

Mercury Control Research: Effects of Fly Ash and Flue Gas Parameters on Mercury Speciation

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ABSTRACT

In flue gas from combustion systems, mercury (Hg) is typically in the vapor phase at flue gas cleaning temperatures, and the control of Hg emissions is dependent on the specific Hg compounds that are present (speciation) and the type of air pollution devices employed. In dry and semi-dry scrubbing systems, the control of Hg emissions is dependent on the sorption of Hg by particulate matter (PM) which can be subsequently collected in a PM control device. In wet scrubbing systems, the principal mechanisms of control are the removal of soluble forms of Hg and the collection of particle-bound Hg. At combustion temperatures, Hg is believed to be predominantly in the form of elemental mercury (Hg^0). As the flue gas is cooled, thermochemical equilibrium calculations indicate that Hg^0 is converted primarily to ionic mercury (Hg^{++}) in the form of mercuric oxide (HgO) or mercuric chloride (HgCl_2). Hg^0 is insoluble in water, but HgO has a low solubility while HgCl_2 is highly soluble. The oxidation of Hg^0 to an ionic form depends on the temperature, the time-temperature profile, the flue gas composition, the reaction kinetics, and the presence of solids that may catalyze reactions.

Bench-scale experiments were conducted to study the effects of flue gas and fly ash parameters on the oxidation of Hg^0 in simulated flue gases containing hydrogen chloride (HCl). 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 ($>700^\circ\text{C}$) 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 . On the other hand, a preliminary investigation indicated that the gas-phase reaction of Hg^0 with chlorine (Cl_2) is fast. At 40°C and in the presence of 50 ppm Cl_2 , 100% of the input Hg^0 was oxidized to HgCl_2 in less than 2 seconds, indicating that Cl_2 is a much more active chlorinating agent than HCl.

The effects of fly ash composition were investigated using a fixed-bed reactor containing different model fly ashes (simulated fly ash) consisting of mixtures of some major components found in coal and municipal waste combustor (MWC) fly ashes. Work to date has focused on the

potential catalytic oxidation of Hg^0 by two- and three-component model fly ashes composed of mixtures of: alumina (Al_2O_3), silica (SiO_2), ferric oxide (Fe_2O_3), cupric oxide (CuO), and calcium oxide (CaO). Copper and iron oxides were the only two components that exhibited significant catalytic activity in the surface-mediated oxidation of Hg^0 . The reactivity of these two metals is hypothesized to be affected 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 much more effective in the oxidation of Hg^0 than iron, and its catalytic activity was less sensitive to the presence of oxidation inhibitors (SO_2 and water vapor). The presence of a small quantity of CuO (0.1% wt) in the model fly ash caused a 95% oxidation of Hg^0 in the temperature range of 150 to 250 °C. The same extent of Hg oxidation was obtained by adding 14% (wt) Fe_2O_3 to the model fly ash.

INTRODUCTION

Mercury (Hg) emissions from combustion sources are important environmentally because of their adverse health and ecological effects. Mercury, a trace constituent in a wide variety of solid fuels including municipal solid waste (MSW) and coal, is readily volatilized during combustion, and it most likely passes through existing air pollution control systems (APCS) unless it is removed in a scrubber or adsorbed onto particulate matter (PM) and removed by a PM control device. The chemical form of Hg in combustion flue gases is an important factor influencing its control. Previous EPA studies (1) have shown that controlling oxidized Hg (Hg^{++}) emissions is much easier than controlling elemental Hg (Hg^0) emissions. Mercury emissions from municipal waste combustion (MWC) are believed to be dominated by mercuric chloride (HgCl_2), because the high Hg and chlorine contents in MWC favor HgCl_2 formation (2). Hg^0 is suggested to be the dominant Hg species in coal combustion flue gases due to lower hydrogen chloride (HCl) concentrations (3). However, recent pilot-scale coal combustion test results showed that Hg emissions from combustion of certain types of coal are dominated by the ionic species (4).

Mercury contained in fuels vaporizes completely in the combustion zone of a boiler and leaves this zone as gas-phase Hg^0 . Oxidation of Hg^0 may occur as the flue gas cools to lower temperatures downstream of the combustion zone. Predicting the chemical form of Hg in flue gas emissions is difficult, since the transformations of Hg^0 in the post-combustion region are unknown, and the major reaction pathways for Hg oxidation in combustion flue gases remain to be determined (5). The pathways may include heterogeneous fly-ash-mediated surface reactions, as well as homogeneous gas-phase reactions.

The objective of this study was to conduct bench-scale experiments to identify and characterize the role of flue gas parameters, such as temperature and composition, and fly ash properties on the speciation of Hg. Oxidation of Hg^0 was studied under two different test regimes:

(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. The homogeneous tests were designed to study potential gas-phase oxidation of Hg^0 in the post-combustion region. A preliminary test was also conducted to study the gas-phase oxidation of Hg^0 in the presence of Cl_2 . The tests for heterogeneous gas-solid Hg^0 oxidation were conducted under conditions simulating the baghouse portion of APCS. The effects of fly ash composition on the oxidation of Hg^0 in the presence of HCl were studied using model (simulated) fly ashes which were formulated using oxides of silicon, aluminum, calcium, iron, and copper. These oxides are significant components in a variety of fly ashes ranging from coal to MSW, and they may be instrumental in promoting catalytic surface reactions involving Hg^0 , HCl, and other flue gas components.

EXPERIMENTAL

A schematic of the experimental setup used to study oxidation of Hg^0 is shown in Figure 1. A low concentration (40 ppbv) of Hg^0 vapor was generated by using a Hg permeation tube surrounded by a temperature-controlled water bath. The Hg^0 vapor was carried by a nitrogen (N_2) stream and mixed with carbon dioxide (CO_2), oxygen (O_2), HCl, sulfur dioxide (SO_2), and water vapor (H_2O) at a constant total system flowrate of $300 \text{ cm}^3/\text{min}$ (at a standard temperature of 25°C and pressure of 101.4 kPa). For the gas-phase tests, the Hg^0 -laden simulated flue gas stream passed through the empty oxidation reactor, surrounded by a temperature-controlled furnace, with 2 seconds of residence time at 850°C . For the heterogeneous tests, 0.25 g of the model fly ash to be studied was placed in the oxidation reactor which was maintained at the desired bed temperature by a temperature-controlled heating tape. The heterogeneous tests were performed at much lower temperatures (e.g., 250°C) than the gas-phase tests.

