

**Development of Novel Activated Carbon-Based Adsorbents for Control of Mercury
Emissions from Coal-Fired Power Plants**

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ABSTRACT

The overall objective of this study is to evaluate pertinent design and operational parameters that would enable successful application of activated carbon adsorption for the reduction of mercury emissions from coal-fired power plants.

The study will evaluate the most suitable impregnate such as sulfur, chloride and other chelating agents for its ability to enhance the adsorptive capacity of activated carbon for mercury vapor under various process conditions. The main process variables to be evaluated include temperature, mercury concentration and speciation, relative humidity, oxygen content, and presence of SO₂ and NO_x in the flue gas. The optimal amount of impregnate for each of these carbons will be determined based on the exhibited performance.

Another important parameter which governs the applicability of adsorption technology for the flue gas clean up is the rate at which vapor phase mercury is being removed from the flue gas by activated carbon. Therefore, the second part of this study will evaluate the adsorption kinetics using the impregnated activated carbons listed above. The rate of mercury uptake will also be evaluated under the process conditions that are representative of coal-fired power plants.

Concerned with the ability of the adsorbed mercury to migrate back into the environment once saturated adsorbent is removed from the system, the study will also focus on the mercury desorption rate as a function of the type of impregnate, loading conditions, and the time of contact prior to disposal.

TABLE OF CONTENTS

	page
EXECUTIVE SUMMARY.....	1
INTRODUCTION.....	2
RESULTS AND DISCUSSION.....	3
CONCLUSION.....	7
REFERENCES.....	8

EXECUTIVE SUMMARY

The objective of this study during the first six-month period was to optimize the sulfur impregnation procedure that would offer a significant enhancement of activated carbon capacity for vapor phase mercury. Removal efficiency of commercially available sulfur-impregnated carbon (HGR) and bituminous coal-based activated carbon impregnated with sulfur at 250 °C, 400 °C and 600 °C (BPL-S) for vapor-phase elemental mercury was evaluated as a function of temperature, influent mercury concentration and empty bed contact time.

Based on the fixed-bed breakthrough experiments, both HGR and BPL-S carbon exhibited improved mercury removal efficiency compared to the virgin carbon (BPL). However, the BPL-S series had higher mercury uptake capacity than that of HGR for the influent mercury concentration of 55 µg/m³ and at the operating temperature of 140 °C. For the BPL-S series, impregnation temperature was an important factor which affected the capacity for mercury uptake. BPL-S impregnated at 600 °C (BPL-S-600) had the highest removal capacity, while BPL-S-400 exhibited slightly lower capacity. BPL-S-250 exhibited significantly lower capacity when compared to BPL-S-600 and BPL-S-400. The actual sulfur content for HGR and BPL-S series were almost the same (10%), except in the case of BPL-S-250 which had much higher sulfur content of 36%.

Bonding between sulfur and carbon, as determined by thermogravimetric analysis (TGA), was dependent on the impregnation procedure. Higher impregnation temperatures promote more uniform distribution of low molecular weight sulfur allotropes on the carbon surface.

At low influent mercury concentrations and low temperatures, HGR and BPL-S-600 performed similarly in the removal of mercury vapor. However, as the temperature was increased above the melting point of sulfur, the performance of HGR deteriorated significantly, while the performance of BPL-S slightly improved.

INTRODUCTION

Environmental control agencies and researchers have become increasingly concerned with the mobilization of trace elements to the environment from fossil fuel burning. Mercury is a trace element of particular concern since, during coal combustion, most of the mercury present in coal is transferred into vapor phase due to its high volatility, while currently used pollution abatement technologies are not capable of controlling gas-phase mercury emissions. Once discharged into the atmosphere, mercury persists in the environment and creates long-term contamination problems. Furthermore, well documented food chain transport and bio-accumulation of mercury require strict control of mercury emissions from coal-fired power plants (1). Activated carbon adsorption is a unit process that offers great promise for achieving high quality air emissions with respect to mercury and other trace elements that might be present in gases emitted from coal-fired power plants. Granular activated carbon (GAC) used in packed bed configuration offers potential for the recovery of mercury from gas streams, and desirable handling properties with respect to final disposal of mercury (2).

The proposed research work will evaluate pertinent design and operational parameters that would enable successful application of this efficient technology for mercury control. The key tasks of this study are: 1) optimize the type and percent impregnate as well as the impregnation procedure that would provide the most significant enhancement of activated carbon capacity for vapor phase mercury, 2) establish the dependency of activated carbon adsorptive capacity on temperature and mercury concentration; 3) evaluate possible interference of other compounds in the vapor phase with mercury removal mechanism; and 4) develop scale-up procedure for correlating the performance of laboratory and pilot-scale granular activated carbon adsorbers.

