg^0 in the post-combustion region of coal combustion processes. This oxidation (if any) may occur in the duct region (in-flight oxidation) upstream of the APCS, or dry particulate collectors (prior to scrubbers), in residence times of the order of seconds. The "base case" simulated flue gas in

these tests consisted of 40 ppbv Hg^0, 5% (mole) CO_2, 2% (mole) O_2, and a balance of N_2. The effect of HCl was studied at three concentrations: 50, 100, and 200 ppmv (typical of coal combustion processes). The effects of SO_2 and water vapor were studied at concentrations of 500 ppmv and 1.7% (mole), respectively. No oxidation of Hg^0 in the empty reactor (gas-phase) was observed at temperatures lower than 500°C (residence times of 3-4 seconds). This is in agreement with the results of Senior et al. [13], and once again indicates that the assumption of gas-phase equilibrium for mercury species in coal combustion flue gases is not valid. Equilibrium calculations predict complete oxidation of Hg^0 to $HgCl_2$ at temperatures lower than 600°C and in the presence of 50-200 ppmv HCl [13, 14].

Gas-phase oxidation of Hg^0 vapor proceeded at measurable, steady-state rates at temperatures greater than 500°C. Figure 2 shows the effects of temperature and HCl concentration on the gas-phase oxidation of Hg^0 in the absence of SO_2 and water vapor (base case flue gas). Relatively significant oxidation of Hg^0 (about 27%) was observed at high temperatures (>700°C) and high HCl concentration (200 ppm). These results show that gas-phase Hg^0 reactions with HCl are relatively slow even at temperatures as high as 700°C. Increasing HCl concentration caused an increase in Hg^0 oxidation at a high temperature (754°C). These results agree with the observations of Hall et al. [10] and MWC field test results, confirming the fact that, in waste incinerators at high HCl concentrations (1000-2000 ppmv), significant oxidation of Hg^0 to $HgCl_2$ may occur near the combustion zone. On the other hand, the gas-phase oxidation of Hg^0 in coal combustion flue gas is not expected to be as significant due to its relatively low HCl concentration.

Gas-phase reaction of Hg^0 with HCl may be affected by the presence of SO_2 and water vapor. Figure 3 shows the effect of adding either 500 ppmv SO_2 or 500 ppmv SO_2 plus 1.7% (mole) water vapor to the base case flue gas on the gas-phase oxidation of Hg^0 at the highest temperature (754°C) selected for this study. The presence of SO_2 and water vapor inhibited the gas-phase oxidation of Hg^0. To better understand this inhibition effect, one has to obtain a complete understanding of the detailed Hg^0 oxidation mechanism. The detailed mechanistic reactions of Hg^0 and HCl are not well understood. There are no obvious reaction pathways for the gas-phase oxidation of Hg^0 by HCl. The ones identified as candidates are complicated; they

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probably involve many unknown elementary steps [15]. A chlorinating agent (such as chlorine free radical, or Cl_2) is most probably needed in the gas-phase Hg^0 oxidation mechanism. Chlorine free radicals (or Cl_2 molecules) may be produced in trace quantities from the HCl in the flue gas; not much is known on this subject. The inhibition effect of SO_2/water vapor may be related to a chlorine free radical scavenging effect caused by these species.

A preliminary investigation, however, indicated that the gas-phase reaction of Hg^0 and Cl_2 is very fast. At temperatures as low as $40\,^\circ C$ and in the presence of 50 ppmv Cl_2, complete oxidation (100%) of Hg^0 was observed in the gas phase at reaction times of less than 2 seconds. These results are in agreement with those from studies conducted by Hall et al. [15]. They showed that at room temperature as little as 2 ppmv Cl_2 was sufficient to oxidized half the elemental mercury in about 1 second (starting with a mercury concentration of 12 ppbv). The results obtained in this investigation and those obtained by Hall et al. [15] indicate that Cl_2 is a much more reactive chlorinating agent than HCl, and it may be an intermediate species in the oxidation reaction of Hg^0 and HCl. Thus, the important gas-phase parameter that influences the oxidation of Hg^0 is the ratio of HCl/Cl_2 in coal or waste combustion flue gases. No quantitative data are available on this ratio; therefore, future research on quantifying the effects of combustion parameters on the HCl/Cl_2 ratio in flue gas could provide important information on the oxidation of Hg^0 by HCl.

In summary, the homogeneous gas-phase oxidation of Hg^0 in the presence of HCl is very slow and proceeds at significant rates only at high temperatures ($>700\,^\circ C$) and high HCl concentrations (>200 ppmv). The presence of SO_2 and water vapor inhibits the oxidation of Hg^0 by HCl. All indications have shown that conditions existing in coal combustion processes are not favorable for a gas-phase oxidation of Hg^0 because of low HCl concentration and high SO_2 and moisture contents in coal combustion flue gases. On the other hand, homogeneous gas-phase oxidation of Hg^0 in the presence of Cl_2 is very rapid. The HCl/Cl_2 ratio in coal combustion flue gases needs to be characterized and quantified in order to obtain a better understanding of oxidation of Hg^0 in the gas phase.

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3.2 Heterogeneous Catalytic Oxidation of Hg^0

These experiments were designed to simulate conditions in baghouses of the coal-fired power plants. In baghouses, the flue gas penetrates a filter cake (fixed-bed) of fly ash at temperatures lower than 250 °C. Oxidation of Hg^0 may occur at these temperatures on the surface of fly ash through heterogeneous catalytic reactions. If this is indeed the case, one has to identify components of fly ash that catalytically enhance oxidation of Hg^0 in the presence of HCl. Of interest is the effect of the individual components on the extent of Hg^0 oxidation and the effect of flue gas species such as SO_2 and water vapor. The fixed bed of fly ash build-up in a baghouse was simulated by the fixed-bed oxidation reactor (Figure 1). The effects of coal fly ash components and composition were studied using model fly ashes (particle size of less than 300 mesh). The fixed-bed reactor was packed with the model fly ash, and the extent of Hg^0 oxidation across the bed was determined (cf. Experimental Procedure). The base case flue gas composition during the heterogeneous tests was as follows: 40 ppbv Hg^0, 50 ppmv HCl, 5% (mole) CO_2, 2% (mole) O_2, and balance N_2. Water vapor (1.7%, mole) and SO_2 (500 ppmv) were added to the base case flue gas during selected tests to deduce the effects of these species.