At the beginning of each test, the concentration of Hg^0 generated by the permeation tube (inlet concentration, Hg_{in}) was measured by an on-line ultraviolet (UV) Hg^0 analyzer, which does not respond to oxidized forms of Hg. During each test, the post-reaction or outlet Hg^0 concentration (Hg_{out}) was measured continuously using the UV analyzer. Since Hg in the flue gas exists as either elemental or oxidized forms, the difference between the Hg_{in} and the Hg_{out} concentrations 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:

$$\% \text{ Oxidation} = 100 \times (\text{Hg}_{\text{in}} - \text{Hg}_{\text{out}}) / \text{Hg}_{\text{in}}$$

Because H_2O creates interferences in the UV analyzer, it was selectively removed from the simulated flue gases by a gas sample dryer prior to entering the analyzer. The entire reaction system showed no affinity toward Hg^0 and acids present in the flue gas. The UV analyzer used in this study responds to SO_2 as well as Hg^0 . Contributions from SO_2 were corrected by placing a

SO₂ analyzer (UV, model 721AT2, Bovar Engineering, Inc.) on-line, downstream of the Hg⁰ analyzer. The SO₂ analyzer is incapable of responding to Hg in the concentration range used in this study. By subtracting the SO₂ concentration measured by the SO₂ analyzer from the concentration measured by the Hg⁰ analyzer, the outlet Hg⁰ concentration was obtained.

Experiments were conducted over two temperature ranges: a high range (515 to 754 °C) and a low range (150 to 250 °C). The high range represents temperatures downstream of combustion chambers where equilibrium calculations indicate that the speciation of Hg⁰ is beginning to shift to oxidized forms of Hg. The low range represents temperatures where fly ash is removed from flue gases by PM control devices (electrostatic precipitators and fabric filters). The range of experimental temperatures and simulated flue gas compositions explored during the first phase of the Hg⁰ oxidation tests are summarized in Table 1. The compositions of model fly ashes used during the experiments are given in Table 2.

RESULTS AND DISCUSSION

Homogeneous Gas-Phase Oxidation

The gas-phase experiments were designed to study the gas-phase oxidation of Hg⁰ in the post-combustion region of a boiler, including the duct region (in-flight oxidation) upstream of the APCS, or dry particulate collectors (prior to scrubbers), for residence times of several seconds. The "base case" simulated flue gas (dry) used in these tests consisted of 40 ppbv Hg⁰, 5% (mole) CO₂, 2% (mole) O₂, and a balance of N₂. The effect of HCl was studied at three HCl concentrations: 50, 100, and 200 ppmv, typical of U.S. coal combustion processes. The effects of SO₂ and H₂O were studied at concentrations of 500 ppmv and 1.7% (mole), respectively, to simulate the combustion of a low sulfur-containing fuel such as coal.

No gas-phase oxidation of Hg⁰ was observed at temperatures below 500 °C with residence times of 3 to 4 seconds, which is in agreement with a previous study (5). This indicates that the Hg species in simulated combustion flue gases did not achieve chemical equilibrium; equilibrium calculations predict complete oxidation of Hg⁰ to HgCl₂ at temperatures below 600 °C with 50 to 200 ppmv HCl (5, 6). As indicated by the results shown in Figure 2, significant oxidation of Hg⁰ (about 27%) was observed at the highest test temperature (754 °C) and highest HCl concentration (200 ppmv). The results also show that increasing the HCl concentration caused an increase in the Hg⁰ oxidation at each of the high test temperatures. These observations are in agreement with the MWC field test results which indicated that significant oxidation of Hg⁰ to HgCl₂ may occur in the post-combustion zone of a waste incinerator which has relatively high HCl concentrations (7). The gas-phase oxidation of Hg⁰ in coal combustion flue gas is not expected to be as high due to the relatively low HCl concentrations.

The effects of adding either 500 ppmv SO₂, or 500 ppmv SO₂ plus 1.7 % (mole) of H₂O to the base case flue gas on the gas-phase oxidation of Hg⁰ were studied at a temperature of 754 °C. The results are shown in Figure 3. It was found that the presence of SO₂ and H₂O inhibit gas-phase Hg⁰ oxidation. The mechanisms of this inhibition are not known. The gas-phase oxidation reactions of Hg⁰ are not well understood, and they may include many elementary reactions between Hg⁰ and compounds of O₂, H₂, Cl₂, and S (8). A chlorinating agent, such as the Cl-free radical, is most probably needed in the gas-phase Hg⁰ oxidation reactions. The observed inhibition effects may be caused by the scavenging of Cl-free radicals by compounds associated with SO₂ and H₂O.

The results of a preliminary investigation to study the effectiveness of Cl₂ as an oxidation agent show that, at temperatures as low as 40 °C and with 50 ppmv of Cl₂, complete gas-phase oxidation of Hg⁰ was observed at reaction times of less than 2 seconds. These results are in agreement with those from studies conducted by other researchers (8). They indicate that Cl₂ is a much more reactive chlorinating agent than HCl. These results support the postulation that Cl₂ is an intermediate species in the oxidation of Hg⁰ in flue gases containing HCl. Thus, an important parameter that influences the oxidation of Hg⁰ is the ratio of HCl/Cl₂ in coal or waste combustion flue gases.

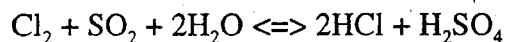
Heterogeneous Catalytic Oxidation

Experiments were conducted to study Hg⁰ oxidation in the presence of fly ash at temperatures typically found in PM control devices. The experiments most closely simulate the conditions in baghouses, where the flue gas penetrates a filter cake of fly ash at temperatures below 250 °C. The potential for fly-ash-mediated reactions was investigated by using a fixed-bed oxidation reactor (Figure 1). The effects of flue gas composition and fly ash composition were studied using model fly ashes composed primarily of metal oxide particles (particle diameter smaller than 50 μm). The fixed-bed reactor was packed with the model fly ash, and Hg⁰ oxidation across the bed was effected by passing simulated flue gases through the bed. The base case flue gas composition during the heterogeneous tests was: 40 ppbv Hg⁰, 50 ppmv HCl, 5% (mole) CO₂, 2% (mole) O₂, and balance N₂. H₂O (1.7%, mole) and SO₂ (500 ppmv) were added to the base case flue gas during selected tests to deduce the effects of these species.

