

**IMPACT OF TEMPERATURE AND FLUE GAS COMPONENTS ON MERCURY
SPECIATION AND UPTAKE BY ACTIVATED CARBON SORBENTS**

by

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Bachelor of Technology, Indian Institute of Technology Guwahati, 2004

Submitted to the Graduate Faculty of
School of Engineering in partial fulfillment
of the requirements for the degree of
Master of Science

University of Pittsburgh

2007

UNIVERSITY OF PITTSBURGH

SCHOOL OF ENGINEERING

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The impact of different flue gas constituents and bed temperature on mercury uptake capacity and mercury speciation were evaluated using a fixed bed experimental system. Two activated carbons were selected for the study: FGD activated carbon (Norit America Inc.) and a novel activated carbon manufactured by Corning Inc. After the experimental setup was tested and validated, evaluation of sorbents' performance was conducted using simulated PRB coal flue gas.

A substantial increase in the mercury uptake capacity of both sorbents was observed in the absence of SO₂ from the flue gas. Temperature programmed desorption (TPD) run on spent FGD sorbent revealed that mercury present on the surface of the spent sorbent was mostly in the elemental form.

An instant breakthrough of mercury was observed with both sorbents when HCl was removed from the flue gas. This led to a significant decrease in the mercury adsorption capacity of both sorbents. Absence of water from the flue gas caused an increase in mercury uptake capacity and a decrease in mercury oxidation with both the sorbents.

Removal of NO and NO₂ had variable impact on different sorbents. Removal of NO or NO₂ from the flue gas caused an increase in mercury uptake capacity of FGD sorbent. Removal

of NO from the flue gas also led to an increase in mercury oxidation catalyzed by FGD sorbent. On the other hand, removal of NO or NO₂ from simulated PRB gas not only caused a decrease in the mercury uptake capacity of the Corning sorbent, but also led to a significant decrease in mercury oxidation catalyzed by this sorbent.

A 100 °C increase in bed temperature (from 140 °C to 240 °C) caused an instant breakthrough of mercury with both sorbents under simulated PRB coal flue gas conditions. It also caused a significant decrease in the oxidation of mercury.

Based on the findings of the study, a mechanistic model explaining the mechanism for mercury uptake and oxidation by activated carbon through competition between Cl and SO₂ for active sites on the surface of the activated carbon is proposed.

Keywords: Flue Gas, Activated Carbon, Mercury Uptake/Adsorption, Mercury Oxidation

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ACKNOWLEDGEMENT

First of all, I would like to thank my thesis and academic advisor Dr. Radisav D Vidic. He has been a great teacher, researcher and mentor to me. His immense energy, superior work ethics and professional standards have always encouraged me to strive for perfection. His professional and personal advises (during paid lunches) are just invaluable.

A great thank goes to Dr. Jason D Monnell who undoubtedly helped me in achieving higher academic and research goals. He made my stay in the department of Civil and Environmental Engineering and in the city of Pittsburgh lot more enjoyable and fulfilling.

I wish to thank Dr. Leonard W. Casson and Dr. Ronald D. Neufeld who have nothing but honest to me in their advice regarding academics, research and career.

I would also like to thank Dr. Amir Koubaa and Dr. J. S. Lin for all of their help, support and concern towards me. I also owe thank to Sonia Suhy and administrative staff of the department especially for their help with official paperwork. A thank goes to Barry Griffith of Valley National Gases for prompt delivery of gas tanks, instrumental parts of my research work.

I am thankful to all of my labmates and classmates who definitely made my stay in the department really wonderful. A thank also goes to my buddy Asitava Mishra for his unflinching support and never-ending sarcasm.

I would like to thank Corning Inc. Corning NY for funding the research work. I would also like thanks officials from Corning Inc for their invaluable feedback.

Finally, I like to thank my parents and my sisters for their concern and care through out the years.

I dedicate this thesis to my Mother and to Soccer, the beautiful game.

1.0 INTRODUCTION

Coal contains very small amounts of mercury which is converted into the vapor phase during the burning of coal for electricity generation or other purposes. This gas phase mercury enters into the environment and eventually enters into water bodies, such as lakes, rivers etc., where it can form an organic compound known as methylmercury. This compound is consumed by fish and through fish consumption it enters into human beings causing negative health impacts, including neurological diseases.

Mercury generally exists in three forms in the coal plant flue gas: elemental, oxidized and particulate bound mercury. Oxidized and particulate bound mercury is easy to remove from flue gas using existing technologies, such as electrostatic precipitators (ESPs) and flue gas desulphurization (FGD) units. However, elemental mercury escapes above mentioned air pollution control devices and a new technology should be used for its control. Activated carbon sorbents can offer a suitable answer to capture elemental mercury. Performance of activated carbon sorbents is governed by many factors such as surface properties of the sorbent, flue gas composition, temperature, etc.

Most of the previous research focused on the impact of variables such as temperature, residence time and impregnation methods for activated carbons. Moreover, the previous studies primarily tested activated carbon performance under simplistic conditions for eg. with N_2 . Little research has been done to evaluate the performance of activated carbons under realistic

conditions of complete flue gas. Hence, the purpose of this study is to evaluate mercury adsorption and speciation by activated carbons in PRB coal flue gas. Impact of flue gas constituents and bed temperature was also studied on mercury uptake and oxidation by activated carbons.

2.0 LITERATURE REVIEW

2.1 MERCURY EMISSIONS

Coal-fired power plants (CFPPs) are currently the largest single source of anthropogenic mercury emissions in the United States. Environmental Protection Agency's (EPA) Information Collection Request (ICR) indicated that total mercury emission from 1149 units at 464 U.S. power plants was 43 tons in 1999. Emissions are projected to increase to 60 tons by 2010. Recent estimates of mercury emissions from power plants have varied between 40 and 52 tons/year^(1, 2, 3), contributing about one-third of the total anthropogenic mercury emissions in the US.

The amount of mercury emitted from CFPPs depends on the type of coal used. A study showed⁽⁴⁾ that the concentration of mercury in coal typically varies between 0.012–0.33ppm, whereas another study⁽⁵⁾ found the average mercury concentration in coal to be 0.085ppm with 0.047ppm as standard deviation.

Mercury emitted from CFPPs exists in three different forms: elemental mercury (Hg^0), oxidized mercury (Hg^{+2}) (as HgCl_2 , HgO and HgS) and particulate bound mercury (Hg^P). The relative amount of different mercury forms present in the flue gas depends on coal type and combustion systems. Studies done on pilot and full-scale systems indicated that amount of oxidized mercury ranges from 10-80% of the total vapor phase mercury^(6, 7, 8).

The efficacy of mercury control methods depends on the species of mercury (elemental vs oxidized) as well as on the form of mercury (gaseous vs particulate) present in the flue gas. Particulate associated mercury (Hg^{P}) can be removed from flue gas by using conventional air pollution control devices such as electrostatic precipitator (ESP), whereas oxidized mercury can be captured in wet flue gas desulfurization systems. However, Hg° is most likely to escape these air pollution control devices into the environment.

In United States, western sub-bituminous coal (from MT, WY, ID, UT, CO, AZ, NM) and eastern bituminous coal (from PA, OH, WV, KY, IL) accounts for 75% of coal production and 81% of mercury entering CFPPs⁽⁹⁾. The western coal contains only half as much mercury as eastern bituminous coal. However, the higher chlorine and sulfur content in the eastern coal leads to higher amount of oxidized mercury in the flue gas, which eventually leads to better capture or removal of mercury from the flue gas.

Activated carbon sorbents can offer a potential answer for controlling elemental mercury emissions since they have high specific surface area, which can be used to adsorb mercury. A comparison between soot particles generated by the incineration of sewage sludge (EP ash) and activated carbon⁽¹⁰⁾ revealed that mercury adsorptive capacity was two orders of magnitude greater for activated carbon samples compared to EP ash samples at room temperature. In addition, very little mercury was adsorbed at higher temperatures for both samples.

The surface of activated carbons can be impregnated by chemicals to further enhance mercury adsorption capacity. Granite *et al.*⁽¹¹⁾ tested a large number of sorbents for mercury uptake. When chemically promoted by the use of sulfur, iodine, chlorine and nitric acid, all activated carbons exhibited a far greater capacity for elemental mercury. It was explained that

non-impregnated carbons capture mercury by physical sorption, whereas chemically impregnated carbons can capture mercury by both physical and chemical sorption.

Teller and Quimby⁽¹³⁾ found that the best chloride salt impregnated carbons had as much as 300 times greater capacity for mercury removal at temperatures of 149 °C and 260 °C than traditional untreated carbons or sulfur impregnated carbons. Also, carbons treated by HCl exhibited greater capacity than untreated activated carbons.

The mercury sorption mechanism on activated carbon is a complex phenomenon. Huggins *et al.*⁽¹⁴⁾ postulated that many factors will influence the sorption and sorption rate, including the nature of the active sites on the carbon, the speciation of sulfur and chlorine in the gas phase, the gas-phase interaction between sulfur and chlorine, and temperature.

Apart from chlorine and sulfur content, extent of mercury oxidation and removal from the flue gas depends on other factors, such as NO_x and moisture content present in the flue gas as well as on the surface, and bed temperature of activated carbon.

2.2 IMPACT OF FLUE GAS COMPONENTS ON MERCURY SPECIATION AND MERCURY UPTAKE BY ACTIVATED CARBON

2.2.1 Carbon Dioxide (CO₂)

Carbon dioxide in flue gas behaves as an inert gas, i.e., it neither impacts adsorption capacity of activated carbon nor does it affect the oxidation of mercury. Liu⁽²¹⁾ observed no change in the adsorption capacity of a sulfur impregnated carbon tested under different CO₂ concentration (5 and 15%).

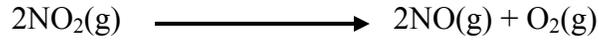
2.2.2 Oxygen (O₂)

Hall *et al.*⁽²²⁾ reported no homogeneous gas phase reaction between Hg[°] and oxygen during a reaction time of 1 hour in the temperature range of 20–700 °C. However, in the presence of activated carbon or fly ash, at temperatures of 100–300 °C, adsorption of mercury increased with increasing oxygen concentration. In an another study, Hall *et al.*⁽²³⁾ found that oxidation of mercury in the presence of activated carbon increased as the concentration of oxygen increased. It was also observed that on increasing the temperature from 200 to 400 °C, with 100 °C step, oxidation of mercury decreased.

Teller and Quimby⁽²⁴⁾ also observed that on using compressed air as the carrier gas for mercury instead of nitrogen, led to a doubling of mercury removal capacity for chloride treated carbons. Liu⁽²¹⁾ observed that mercury uptake by activated carbon was negligible at low oxygen concentration (3%). However, at higher concentrations (6 and 9%) mercury uptake by the same activated carbon sorbent increased by 16 and 33%, respectively.

2.2.3 Nitrogen Dioxide (NO₂)

Hall *et al.*⁽²³⁾ studied the homogeneous reaction between NO₂ and Hg[°]. A small but significant (16.7%) oxidation of Hg[°] was observed at 340 °C when the NO₂ concentration was 400ppm. The oxidation of mercury increased upto 30% on increasing the NO₂ concentration to 1000ppm. However, at higher temperatures (i.e. above 500 °C) almost no oxidation of mercury was observed. This is so because NO₂ is believed to decompose into NO and O₂ according to the following reaction⁽²²⁾:



A probable reaction between Hg° and NO_2 is the formation of $\text{HgO}(\text{s,g})$ ⁽²²⁾:



Miller *et al.*⁽¹⁶⁾ observed 100% breakthrough of mercury within 20 minutes when a lignite-based activated carbon was subjected to a gas mixture containing 6% O_2 , 12% CO_2 , 8% H_2O and balance N_2 . However, on adding 20ppm NO_2 to the above mentioned gas mixture, the activated carbon showed 90-100% adsorption of mercury for 8 hours. The capture of the influent mercury was confirmed by mass balance closure. A rapid breakthrough of mercury was observed when 1600ppm of SO_2 was added to the above gas mixture containing 20ppm NO_2 . Thus, a possible interaction between SO_2 and NO_2 was proposed, causing an instant breakthrough of mercury on the addition of SO_2 .

2.2.4 Sulfur Oxide (SO_2)

Miller *et al.*⁽¹⁶⁾ found that the addition of 1600ppm SO_2 to the baseline gas mixture (6% O_2 , 12% CO_2 , 8% H_2O and balance N_2) caused mercury in the effluent stream to instantly increased to 50% level, and reached to 100% breakthrough within 1hour. However, no oxidation of elemental mercury was observed. In an another test, same amount of SO_2 was added to the gas matrix containing 20ppm NO_2 along with the baseline gas mixture after 2.5 hours of the start of experiment. During this test, a rapid breakthrough as well as 100% oxidation of mercury was observed. This effect was observed at 107 °C and at 163 °C irrespective of the presence or

absence of NO or HCl. However, for the first 2.5 hours of the test almost 100% removal of elemental mercury was reported. It was concluded that the interaction between SO₂ and NO₂ on the surface caused a drastic decrease in the mercury uptake capacity of the sorbent and also led to the complete oxidation of the mercury. Butz *et al.*⁽¹⁷⁾ also reported a large reduction in mercury adsorption capacity of a metal sorbent due to the addition of SO₂ and NO₂.

The mercury adsorption capacity of the activated carbon was found to be inversely proportional to the concentration of SO₂⁽¹⁹⁾. Reduction in the adsorption capacity due to SO₂ presence was observed at concentrations as low as 100ppm. Carey *et al.*⁽²⁸⁾ also reported that the removal of SO₂ from the flue gas led to an increase in the adsorption capacity of activated carbon.

Dunham *et al.*⁽¹⁹⁾ and Olson *et al.*⁽²⁰⁾ proposed a mechanism to explain the effects of NO₂ and SO₂ (Figure 2.1). In the presence of NO₂, Hg⁰ is catalytically oxidized on the surface to form the nonvolatile nitrate Hg(NO₃)₂, which is bound to basic sites on the carbon. Capture continues until the binding sites are used up and breakthrough occurs. In the presence of SO₂, some of the catalytic sites are converted to a sulfate form where Hg(NO₃)₂ is no longer formed. However, mercury is still oxidized on the surface with NO₂ acting as the oxidizing agent (electron sink), but the product formed is a labile sulfur compound, mercury bisulfate [Hg(SO₄H)₂]. The bisulfate in turn reacts with NO₃⁻ to form a stable but volatile acidic form of mercuric nitrate. The emission of Hg(NO₃)₂ or the hydrate Hg(NO₃)₂·H₂O has been confirmed by solvent trapping and gas chromatography analysis. Sulfurous acid that accumulates from the hydration of SO₂ converts the previously formed nonvolatile basic mercuric nitrate into the volatile form, which explains the slow release of previously captured mercury over time in the presence of NO₂ and SO₂.

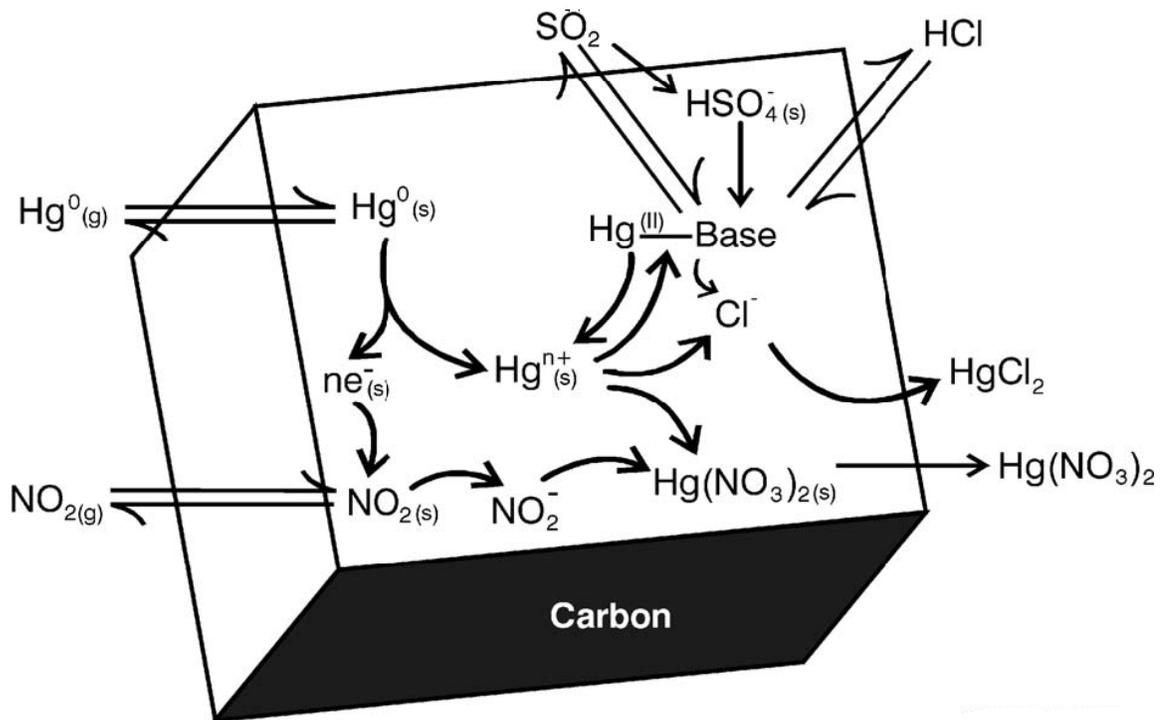


Figure 2.1 Suggested heterogeneous model for mercury capture showing potential impact of SO₂ and NO₂ ^(19,20)

2.2.5 Nitric Oxide (NO)

In a full factorial study done by Miller *et al.*⁽¹⁶⁾, 100% breakthrough of mercury was observed within 20 minutes when a lignite-based activated carbon was subjected to a gas mixture containing 6% O₂, 12% CO₂, 8% H₂O and balance N₂. However, addition of 300ppm NO to the above gas mixture (of 6% O₂, 12% CO₂, 8% H₂O and balance N₂) led to 95-100% mercury removal by the activated carbon. But in another study, Liu⁽²¹⁾ observed no change in adsorption capacity of virgin activated carbon and sulfur impregnated carbon by adding 500ppm NO to the balance N₂ (instead of using pure N₂).

Zhao *et al.*⁽²⁶⁾ reported that addition of NO to a gas mixture containing 13ppm Cl₂, 8% H₂O and balance N₂ led to a decrease in the oxidation of Hg⁰ under homogeneous conditions. However, the inhibiting effect of NO on mercury oxidation was not observed when H₂O was not present in the gas mixture. It was postulated that interaction between H₂O and NO led to development of reducing environment. In the reverse experiment, reduction of Hg⁺² was also observed when 300ppm of NO was added to the gas mixture of 13ppm Cl₂ and 8% H₂O.

Moreover, in a study done by Norton *et al.*⁽²⁵⁾ on fly ash samples, it was observed that addition of 300ppm NO to baseline gas mixture (100ppm CO, 12% CO₂, 50ppm HCl, 20ppm NO₂, 6% O₂, 1600ppm SO₂ and balance N₂) led to a 50% decrease in the oxidation of elemental mercury. However in this study, unlike the previous study⁽²⁶⁾, water vapor was not present in the gas mixture.