The model fly ash studies were started using the base case simulated fly ash. Its composition (base composition; two-component) is illustrated in Table 1. The effect of fly ash composition was studied by individually adding a number of metallic oxides to the base case (three-component fly ashes, Table 1). The primary focus was on the most commonly found metallic oxides in coal-derived fly ash: Iron(III) oxide (Fe_2O_3, Puratronic, 99.99%, Alfa Aesar), calcium oxide (CaO, 99.95%, Alfa Aesar), and cupric oxide (CuO, 99.9%, Alfa Aesar). Different compositions of these compounds in the three-component model fly ashes were prepared (Table 1). These compositions reflect those ranges typically measured in coal fly ashes [16].

Initial heterogeneous tests with the two-component fly ash (Table 1) yielded no oxidation of Hg^0 in the presence or absence of SO_2/water vapor in the flue gas over a temperature range of 150-250 °C. Thus, alumina (Al_2O_3, fused, 99+%, Aldrich Chemical Company) and silica (SiO_2, fused amorphous powder, 99.9%, Alfa Aesar) could be considered to be inert since they do not play a role in the oxidation of Hg^0 in the simulated flue gas and model fly ash tested.

Heterogeneous tests on the three-component model fly ashes were continued using the

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high iron (Fe) content fly ash (14% Fe_2O_3, Table 1). Significant oxidation of Hg^0 was observed across the fixed bed of this simulated fly ash. The extent of Hg^0 oxidation as a function of time of exposure of the fly ash to the base case flue gas (no SO_2/water vapor) and bed temperature is shown in Figure 4. On average, steady state oxidation of Hg^0 across the bed of fly ash was achieved after 15-20 minutes of exposure to the simulated flue gas and maintained for at least 2 hours. The initial 20 minutes of the oxidation process can be referred to as the "induction" period. The reaction mechanisms during the induction period are not understood at this time. In a separate test, the model fly ash was first exposed to HCl (no Hg^0) and then exposed to Hg^0 (no HCl). No oxidation of Hg^0 was observed. This indicates that HCl is needed during the oxidation of Hg^0, and the catalysts are not being activated by HCl during the induction period.

In the steady-state region after the induction period shown in Figure 4, the fly ash exhibited its best catalytic activity under a particular condition, and continuously catalyzed the oxidation of Hg^0. The heterogeneous mechanisms of Hg^0 oxidation are not well understood. It is probable that iron oxide in the fly ash produces an active chlorinating agent from the gas-phase HCl. This chlorinating agent can be the fly ash on which a surface chlorine radical is attached, a gas-phase chlorine free radical, or a gas-phase chlorine (Cl_2) molecule. Subsequently, the chlorinating agent attacks Hg^0 molecules, resulting in the most probable oxidation state of Hg^0; i.e. $HgCl_2$. The process can be described in terms of a detailed kinetic mechanism consisting of elementary gas-phase and gas-solid reactions. Future research with focus on constructing such detailed mechanisms is needed in order to obtain a better understanding of catalytic oxidation of Hg^0.

The effect of bed temperature is also illustrated in Figure 4. Like any kinetically controlled process, catalytic or non-catalytic, increasing the reaction temperature increases the rate of reactions, and here leads to higher steady-state oxidation of Hg^0. Hg^0 oxidation as high as 95% was observed when 14% Fe_2O_3 was present in the model fly ash. The high iron content found in a Pittsburgh coal fly ash [16] suggests that the high $HgCl_2$ emissions measured when burning this coal are resulting from heterogeneous catalytic oxidation of Hg^0 [12].

Coal combustion flue gas contains a significant amount of SO_2 and moisture. The oxidation of Hg^0 over high iron containing fly ash was studied under more realistic conditions;

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i.e., the presence of 500 ppmv SO_2 and 1.7% (mole) H_2O. Steady-state Hg^0 oxidation results are shown in Figure 5. The presence of SO_2 in the simulated flue gas caused a slight decrease in Hg^0 oxidation at temperatures of 200 and 250°C. It caused a slight increase at 150°C, which can not be explained at this time. However, the presence of both SO_2 and water vapor caused a drastic decrease in the catalytic oxidation of Hg^0, especially at the lower temperatures. Similar to the gas-phase tests, the effect of SO_2/water vapor can be related to a scavenging of the catalytically generated chlorinating agent(s) such as Cl_2. One possible global scavenging reaction is shown below:

$$Cl_2 + SO_2 + 2H_2O \rightarrow 2HCl + H_2SO_4$$
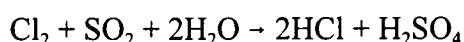
Thus, in practical situations, the inhibition effect of SO_2/water vapor is also an important factor which needs to be considered when the coal combusted contains sufficient iron and other catalytic metals for catalytic Hg^0 oxidation to occur.

The potential catalytic activities of CaO and CuO and the effects of the iron and copper contents of the three-component model fly ashes on the oxidation of Hg^0 were also investigated. Table 1 lists all the three-component model fly ashes used for the present study. The steady-state Hg^0 oxidation results under the base case flue gas (no SO_2/water vapor) are shown in Figure 6. Since the CaO-containing model fly ash did not exhibit any Hg^0 oxidation, it may be considered to be inert fly ash component. As shown in Figure 6, CuO is a much more active catalyst than Fe_2O_3. This is apparent for the 200°C and 250°C data shown in Figure 6 when comparing the same percentages of the two additives. A model fly ash containing 0.1% CuO exhibited similar catalytic activity for Hg^0 oxidation as did a model fly ash containing 14% Fe_2O_3. The high catalytic reactivity of CuO on chlorinating agent formation from HCl is also indicated by the formation of dioxins at low temperatures in the presence of MWC fly ash. Chlorination of aromatic compounds such as phenol is enhanced by the presence of a copper (I) chloride catalyst [17] or MWC fly ash [18]. The mechanism for the chlorinating agent formation is presumed to be the Deacon process reaction:

$$2HCl + \tfrac{1}{2}O_2 \rightleftharpoons Cl_2 + H_2O$$
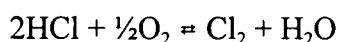
in which HCl is converted to Cl_2 in the presence of a metal catalyst. This conversion promoted by the cuprous chloride catalyst (CuCl) was directly observed by Gullett et al. [17] in a

laboratory flow reactor. At 400°C, approximately 40% conversion of HCl to Cl_2 was measured. It is suggested by this case that copper is very reactive in generating a chlorinating agent through the Deacon process reaction. The chlorinating agent (Cl_2) was possibly produced at a much higher rate in the presence of Cu than in the presence of Fe and led to greater oxidation of Hg^0 and formation of $HgCl_2$. It should be noted that the homogeneous gas-phase test results also suggested that Cl_2 may be the required intermediate species in the oxidation of Hg^0 by HCl.

