DEVELOPMENT OF AN EXPERIMENTAL SYSTEM TO STUDY MERCURY UPTAKE BY ACTIVATED CARBONS UNDER SIMULATED FLUE GAS CONDITIONS

by

John L. Stuart

B.S. in Chemical Engineering, University of Michigan, 1996

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

2002

UNIVERSITY OF PITTSBURGH

School of Engineering

This thesis was presented

by

John L. Stuart

It was defended on

October 23rd, 2002

and approved by

Radisav D. Vidic, Associate Professor, Department of Civil and Environmental Engineering

Ronald D. Neufeld, Professor, Department of Civil and Environmental Engineering

Leonard W. Casson, Associate Professor, Department of Civil and Environmental Engineering

Thesis Advisor: Radisav D. Vidic, Associate Professor, Department of Civil and Environmental Engineering

ABSTRACT

DEVELOPMENT OF AN EXPERIMENTAL SYSTEM TO STUDY MERCURY UPTAKE BY ACTIVATED CARBONS UNDER SIMULATED FLUE GAS CONDITIONS

John L. Stuart, M.S.

University of Pittsburgh, 2002

Mercury is an increasing environmental concern because of its high volatility in the vapor phase in flue gas streams and the ineffectiveness of existing control technologies to remove the vapor phase mercury. Previous research has documented that activated carbon can be an effective adsorbent for vapor phase mercury in a variety of conditions. Mercury speciation has a large impact on the adsorption by activated carbon because oxidized forms of mercury (Hg^{2+}) can be removed much more easily than elemental mercury (Hg^0).

An experimental system was developed in this study to test the impact of a simulated flue gas on the adsorption of mercury under more realistic process conditions. Mass flow controllers (to control gas flow rates), a water bath (to add moisture), an oil bath (to keep a steady mercury concentration), two gas washing bottles (to remove acid gases and oxidized mercury), and a Nafion dryer (to remove moisture) were utilized in the experimental system. All the components of the experimental system were verified to produce stable flue gas composition and flow rate. Analytical procedures for mercury measurement were developed and tested. It was discovered that approximately 15% of the total mercury in flue gas consists of oxidized mercury and 85% of elemental mercury.

Systematic calibration and tests of analytical equipment and all components of the experimental system are critical to the proper functioning of this experiment.

Two commercial adsorbents were tested for mercury uptake in a simulated flue gas. Elemental mercury capacity of both BPL and FGD carbon increased dramatically as compared to tests with the same adsorbent under nitrogen conditions. The increased capacity is likely caused by the oxidation and acidification of the carbon surface along with the oxidizing conditions within the flue gas. The exact mechanism of the reaction between the flue gas components and the carbon surface are very complex and poorly understood and were not the subject of this study. The main conclusion of this study is that the adsorbent performance in a nitrogen atmosphere is not relevant for full-scale applications where flue gas components produce numerous reactions on the carbon surface and yield drastically different mercury uptake capacity.

DESCRIPTORS

Activated Carbon
Adsorption
Coal-Fired Power Plants
Flue Gas
Mercury
Mercury Measurement
Mercury Speciation

ACKNOWLEGEMENTS

I would like to thank all of my family and friends who have helped me while I’ve been writing this thesis. But in particular, I wish to thank Dr. Radisav Vidic, Nicole (Xiaozhou) You and my parents.

TABLE OF CONTENTS

Page

Page

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

The increasing release of trace metals from fossil fuel burning and municipal waste combustion has caused significant concern for their environmental impact. Mercury is of particular concern because its high volatility in the vapor phase of flue gas streams. Existing pollution abatement technologies, such as flue gas desulfurization and baghouses, are ineffective for the removal of vapor phase mercury. Once it is released into the atmosphere, mercury creates a long-term contamination problem because it persists in the environment and a well-documented food chain transport mechanism results in bioaccumulation that leads to high toxicity to plants and animals. The greatest source of mercury to the population is the ingestion of fish contaminated with mercury.(1) On December 14, 2000, The Environmental Protection Agency (EPA) announced that it would propose regulations for mercury emissions from power plants by December 2003 with promulgation to be launched before December 2005 and full compliance expected by 2007.(2)

Mercury is present in coal in trace amounts and is vaporized during the combustion in coal fired power plants. Previous research has documented that activated carbon can be an effective adsorbent for vapor phase mercury in a variety of conditions, including those in coal fired power plants and municipal waste combustors. Much of the previous work was focused on mercury uptake in an inert nitrogen atmosphere. These studies concluded that virgin activated carbon has a very low mercury uptake capacity, which can increase dramatically with the impregnation of elemental sulfur on the carbon surface.

Researchers have proposed the use of several approaches, including the use of wet scrubbers and powder activated carbon injection for mercury removal, but sorbent capacity is highly dependent on temperature, mercury speciation, and other flue gas constituents.

Mercury speciation is of great importance in coal fired power plants because it has a large impact on mercury removal by adsorption. When combusted, mercury primarily exists in elemental form (Hg^0) while the oxidized form (Hg^{2+}) occurs as the flue gas cools. Mercury speciation is important because oxidized mercury is much more easily removed since it is soluble in water than elemental mercury by both adsorption on activated carbon or wet scrubbing systems. In addition, various flue gas constituents are likely to influence activated carbon capacity for mercury. Some, like sulfur dioxide, will reduce capacity(49) while other constituents, like hydrogen chloride, will enhance mercury adsorption capacity.

The purpose of the current study is to develop an experimental system that can be used to test the impact of flue gas constituents on adsorption of mercury and provide realistic process conditions for sorbent evaluation. First, verification of analytical procedures for mercury measurement must be completed, including mercury speciation between elemental and oxidized forms. After that, evaluation of the performance of common sorbents for mercury uptake under simulated flue gas conditions can be accomplished to compare these results with those obtained using pure nitrogen as a carrier gas. Finally, the results of this study will be used to offer general guidelines for the testing and evaluation of sorbents.

2.0 LITERATURE REVIEW

2.1 Mercury Emission Sources

2.1.1 Coal Fired Power Plants

Coal fired power plants (CFPP) are a major source of energy generation in the United States and other countries. The coals that are burned in these power plants have varied mercury concentrations based on the location and type of coal. One study(3) showed mercury concentrations of coal varying between 0.012 and 33 ppm with an average of 0.2 ppm. Another study(4) sampled 154 different coals and found the average mercury concentration to be 0.085 ppm with a standard deviation of 0.047 ppm. Yet another study(1) suggested that the concentration of mercury in US Coals is between 0.05 to 0.2 ppm by weight.

It is estimated that 25-50 tons per year(1) of mercury are emitted into the atmosphere in the United States through coal combustion. The projected increase of coal usage over the next two decades in China, India, and Indonesia is expected to dwarf the emissions from US coal sources. Estimates of mercury emissions from coal fired power plants as a function of the plant's capacity are shown in Table 1.

Table 1 Mercury Emissions from Coal Fired Power Plants

Capacity of Power Plant, MW	Mercury Emissions (kg/day)
180 (5)	0.14
240 (6)	0.25
500 (7)	0.31
775 (3)	2.3
2150 (8)	1.7-3.4

Estimates of the uncontrolled flue gas composition from coal fired power plants are summarized in Table 2.(8)

Table 2 Uncontrolled Flue Gas Composition for Coal Fired Power Plants

Temperature, ^{o}C	121-177
Mercury Concentration, $\mu g/m^3$	1-10
SO_2 Concentration, ppm (by volume)	100-3000
HCl Concentration, ppm (by volume)	5-100
Excess Air, %	15-25

Mercury concentration in power plant flue gas that has been reported in the literature varies greatly as can be seen in Table 3.

Table 3 Mercury Concentration in Power Plant Flue Gas

Source	Mercury Concentration, $\mu g/m^3$
Billings *et al.* (3)	31
Lindberg (9)	20
Young *et al.* (10)	2-15
Meij (11)	4.1 +/- 5.8
DeVito and Rosenhoover (12)	2.9-7.5

Power plant emissions fall in the 2-31 $\mu g/m^3$ range, which is much higher than mercury concentration in ambient urban air (0.002-0.004 $\mu g/m^3$). Elemental mercury (Hg^0) is very stable and can stay in the atmosphere for several months and be evenly distributed throughout the troposphere. Most of the mercury emitted from a coal fired power plant will remain airborne for tens of kilometers but some of it can be deposited locally leading to a slow increase in mercury concentration in local soils and local surface runoff.(13) One study(14) found soil around a coal fired power plant in Michigan to be enriched in heavy metals and showed that the concentrations correlate with wind patterns and the metal content of the coal. Mercury was the only exception since it showed only a slight increase, suggesting that mercury is more widely dispersed into the environment and causes more of a global impact.

Klein *et al.*(6) analyzed the pathways of 37 trace elements in a coal fired power plant to determine the fate of each element. Class I elements were defined as those that did not evaporate during combustion, remained in the condensed state, and were incorporated into the slag. The following elements belong to this group: Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti. Class II elements were defined as metals that evaporated during combustion and were poorly incorporated into the slag due to limited contact time in the combustion zone. These elements were incorporated into the fly ash and removed in the air pollution control devices. The following elements belong to this group: As, Cd, Cu, Ga, Pb, Sb, Se, Zn. Class III elements include highly volatile elements. The following elements were included in this group: Br, Cl, Hg. The mass balances for Class I and Class II elements were fulfilled, whereas the mass balances were not accomplished for Class III elements. The conclusion was that Class III elements are discharged into the atmosphere and existing pollution control technologies are ineffective for their capture. It is believed that the physical characteristics, such as high volatility and small particle diameters, were the major reason for this observation.

During combustion, mercury is evaporated into the gas phase, and in the presence of other gases such as O_2 and HCl, many reactions may occur. In the furnace, mercury is mostly present in the elemental form due to the high temperatures (1500 ^{o}C). In the post-combustion zone, the temperature will drop to about 300 ^{o}C in several seconds. Only the reactions with fast kinetics can take place in this zone. Mercury may react with HCl or Cl_2 to form $HgCl_2$. It is not likely that mercury will react with oxygen, even though it is readily available, because of slow kinetics. Elemental mercury will make up about 30-60% of the post combustion flue gas.(15) Most of the oxidized mercury forms can be removed by the existing air pollution control devices(12) (e.g., Wet Scrubbers, Fabric Filters) but the majority of the mercury emitted into the atmosphere is in elemental form.

2.1.2 Municipal Waste Combustors

The sources of mercury in a municipal waste combustor (MWC) are predominantly found in organic material, paper and in fines. Results of one study(16) to determine the mercury distribution in the waste of a MWC are detailed in Table 4.

Table 4 Mercury Distribution in Waste of a MWC

Waste Group	Waste, %	Mercury, %
Paper	38.51	31.3
Plastic	8.19	2.2
Organic	34.81	35.4
Ferrous Material	3.52	10.9
Non-ferrous material	0.98	0.6
Glass	1.79	0.8
Inorganic	1.56	
Small appliances	0.26	
Batteries	0.03	4.2
Fines	7.56	14.6
Others	2.89	0.0
Total	100	100

Most metals are either collected in the bottom ash or fabric filter residue in municipal waste combustors (MWC) but mercury is an exception. Mercury tends to escape with the stack emissions. In the same study(16), it was concluded that 59.2% of the mercury exited in the stack gas as opposed to zinc and aluminum, which had extremely low atmospheric emissions.

It is clear that the majority of mercury is escaping through the stack, which will cause regional environmental problems if no air pollution control devices were implemented. Composition of an uncontrolled flue gas from a municipal waste combustor(7) is summarized in Table 5.

Table 5 Uncontrolled Flue Gas Concentrations for Municipal Waste Combustors

Temperature, °C	177-299
Mercury Concentration, μg/m^3	100-1000
SO_2 Concentration, ppm by volume	100-300
HCl Concentration, ppm by volume	100-1000
Excess Air, %	50-110

The concentration of mercury emissions will vary from site to site with mercury concentration estimates varying from 100-1000(15) to 1000-2000 μg/m^3.(10) Comparing Table 2 with Table 5, it is clear that the concentration of mercury in the flue gas is one to three orders of magnitude greater in municipal waste combustors than in coal fired power plants.

Municipal waste combustors have higher HCl concentrations and lower SO_2 concentrations than coal fired power plants, so mercury will predominantly exist as oxidized mercury(7) (mercuric chloride and other oxidized mercury forms) as opposed to CFPP where it tends to be in the elemental form.(9) Because the mercury tends to be in the oxidized form, it can be easily removed by wet scrubbers. Mercuric chloride ($HgCl_2$) has the solubility of 69.0 g/L in water, whereas elemental mercury has the solubility of 6×10^{-5} g/L at 25 °C.(17)

2.1.3 Other Sources

It is estimated that 65 tons/year of mercury were emitted in 1995 by about 2300 medical waste incinerators in the United States.(18) The Hospital/Medical/Infectious Waste Incinerator

Rule (HMIWI) regulates the release of mercury along with several other components.(19) The standard emission limit for mercury was set at 0.55 mg/dscm or 85% reduction without consideration of the size of the incinerator.(19)

It was estimated that 5 tons/year of mercury were emitted in 1990 by cement factories.(20) Limestone is the main ingredient of cement and mercury concentrations in cement vary between 0.07 to 0.22 ppm.(18, 21, 22) It was estimated that 70 tons/year of mercury are emitted by smelting and refining processes.(23) Other sources of mercury include emissions from commercial sources, lamp breakage, geothermal power, wood combustion and secondary mercury production (such as mercury recycling).(24)

2.2 Adsorption-Based Technologies for Mercury Removal

2.2.1 Virgin Activated Carbon

Activated carbon adsorption offers the potential for controlling mercury emissions since it has a high specific surface area and is considered an excellent adsorbent. A comparison between soot particles generated by the incineration of sewage sludge (EP ash) and activated carbon(25) 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.

Other studies(26) have tested activated carbons for the removal of mercury compounds such as mercuric chloride. Virgin activated carbon was able to capture nearly all $HgCl_2$ vapor present even at temperatures as high as 200 ^{o}C, though poor adsorptive capacity was observed for elemental mercury.

Livengood *et al.*(27) tested mercury uptake by activated carbon using a fixed bed reactor. Virgin activated carbon displayed very little mercury adsorptive capacity. They discovered that mercury removal with activated carbon decreases with increasing temperature, particle size, and mercury concentration. Pretreating the carbon with sulfur or $CaCl_2$ can greatly increase the adsorptive capacity of that carbon, which is believed to be caused by the formation of other compounds such as mercury sulfide.

McLaughlin(28) found that activated carbon (F-400) showed poor adsorptive capacity for elemental mercury. Korpiel(29) investigated the impact of empty bed contact time, mercury concentration and temperature on the performance of virgin activated carbon (BPL), which again showed negligible mercury uptake.

Other researchers(30) tested the use of powdered activated carbon (PAC) (a small amount of carbon injected in the flue gas stream upstream of the particulate control devices) on mercury uptake. They discovered that as mercury inlet concentration decreases, the mercury removal attributable to activated carbon adsorption decreases exponentially and concluded that activated carbon injection would provide only about 5% additional mercury removal for coal fired electric utilities.

Likewise, Krishnan *et al*.(31) used PAC and discovered that virgin activated carbon would capture more mercury than Ca-based sorbents as the temperature was raised from 100 to 140 ^oC. Also, activated carbon showed significant capture of elemental mercury at both temperatures, though oxidized mercury was removed more easily than elemental mercury.

Serre and Silcox(32) tested various fly ashes to evaluate them in the use of mercury removal from flue gas streams. A significant amount of Hg^0 was adsorbed by fly ash with carbon contents ranging from 2 to 35% and was proportional to the carbon content and surface area of the fly ash.

Hsi *et al.*(33) compared the adsorptive ability of Illinois coal-derived activated carbons (ICDAC) with a commercially available activated carbon (FGD). They discovered that the adsorptive capacities were comparable. Also, it was found that ICDAC produced from high organic sulfur coal had a 2-4 times higher adsorptive capacity(34) than ICDAC produced from low organic sulfur coal.

2.2.2 Impregnated Carbons

The first researchers to use sulfur impregnated carbon to adsorb mercury vapors were Sinha and Walker.(35) Using sulfur loadings from 1.0 to 11.8%, it was determined that the virgin activated carbon performed better than the sulfur impregnated carbons at 25 ^{o}C. But, the mercury uptake by virgin activated carbon was negligible compared to the sulfur impregnated carbons at 150 ^{o}C.

In contradiction to Sinha and Walker(35), Otani *et al.*(36) found that increasing the sulfur content (from 0 to 13.1%) increased the removal of mercury. This is explained by Otani *et al.* to be due to the difference in surface areas.

Other researchers(37) have tried oxidizing activated carbon with 7 N nitric acid solution. Mercury adsorption increased by as much as 20 times by this technique and iodizing the carbon increased sorption by about 160 times as compared to virgin activated carbon at 30 ^{o}C and mercury influent concentration of 40 mg/m^3. They suggested that surface acidic groups on the oxidized active carbon, along with finely porous and microcrystalline carbon structure, could explain such behavior.

Teller and Quimby(38) found that the best chloride salt impregnated carbons had as much as 300 times greater capacity for mercury removal at temperatures of 300 °F (149 °C) and 500 °F (260 °C) than traditional untreated carbons or sulfur impregnated carbons. Also, carbons treated by HCl exhibited greater capacity than untreated activated carbons.

McLaughlin(28) studied the adsorption of a sulfur impregnated carbon (F-400S) and compared it to a commercially available carbon (HGR). The adsorptive capacity of the sulfur impregnated carbon was much larger than that of the virgin activated carbon. It was also discovered that the mercury removal by HGR is highly temperature dependent. The sulfur impregnated carbon (F-400S) performed better than HGR though it contained 21% less sulfur. Such behavior was explained by the fact that F-400S was impregnated at 600 °C, which promotes a more uniform distribution of sulfur in the activated carbon pore structure.

Korpiel(29) further developed sulfur impregnated carbon (BPL-S) using a commercially available carbon (BPL) as support. Again, due to the sulfur impregnation method, the mercury uptake of this sulfur impregnated carbon was better than HGR at low mercury concentrations due to the weak sulfur bonding in the HGR. At high mercury concentrations, HGR performed better than BPL-S believed to be due to blocking of the pores and limited internal diffusion caused by HgS formation.

Liu(39) continued with the sulfur impregnation process and developed new sulfur impregnation methods. He concluded that impregnation temperature and initial sulfur to carbon ratio are the key parameters in the impregnation procedure. The higher impregnation temperature was believed to result in the formation of shorter chains, more reactive sulfur molecules and the ability of the carbon to retain the high surface area. At these high temperatures, strong sulfur-carbon bonding was observed.

Carey *et al*.(40) used bench and pilot scale tests to determine the ability of sorbents to adsorb mercury in simulated and actual flue gases. They found that laboratory results agreed reasonably well with results in the field and that adsorption capacity increases as the temperature decreases, mercury concentration increases, NO_x concentration decreases, and HCl concentration increases.

Ghorishi *et al*.(41) completed a bench scale study on mercury/sorbent reactions by testing the effects of temperature, sulfur dioxide, HCl, and water vapor on two thermally activated carbons and two calcium based sorbents. $HgCl_2$ is easily adsorbed by the calcium based sorbents due to the presence of alkaline sites. They suggested that the number of active sites on activated carbon is limited, which may explain why elemental mercury control is more difficult.

Granite *et al*.(42) 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.

Huggins *et al*.(1) concluded that the mechanism of mercury sorption on activated carbon can be very complex. They 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.

Hsi *et al*.(33) discovered that sulfur impregnation at 120-200 ^oC did not improve the adsorptive capacity of ICDAC because of blockage of the pore structure of the coals, though increased reactivity and $HgCl_2$ uptake demonstrated that sulfur content was a key feature of the coal. When impregnation was completed at 600 ^oC, the low sulfur ICDAC reached capacity levels similar to the carbons derived from the high organic sulfur coals. The formation of effective sulfur functional groups from sulfur deposition was believed to be the reason for this increased capacity.

2.3 Parameters Influencing Mercury Adsorption by Activated Carbon

A typical composition of gases in CFPP and MWC is compared in Table 6.

Table 6 Typical Gas Composition in Coal Fired Power Plants And Municipal Waste Combustors(15)

Gas	CFPP	MWC
O_2	4-10%	6-15%
CO_2	10-16%	5-14%
CO	10-100 ppm	10-100 ppm
NO	100-1000 ppm	100-1000 ppm
NO_2	5-50 ppm	5-50 ppm
SO_2	100-2000 ppm	100-300 ppm
HCl	1-100 ppm	400-1000 ppm
NH_3	5 ppm	<1 ppm
N_2O	5-200 ppm	<1 ppm
Hg	1-5 $\mu g/m^3$	100-1000 $\mu g/m^3$

2.3.1 Gas Temperature

Increasing the temperature of the flue gas will decrease the mercury capacity of both virgin and sulfur impregnated activated carbons. Chang and Offen(7) studied the effects of lowering the flue gas temperature when activated carbon is injected upstream of a pulse-jet baghouse. The total vapor phase mercury removal efficiency increased from 0 to 37% when the temperature decreased from 345 ^oF (174 ^oC) to 250 ^oF (121 ^oC). Further tests at 200 ^oF (93 ^oC) indicated that the removal could reach 90% in some cases. Carey *et al.*(43) reported that FGD carbon showed a decrease in equilibrium capacity for elemental mercury and mercuric chloride as the temperature increased. Livengood *et al.*(44) reported that mercury removal capacity is increased with decreasing temperature on both virgin and sulfur impregnated activated carbons. Jozewicz and Gullett(45) reported that after 5 hours, a carbon tested at 23 ^oC exhibited better mercury sorption than another tested at 140 ^oC, with similar results observed for a sulfur impregnated carbon (HGR). Chang(46) found that higher temperatures resulted in lower overall mercury uptake. Korpiel(29) found that the dynamic mercury adsorptive capacity of virgin GAC decreased by a factor of 46 as the temperature increased from 50 to 140 ^oC. Liu(39) determined that mercury uptake by sulfur impregnated carbon decreased by a factor of 485 as the temperature increased from 140 ^oC to 250 ^oC. Serre and Silcox(32) found the amount of Hg^0 adsorbed decreases as the temperature was increased from 121 to 177 ^oC. This phenomenon seems indicative of a physical adsorption process.

2.3.2 Inlet Mercury Concentration

Increasing the inlet concentration of mercury will increase the capacity of both virgin and sulfur impregnated activated carbons. Livengood *et al.*(44) suggested that greater adsorption driving force due to the higher mercury concentration increased the utilization of the carbon. Jozewicz and Gullett(45) observed that the increase in sorption rate is not linearly related to the increase in inlet mercury concentration. Chang(46) suggested that this behavior is due to the nature of the driving force. Since there will be greater driving force at higher mercury concentrations, more mercury molecules can be adsorbed on the surface of the carbon.

2.3.3 Moisture Content

Moisture in the flue gas typically reduces the capacity of the carbon. Sinha and Walker(35) reported that a Saran carbon showed reduced breakthrough time (from 68 to 14 minutes) because of the addition of 1.5% (by volume) moisture in the feed gas. Liu(39) reported that no change in mercury uptake by sulfur-impregnated carbon was observed at a 5% water vapor concentration, but the capacity of the carbon was decreased by 25% when the water vapor concentration was increased to 10%. It was postulated that water molecules were able to fill micropores, thereby blocking adsorption sites for mercury. Another possibility is hydrogen formation due to dissociation of water by the carbon. Another researcher(47) suggests that the presence of some moisture on the carbon surface may serve to promote mercury bonding after testing two activated carbons by heating them to 110 ^{o}C to drive off the moisture. It was discovered that the mercury capacity was drastically reduced after this was done.

2.3.4 Sulfur Dioxide (SO_2)

Sulfur dioxide appears to reduce oxidized mercury back into the elemental form. Senior *et al.*(48) suggested that oxidized mercury will be reduced into elemental form by reaction with SO_2. The relevant reaction is:(15)

$$\text{Reduction: } HgO\,(s,g) + SO_2\,(g) = Hg^0\,(g) + SO_3\,(g) \qquad (1)$$

Carey *et al.*(43) reported that removing SO_2 from the flue gas will increase the adsorption capacity of the activated carbon. One researcher(1) suggests that acidic components H_2SO_4 and HCl are the prevalent species adsorbed on the surface of the carbon. It appears that both a lignite activated carbon (LAC) and a sulfur impregnated carbon reacted with this H_2SO_4 to form sulfate species. Liu(39) reported no reaction between the activated carbon and SO_2 and no change in mercury uptake when using 300ppm SO_2 in nitrogen. Miller *et al*.(49) suggested that there may be a significant interaction between SO_2 and NO_2 that causes a rapid breakthrough of mercury with or without the presence of HCl and NO. Tests on fly ash(32) in the presence of SO_2 in the flue gas resulted in 40% reduction in Hg^0 adsorption. It was postulated that this was caused by SO_2 competing for adsorption sites. Ghorishi and Sedman(50) discovered that calcium based sorbents showed insignificant elemental mercury removal in the absence of SO_2, but the uptake was enhanced by 10-40% in the presence of SO_2. Reaction with hydrated lime resulting in pore mouth closure was the postulated reason for this result that suggests that Hg^0 and SO_2 do not compete for the same active sites. Conversely, the presence of SO_2 decreased the removal of $HgCl_2$, with it explained that alkaline sites were instrumental in the capture of $HgCl_2$ and SO_2 competed for these same sites.