2.2.6 Hydrogen Chloride (HCl)

Miller *et al.*⁽¹⁶⁾ reported that addition of 50ppm HCl to the baseline gas mixture of 6% O₂, 12% CO₂, 8% H₂O and balance N₂ led to 100% removal of mercury for 3 hours by an activated carbon. Ghorishi and Gullett⁽²⁷⁾ also reported a significant increase in the adsorption capacity of the FGD sorbent when 50ppm HCl was added to the baseline N₂ gas. X-ray fluorescence (XRF) spectroscopy analysis indicated an increased concentration of chlorine atoms on the surface of the spent sorbent. It was postulated that Cl atoms get adsorbed on the surface of the sorbent and facilitate formation of Hg-Cl bond, which in turn increased the uptake of Hg⁰.

In another study by Carey *et al.*⁽²⁸⁾, HCl gas in different concentrations was added to the baseline gas mixture of 6% O₂, 12% CO₂, 7% H₂O and balance N₂ to observe a change in adsorption capacity of FGD carbon at 140 °C. It was reported that the adsorption capacity

increased linearly on increasing the concentration of HCl from 0-50ppm. Even the uptake capacity of FGD sorbent for HgCl_2 also increased on increasing HCl concentration. However, the presence of SO_2 in the above gas mixture diminished the positive impact of HCl on mercury uptake. Moreover, in the presence of SO_2 , oxidation of elemental mercury also decreased even when HCl was present in the gas mixture.

In another study done by Galbreath *et al.*⁽²⁹⁾ on a 7KW coal combustion system burning lignite coal, it was reported that the addition of 100ppm HCl to the flue gas led to an enhanced Hg^0 uptake by the fly ash in the system. It was proposed that presence of HCl probably activated the adsorption sites on the fly ash leading to a higher adsorption.

Hall *et al.*⁽²²⁾ observed that an increase in the HCl concentration from 10-100ppm led to a logarithmic increase in the vapor-phase oxidation of elemental mercury. However, further increase in the concentration (i.e. above 100ppm) did not cause as much increase in the mercury oxidation.

Norton *et al.*⁽²⁵⁾ reported that the addition of 50ppm HCl to a gas mixture (100ppm CO, 12% CO_2 , 300ppm NO, 20ppm NO_2 , 6% O_2 , 1600ppm SO_2 and balance N_2) led to an increase in the oxidation of mercury catalyzed by different fly ash samples.

2.2.7 Water (H_2O)

In general, water present in the flue gas is known to decrease the adsorption capacity of activated carbons. Carey *et al.*⁽²⁸⁾ reported the effect of water concentration on mercury adsorption capacity of FGD under simulated flue gas mixture comprised of 1600ppm SO_2 , 50ppm HCl, 300ppm NO, 20ppm NO_2 , 6% O_2 , 12% CO_2 and balance N_2 . It was observed that the capacity of the sorbent for elemental mercury at 275 °F decreased significantly as the

concentration of water was increased from 1 to 10%. Decrease in the HgCl_2 uptake was even more than the decrease in the Hg° uptake. However, Ghorishi *et al.*⁽²⁷⁾ reported that the addition of 5% H_2O to the gas mixture comprised of 100ppm SO_2 , 50ppm HCl and balance N_2 caused an increase in the Hg° uptake capacity at 100 and 140 °C.

Zhao *et al.*⁽²⁶⁾ reported that in the presence of water, SO_2 and NO had pronounced inhibitory effect on vapor-phase Hg° oxidation at high temperature. It was observed that the addition of 8% H_2O to a gas mixture of 13ppm Cl_2 , 600ppm NO and balance N_2 caused a decrease in the oxidation of Hg° from 40% to 5%. Almost identical decrease was observed on the addition of H_2O when the above gas mixture contained 2000ppm SO_2 (instead of 600ppm NO). Inhibitory reduction effect was observed even when HgCl_2 was used instead of Hg° . The reduction of HgCl_2 increased from 40% to 80% upon adding water to either of the above gas mixtures. However, no decrease in the oxidation of elemental mercury (or increase in the reduction of HgCl_2) was observed in the absence of H_2O from the gas mixtures. Thus, it was proposed that SO_2 reacts with Cl_2 , which is responsible for the formation of HgCl_2 , to SO_2Cl_2 and SO_2Cl as per the following reactions⁽²⁶⁾:



However, almost no mercury oxidation was observed when SO_2 alone was present in the gas mixture without water. Thus, it was speculated that SO_2Cl_2 and SO_2Cl were capable of

decomposing back to Cl and Cl₂ or have almost the same oxidizing ability as Cl and Cl₂. But SO₂Cl₂ and SO₂Cl have the property to readily react with H₂O as per the following reactions⁽²⁶⁾:



As per the above reactions, chlorinating/oxidizing species were hydrolyzed by H₂O rendering less Cl and Cl₂ in the gas phase and ultimately causing a decrease in the oxidation of Hg^o.

NO has the same properties as SO₂ and hence forms NOCl and NOCl₂ through reactions with Cl and Cl₂ respectively⁽²⁶⁾.



Compounds formed, NOCl and NOCl₂, in turn react with H₂O and lead to less Cl and Cl₂ in the gas causing decrease in the oxidation of Hg^o as per the following reactions⁽²⁶⁾:



2.3 IMPACT OF TEMPERATURE ON MERCURY UPTAKE AND MERCURY OXIDATION BY ACTIVATED CARBON

Carey *et al.*⁽²⁸⁾ studied the impact of temperature on elemental mercury uptake capacity of FGD sorbent in a constant flow of N₂. A consistent decrease in the uptake capacity was observed on increasing the temperature from 60 °C to 100 °C to 140 °C. McLaughlin and Vidic⁽³³⁾, Karatza *et al.*⁽³⁴⁾ and Krishnan *et al.*⁽³⁵⁾ also reported a decrease in adsorption capacity of different activated carbons with an increase in temperature. However, in the presence of SO₂, it was observed that elemental mercury capacity of activated carbon increased with an increase in temperature⁽²⁸⁾.

Ghorishi *et al.*⁽³⁶⁾ also reported a decrease in the adsorption capacity of Cl-impregnated activated carbon with an increase in temperature under entrained flow conditions in N₂. However, upon increasing the amount of activated carbon no effect of temperature increase was observed on the adsorption capacity. It was concluded that to negate the effect of temperature on the adsorption capacity a minimum carbon-to-mercury ratio should be maintained.

Hall *et al.*⁽²²⁾ studied the impact of temperature on mercury oxidation in the presence of activated carbon subjected to different O₂ concentrations balanced by N₂. At bed temperature of 200 °C, a linear increase in the oxidation of mercury was observed as the O₂ concentration was increased from 0 to 10%. Almost 30% mercury oxidation was observed at 10% O₂ concentration. However, on increasing the bed temperature to 400 °C no mercury oxidation was observed even at 10% O₂ concentration.

Zhuang *et al.*⁽³⁷⁾ studied the impact of temperature on oxidation of elemental mercury under sub-bituminous coal flue gas. Almost no oxidation of elemental mercury was observed at

higher bed temperatures such as 275 °C and 400 °C. However, 50% oxidation of influent mercury was observed at 150 °C even in the presence low sulfur and low chlorine in the flue gas.

2.4 EFFECT OF ACTIVATED CARBON SURFACE ON MERCURY UPTAKE AND MERCURY OXIDATION

Li *et al.*⁽³⁰⁾ studied the effect of surface moisture on Hg⁰ adsorption capacity of two activated carbon sorbents. Experiments were conducted in N₂ environment at room temperature. It was observed that heating the sorbents to 110 °C, to remove surface moisture, led to a 70% decrease in mercury uptake by the sorbents. Temperature programmed desorption (TPD) on the spent sorbent revealed that mercury is desorbed from the surface at high temperatures, indicating that mercury was chemisorbed on the surface. X-ray absorption fine structure (XAFS) analysis indicated possible surface oxygen complexes could serve as the active centers for mercury binding. It was speculated that the adsorbed H₂O molecules on the activated carbon surface were closely associated with surface oxygen complexes, which in turn were facilitating the adsorption of mercury. Thus, during heat treatment H₂O molecules were removed from the surface causing a decrease in mercury uptake. However, it should be noticed that moisture present on the activated carbon surface is different from the moisture content in the flue gas which causes decrease in the mercury uptake capacity of activated carbon.

Laumb *et al.*⁽³¹⁾ studied the surface of spent activated carbon sorbents using X-ray photoelectron spectroscopy (XPS). Sorbents were exposed to bituminous coal flue gas i.e., flue gas containing 1600ppm SO₂, 20ppm NO₂ and 50ppm HCl. Concentrations of acid gases were varied in the baseline gas mixture of 6% O₂, 12% CO₂, 8% H₂O and balance N₂. When HCl was

excluded from the gas matrix, no Cl was observed on the surface. It was reported that the concentration of Cl atoms on the sorbent surface was the highest when SO₂ was not present in the flue gas. When SO₂ was added to the flue gas, concentration of Cl atoms on the surface decreased ten times. Moreover, no Cl atoms were found on the sorbent surface when experiments were run long after 100% breakthrough of mercury. A competition between Cl and S was suggested for the active binding sites on the surface. X-ray Photoelectron Spectroscopy (XPS) analysis showed that the chlorine on the surface was present as chloride and/or organic chlorine.

Analyses of sulfur on the sorbent surface showed that omission of SO₂ from gas matrix resulted in very low concentration of sulfur species⁽³¹⁾. Sulfur content was found to be the highest after the longest run performed using a complete bituminous coal flue gas. S(IV) form was the most dominant form of sulfur on the sorbent surface. It was suggested that SO₂ was converted to S(VI) form, such as sulfate, bisulfate or sulfuric acid, on the surface of the sorbent. However, absence of NO₂ or H₂O, led to a much lower concentration of S(VI) concentration on the surface. The absence of NO₂ contributed to slower oxidation of the SO₂ to sulfuric acid. Similarly, the absence of H₂O from the gas matrix led to lower hydration of sulfur trioxide and/or sulfurous acid and subsequent oxidation to sulfuric acid⁽³¹⁾.

Olson *et al.*⁽³²⁾ analyzed the surface of an activated carbon sorbent subjected to low rank coal flue gas containing 6% O₂, 12% CO₂, 15% H₂O, 580ppm SO₂, 120ppm NO, 6ppm NO₂, 1ppm HCl and balance N₂. XPS analysis of samples collected after different exposure time revealed a change in the concentration of elemental carbon, sulfur, oxygen and chlorine. The atom percentage of carbon decreased over the time, whereas concentration of S(VI) continuously increased on the surface of the sorbent. Chlorine atoms were not observed on the samples collected in the beginning but presence of chlorine atoms was detected on the samples collected

in the middle of experiments. Chlorine concentration on the surface decreased when Hg breakthrough level reached the inlet concentration. Moreover, sorbent samples from longer runs did not show any presence of chlorine atoms on the surface. On the other hand, oxygen concentration increased on the surface with time. It was postulated that the increase in oxygen was due to the addition of SO₂ and subsequent oxidation and hydration of SO₂ to S(VI) form.

Mercury accumulation on the activated carbon surface correlated inversely with the accumulation of S(VI)⁽³²⁾. A competition was proposed to be existing between Hg⁺², S(VI) and HCl for the basic sites on the surface, which was eventually won by S(VI) species.

3.0 MATERIALS AND EXPERIMENTAL METHODS

3.1 ACTIVATED CARBONS

The main objectives of this study were to analyze the performance of various types of activated carbons in removing mercury from coal fired power plant (CFPP) flue gas and to determine the effect of different flue gas constituents and temperature on sorbent performance and mercury speciation.

The main sorbents used for the study includes FGD sorbent, carbon black and a novel sorbent manufactured by Corning Inc. FGD sorbent is a commercially available lignite coal-based powdered activated carbon supplied by the manufacturer (Norit Americas Inc., Atlanta, GA) in 325 mesh size (45 μ m). This carbon is designed to remove heavy metals typically found in flue gas streams. In this study, FGD was used as the standard to compare the performance of other sorbents.

Cabot Black Pearl 460 was used as the substitute for carbon black in the study. It is a commercially available carbon from Cabot Corporation, Billerica, MA. It was obtained in particle form but was crushed and sieved to 325 mesh size (45 μ m) before using in the experiment.

Novel sorbent from Corning Inc. was analyzed for its performance in removing mercury from PRB coal flue gas. This sorbent is a carbon based sorbent impregnated with a chelating

agent and an oxidizing agent. These agents were added to the base carbonaceous material to improve the performance and possibly to achieve higher efficiency than commercially available sorbents. The performance of this sorbents was compared to that of the FGD sorbent.

3.2 FLUE GAS COMPOSITION

Flue gas used in this study was designed to simulate gas from plants burning powdered river basin (PRB) coal. Concentration of various flue gas constituents are shown in Table 3.1. The stock concentration column in the table shows the concentration of gases in the gas cylinders obtained from the industrial supplier. For cylinders with NO, NO₂, SO₂ and HCl, balance gas is N₂. The flow rate of the simulated flue gas in all the experiment was maintained at 1L/min.

Table 3.1 Composition of the PRB Flue Gas ^(38, 39, 40)

Constituents	Concentration in PRB Flue Gas	Stock Concentration in gas Tanks	Flow Rate of Gases (ml/min)
NO ₂	20 ppm	488 ppm	40.98
NO	300 ppm	3027 ppm	99.1
HCl	5 -10 ppm	1022 ppm	5-10
SO ₂	300 ppm	1.01%	29.7
O ₂	6%	99.99%	60
CO ₂	13.5%	99.99%	135
H ₂ O	6%	99.99%	60
N ₂	Balance	99.99%	565.22-570.22

3.3 GAS PHASE MERCURY

A mercury permeation tube manufactured by VICI Metronics (Santa Clara, CA) was used as the source of elemental mercury (Hg°) throughout the study. The tube was kept in a glass U-tube, which also contained small glass beads to heat the incoming carrier gas to the designed temperature. The U-tube setup was placed in a water bath to maintain the constant temperature. Water in the bath was topped with a thin layer of oil to reduce the evaporation loss. The carrier gas (carbon dioxide, CO_2) was sent from the left arm of the tube to pick mercury and leaving the tube from the right arm. Complete arrangement for elemental mercury generation is shown in Figure 3.1.

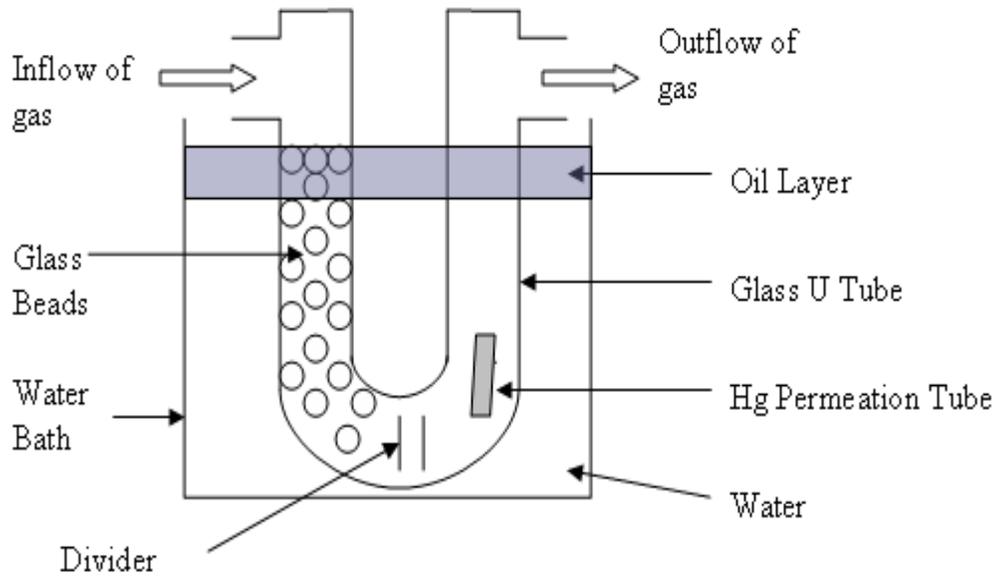


Figure 3.1 Arrangement for elemental mercury generation

Mercury permeation tube is designed to provide a constant Hg° concentration (ng/min) as a function of temperature. The calibration curve, shown in Figure 3.2, of the permeation tube was provided by the manufacturer (VICI Metronics). Calibration curve was also verified experimentally using the atomic fluorescence detector.

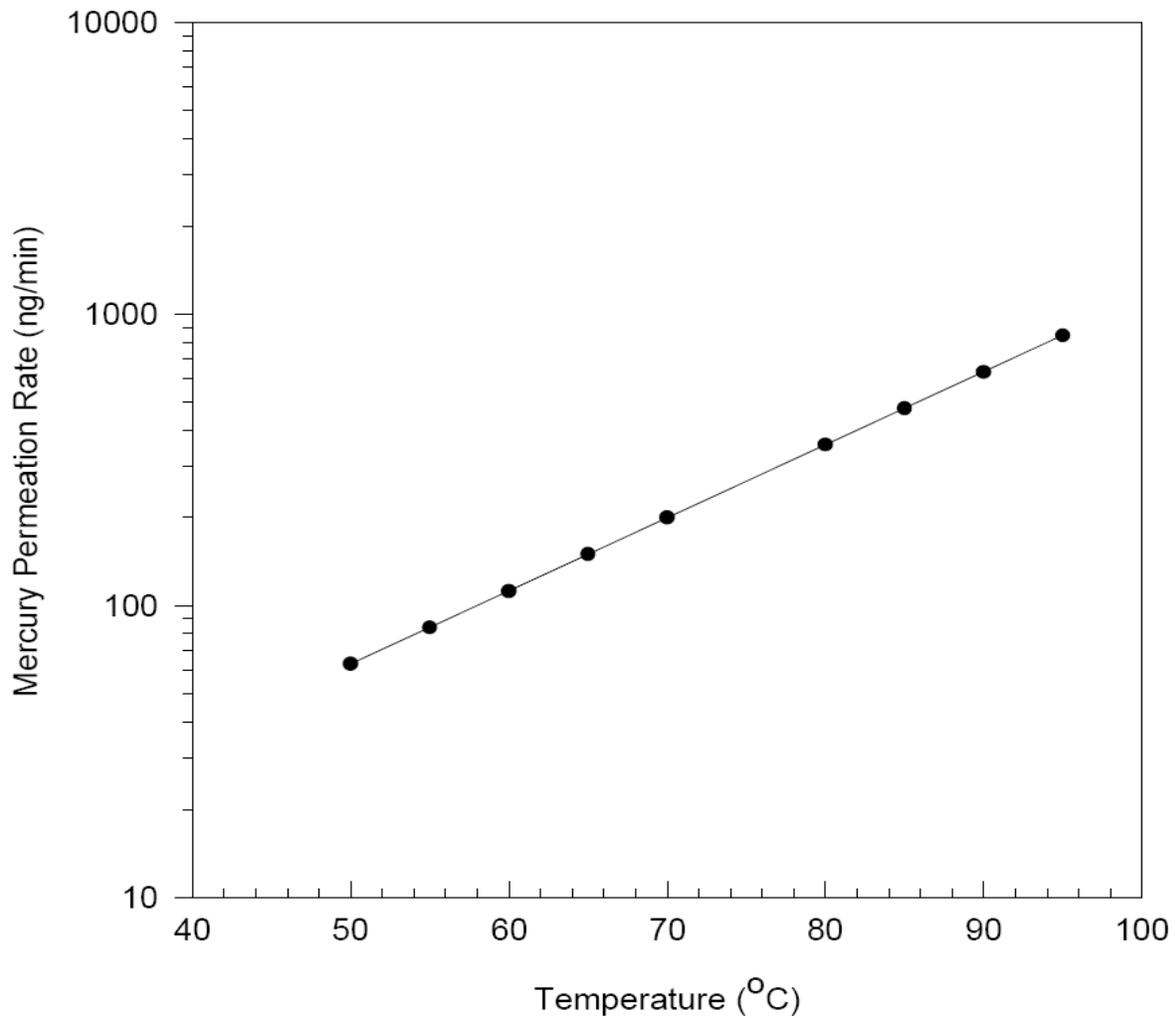


Figure 3.2 Mercury permeation rate curve: Mercury permeation rate as a function of temperature

For most of the experiments with flue gas, carbon dioxide CO₂ was used as the carrier gas for Hg⁰. A mass flow controller connected to read-out/control box was used to control the flow rate of CO₂ to the mercury permeation tube. Two 3-way valves were placed before and after the U-tube to by-pass the tube to conduct experiments without mercury or to purge the system. A 3-way valve was also used so that N₂, instead of CO₂, can be used as the carrier gas for mercury. The flow rate of N₂ was controlled by a mass flow controller manufactured by Aalborg (Orangeburg, NY).