As illustrated in Figure 6, lowering the amounts of iron and copper in the three-component model fly ashes reduced the heterogenous oxidation of Hg^0. A model fly ash containing 1% CuO was the most active catalyst in these tests. The oxidation of Hg^0 reached approximately 95% in the temperature range of 150-250°C, while temperature had no effect on oxidation.

Figure 7 shows the effect of SO_2/water vapor on the oxidation of Hg^0 across the fixed beds of the three-component model fly ashes at a bed temperature of 250°C. The inhibition effect of SO_2/water vapor was observed to be very drastic for the iron-containing model fly ashes, and a less significant inhibition effect was observed for the copper-containing model fly ashes. The diminished inhibition effect may be due to the superior catalytic activity of copper.

A three-component model fly ash containing 7% CaO exhibited a very interesting and unique behavior in the presence of SO_2/water vapor; it did not cause any Hg^0 oxidation in the presence of HCl. In another words, it did not catalyze the formation of chlorinating agent(s) from HCl. However, unlike the iron and copper catalysts, the presence of SO_2 induced little Hg^0 oxidation across this model fly ash. One possible explanation for this observation is that CaO is a good SO_2 sorbent. Adsorption of SO_2 may create active sulfur (S) sites on the surface of the CaO-containing model fly ash. An oxidation reaction between the Hg^0 molecules in the gas phase and the active "S" sites produces mercuric sulfide (HgS) molecules which either remain on the surface or are released back into the simulated flue gas. The outcome of this process is a low oxidation of Hg^0 (15%) to HgS mediated by gas-phase SO_2 and solid-phase CaO in the model fly ash.

In summary, it appears that coal fly ashes rich in iron and copper may catalyze the oxidation of Hg^0 in baghouses through the chlorinating agents produced by a Deacon type

reaction. Copper has a much more pronounced catalytic activity than iron even in the presence of oxidation inhibitors, such as SO_2 and water vapor.

4. CONCLUSIONS

The formation of oxidized mercury species from Hg^0 vapor in simulated coal combustion flue gases was investigated. Although high temperature combustion reactions convert mercury in coal to gaseous elemental mercury (Hg^0), certain coal fly ash and flue gas parameters may be influential in converting Hg^0 vapor to gaseous mercuric chloride ($HgCl_2$) in post-combustion regions, including air pollution control systems (APCSs). Research has indicated the relative ease of controlling $HgCl_2$ emissions in APCSs as opposed to those of Hg^0.

Gas-phase studies revealed that Hg^0 oxidation in the presence of hydrogen chloride (HCl) is very slow and proceeds at measurable rates only at high temperatures ($>700\,^\circ C$) and high HCl concentrations (>200 ppm). Furthermore, the presence of high sulfur dioxide (SO_2) concentration in coal combustion flue gases inhibits such oxidation. On the other hand, gas-phase reaction of Hg^0 and chlorine (Cl_2) proceeds rapidly even at low temperatures ($40\,^\circ C$). No data are available on the quantitative ratio of Cl_2/HCl in coal combustion flue gases. Assuming that this ratio is small, one may conclude that the conditions in coal combustion processes are not favorable for a gas-phase oxidation of Hg^0.

The effects of coal fly ash parameters on the oxidation of Hg^0 were studied using model (simulated) fly ashes. The focus was on the inorganic constituents of coal fly ashes: alumina (Al_2O_3), silica (SiO_2), iron(III) oxide (Fe_2O_3), calcium oxide (CaO), and copper (II) oxide (CuO). CuO and Fe_2O_3 exhibited significant catalytic activity in oxidizing Hg^0 in the presence of 50 ppm HCl and in the temperature range of $150-250\,^\circ C$. Initial indications are that these transition metals, through a multi-step heterogeneous Deacon process, produce an active chlorinating agent, most probably Cl_2, from HCl. Subsequent reaction of this agent and gaseous Hg^0 proceeds quickly and results in large quantities of $HgCl_2$, the most probable oxidation state of Hg^0. CuO is a much more active catalyst than Fe_2O_3. A simulated fly ash consisting of a 3.5/1 ratio of alumina to silica base and 0.1% (wt) CuO exhibited the same catalytic activity (95% Hg^0 oxidation) as a model fly ash containing of 14% Fe_2O_3 with identical alumina and silica contents in the

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temperature range of 150-250°C. It appears that the production of the chlorinating agent from HCl in the presence of a copper catalyst proceeds much faster compared to that of iron. Overall, increasing the bed temperature increased the catalytic activity of the model fly ashes, indicating that the oxidation process is kinetically controlled.

The presence of SO_2/water vapor in the simulated flue gas inhibited the catalytic activity of the iron-containing fly ashes more drastically than those having copper catalysts. The inhibition effect was more pronounced at the lower temperature studied (150°C). Calcium oxide (CaO) exhibited a different behavior from those of iron and copper catalysts. It did not show any catalytic activity in oxidizing Hg^0 in the presence of HCl and absence of SO_2. However, when SO_2 was added to the simulated flue gas, a low oxidation of Hg^0 (15%) was observed across the fixed bed of the CaO model fly ash. This low oxidation may have been caused by the formation of Hg-S bonds on the surfaces of CaO.

In summary, it appears that coal fly ashes with high iron and copper contents catalyze the oxidation of Hg^0 in baghouses. Copper is a much more active catalyst than iron even in the presence of oxidation inhibitors such as SO_2 and water vapor.

5. FUTURE RESEARCH (PHASE II)

There have been indications that oxidation of Hg^0 in the presence of chlorine (Cl_2) proceeds faster than in the presence of HCl [15]. In this study, it was also hypothesized and shown that Cl_2 may be the critical intermediate reaction species during oxidation of Hg^0 by HCl. Additional heterogeneous tests will be performed using Cl_2, instead of HCl, in the simulated flue gases. Heterogeneous oxidation of Hg^0 will be studied in the presence of Cl_2. The effects of Cl_2 concentration, flue gas temperature, and coal fly ash components and composition will be investigated. There have also been indication that nitric oxide (NO), a significant component of coal combustion flue gases, may affect mercury speciation. Oxidation of Hg^0 will be investigated in the presence of NO in the simulated flue gas.