RESULTS AND DISCUSSION

1 Materials and Methods

Several types of sulfur impregnated activated carbon were used in this study. HGR, a commercially available sulfur-impregnated carbon, was supplied by the manufacture (Calgon Carbon Corporation, Pittsburgh, PA). BPL-S series carbons were produced by impregnating a bituminous coal-based virgin activated carbon, BPL (Calgon Carbon Corporation, Pittsburgh, PA), with sulfur in a pure nitrogen atmosphere at different temperatures.

A fixed bed reactor column was designed and installed for the vapor phase mercury removal test. Figure 1 shows the layout of the devices. The column packed with sulfur-impregnated carbon was placed inside the oven to allow experimental investigation at different operating temperatures. Mercury source was a mercury permeation cell (VICI Metronics, Santa Clara, CA) submerged in a temperature controlled oil bath. By varying the oil bath temperature and the carrier gas flow rate, a wide range of mercury concentrations could be generated. A Perkin-Elmer Model 403 atomic adsorption spectrophotometer (AAS) was used to continuously monitor the concentration of elemental mercury vapor. Industrial grade nitrogen was used as a carrier gas for all experiments. During the preparatory phase of each experiments, mercury-laden gas by-passed the adsorber and was monitored by the AAS until stable levels were established. At the same time, oven temperature was gradually increased to reach the desired level. Once the mercury concentration was stabilized, the mercury-laden gas was introduced into the reactor in a down flow mode and time was recorded as zero. The experiment was terminated when the AAS indicated that the effluent concentration from the column was the same as the inlet concentration.

A mercury trapping impinger solution was used to collect batch mode mercury samples in order to calibrate the atomic adsorption spectrophotometer and to determine the total mercury concentration in the effluent stream from the fixed-bed carbon adsorber. The impinger solution used for this purpose was prepared with 1.5% potassium permanganate in 10% sulfuric acid.

The sulfur content for each carbon was examined by a Leco Model SC 132 sulfur determinator (Leco Corporation, St. Joseph, MI). The specific surface area and pore size distribution for these samples was measured by an Orr Surface-Area Pore-Volume Analyzer Model 2100 (Micromeritics Instrument Corporation, Atlanta, GA) using a nitrogen BET method.

In order to obtain reliable and reproducible data, the following quality control and quality assurance procedures have been used throughout each experimental step: 1) the AAS readings vs. mercury concentration was calibrated based on EPA Method 29 (a linear relationship between absorbance and mercury concentration was always established); 2) the effluent gas from each column run was periodically collected in an impinger solution, and the amount of total mercury in the impinger solution was compared to gas phase elemental mercury measurements; 4) the spent carbon was burned in a combustor and the effluent gas from that combustor was collected in impingers to verify the mass balance on mercury.

2 Results and Discussion

2.1 Effect of impregnation temperature on mercury uptake

HGR is manufactured by condensing sulfur vapor onto BPL carbon at a relatively low temperature (somewhere in the range of 150-200 °C). BPL-S series was produced by impregnating sulfur onto BPL carbon at 250 °C, 400 °C and 600 °C, respectively. Based on the impregnation temperature, the newly derived carbon series were denoted as BPL-S-250, BPL-S-400 and BPL-S-600.

Figure 2 shows the result of column runs for these carbons at 140 °C using the influent mercury concentration of 55 µg/m³ (9.267×10⁻⁸ lb/yd³), 100 mg (2.2×10⁻⁴ lb) of sulfur impregnated carbon and a N₂ flow rate of 1.0 L/min (0.264 gal/min). HGR carbon showed the lowest capacity for mercury uptake and it reached 100% breakthrough only after 3 hours. BPL-S series generally exhibited higher capacity than that of HGR. As the impregnation temperature increased, the capacity of the corresponding BPL-S carbon also increased. For example, BPL-S-250 reached 100% breakthrough after 4 days, while BPL-S-400 reached 100% breakthrough after 8 days.