The composition of simulated fly ashes used in these studies is shown in Table 2. The effect of potentially reactive fly ash components was studied by adding a number of metallic oxides to a base-case two-component mixture consisting of alumina and silica. The primary focus was on metallic oxides commonly found in fly ash: ferric oxide (Fe₂O₃), calcium oxide (CaO), and cupric oxide (CuO). Initial tests with the two-component base-case fly ash over a temperature range of 150 to 250 °C did not display oxidation of Hg⁰ in these simulated flue gases either in the presence or absence of SO₂ and H₂O. Thus, neither alumina nor silica appears to be active in promoting the oxidation of Hg⁰ at flue gas cleaning temperatures.

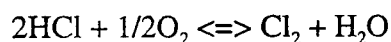
Experiments with the three-component model fly ashes, conducted using the high iron content fly ash, showed significant oxidation of Hg^0 . The gas residence time in the empty reactor was approximately 2 seconds. As shown in Figure 4, steady state oxidation conditions across the model fly ash bed were achieved after 15 to 20 minutes of exposure to the simulated flue gases. These steady state oxidation conditions were maintained for up to 2 hours, the time limit of the experiments. The heterogeneous mechanisms of Hg^0 oxidation are not well understood. It is probable that Fe_2O_3 produces an active chlorinating agent from gas-phase HCl , which subsequently attacks Hg^0 molecules and results in the formation of HgCl_2 . Hg^0 oxidation levels as high as 95% were observed when 14% Fe_2O_3 was present in the model fly ash. The high Fe content found in a Pittsburgh coal fly ash (9) suggests that the high Hg^{++} concentrations measured when burning this coal resulted from the heterogeneous catalytic oxidation of Hg^0 (4).

The oxidation of Hg^0 over high-iron-containing fly ash was studied with 500 ppmv SO_2 and 1.7% (mole) H_2O added to the base-case flue gas. The 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, but it appeared to cause a 15 or 20% increase at 150 °C. However, the presence of both SO_2 and H_2O caused a drastic decrease in the catalytic oxidation of Hg^0 , especially at the lower temperatures. The inhibition effect of SO_2 and H_2O may be attributed to the scavenging of a catalytically generated chlorinating agent such as Cl_2 through a possible reaction shown below:



The inhibition effect of SO_2 and H_2O on catalytic Hg^0 oxidation needs to be considered when burning sulfur-containing fuels such as coal.

The potential catalytic activities of CaO and CuO and the effects of the Fe and Cu contents of the three-component model fly ashes on the oxidation of Hg^0 were also investigated. The results are shown in Figure 6. The CaO -containing model fly ash did not cause Hg^0 oxidation in absence of SO_2 and H_2O , suggesting that CaO is an inert fly ash component relative to Hg^0 . CuO is a much more active catalyst than Fe_2O_3 . A model fly ash containing 0.1% CuO exhibited catalytic activity for Hg^0 oxidation similar to that for 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 in MSW combustors (10). The mechanism for the chlorinating agent formation is presumed to be the Deacon process reaction shown below:



The chlorinating agent (Cl_2) was possibly produced at a much higher rate in the presence of Cu compared to that in the presence of Fe and led to higher oxidation of Hg^0 and formation of HgCl_2 . As illustrated in Figure 6, lowering the amounts of Fe and Cu in the three-component model fly ashes reduced the heterogeneous oxidation of Hg^0 . A model fly ash containing 1% CuO was the

most active catalyst in these tests; oxidation of Hg^0 reached approximately 95% over the temperature range of 150 to 250 °C. While changes in temperature did not significantly affect the rate of Hg^0 oxidation for the 0.1% Fe_2O_3 fly ash (little oxidation) or the 1.0% CuO model fly ash (>95% oxidation), it significantly affected Hg^0 oxidation rates for the three other model fly ashes. Increasing reactor temperatures resulted in increasing oxidation rates.

The effect of SO_2 and H_2O on the oxidation of Hg^0 across the fixed beds of the three-component model fly ashes was studied at a bed temperature of 250 °C. Results are shown in Figure 7. The inhibition effect of $\text{SO}_2/\text{H}_2\text{O}$ was observed to be very strong for the Fe-containing model fly ashes, while a less significant inhibition effect was observed for the Cu-containing model fly ashes. The three-component model fly ash containing 7% CaO exhibited very interesting behavior in the presence of SO_2 and H_2O . It did not show any Hg^0 oxidation in the presence of HCl without SO_2 and H_2O . However, after an induction period of approximately 20 minutes, the presence of SO_2 and H_2O resulted in a steady state Hg^0 oxidation of approximately 15% across this model fly ash. Adsorption of SO_2 by CaO may have created active sulfur sites on the surface of the CaO-containing model fly ash, which reacted with the Hg^0 molecules in the gas phase to produce mercuric sulfide (HgS) molecules on the ash surface. Sulfite or sulfate may be the active sites, created by reaction between SO_2 and CaO.

CONCLUSIONS

The results of the gas-phase experiments suggest that Hg^0 oxidation occurring in simple simulated combustion flue gas mixtures in the presence of HCl is very slow and proceeds at measurable rates only at high temperatures (>700 °C) and relatively high HCl concentrations (>200 ppm). A concentration of 500 ppm SO_2 in flue gases inhibits oxidation by HCl. However, the gas-phase reaction of Hg^0 and Cl_2 is very fast even at low temperatures (40 °C). The observed SO_2 effect suggests that homogeneous gas-phase Hg^0 oxidation is unlikely to occur in coal combustion processes, as U.S. coals typically have relatively high sulfur and low chlorine contents.