Coal fly ash is a complex mixture of many metal oxides which are formed from minerals present in coal. The study described here (under Phase I) used simulated fly ashes which contained three metal oxides. Hg^0 oxidation studies on more complex fly ashes which contain

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more metal oxides need to be performed in order to better understand the synergistic or antagonistic effects of individual metal oxides. Four-component model fly ashes will be studied. These model fly ashes will contain Al_2O_3, SiO_2, Fe_2O_3 (or CuO), and CaO at different concentrations. Following the four-component fly ash tests, a more complex model fly ash will be developed to simulate the oxidation behavior of Hg^0 in coal combustion flue gases. Initial components of this fly ash are anticipated to be: SiO_2, Al_2O_3, Fe_2O_3, CaO, CuO, Na_2O, TiO_2, MgO, and MnO_2. Pending the initial results, the composition of the complex model fly ash will be further improved to represent more realistic conditions.

In the presence of sufficiently high chlorine (HCl or Cl_2) in the gas phase, the metallic compounds in the fly ash may be in the form of chlorides. Metal chlorides may also be the dominant form of minerals in MWC fly ash. Additional heterogeneous tests will be performed in the presence of simulated fly ashes containing copper and iron chlorides. These results will be compared with those obtained in the presence of copper and iron oxides.

Coal cleaning prior to its combustion has been considered as a method of pollution prevention. The cleaning process significantly changes the properties and characteristics of coal combustion fly ashes. Samples of fly ashes from combustion of raw and cleaned coal will be obtained. Oxidation of Hg^0 across these two different types of fly ashes will also be investigated.

Recent research results obtained at the Babcock & Wilcox Clean Environment Development Facility (B&W CEDF) have indicated that major portions of oxidized mercury can undergo reduction to Hg^0 in the specific sections of the APCS [19]. The Hg^0 oxidation studies will be followed by a preliminary investigation into the reduction of $HgCl_2$ across the fixed bed of the complex model fly ash.

Besides baghouses, other air pollution control devices may also be instrumental in affecting mercury speciation in coal-fired combustion processes. A detailed bench-scale investigation will be designed to specifically answer the following questions:

- What is the effect of wet scrubber (WS) design and operating conditions on mercury speciation?

- What WS parameters, such as pH and temperature, affect mercury speciation?

- How does the chemistry in a single stage limestone WS system commonly used for coal-

fired boilers affect mercury speciation and control?

- What are the effects of other likely utility APCS devices such as electrostatic precipitators (ESPs) on mercury speciation?

- What operating parameters (such as electric field) are most likely to control mercury speciation in an ESP?

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Table 1. Model Fly Ash Compositions (wt%)