Sulfur exists in several allotropes, including S_λ (S₈ rings), S_π (S₈ chains), and S_μ (chains of variable length). Meyer (3) summarized the relationship between temperature and major sulfur allotropes in vapor-phase (Table 1):

Table 1. Dominant Sulfur Allotropes at Different Temperatures

Temperature [°C]	S ₈	S ₇	S ₆	S ₅	S ₂
180	65%	15%	15%		
250	49%	27%	21%		
400	22%	36%	28%	5%	2%
600			58.8%		16.4%

It can be seen clearly that low molecular weight, short chain allotropes of sulfur are dominant forms at higher temperatures, while the high molecular weight, long chain or ring-structured allotropes are the major sulfur components at low temperatures. If the predominant form of sulfur on the carbon surface is comprised of smaller sulfur molecules such as S₂, then the weight fraction of active terminal atoms that can react with mercury is much greater than in the case of larger sulfur molecules. In addition, the smaller sulfur chains can more easily migrate into the narrower pores of the carbon matrix, which results in a more uniform sulfur distribution throughout the carbon surface.

Based on the discussion presented above, it is believed that the sulfur in HGR carbon is predominantly in the form of S₈ rings. On the other hand, the BPL-S series carbons have more sulfur in the form of smaller, shorter chains as the impregnation temperature increases. Since lower amount of active terminal sulfur atoms are available in HGR than in BPL-S series, lower amount of mercury can be adsorbed by HGR carbon and early breakthrough will occur.

Table 2 summarizes mercury removal capacities for these carbons. Mercury uptake was calculated by integrating the area above the breakthrough curves given in Figure 2.

Table 2. Capacity of Mercury Removal for HGR and BPL-S Series

Sulfur Impregnated Carbon Type	Time for 100% Breakthrough, [hr]	Mercury Uptake, [$\mu\text{g Hg/g carbon}$] (10^{-6} lb/lb)
HGR	3	44
BPL-S-250	96	594
BPL-S-400	192	1687
BPL-S-600	408	2376

Thermogravimetric analysis (TGA) was conducted by heating samples of BPL-S-600 and HGR carbon up to 400 °C in an argon atmosphere. Figure 3 shows that BPL-S-600 underwent negligible decrease in weight, while the weight of the HGR carbon sample decreased by 8.5%. Since both BPL-S-600 and HGR carbon were manufactured by impregnating BPL carbon with sulfur, this outcome implies that BPL-S-600 carbon lost a negligible amount of its impregnated sulfur, while HGR carbon lost 88% of its sulfur content. This shows that the bonding of sulfur molecules to the carbon matrix is much stronger in BPL-S-600 than in HGR carbon.

The experimental data presented in Figure 2 were collected at 140 °C, while the melting point of sulfur is 115.2 °C. At 140 °C, the weakly bonded sulfur on the surface of HGR carbon tended to melt, migrate and agglomerate along the internal pores. As a consequence, agglomerated sulfur blocked a large portion of internal pores that mercury could then not access to react with the available sulfur, resulting in a relatively low HGR capacity for vapor-phase elemental mercury. On the other hand, the TGA results indicated that the sulfur-carbon bonding force for BPL-S series was strong enough to minimize sulfur-melting effect, resulting in much higher uptake capacity for elemental mercury.

2.2 BET surface area measurements

A classical BET method was used to further study the micro-structure of all the carbons used in this study. Specific surface area for each carbon sample was calculated and listed in Table 3. For the BPL-S series, the specific surface area decreased with a decrease in the impregnation temperature. The difference in specific surface areas between BPL-S-600 and BPL-S-400 was only 23%. But the specific surface area of BPL-S-250 was drastically reduced. Comparing to BPL-S-600, the surface area of BPL-S-250 is merely 20%. Since the major form of sulfur allotropes at low temperature is S_8 , the ring-structured molecules would occupy large volume and could easily form clusters or generate multi-layers during the impregnation process, which blocks pore entrances and reduces the measurable surface area. As for the BPL-S-400 and BPL-S-600, this steric hindrance is not obvious due to the high impregnation temperature.

Table 3. BET Surface Area of Carbons Used in The Study

Carbon Type	Specific Surface Area, [m ² /g]	Specific Surface Area, (yd ² /lb)
BPL	1040	5.572×10 ⁵
HGR	482.4	2.618×10 ⁵
BPL-S-250	164.4	8.928×10 ⁴
BPL-S-400	634.4	3.445×10 ⁴
BPL-S-600	823.7	4.473×10 ⁵

2.3 Influence of temperature on the performance of HGR and BPL-S-600

Adsorber experiments using 200 mg of 60×80 U. S. mesh carbon were conducted for a duration of 10 hours at mercury concentration of 55 µg/m³ (9.267×10⁻⁸ lb/yd³), a flow rate of 1.0 L/min (0.264 gal/min), and at temperatures of 25, 90 and 140 °C. The breakthrough curves illustrated in Figure 4 show that HGR and BPL-S-600 carbons performed similarly in the uptake of mercury vapor at 25 and 90 °C. However, when the temperature was increased to 140 °C, the performance of BPL-S-600 carbon improved slightly while HGR carbon exhibited significant deterioration in the ability to remove mercury from the feed stream. This may be due to the fact that 140 °C is above the melting point of sulfur, which induces the sulfur that is weakly bonded to the surface of HGR carbon to melt and agglomerate as a liquid in the form of long polymer chains and decreases the sulfur surface area available for contact with the incoming mercury molecules.