2.3.5 Hydrogen Chloride (HCl)

Adding hydrogen chloride will increase the capture of mercury. Elemental mercury can be oxidized by HCl in the flue gas. Krivanek(51) reported that adding 100 ppm of HCl to the flue gas will increase mercury capture regardless of the sulfur dioxide in the flue gas. Teller(38) postulated that HCl would impregnate carbon in-situ with the result being increased mercury capacity. Such results are consistent with results in which acid-treated carbons are more effective sorbents than virgin activated carbons.(37) Miller *et al*.(49) found that adding HCl increases the effectiveness of the carbon and Carey *et al*.(43) found that removing HCl from the simulated flue gas made FGD carbon unable to adsorb any mercury. Huggins *et al*.(1) suggests that the acidic components H_2SO_4 and HCl are the prevalent species adsorbed on the surface of activated carbon. They also determined that lignite activated carbons (such as FGD) are very efficient in extracting HCl from the flue gas.

2.3.6 Oxygen (O_2)

Oxygen will generally increase the capacity of activated carbons for mercury. Oxygen in excess air, which is provided to improve burning efficiency of the coal, can oxidize elemental mercury into mercuric oxide (HgO) at high temperatures. Teller and Quimby(38) observed that with the use of compressed air as a carrier of mercury led to twice the mercury vapor removal capacity as compared to a nitrogen carrier for chloride treated carbons. One possible explanation for this result is the formation of mercury (II) oxychloride ($HgCl_2 \cdot 2HgO$) on the adsorbent. Korpiel(29) found that the presence of oxygen in the carrier gas increased mercury adsorptive capacity of sulfur impregnated granular activated carbons. The oxygen facilitates HgO formation on the surface of the carbon, which acts like a catalyst for the reaction. Liu(39) noticed that that no reaction occurs between O_2 and Hg without the presence of carbon. In the presence of carbon and at low O_2 concentrations (3%), the mercury uptake was unchanged. But at higher concentration (6 and 9%) the mercury uptake increased by 16 and 33%, respectively. The presence of oxygen increases the acidic functional groups on the carbon but it was postulated that the carbon acted as a catalyst to promote the reaction between O_2 and Hg.

2.3.7 Carbon Dioxide (CO_2)

Carbon dioxide behaves as an inert gas and does not affect the performance of the adsorbent and does not react with mercury or interfere with any sulfur-mercury reactions. Liu(39) tested flue gas containing 5% and a 15% CO_2 (balance N_2) using a sulfur-impregnated BPL carbon and showed that the capacity of the carbon remained unchanged.

2.3.8 Nitric Oxide (NO)

It is believed that the addition of nitric oxide will increase the effectiveness of carbon for the removal of mercury. Miller *et al.*(49) reported that adding 300 ppm NO in a baseline gas including 6% O_2, 12% CO_2, 8% H_2O and balance N_2 had a positive effect on the removal of elemental mercury as the initial mercury capture increased from 85-95% to 100% after 2.5 hours. There are several postulated reactions(52) between nitric oxide and carbon:

$$C + 2\,NO = CO_2 + N_2 \qquad (2)$$

$$C + NO = CO + \tfrac{1}{2}\,N_2 \qquad (3)$$

$$CO + NO = CO_2 + \tfrac{1}{2}\,N_2 \qquad (4)$$

Liu(39) showed no difference in carbon capacity between pure nitrogen gas and a 500ppm NO with balance N_2 gas using both virgin activated carbon (BPL) and sulfur-impregnated activated carbon. In addition, there was no weight gain or loss for activated carbon exposed to NO, which led to the conclusion that NO was not adsorbed by the carbon and that the carbon was not gasified. This result is likely caused by a very low concentration of NO in the experiment.

2.3.9 Nitrogen Dioxide (NO_2)

Nitrogen dioxide typically increases mercury removal capacity of carbon. Miller *et al.*(49) reported that adding 20 ppm of NO_2 in a 6% O_2, 12% CO_2, 8% H_2O with a balance N_2 gas increased the effectiveness of the carbon in removing mercury. There is a significant interaction between SO_2 and NO_2, which caused a rapid breakthrough of Hg with or without the presence of HCl and NO.

2.4 Impact of Gas Constituents on Mercury Speciation

Each of the gas constituents in the flue gas has an impact on mercury speciation. Elemental mercury can be oxidized by HCl, Cl_2, NO_2, and O_2 in the presence of activated carbon. Senior *et al.*(48) suggested that the addition of HCl will lead to the formation of $HgCl_2$(g) at temperatures between 750 and 900 K (477 and 627 °C). Therefore, at temperatures representative of the inlet to air pollution control devices all mercury should be present as $HgCl_2$(g) if equilibrium has been attained. But, according to their measurements, only 75% of total mercury is present as oxidized mercury. The reaction with HCl is fast above 700 K (427 °C), and proceeds slowly under 600 K (327 °C), while the reaction with Cl_2 is fast even at 283 K (10 °C). Galbreath and Zygarlicke(53) observed that at temperatures below 450 °C, $HgCl_2$ is the dominant form of Hg. But with increasing temperatures, $HgCl_2$ can react with water to form:

$$HgCl_2\,(g) + H_2O\,(g) = HgO\,(g) + 2\,HCl\,(g) \qquad (5)$$

HgO can gradually decompose according to:

$$HgO\,(g) = Hg^0\,(g) + \tfrac{1}{2}\,O_2\,(g) \qquad (6)$$

Therefore, the relative amount of HgO is minor as compared to $HgCl_2$ and Hg^0. Sliger *et al.*(54) showed that as the temperature of the gas decreases, the equilibrium shifts to $HgCl_2$. The 50/50 split between elemental and oxidized mercury occurs at about 550 °C at a HCl concentration of 50 ppm and at 675 °C for a HCl concentration of 500 ppm. But at 900 °C, mercury oxidation occurs rapidly (0.7 sec), which seems to contradict the findings discussed above. Hall *et al.*(15) described possible oxidation reactions as:

$$Hg^0 (g) + Cl_2 (g) = HgCl_2 (s,g) \quad (7)$$

$$2 Hg^0 (g) + Cl_2 (g) = Hg_2Cl_2 (s) \quad (8)$$

$$Hg^0 (g) + 2 HCl (g) = HgCl_2 (s,g) + H_2 (g) \quad (9)$$

$$2 Hg^0 (g) + 4 HCl (g) + O_2 (g) = 2 HgCl_2 (s,g) + 2 H_2O (g) \quad (10)$$

$$4 Hg^0 (g) + 4 HCl (g) + O_2 (g) = 2 Hg_2Cl_2 (s) + 2 H_2O (g) \quad (11)$$

Senior *et al.*(48) suggested that elemental mercury can be oxidized by O_2 in the presence of activated carbon. Hall *et al.*(15) also proposed the reactions that are relevant to mercury speciation in coal fired power plants:

$$2 Hg^0 (g) + O_2 (g) = 2 HgO (s,g) \quad (12)$$

$$2 Hg^0 (g) + 4 HCl (g) + O_2 (g) = 2 HgCl_2 (s,g) + 2 H_2O (g) \quad (13)$$

$$4 Hg^0 (g) + 4 HCl (g) + O_2 (g) = 2 Hg_2Cl_2 (s) + 2 H_2O (g) \quad (14)$$

Hall *et al.*(55) also determined that the temperature of the flue gas will be greater than 600 ^oC before it enters the duct and thus, no HgO will be formed. But as the gas cools along the duct, it will reach a temperature of 300-500 ^oC, where the oxidation of elemental mercury may occur:

$$Hg^0 (g) + \tfrac{1}{2} O_2 (g) = HgO (g) \quad (15)$$

This reaction is probably too slow under 300 ^oC.

Senior *et al.*(48) also suggested that elemental mercury may be oxidized by NO_2 in the presence of activated carbon. Hall *et al.*(15) suggested that the mercury oxidation with NO_2 that is relevant to mercury speciation can occur according to the following reaction:

$$Hg^0\,(g) + NO_2\,(g) = HgO\,(s,g) + NO\,(g) \qquad (16)$$

2.5 Mercury Measurement Methods

The measurement of mercury concentration can be categorized into two main approaches: Batch and on-line measurements. Batch methods include the following:(53)

- U.S. Environmental Protection Agency (EPA) Method 29, EPA Method 101A and Modified Method 101A. These methods employ glass fiber filters and acidic impinger solutions for sampling and cold-vapor atomic absorption spectroscopy (CVAAS) for mercury measurement.
- Mercury Speciation Adsorption (MESA), Hazardous Element Sampling Train (HEST), and Massachusetts Institute of Technology (MIT) methods. These methods use solid sorbents for sampling and cold-vapor atomic fluorescence spectroscopy (CVAFS), energy-dispersive X-ray fluorescence spectrometry, and instrumental neutron activation analysis, respectively, for quantification.
- Use of KCl and Ag Denuder tubes or a gold-coated screen for sampling and an analyzer that measures Hg concentrations in solution based on the adsorption of Hg on a gold plate and the resulting change in resistance.

On-line measurements utilize analytical instruments capable of measuring mercury at all times. These instruments typically employ an ultraviolet detector.

2.5.1 Batch Methods

The most widely used method to sample mercury is EPA Method 29.(12, 54, 56) This method is recognized as the way to measure total mercury though concerns have been voiced on its ability to distinguish between elemental and oxidized mercury due to interference of SO_2 and Cl_2 with the measurement of elemental mercury.(54, 57) This sampling method along with many other methods uses cold vapor atomic absorption spectroscopy (CVAAS) for mercury measurement.(15, 33, 34, 40, 43, 55, 58-60) Detection limits for this process can vary with early estimates ranging from 3-10 $\mu g/m^3$ (15, 55) to later measurements using EPA Method 7470A, SW-846 having an estimated accuracy of ±10% or ± 0.02 $\mu g/L$,(60) whichever is greater.

Though these methods may be the most common, other techniques have been used. Hsi *et al.*(33, 34) used a gold amalgamation column housed in a tubular furnace where the mercury laden gas would pass and be captured before being thermally desorbed and sent to a CVAA for analysis. The mercury laden gas was first passed through a $SnCl_2$ impinger to reduce oxidized mercury to elemental form and a Na_2CO_3 impinger to remove acid gases from the stream in order to protect the downstream analytical equipment.(40) The measurement of oxidized mercury was completed by replacing the $SnCl_2$ impinger with a tris(hydroxylmethyl)-aminomethane (Tris) solution to trap any oxidized species, allowing only elemental mercury to be recorded downstream. The difference between the measured total mercury and elemental mercury would be the oxidized mercury.

Another batch method is the Mercury Speciation Adsorption (MESA) method used by Sjostrom *et al.*(61). This method uses two KCl impingers to collect oxidized mercury followed by two iodine-impregnated activated carbons designed to capture Hg^0. Concerns have been noted with this method as elemental mercury can be adsorbed in the first two traps, particularly in flue gas with high NO_x and SO_2 concentrations.(57) Other researchers(1) have used techniques like X-ray absorption fine structure (XAFS) spectroscopy. This process is capable of providing detailed speciation information on the carbon and is well suited on obtaining information on the local structure and bonding of elements on the activated carbon surface.

2.5.2 On-line Methods

Several on-line instruments have been used to directly measure elemental mercury concentration. Miller *et al*.(49, 56, 62) used a Semtech 2000 mercury analyzer to continuously measure concentration of elemental mercury. To monitor oxidized mercury, a $SnCl_2$ reduction cell was placed prior to the analyzer to convert all forms of mercury to the elemental form.

Researchers at Triangle Park, NC(31, 47, 50, 63, 64) used an on-line ultraviolet (UV) detector to record elemental mercury concentration. A furnace at 850-900 ^{o}C was placed prior to the analyzer to convert any oxidized mercury into the elemental form, as thermodynamics predicts.(31) A Nafion dryer was also placed before the UV detector to remove moisture. A SO_2 analyzer was placed downstream of the online UV detector because SO_2 would interfere with the mercury detection. The SO_2 signal would be subtracted from the overall signal to determine the mercury concentration.

Another on-line detector is the Brooks Rand CVAFS-2 cold vapor atomic fluorescence spectrophotometer (AFS),(42) which is an ultraviolet detector. The detection limit of the instrument is 0.1 ppb. Argon is used as the carrier gas as the sensitivity of the system can be large depending on the carrier gas.

Finally, several researchers have used Perkin-Elmer brand atomic absorption spectrophotometers (AAS). Sinha and Walker(35) used a Perkin-Elmer Model 303, Daza *et al*.(65)

used a Perkin-Elmer Model 3030 and researchers at the University of Pittsburgh(28, 29, 39, 46) have used a Perkin-Elmer 403 AAS.

3.0 MATERIALS AND METHODS

3.1 Adsorbents

Two adsorbents were tested to determine their capacity for mercury under simulated flue gas conditions. These include BPL and FGD. BPL is a commercially available bituminous coal-based activated carbon and was supplied by the manufacturer (Calgon Carbon Corporation, Pittsburgh, PA) in 4x10 U.S. mesh size. FGD is a powdered lignite activated carbon from Norit Americas Inc. (Atlanta, GA).

3.1.1 Preparation of Adsorbents

BPL was washed in deionized water to remove fines, dried in an oven at 140 ^{o}C for at least 24 hours and stored in a dessicator. It was then ground to 50x80 mesh size. This particle size was produced by grinding the carbons using a coffee grinder and sieving to reach the desired range.

FGD was provided as a powder and was not washed. The FGD sample was stored in a dessicator.

Nitric acid treatment of BPL carbon (4x10) was completed by soaking in 15 N nitric acid (EM Industries, Inc., Gibbstown, NJ) at a ratio of 5 ml/g of carbon for 24 hours with continuous stirring at room temperature. Treated BPL carbon was washed with deionized water until a stable pH was obtained and dried at 140 ^{o}C overnight.

3.2 Elemental Mercury Source

A mercury permeation tube (VICI Metronics, Santa Clara, CA) was used as the source of elemental mercury. This tube included metallic mercury in a silicone tube designed to provide uniform and stable release of elemental mercury (Hg^0) at a given temperature. Figure 1 shows the mercury permeation rate as a function of temperature as provided by the manufacturer. The permeation tube was placed in a glass U-tube that included inlet and outlet ports. Glass beads were placed upstream of the permeation tube to facilitate heat exchange. The U-tube was placed in a temperature controlled oil bath (Precision Scientific, Chicago, IL) which was maintained at 70 ^oC throughout the experiments in order to maintain constant release of mercury from the permeation tube.

3.3 Simulated Flue Gas

A diagram of the experimental system used to prepare simulated flue gas is shown in Figure 2. The nitrogen from one of the tanks is mixed with oxygen and carbon dioxide and sent to an empty flask that was used to prevent backflow of water before entering the water bath. The temperature of the water bath was adjusted until the moisture content in the total gas flow reached 8%. The exit line from the water bath was heated to 140 ^oC in order to prevent water condensation in the tubing prior to the column. The nitrogen from the second tank was directed to the mercury permeation device that was submerged in the oil bath. The SO_2, NO, NO_2 and HCl were added to the nitrogen stream containing mercury after the permeation tube. Bypass lines were added around both the mercury permeation cell and the water bath. The two main lines are merged and heated with a heating tape to maintain the gas at 140 ^{o}C and prevent water condensation in the lines.

In order to simulate a coal fired power plant gas emission, the following gases were used: nitrogen (N_2), carbon dioxide (CO_2), oxygen (O_2), sulfur dioxide (SO_2) in nitrogen, nitric oxide (NO) in nitrogen, nitrogen dioxide (NO_2) in nitrogen, and hydrogen chloride (HCl) in nitrogen. The flows and concentrations are listed in Table 7.

Table 7 Gas Composition of Simulated Flue Gas

Gas	Concentration in the Feed Tank	Flow (ml/min)	Concentration in the Total Flow
Carbon Dioxide (CO_2)	99%	120	12%
Oxygen (O_2)	99%	60	6%
Sulfur Dioxide (SO_2)	1.5%	100	1500 ppm
Nitric Oxide (NO)	3000 ppm	100	300 ppm
Nitrogen Dioxide (NO_2)	1000 ppm	20	20 ppm
Hydrogen Chloride (HCl)	1250 ppm	40	50 ppm
Nitrogen (N_2)	99%	560	Balance

The gases were supplied by Praxair Inc. (Pittsburgh, PA) and the flow rate of each gas was regulated by a mass flow controller (Tylan General, Torrance, CA and Kobold Instruments Inc, Pittsburgh, PA).

3.4 Analytical Techniques

3.4.1 Sulfur Analysis

Sulfur concentration was determined using a Leco Model SC 132 Sulfur Determinator (Leco Co., St. Joseph, MI). After preheating the furnace to a temperature of 1200 °C, a ceramic boat with approximately 100mg of the sample was placed inside the furnace. Sulfur in the carbon sample is oxidized by oxygen (Praxair Inc. Pittsburgh, PA) to sulfur dioxide during the combustion and detected by an infrared (IR) detector. Output signals are calculated by a computer system connected to the sulfur determinator and the results are displayed in terms of percent sulfur. Standard samples (Leco Co., St. Joseph, MI) of known sulfur content (3.87% ± 0.06%) were used for the calibration of the sulfur determinator. Good accuracy was observed when sulfur content was in the 0-7% (wt%) range. Samples with higher sulfur content were accurately weighed and mixed with sand (sulfur content of sand is less than 0.005%) to reach the appropriate range on the calibration curve.

3.4.2 Titration of Oxygen-Containing Surface Functional Groups

Boehm Titration(66, 67) was used to quantify the oxygen-containing acidic functional groups on the surface of BPL carbon.

Two grams of a carbon sample was accurately weighed and soaked in 100ml of an appropriate base solution in a 160 mL glass vial. Teflon stoppers and aluminum caps were used to seal the vials in order to prevent interference of carbon dioxide in the air. The vials were placed in a rotator and rotated end over end for 24 hours. The reaction solution was separated by filtration through a 0.45 μm nylon membrane and titrated to determine the remaining base.

After removing carbon from the solution, the amount of remaining base was titrated to pH 7 using standardized HCl solution. Base consumed by the acidic functional groups on the carbon surface was calculated as the difference between the amount of acid required to titrate the remaining base in the filtrate and the amount of acid required to titrate the control blank to the same endpoint (pH 7).

Standard Methods (Methods 2310B and 2320B)(68) were used to measure the original concentration of a 0.05 N HCl agent. A standardized NaOH solution was used to determine the concentration of 0.05 N HCl by titrating the solution to pH 7. The standardized HCl was then used to measure other basic solutions by titrating the solutions to pH 7.

3.4.3 Outgassing of Carbon Samples

Outgassing carbon samples to remove surface functional groups was performed in a Lindberg Hevi-Duty furnace (Lindberg, Watertown WI) fitted with a mullite tube. BPL virgin carbon (4x10) in the sealed mullite tube was heated at a rate of 200 ^{o}C/hr until 900 ^{o}C was reached with nitrogen gas flushing the tube at 60 ml/min. The carbon was outgassed overnight for approximately 18 hours. The furnace was then cooled at 200 °C/hr until room temperature was reached.

3.4.4 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was conducted using a Thermogravimetric Analyzer TGA7 (Perkin-Elmer Corporation, Norwalk, CT), to investigate the thermal stability of carbon samples by measuring the percentage weight loss of the samples during heat treatment. A sample was heated from room temperature to 100 ^{o}C at a heating rate of 7 ^{o}C/min where it was kept for one hour to remove moisture. It was then heated to 500 ^{o}C at a heating rate of 20 ^{o}C/min where it was kept for 2 hours to remove any sulfur (sulfur boiling point is 445 ^{o}C). Finally, it was heated to 900 ^{o}C at a heating rate of 20 ^{o}C/min where it was kept for two hours before being cooled back to room temperature. Prior to thermogravimetric analysis, both weight and temperature calibrations were completed to ensure data reliability.

3.5 System Operation

After mixing, the simulated flue gas was directed to the column that was enclosed in a laboratory oven. Approximately three meters of teflon tubing (Fisher Scientific) were added inside the oven upstream of the column to ensure that the gas mixture reaches 140 ^{o}C before reaching the adsorber. The oven was maintained at 140 ^{o}C for all experiments in this study. A stainless steel column was equipped with swage-lock fittings and installed in the oven to act as a fixed-bed adsorber. The column measured 6 in. in length with an outer diameter of 0.25 in. Three-way valves were added to the system so that the oven and the column could be bypassed at any point during experimental runs.

The effluent from the adsorber was then directed to two gas washing bottles. The first bottle contained Potassium Chloride (KCl) and was used to remove any oxidized mercury and acid gases.(12, 61) The second gas washing bottle containing Sodium Hydroxide (NaOH) was used to remove the remainder of the acid gases. Removal of the acid gases is important in the analysis since these acid gases will interfere with the reading of the AAS.(39) The gases were then sent to an empty flask to remove any aerosols or sodium hydroxide droplets that could damage the Nafion dryer, which is used to remove moisture and prevent interference with the AAS reading. The first twelve inches of the Nafion dryer were heated to 70 ^{o}C to ensure the moisture would stay in the vapor phase while drying. This purified gas was then sent to the atomic absorption spectrophotometer (AAS) for elemental mercury analysis. Potassium permanganate impingers were placed in-line for total mercury analysis.

3.6 Quality Assurance

3.6.1 Atomic Absorption Spectrophotometer (AAS)

The concentration of mercury was measured using a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer (AAS) (Perkin-Elmer, Norwalk, CT) that was fitted with an 18 cm hollow quartz gas cell (Varian Australia Pty. Ltd., Mulgrave, Victoria, Australia). The AAS was the primary equipment for data collection. The AAS was turned on and allowed to warm up for 2 hours before each experiment. During this time, nitrogen gas at about 0.5 L/min was passed through the AAS quartz tube to ensure no mercury was present in the tubing or quartz cell. The AAS was set at a wavelength of 253.7 nm and the intensity was set at 0.255. After two hours, the AAS was auto-zeroed and then placed on-line. Throughout runs, the mercury-laden gas would be directed to a mercury trap (commercial sulfur impregnated carbon) after the AAS to prevent any release of mercury into the hood. From time to time, the mercury-laden gas would be sent to another mercury trap and clean nitrogen would be used to purge the AAS followed by auto-zeroing the AAS to ensure consistency in measurements.

Two forms of calibration were used in this study: Jerome Calibration and Potassium Permanganate impingers.

3.6.2 Jerome Calibration

The Jerome vessel (Arizona Instrument Corporation, Phoenix, AZ) is a thermos style bottle containing liquid mercury sealed with a rubber stopper. A thermometer was fitted through the rubber stopper to precisely determine the temperature inside the bottle. Based on the ideal gas law, the concentration of mercury in the vapor phase could then be calculated. The rubber stopper has a small slit through which a syringe can be inserted to extract a known volume of mercury-containing vapor, which was then transferred to the quartz cell of the AAS through a rubber septum. A very low flow rate of nitrogen was then sent through the quartz tube to ensure no mercury deposition on the quartz tube. Since the volume of the quartz cell (30.4 ml) and mass of mercury is known, the mercury concentration within the quartz tube can be calculated. A calibration curve can be obtained from the maximum absorbance reading corresponding to different volumes of mercury-containing vapor injected into the quartz cell. This provided another check on the system to determine if the AAS was still working satisfactorily in comparison to impinger analysis.

3.6.3 Potassium Permanganate Impinger Calibration

A mercury trapping impinger was prepared to calibrate the AAS and to determine the concentration of total mercury in the gas streams. The impinger solution used for complete collection of the gas phase mercury species was made with a 1.5% potassium permanganate in a 10% sulfuric acid solution.(69) The 3.6 N sulfuric acid solution was prepared by diluting 36 N sulfuric acid (Fisher Scientific, Pittsburgh, PA) with deionized water. This potassium permanganate solution was always mixed for two hours while all the glassware was covered with aluminum foil due to the instability of the impinger solution in the presence of light. The solution was always used on the day it was prepared.

