

## REMOVAL OF MERCURY FROM STACK GASES BY ACTIVATED CARBON

Radisav D. Vidic  
University of Pittsburgh  
943 Benedum Hall  
Pittsburgh, PA 15261  
412-624-1307

### INTRODUCTION

On combustion, the trace elements in the incinerator feed stream are partitioned between the bottom ash (slag) stream, and a flue gas stream containing suspended fly ash and vapors of volatile elements or compounds. A further partitioning of the flue gas stream takes place in the particulate emission control devices that efficiently remove larger fly ash particles but are less efficient for vapors and finer particles. Ash from the bottom of the combustion chamber and ash removed by the particulate control devices are flushed with water to ash ponds, where elements may be leached from the ash and enter the aquatic environment in runoff. Small particles and vapors are discharged to atmosphere through exhaust stacks and enter the terrestrial and aquatic environments by wet or dry deposition.

Environmental control agencies, researchers, and general public have become increasingly concerned with the mobilization of trace elements to the environment from solid and hazardous waste incinerators. Mercury is the trace element of particular concern since, during combustion, most of the mercury present in the influent stream is transferred into the vapor phase due to its high volatility. There is a considerable evidence in the literature that currently used pollution abatement technologies (flue gas clean-up and particulate control devices) are not capable of controlling gas phase mercury emissions.

Once discharged to the atmosphere, mercury persists in the environment and creates long term contamination problem. Furthermore, well documented food chain transport and bioaccumulation of mercury, together with high toxicity to mammals and severe health problems caused by the ingestion of mercury even at low levels, require strict control of mercury emissions from solid and hazardous waste incinerators.

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 solid and hazardous waste incinerators. This study is designed to evaluate the rate of vapor-phase mercury removal by virgin and sulfur impregnated activated carbons under various process conditions. The specific process conditions that will be evaluated for their effect on the rate and mechanism of mercury uptake include temperature, moisture content, oxygen partial pressure, and presence of other compounds and trace elements in the vapor-phase. Accurate description of the kinetics of mercury removal by activated carbon is an essential component in establishing design procedures that would ensure successful application of this efficient technology for mercury control.

### METHODOLOGY

Experimental set-up that is used in this study is shown in Figure 1. Carrier gas used in the experiments is first passed through a drier and a 0.22  $\mu\text{m}$  nylon filter to remove impurities and is then split into two streams. One stream goes through a regulating valve, mass flow controller, gas moisturizer

(if needed), and into a mixing chamber. The other gas stream goes through a regulating valve, mass flow controller and a mercury generator. Hydrogen chloride can also be added to this gas stream.