A continuous flow of CO₂ at 135 mL/min was maintained through the U-tube containing mercury permeation tube even when no experiment was running. The flow was maintained to avoid deposition of mercury in the tubings and to obtain constant mercury readings when experiments were initiated.

3.4 EXPERIMENTAL SETUP

The whole experimental set up can be divided into four major parts:

1. Flue gas preparation section
2. Furnace and reactor section
3. Mercury conversion section
4. Mercury analysis section (Sir Galahad II: Atomic fluorescence based mercury detector)

3.4.1 Flue gas preparation section

PRB coal flue gas was generated by mixing different constituent gases. The source gas cylinders were obtained from Valley National Gases (West Mifflin, PA). Gas regulators were used to maintain the pressure of each constituent gas at 20psi. Flow rate of the gases was controlled by mass flow controllers (Aalborg, Orangeburg, NY). For SO₂, NO and NO₂, a ¼” outer diameter (OD) stainless steel tubing (McMaster-Carr, Aurora, OH) was used to transport gases from gas tanks to regulators, and from regulators to the experimental set up. For all the other gases, a ¼” inner diameter (ID) Tygon tubing (Saint-Gobain Performance Plastic Corp., Aurora, OH) was used to transfer the gases.

Nitrogen was used to pick the moisture from the water bath which was maintained at 48 °C. Figure 3.3 illustrates the arrangement for moisture generation and introduction into the flue gas. The tubing from the bath to the reactor was ¼” outer diameter Teflon tubing (Fisher Scientific). Heating tape was used to heat the Teflon tubing so as to avoid water vapor condensation in the tubing. Teflon tubing was specifically used to carry water vapor as it can withstand high temperatures needed to keep the water in the vapor phase.

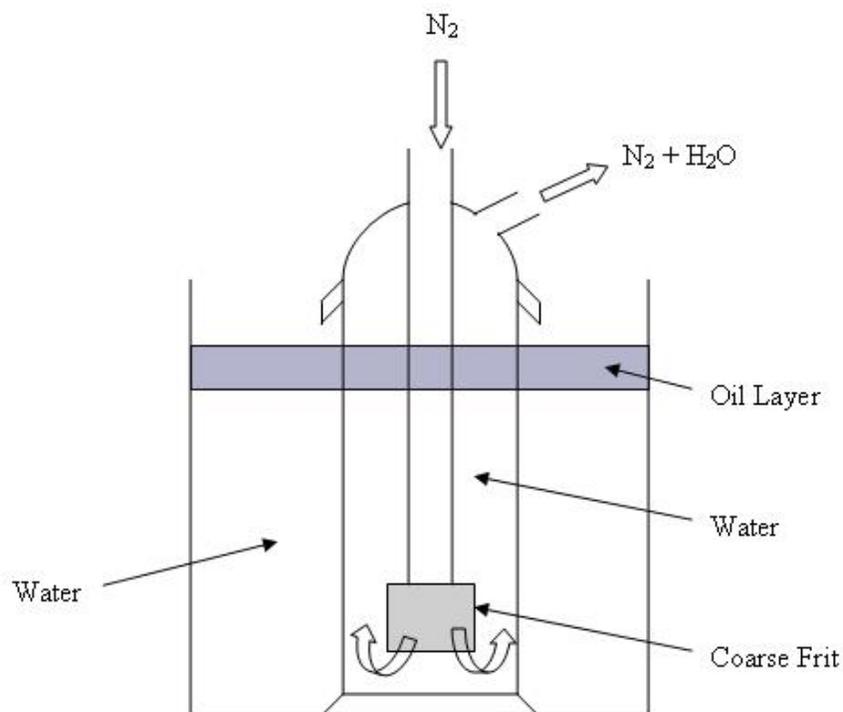


Figure 3.3 Arrangement for moisture generation

Nitrogen stream containing moisture was then mixed with other gases to simulate complete PRB coal flue gas. The simulated flue gas then proceeded to the reactor which was placed inside the furnace to maintain constant temperature.

3.4.2 Furnace and Reactor section

The reactor used in all the experiment to contact simulated flue gas with the sorbent was made of quartz glass and was 55cm long with 22mm inner diameter. A coarse frit was used to support the sorbent and also to prevent sorbent from leaking during experimental runs. Figure 3.4 illustrates the reactor and its cap used during experiments.

The reactor was placed inside a clam-shell electric furnace (Lindeberg, New Columbia, PA). The temperature of the furnace was controlled by a temperature controller (Eurothem, Reston, VA) with digital display/control panel. The temperature of the reactor was maintained at 140 °C unless stated otherwise.

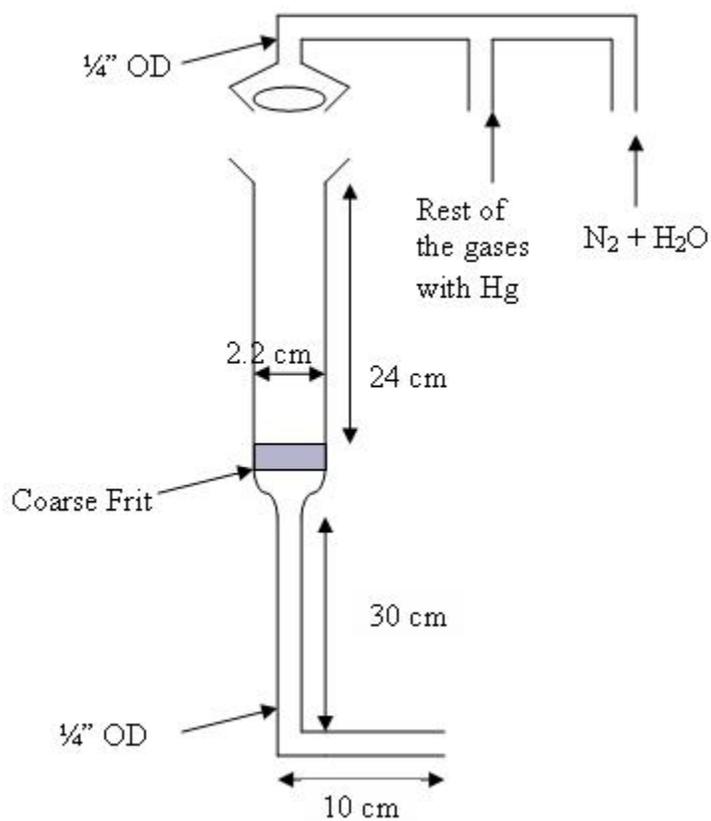


Figure 3.4 Reactor and cap used during the experiments

3.4.3 Mercury conversion section

This section was used to facilitate the analyses of total and elemental mercury concentration in the flue gas. It also aided in removing acid gases (CO₂, NO, NO₂ and HCl) from the flue gas. The setup consisted of three main parts, namely

- a. Heating box
- b. Impingers
- c. Chillers/condensers

3.4.3.1 Heating Box

The main purpose of the heating box was to maintain the incoming flue gas at elevated temperature and prevent condensation in the lines. The incoming flue gas was divided in two equal parts of 500mL/min and the temperature of both parts was maintained at 180 °C.

Teflon tubing was used to divide the incoming flue gas into two equal parts. An exhaust valve was also maintained to release the gas out of the system in the case of emergency or for maintenance. Needle valves were used to split the incoming 1L/min flue gas. These valves were adjusted to get approximately the same flow through both total and elemental sides that were sent to different impingers.

Figure 3.5 shows the schematic diagram of the tubings inside the heating box.

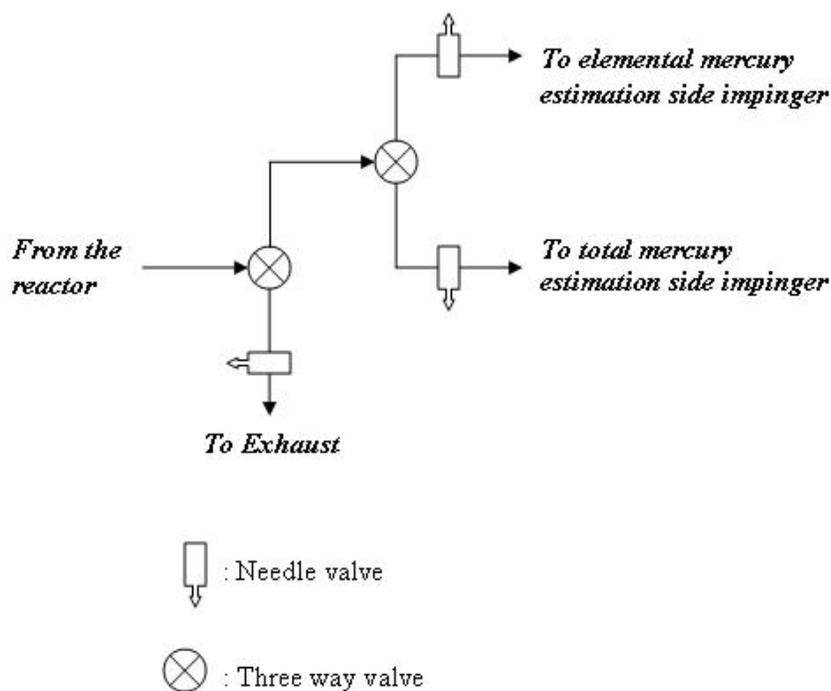


Figure 3.5 Schematic diagram of tubing inside the heating box

3.4.3.2 Impingers

Two impingers were used to facilitate the measurement of total and elemental mercury. An impinger containing 20% NaOH and 2% SnCl₂ solution was used for total mercury measurement. The function of NaOH was to remove all acid gases whereas SnCl₂ was used to reduce all mercury into elemental form.

An impinger containing 20% NaOH and 10% KCl was used for elemental mercury measurement. NaOH in this impinger also served to remove all acid gases, however KCl in the solution was used as a chelating agent to form complex compound with oxidized mercury and remove it from the gas phase. Thus, only elemental mercury was present in the gas coming out of this impinger. Figure 3.6 shows the schematic diagram of an impinger.

The difference between total and elemental mercury gave the concentration of oxidized mercury in the flue gas.

The solutions in impingers were continuously replenished by a peristaltic pump which was pumping fresh solution to the impingers. The same pump was used to drain the solution from the chillers/condensers.

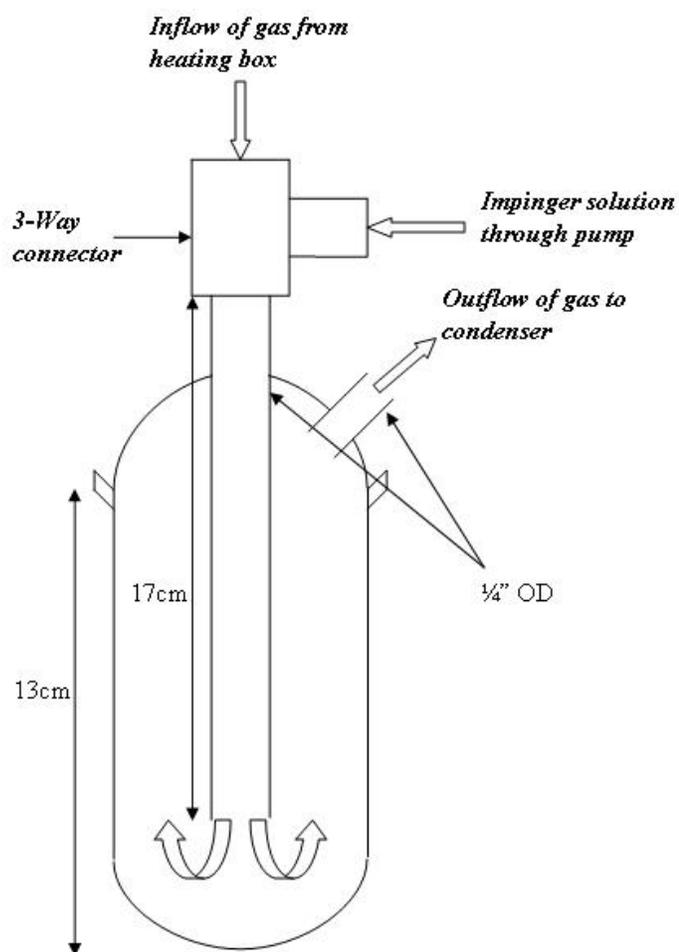


Figure 3.6 Impinger

3.4.3.3 Chiller or condensers

The main function of condensers/chillers was to remove moisture from the flue gas before it enters into the atomic fluorescence unit. They also served to collect the carry over solution, from impingers, which was finally drained out by peristaltic pump. Two separate chillers were maintained; one each for elemental and total mercury measurement sides. Chillers were maintained at 4 °C. Figure 3.7 shows the chiller used in the setup.

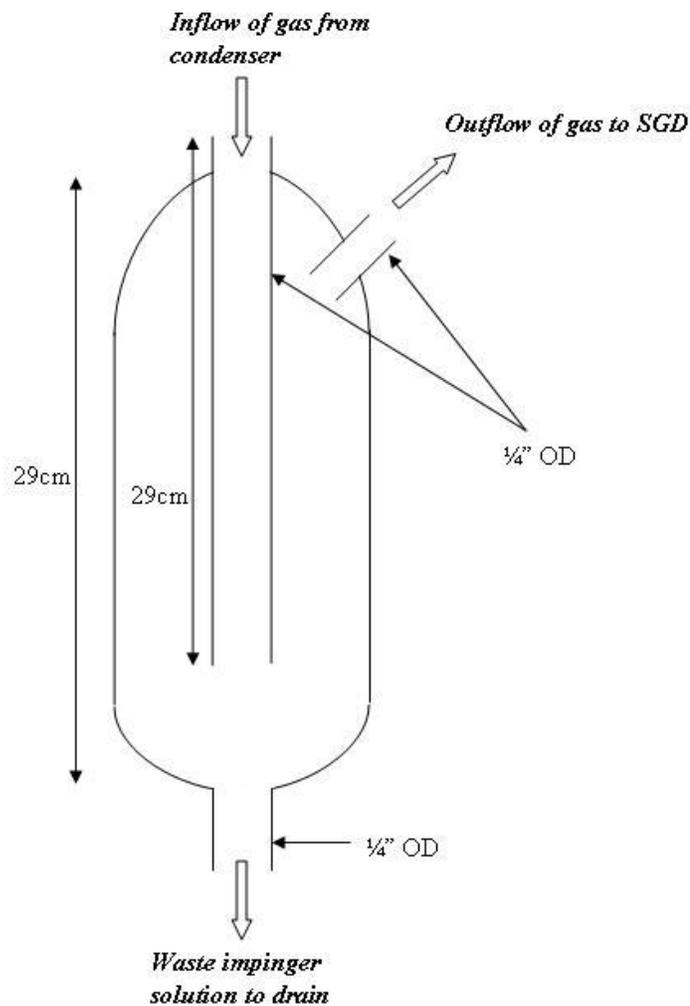


Figure 3.7 Chiller or condenser

3.4.4 Mercury analysis section

An atomic fluorescence unit known as Sir Galahad II (PS Analytical, Orpington, Kent, UK) was used to measure the concentration of elemental mercury in the flue gas. Working of the unit is explained in the sections below.

3.4.4.1 Operation

The Sir Galahad instrument contains a gold coated sand trap, which is used to adsorb elemental mercury from the flue gas. The instrument has four cycles:

- a. **Flushing:** At the start of the measurement, gold coated sand trap is flushed with argon gas which was used as flushing and carrier gas. The gas was maintained at 35 psi and at a flow rate of 14L/min. The purpose of flushing cycle was to remove any mercury left over from previous measurement cycles. Flushing cycle also cleaned the ambience around the gold trap of any contamination. A valve before the trap turns on automatically so that argon gas can enter.
- b. **Adsorption:** Adsorption cycle follows the flushing cycle. In this cycle, flue gas carrying mercury was passed over the gold coated sand trap, which adsorbed elemental mercury from the gas. The flow rate of the influent gas was set at 200mL/min and the time during which the influent gas was passed over the trap was set as 1min.
- c. **Heating:** In the heating cycle which followed after adsorption cycle, the flow of flue gas was stopped and the gold coated sand trap was heated to 500 °C to desorb elemental mercury collected on the trap. The desorbed mercury was then carried by argon gas to UV chamber where mercury atoms were excited by a UV light of 253.7nm wavelength. The excited mercury atoms fluoresce at same wavelength and the intensity of emitted

light was measured by a photodiode. The mass of elemental mercury was determined using the calibration curve and it was divided by the known volume of the influent gas sampled during the adsorption to calculate the concentration of mercury in $\mu\text{g}/\text{m}^3$.

- d. Cooling:** Cooling was done to bring down the trap to room temperature and prepare it for next round of sampling. The cooling could be carried out by either N_2 or air. However, in this study air at 35 psi was used as the cooling gas.