Model Fly Ash	Content				
	Al_2O_3	SiO_2	Fe_2O_3	CuO	CaO
Base Composition (Two-Component)	22	78	0	0	0
Three-Component, High Fe	19	67	14	0	0
Three-Component, Medium Fe	22	77	1	0	0
Three-Component, Low Fe	22	78	0.1	0	0
Three-Component, High Cu	22	77	0	1	0
Three-Component, Medium Cu	22	78	0	0.1	0
Three-Component, High Ca	21	72	0	0	7
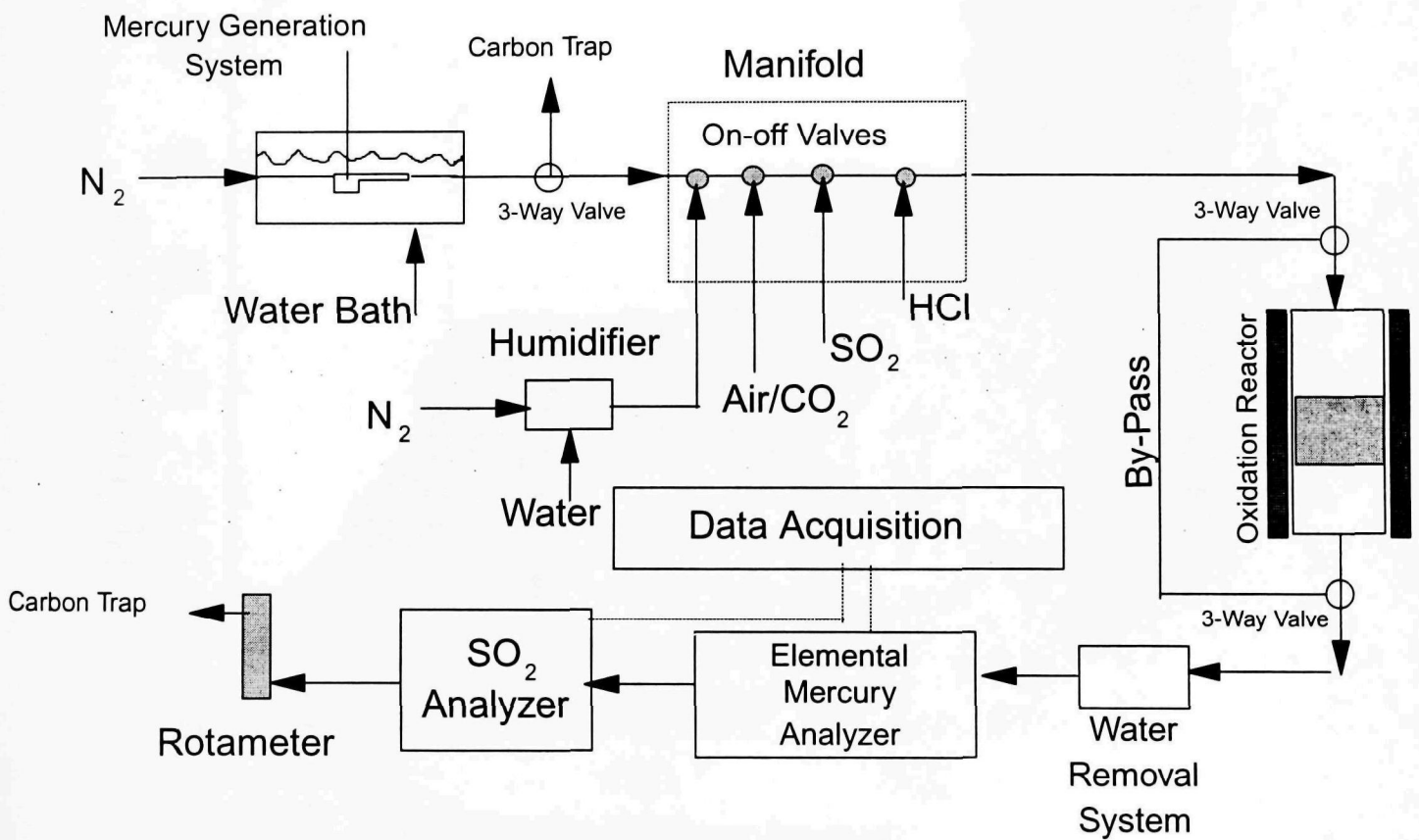
Figure 1.   Schematic of the elemental mercury oxidation reactor system.
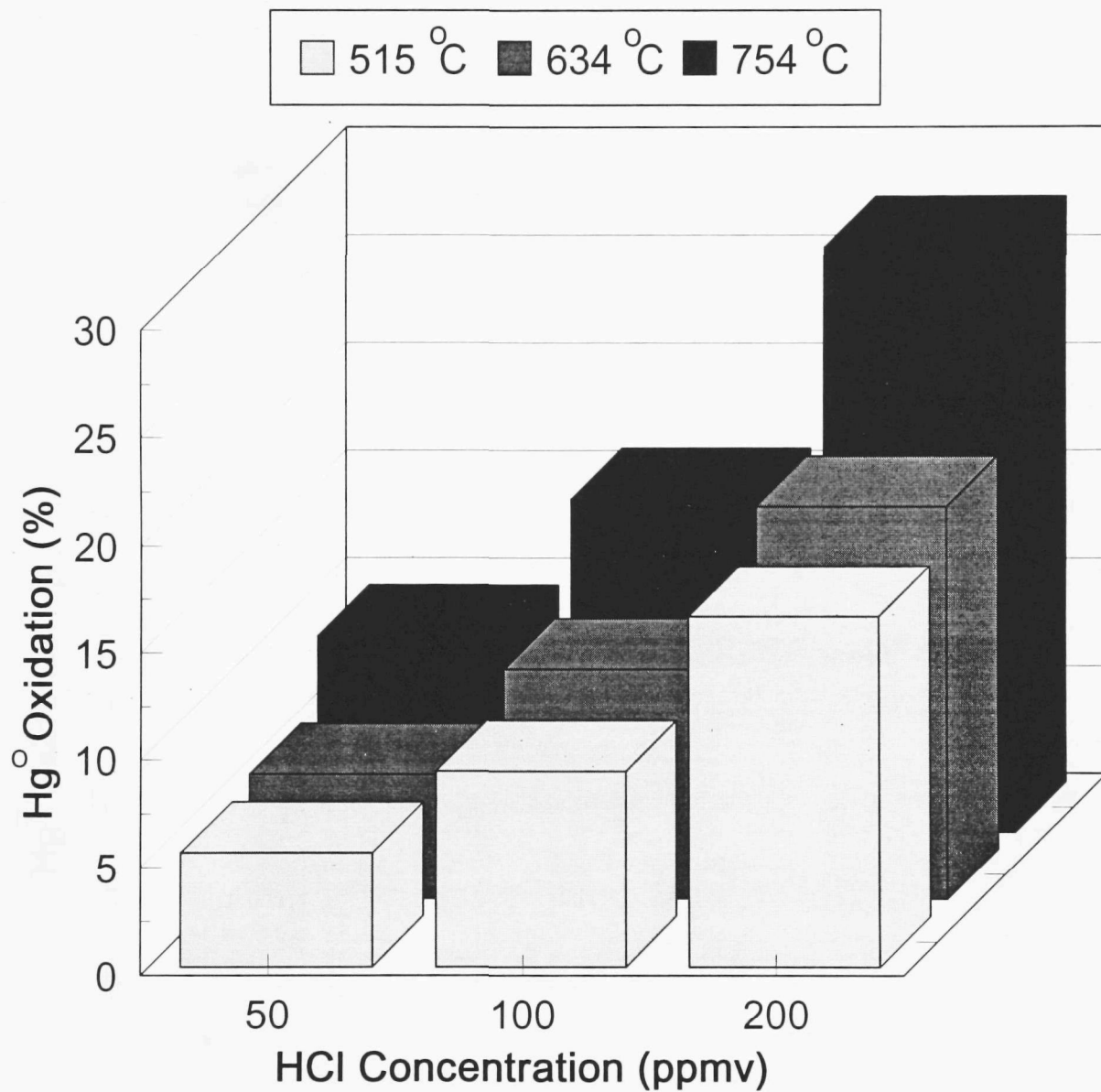