The effects of fly ash parameters on the oxidation of Hg^0 were studied using model fly ashes which contained major fly ash inorganic constituents. CuO and Fe_2O_3 showed significant catalytic activity in oxidizing Hg^0 with 50 ppmv of HCl in the simulated flue gas over the experimental temperature range of 150 to 250 °C. It is speculated that these two transition metal oxides produce an active chlorinating agent, probably Cl_2 , from HCl through a multi-step heterogeneous Deacon process reaction. Subsequent rapid reaction of the chlorinating agent with the gaseous Hg^0 produces large quantities of HgCl_2 . CuO is a much more active catalyst than Fe_2O_3 , and the production of the chlorinating agent from HCl in the presence of this Cu catalyst appears to proceed much faster than with Fe. The increases in catalytic activity of the model fly ashes with increasing reaction temperature suggest that the catalytic Hg^0 oxidation process is

kinetically controlled. The presence of SO₂ and H₂O in the simulated flue gas inhibited the catalytic activity of the Fe-containing fly ashes more strongly than did the Cu-containing model fly ashes. The catalytic Hg⁰ oxidation may not be significant in combustion of sulfur-containing fuels such as coal. CaO exhibited a different behavior than did the Fe and Cu oxide catalysts. Low oxidation of Hg⁰ (15%) was observed for the Ca-containing model fly ashes when SO₂ was added to the simulated flue gas. Oxidation of Hg⁰ may be caused by the formation of Hg-sulfur bonds on the surfaces of CaO.

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Table 1. Summary of Experimental Temperatures and Simulated Flue Gas Compositions

<u>Temperature* (°C)</u>			
Low Temperature Tests	150	200	250
High Temperature Tests	515	634	754
<u>Flue Gas Composition**</u>			
Concentration of HCl (ppmv)	50	100	150
Concentration of SO ₂ (ppmv)	0	500	
Concentration of H ₂ O (mole%)	0	1.7	
Concentration of CO ₂ (mole%)	5		
Concentration of O ₂ (mole%)	2		
Concentration of N ₂ (mole%)	Balance		

* with ± 5.0 °C measurement uncertainty

** with $\pm 2.8\%$ measurement uncertainty

Table 2. Model Fly Ash Compositions (wt%*)

Model Fly Ash	Content				
	Al ₂ O ₃	SiO ₂	Fe ₂ O 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

* with ±0.0017% measurement uncertainty

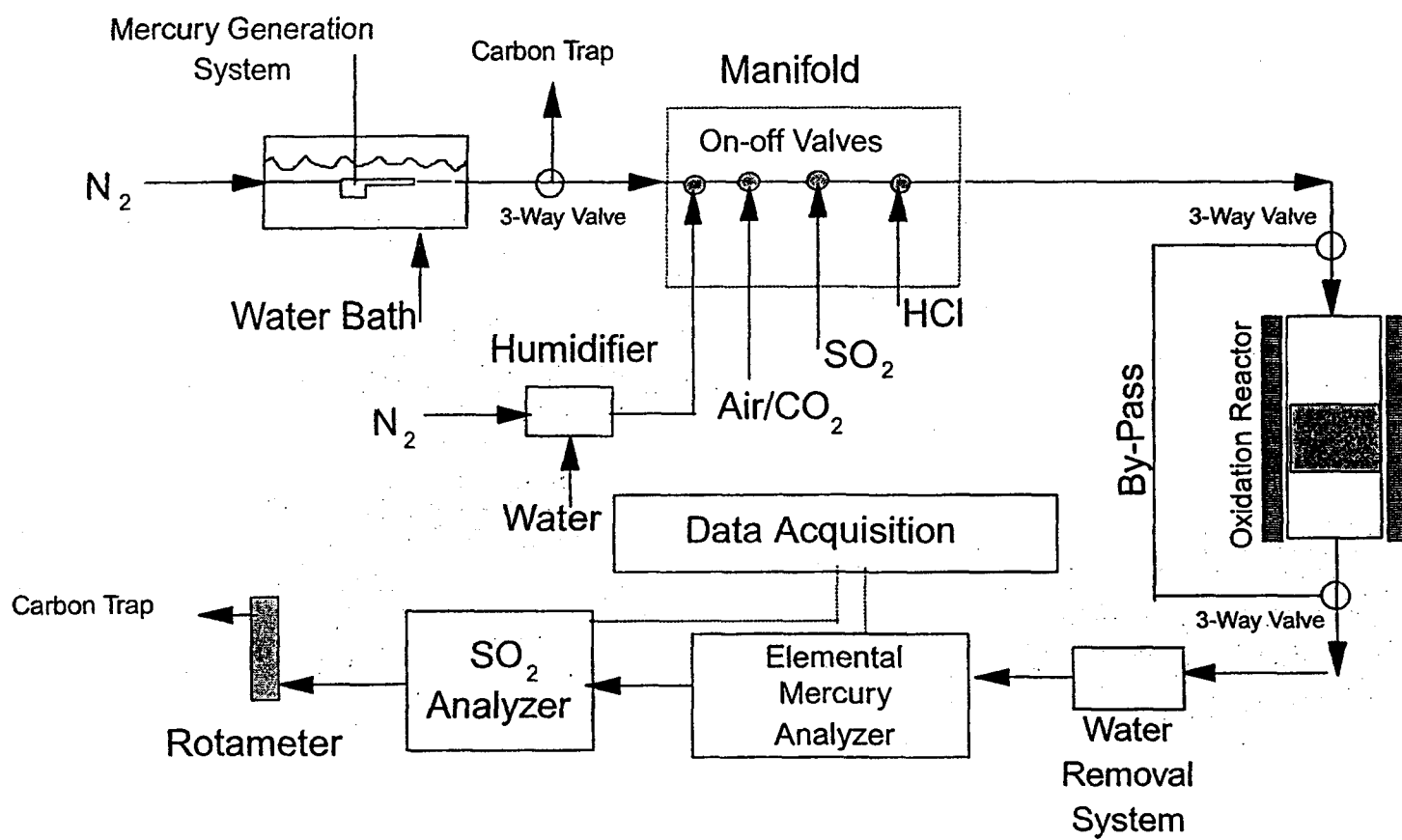


Figure 1. Schematic of the elemental mercury oxidation reactor system.