3.4.4.2 Calibration of the instrument

Calibration of the instrument was done by injecting known volumes of elemental mercury vapor at a known temperature. Calibration software calculates the total mass of elemental mercury injected based on the temperature and volume of the sample. A calibration vessel (Arizona Instrument LLC, Tempe AZ) was used as the source of elemental mercury vapor at a precisely monitored temperature. A typical calibration curve of the instrument is shown in Figure 3.8

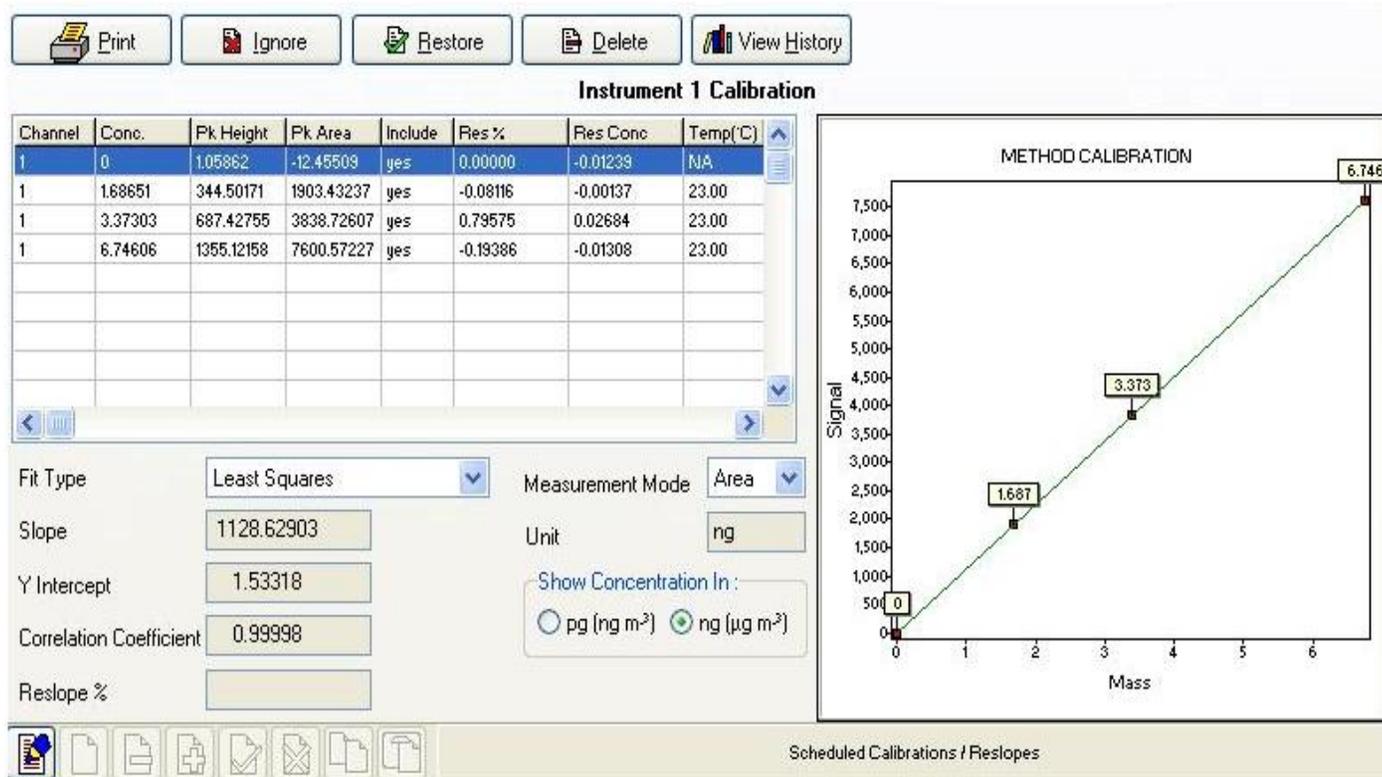


Figure 3.8 Calibration curve of the atomic fluorescence unit

A solenoid valve was used before the Sir Galahad instrument to send gas either from elemental side or total side to the instrument. In other words, elemental mercury sampling was done when the solenoid valve was off and total mercury sampling was done when solenoid valve was on.

The schematic diagram of the complete laboratory setup is shown in the Figure 3.9.

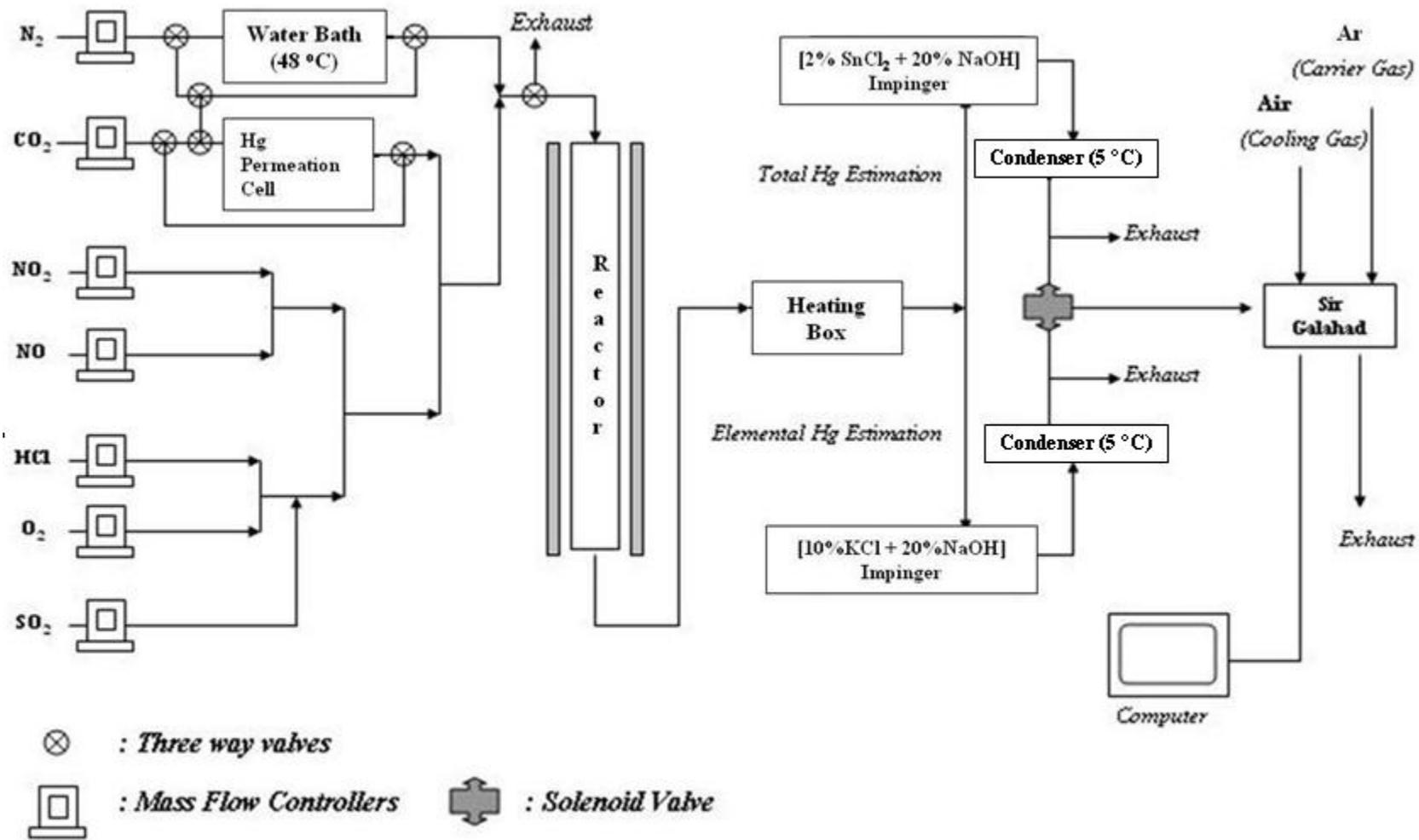


Figure 3.9 Schematic diagram of laboratory setup

3.5 EXPERIMENTAL PROCEDURE

Before the start of any experiment, background mercury readings were observed by sending the flue gas through the experimental setup to verify that stable readings for total and elemental mercury were obtained. It was also important to verify that elemental and total mercury concentrations in the flue gas were identical.

For all the experiments, 40mg of sorbents was mixed with 1g of 150-212 μm size glass beads (Sigma Aldrich, St. Louis, MO). To remove any contamination from the beads, they were washed with aqua-regia and deionized water, and then dried in a furnace at 500 $^{\circ}\text{C}$. Sorbents were mixed with the beads to provide sufficient sorbent bed depth in the reactor. The mix was placed in the reactor on top of 3g of glass beads, which were used to protect sorbent from escaping through the coarse frit in the reactor.

Experiments were conducted in four major phases:

1. Adsorption
2. Flushing
3. Temperature programmed desorption (TPD)
4. Re-adsorption

3.5.1 Adsorption

Adsorption phase was started by sending 1L/min of coal flue gas through the sorbent mix, which was maintained at 140 $^{\circ}\text{C}$. During this phase, mercury concentration in the flue gas

was maintained at 15-20 $\mu\text{g}/\text{m}^3$. Adsorption phase was carried out until 100% breakthrough of mercury was achieved. After 100% breakthrough, experiment was either stopped or proceeded to the flushing phase.

3.5.2 Flushing

In the flushing phase, spent sorbent was flushed with 1L/min of N_2 (no mercury was present in the N_2 gas stream). Temperature of the sorbent was still maintained at 140 °C. Flushing was done to remove all physisorbed mercury from the surface of the spent sorbent. This phase was conducted till sufficiently low concentration (below $2\mu\text{g}/\text{m}^3$) of mercury was observed in the effluent.

3.5.3 Temperature programmed desorption

This phase was initiated, after the flushing phase, by using 1L/min of N_2 . Temperature of the furnace was increased from 140 °C to 350 °C at a rate of 1 °C /min. During this desorption of the chemisorbed mercury was monitored as a function of temperature.

3.5.4 Re-adsorption

After temperature programmed desorption was terminated, the furnace was cooled down to 140 °C and the sorbent was again subjected to initial gas matrix used in the adsorption phase. This phase was also carried out until 100% mercury breakthrough was achieved. This phase was

done to estimate the adsorption capacity of the spent sorbent following the thermal regeneration step as simulated by the temperature programmed desorption.

3.6 TROUBLESHOOTING

During the course of this study, many problems with experimental system were observed. Problems were expected to happen as the system was pretty complex and had many supply lines, valves etc. This section of the document is included to assist/aid in troubleshooting the system. Some of the major problems that were encountered and how they were resolved are listed below.

3.6.1 Cleaning of the valves

The flue gas preparation involves many three-way and two-way valves to direct the constituent gases to different paths. These valves can pose a risk of becoming contaminated. Thus, it is important to regularly clean the valves with dilute HCl solution.

3.6.2 Cleaning of the calibration port

The calibration port of the Sir Galahad instrument contains a small rubber stopper which allows one way entry of known sample of elemental mercury. This stopper prevents gas from leaking out of the instrument. The stopper gets contaminated by continuous use and thus needs to be replaced at least once a month.

3.6.3 Use of proper clean syringe during the calibration

Syringe used to draw known volume of gas phase elemental mercury from calibration vessel gets clogged very often. Because of the clogging, it can't aspirate desired amount of gas, which could lead to faulty calibration. It is advisable to clean or change the syringe every other month.

3.6.4 Regular inspection of Tygon tubing

Tygon tubing is used to transport gases to the reactor and also from the impingers to the Sir Galahad. Over the time, tubing carrying gases get some deposition of brown color and needs to be replaced. Tubing after impingers, especially tubing for total mercury estimation side, gets high amount of white precipitate after consistent use. These tubings should be replaced as white precipitation can enter into the Sir Galahad and can contaminate the gold sand trap.

3.6.5 Clogging of impinger

Clogging of impingers is a serious problem which should be avoided at all cost. A clogged impinger can cause the solution in the impinger to get into the tubings and finally into the Sir Galahad instrument. Once solution enters into the instrument, it can contaminate valves, gold trap and tubings inside the instrument. To avoid the clogging, consistent and equal flow of gases and solutions should be maintained throughout the experiment. Also, draining of solutions from chiller needs to be ensured continuously.

4.0 RESULTS AND DISCUSSION

The glass beads used as base material in all experiments were washed with aqua-regia and dried in furnace at 500 °C. Experimental runs with dried glass beads and 1L/min N₂ or PRB coal flue gas confirmed no adsorption or oxidation of mercury by the beads. All experimental runs used 40mg of as-received activated carbon mixed with 1g of glass beads. The sorbent was placed on top of 3g of glass beads. Experiments were performed at 140 °C unless stated otherwise and inlet mercury concentration during the experiments varied from 15.5–20.5 µg/m³.

A run with FGD sorbent and 1L/min of N₂ was performed to verify the performance of the experimental setup. Breakthrough data, shown in Figure 4.1, reveal that FGD has very little mercury uptake capacity under 1L/min of N₂. Also, no oxidation of mercury was observed. The results obtained are in accordance with the results reported elsewhere in literature⁽¹⁶⁾.

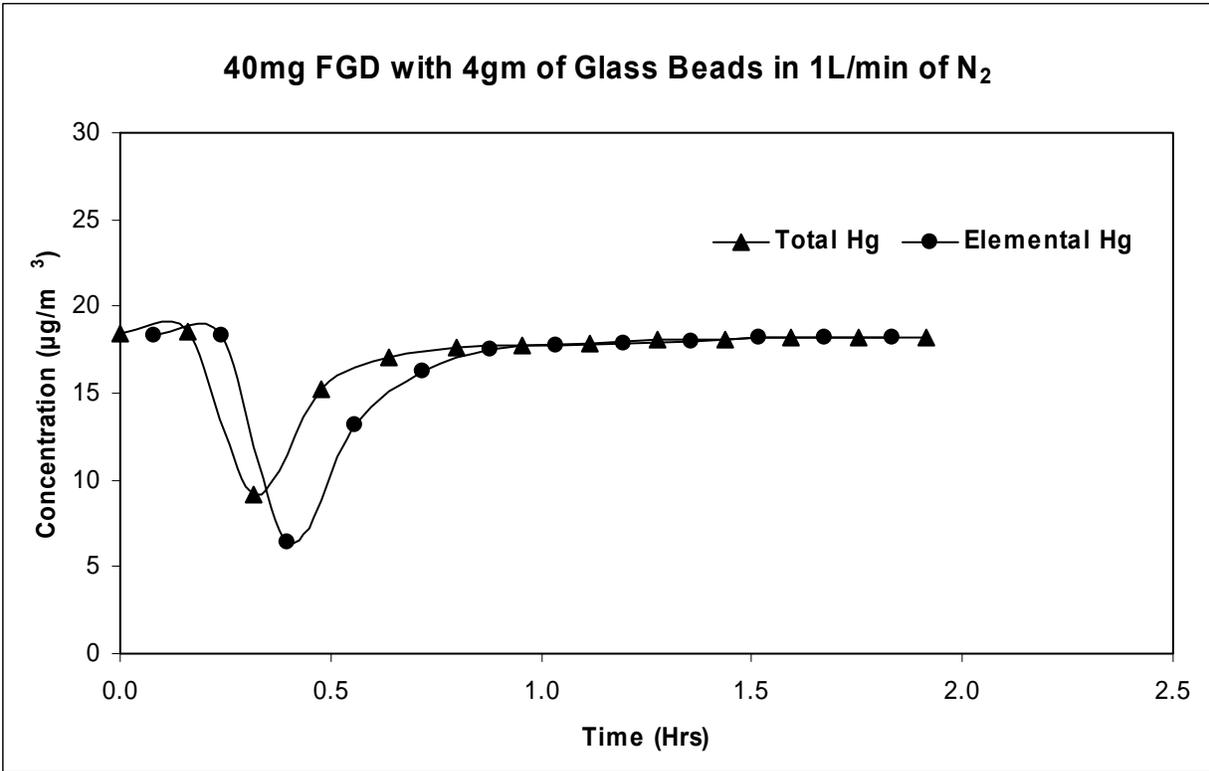


Figure 4.1 Impact of N_2 : A run with 40mg FGD sorbent with 1g glass beads in 1L/min N_2 at 140 °C

An experimental run with FGD sorbent and 1L/min of simulated PRB coal flue gas without moisture is shown in Figure 4.2. The run was performed for all the phases i.e. adsorption, flushing, TPD and readsorption. The mass balance on the mercury was performed in this experiment. Amount of mercury adsorbed by the FGD sorbent during the adsorption phase was 12.790 μg , whereas the masses of mercury released during flushing and TPD phase were 1.725 μg and 4.05 μg , respectively. Flushing and TPD experiments did not recover all the mercury adsorbed on this sorbent since the TPD experiment was not conducted long enough. The regenerated FGD sorbent (during TPD phase) adsorbed 10.845 μg of mercury during the readsorption phase.

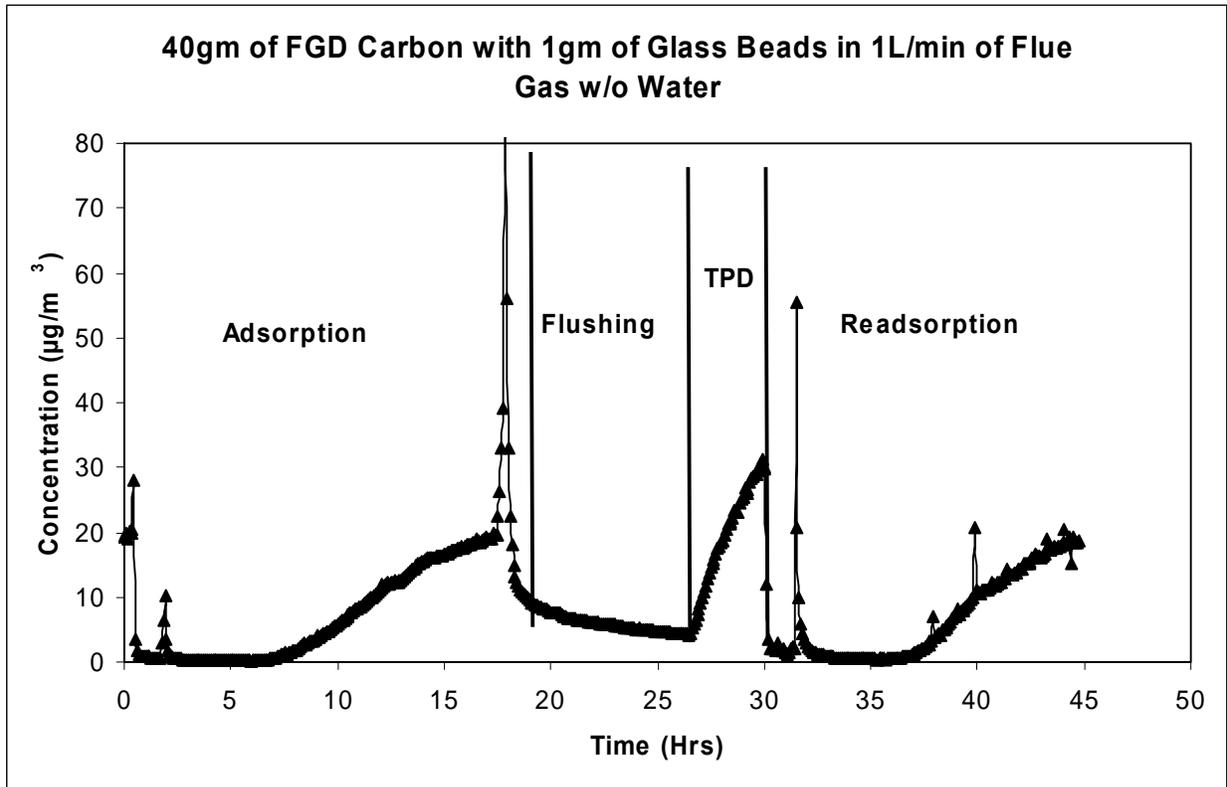


Figure 4.2 A run with 40mg FGD sorbent with 1g glass Beads in 1L/min PRB coal flue gas without water at 140 °C

Another experiment with 1L/min PRB coal flue gas without moisture was performed with 40mg Corning sorbent. Results for all the four phases are shown in Figure 4.3. The mass balance calculation revealed that 16.780µg of mercury was adsorbed in the adsorption phase. However, only 0.114µg and 6.926µg of mercury was released during the flushing and readsorption phase, respectively. The mass of mercury released was only 42% of the mass of mercury adsorbed because the TPD run was not conducted long enough. The regenerated Corning sorbent adsorbed 8.679µg of mercury during the readsorption phase.