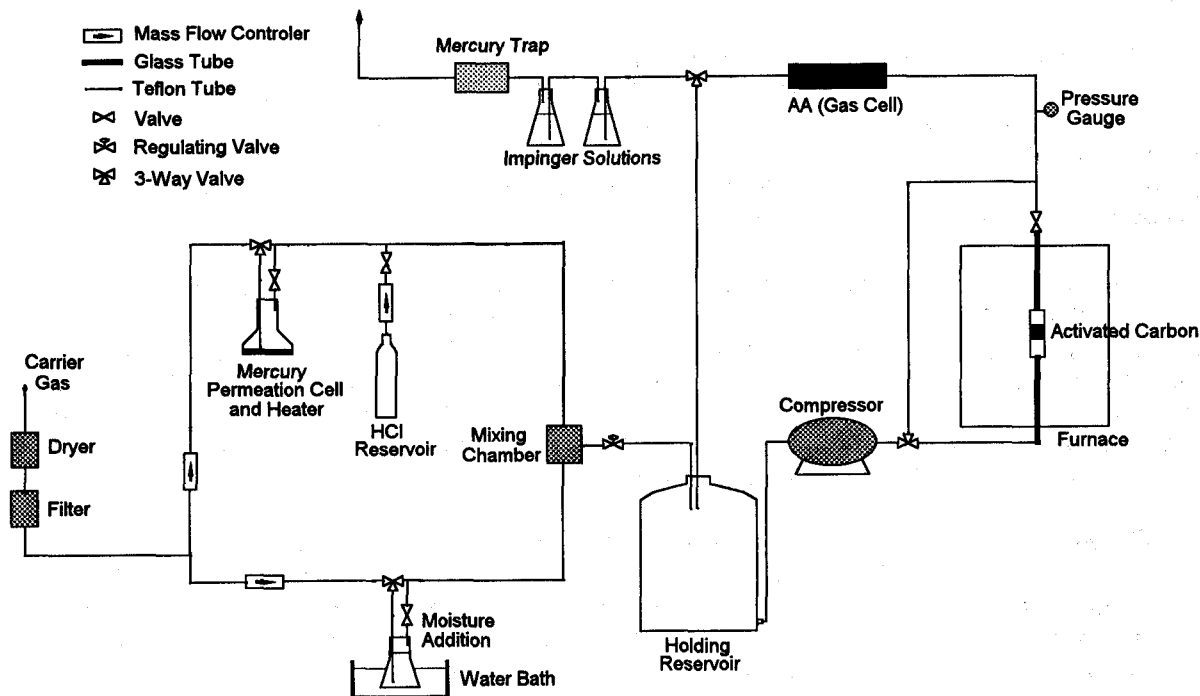


Figure 1. Schematic Representation of Experimental System

Mercury is added to the gas stream by passing the gas around a permeation cell that contains mercury and is submerged into a constant-temperature water bath. Desired mercury concentrations in the vapor phase is accomplished by adjusting the temperature of the water bath. HCl is added to the gas stream by injecting a known flowrate of a gas which contains a known concentration of hydrogen chloride in nitrogen. After the mixing chamber, the mercury laden gas stream passes through a holding reservoir that is placed into the system to increase the total system volume and improve the accuracy of experimental results. During the preparation phase, which precedes each measurement of mercury uptake by activated carbon, the gas stream is directed around the activated carbon bed until a steady-state conditions with respect to gas composition are achieved.

Gas stream then passes through a quartz cell placed in a light path of an atomic absorption spectrophotometer (AAS) which enables direct and continuous measurement of elemental mercury in the vapor phase. Finally, the gas stream is passed through appropriate impinger solutions to facilitate measurements of other forms of mercury in the gas phase as well as other trace compounds that might be present in the gas stream. Impinger solutions are placed in 250 mL gas washing bottles. The collection of a particular compound from the gas phase into an impinger solution is performed for a period of 60 minutes after which the fresh solution will be placed on line. The mercury trap at the exit from the system is a GAC column charged with 100 g of sulfur impregnated activated carbon (HGR).

Once the composition of the gas stream is stabilized at predetermined levels, the regulating valve is closed to prevent any infusion of mercury into the holding reservoir and the gas stream exiting the AAS is directed back into the holding reservoir thereby, forming a completely closed system. The compressor in the system is operated at a very high flow rate (up to 3 cfm) to ensure complete mixing in

the system throughout the experiment. The flow of the gas is then directed to a differential (short) activated carbon bed positioned inside the furnace and the uptake of mercury by activated carbon is monitored with time.

Elemental mercury in the gas stream is measured continuously at a wavelength of 253.7 nm using a quartz gas cell placed in the AAS system which is first calibrated according to the procedure described by Shendrikar *et al.* (1) while the total mercury is determined by directing a gas through a 200 mL impinger solution containing 1.5%  $\text{KMnO}_4$  and 10%  $\text{H}_2\text{SO}_4$  that collects all mercury species from the gas phase. The total mercury concentration in the impinger solution is then analyzed using a cold vapor atomic absorption spectrophotometric method (2).

The proposed research objectives will be accomplished through the following activities:

1) Evaluate the effect of temperature and mercury concentration in the gas phase on the rate of mercury adsorption by virgin and sulfur impregnated activated carbons for a wide range of mercury concentrations (100 - 1000  $\mu\text{g}/\text{m}^3$ ) and temperatures (80-200 °C) that are representative of gaseous emissions from incineration plants. Activated carbons selected for this part of the study are bituminous-coal based virgin activated carbon designed for vapor-phase applications (BPL) and sulfur impregnated activated carbon (HGR) (Calgon Carbon Corporation, Pittsburgh, PA).