For each set of experimental conditions, the AAS reading would be recorded and the mercury containing gas stream would be sent through a series of potassium permanganate impingers. By measuring the mass of mercury in the impingers, the concentration in the gas stream could be calculated as:

$C_{Hg} = M/(Q*t)$

where C_{Hg} = concentration of gas phase mercury (μg/m^3)

M = mass of mercury in impinger train

Q = flow rate of gas stream (m^3/min)

t = time of impinger run (min)

The impinger train consisted of two 250 ml gas washing bottles (Corning Inc., Horsehead, NY) each containing 200 ml of the impinger solution. The gas stream was passed through these impinger bottles for a predetermined period of time, usually one hour, and each impinger solution was transferred into a plastic bottle. The results showed that the first impinger collected nearly all of the total mercury that was present in the gas phase. Each impinger bottle was washed with 10ml of concentrated aqua regia to remove any mercury that may have condensed on the glass impinger bottles and the aqua regia rinse was poured into the corresponding beaker. Aqua Regia was prepared by adding 18 ml of 16 N Nitric Acid (J.T. Baker, Phillipsburg, NJ) to a volumetric flask, filling to 100 ml with 36.5-38.0% Hydrochloric Acid (J.T. Baker, Phillipsburg, NJ), and allowing the flask to sit until bubbles began to form after approximately thirty minutes. 100ml of the impinger solution was transferred into a 150 ml PTFE bottle. To prevent interference of permanganate with the AAS analysis, 15 ml of a decolorizing solution (12% sodium chloride, 12% hydroxylamine sulfate in DI water) was added to the bottles to reduce excess permanganate and the bottles were shaken and vented to release gases that were generated through the reduction of permanganate.

Liquid phase mercury standards were prepared by adding a known volume of 1020 μg/ml mercury atomic absorption solution (Aldrich Chemical Company, Milwaukee, WI) into the permanganate solution. Dilutions were made to make standard solutions between 0 and 31.46 µg/L. Five standards of 100 ml each were prepared and transferred to 150 ml PTFE bottles. Again, 15 ml of the decolorizing solution was added and the bottles were shaken and vented.

3.7 Mercury Recovery

At the completion of the experiment, the carbon was removed from the column, placed in a clean and dry vial, labeled and placed in a desiccator. Mercury adsorbed on the carbon was extracted with aqua regia by successive extractions. Approximately 100 ml of aqua regia and mercury containing carbon were poured into the 250 ml beaker and stirred for approximately two hours. The contents of the beaker were then poured through a fritted glass vacuum filtration flask (Kontes, Vineland, NJ) and a 47 mm diameter 0.45 µm acid resistant glass microfibre filter paper (Whatman Inc, Clifton, NJ) to filter the carbon. The beaker was continually washed with small amounts of aqua regia to remove any carbon still remaining in the beaker. Small volumes of the remaining aqua regia were poured through the filter paper to leach out any remaining mercury on the carbon.

The filtrate was collected on the bottom and diluted with the potassium permanganate impinger solution for mercury analysis. 15ml of the decolorizing solution was added to this mixture and then the bottles were shaken and vented. The total mercury concentration was analyzed in the same manner as described in Section 3.6.3. The mass of mercury on the carbon could be calculated based on the concentration in the sample, the dilution factor of the sample, and the volume of aqua regia used.

3.8 Mercury Measurement

The measurement of the mercury in the liquid phase was completed with the use of a MHS-10 Mercury/Hydride System (Perkin-Elmer), a cold vapor technique in conjunction with the Perkin-Elmer AAS. Nitrogen was used at a flow rate of 1.1 L/min as the inert gas to operate the pneumatic and purging system. A 5% $SnCl_2.2H_2O$ in 10% HCl was used as the reductant and placed in the reductant reservoir. A 30ml sample was collected and placed in the reaction flask and then sealed onto the analyzer. The plunger would be pressed and held down, forcing the reductant into the reaction cell and reducing the oxidized mercury into the elemental form and forcing the gas flow into the quartz cell of the AAS. The plunger would be held down until a peak reading was observed on the AAS. The reaction flask would be removed and washed in preparation for the next sample. The immersion tube would be rinsed with deionized water and dried.

4.0 RESULTS AND DISCUSSION

4.1 Development of Experimental System and Analytical Procedures

The first action that was completed was the systematic development of the experimental system, including calibration of mass flow controllers, the water bath, oil bath and the addition of elements to remove acid gases and moisture in order to avoid interference of the elemental mercury reading on the AAS. Next, the development of analytical procedures to measure the elemental and total mercury concentrations were completed with the use of potassium permanganate impingers being used to capture the total mercury concentration.

Following the development of the system, BPL carbon was tested to determine if this system would be effective in mercury uptake experiments. Problems developed when BPL began to be a more effective adsorbent than previous researchers had observed. A series of experiments were completed to determine the cause of the increased effectiveness of BPL. Finally, BPL and FGD carbon were tested in the simulated flue gas system to show the functioning of the system and preliminary data on the vast difference between tests under nitrogen and simulated flue gas conditions.

4.1.1 Gases and Mass Flow Controllers (MFC)

The flow rates of different gases were regulated by one of two different mass flow controllers -- Tylan and Kobold Flow Meters. The flow of each gas was calibrated with a bubble flow meter and a stopwatch. The mass flow controller was then set at a desired reading to accomplish the desired flow rate as can be seen in Table 8.

Table 8 Mass Flow Controller Readings

Gas	Flow Meter	Reading	Flow
Nitrogen 1	Kobold	404	400 ml/min
Nitrogen 2	Kobold	176	160 ml/min
Carbon Dioxide	Kobold	110	120 ml/min
Sulfur Dioxide	Tylan	84.9	100 ml/min
Nitric Oxide	Tylan	33.4	100 ml/min
Oxygen	Kobold	46	60 ml/min
Hydrogen Chloride	Kobold	30.0	40 ml/min
Nitrogen Dioxide	Kobold	20.0	20 ml/min

The flow meters were re-calibrated every few months to ensure accuracy of the flow meter readings. An example of calibration results is shown in Figure 3 for a Tylan Flow meter with a maximum flow rate of 5 L/min. The resulting correlation for this meter was then used throughout the experiment.

$$\text{Tylan Reading} = 16.999 * \text{Flow (L/min)} - 1.5287 \qquad (18)$$

One mass flow controller was corroded by HCl gas. It is believed that this corrosion occurred for one of two reasons. First, the connection was not tight enough and HCl gas leaked to enable the metal to corrode. Second, early in the process, the gas cylinders were not being bled (to reduce the pressure on the pressure regulators on the gas cylinders), thus some gas still remained in the gas line and in the mass flow controller itself. These two reasons may have contributed to the corrosion. The HCl was switched to another Kobold mass flow controller without any further problems.

The Kobold mass flow controllers for sulfur dioxide and nitric oxide began to malfunction and the readings on the mass flow controllers were inaccurate. Since sulfur dioxide and nitric oxide were two key (and expensive) gases, they were switched to Tylan controllers to ensure accurate flow control. The oxygen and second nitrogen tank were switched to the mass flow controllers previously used by SO_2 and NO. The flow of these was then controlled by pressure regulators and the reading was set on the mass flow controller.

The flow of the system was tested frequently. When the flow decreased by more than 5%, leaks were the most likely explanation. Leaks were common throughout the runs and were fixed as soon as detected. The most common leaks were found to be in one of four places: the U-tube housing the mercury permeation device, the water bath, the fixed-bed column, and the gas washing bottles. The first place to check was the column, which had to be fastened tightly to prevent any leaks. The second place to inspect was the gas washing bottles. Originally, teflon tape was used to seal the bottles but it was discovered that this did not prevent leaks and may have even contributed to them. So, the teflon tape was removed and the bottles were sealed by the fritted glass. Since the solution in these gas washing bottles had to be changed every day this was an important step. Another common problem area was the empty flask before the Nafion dryer since the rubber stopper “popped off” due to the pressure on several occasions.

4.1.2 Water Bath

Relative humidity was measured with a Humidity/Temperature Testo 610 (Testo GmbH & Co., Lenzkirch, Germany) probe and converted to percent water vapor using the following relationship:

$\text{Vol. \%} = P_{sat,T} \times RH/P_{Total}$

Where Vol. % = Water Vapor Concentration

$P_{sat,T}$ = Vapor Pressure of Water at Temperature T (kPa)

RH = Relative Humidity

P_{Total} = 101.325 kPa

The temperature of the bath was adjusted until water vapor reached 8% by volume.

The water bath was periodically bypassed so that it could be refilled with water. When the flow through the water bath was resumed, a pressure buildup would occur and water would be forced back into the line. Because of this, an empty flask was introduced into the system prior to the water bath. This flask was periodically emptied because the water accumulated in it over time.

Heating tape was placed around the teflon tubing leading from the water bath to the oven. This tape was maintained at 140 ^{o}C to prevent condensation of water prior to entering the oven and the column.

4.1.3 Oil Bath with Mercury

Nitrogen was flushed through the U-tube containing the mercury permeation device almost constantly during the course of this work. The purpose was to prevent condensation of mercury on the walls of the U-tube or tygon tubing. When nitrogen was not sent through the mercury permeation device for any reason, nitrogen was sent to flush the U-tube for at least 24 hours to remove any residual mercury before the continuation of the experiment.

One mercury permeation device was used in the course of this work. Mercury permeation rate was linearly dependent on water bath temperature as can be seen in Figure 1.

4.1.4 Gas Washing Bottles and Dryer

In order to properly and accurately detect elemental mercury in the carrier gas by atomic absorption spectrophotometry, it is necessary to remove acid gases (HCl, SO_x, NO_x) that absorb at the wavelength close to that of elemental mercury.(39) For example, when mixing 900 ml/min of nitrogen gas with 100 ml/min of 1.5% SO_2 in nitrogen, the AAS reading would increase to 0.045. Likewise, when N_2, SO_2, NO, NO_2 and HCl were passed into the AAS, the reading would increase to 0.047. The first approach to remove acid gases was by the reaction with sodium bicarbonate pellets. However, when the pellets were placed into an empty flask, pressure drop was so high that almost no flow was possible through the pellets and this setup was abandoned.

The next approach was to use wet scrubbing to remove the gases that would interfere with the AAS reading. When a mixture of SO_2 and N_2 as listed above was passed through the Potassium Chloride (KCl) and Sodium Hydroxide (NaOH) impingers, the AAS reading would go to 0.000. Again, when N_2, SO_2, NO, NO_2 and HCl were passed through the potassium chloride and sodium hydroxide gas washing bottles, the AAS reading returned to 0.000.

It was also necessary to dry the gas before sending it to the AAS because moisture would interfere with the reading on the AAS.(39) A Gas Purifier dryer unit (W.A. Hammond Drierite Co., Xenia, Ohio) with pellets was placed after the gas washing bottles to dry the gas. Remarkably, the dryer pellets interfered with the experiment by removing mercury as detected on the AAS. The dryer pellets would also saturate with water quickly and need to be replaced frequently.

Finally, a Nafion Dryer (Perma Pure Inc., Toms River NJ) was used to remove moisture from the gas stream. The dryer consists of a membrane housed inside a stainless steel shell. Water absorbs onto the membrane and permeates to the other side where it is removed with a countercurrent 2 L/min nitrogen flow. The integrity of the dryer was tested periodically to ensure that it was working properly by first bypassing mercury laden gas around the Nafion dryer. After the reading stabilized on the AAS, the flow would then be directed into the Nafion Dryer and the reading on the AAS would be recorded. If the numbers were identical, then the dryer was still functioning properly.

The Nafion dryer could be damaged by sodium hydroxide droplets that may be carried over from the impinger placed immediately before it in the system. Because of this potential problem, a coalescing filter was placed in the system between the NaOH gas washing bottle and the Nafion dryer. The purpose of this filter was to prevent any NaOH globules, water or any aerosols from interfering with the dryer. After using the coalescing filter for some time, it began to cause problems. The reading on the AAS would decrease compared to that when the flow bypassed the coalescing filter. Also, the flow rate of the system was reduced going through this filter. Because of this, the filter was removed and an empty flask was placed immediately before the dryer to eliminate any NaOH globules, water or any aerosols that may interfere with the dryer. No problems occurred with the dryer after the empty flask was placed in the system.

The first 12 inches of the dryer was heated to 70 ^{o}C in order to prevent any water or sodium hydroxide vapor from condensing on the walls of the membrane.

4.1.5 Reduction of Mercury

Because the AAS can only detect elemental mercury, it is necessary to collect information about either oxidized or total mercury to fully account for all mercury species in the breakthrough experiments. Therefore, by determining both total and elemental mercury concentrations in the gas stream, it is possible to determine the oxidized mercury concentration as the difference between these two values. The easiest way to determine total mercury would be to reduce all oxidized mercury into elemental form and analyze by the AAS. Two possible approaches were used for this purpose.

First, a one-inch diameter quartz reaction tube contained in a furnace heated to 850 ^{o}C was placed in the system after the column and before the gas washing bottles. At this temperature, all mercury should be reduced into the elemental form.(31, 47, 50, 63, 64) Three problems with this approach became evident in the testing phase. First, a white substance was developing on the surface of the quartz tube. Second, when 60 ml/min oxygen was added to 940 ml/min nitrogen, the reading on the AAS decreased by 25%. Third, the tube could not withstand the heat of the furnace for a long period of time. So, while testing the tube, the tube would shatter within one month of use.

The second approach was to place a tin chloride solution in the system after the column and before the gas washing bottles. A 5% $SnCl_2$ solution in 10% HCl was used. The $SnCl_2$ should reduce the oxidized mercury into the elemental form. With all mercury in the elemental form, the AAS could determine the total mercury concentration. When only the elemental mercury concentration in the flue gas was being measured, the $SnCl_2$ solution would be bypassed. In this approach, a third gas washing bottle containing only water was added following the NaOH gas washing bottle in order to maintain identical pressure in the system for all flow configurations and to ensure removal of all the gases and oxidized mercury from the gas line. Two problems became evident with this approach. First, after running for only a few minutes, the $SnCl_2$ solution would turn a yellowish brown color that is likely a result of the reaction with sulfur dioxide. Second, and more importantly, the reading on the AA would decrease. The AAS would read 0.022 indicating an elemental mercury concentration of 50 $\mu g/m^3$ when bypassing the $SnCl_2$ impinger. However, this reading would decrease to 0.014 when the gas was sent through the $SnCl_2$ impinger. Thus, the $SnCl_2$ was not reliable in giving a good reading on the AAS and was not used.

The final option was to collect mercury in potassium permanganate in sulfuric acid impingers immediately after the column and analyze them in order to determine the total mercury concentration. Although this approach could not provide continuous total mercury analysis, it was the only one that worked reliably.

4.1.6 AAS

The reading on the AAS was not stable throughout the day. A two hour warm-up period was necessary every day to allow a stable reading. Even then, nitrogen was periodically flushed through the quartz cell and the AAS was auto-zeroed during experiments. Also, the "Gain" of the AAS was checked frequently and readjusted to 0.255. Over the course of the day, the "Gain" would change. After several hours, the AAS would stabilize but these steps were always done to ensure reliable data. The reading on the AAS would rise over the course of the day even with only nitrogen running through the quartz tube, and the AAS had to be zeroed periodically. The AAS was calibrated frequently by Jerome Calibration and collection of potassium permanganate impingers.

4.1.7 Analysis of Mercury in Aqueous Samples

To analyze mercury in the aqueous phase, the MHS-10 Mercury/Hydride System was used. The purge flow rate using nitrogen was set at 1.1 L/min, which was suggested by the manufacturer. Experiments were conducted at varying flow rates though, but results with lower flow rates were inconsistent.

The $SnCl_2$ was fed into the reaction cell from a plastic cone. Sometimes that cone would dislodge from its proper place, which would result in erroneous readings. Care was taken to prevent dislodging of the cone.

The maximum sample volume for the MHS-10 is specified at 50ml. Therefore, a volume of 30 ml was chosen as the consistent sample volume throughout all experiments. The manufacturer suggested that a peak reading from the MHS-10 system could be used in order to improve the detection limit and a test was completed to verify this. Five calibration standards were prepared at 0, 2.6, 6.4, 12.8 and 31.9 μg/L and two impingers were collected. Table 9 compares instrument calibration using the peak values only and using the entire peak area. The area was calculated by taking readings every five seconds and plotting this data with the area being the area under the curve. Peak values correspond to the peak reading observed on the AAS.

Table 9 Comparison of Peak and Area Readings

	Calculated Mercury Concentration, $\mu g/m^3$
Peak Value	128
Area	119

Comparing the two approaches reveals similar results. Therefore, maximum peak reading was used for simplicity.

$SnCl_2$ was made fresh on the day of use because when tests were done with one-day old solution, the results were not as consistent.

4.2 Testing the System

4.2.1 Tests with Nitrogen

The adsorbent selected for baseline testing was BPL. It was important to test BPL to determine if it responded similarly in this system compared to previous studies(29) that also used only nitrogen as a carrier gas. This BPL carbon was labeled BPL1 and used throughout the experiments, except when noted.

Previous experiments with BPL were performed under the conditions listed in Table 10 and those conditions were used in the initial phase of this study, except for the column temperature that was set at 140 ^{o}C.

Table 10 Experimental Conditions for tests with BPL in Nitrogen

Flow Rate	1.0 L/min
Initial Mercury Concentration	55 $\mu g/m^3$
Temperature of Column	50 ^{o}C
Gas	Nitrogen
Mass of Carbon	100 mg

Previous research(7, 29, 32, 39, 43, 44, 46) has shown that as the temperature of the carbon bed increases, breakthrough occurs more rapidly. A comparison with a previous study(29) in Figure 4 was done to demonstrate proper functioning of the system.

The breakthrough profiles of the four trials were similar, all reaching 80% breakthrough within approximately fifteen minutes and total breakthrough within an hour. With this result, it was concluded that the system was operating similar as in the previous study so further experiments could now be conducted.

4.2.2 Tests with Gas Mixture

With the success of the experiments with nitrogen as a carrier gas, the complete gas matrix was set up. The conditions listed in Table 11 were followed in these experiments.

Table 11 Experimental Conditions for Gas Experiments with Simulated Flue Gas

Flow Rate	1.0 L/min
Initial Mercury Concentration	50 μg/m^3
Temperature of Column	140 ^{o}C
Gases	All
Mass of BPL Carbon	100 mg

The BPL Carbon was mixed with 0.5g of sand in these experiments. From a previous study,(29) it was discovered that activated carbon mixed with sand had higher mercury uptake capacity than the carbon tightly packed in the reactor. It was postulated that the incoming gas might be short circuiting and allowing the gas flow through the reactor without encountering all the carbon. Also, 0.25g of sand was placed at the bottom of the column and on top of the carbon-sand mix to prevent any carbon breakthrough out of the column. Two runs were conducted under these conditions and the results are depicted in Figure 5.

After 70-100 hours, little to no breakthrough was observed. Most of the readings were believed to be variance of the AAS during the day as opposed to actual mercury breakthrough. BPL was previously(29, 39) considered a poor mercury adsorbent and this result was quite surprising. To ensure that these results were valid, re-testing of this sorbent with nitrogen as a carrier gas was deemed an appropriate next step.

To determine if and where a problem existed in the system, the first step was to perform another experiment with BPL using only nitrogen as a carrier gas. The experiment was only altered by mixing the carbon with sand. This BPL carbon was tested twice under the conditions listed in Table 12.

Table 12 New Experimental Conditions

Flow Rate	1.0 L/min
Initial Mercury Concentration	50 $\mu g/m^3$
Temperature of Column	140 ^oC
Gas	Nitrogen
Mass of Carbon	100 mg
Sand	0.5g mixed

A previous study(29) tested BPL mixed with 3.2g of sand with complete mercury breakthrough occurring after four to five hours. A comparison of these results with the ones collected in this system is shown in Figure 6.

After 25 hours, breakthrough of only 80% was being observed. Compared to the previous research, the results were not expected and it was decided to retest the system to determine where or if there was a problem.

4.2.3 Evaluation of the System with previously Tested Sorbents

Each part of the system was tested to determine if it was responsible for the observed increase in mercury uptake shown in Figure 6. The first item to be tested was the sand. In previous experiments,(29) sand showed negligible mercury uptake. Also, the mercury uptake of the sand was tested by first bypassing the column until a stable reading was observed on the AAS and then sending the mercury laden gas through the column containing only 0.5g of sand. The reading on the AAS would quickly return to its previously value, indicating negligible uptake of mercury.

Also, one gram of sand was placed in the column. First, 1 L/min of mercury laden nitrogen was passed through the column to determine the mercury uptake of the sand. Following that test, one gram of sand was placed in the column and 1 L/min of the mixed gas laden with mercury was passed through the column to determine the mercury uptake of the sand. Figure 7 compares results of these experiments.

It can be concluded from these results that the mercury uptake by the sand was negligible in both experiments since there is very little mercury uptake and sand was considered inert within the column. Also, since sand is not causing the increased mercury uptake, this test showed that the problem in the previous experiment was likely either caused by the carbon, column, or AAS.

The next step was to determine if BPL carbon that was used in the test had changed in some way. The same experimental procedure as shown in Table 12 was used but no sand was placed in the column this time. The results can be seen in Figure 8.

The results were drastically different than the identical tests from before (Figure 4). After approximately three hours, only 30-40% breakthrough was observed, whereas complete breakthrough occurred in less than an hour in the previous experiment.

Another experiment was conducted with identical conditions but with only 29 mg of BPL carbon in the column. This test was conducted to determine how the mass of carbon can affect the mercury capacity of the carbon. As can be seen in Figure 9, the results for this test were similar to those with 100 mg in the column. After two to three hours, the breakthrough was similar to that in the experiment with 100 mg of sorbent.

4.2.4 Acid Rinse for Mass Balance

Two more tests with BPL were completed with conditions summarized in Table 13. The mercury adsorbed on the carbons was recovered using an aqua regia acid rinse. The results of the experiment are shown in Table 14.

Table 13 Conditions for Runs with Acid Rinse

Flow Rate	1.0 L/min
Initial Mercury Concentration	50 $\mu g/m^3$
Temperature of Column	140 ^oC
Gas	Nitrogen
Mass of Carbon	100 mg

Table 14 Mass Balance Check Using Acid Rinse

	Mass of Mercury Supplied	Mass of Mercury Recovered	Recovery
Trial 1	30.4 μg/L	25.1 μg/L	82%
Trial 2	33.2 μg/L	43.8 μg/L	132%

Trial 1 was conducted for 2.5 hours and Trial 2 was conducted for 2.75 hours with neither showing any breakthrough. Trial 1 showed mercury recovery of 82% while Trial 2 showed a recovery of 132%. Even though both trials do not show exactly 100% breakthrough, these experiments indicate that the carbon was capturing mercury supplied to the column.

4.2.5 Sources of Experimental Error

A fresh BPL carbon (labeled BPL2) was prepared as described earlier (Section 3.1.1) because of these unexpected results. On the same day that BPL2 was prepared, a sample of both BPL1 and BPL2 were tested under identical conditions and the results are compared in Figure 10. After nearly 3 hours, both tests were showing approximately 30% breakthrough. BPL2 was performing similarly to BPL1, which led to the conclusion that the BPL carbon was not the reason for the increased mercury uptake witnessed during previous experiments.

Because of these results, a different activated carbon was prepared and tested (HGR) due to its availability and a well known performance.(28, 29, 39) Figure 11 shows the performance of HGR determined in previous studies. All previous studies used conditions identical to those shown in Table 13 except that the initial mercury concentration was 55 $\mu g/m^3$. In all cases, complete breakthrough occurred in 4 to 6 hours with 50% breakthrough occurring in about one hour.

Two experiments with HGR were conducted in this study under the conditions shown in Table 13. The results of these experiments are shown in Figure 12. Trial 1 was conducted for just over an hour but since almost no breakthrough was observed, it was taken off-line. The second trial was performed for just over 4 hours with no significant breakthrough at all. These results suggested that the column or the tubing was affecting the results.

The column itself was then checked to ensure that it was not interfering or acting as a catalyst for mercury removal. To do this, another column was set up. This column was larger with an internal diameter of 1 inch and a length of 6 inches. To ensure that mercury breakthrough would occur, the concentration of mercury was increased. Trial 1 used 100 mg BPL2 carbon with an initial mercury concentration of 125 $\mu g/m^3$ with a flow rate of 1 L/min. Trial 2 used 100 mg BPL2 carbon at an initial mercury concentration of 175 $\mu g/m^3$ with a flow rate of 1 L/min. Also, BPL2 used in Trial 2 was mixed with 3g of sand. Figure 13 depicts the results from these trials.