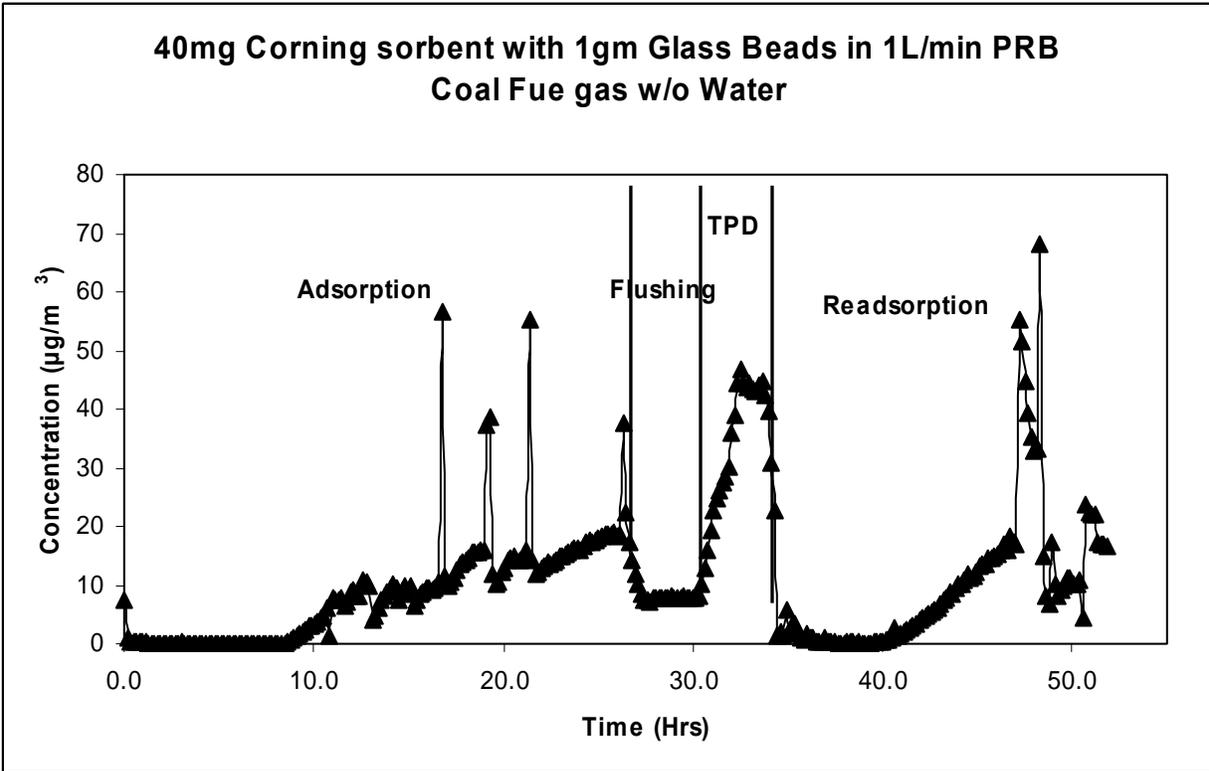


Figure 4.3 A run with 40mg Corning sorbent with 1g glass Beads in 1L/min PRB coal flue gas without water at 140 °C

4.1 EXPERIMENT WITH SIMULATED PRB COAL FLUE GAS

An experimental run was performed with FGD sorbent under 1 L/min of simulated PRB coal flue gas (shown in Table 3.1). One of the goals of the test was to reconfirm the consistency of the experimental setup when simulated PRB coal flue gas was used. The results obtained are shown in Figure 4.4. Mercury uptake capacity of FGD sorbent under PRB coal flue gas was comparable to the results reported by Miller *et al.*⁽¹⁶⁾.

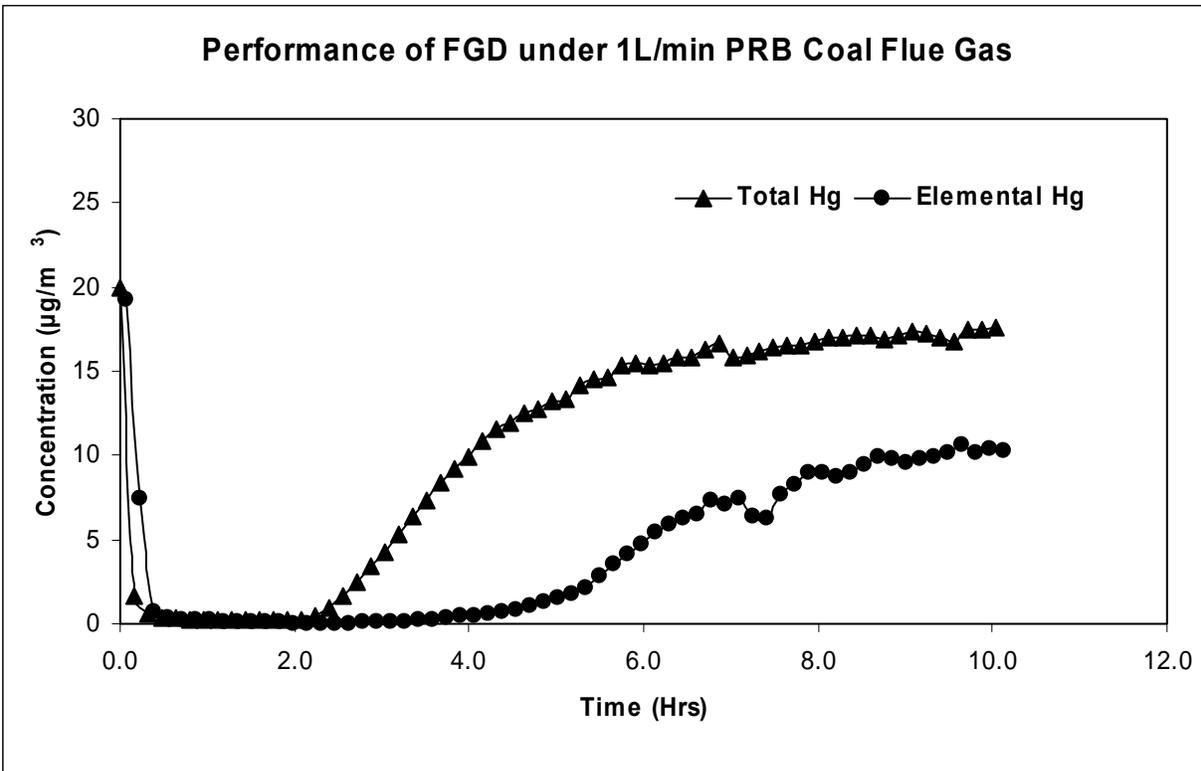


Figure 4.4 Impact of PRB coal flue gas on FGD sorbent: 40mg of FGD sorbent with 1g of glass beads in 1L/min of PRB coal flue gas at 140 °C

The data shown in Figure 4.4 reveal that the presence of FGD sorbent led to almost 50% oxidation of mercury in the effluent stream. However, no oxidation of mercury was observed (in the absence of activated carbon sorbent) when only 3g of glass beads were present in the reactor. This result emphasizes that the activated carbon surface catalyzes mercury oxidation even in the flue gas representative of low chlorine and low sulfur containing coal.

Another test under identical flue gas conditions was performed with the Corning sorbent. The results shown in Figure 4.5 demonstrate almost 50% oxidation of mercury with this sorbent as well. However, Corning sorbent showed better mercury uptake capacity than the FGD sorbent, which due to the presence of chelating and oxidizing agent on the surface of the Corning sorbent.

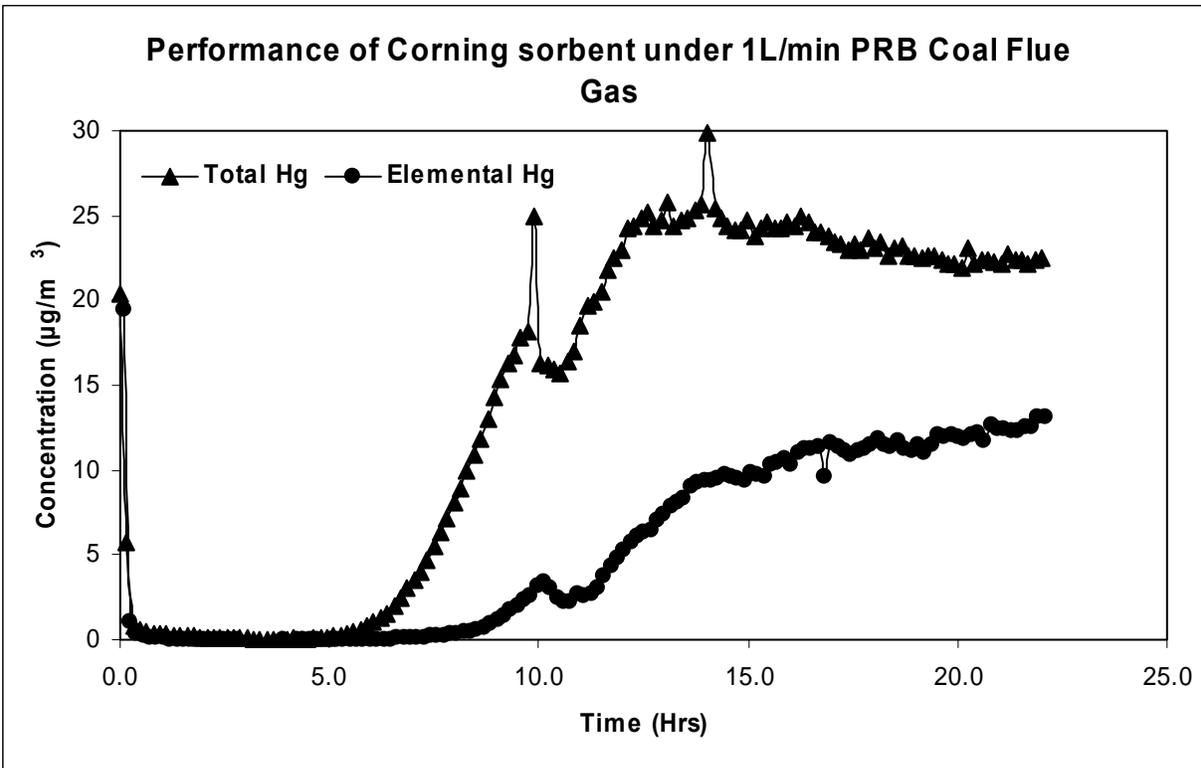


Figure 4.5 Impact of PRB coal flue gas on the Corning sorbent: 40mg of Corning sorbent with 1g of glass beads in 1L/min of PRB coal flue gas at 140 °C

A test with Cabot Black Pearl 460 (representative of carbon black) was performed under complete PRB coal flue gas. In this experiment an instant breakthrough of mercury was observed as shown in Figure 4.6. Moreover, a very low oxidation of mercury was observed as compare to other two sorbents. The difference in the mercury oxidation and uptake capacity can be attributed to different surface areas of Cabot Black Pearl 460 as compared to the other two sorbents. BET analysis of Cabot Black Pearl 460 showed a surface area of 72.5 m²/g, whereas FGD and the Corning sorbent have the surface areas above 700m²/g.

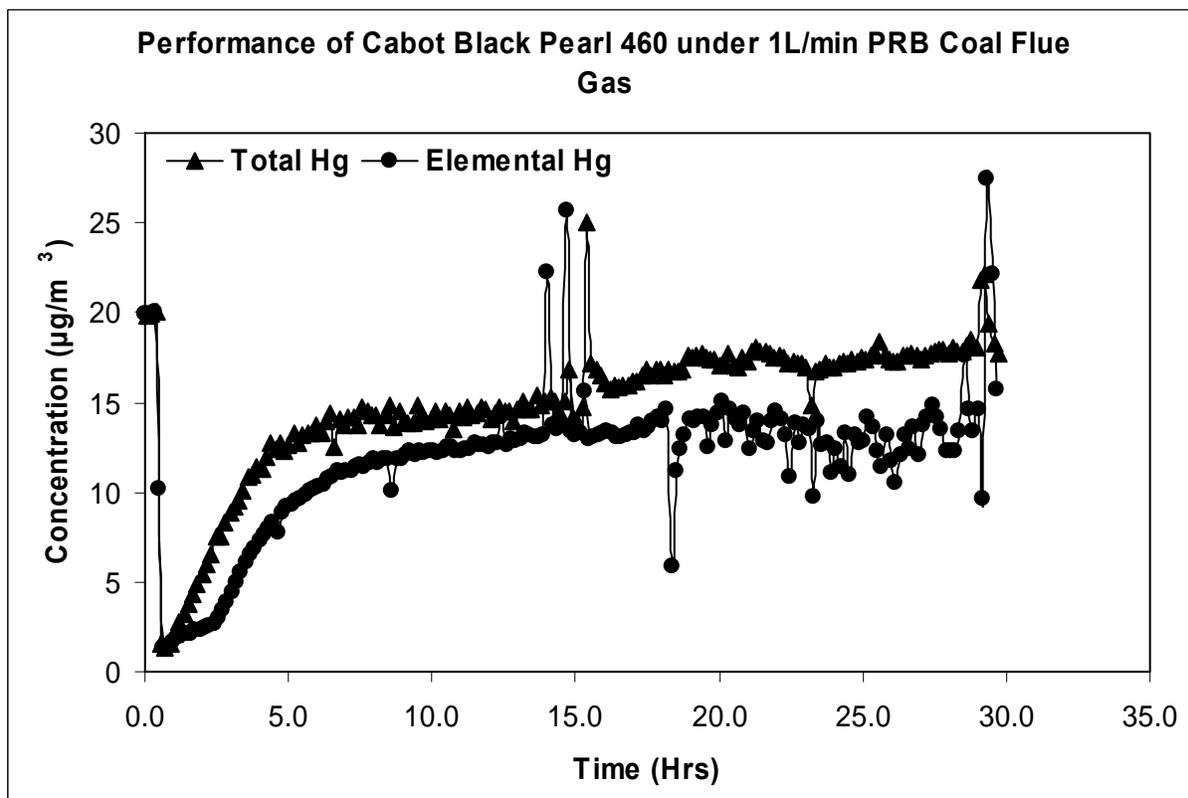


Figure 4.6 Impact of PRB coal flue gas on Cabot Black Pearl 460 (carbon black): 40mg of Cabot Black Pearl 460 with 1g of glass beads in 1L/min of PRB coal flue gas at 140 °C

4.2 IMPACT OF WATER

To study the impact of water on mercury oxidation and on mercury uptake capacity of activated carbon sorbents, water was taken out of the simulated PRB coal flue gas but the flow rate was still maintained at 1L/min. Results obtained for the experimental run performed on FGD sorbent are shown in Figure 4.7.

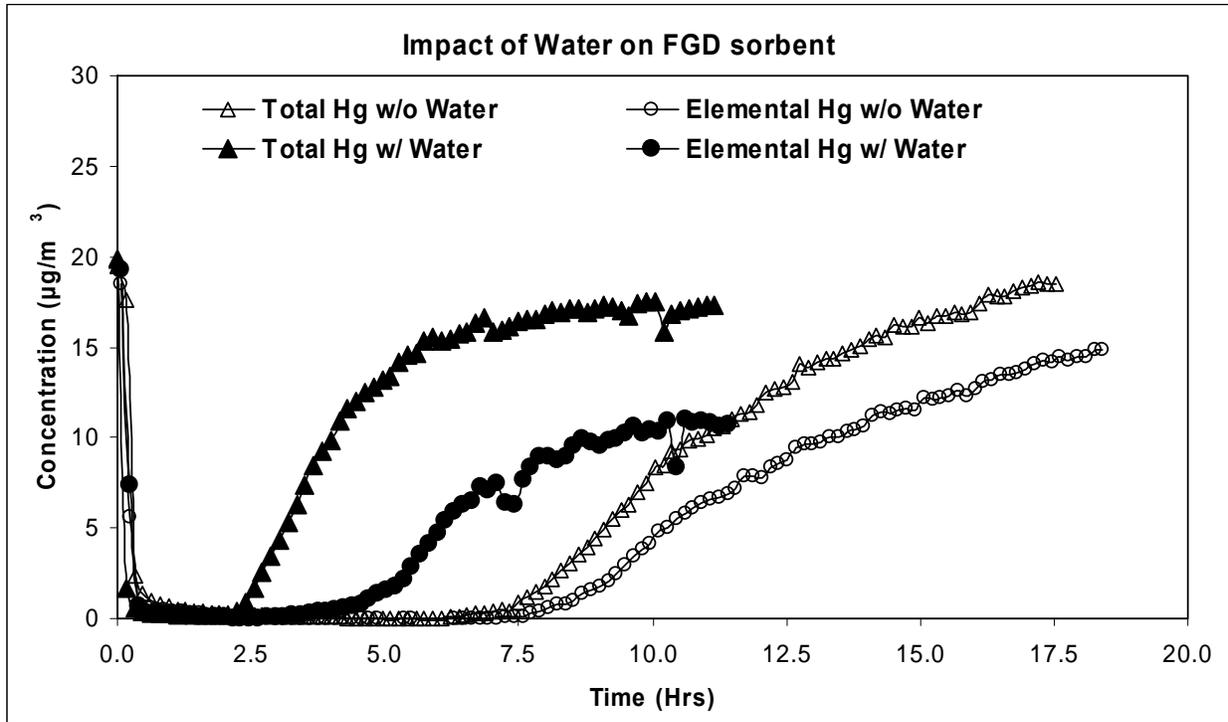


Figure 4.7 Impact of water on FGD sorbent: Experimental runs with 40mg FGD sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without water at 140 °C

It is clear from the above figure that the removal of water from the flue gas led to a more than doubling of mercury uptake capacity of FGD sorbent. Results in the above figure are in contradiction with the result reported by Ghorishi *et al.*⁽²⁷⁾ which found an increase in mercury uptake on adding water to N_2 . On the other hand, Carey *et al.*⁽²⁸⁾ reported decrease in the mercury uptake capacity of activated carbons upon addition of water to the flue gas. This result with FGD sorbent reveals the importance of performing tests under realistic flue gas conditions. Decrease in the adsorption capacity of the FGD sorbent could be due to the condensation of water on the active sites or due to conversion of SO_2 to S(IV) form due to oxidation and hydration in the presence of water, which inhibit the mercury uptake by carbonaceous sorbents.

The absence of water from the flue gas led to a 50% decrease in mercury oxidation by the FGD sorbent. This oxidation result is in contradiction with the results reported by Zhao *et al.*⁽²⁶⁾ who reported inhibitory effect of H₂O on vapor phase mercury oxidation in the presence of NO and SO₂ at high temperatures. Zhao *et al.*⁽²⁶⁾ proposed that on addition of H₂O consumes Cl atoms (the main oxidizing agents) in the vapor phase through the formation of HCl. This decrease in Cl atoms in turn causes a decrease in mercury oxidation. In the results shown above HCl was already present in the gas stream. The contradiction could be because of different phase (i.e. homogeneous vs heterogeneous) reactions. This result also highlights the catalytic effect of the FGD sorbent on mercury oxidation in the presence of water.

Another experiment to study the impact of water was performed with the Corning sorbent. Results shown in Figure 4.8 reveal a slight increase in mercury uptake and almost no oxidation of mercury in the absence of water from flue gas.