Figure 2.   Effects of temperature and HCl concentration on the gas-phase oxidation of Hg^0 in the absence of SO$_2$/water vapor.
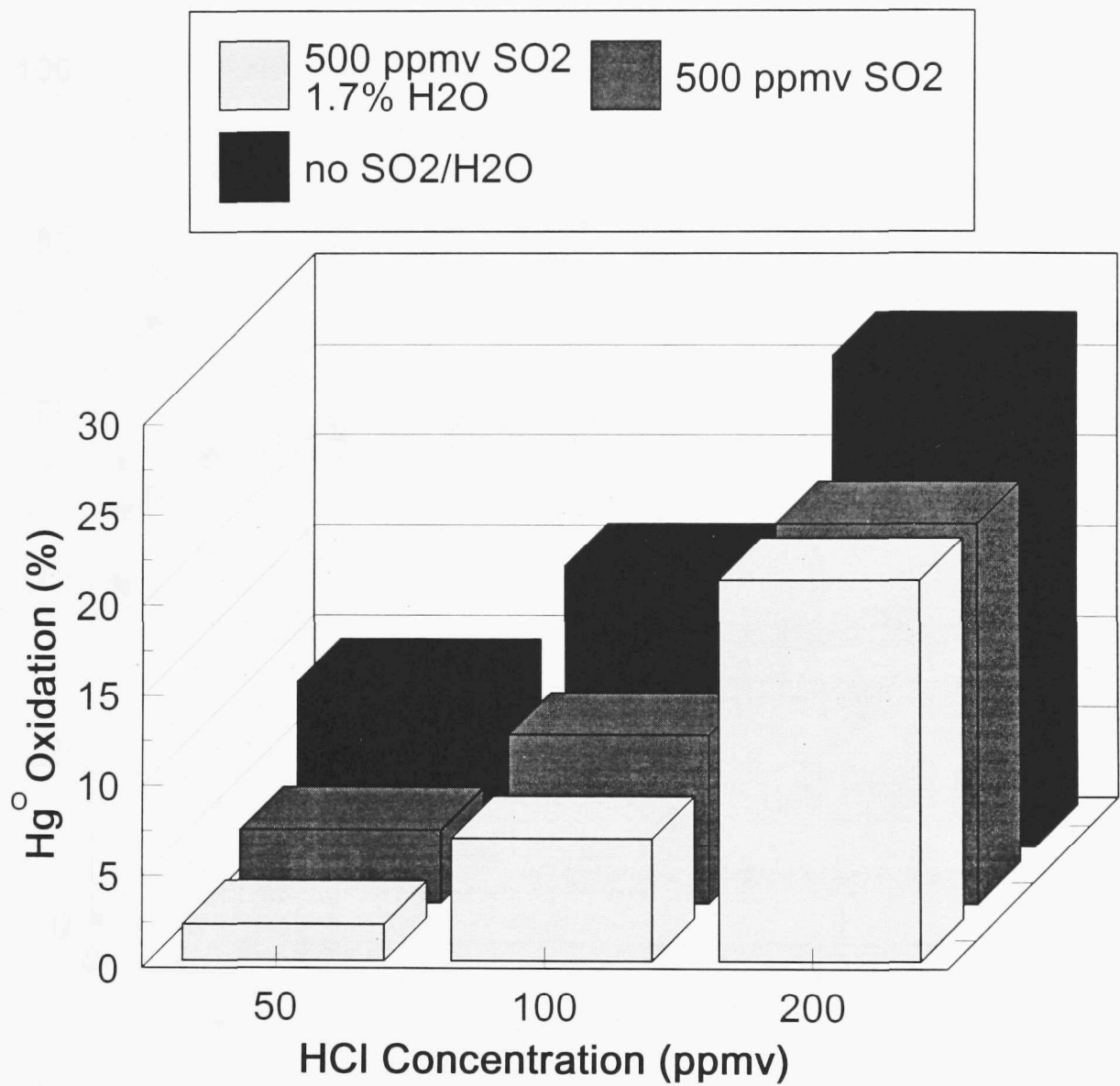
Figure 3.   Effects of SO_2 and water vapor on the gas-phase oxidation of Hg^0 at 754°C and three different HCl concentrations.
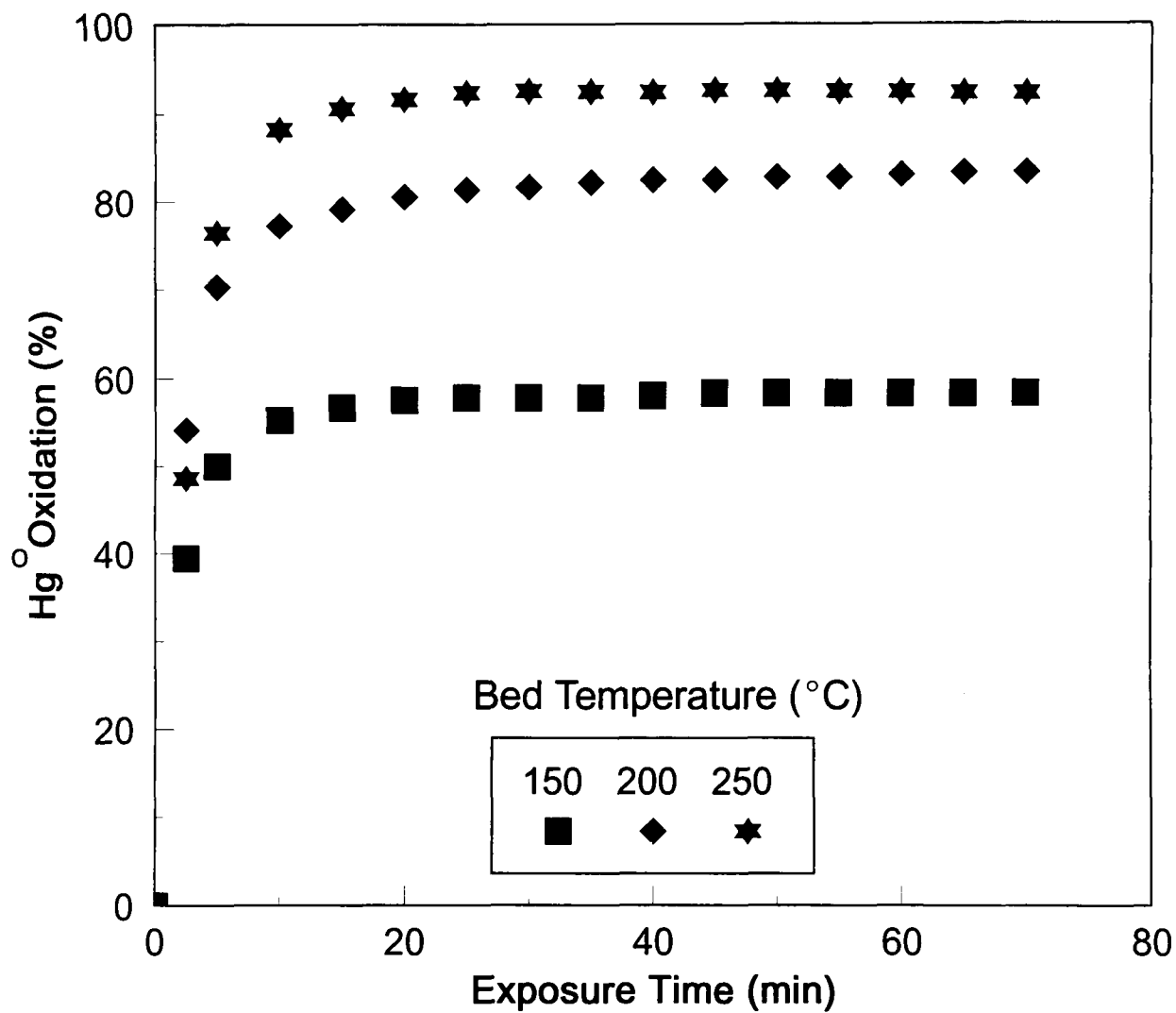
Figure 4.   Heterogeneous oxidation of Hg^0 across the high Fe model fly ash (see Table 1) in the presence of 50 ppm HCl and the absence of SO_2/water vapor; effects of time of exposure and bed temperature.
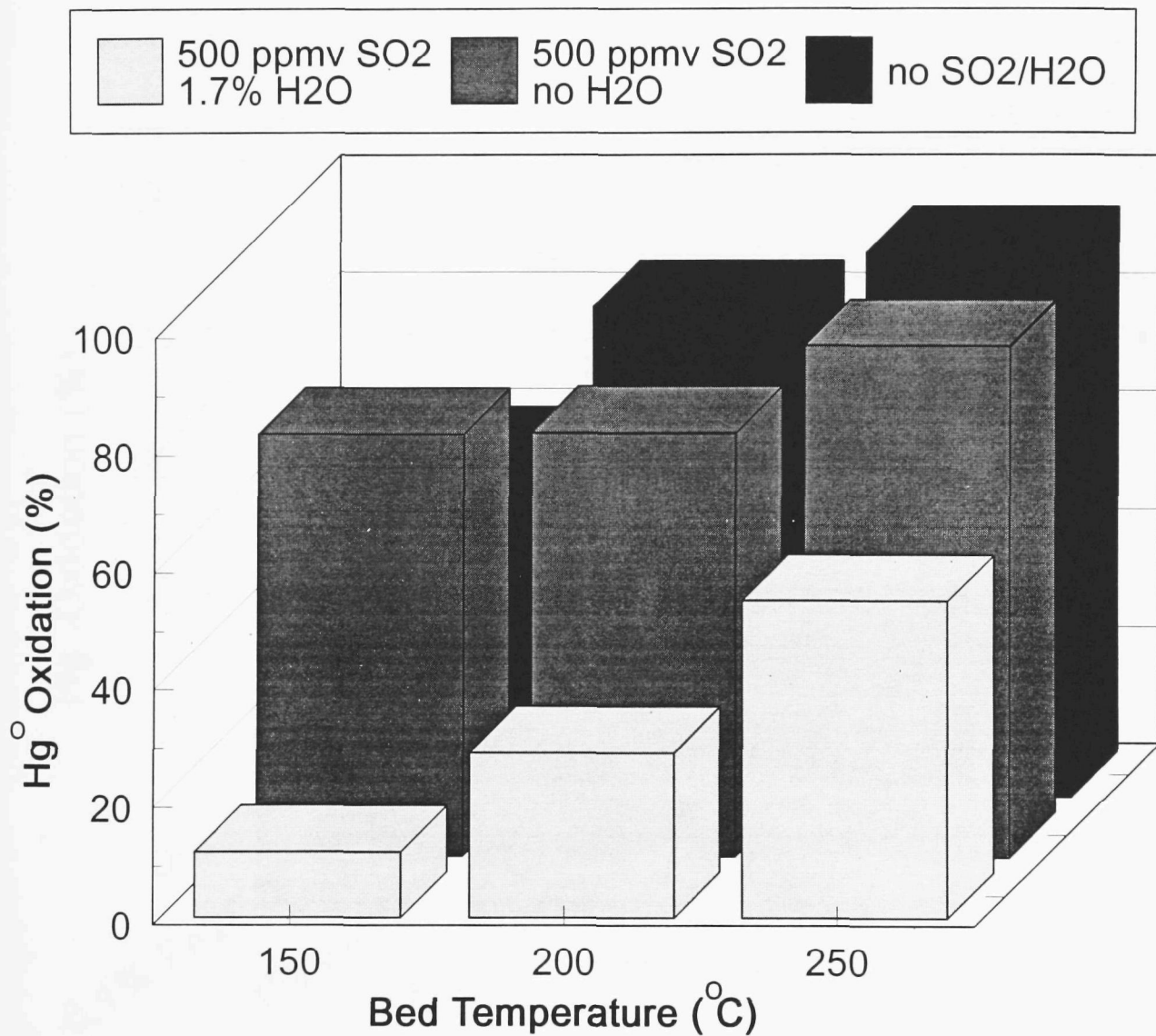