2.4 GAC performance at short empty bed contact time (EBCT)

All adsorber experiments conducted at short EBCT (≤ 0.11 second) utilized 60×80 U. S. mesh size GAC. As shown in Figure 5, the performance of HGR carbon improved as the flow rate increased from 0.1 to 5.0 L/min (0.0264 to 1.32 gal/min). Although the dynamic mercury adsorptive capacity was observed to increase with increasing flow rate, it was in all cases negligible compared to the capacity predicted by the stoichiometry of HgS formation ---0.607 g Hg/g HGR (lb Hg/lb HGR).

External mass transfer resistance and internal mass transfer resistance are typically not considered as rate limiting steps for gas phase applications of activated carbon. In addition, it has already been suggested that sulfur in HGR carbon is located in a macroporous region of a GAC particle, making it easily accessible for mercury molecules. The only other possibility is that the rate of mercuric sulfide formation and subsequent diffusion into the sulfur bulk phase is the rate limiting step in the adsorption dynamics of HGR carbon. As the flow rate is increased at a given mercury concentration, the mercury loading rate (µg/min) increases, causing an increase in the amount of mercury molecules which contact the sulfur surface in a given time period. Higher mercury loadings establish a surface excess of mercury, which increases the rate of HgS formation and drives the HgS molecules to diffuse more rapidly into the sulfur bulk phase. The increasing mercury loading rates accelerate the exothermic reaction of HgS formation, resulting in thermal

agitation which breaks up the sulfur chains more rapidly. The resulting increase in the number of sulfur terminal atoms causes the reactivity of the impregnated sulfur to increase (4).

2.5 Liquid state diffusion limitation for HGR

In order to confirm the liquid phase diffusion limitation of HGR, an adsorber experiment was conducted at 140 °C using the influent mercury concentration of 55 $\mu\text{g}/\text{m}^3$ (9.267×10^{-8} lb/yd³), a flow rate of 1.0 L/min (0.264 gal/min), and 100 mg (2.2×10^{-4} lb) of 60×80 U.S. mesh HGR carbon in which the mercury laden gas was periodically diverted around the adsorber while the temperature of the adsorber was maintained at 140 °C. As shown by the breakthrough curve (Figure 6), four mercury loading steps were performed over a period of 8 days. Note that in the first two loading steps, after 100% breakthrough was reached and the adsorber was bypassed for over a day, the adsorber exhibited additional capacity after it was placed back on-line. The performance of HGR in each mercury loading step is summarized in Table 3.

Table 4. Summary of HGR Performance in Each Mercury Loading

Hg Loading Step	Duration , [hr]	Hg uptake, [$\mu\text{g}/\text{g}$] (10^{-6} lb/lb)	Cumulative Hg uptake, [$\mu\text{g}/\text{g}$] (10^{-6} lb/lb)
1	4.1	34.9	34.9
2	4.6	45.4	80.3
3	12.5	155.0	235.3
4	21.1	263.0	498.3

CONCLUSION

Physical characteristics and adsorption properties for vapor-phase elemental mercury of several sulfur impregnated carbons were investigated in this study. The sulfur impregnation procedure exhibited strong impact on the carbon pore structure. Results of the BET surface area analysis suggest that specific surface area increases as the impregnation temperature increases. Consequently, more mercury can be adsorbed onto the carbon whose surface area is larger (5).

TGA analysis of sulfur impregnated carbons showed that sulfur is weakly bonded to the carbon matrix with large ring-structured molecules in the case of HGR carbon. The loosely bonded sulfur in HGR carbon tends to melt and agglomerate inside the carbon pores at elevated temperatures resulting in deterioration of dynamic mercury uptake capacity. This is unlikely to happen for BPL-S carbons since the bonding force between sulfur and carbon surface is very strong.

At low temperature, HGR and BPL-S -600 carbons performed similarly in the removal of mercury vapor. However, as the temperature was increased above the melting point of sulfur, the performance of HGR carbon deteriorated significantly, while the performance of BPL-S-600 carbon slightly improved. This is due to the weak bonding of sulfur to the surface of HGR carbon, which cannot prevent the sulfur molecules from agglomeration as large, less reactive globules, leading to the liquid state diffusion limitations in the performance of this carbon.