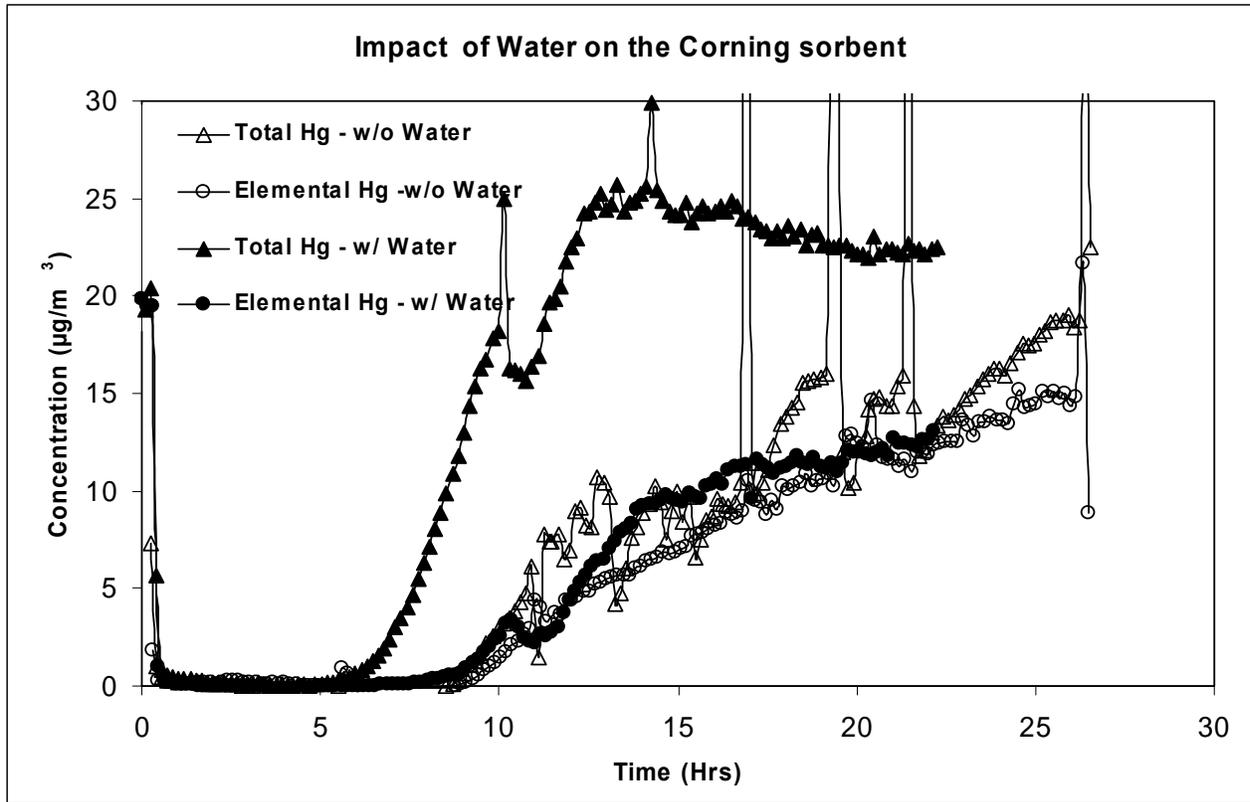


Figure 4.8 Impact of water on the Corning sorbent: Experimental runs with 40mg Corning sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without water at 140 °C

4.3 IMPACT OF SO_2

The impact of SO_2 on mercury uptake capacity and mercury oxidation by FGD sorbent was studied by removing SO_2 from the PRB coal flue gas and replacing it by N_2 to maintain the flow rate at 1L/min. Results shown in Figure 4.9 reveal that no mercury was observed in effluent for 16 hours. To verify the influent mercury readings, reactor was taken offline at different times during the experimental run and it was observed that influent mercury readings were equal to the influent mercury reading at the beginning of the experiment. It is clear that the presence of SO_2 in the flue gas has a very high detrimental impact on mercury uptake by the FGD sorbent.

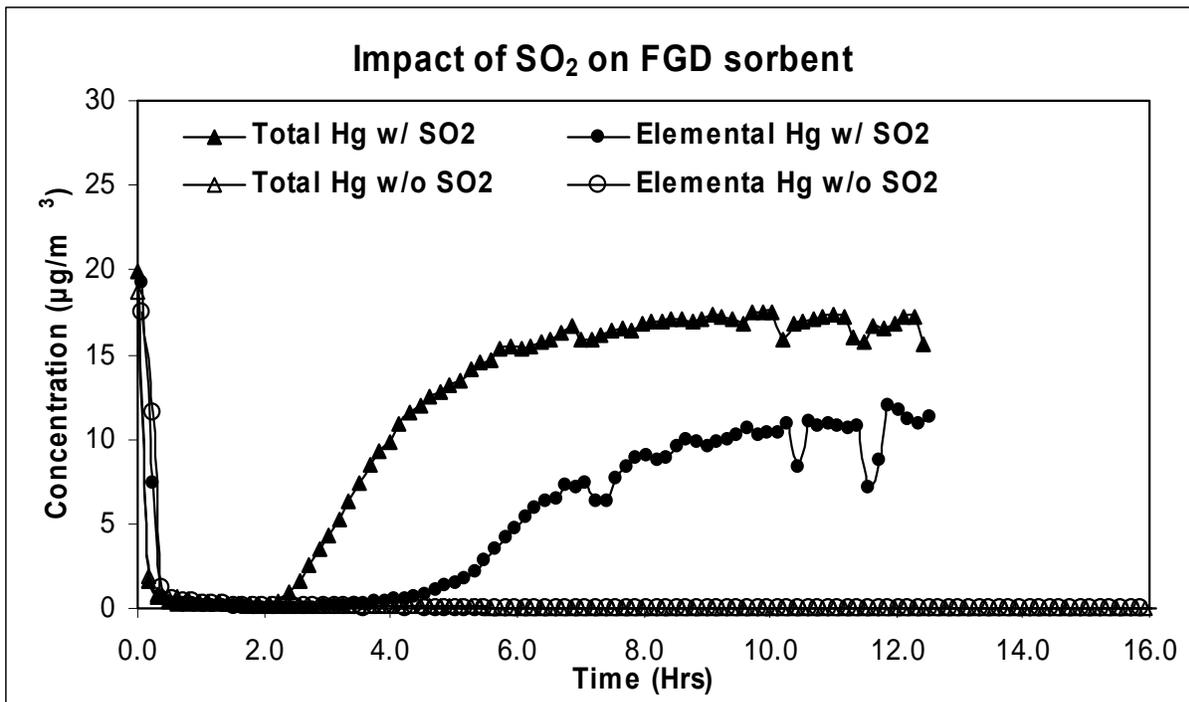


Figure 4.9 Impact of SO_2 on FGD: Experimental runs with 40mg FGD sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without SO_2 at 140 °C

To determine mercury species present on the spent FGD sorbent, temperature program desorption (TPD) experiment was performed on the spent sorbent after 24 hours run (shown in Figure 4.9). Results shown in Figure 4.10 clearly indicate that the mercury present on the surface of the FGD sorbent was mostly in elemental form.

The mass of mercury adsorbed during 24hrs adsorption run (Figure 4.9) was 28.8 μg . On the other hand, the mass of mercury desorbed during TPD run (Figure 4.10) was 17.7 μg . Thus, a complete mass balance closure was not achieved because the TPD experiment was terminated before all of the mercury was desorbed from the surface.

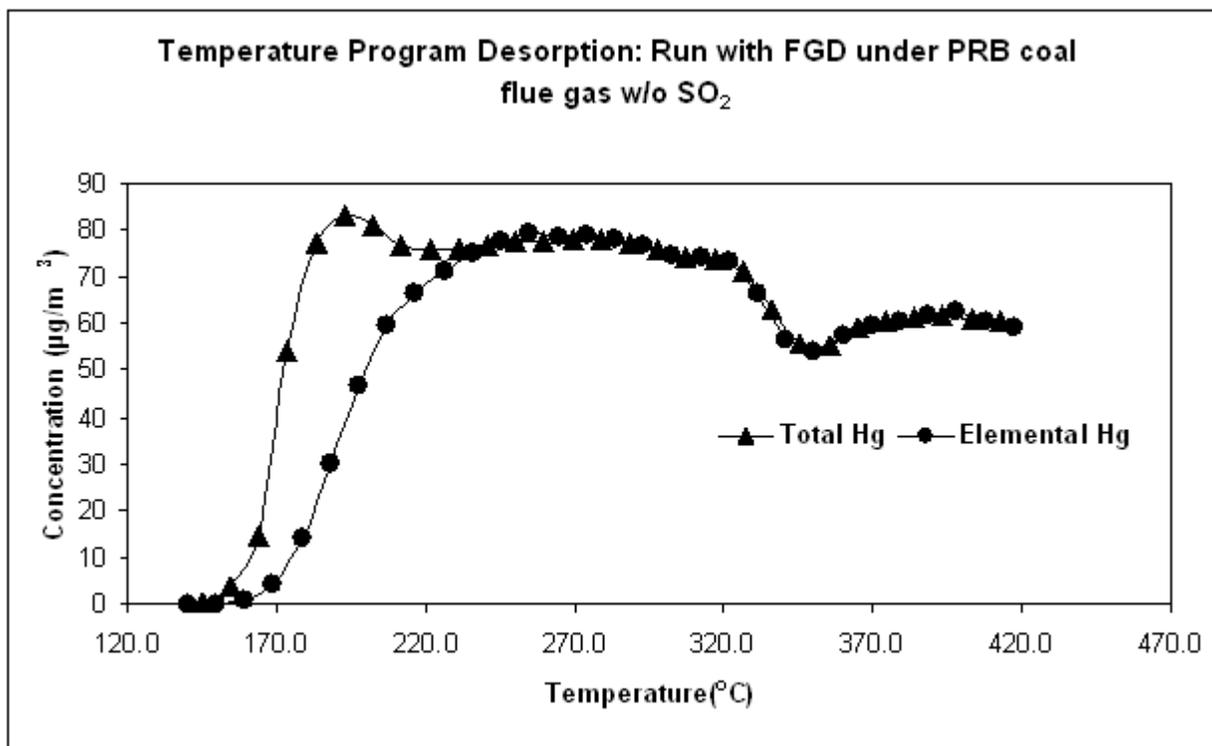


Figure 4.10 Temperature programmed desorption (TPD) run on the spent FGD sorbent subjected to PRB coal flue gas without SO₂

Miller *et al.*⁽¹⁶⁾ and Butz *et al.*⁽¹⁷⁾ reported manifold increase in mercury uptake capacity of activated carbon on removing SO₂ from the flue gas mixture. Miller *et al.*⁽¹⁶⁾ proposed a possible interaction between SO₂ and NO₂ on the surface of the sorbent causing a comparatively earlier breakthrough of mercury from the surface. Olson *et al.*⁽³²⁾ reported progressive accumulation of S(IV) species on the surface of sorbent eventually causing the breakthrough of mercury from the surface. They also proposed a competition between S(IV) and Hg⁰ (and Cl) species for active sites on the surface, which was eventually won by the S(IV) species. The above results confirm that the absence of SO₂ leads to a tremendous mercury uptake capacity improvement implying no competitor against Hg⁰ for the active sites on the surface.

Dunham *et al.*⁽¹⁹⁾ and Olson *et al.*⁽²⁰⁾ proposed that in the absence of SO₂ oxidation of Hg⁰ by NO₂ leads to the formation of Hg(NO₃)₂. However, this was not observed during the TPD run performed on the FGD sorbent which was subjected to flue gas without SO₂. Most of the desorbed mercury during the TPD run was in elemental form.

The Corning sorbent also showed very high mercury uptake capacity in the absence of SO₂ from the flue gas, as can be seen in Figure 4.11. No mercury in the effluent gas was observed for 24 hours.

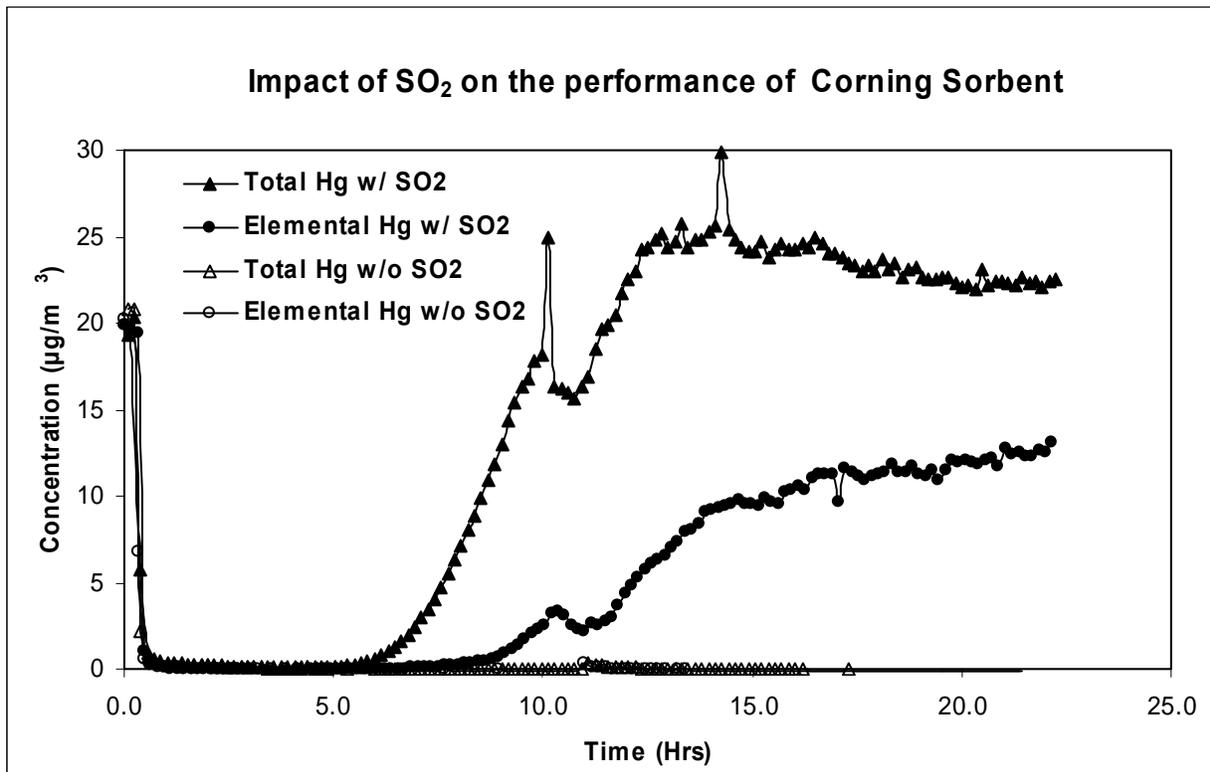


Figure 4.11 Impact of SO₂ on the Corning sorbent: Experimental runs with 40mg Corning sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without SO₂ at 140 °C

4.4 IMPACT OF HCl

Impact of HCl on mercury oxidation and mercury uptake capacity of the FGD sorbent was studied by removing HCl from the PRB coal flue gas and replacing it with N₂. Results shown in Figure 4.12 indicate that the absence of HCl led to an immediate breakthrough of mercury. Miller *et al.*⁽¹⁶⁾ and Carey *et al.*⁽²⁸⁾ reported positive impact of HCl on mercury uptake capacity of activated carbons. A tremendous decrease in mercury uptake capacity was reported on removing HCl from the flue gas.

Olson *et al.*⁽³²⁾ reported an increase in the Cl atom concentration as the breakthrough experiment proceeded. However, at the end of the breakthrough experiment no Cl was observed on the carbon surface. A competition between Cl and S(IV) was reported⁽³²⁾, which was eventually won by the S(IV) species. The disappearance of Cl atoms was correlated with the release of mercury during the breakthrough experiment. Thus, it was concluded that Cl atoms from HCl are facilitating the mercury uptake. Results shown in Figure 4.12 confirm the facilitating effect of HCl on mercury uptake by the FGD sorbent.

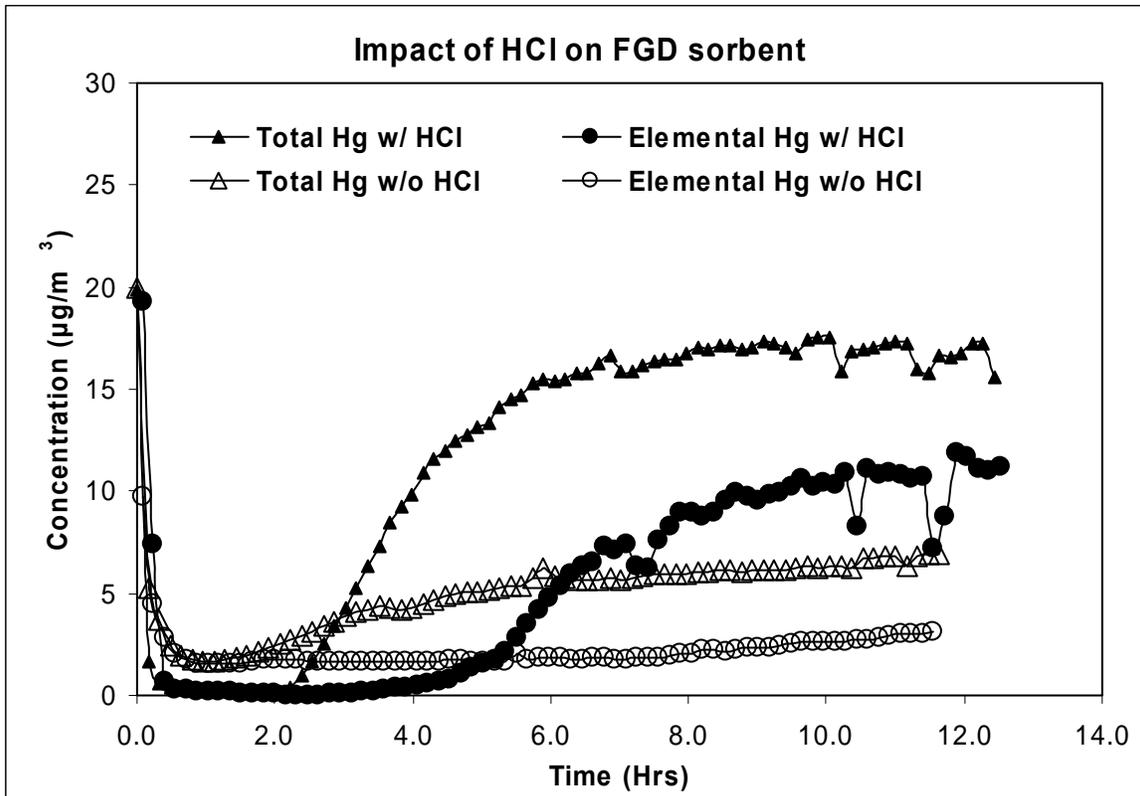


Figure 4.12 Impact of HCl on FGD sorbent: Experimental runs with 40mg FGD sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without HCl at 140 °C

In the absence of HCl from PRB coal flue gas, Corning sorbent also showed a decrease in mercury uptake capacity (Figure 4.13). Almost instant breakthrough of mercury was observed in the absence of HCl from the flue gas. However, Corning sorbent showed better mercury uptake than the FGD sorbent, which could be due to presence of chelating and oxidizing agent present on the surface of the Corning sorbent.