Figure 5.   Effects of SO$_2$, water vapor, and bed temperature on the steady-state heterogenous oxidation of Hg^0 across the High Fe model fly ash (see Table 1) in the presence of 50 ppm HCl.
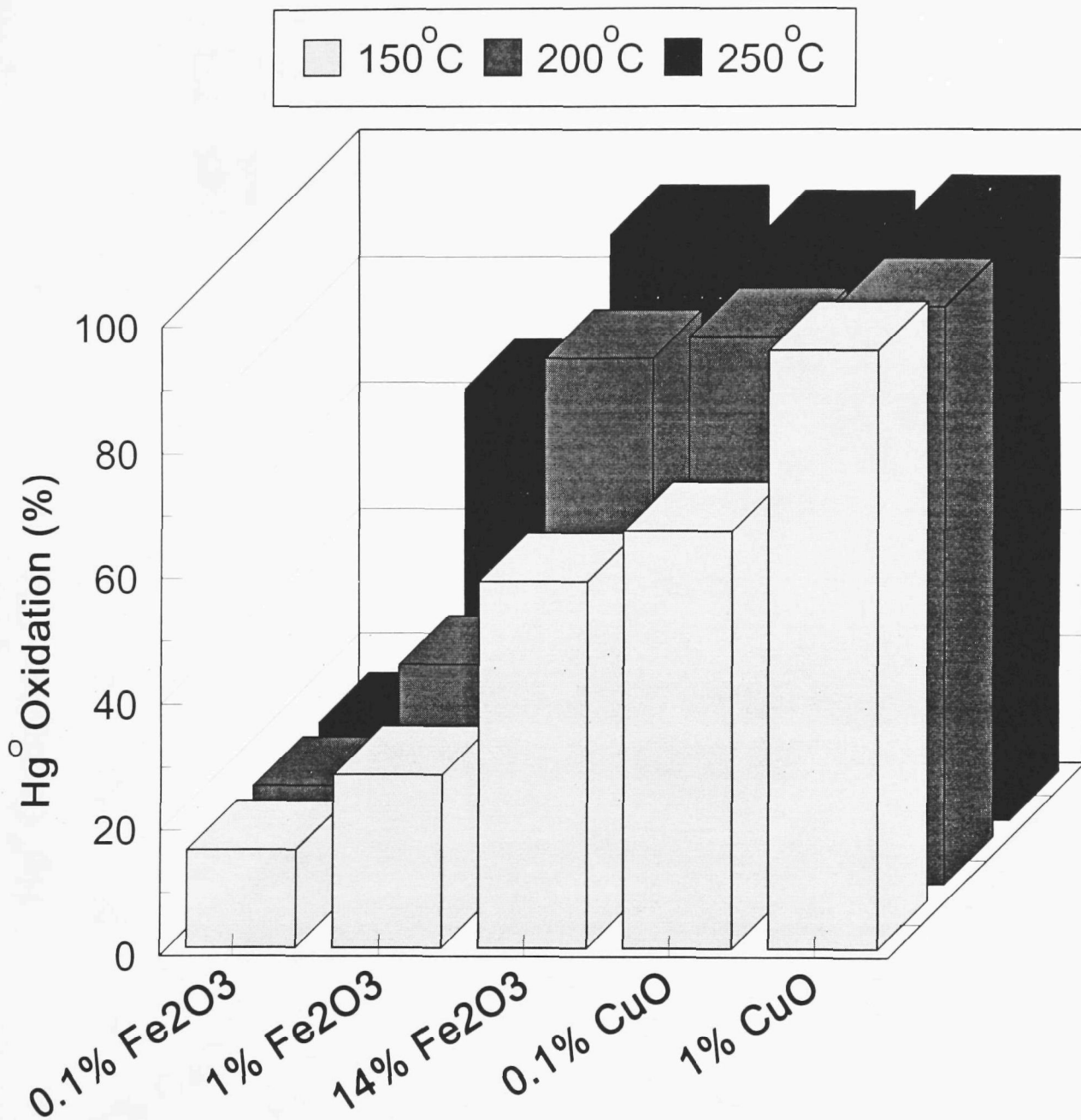
Figure 6.   Effects of coal fly ash components/compositions and temperature on the steady-
            state heterogeneous oxidation of Hg^0 across model fly ashes (see Table 1) in the
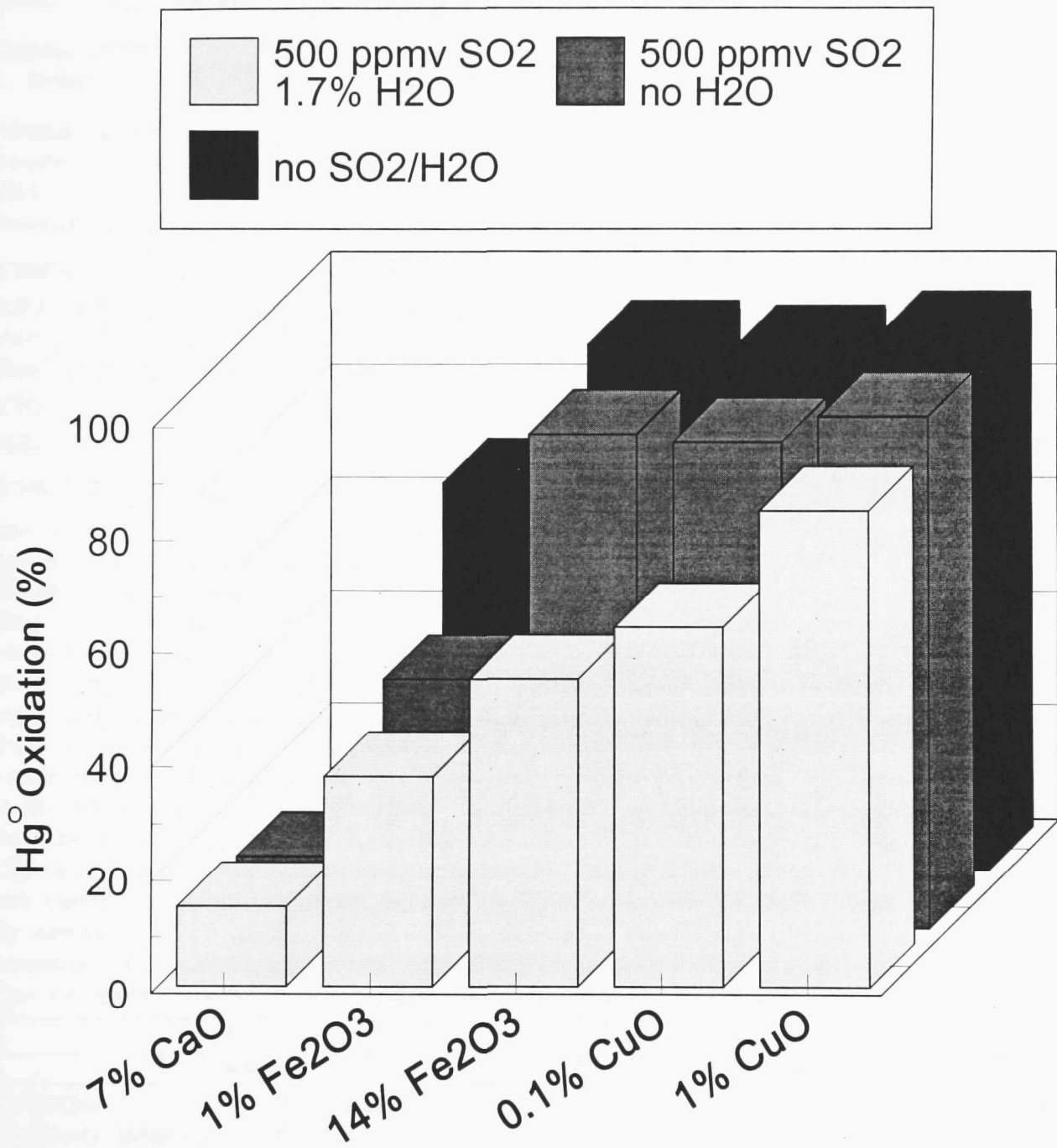   presence of 50 ppm HCl and the absence of SO_2/water vapor.