Trial 1 had reached only 34% breakthrough after 43 minutes before the run was stopped. Trial 2 was performed for 42 hours before being terminated after reaching only 10%

breakthrough. Since these results were similar to those performed by the original reactor column, it was likely that the original column itself was not causing interference with mercury adsorption.

Since breakthrough in these trials was occurring so slowly, the concentration of mercury in the subsequent trial was increased to 300 $\mu g/m^3$ and the mass of carbon in the column was decreased to 30 mg. Both of these conditions should result in faster breakthrough.(44-46) If the time for breakthrough did decrease, this result would indicate that the increased mercury uptake observed by this carbon was real and oxidation of the carbon surface may have occurred. If the time for breakthrough did not decrease, this would indicate other factors within the system may be causing the increased mercury uptake observed in these experiments. With these new conditions, BPL2 was again tested and the results are depicted in Figure 14. BPL2 reached breakthrough after 50 minutes and 80% breakthrough was observed after 9 minutes. This result appeared more consistent with previous results (Figure 4) but this was only observed after the mercury concentration was increased six times and the carbon mass decreased by 70%. Since breakthrough had occurred more rapidly, it was concluded that the carbon properties had changed and the next step was to determine what might have caused this outcome.

A simple test was done periodically to ensure that the setup was working properly. The mercury laden nitrogen gas would first bypass the column until the reading on the AAS stabilized at a consistent value. After that, the flow of the gas would be directed through an empty column until an identical AAS reading was achieved. Any residual mercury left in the system would be flushed out during the tests. At one point, a 60% drop in the concentration of mercury was observed on the reading of the AAS (Table 15).

Table 15 Mercury Concentrations Flowing Through
And Bypassing Column

	Mercury Concentration, $\mu g/m^3$
Flow Bypassing Column	50
Flow Through Column	20

This result suggested that some of the sorbent had deposited on the surface of the tubing or column and was adsorbing mercury. Each of the three components in the oven – upstream teflon tubing, the column, and downstream teflon tubing – was systematically checked to determine their ability to remove mercury by passing the mercury laden nitrogen gas only through that component and bypassing the other two. By this method, it was observed that all three components were removing mercury.

Approximately every two weeks, the teflon tubing upstream and downstream of the column would be removed and washed with 10% sulfuric acid followed by a tap water wash. Also, the column would be brushed, washed and cleaned every week or so. Cleaning of the column resulted in no mercury removal through it, but the upstream and downstream teflon tubing was still removing mercury even after repeated rinsings, including 2 liters of 1 M NaOH. The tubing was clearly compromised and was replaced.

4.3 Impact of Adsorbent Properties on Mercury Uptake

4.3.1 Impact of Sulfur Content on Mercury Uptake

Since impregnation with sulfur is known to increase adsorptive capacity of activated carbons for mercury,(39) the BPL samples were tested for sulfur content. From a previous study,(39) BPL was found to have a sulfur content of 0.51-0.73% by weight. Table 16 shows the sulfur content for all of the sorbents that were available for laboratory testing. The number of times sampled is the number of distinct times that carbon was tested for its sulfur content.

Table 16 Sulfur Analysis of Various Carbons

Carbon	Number of Times Sampled	Sulfur Content, wt%
BPL1	3	0.838
BPL2	1	0.787
BPL3	3	0.858
BPL – HNO_3 treated	1	0.750
BPL – outgassed	1	0.826
FGD	3	1.287
FGD – HNO_3 treated	2	0.335
Centaur	3	0.824
MERSORB	3	17.012
HGR	3	12.612

BPL3 was the BPL carbon that was prepared for the final tests that will be discussed later. The sulfur content of the BPL carbon was fairly consistent between samples, averaging around 0.8% which is in-line with previous results. It can therefore be concluded that sulfur accumulation on the carbon surface was not a likely reason for the increased mercury uptake depicted on Figure 6.

4.3.2 Oxygen-Containing Surface Functional Groups

BPL2 was then outgassed to remove any surface functional groups from the carbon. A sample of 80mg was outgassed and then placed in the system to be tested. On the same day, another sample of BPL2 that had not been outgassed was tested. Both experiments were completed under the experimental conditions listed in Table 13 except that 80mg were used for each carbon. Figure 15 compares the performance of these two sorbents.

The breakthrough of the outgassed carbon was nearly immediate, reaching 80% breakthrough in 4 minutes and 100% breakthrough in just 13 minutes. This result compared favorably to previous studies with BPL (Section 4.2.1). The BPL that was not outgassed only reached 75% breakthrough after nearly two hours. From the differing mercury uptake results, it was clear that the surface of the BPL carbon had been altered, likely oxidized, to result in the increased mercury uptake.

Because the ability of acidic functional groups to influence the adsorption of activated carbon was demonstrated,(70-72) a Boehm titration was completed on BPL2 carbon to determine the total acidity. One gram of BPL was titrated by the procedure outlined in Section 3.4.2 and the results are shown in Table 17.

Table 17 Titration Results of Two BPL2 Samples

Sample	Total Acidity (μeq/g)
Test 1	293
Test 2	235

The total acidity of the BPL2 carbon averaged 264 μeq/g. A previous study(73) found a total acidity of BPL to be 249 μeq/g. From this similarity, no evidence of additional functional groups could be found.

Even though Boehm titration did not indicate any increase in oxygen-containing acidic groups on the surface of the carbon, outgassed BPL carbon was treated with nitric acid to replenish acidic functional groups on the surface of the carbon because some studies(70-72) showed that acid treatment of activated carbon leads to better performance of that sorbent. This Nitric Acid treated carbon was then tested for mercury breakthrough under experimental conditions listed in Table 12 and the results are compared to performance of virgin and outgassed BPL carbons in Figure 16. The acidified BPL had larger mercury uptake compared to the outgassed activated carbon but did not attain the mercury uptake of the virgin BPL1. This result may partially explain the increased mercury uptake but other factors must still be investigated.

A sample of BPL2 was then heated in the Thermogravimetric Analyzer (TGA) with the weight loss shown in Figure 17. Negligible weight loss mostly due to water can be observed in this test. This result fortified the belief that sulfur had not deposited on the surface of the carbon. Also, other functional groups had not deposited on the surface of the carbon and hence possibly explain the increased mercury uptake capacity of BPL2.

Another sample of BPL was prepared in the lab (labeled BPL3) using the approach described in Section 3.1.1. This carbon was tested for mercury uptake using experimental conditions listed in Table 13. As can be seen in Figure 18, immediate breakthrough of mercury occurred for this sorbent. Since the BPL2 sorbent showed significantly better performance (Figure 18), it is postulated that the source of BPL2 carbon was different than the source for BPL3 (most likely, BPL2 may have been oxidized during prolonged storage in the laboratory). BPL3 was then mixed with 0.5g of sand and tested under the same conditions listed in Table 13 to facilitate direct comparison with previous results (Section 4.2.2) on Figure 18. Performance of BPL3 mixed with 0.5g of sand was comparable to previous results with BPL carbon(29) and it was decided to complete the remaining experiments with this freshly prepared BPL sample (BPL3).

4.4 Comparison of Mercury Sorbents Under Simulated Flue Gas Conditions

The complete gas matrix was established and passed through the system until a stable reading was observed on the AAS. This reading indicated an elemental mercury concentration of 210 $\mu g/m^3$. Potassium Permanganate impingers were then placed prior to the AAS to verify elemental mercury concentration in the simulated flue gas. This test revealed elemental mercury concentration of 207 $\mu g/m^3$, which is in good agreement with AAS results. Potassium Permanganate impingers were then placed prior to the gas washing bottles to obtain the total mercury concentration in the simulated flue gas. This test revealed a total mercury concentration of 259 $\mu g/m^3$. It is clear from these results that 207-210 $\mu g/m^3$ is in the elemental mercury concentration in the simulated flue gas and that oxidized mercury species account for 49-52 $\mu g/m^3$.

Following this set of experiments, only nitrogen was used as the carrier gas. With this setup, no oxidized mercury should be present in the system. Pottasium permanganate impingers were placed prior to the AAS to verify the total mercury concentration. Impinger analysis indicated both total and elemental mercury concentration of 242 $\mu g/m^3$. This is in reasonably close agreement with the total mercury concentration analyzed in the simulated flue gas (259 $\mu g/m^3$).

Hence, approximately 15-20% of the mercury in the simulated flue gas is in the oxidized form and the potassium permanganate impingers must be placed prior to the gas washing bottles to determine the total mercury concentration exiting the column. On the other hand, the reading on the AAS would reflect only the elemental mercury concentration and potassium permanganate impingers were occasionally placed prior to the AAS to verify elemental mercury readings by this instrument.

4.4.1 Performance of BPL Carbon

The mass of BPL carbon used in these tests was only 10 mg in order to reach breakthrough in a reasonable period of time. BPL carbon was mixed with 1g of sand and placed in an oven maintained at 140 ^{o}C, and tested for mercury uptake under experimental conditions listed in Table 18. Mercury breakthrough is shown in Figure 19.

Table 18 Experimental Conditions for Complete Mix Gas Experiments

Flow Rate	1.0 L/min
Initial Mercury Concentration	250 $\mu g/m^3$
Temperature of Column	140 ^{o}C
Gases	All
Mass of BPL Carbon	10 mg

The complete breakthrough of total mercury was accomplished after 263 hours, whereas the elemental mercury concentration reached 91% breakthrough during that time period. There was approximately 15% difference between the elemental and total mercury concentrations during the experiment.

As compared to experiments with nitrogen as the carrier gas, this result shows a dramatic increase in mercury uptake. Even comparing the results to the oxidized BPL1 sample, the mercury uptake is drastically improved. The cause of the increased uptake is likely the oxidation of both the carbon surface with some oxidation of the inlet mercury. The complete gas matrix is complex with many reactions potentially occurring but it is these interactions that are causing the increased mercury uptake by BPL carbon. This result indicates assessing the effectiveness of adsorbents tested in a nitrogen atmosphere is not relevant for field application.

This result could likely be predicted from previous research. First, the capacity of the carbon is likely to increase solely due to the higher concentration of mercury which will cause a higher driving force for adsorption.(44, 46) Though moisture and SO_2 tend to decrease the capacity for mercury, the introduction of other gas constituents may offset this phenomenon. It is postulated that moisture may block the micropores of the carbon surface,(39) but moisture certainly leads to the acidification of the carbon surface through the reaction with acid gases. Such deposition of acidic groups on the carbon surface will improve mercury uptake.(37, 42) Sulfur dioxide in the presence of moisture is expected to form H_2SO_4, which can both acidify the carbon surface and dissolve mercury vapor. Both of these processes increase the mercury capacity of an activated carbon.

It was reported(51) that the introduction of HCl will increase the capture of mercury irrespective of the SO_2 concentration in the flue gas. As suggested,(38) perhaps the HCl impregnates the carbon in-situ, causing the increase its mercury capacity. Another factor is the addition of O_2 to the flue gas. The introduction of O_2 alone appears to increase the mercury capacity of activated carbons.(38, 39) Perhaps, a formation of mercury (II) oxychloride ($HgCl_2{\cdot}2HgO$) or mercuric oxide (HgO) is the reason for the enhanced removal of mercury since the removal of oxidized mercury is much easier(26, 31, 41) than elemental mercury. Another factor is the introduction of NO_x, which tends to increase the effectiveness of activated carbon,(49) though the precise mechanism of this interaction is not fully understood.

4.4.2 Performance of FGD Carbon

The second experiment with the full gas matrix was completed with another commercially available activated carbon, FGD. Again, 10 mg of FGD was mixed with 1g of sand and placed into an oven at 140 ^oC. About 0.3 g of sand were placed on top and on bottom of this mixture to prevent loss of this pulverized carbon from the column. The results of this experiment are shown in Figure 20. After 191 hours, only 45% total mercury breakthrough was observed, with approximately 20% of the mercury in the oxidized form.

Experiments were also conducted on FGD under nitrogen conditions. Experimental conditions were the same as listed in Table 13 except 30mg of the adsorbent was used and was mixed with 1g of sand, with about 0.3g of sand placed on top of the carbon/sand mixture and 0.3g of sand placed on the bottom of the mixture to prevent loss of sorbent. The results of three experiments under various conditions can be seen in Figure 21. The outgassed FGD performed worse than the original sample, indicating that the surface of the FGD carbon was oxidized since it performed similarly to FGD treated with nitric acid. The breakthrough, though, reached 85% within one hour for each sorbent.

So, there is a large difference between the mercury uptake by FGD between the experiments conducted using only nitrogen as a carrier gas and the simulated flue gas. This result leads to the conclusion that assessing adsorbent effectiveness in a nitrogen atmosphere as opposed to a simulated flue gas is not relevant. Many of the same factors for this difference can be reiterated from the previous section. The FGD carbon is likely heavily acidified and oxidized and the matrix of gases has oxidized some of the mercury prior to entering the column. It appears that lignite activated carbons (LAC), such as FGD, will react with H_2SO_4 to form sulfate species on the surface of the carbon.(1) Perhaps reaction of these species with mercury are causing the increased mercury uptake. Also, it was observed that LAC are very efficient in the extraction of HCl from the flue gas.(1) The increased acidification of the carbon surface could be a large factor in the increased mercury uptake. Carey *et al*.(43) observed that the presence of HCl is critical for the uptake of mercury by FGD since the removal of this gas renders FGD unable to remove any mercury.

4.4.3 Comparison Between BPL and FGD

A comparison of the elemental breakthrough for both BPL and FGD is depicted in Figure 22. It clearly shows that FGD shows a higher capacity of mercury compared to mercury. Table 19 lists the time of 30% and 90% breakthrough for both BPL and FGD for both elemental and total mercury.

Table 19 Total and Elemental Breakthrough Times for BPL and FGD Under Simulated Flue Gas Conditions

	30% Breakthrough (hours)		90% Breakthrough (hours)	
	Hg^0	Hg_{Tot}	Hg^0	Hg_{Tot}
BPL	39.5	18	262.5	181
FGD	146	98	N/A	N/A

FGD reached 30% breakthrough in elemental and total mercury 3.5 and 5 times slower than BPL. The reactions occurring on the surface of the carbon along with oxidizing and acidifying conditions of the flue gas are large factors for these results. The reactions with H_2SO_4 on the carbon surface of FGD and the efficiency of the lignite activated carbons in removing HCl could be factors in the increased mercury uptake by FGD. But an even larger factor could be the particle size of the two carbons. FGD was in powder form, a particle size on the order of 5 μm whereas the particle size of BPL is in the 177-300 μm range. The kinetics of the reactions along with the chemical reactions on the carbon particle surface could be larger factors in the difference in performance of the particles. For true comparisons, adsorbents should be of the same particle size. However, FGD is only available in powder form while BPL is supplied in granular form.

5.0 SUMMARY AND CONCLUSIONS

The first step in this study was to build an experimental system to test the impact of simulated flue gas on mercury uptake by carbon adsorbents. Mass flow controllers were installed, calibrated and set at a desired flowrate. Both a water bath and an oil bath were installed to accomplish 8% moisture in the flue gas and a steady mercury concentration in the carrier gas. Two gas washing bottles (KCl and NaOH) and a Nafion dryer were installed after testing several methods to remove any interference by acid gases on the elemental mercury reading by the AAS. A system was then devised to measure both the total and elemental mercury readings. The elemental mercury measurement would be continuously performed by the AAS. After testing several methods, potassium permanganate impingers were used to determine the total mercury concentration in the gas phase. These mercury measurement methods were calibrated and tested many times to ensure the reliability of the data, analytical techniques, and proper functioning of the system.

After various tests, it became evident that the original sample of BPL carbon must have been somehow altered to exhibit significant increase in mercury uptake capabilities. Each component of the system was separately tested, including sand, tubing, and AAS, and fresh samples of BPL and various other sorbents were tested to determine the cause of the increased mercury uptake observed with the original BPL sample. It was observed that the tubing around the column was removing mercury probably because of sorbent accumulation from previous runs with powdered sorbent. This problem was resolved by replacing the tubing. Eventually, the BPL carbon was outgassed and it performed as expected. Further studies were performed to determine the cause for this behavior. After testing its sulfur content, surface acidic groups, and thermogravimetric analysis, no definite conclusion could be made.

The main conclusions that can be made from this phase of the study are as follows:

- An experimental system to test mercury uptake by various adsorbents under flue gas conditions was successfully developed.
- Sampling and analytical protocols were developed to ensure proper functioning of the system.
- Gas washing bottles and a Nafion dryer were important in order to eliminate interference of flue gas components with elemental mercury analysis by the AAS.
- About 15% of the inlet mercury to the column would be in the form of oxidized mercury.
- Systematic calibration and testing of the system and analytical equipment is critical for proper functioning of an experiment.
- Each component of the system must be tested to determine where problems may exist and each possibility must be investigated.

Finally, a fresh sample of BPL carbon was prepared for testing and its performance in nitrogen atmosphere was verified by comparison with previous results. This carbon was then tested under simulated flue gas conditions and its capacity increased drastically. The breakthrough of oxidized mercury was approximately 15% higher than for elemental mercury. The reason for the increased mercury uptake is likely caused by the oxidation and acidification of the carbon surface along with oxidizing conditions of the flue gas. Many of the key gases from the flue gas will either cause some oxidation of the flue gas or deposit acids onto the surface of the carbon. The interactions between the carbon surface and the flue gases can be very complex and very hard to predict. The simulated flue gas causes an oxidizing and acidifying situation where much more mercury is captured on the carbon surface.

It is concluded that tests in nitrogen are not relevant for assessing adsorbent performance in the field because of the vast difference between mercury uptake capacity by virgin activated carbons in a nitrogen atmosphere compared to those in a simulated flue gas atmosphere.

It is important to not compare the results of FGD and BPL directly to each other because the carbon particles of these sorbents are vastly different. BPL has a size of approximately 177-300 μm, whereas the particle size of FGD is on the order of 5 μm. The kinetics of the adsorption and chemical reactions on the surface of the carbon particle may be the reasons for the observed differences in performance. Thus, identical particle sizes should be used for comparison.

FGD carbon is the standard activated carbon sorbent used by most researchers in this field to test and compare mercury uptake experiments. It is important to compare mercury uptake experiments of different sorbents to FGD Carbon for this reason.

6.0 RECOMMENDATIONS FOR FUTURE WORK

Further tests could be completed to determine the best conditions on how to determine the elemental and total mercury concentrations by re-testing the use of $SnCl_2$, a furnace or continued impinger collection. This could be important to save time and also ensure the accuracy of the measurements.

Evidence that photochemical oxidation(59) may occur in the quartz cell should be examined as it could also be a cause of mercury removal in the system.

There are various research topics that could be continued from this research. First, a comparison of fixed bed results with powder activated carbon tests will give more realistic data since coal fired power plants would use powder activated carbon injected into the flue gas to control mercury.

The effect of sand mixing could be analyzed by experimenting with different masses of sand to determine at what point short circuiting begins. This could help understand this phenomenon to prevent it from happening.

Now that the system seems to be operating properly, duplicates could be done of each sorbent along with testing a large range of different sorbents to determine their effectiveness in a simulated flue gas. Different masses of carbon could be tested to determine how carbon loading will affect the mercury uptake of the carbon. Then, these sorbents could potentially be used in a pilot test to compare results in a lab and pilot setting.

Testing the sorbents with a wide variety of gas combinations may pinpoint which gases are more critical in the oxidizing and acidifying of the carbon surface, which could be critical in predicting how a sorbent may work in different field conditions.