2) Evaluate the effect of activated carbon particle size on the rate of mercury uptake from the gas phase. Smaller particle sizes would provide easier access of mercury to the surface active sites where adsorption occurs, thereby improving the kinetics of adsorption. However, injecting smaller GAC particle sizes would facilitate faster build-up of pressure drop at the fabric filter which is used to control particulate emissions. Consequently, the frequency of fabric filter cleaning would increase leading to lower run times. Therefore, it is necessary to determine an optimal particle size that would satisfy these opposing requirements. The intention of this task of the study is to determine the extent of the improvement in adsorption kinetics with the reduction in activated carbon particle size. Activated carbon particle sizes that will be used in such experiments include 30x40, 60x80, and 170x230 U.S. Standard Mesh sizes. These kinetic experiments will be performed at 140 °C using an influent mercury concentration of 500  $\mu\text{g}/\text{m}^3$  as representative of incinerator flue gas conditions. Once the optimum activated carbon particle size is established during this phase of the study, it will be used in the rest of the experiments outlined below.

3) Determine the effect of environmental conditions on the rate mercury uptake by activated carbon. The key environmental conditions that need to be evaluated include moisture content and oxygen partial pressure in the gas stream. Effects of moisture on the adsorption kinetics will be evaluated using dry and moisture saturated nitrogen as a carrier gas. Dry nitrogen and dry air will be used as carrier gases in the experiments designed to evaluate the effect of oxygen partial pressure on the adsorption kinetics. All the kinetic experiments included in this task of the study will be conducted at three different temperatures (80, 140, and 200 °C) using an influent mercury concentration of 500  $\mu\text{g}/\text{m}^3$ . All possible combinations of moisture content and oxygen partial pressure in the gas stream will be employed to study the effect of temperature on chemical interactions between mercury, oxygen, and moisture, and the related impact on the rate of mercury uptake by activated carbon.

4) Evaluate the effect of the presence of halogen compounds (most notably chlorine, Cl) in the gas stream on the kinetics of mercury uptake by activated carbons. Cl can react with elemental mercury and change its oxidation state and therefore, influence the affinity of mercury towards the carbon surface. This task of the study includes kinetic experiments at three different temperatures (80, 140 and 200 °C) using different ratios of mercury and chlorine concentrations in the influent stream. Typical chlorine in-stack vapor-phase concentrations for incineration plants range from 400 to 1000  $\mu\text{L}/\text{L}$  as hydrogen chloride, HCl (3). Two different HCl concentrations will be tested in this study, namely 400 and 1000  $\mu\text{L}/\text{L}$  while the concentration of mercury in both cases will be 500  $\mu\text{g}/\text{m}^3$ .

## RESULTS

An experimental system capable of producing constant concentrations of vapor-phase mercury was successfully constructed and tested at the outset of this study. Furthermore, an AAS was calibrated by trapping a carrier gas containing different concentrations of vapor-phase mercury in the impinger solutions. It was discovered that mercury adsorbs to glass walls of the impinger bottles and the problem was solved by rinsing the glassware with concentrated nitrohydrochloric acid. The calibration curve generated from these experiments is shown in Figure 2.

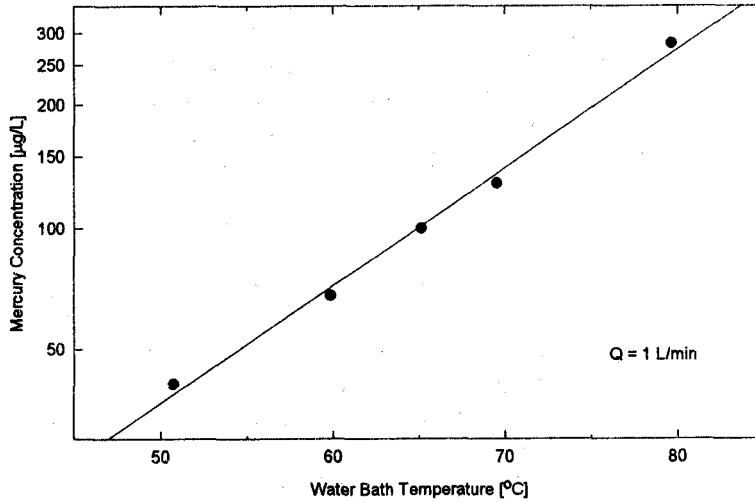


Figure 2. Vapor-Phase Mercury Concentration as a Function of Water Bath Temperature