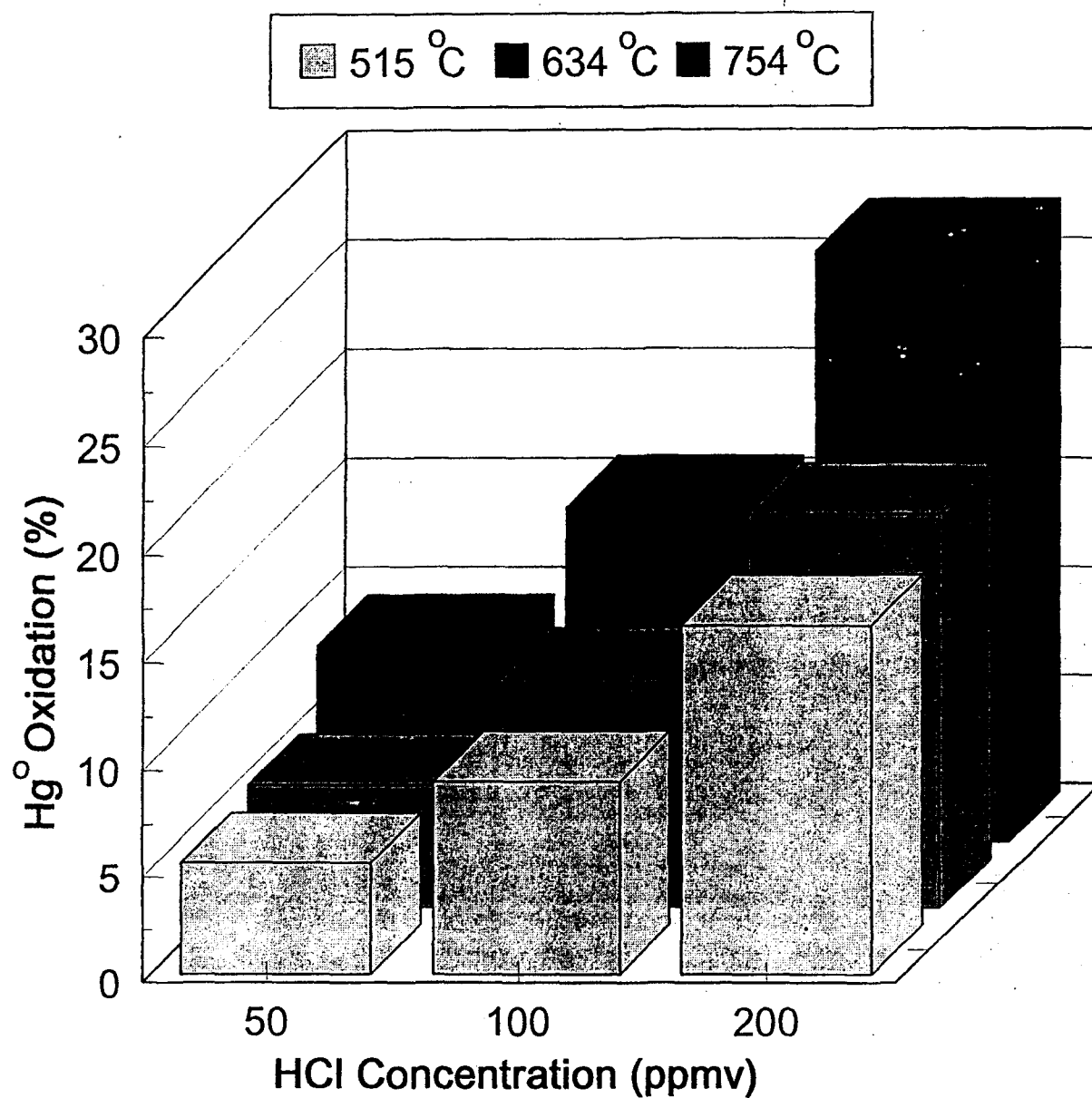


Figure 2. Effects of temperature and HCl concentration on the gas-phase oxidation of Hg^0 in the absence of SO_2 and H_2O .