APPENDIX

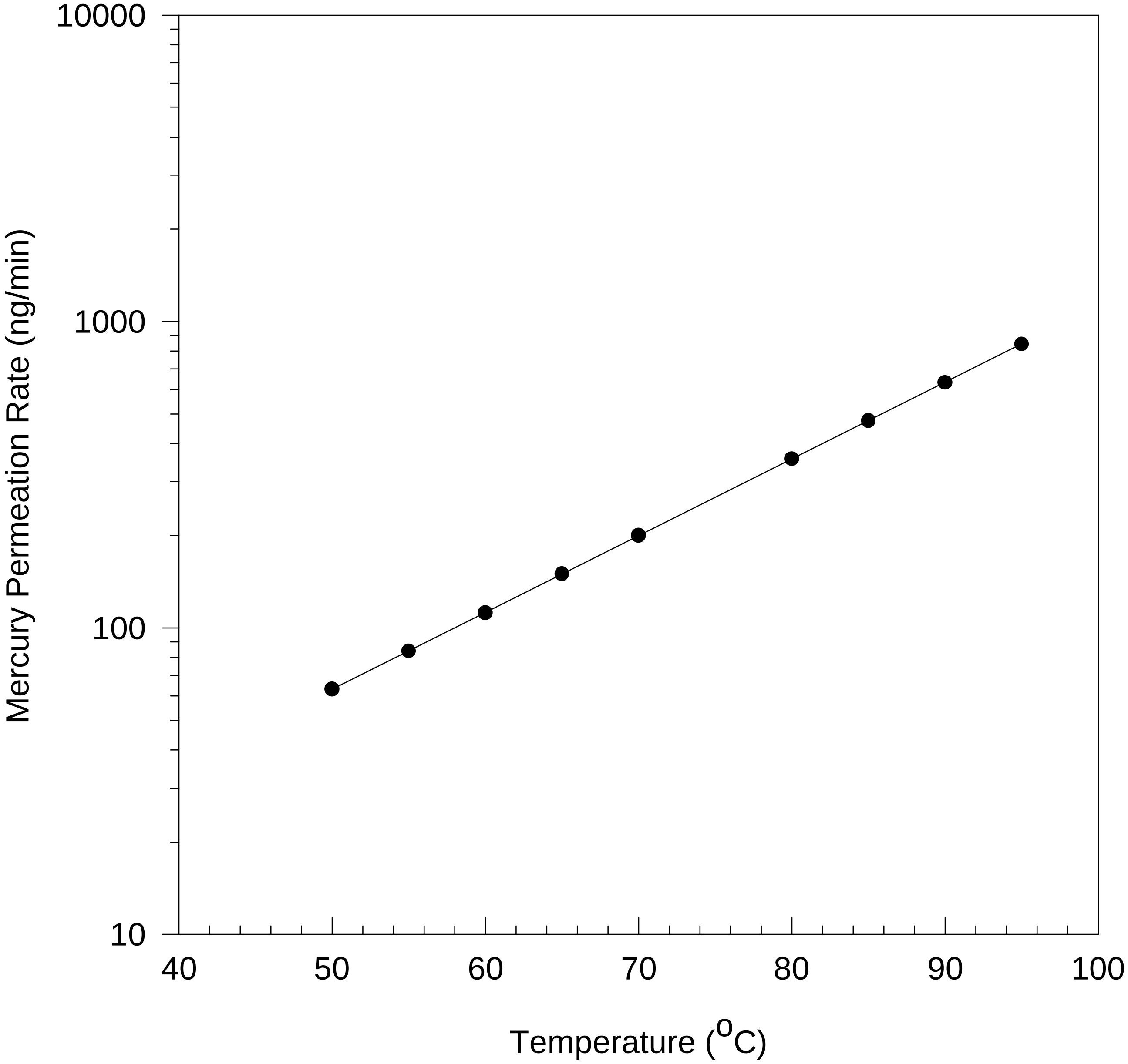

Figure 1 Mercury Permeation Rate as a Function of Temperature

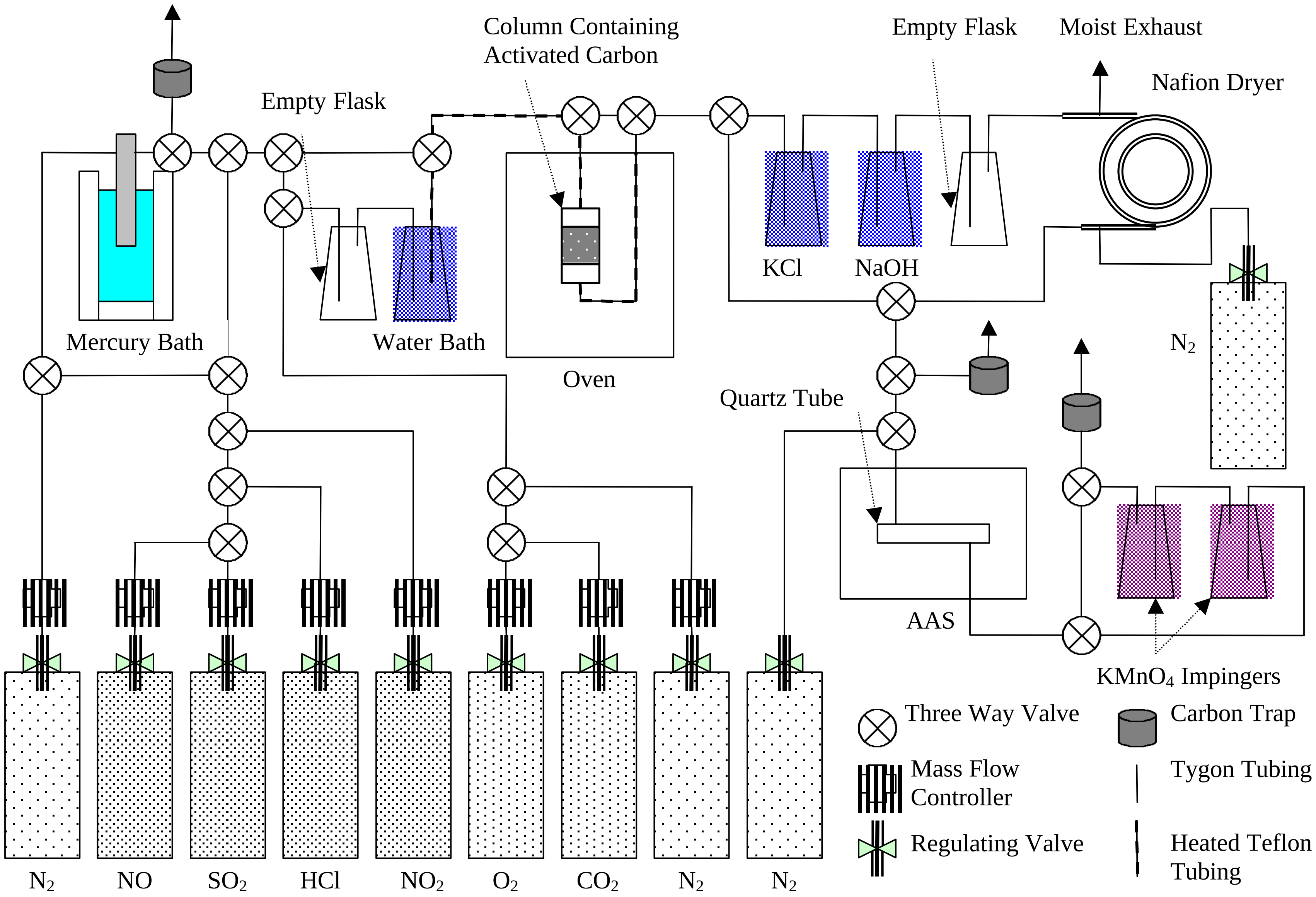

Figure 2 System Schematic

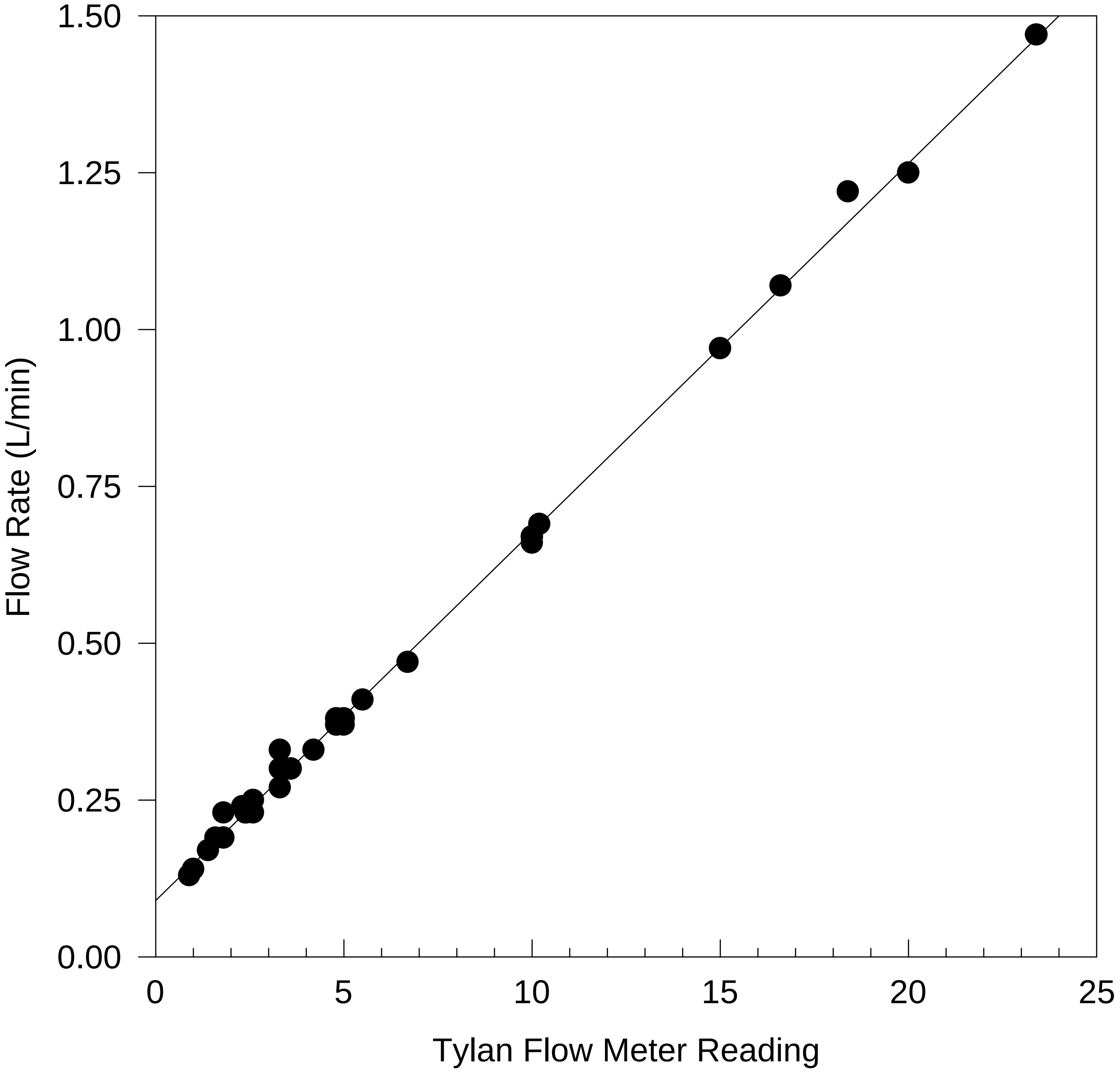

Figure 3 Tylan Flow Meter Calibration – Tylan Flow Meter Reading versus Actual Flow Rate