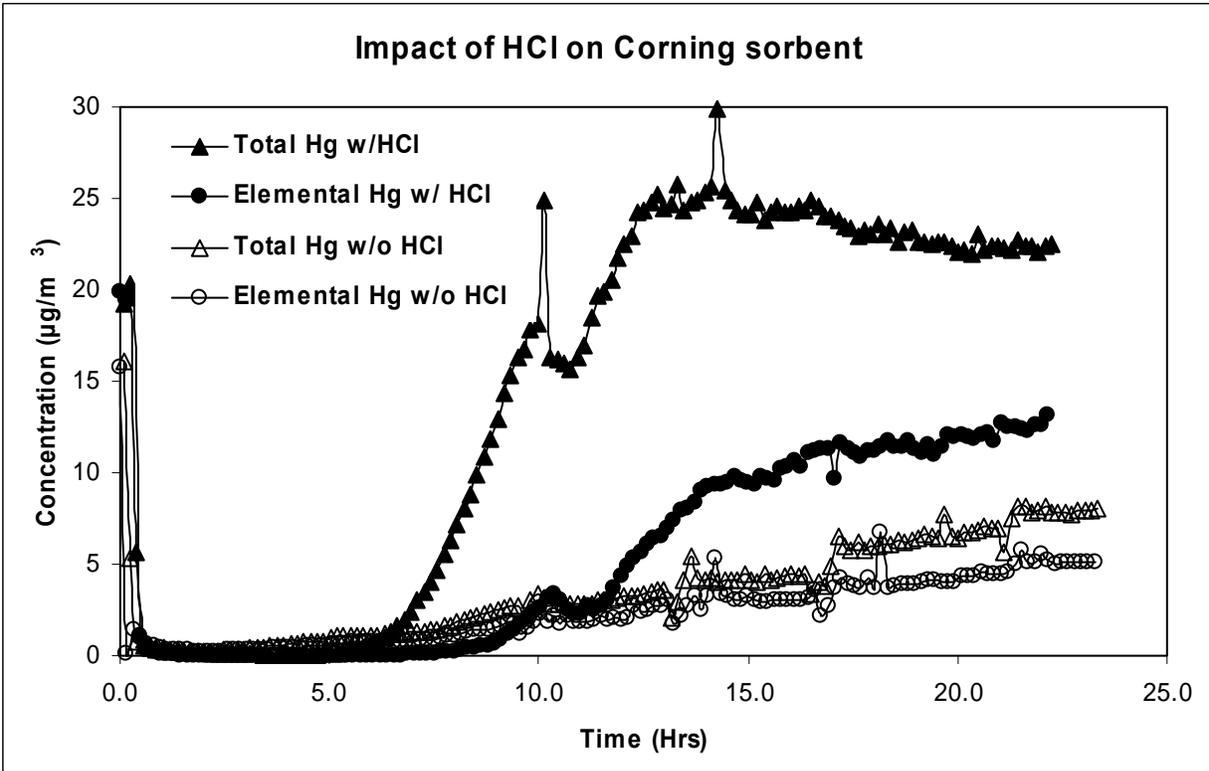


Figure 4.13 Impact of HCl on the Corning sorbent: Experimental runs with 40mg Corning sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without HCl at 140 °C

4.5 IMPACT OF NO

Impact of NO on mercury oxidation and mercury uptake by two sorbents was studied by removing NO from the flue gas and replacing it with N₂. Results obtained for the run with FGD are shown in the Figure 4.14. It is clear that the removal of NO not only led to an increase in mercury uptake capacity but also caused almost complete oxidation of effluent mercury.

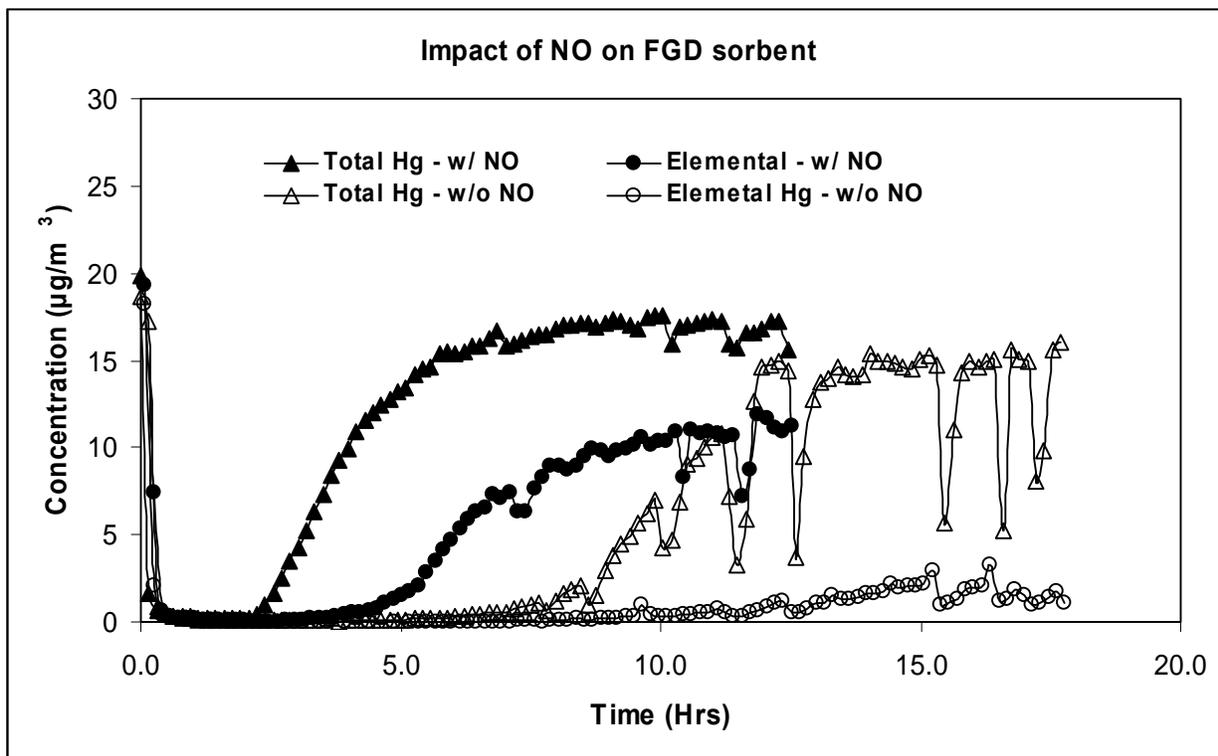


Figure 4.14 Impact of NO on FGD sorbent: Experimental runs with 40mg FGD sorbent with 1gm of glass beads under 1L/min PRB coal flue gas with and without NO at 140 °C

In another experiment, Corning sorbent was used to study the impact of NO. Results shown in Figure 4.15 reveal that the removal of NO from the flue gas led to a decrease in the adsorption capacity as well as a decrease in mercury oxidation. Results obtained with the Corning sorbent are contrary to that obtained with FGD, which could be due to the presence of chelating and oxidizing agent present on the surface of the Corning sorbent.

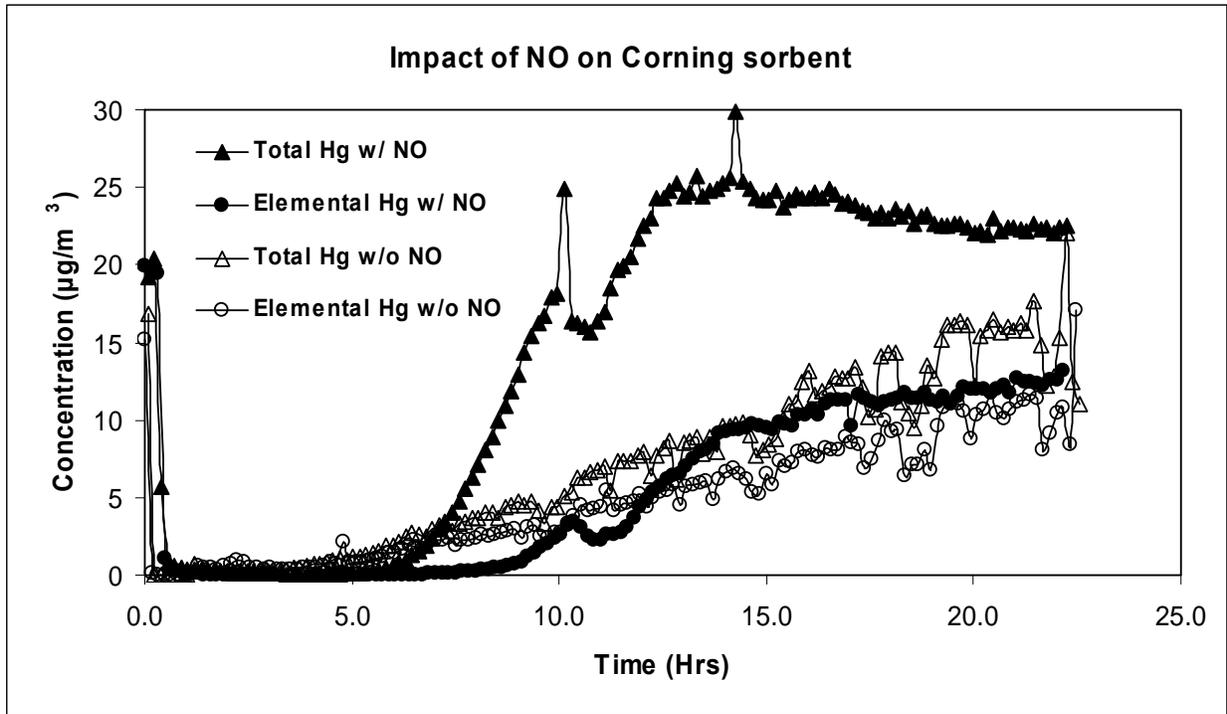


Figure 4.15 Impact of NO on Corning sorbent: Experimental runs with 40mg Corning sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without NO at 140 °C

Miller *et al.*⁽¹⁶⁾ reported an increase in mercury uptake capacity of activated sorbent on adding NO to the flue gas. In a study with different fly ashes, Norton *et al.*⁽²⁵⁾ reported a decrease in the oxidation of mercury upon the addition of NO to the gas stream. Zhao *et al.*⁽²⁶⁾ also reported inhibitory impact of NO on the vapor phase mercury oxidation, though in the presence of water. Mercury oxidation results shown above for FGD sorbent are in accordance with the results reported elsewhere in literature, however the result for the Corning sorbent are in sharp contradiction. FGD and Corning sorbent have almost same physical properties (like surface area, particle size, sulfur and carbon content etc), thus difference between the results could be due to the presence of chelating and oxidizing agent on the surface of the Corning sorbent.

4.6 IMPACT OF NO₂

To study the impact of NO₂ on mercury oxidation and mercury uptake, FGD and Corning sorbents were subjected to simulated PRB coal flue gas without NO₂, which was replaced by N₂ to maintain the flow rate at 1L/min. Results obtained for FGD and Corning sorbents are shown in Figure 4.16 and Figure 4.17, respectively. Removal of NO₂ from PRB coal flue gas led to an increase in mercury uptake by FGD sorbent. However, not a significant impact on mercury oxidation was observed.

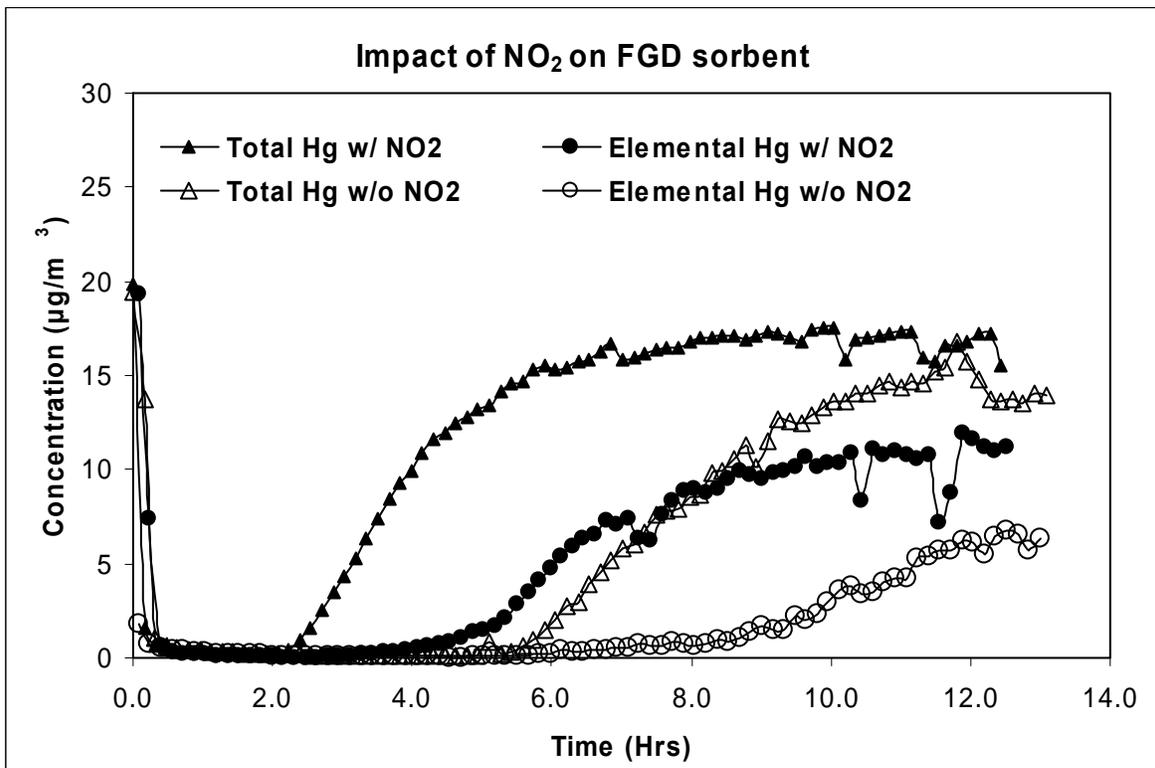


Figure 4.16 Impact of NO₂ on FGD sorbent: Experimental runs with 40mg FGD sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without NO₂ at 140 °C

In the absence of NO₂ from flue gas, a decrease in mercury oxidation and a decrease in mercury uptake capacity of the Corning sorbent were observed (Figure 4.17). The results obtained with Corning sorbent are in contradiction with those obtained for FGD sorbent.

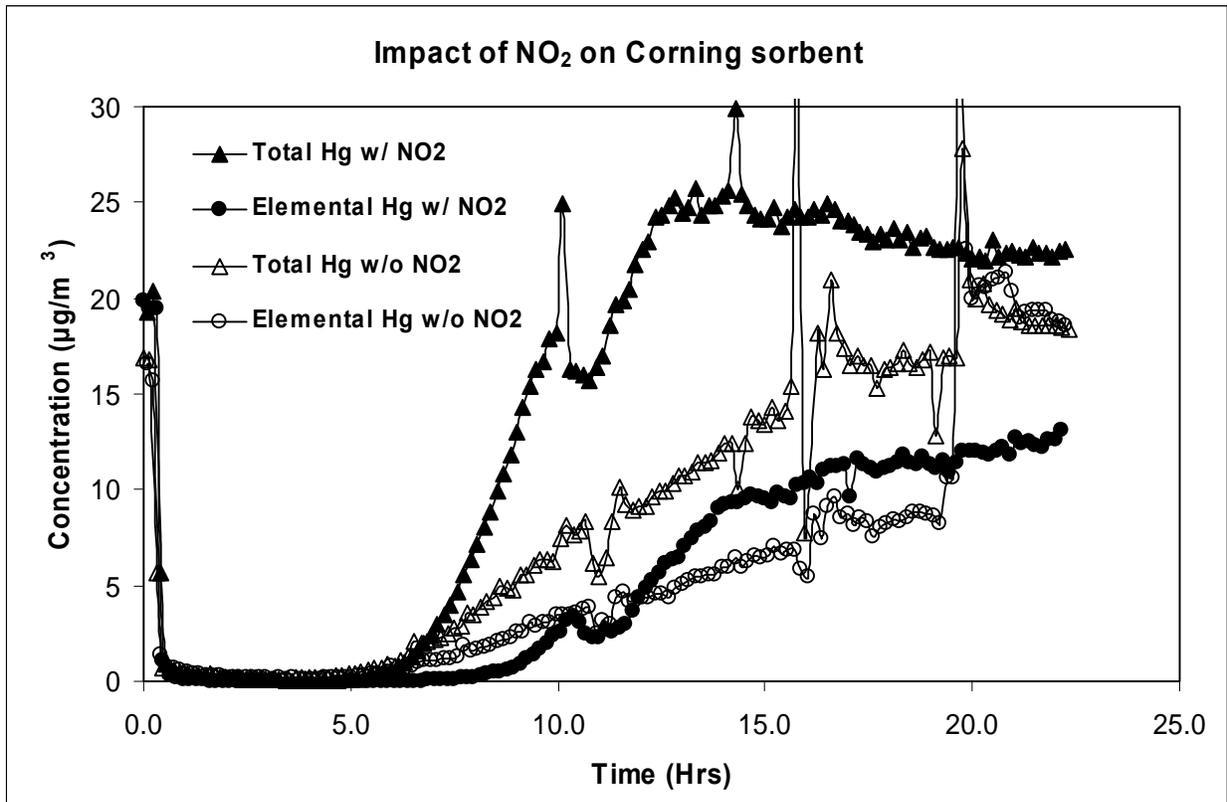


Figure 4.17 Impact of NO₂ on Corning sorbent: Experimental runs with 40mg Corning sorbent with 1g of glass beads under 1L/min PRB coal flue gas with and without NO₂ at 140 °C

Miller *et al.*⁽¹⁶⁾ reported an increase in mercury uptake capacity of activated carbon upon the addition of NO₂ to flue gas. However, in the presence of SO₂, a NO₂-SO₂ interaction was implicated causing faster breakthrough leading to a lower mercury uptake capacity of activated carbon. In the above results, FGD sorbent showed a decrease in mercury uptake in the presence of NO₂, however this was not observed with the Corning sorbent. Difference in results with the

sorbents could be due to the presence of chelating and oxidizing agent on the surface of Corning sorbents.

4.7 IMPACT OF TEMPERATURE

To study the impact of temperature on mercury uptake by carbonaceous sorbents, experiments were conducted at 240 °C under complete PRB coal flue gas. Results obtained with FGD sorbent, shown in Figure 4.18, reveal that an increase in temperature to 240 °C caused an instant breakthrough of mercury and a tremendous decrease in mercury uptake capacity of the FGD sorbent. Apart from drop in the adsorption capacity, almost no oxidation of mercury was observed. Decrease in the adsorption capacity of sorbents and mercury oxidation with an increase in temperature is reported elsewhere in the literature ^(33, 34, 35, 36, 37).