For both types of carbons, the observed mercury adsorptive capacities are far below the capacities predicted by stoichiometry. The sulfur in HGR carbon is very accessible, but agglomeration which occurs at high temperatures causes the sulfur to be relatively unreactive. In BPL-S series, the sulfur remains in a highly reactive form, but its location deep in the internal pores makes it relatively inaccessible and prone to blockage by HgS formation.

The pending tasks of our research include continuation of the column tests using BPL-S series carbons to optimize their adsorptive capacities and kinetics by varying the sulfur to carbon ratio (SCR) during the impregnation procedure. Also, the composition of the carrier gas stream will be modified in order to simulate the flue gas condition. Especially, the influence of oxygen, SO₂ and NO_x on the mercury removal capacity will be studied. In addition, virgin BPL carbon will be impregnated with other compounds such as chloride and chelating agents to evaluate the mercury removal efficiency of carbons when these chemicals are present. Varying proportions of flow rates, carbon masses, and carbon sizes will be used to determine whether the results can be scaled up to predict the performance of full-scale adsorbers.

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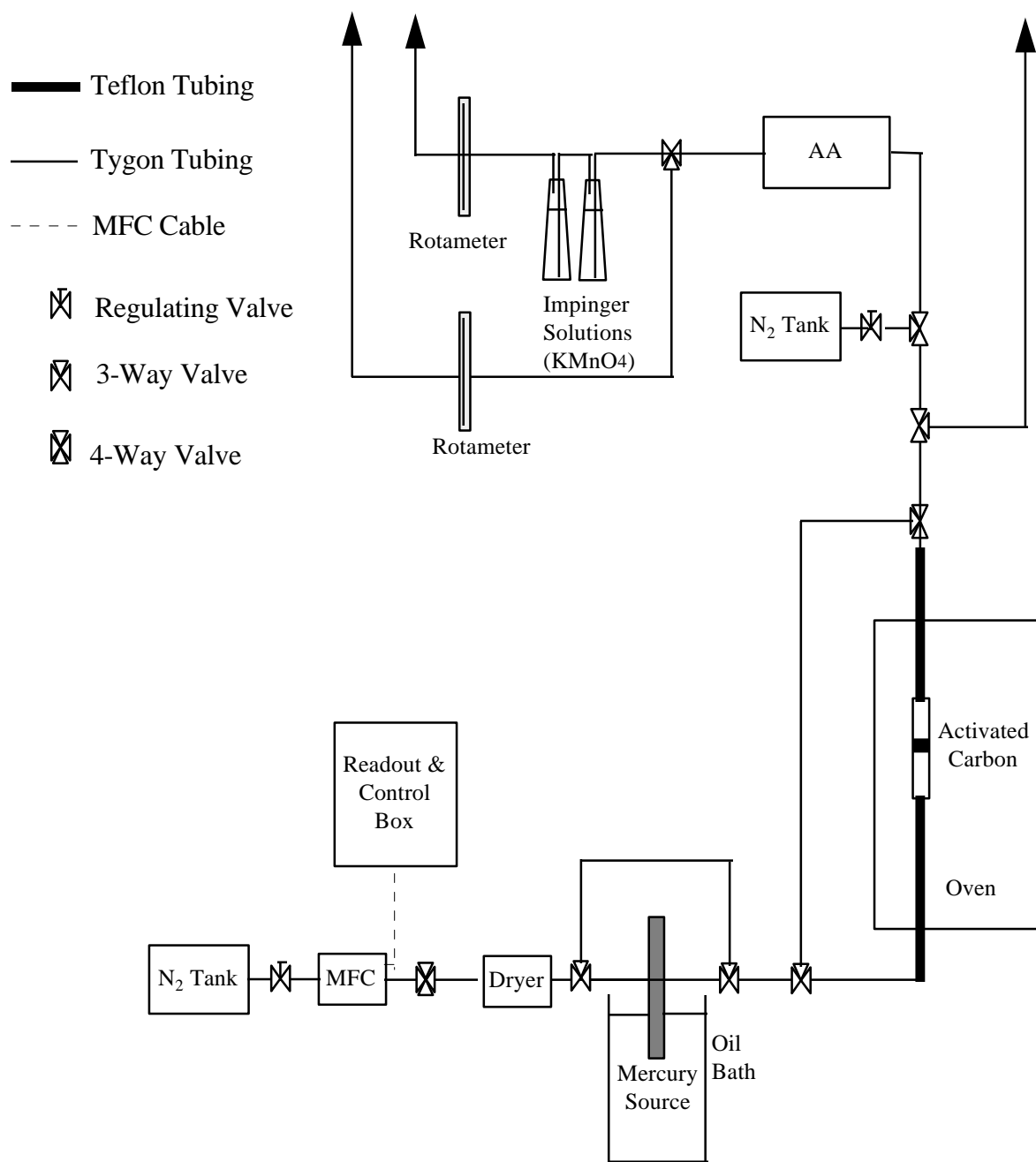