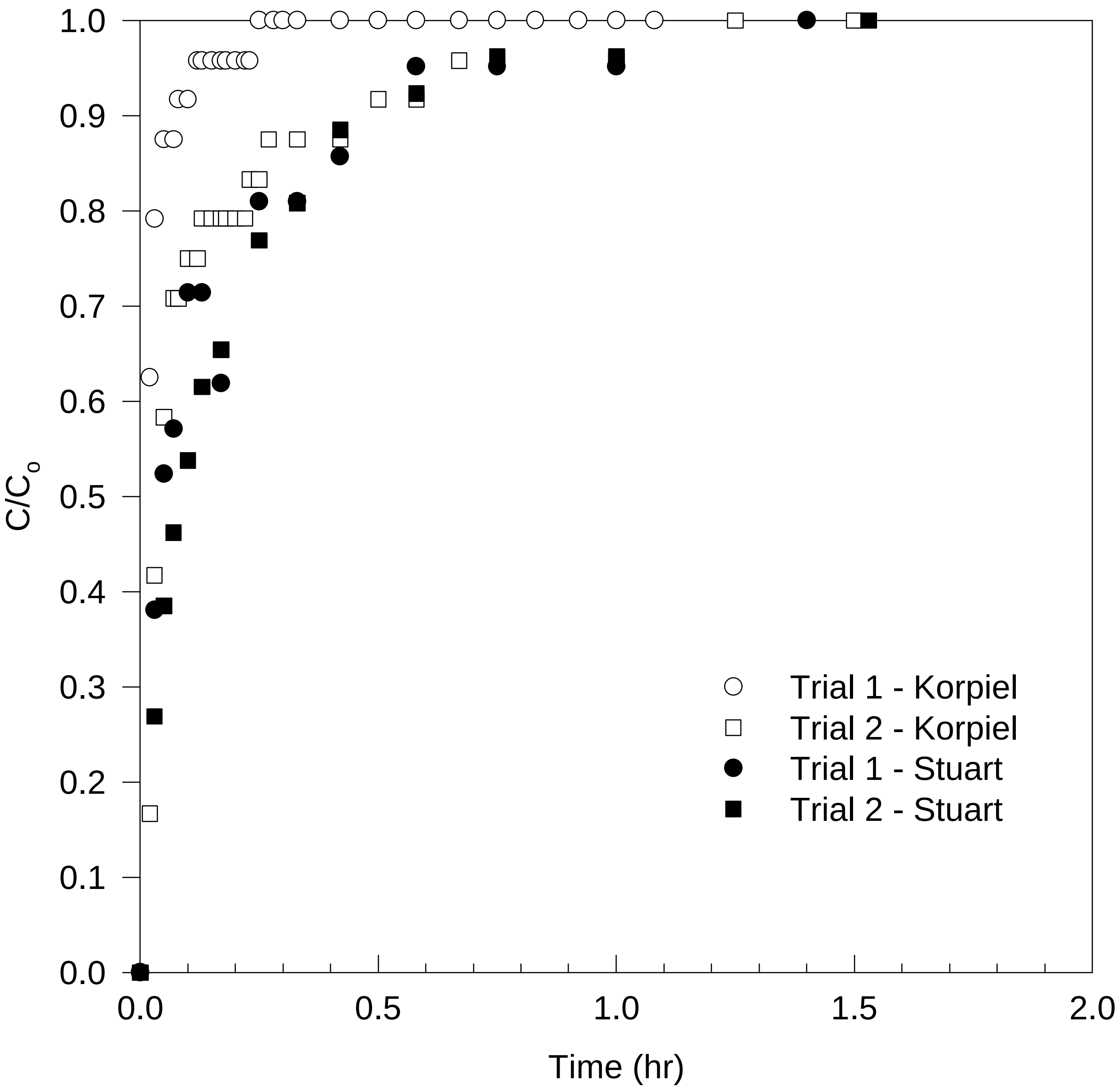

Figure 4 Mercury Breakthrough of BPL in a Nitrogen Atmosphere

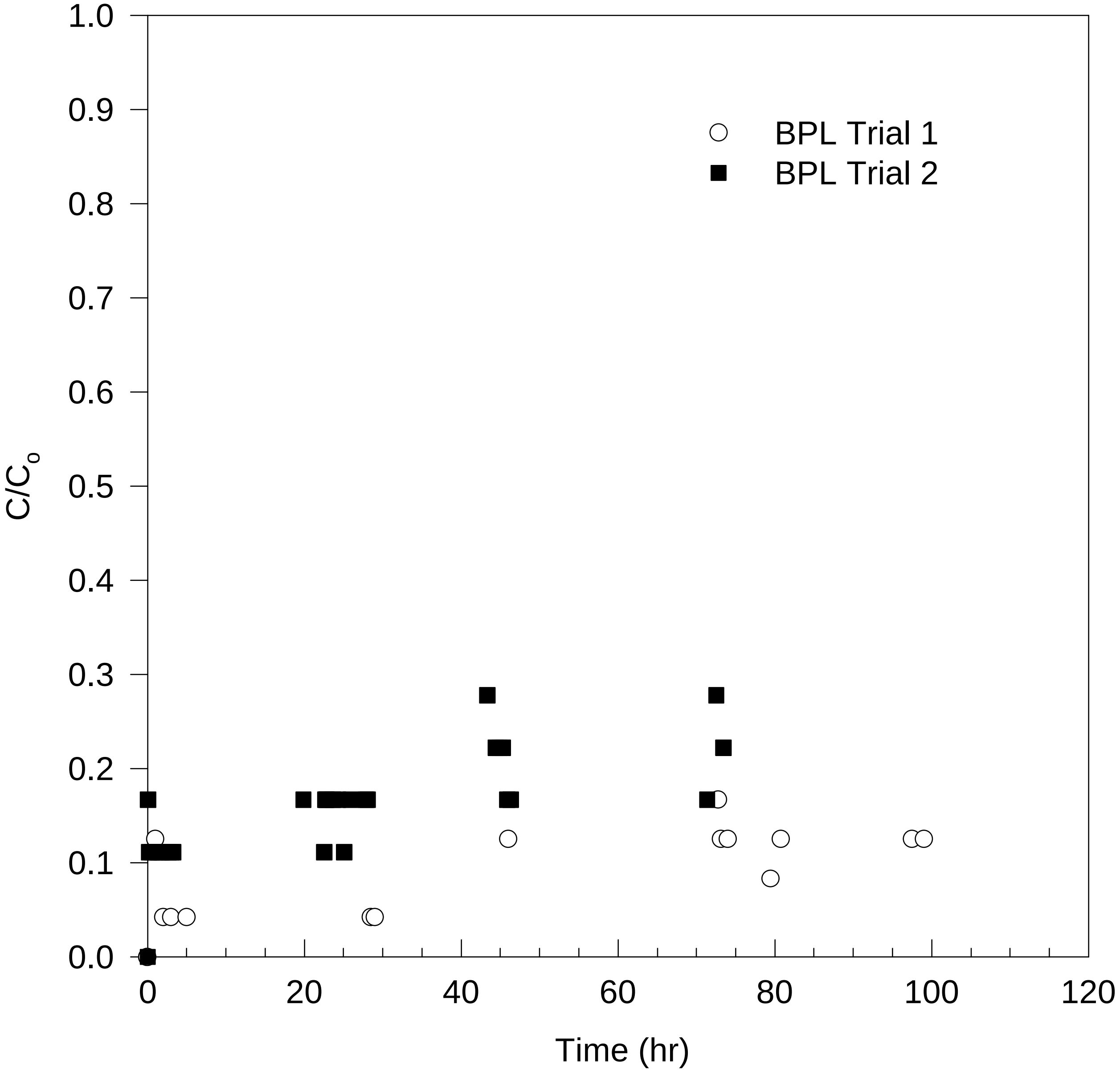

Figure 5 Mercury Breakthrough of BPL in Simulated Flue Gas Atmosphere

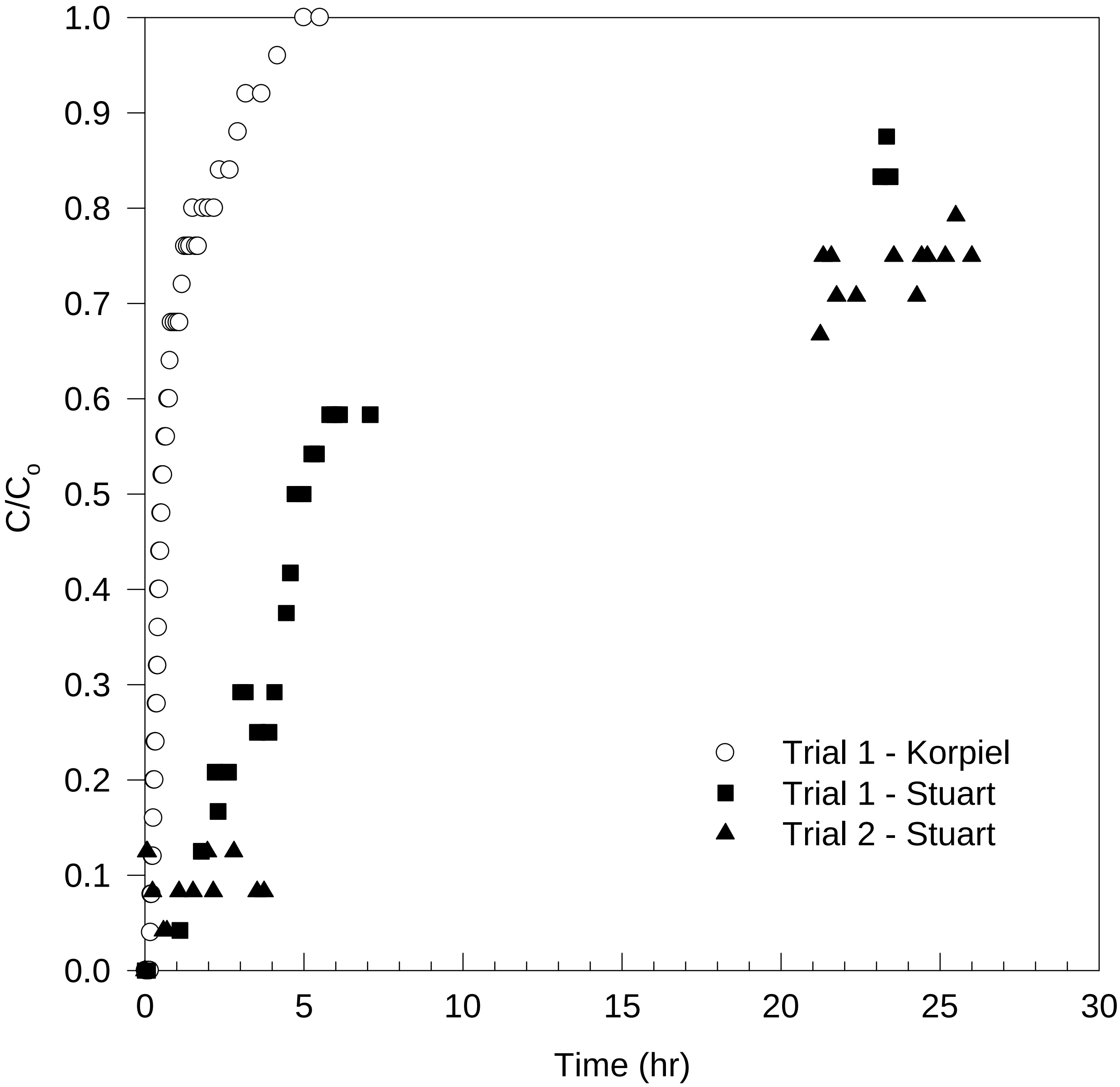

Figure 6 Mercury Breakthrough of BPL1 in a Nitrogen Atmosphere

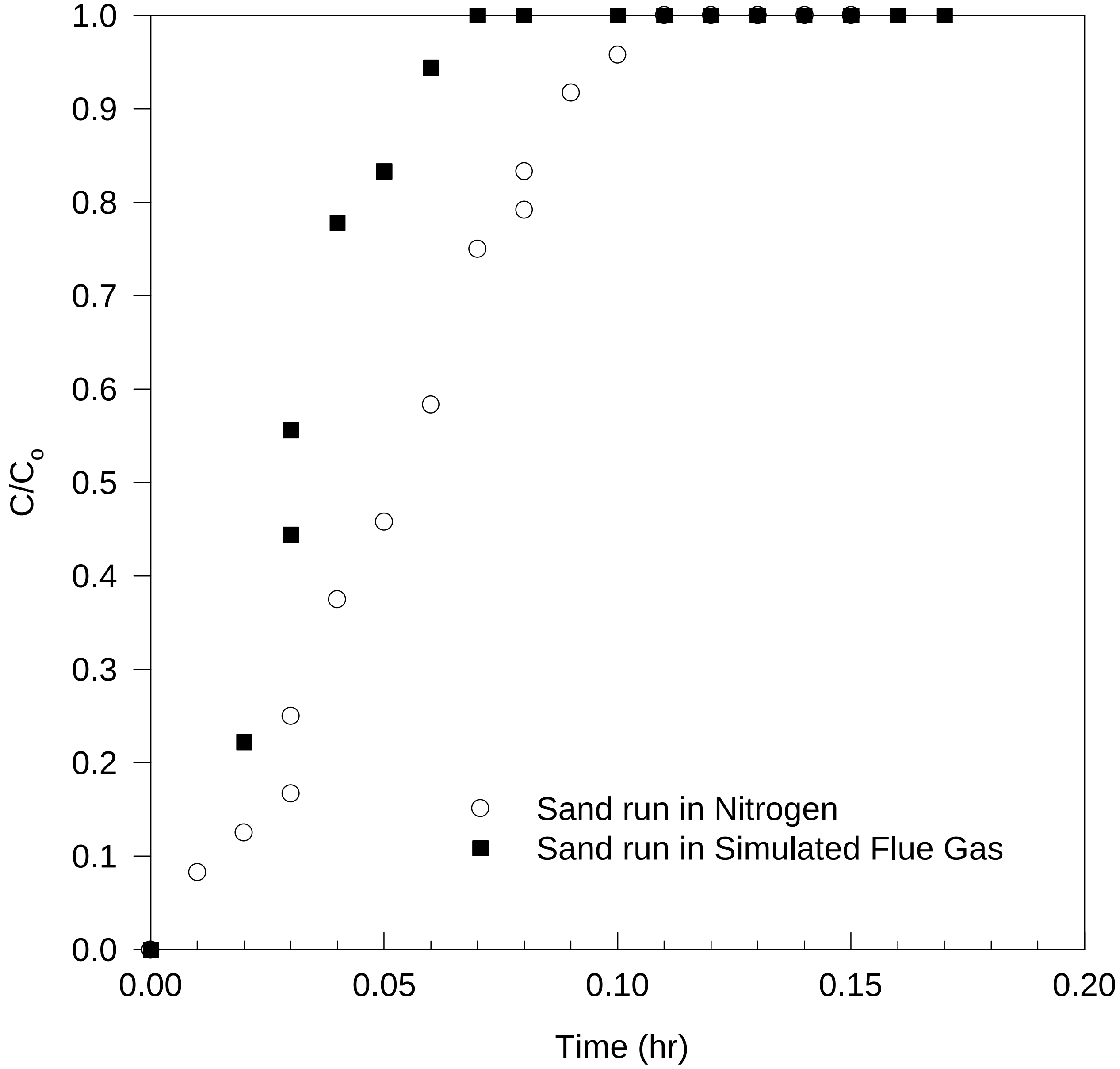

Figure 7 Mercury Uptake by Sand in Nitrogen and Simulated Flue Gas

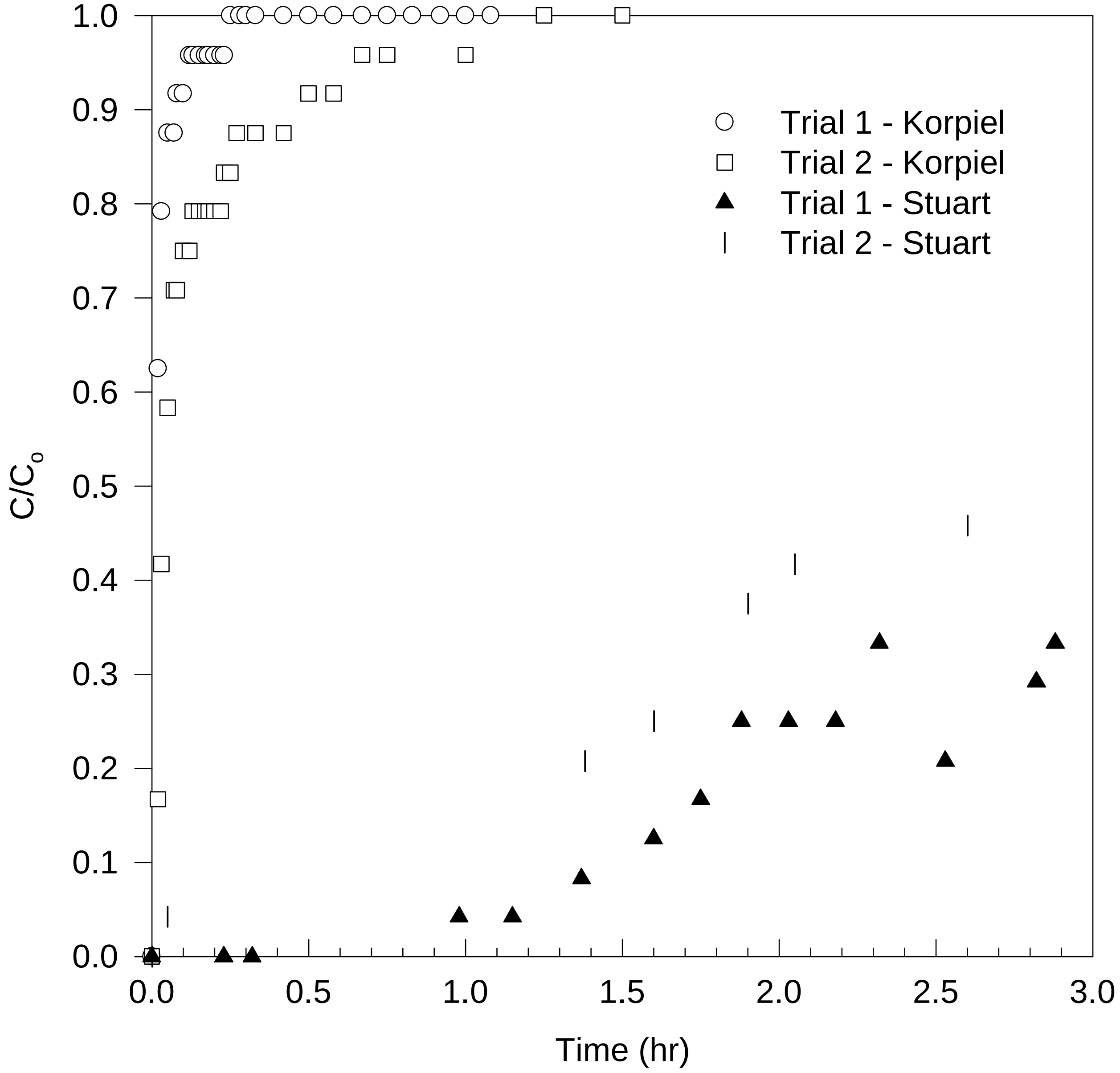

Figure 8 Mercury Breakthrough in Nitrogen Atmosphere with BPL1 Sorbent

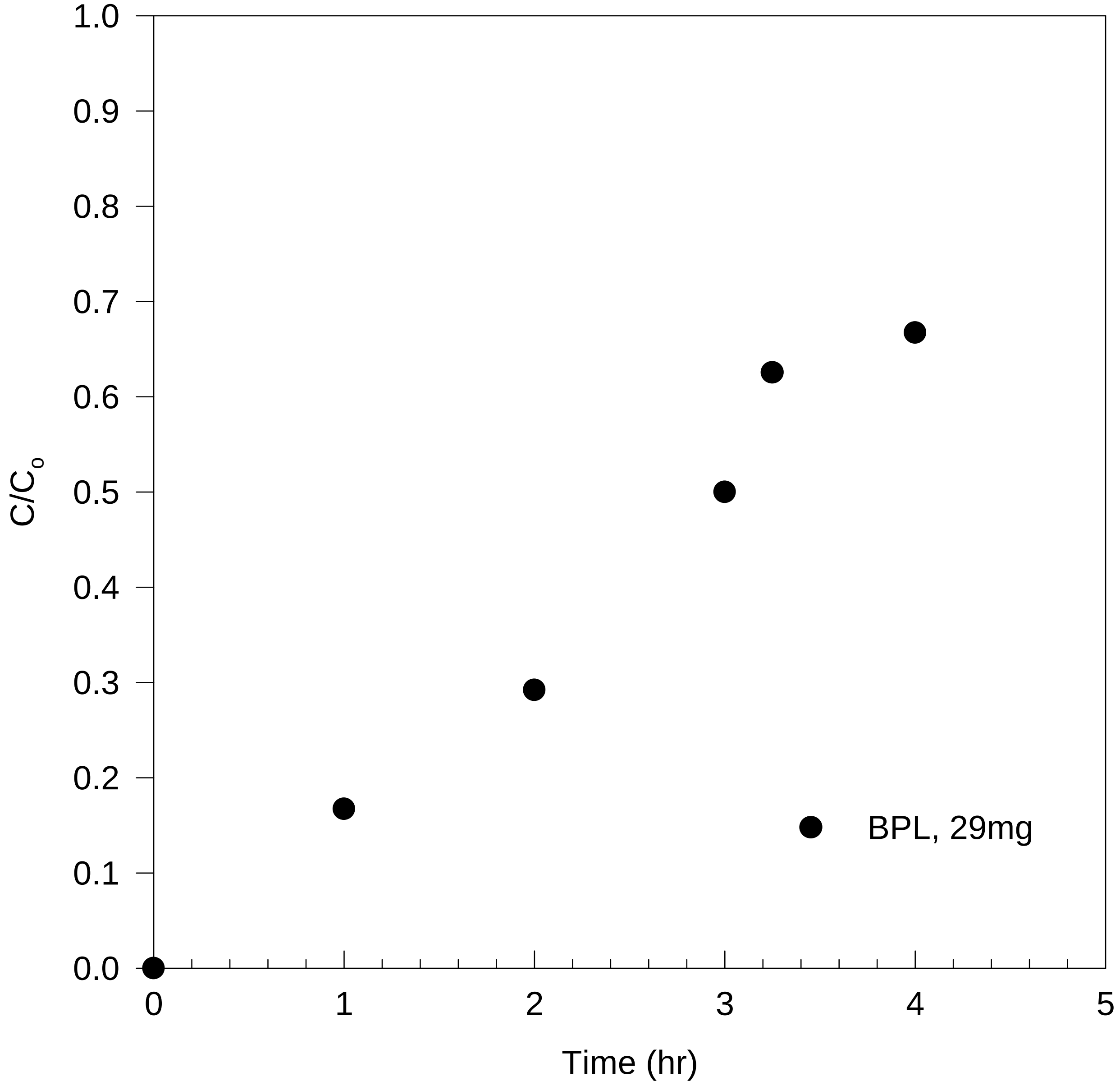

Figure 9 Effect of Carbon Mass on Mercury Uptake

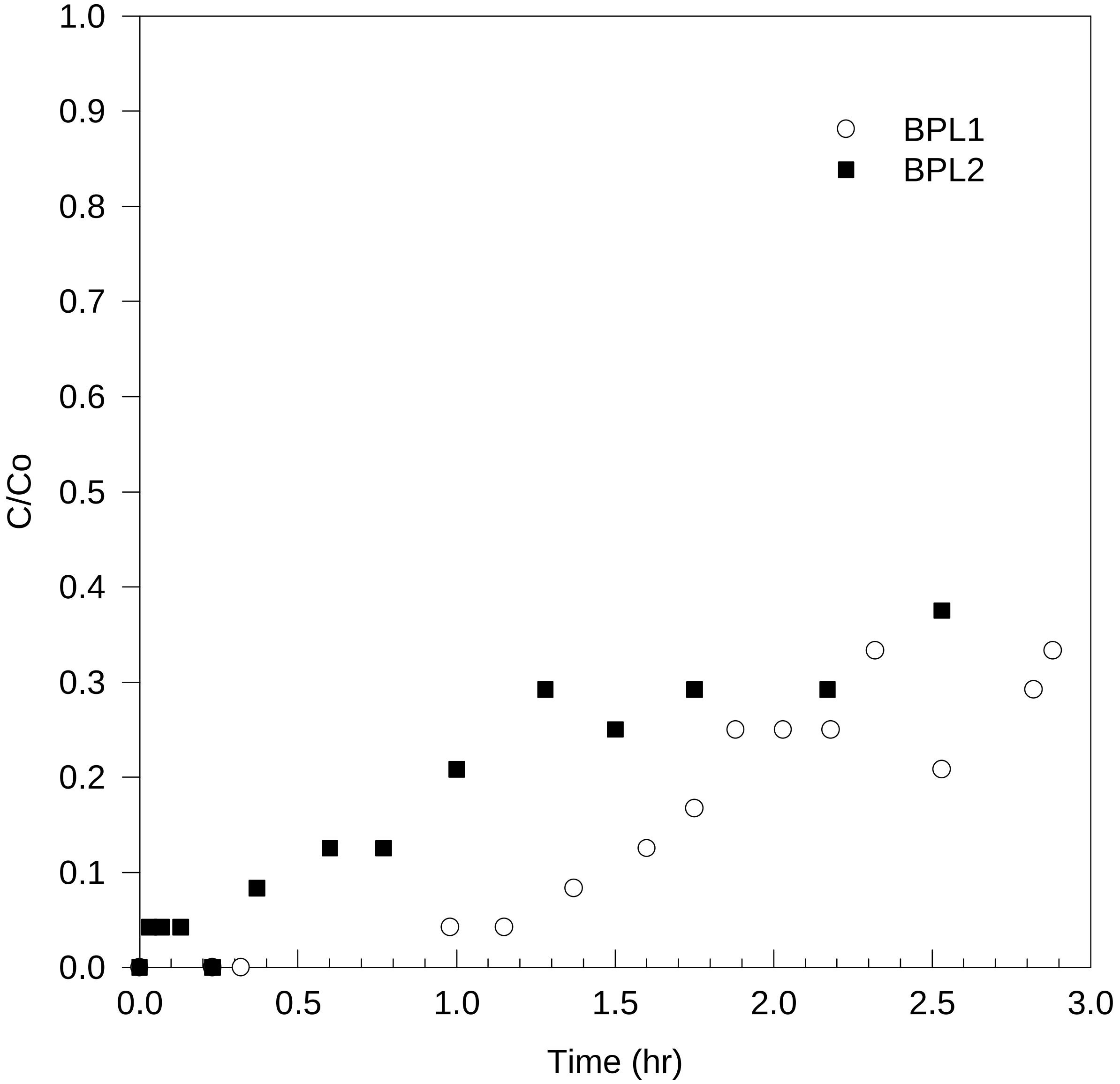

Figure 10 Comparison of BPL1 and BPL2 Performance in Nitrogen Atmosphere

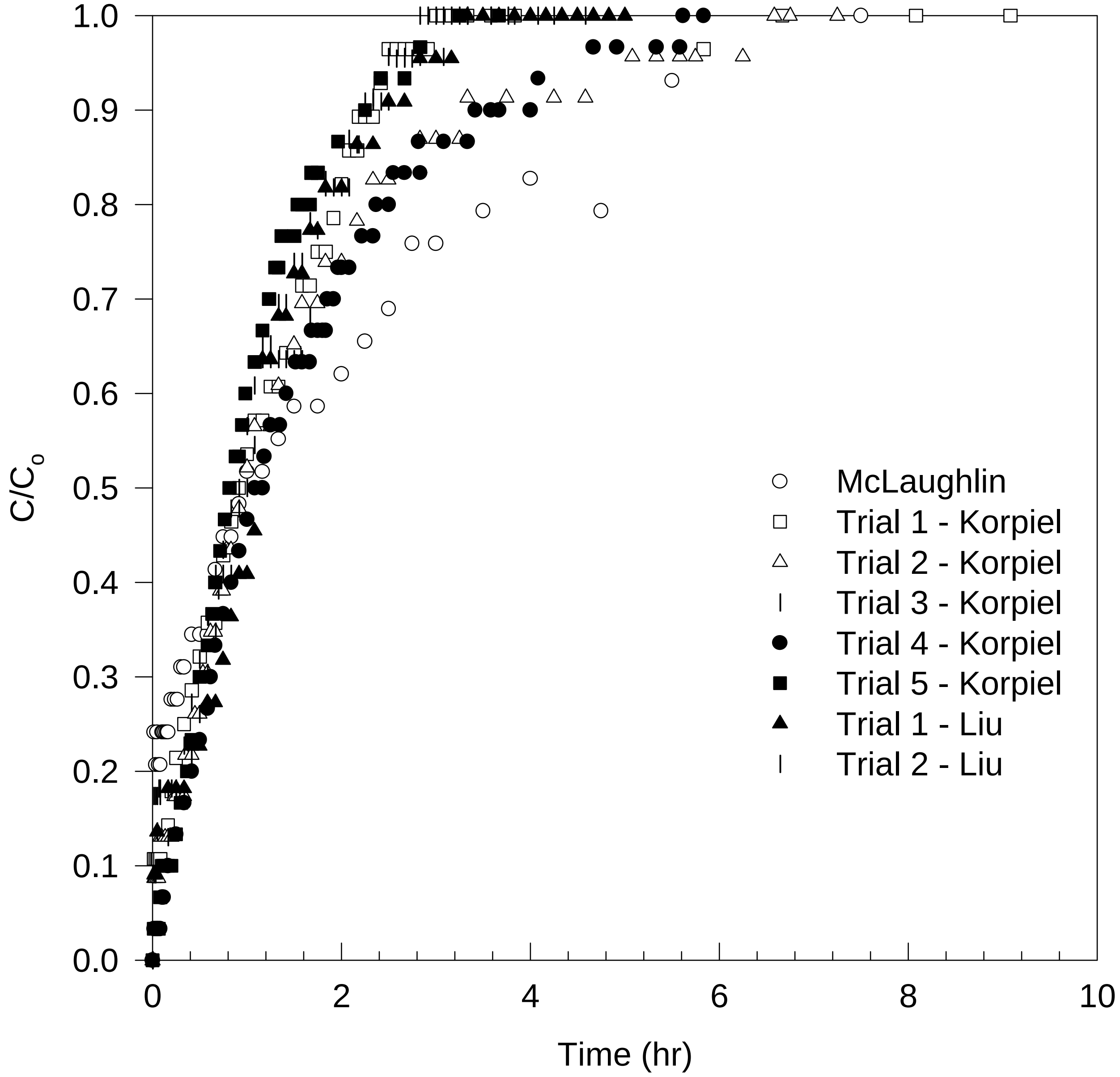

Figure 11 Mercury Breakthrough of HGR in Nitrogen Atmosphere Obtained by Previous Researchers

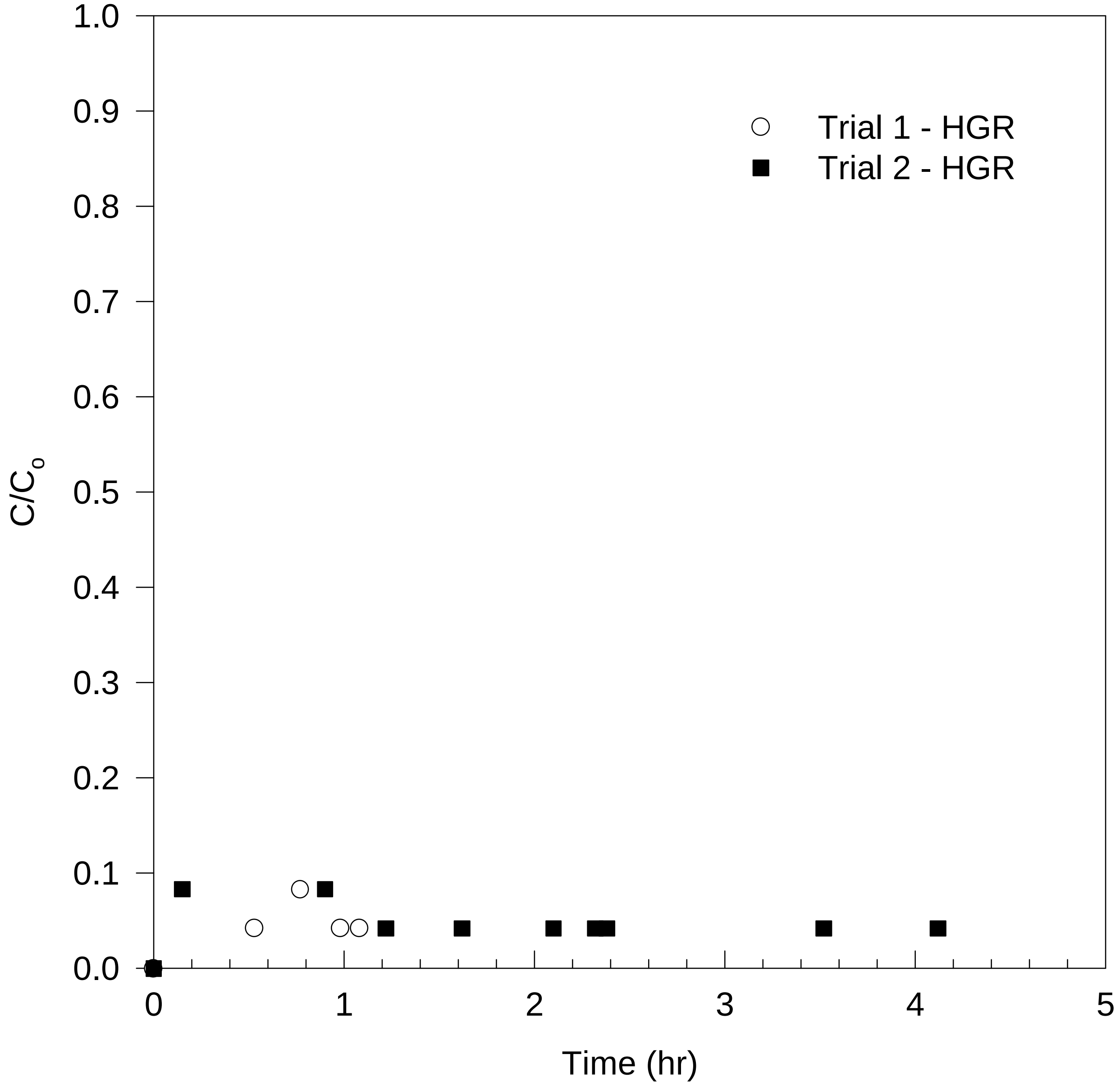

Figure 12 Mercury Breakthrough of HGR in Nitrogen Atmosphere

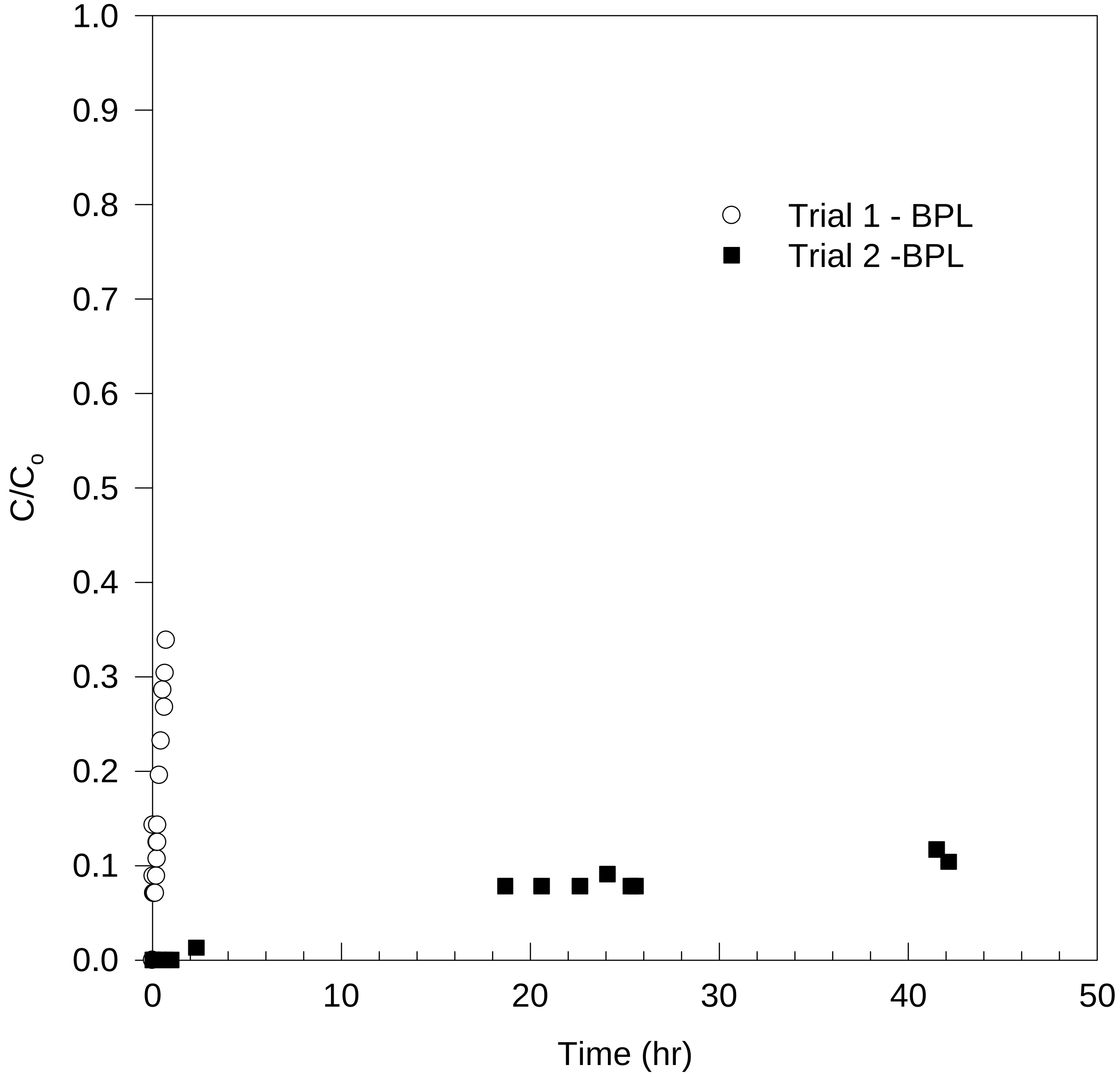

Figure 13 BPL Experiments in a Nitrogen Atmosphere Conducted in a Larger Column

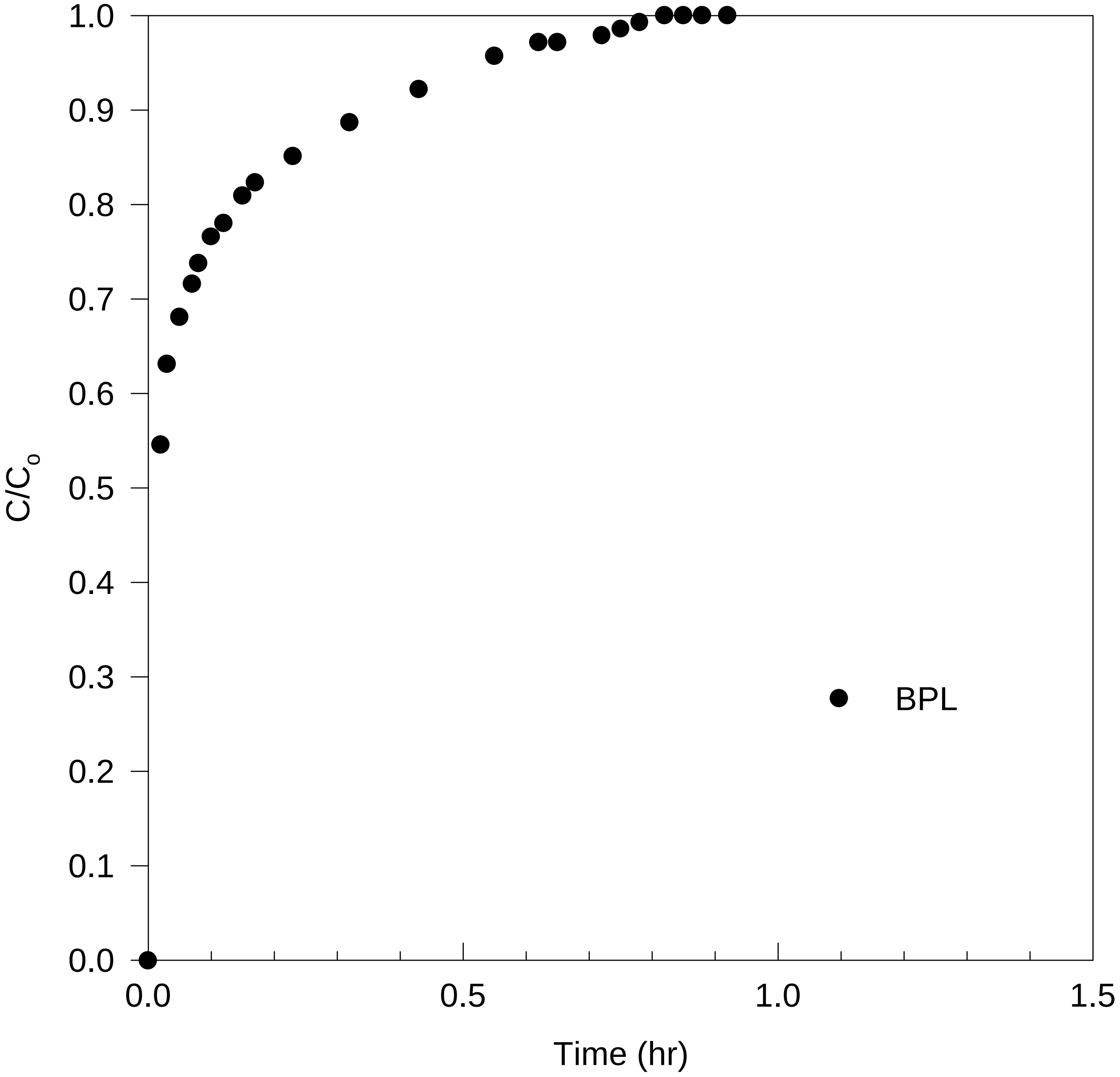

Figure 14 BPL Experiment in a Nitrogen Atmosphere with Inlet Mercury Concentration of 300 μg/m^3 and a Carbon Mass of 30 mg