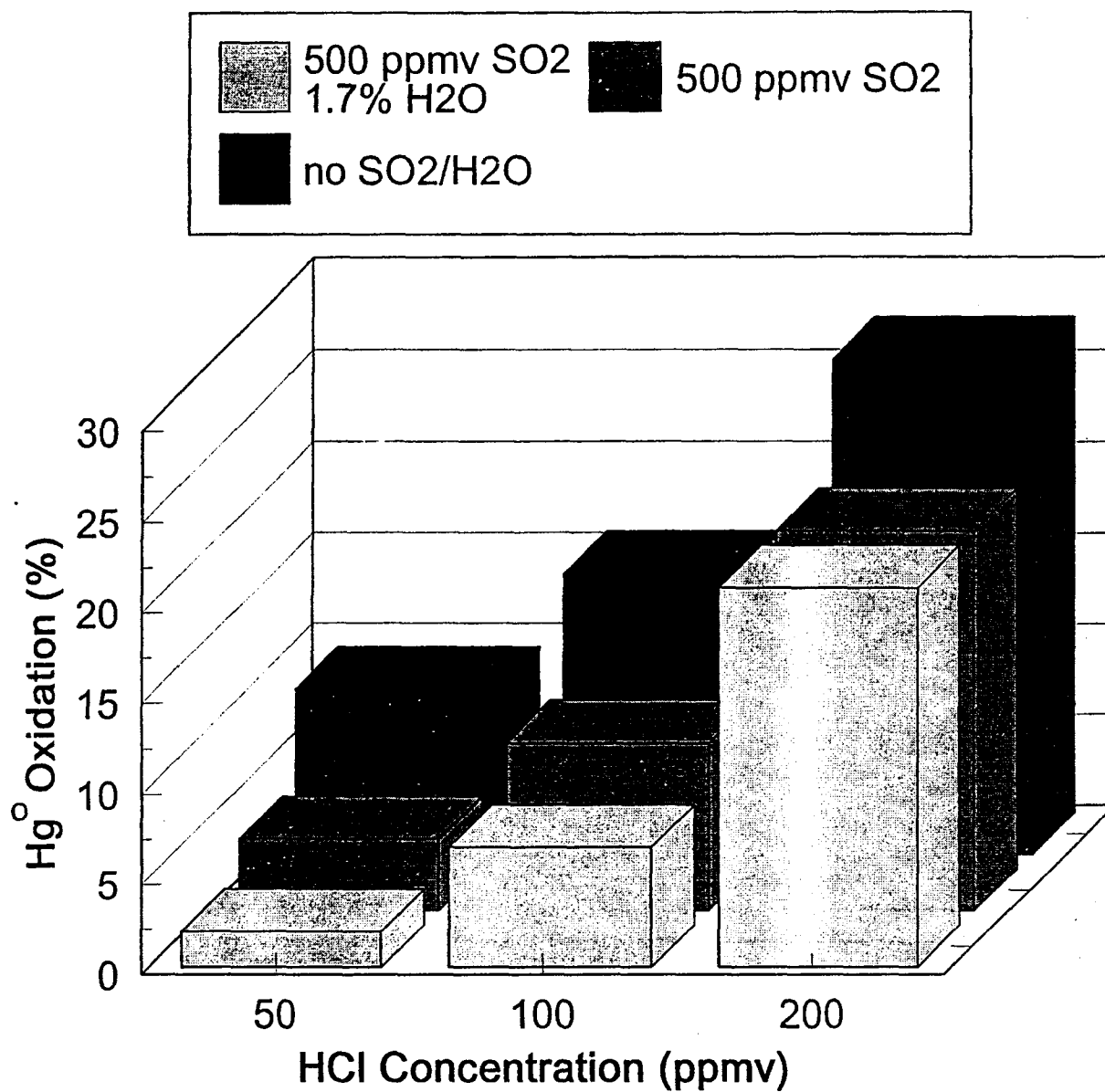


Figure 3. Effects of SO₂ and H₂O on the gas-phase oxidation of Hg⁰ at 754°C and three different HCl concentrations.

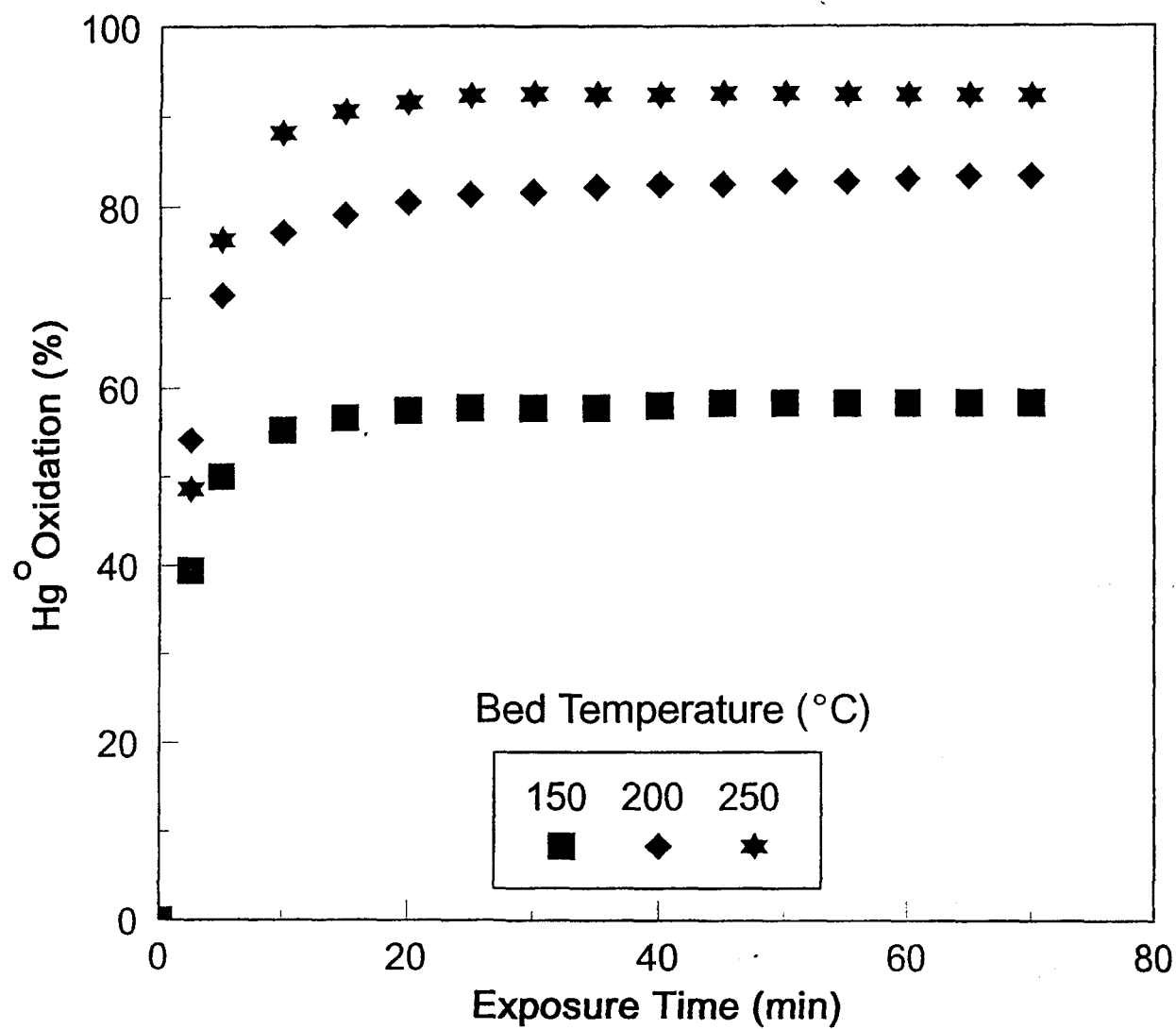


Figure 4. Heterogeneous oxidation of Hg⁰ across the high Fe model fly ash (see Table 1) in the presence of 50 ppm HCl and the absence of SO₂ and H₂O; effects of time of exposure and bed temperature.