Figure 1. Experimental Setup

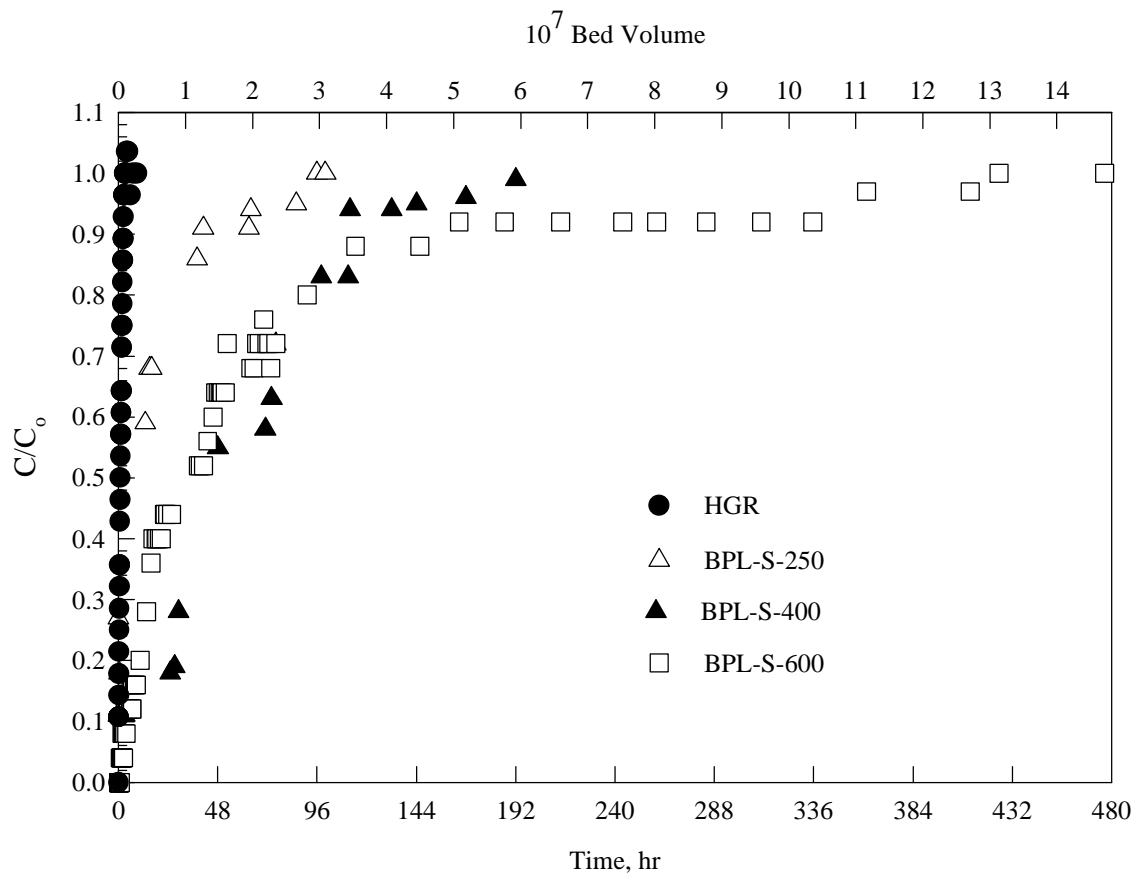


Figure 2. Breakthrough Curve for HGR and BPL-S Series

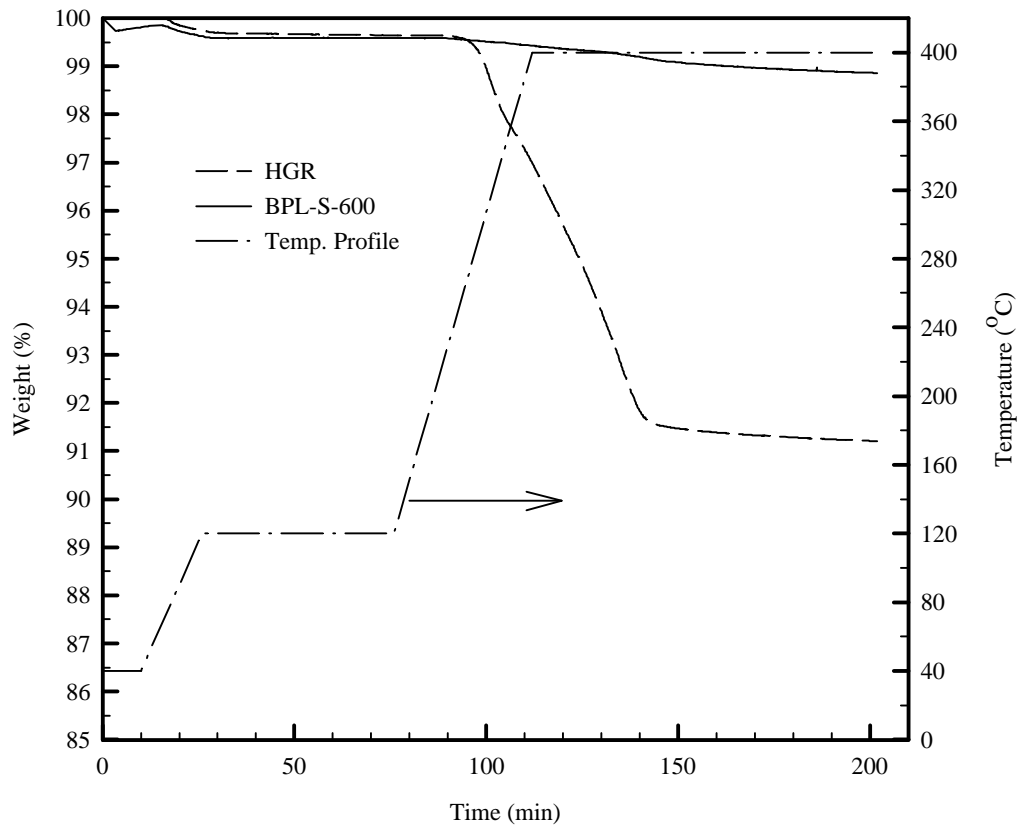