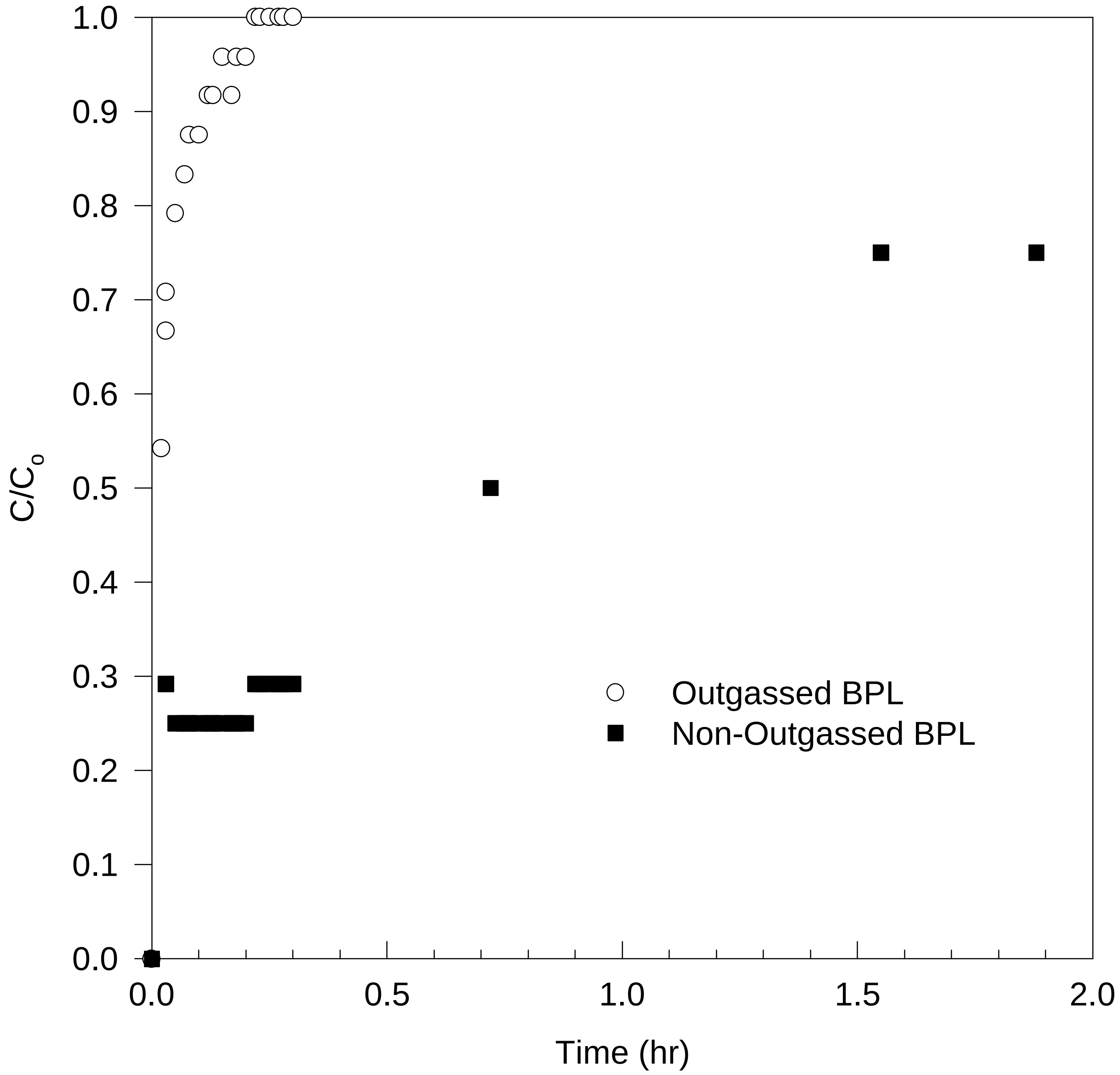

Figure 15 Comparing Performance of Outgassed and Non-Outgassed Sorbents in Nitrogen Atmosphere

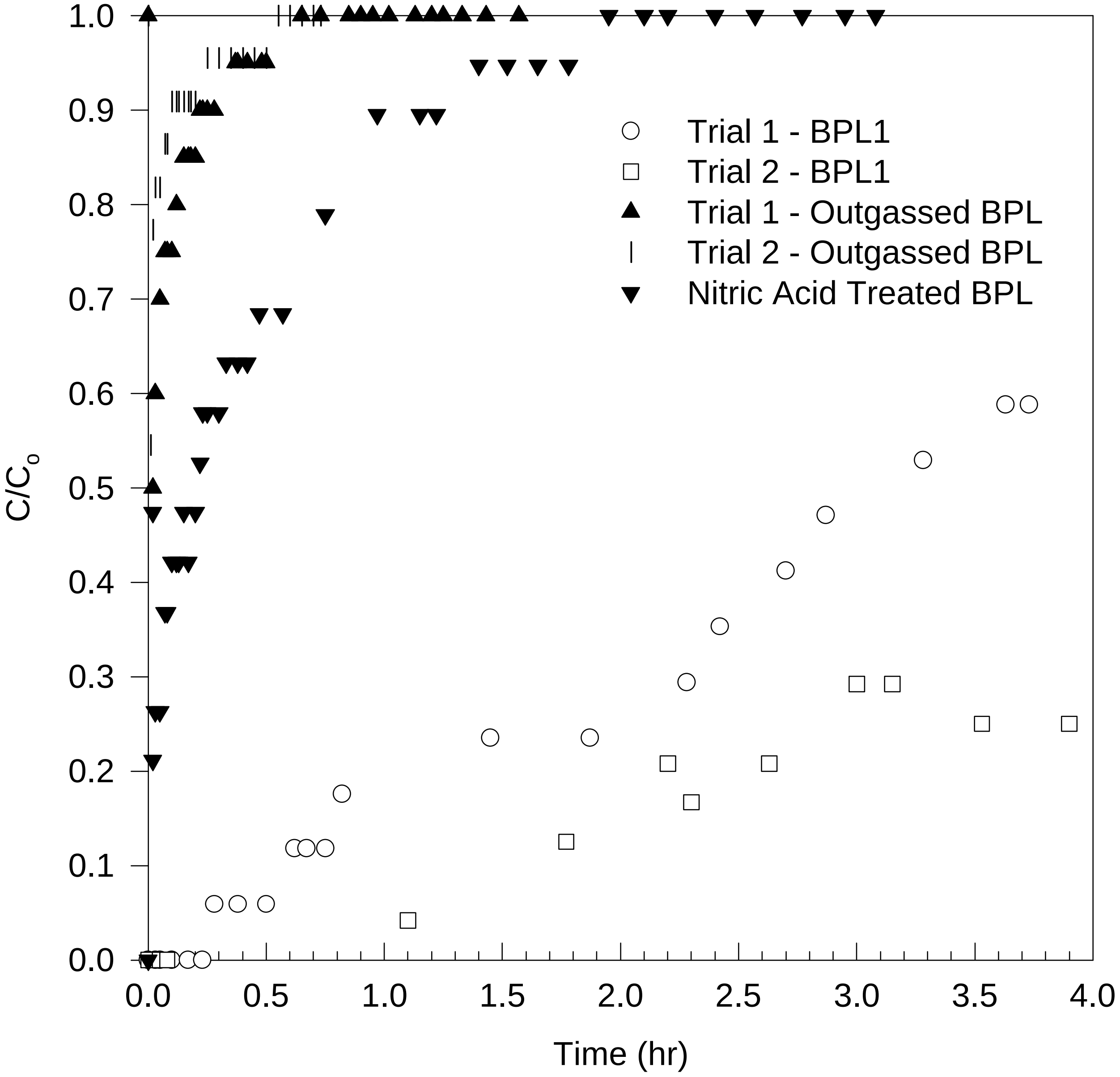

Figure 16 Mercury Breakthrough in Nitrogen Atmosphere from Adsorber Charged with Different BPL Samples

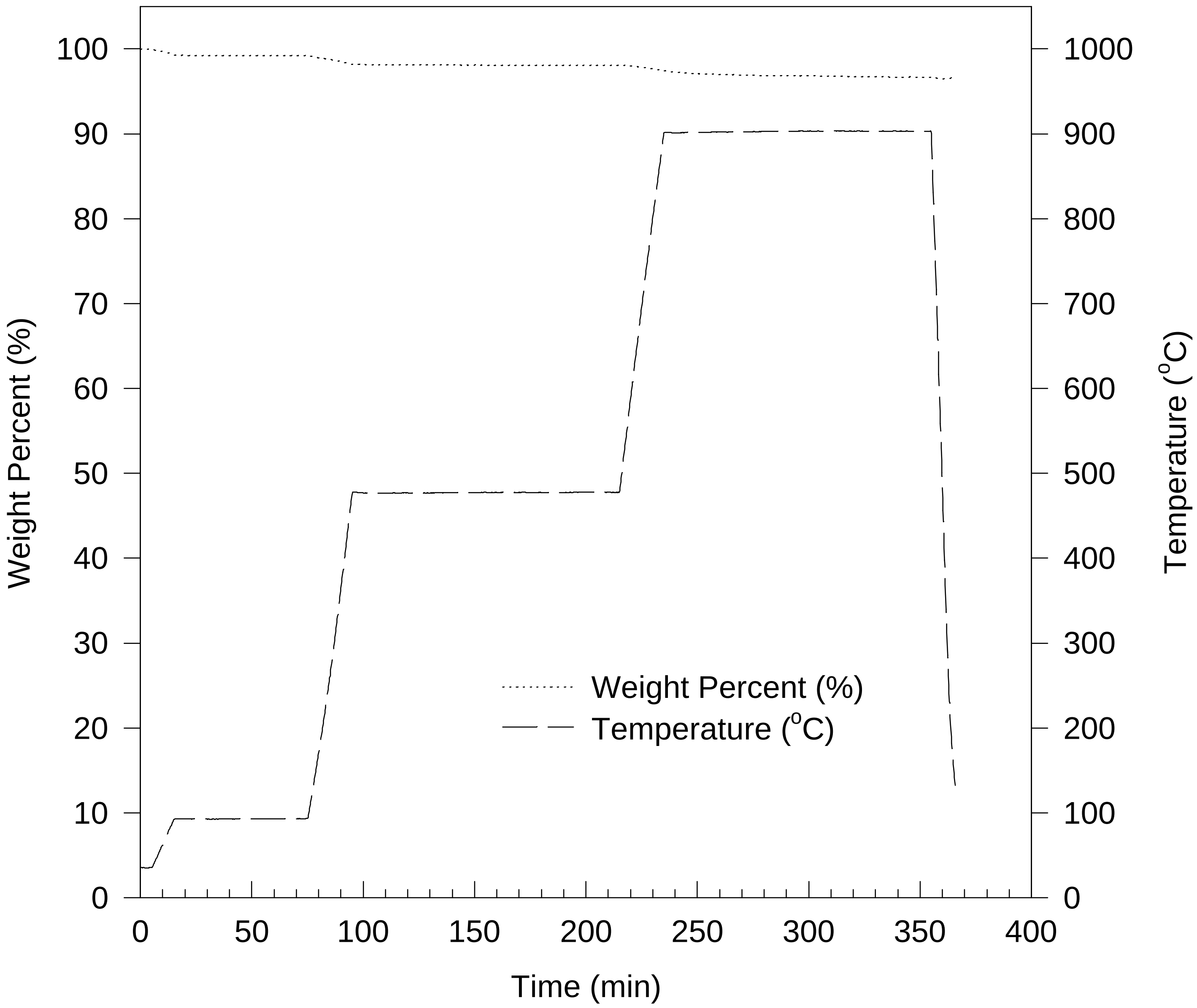

Figure 17 Thermogravimetric Analysis of BPL2 Carbon

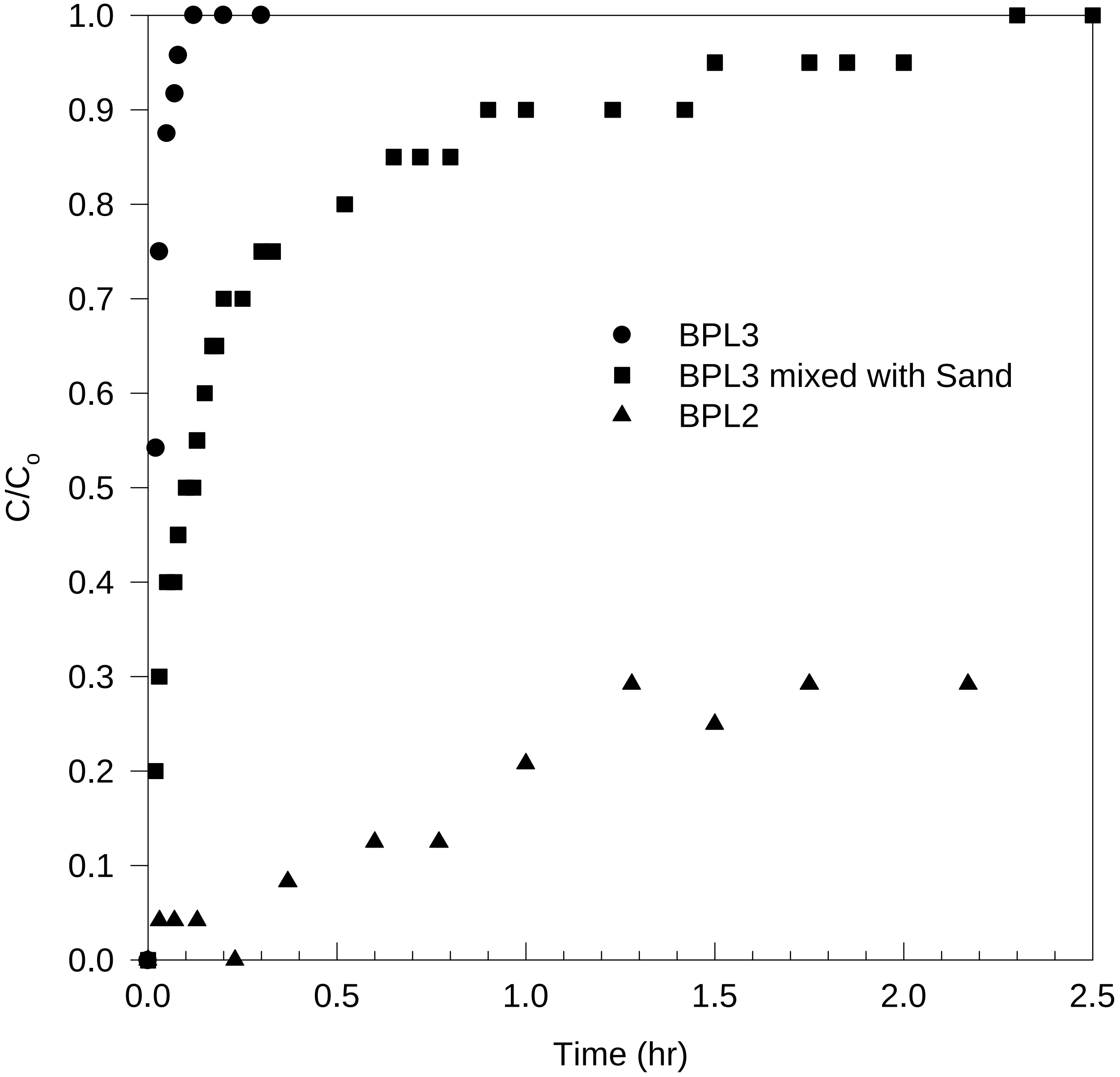

Figure 18 Comparison of BPL2 and BPL3 Performance in Nitrogen Atmosphere

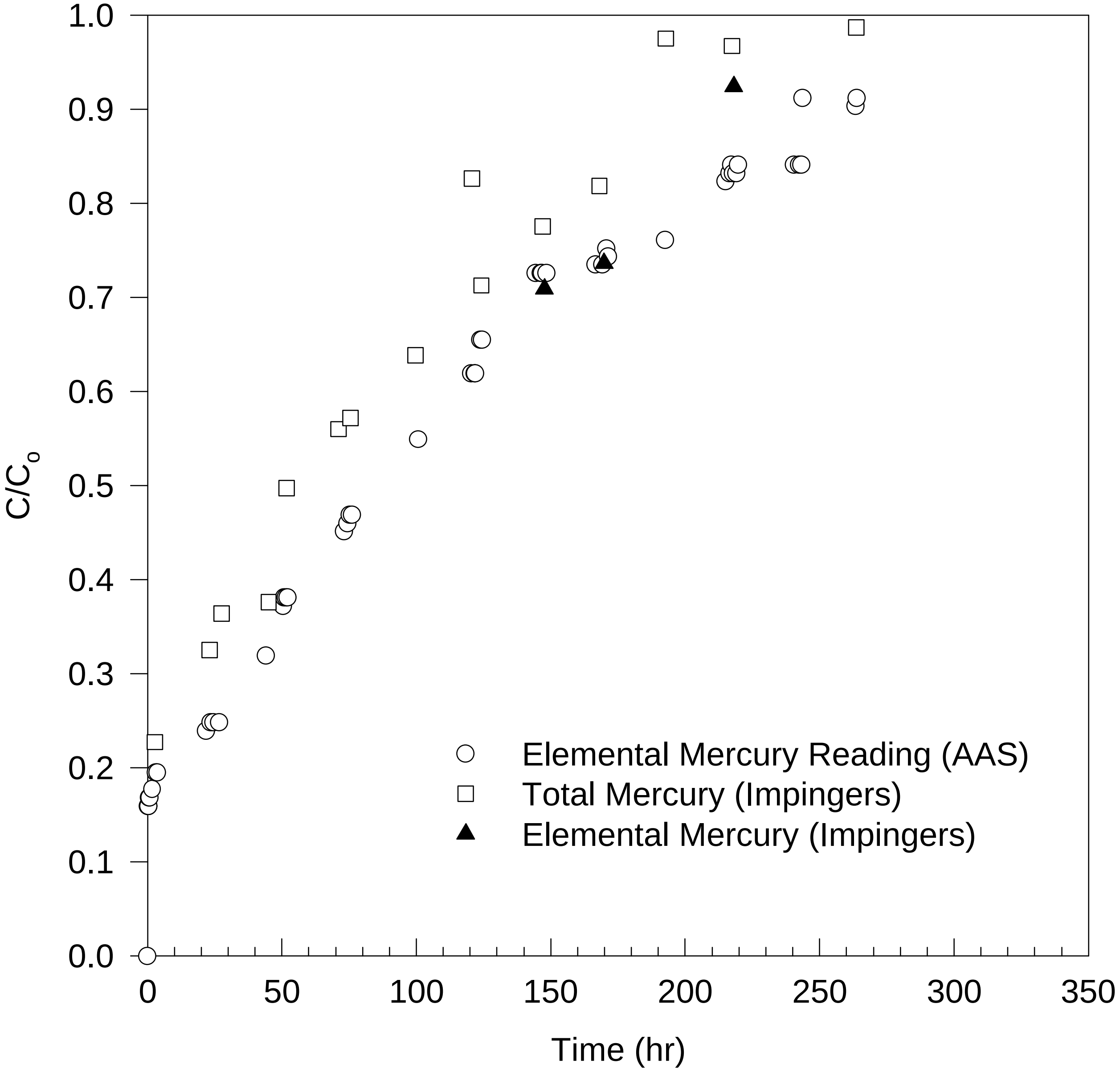

Figure 19 Mercury Breakthrough of BPL in a Simulated Flue Gas

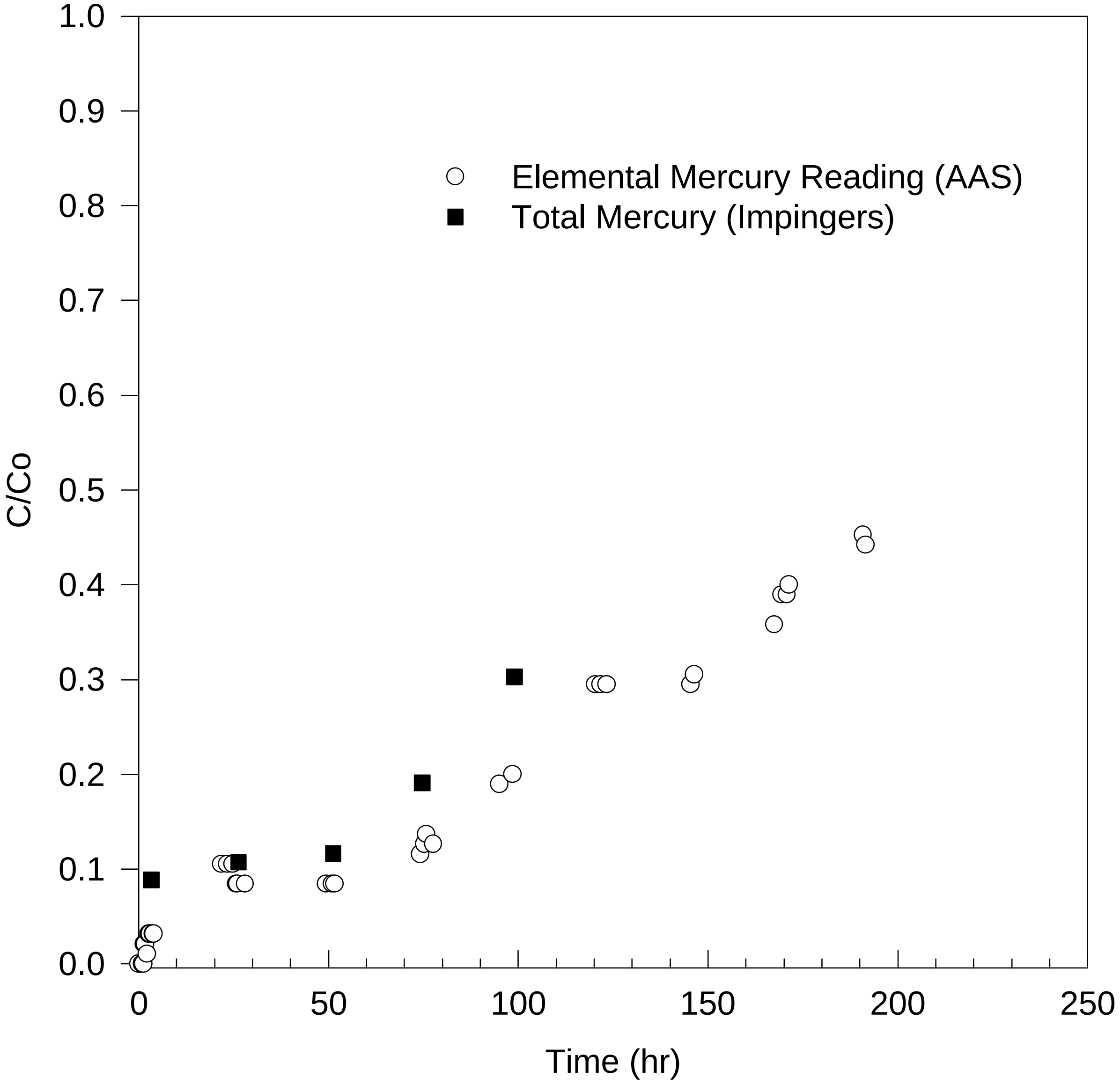

Figure 20 Mercury Breakthrough of FGD Carbon in a Simulated Flue Gas

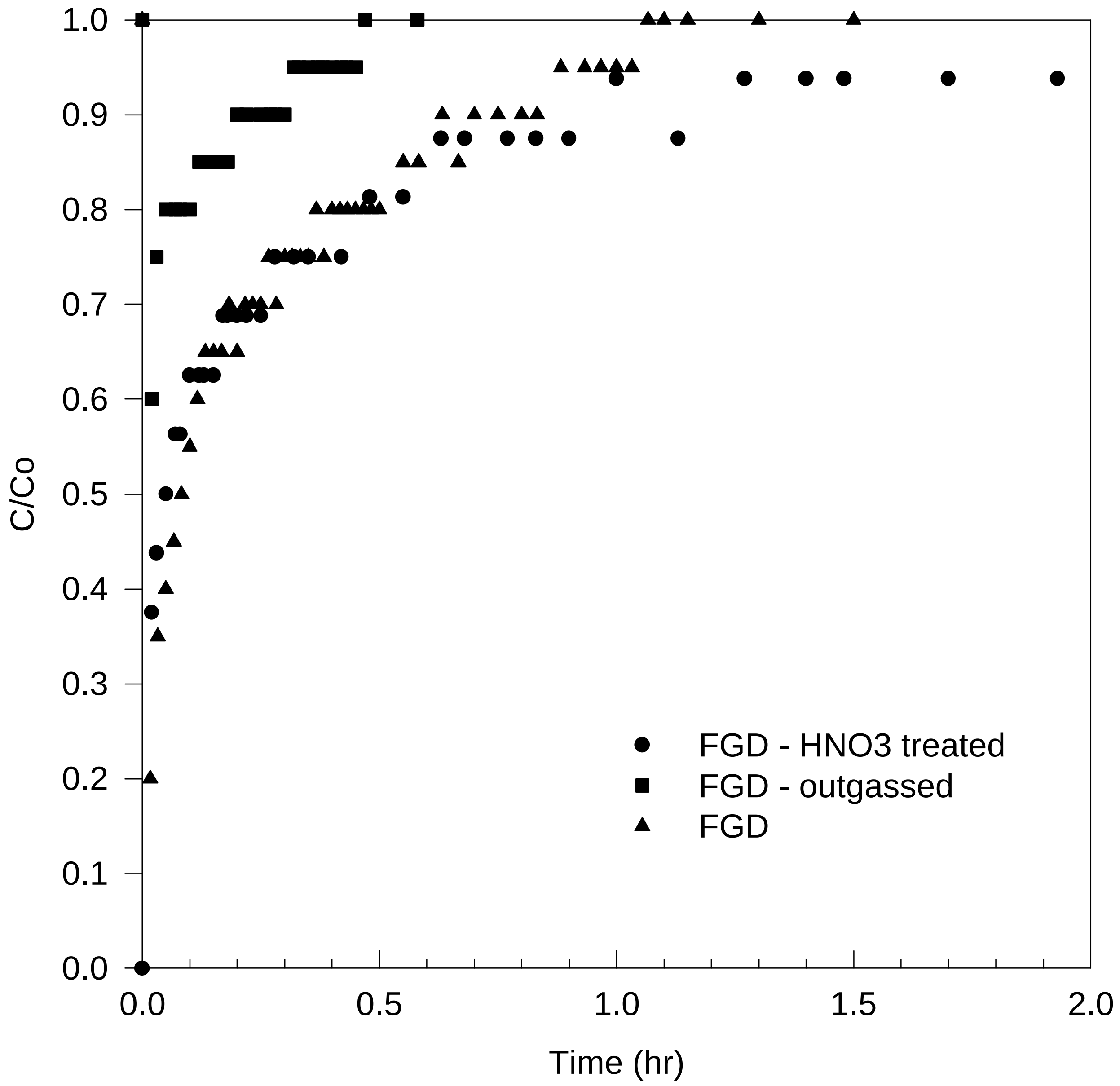

Figure 21 Mercury Breakthrough in Nitrogen Atmosphere from Adsorber Charged with Different FGD Samples