Figure 7.   Effects of SO_2 and water vapor on the steady-state heterogeneous oxidation of Hg^0 across model fly ashes (see Table 1) at 250°C and in the presence of 50 ppm HCl.

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16. ABSTRACT The report describes the progress of an experimental investigation of the speciation of mercury in simulated coal combustion flue gases. The effects of flue gas parameters and coal fly ash on the oxidation of elemental mercury (Hgo) in the presence of hydrogen chloride (HCl) in a simulated post-combustion region, including the baghouse portion of air pollution control systems, were studied using a bench-scale setup. Results of the gas-phase experiments indicate that the in-flight post-combustion oxidation of Hgo in the presence of HCl in a simulated flue gas is slow and proceeds at measurable rates only at high temperatures (> 700 C) and high HCl concentrations (> 200 ppmv). The presence of sulfur dioxide (SO2) and water vapor in the simulated flue gas significantly inhibits the gas-phase oxidation of Hgo in the presence of HCl. However, results of a preliminary investigation indicate that the gas-phase reaction of Hgo with chlorine (Cl2) proceeds rapidly, suggesting that Cl2 is a much more active chlorinating agent than HCl. The effects of the coal fly ash component and its composition were investigated using a fixed bed of model fly ashes. The primary focus was to evaluate the catalytic activity of major mineral constituents of coal fly ashes. Copper and iron oxides were the only two components that exhibited significant catalytic activity toward surface-mediated oxidation of Hgo.

17.	KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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