Figure 3. TGA Analysis of HGR and BPL-S-600

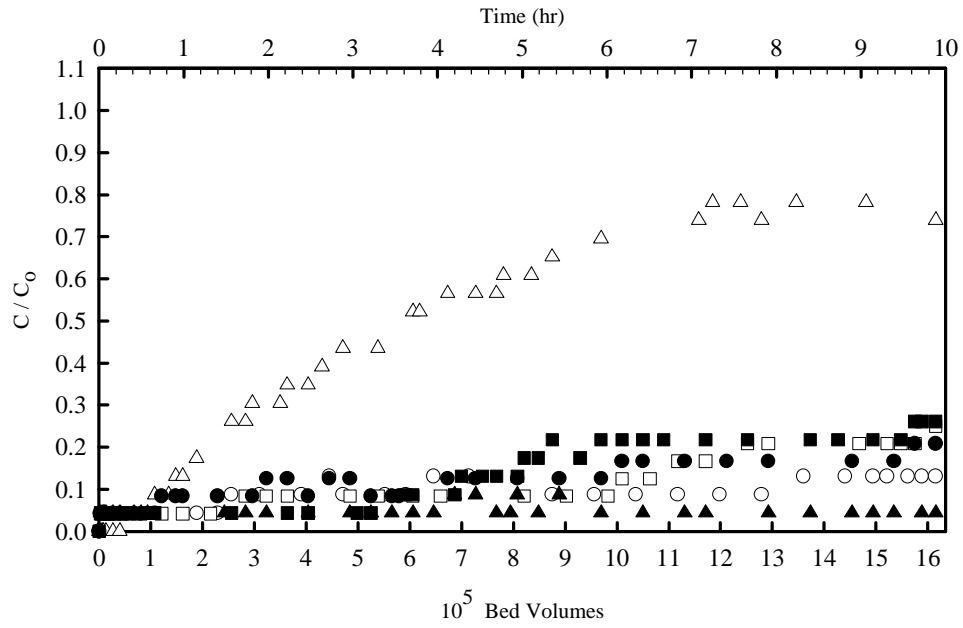


Figure 4. Effect of Temperature on HGR and BPL-S-600 Carbons

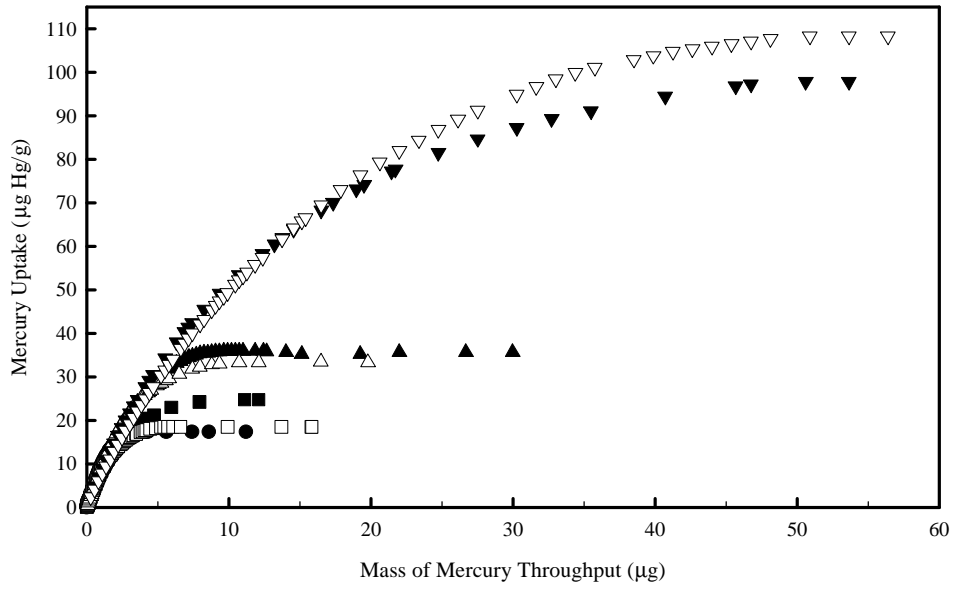