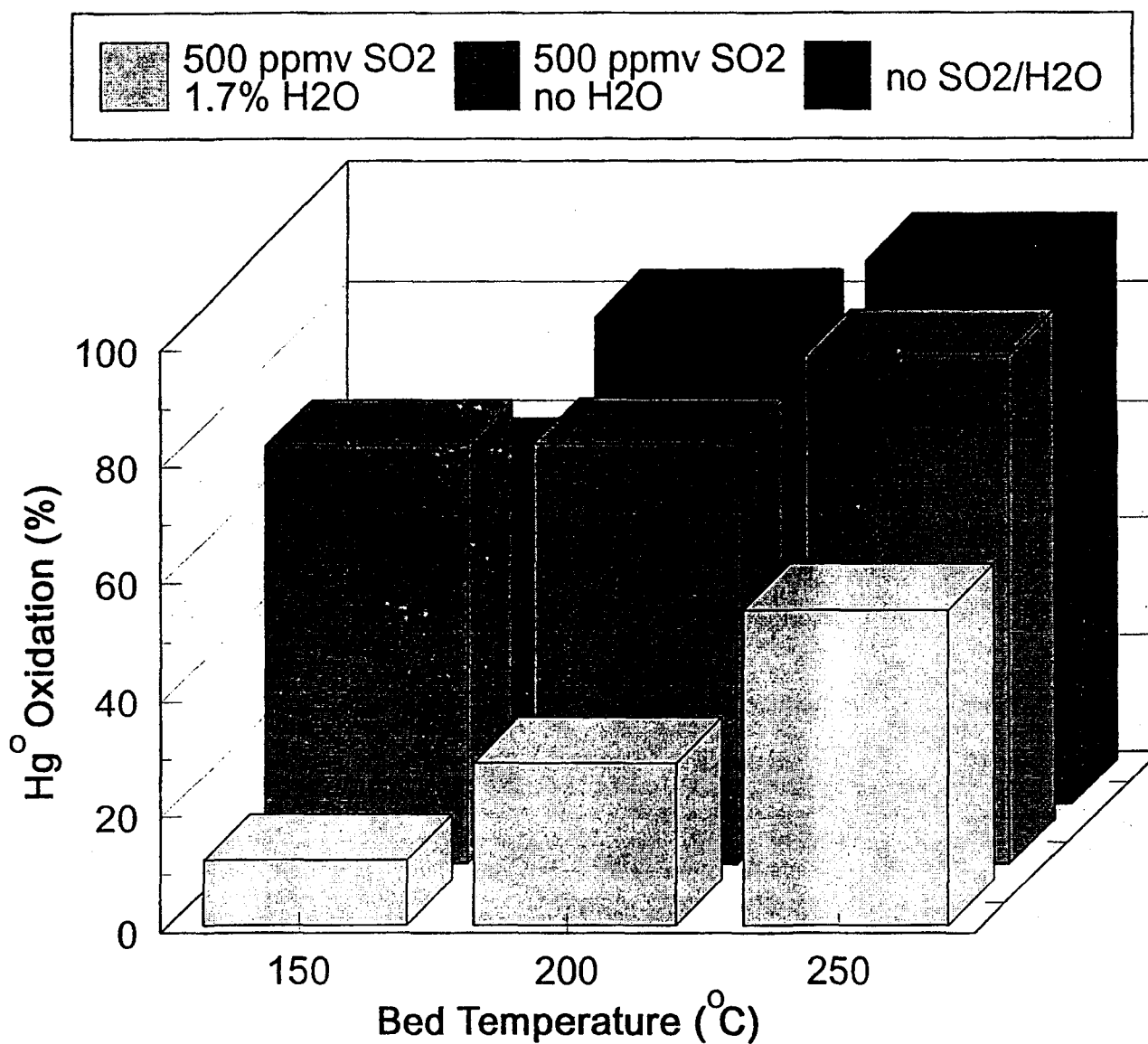


Figure 5. Effects of SO₂, H₂O, and bed temperature on the steady-state heterogenous oxidation of Hg⁰ across the high Fe model fly ash (see Table 1) in the presence of 50 ppm HCl.

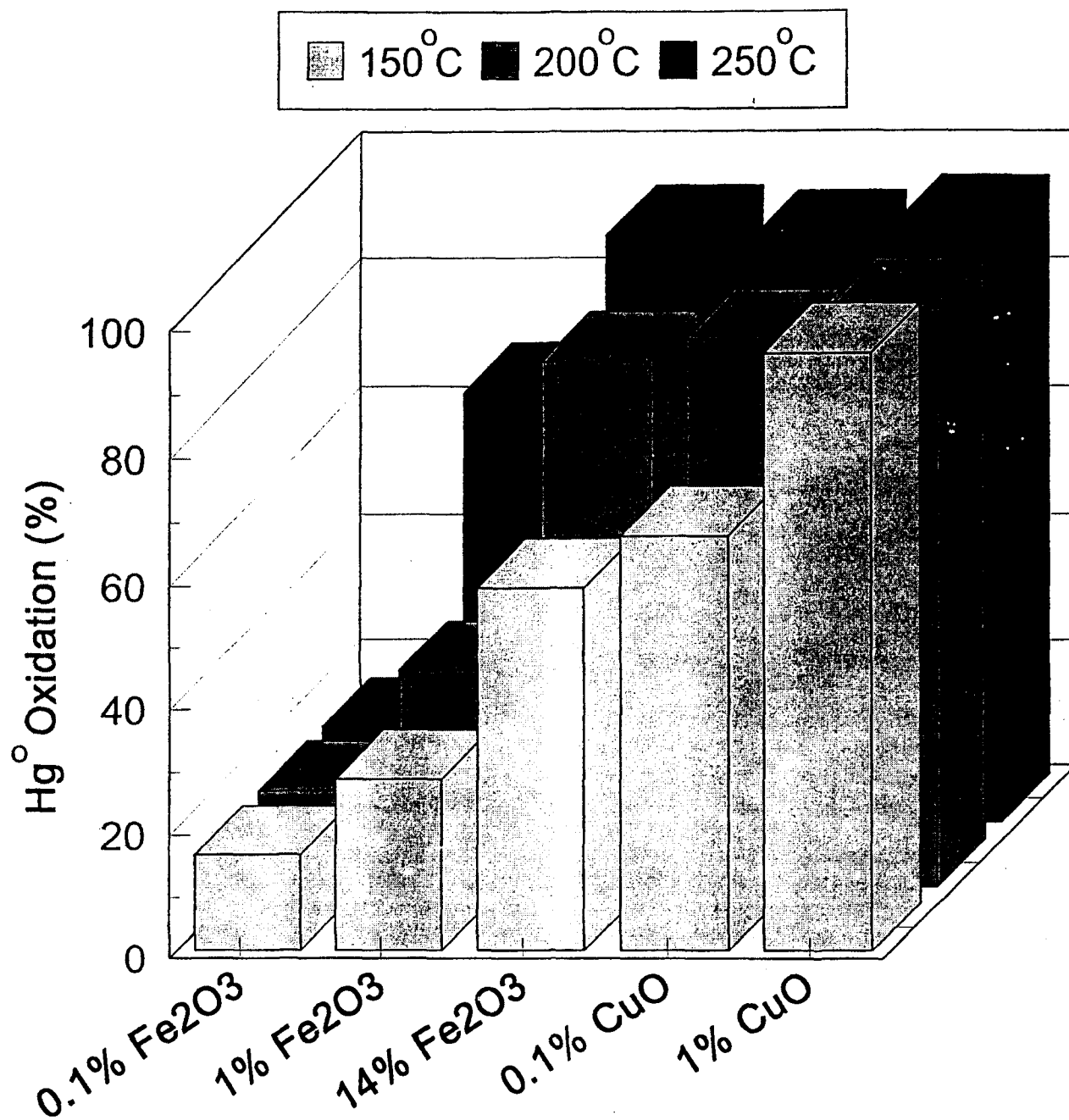


Figure 6. Effects of coal fly ash components/compositions and temperature on the steady-state heterogeneous oxidation of Hg^0 across model fly ashes (see Table 1) in the presence of 50 ppm HCl and the absence of SO_2 and H_2O .