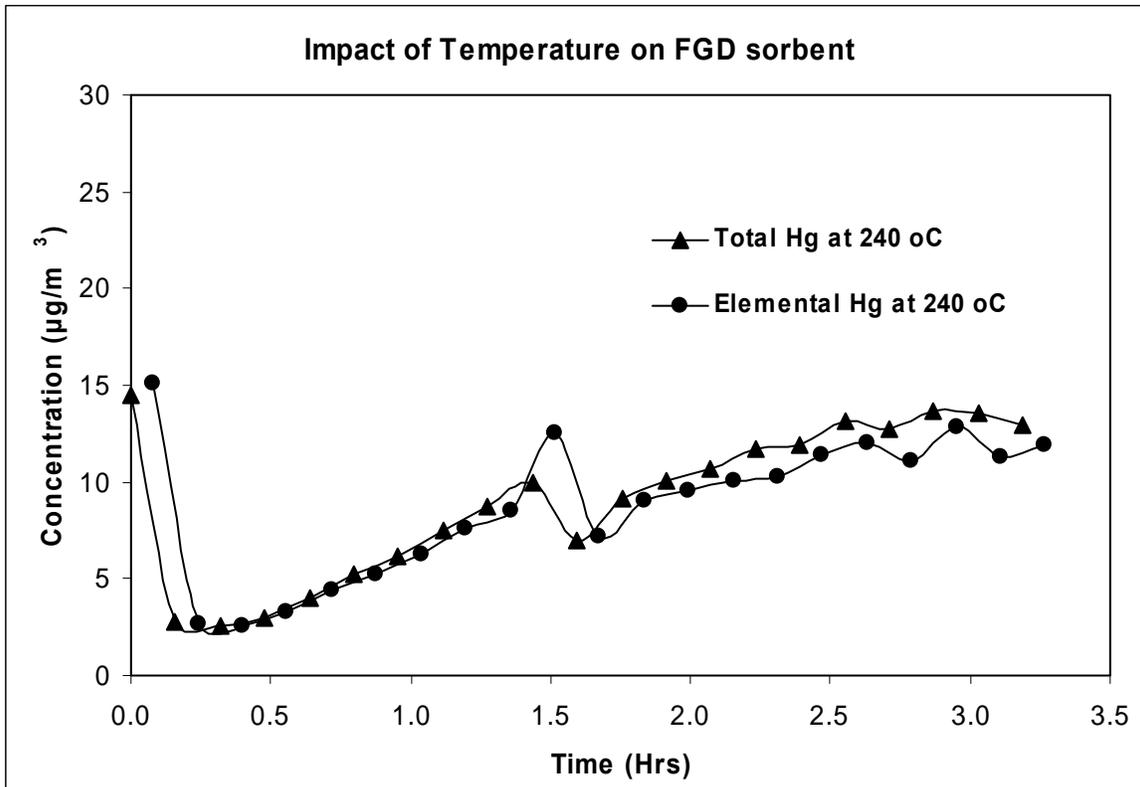


Figure 4.18 Impact of Temperature on FGD sorbent: Experimental run with 40mg FGD with 1gm of glass beads under 1L/min PRB coal flue gas at 240 °C

Results obtained for the impact of increase in bed temperature on Corning sorbent are reported in the Figure 4.19. From the data it is clear that an increase in bed temperature led to a decrease in adsorption capacity of the Corning sorbent. Moreover, no oxidized mercury was observed in the effluent stream.

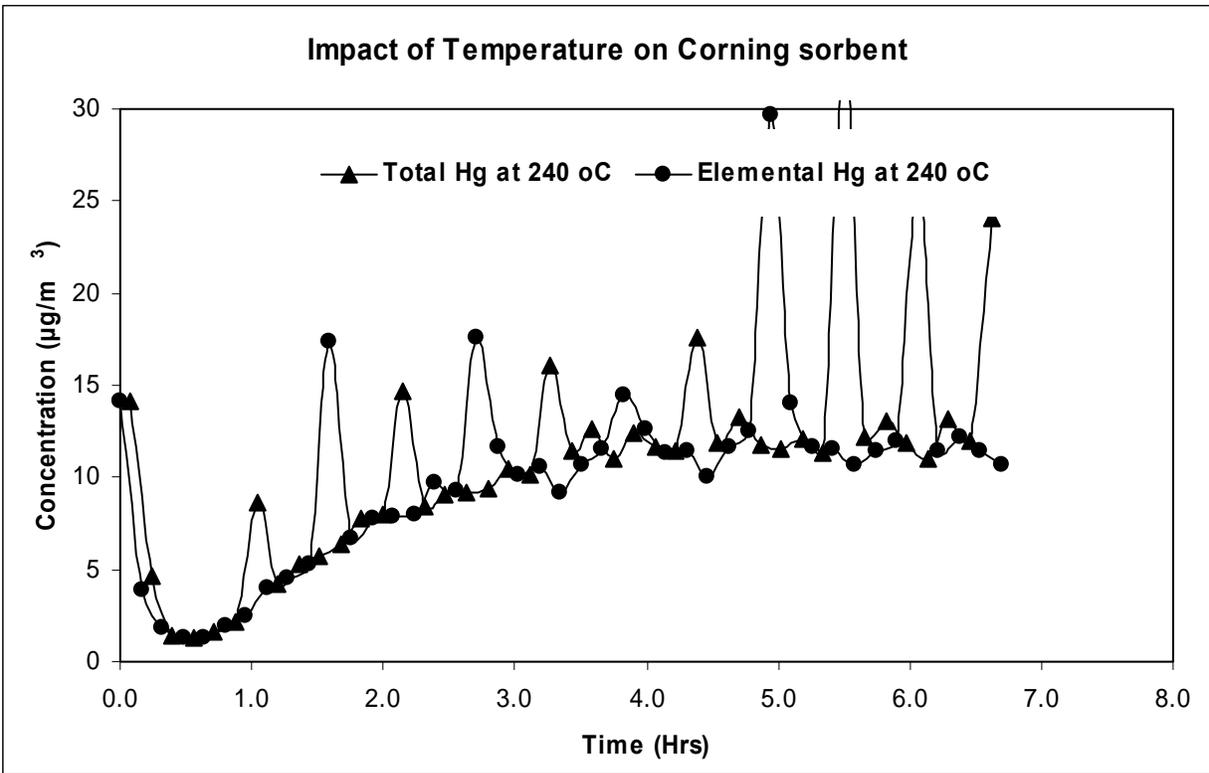


Figure 4.19 Impact of Temperature on Corning sorbent: Experimental run with 40mg Corning sorbent with 1gm of glass beads under 1L/min PRB coal flue gas at 240 °C

4.8 MECHANISTIC MODEL FOR MERCURY UPTAKE AND OXIDATION BY ACTIVATED CARBONS

Laumb *et al.*⁽³¹⁾ and Olson *et al.*⁽³²⁾ studied the surface of sorbents sampled at different times during the breakthrough curve, which were subjected to different flue gases. They reported a competition between Cl and S(IV) species for active sites present on the surface of activated carbon, which was eventually won by S(IV) species. Mercury breakthrough was reported to be in correlation with the concentration of Cl on the surface with the Cl concentration found to be the

lowest at the time of breakthrough. It was also reported that on the surface Cl was present in the chloride form.

Based on the results reported by Laumb *et al.*⁽³¹⁾ and Olson *et al.*⁽³²⁾, and the findings of this study, a simplistic model for mercury uptake and oxidation in the presence of activated carbon surface is developed. Initially HCl present in the flue gas attaches itself to the surface of activated carbon creating active sites for mercury adsorption. The HCl-coated active sites are then used to bind mercury in the flue gas, which stays in the elemental form on the surface. As the experiments proceed, SO₂ gets accumulated on the surface of activated carbon. The presence of O₂ and H₂O facilitates oxidation and hydration of SO₂ producing H₂SO₄ which is less volatile than HCl (which is already present on the surface). Over the course of experiment, H₂SO₄ dislodges HCl from the surface and in turn dislodges mercury bonded to the surface through HCl. During the release of mercury from the surface, a part of it gets oxidized with activated carbon surface acting as a catalyst. The model is represented diagrammatically in Figure 4.20-4.25.

Sulfur dioxide (SO₂) in the flue gas acts as poison causing a decrease in mercury uptake capacity, whereas HCl facilitates mercury binding to the surface. During the breakthrough, oxidation of mercury is catalyzed by the surface of activated carbon. The model does not include the role of NO and NO₂ present in the flue gas due to the lack of conclusive results.

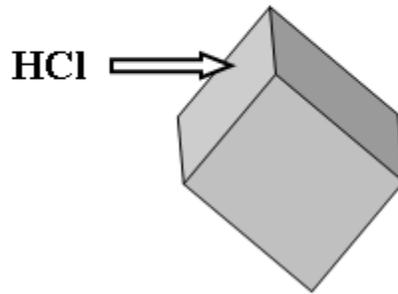


Figure 4.20 Step1: Attaching of HCl to the surface of activated carbon

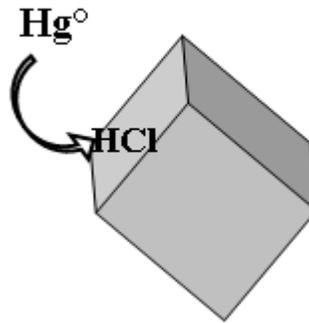


Figure 4.21 Step 2: Binding of Hg° onto the HCl-active sites on the surface of activated carbon

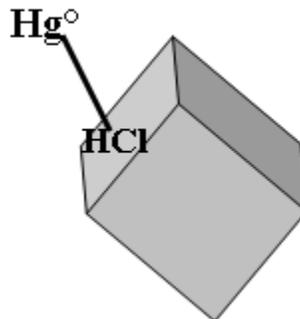


Figure 4.22 Step 3: Bond between Hg° and HCl active sites on the surface of activated carbon

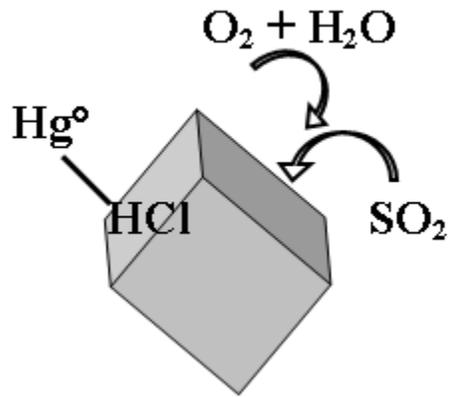


Figure 4.23 Step 4: Attack of SO_2 , H_2O and O_2 on the surface of activated carbon

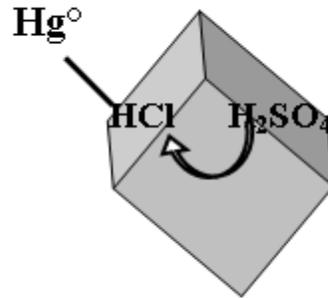


Figure 4.24 Step 5: Formation of H_2SO_4 causing release of HCl from the surface of activated carbon

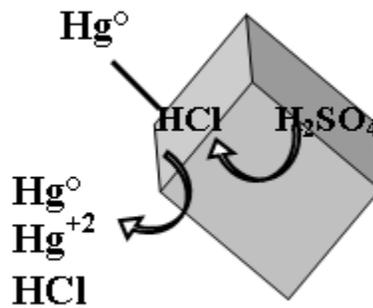


Figure 4.25 Step 6: Release of HCl and Hg° from the surface of activated carbon and oxidation of Hg° to Hg^{+2} catalyzed by the carbon surface

In the absence of SO₂ step 4 is not initiated, which leaves higher number sites on the surface available for HCl to get adsorbed. The increased HCl-coated active sites in turn causes higher mercury uptake. Also, step 4 gets delayed in the absence of moisture from the flue gas causing an increased mercury uptake capacity by sorbents.

The impact of HCl on mercury bonding is evident when the bed temperature was increased. Due to the increased temperature, volatility of HCl in the flue gas was further increased causing a decrease in the mercury uptake by activated carbons. The less amount of mercury present on the surface in turn led to a decrease in mercury oxidation.

Model proposed by Dunham *et al.*⁽¹⁹⁾ and Olson *et al.*⁽²⁰⁾ suggests oxidation of mercury by NO₂, even in the absence of SO₂, on the surface of activated carbon. However, results in this study revealed almost no oxidation of mercury on the surface in the absence of SO₂ from the flue gas. The model shown above suggests the presence of elemental mercury bonded to the surface.

5.0 SUMMARY AND CONCLUSIONS

The first step in this study was to develop an experimental system to generate simulated flue gas representative of gas from coal fired power plants using sub-bituminous coal. Mass flow controllers were installed and calibrated to obtain desired flow rates of different components of the simulated flue gas. A water bath was used to produce 6% moisture content which was picked and introduced by N_2 to other constituents of flue gas. Another water bath containing mercury permeation device was installed to generate elemental mercury. Mercury was introduced into the flue gas by CO_2 . A wet chemistry setup was installed to remove acid gases as well as moisture from the flue gas and also to prepare the flue gas for total and elemental mercury measurement. The setup contained two impingers and condensers. Total mercury side impinger contained [20% NaOH + 2% $SnCl_2$] solution whereas elemental side impinger contained [20% NaOH + 10% KCl] solution. NaOH in the impingers was used to remove acid gases from the flue gas. The usage of $SnCl_2$ in the total side impinger solution was to reduce all the oxidized mercury into elemental form and hence prepare the flue gas for total mercury measurement. On the other hand, KCl in elemental side impinger solution was used to remove oxidized mercury from the gas phase and to prepare the flue gas for only elemental mercury measurement. Condensers in the wet chemistry setup were used to remove moisture from the flue gas, which otherwise could cause potential damage to atomic fluorescence unit.

Fixed bed experiments were conducted to study the impact of different flue gas components and bed temperature on mercury uptake and oxidation by activated carbon sorbents. Two activated carbon sorbents were selected for the study: FGD sorbent and a novel sorbent manufactured by Corning Inc. Experiments were conducted with 1L/min of flue gas at bed temperature of 140 °C and 240 °C. Flue gas components studied were H₂O, SO₂, HCl, NO₂ and NO.

Following conclusions are drawn from the study:

1. FGD sorbent at 140 °C with 1L/min N₂ did not show any mercury uptake as well as no mercury oxidation. However, FGD sorbent with simulated PRB coal flue gas showed no breakthrough of mercury till 2.5 hours. Also a 50% oxidation of mercury was observed. This result emphasized the need for tests to be conducted in realistic conditions.
2. FGD and Corning sorbent with 1L/min simulated PRB coal flue gas showed almost 50% oxidation of mercury during breakthrough, whereas carbon black substitute did not show any significant oxidation of mercury. The difference is due to the significantly higher surface areas of FGD and Corning sorbents than the carbon black substitute.
3. Absence of H₂O from the flue gas led to a 50% increase in mercury uptake capacity of both sorbents. On the other hand, a 50% decrease in mercury oxidation was observed with FGD sorbent and a 100% decrease with Corning sorbent.
4. Absence of SO₂ from simulated flue gas led to a tremendous increase in mercury uptake by FGD and Corning sorbent. No trace of mercury was observed in effluent for 24 hours. TPD run on spent FGD sorbent revealed that mercury present on the surface of the sorbent was mostly in elemental form.

5. Absence of HCl from the flue gas caused an instant breakthrough of mercury with FGD sorbent. With Corning sorbent, breakthrough was observed within one hour of the experiment. In both cases, a significant decrease in mercury uptake by the sorbents was observed.
6. Absence of NO from the flue gas caused a 100% increase in mercury uptake as well as a 95-100% increase in mercury oxidation by FGD sorbent. However, a 50% decrease in mercury uptake with the Corning sorbent was observed in the absence of NO. The difference in the results could be due to the presence of chelating and oxidizing agent on the surface of the Corning sorbent.
7. Absence of NO₂ from the simulated PRB coal flue gas led to a 50% increase in mercury uptake by the FGD sorbent, whereas with Corning sorbent a 50% decrease was observed. However, not a significant change in the mercury oxidation was observed with both sorbents.
8. A 100 °C increase in bed temperature (from 140 °C to 240 °C) caused an instant breakthrough of mercury and a 100% decrease in mercury oxidation by both FGD and Corning sorbent.

A mechanistic model explaining the adsorption and oxidation of mercury by activated carbon is proposed. Initially, HCl gets adsorbed onto the surface providing Cl-active sites which can be used to attach elemental mercury onto the surface of activated carbon. Thus mercury is present on the surface in elemental form. As the breakthrough run proceeds SO₂ gets accumulated on the surface of the carbon and gets converted into H₂SO₄ through oxidation and hydration. Sulfuric acid being less volatile than HCl dislodges HCl from the active sites on the surface which in turn

causes the release/breakthrough of mercury. Mercury gets oxidized during the breakthrough process from the surface.

6.0 ENGINEERING SIGNIFICANCE

Oxidized mercury can be controlled by wet scrubbers and flue gas desulfurization systems; whereas release of particulate bound mercury can be controlled by electrostatic precipitators. However, elemental mercury escapes these control technologies and currently there are no elemental mercury commercial technologies. Results of this study indicate that activated carbons can be successfully used to capture elemental mercury from the coal-fired power plant flue gas under realistic process conditions. Thus, activated carbon adsorption can prove to be a competent technology to control the release of elemental mercury from coal fired power plants using sub-bituminous and lignite coals. These coals contain low chlorine, which leads to lower amount of oxidized mercury (and more elemental mercury) in the flue gas.

Breakthrough (BT) capacities of FGD and Corning sorbent under various gas compositions are shown in the Table 6.1.

Table 6.1 Breakthrough (BT) capacities of FGD and Corning sorbent in different gas mixtures

Condition	BT Capacity of FGD Sorbent	BT Capacity of Corning Sorbent
	µg Hg /mg Sorbent	µg Hg /mg Sorbent
PRB flue gas	0.182	0.274
Absence of H ₂ O	0.344	0.559
Absence of NO	0.336	0.332
Absence of NO ₂	0.256	0.265
Absence of HCl	0.268	0.468
Absence of SO ₂	0.789	0.660

Under simulated PRB coal flue gas condition, BT capacity of FGD sorbent was 50.5% higher than the BT capacity of FGD sorbent. Also, in most of the other gas compositions Corning sorbent performed better than FGD sorbent. In the absence of SO₂, experimental run with Corning sorbent was stopped at 22 hours whereas run with FGD sorbent was stopped at 28 hours. Due to the above reason, BT capacity of FGD sorbent is higher than that of Corning sorbent, however with both sorbents no breakthrough of mercury was observed.

Corning sorbent performed better than FGD sorbent, however the BT capacities of Corning sorbent were marginally higher than that of FGD sorbent. Moreover, preparation of Corning sorbent is costlier than FGD sorbent because it has chelating and oxidizing agent on its surface. A cost comparison between FGD and Corning sorbent should be done for the better understanding

Findings in this study also indicated that even the presence of small amounts of SO₂ in PRB coal flue gas are sufficient to inhibit mercury uptake by activated carbon. On the other hand, it was also found that presence of HCl in the flue gas facilitates mercury uptake. Wet scrubbers and flue gas desulfurization units in thermal power plants are used to remove acid gases (like NO_x and SO_x) to control emission of these gases into the environment. These

systems can be used prior to activated carbon to remove SO_2 (and SO_3) from the flue gas. However, these systems will remove HCl (which helps in the capture of mercury on the surface of activated carbons) and will add high amount of moisture to the effluent. Excessive moisture content can be removed by reducing temperature of the gas. It can be achieved by passing the gas through coiled tubing maintained at temperature lower than the room temperature. To increase mercury capture/removal, it would be desirable to add HCl to the gas before it enters into the activated carbon setup.

Lime ($\text{Ca}(\text{OH})_2$) can be used to remove SO_2 from the flue gas in thermal power plants which are not equipped with wet scrubbers or FGD systems. Apart from capturing SO_2 , lime will also serve to capture mercury from the flue gas. However, lime will also remove HCl along with water and O_2 from the flue gas. Thus, the gas coming out of a lime scrubber should be dosed with HCl and optimum amount of water before it enters into the activated carbon injection system. Water can be added to the system by a steam generating setup.

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