Figure 5. Flowrate Effect on the Mercury Removal for HGR

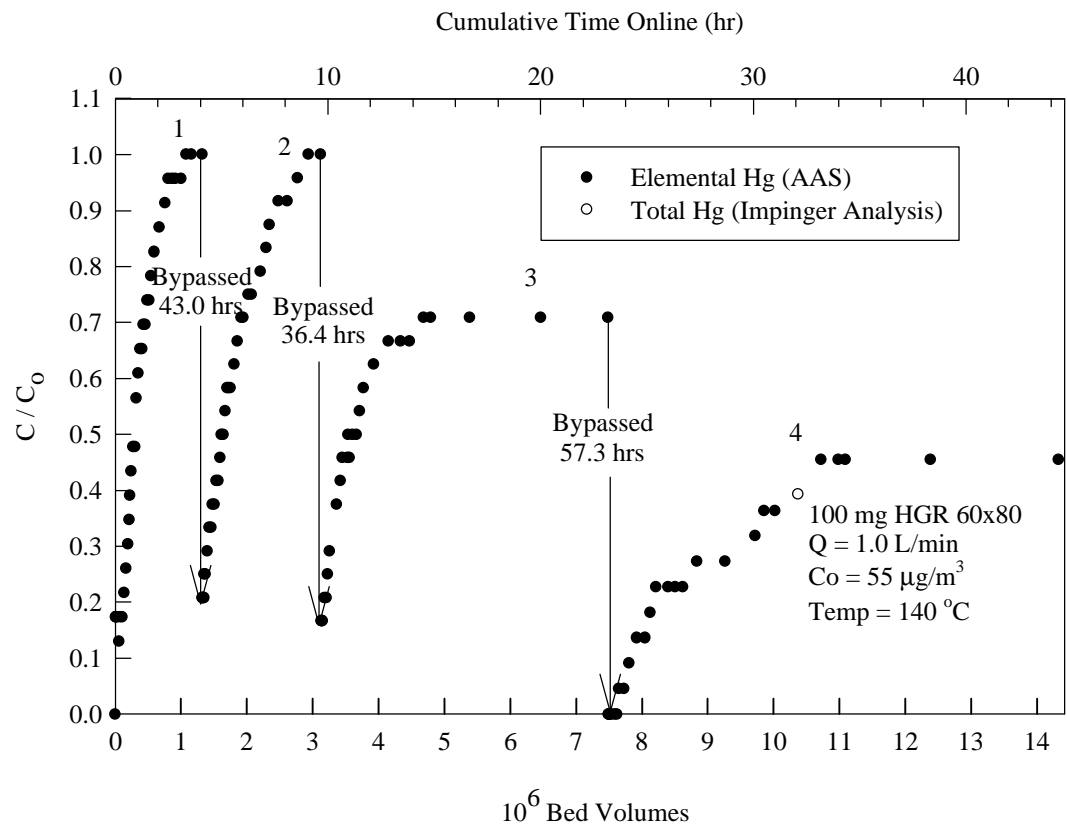


Figure 6. Breakthrough Curves of HGR with Adsorber Bypassed Periodically