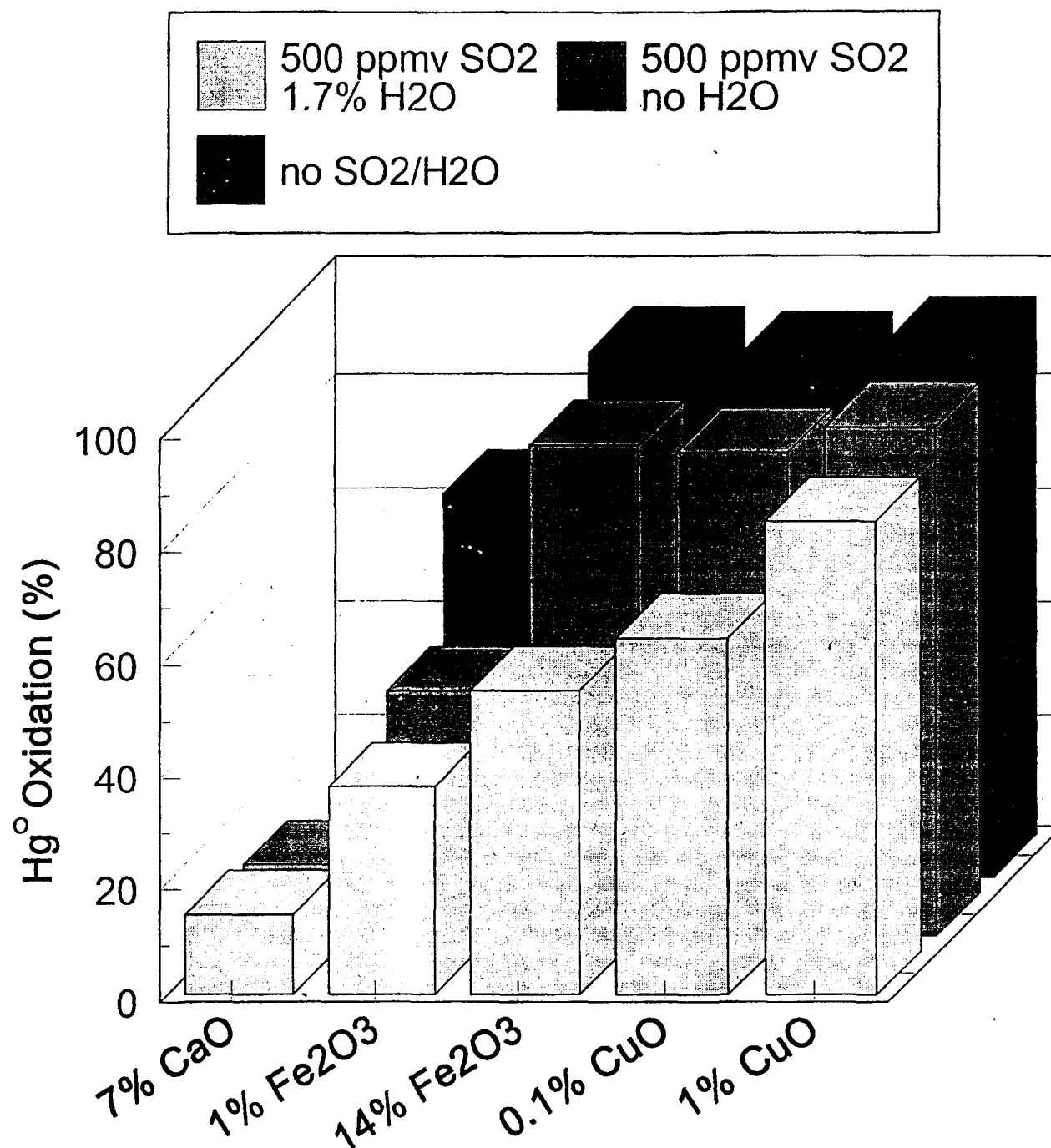


Figure 7. Effects of SO₂ and H₂O on the steady-state heterogeneous oxidation of Hg⁰ across model fly ashes (see Table 1) at 250°C and in the presence of 50 ppm HCl.

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16. ABSTRACT The paper discusses results of bench-scale experiments to study the effects of flue gas and fly ash parameters on the oxidation of elemental mercury (Hgo) in simulated flue gases containing hydrogen chloride (HCl). Gas-phase studies indicate that the in-flight post-combustion oxidation of Hgo 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 (SO2) and water vapor (H2O) in the simulated flue gas significantly inhibits the gas-phase oxidation of Hgo. On the other hand, a preliminary investigation indicates that the gas-phase reaction of Hgo with chlorine (Cl2) is fast. At 40 C and in the presence of 50 ppm Cl2, 100% of the input Hgo was oxidized to mercuric chloride in less than 2 seconds, indicating that Cl2 is a much more active chlorinating agent than HCl. The effects of fly ash composition were investigated using a fixed-bed reactor containing different model fly ashes (simulated fly ash) consisting of mixtures of some major components found in coal and municipal waste combustor fly ashes. Work to date has focused on the potential catalytic oxidation of Hgo by two- and three-component model fly ashes composed of mixtures of alumina, silica, ferric oxide, cupric oxide, and calcium oxide.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Sulfur Dioxide		Pollution Control Stationary Sources	13B
Mercury (Metal) Water			07B
Fly Ash Chlorine			21B
Flue Gases			07D
Oxidation			07C
Hydrogen Chloride			
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