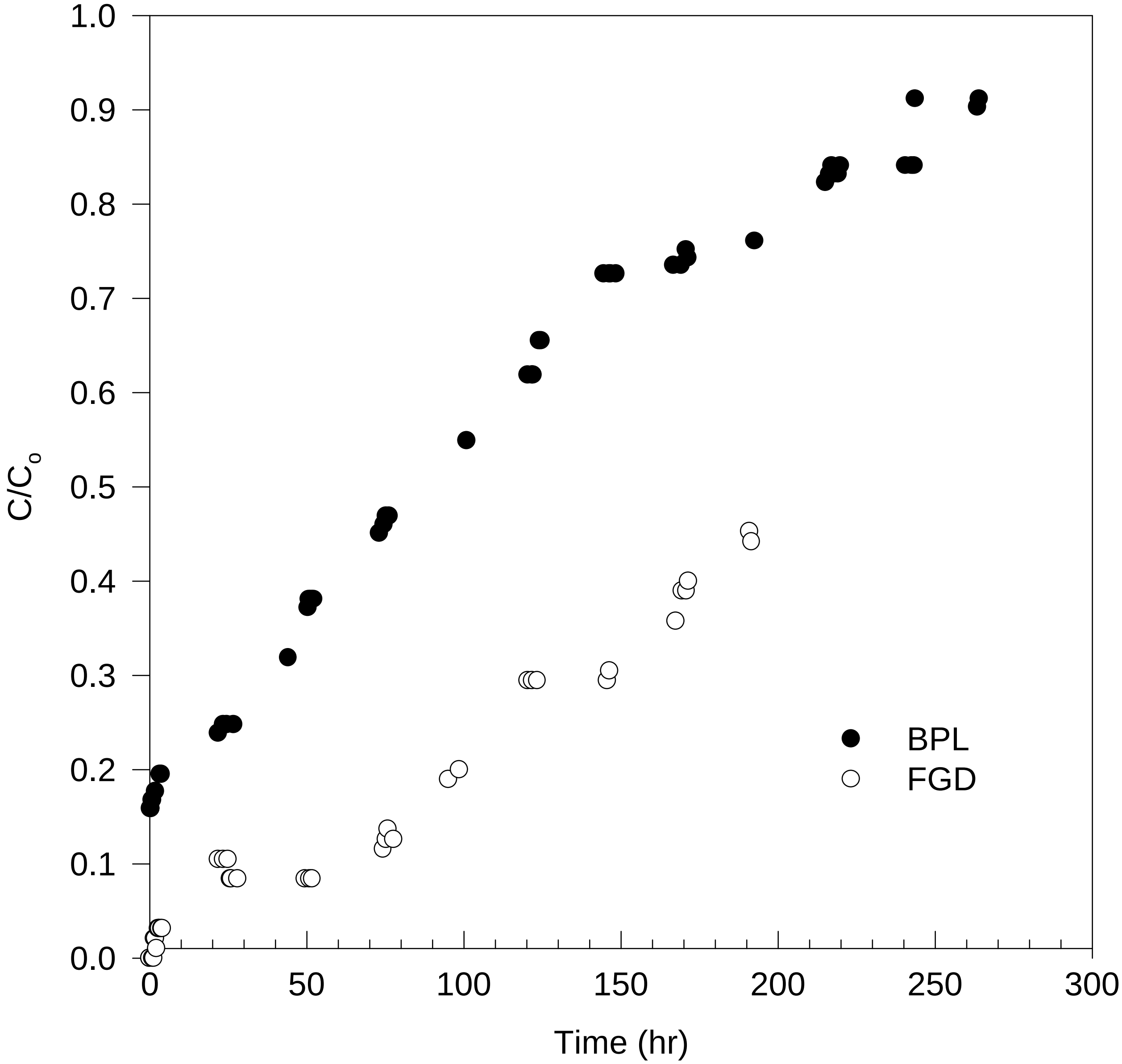

Figure 22 Comparison of Elemental Mercury Breakthrough from BPL and FGD Adsorbers in Simulated Flue Gas

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Huggins, F.E., Huffman, Gerald P., Dunham, Grant E., Senior, Constance L., "XAFS Examination of Mercury Sorption on Three Activated Carbons," Energy & Fuels, Vol. 13, (1999), pp. 114-121.

2. University of North Dakota Energy & Environmental Center, "EPA Decision Directs Mercury Research," Center for Air Toxic Metals Newsletter, Vol. 7, Issue 1 (2000).

3. Billings, C.E., Sacco, A. M., Matson, W. R., Griffin, R. M., Coniglio, W. R., Harley, R. A., "Mercury Balance on A Large Pulverized Coal-Fired Furnace," Journal of the Air Pollution Control Association, Vol. 23, No. 9 (1973), pp. 773-777.

4. Chu, P., Porcella, D. B., "Mercury Stack Emissions from U.S. Electric Utility Power Plants," Water, Air and Soil Pollution, Vol. 80, (1995), pp. 135-144.

5. Kaakinen, J.W., Jorden, R. M., Lawasani, M. H., West, R. E., "Trace Element Behavior in A Coal-fired Power Plant," Environmental Science and Technology, Vol. 9, No. 9 (1975), pp. 862-869.

6. Klein, D.H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W. Q., Lyon, W. S., Ogle, J. C., Talmi, Y., Van Hook, R. I., Bolton, N., "Pathways of Thirty-Seven Trace Elements Through Coal-Fired Power Plant," Environmental Science and Technology, Vol. 9, No. 10 (1975), pp. 973-979.

7. Chang, R.and.Offen, G., "Mercury Emission Control Technologies: An EPRI Synopsis," Power Engineering, Vol. 99, No. 11 (1995), pp. 51-57.

8. Crockett, A.B., and Kinnison, R. R., "Mercury Residues in Soil around A Large Coal-Fired Power Plant," Environmental Science and Technology, Vol. 13, No. 6 (1979), pp. 712-715.

9. Lindberg, S.E., "Mercury Partitioning in A Power Plant Plume and Its Influence on Atmospheric Removal Mechanisms," Atmospheric Environment, Vol. 14, (1980), pp. 227-231.

10. Proceedings of the Pittsburgh Coal Conference, Pittsburgh, PA, Sept. 12-16, 1994, "Carbon Sorption of Trace Mercury Species, by B. C. Young, S. J. Miller, and D. L. Laudal" (Pittsburgh, 1994), pp. 575-580.

11. Meij, R., "The Fate of Mercury in Coal-Fired Power Plants and the Influence of Wet Flue-Gas Desulfurization," Water, Air, and Soil Pollution, Vol. 56, (1991), pp. 21-33.

12. DeVito, M.S., and Rosenhoover, W.A., "Flue Gas Mercury and Speciation Studies at Coal-Fired Utilities Equipped with Wet Scrubbers," (Library, Pa: CONSOL Inc.,undated), unpublished.

13. Lockeretz, W., "Deposition of Airborne Mercury near Point Sources," Water, Air and Soil Pollution, Vol. 3, (1974), pp. 179-193.

14. Klein, D.H., and Russell, P., "Heavy Metals: Fallout around A Power Plant," Environment Science and Technology, Vol. 7, No. 4 (1973), pp. 357-358.

15. Hall, B., Schager, P., Lindqvist, Q., "Chemical Reactions of Mercury in Combustion Flue Gases," Water, Air, and Soil Pollution, Vol. 56, (1991), pp. 3-14.

16. Proceedings of the 1994 National Waste Processing Conference, Boston, MA, June 5-8, 1994, "Metals in MSW --- Where Are They and Where Do They Go in An Incinerator?, by H. G. Rigo, and A. J. Chandler," (New York: ASME, 1994), pp. 49-62.

17. Porcella, D.B. and Jermelov, A., "Global Mercury Pollution and the Role of Gold Mining An Overview," Water, Soil and Pollution, Vol. 97, (1997), pp. 205-207.

18. EPA, "Characterization of Products Containing Mercury in Municipal Solid Waste in the United States, 1970 to 2000," PB92-162596, 1992.

19. Proceedings of the 91st Annual Meeting & Exhibition of the Air and Waste Management Association, San Diego, CA, June 14-18, 1998, "Meeting the New Regulations for Medical Waste Incinerators - A Review of Current Technology, by W. P. Norris and R. G. Patterson," 98-RP108.01.

20. Pai, P., Heisler, S., Joshi, A., "An Emission for Regional Atmospheric Modeling of Mercury," Water, Air and Soil Pollution, Vol. 101, (1998), pp. 289-308.

21. Fukuzaki, N. and Ichikawa, Y., "Determination of Particulate Mercury in Air," Bunseki Kagaku, Vol. 33, (1984), pp. 178-182.

22. Kitamura, M., ed., Mercury, (Tokyo: Kodansha, 1976), pp. 99-100.

23. Nriagu, J.O., ed., "Economic Considerations in Controlling Mercury Pollution, by W.D. Watson, Jr.," The Biogeochemistry of Mercury in the Environment, (New York: Elsevier/North-Holland Inc.,1979), Chapter 3.

24. Shannon, J and Voldner, E. C., "Modeling Atmospheric Concentrations of Mercury and Deposition to the Great Lakes," Atmospheric Environment, Vol. 29, No. 14 (1995), pp. 1649-1661.

25. Otani, Y., Kanaoka, C., Usui, C., Matsui, S., Emi, H., "Adsorption of Mercury Vapor on Particles," Environmental Science and Technology, Vol. 20, (1986), pp. 735-738.

26. Metzger, M and Braun, H., "In-Situ Mercury Speciation in Flue Gas by Liquid and Solid Sorption Systems," Chemosphere, Vol. 16, No. 4 (1987), pp. 821-832.

27. Livengood, C.D., Huang, H. S., Mendelsohn, M. H., Wu, J. M., "Mercury Capture in Bench-Scale Adsorbers," (Argonne, IL: Argonne National Laboratory,undated), unpublished.

28. McLaughlin, J.B., "Activated Carbon Adsorption for the Removal of Mercury from Flue Gas Emissions," (unpublished M.S. Thesis, Department of Civil and Environmental Engineering, School of Engineering, University of Pittsburgh, Pittsburgh, PA, 1995).

29. Korpiel, J.A., "Effect of Sulfur Impregnation Method on Activated Carbon Adsorption of Vapor-Phase Mercury," (unpublished M.S. Thesis, Department of Civil and Environmental Engineering, School of Engineering, University of Pittsburgh, Pittsburgh, PA, 1996).

30. Lowe, P.A. and St. John, B., "Activated Carbon Injection to Control Flue Gas Mercury Emissions," (Potomac, MD: INTECH, Inc,undated), unpublished.

31. Proceedings of the Solid Waste Management: Thermal Treatment and Waste-to-Energy Technologies, Washington, DC, April 18-21, 1995, "Mercury Control by Injection of Activated Carbon and Calcium-Based Sorbents, by S. V. Krishnan, B. K. Gullett, and W. Jozewicz," (U.S. EPA/AEERL and AWMA, 1995).

32. Serre, S.D., and Silcox, Geoffrey D., "Adsorption of Elemental Mercury on the Residual Carbon in Coal Fly Ash," Ind. Eng. Chem. Res, Vol. 39, No. 6 (2000), pp. 1723-1730.

33. Proceedings of the 90th Annual Meeting & Exhibition on the Air and Waste Management Association, Toronto, Ontario, Canada, July 8-13, 1993, "Mercury Vapor Removal from Simulated Flue Gas with Illinois Coal-Derived Activated Carbon, by Hsi, H., Massoud, R. A., Rood, M. J., Chen, S.," 97-RA79B.03.

34. Hsi, H.-C., Chen, Shiaoguo, Rostam-Abadi, Massoud, Rood, Mark J., Richardson, Carl F., Carey, Todd R., Chang, Ramsay, "Preperation and Evaluation of Coal-Derived Activated Carbons for Removal of Mercury Vapor from Simulated Coal Combustion Flue Gases," Energy & Fuels, Vol. 12, No. 6 (1998), pp. 1061-1070.

35. Sinha, R.K. and Walker, P. L., "Removal of Mercury by Sulfurized Carbons," Carbon, Vol. 10, (1972), pp. 754-756.

36. Otani, Y., Emi, H., Kanaoka, C., Uchijima, I., Nishino, H., "Removal of Mercury Vapor from Air with Sulfur-Impregnated Adsorbents," Environmental Science and Technology, Vol. 22, (1988), pp. 708-711.

37. Matsumura, Y., "Adsorption of Mercury Vapor on the Surface of Activated Carbons Modified by Oxidation or Iodization," Atmospheric Environment, Vol. 8, (1974), pp. 1321-1327.

38. Teller, A.J. and Quimby, J. M., "Mercury Removal form Incineration Flue Gas," (Somerville, NJ: Air and Water Technologies, Co, 1991), unpublished.

39. Liu, W., "Development of Novel Adsorbents for the Control of Vapor-Phase Mercury Emissions," (unpublished PhD Thesis, Department of Civil and Environmental Engineering, School of Engineering, University of Pittsburgh, Pittsburgh, PA, 1998).

40. Carey, T.R., Richardson, Carl F., Chang, Ramsay, Meserole, Frank, Rostam-Abadi, Massoud, Chen, Scott, "Assessing Sorbent Injection Mercury Control Effectiveness," Prepared for presentation at the 1999 AIChE Spring National Meeting, Houston, TX, March 14-18, 1999, unpublished.

41. Ghorishi, S.B., Singer, Carl F., Jozewicz, Wojciech S., Sedman, Charles B., Srivastava, Ravi K., "Simultaneous Control of Hg^0, SO_2, and NO_x by Novel Oxidized Calcium-Based Sorbents," (Durham, NC: ARCADIS G&M Inc, undated), unpublished.

42. Granite, E.J., Pennline, Henry W., Hargis, Richard A., "Novel Sorbents for Mercury Removal from Flue Gas," Ind. Eng. Chem. Res., Vol. 39, No. 4 (2000), pp. 1020-1029.

43. Proceedings of the 90th Annual Meeting & Exhibition on the Air and Waste Management Association, Toronto, Ontario, Canada, July 8-13, 1993, "Factors Affecting Mercury Control in Utility Flue Gas Using Sorbent Injection, by Carley, T. R., Hargrove, jr., W. O., Richrdson, C. F., Chang, R., Meserole, F. B," pre-printed, 97-WA72A.05.

44. Proceedings of the 87th Annual Meeting and Exhibition of the Air and Waste Management Association, Cincinnati, OH, June 19-24, 1994, "Experimental Evaluation of Sorbents for the Capture of Mercury in Flue Gases, by C. D. Livengood, H. S. Huang, and J. M. Wu," preprinted, 14 p.

45. Proceedings of the 1993 International Conference on Managing Hazardous Air Pollutions, Washington, DC, July 13-15, 1993, "Bench-Scale Investigation of Mechanisms of Elemental Mercury Capture by Activated Carbon, by W. Jozewicz and B.K. Gullett," (Electric Power Research Institute, 1993), pp. VII-85 - VII-99.

46. Chang, M., "Kinetics of Vapor-Phase Mercury Uptake by Virgin and Sulfur Impregnated Activated Carbons," (unpublished M.S. Thesis, Department of Civil and Environmental Engineering, School of Engineering, University of Pittsburgh, Pittsburgh, PA, 1996).

47. Li, Y.H., Lee, C.W., Gullett, B.K, "The Effect of Activated Carbon Surface Moisture on Low Temperature Mercury Adsorption," (Research Triangle Park, NC: U.S. Environmental Protection Agency, National Risk Management Research Laboratory, undated), unpublished.

48. Proceedings of the Air & Waste Management Association's 90th Annual Meeting and Exhibition, Toronto, Ontario, Canada, "A Fundamental Study of Mercury Partitioning in Coal Fired Power Plant Flue Gas, by C. L. Senior, L. E. Bool III, G. P. Huffman, F. E. Huggins, N. Shah, A. Sarofim, I. Olmez, and T. Zeng," 97-WP72B.08.

49. Miller, S.J., Dunham, Grant E., Olson, Edwin S., Brown, Thomas D., "Mercury Sorbent Development for Coal-Fired Boilers," (Grand Forks, ND: Energy & Environmental Research Center, University of North Dakota, undated), unpublished.

50. Ghorishi, S.B., Sedman, Charles B., "Low Concentration Mercury Sorption Mechanisms and Control by Calcium-Based Sorbents: Application in Coal-Fired Processes," Journal of the Air & Waste Management Association, Vol. 48, (1998), pp. 1191-1198.

51. Proceedings of the 1993 International Municipal Waste Combustion Conference, Williamsburgh, Virginia, March 1993, "Mercury Control Technologies for MWC's; The Unanswered Questions, by C.S. Krivanek, III," pp. 824-840.

52. Teng, H., Suuberg, E. M., Calo, J. M., "Studies of the Reduction of Nitric Oxide by Carbon: The NO-Carbon Gasification Reaction," Energy and Fuels, Vol. 6, (1992), pp. 398-406.

53. Galbreath, K.C., Zygarlicke, Christopher J., "Mercury Speciation in Coal Combustion and Gasification Flue Gases," Environmental Science & Technology, Vol. 30, No. 8 (1996), pp. 2421-2426.

54. Sliger, R.N., Going, David J., Kramlich, John C., "Kinetic Investigation of the High-Temperature Oxidation of Mercury by Chlorine Species," Western State Section/The Combustion Institute, Fall 1998 Meeting, Seattle, Washington, October 26-27, 1998.

55. Hall, B., Lindqvist, Oliver, Ljungstrom, Evert, "Mercury Chemistry in Simulated Flue Gases Related to Waste Incineration Conditions," Environmental Science & Technology, Vol. 24, No. 1 (1990), pp. 108-111.

56. Dunham, G.E., Miller, Stanley J., Chang, Ramsay, Bergman, Perry, "Mercury Capture by an Activated Carbon in a Fixed-Bed Bench-Scale System," Environmental Progress, Vol. 17, No. 3 (1998), pp. 203-208.

57. Proceedings of the Air & Waste Management Association, Nashville, TN, June 23-28, 1996, "Mercury Speciation: A Comparison between EPA Method 29 and Other Sampling Methods, by Laudal, Dennis L., Heidt, Marlys K., Brown, Thomas D., Nott, Babu R., Prestbo, Eric P.," 96-WA64A.04.

58. Proceedings of the Air & Waste Management Association's 90th Annual Meeting and Exhibition, Toronto, Ontario, Canada, June 8-13, 1997, "Enhanced Control of Mercury Emissions Through Modified Speciation, by Livengood, C. David, and Mendelsohn, Marshall H.," 97-WP72B.01.

59. Proceedings of the Seventh Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 11-15, 2000, "Photochemical Removal of Mercury from Flue Gas, by Granite, Evan J., Pennline, Henry W., Stanko, Dennis C.," 25-5.

60. Proceedings of the Seventh Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 11-15, 2000, "Development of a Process for Combined Removal of Mercury and Nitric Oxides from Flue Gas, by Mendelsohn, Marshall H., and Livengood, C. David."

61. Proceedings of the Air & Waste Management Association's 90th Annual Meeting and Exhibition, Toronto, Ontario, Canada, June 8-13, 1997, "Demonstration of Dry Carbon-Based Sorbent Injection for Mercury Control in Utility ESPs and Baghouses, by Sjostrom, Sharon, Smith, Justin, Hunt, Terry, Chang, Ramsay, Brown, Thomas D.," 97-WA72A.07.

62. Proceedings of the 91st Annual Meeting & Exhibition of the Air and Waste Management Association, San Diego, CA, June 14-18, 1998, "Preparation Methods and test Protocol for Mercury Sorbents, by Miller, Stanley J., Olson, Edwin S., Dunham, Grant E., and Sharma, Ramesh K.," 98-RA79B.07(A767).

63. Ghorishi, S.B., Singer, Carl F., Jozewicz, Wojciech S., Sedman, Charles B., Srivastava, Ravi K., "Simultaneous Control of Hg^0, SO_2, and NO_x by Novel Oxidized Calcium-Based Sorbents," (Durham, NC: ARCADIS G&M Inc, undated), unpublished.

64. Serre, S.D., Gullett, Brian K., Ghorishi, S. Behrooz, "Entrained-Flow Adsorption of mercury Using Activated Carbon," (Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, undated), unpublished.

65. Daza, L., and Mendioroz, S., "Mercury Elimination from Gaseous Streams," Applied Catalysis B: Environmental, Vol. 2, (1993), pp. 277-287.

66. Boehm, H.P., Diehl, E., Heck, W., Sappok, R., "Surface Oxides of Carbon," Angewandte Chemie International Edition, Vol. 3, No. 10 (1964), pp. 669-677.

67. Boehm, H.P., "Functional Groups on the Surfaces of Solids," Angewandte Chemie International Edition, Vol. 5, No. 6 (1966), pp. 533-622.

68. APHA-AWWA-WPCF, Standard Methods, (17th, Washington, DC: American Public Health Association, pp. 230-239.

69. Shendrikar, A.D., Damie, A., Gutknect, W. F., "Collection Efficiency Evaluation of Mercury-Trapping Media for the SASS Train Impinger System," (Research Triangle Park, NC: NTIS, 1984), EPA-600/7-84-089.

70. Bagreev, A., Bashkova, S., Locke, D.C., Bandosz, T.J., "Sewage Sludge-Derived Materials as Efficient Adsorbents for the Removal of Hydrogen Sulfide," Environmental Science and Technology, Vol. 35, (2000), pp. 1537-1543.

71. Bagreev, A. and Bandosz, T.J., "Study of Hydrogen Sulfide Adsorption on Activated Carbons Using Inverse Gas Chromotography at Infinite Dilution," Journal of Physics and Chemistry, Vol. 104, (2000), pp. 8841-8847.

72. Bandosz, T.J., "Effect of Pore Structure and Surface Chemistry of Virgin Activated Carbons on Removal of Hydrogen Sulfide," Carbon, Vol. 37, (1999), pp. 483-491.

73. You, Xiaozhou., "Sulfur Impregnation of Activated Carbon Through Hydrogen Sulfide Oxidation," (unpublished M.S. Thesis, Department of Civil and Environmental Engineering, School of Engineering, University of Pittsburgh, Pittsburgh, PA, 2002).