Following the calibration of the instrument, the influence of mercury concentration and ambient temperature on the adsorptive capacity of virgin GAC was evaluated using the fixed-bed breakthrough experiments conducted with 100 mg of GAC and a carrier gas flow rate of 1 L/min. The results of these experiments are summarized in Figure 3.

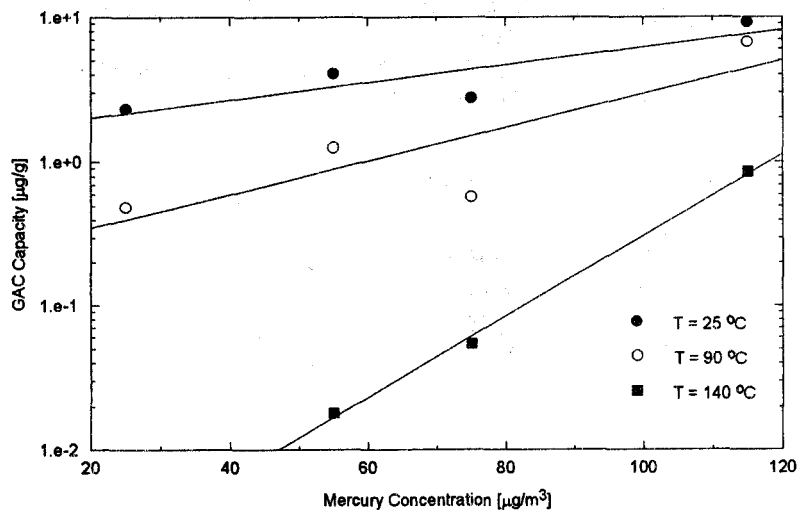


Figure 3. Effect of Temperature and Mercury Concentration on Virgin GAC Adsorptive Capacity

## CONCLUSIONS

As is apparent from Figure 3, the increase in mercury concentration leads to an increase in virgin GAC adsorptive capacity for vapor-phase mercury. However, higher temperatures significantly reduce the ability of virgin activated carbon to remove mercury from the stack gases. Both of these trends were expected since the adsorption process is an exothermic reaction that is driven by the concentration of adsorbate in the fluid phase.

What is also apparent from Figure 3 is that the virgin GAC has very low capacity for the removal of vapor-phase mercury under the conditions that are prevalent in the incineration plant stacks (high temperatures). Furthermore, the presence of other trace inorganic and organic compounds in the stack gas would further diminish its capacity for the retention of mercury due to competitive adsorption. Therefore, it appears that sulfur impregnated carbon would be better suited for the control of mercury emissions from solid and hazardous waste incinerators for the following reasons: a) the capacity of sulfur impregnated GAC is several orders of magnitude above the capacity of virgin GAC; and b) the entire adsorptive capacity of sulfur impregnated GAC can be used exclusively for vapor-phase mercury since this carbon can not adsorb any other trace organic or inorganic compounds in the stack gas.

Next goal in this study is to evaluate the effects of temperature and mercury concentration on the ability of sulfur impregnated activated carbon to remove mercury from the gas phase (similar to those presented in Figure 3 for virgin GAC) followed by the evaluation of the rates of vapor-phase mercury uptake by both carbons. Based on the results of these experimental studies, a mathematical model that accounts for both diffusion rate and the rate of reaction between sulfur and vapor-phase mercury will be developed to assist in predicting the performance of these activated carbons in the control of mercury emissions from solid and hazardous waste incinerators.

## REFERENCES

1. Shendrikar, A.D., Damle, A., and Gutknecht, F. Collection Efficiency Evaluation of Mercury-Trapping Media for the SASS Train Impinger Solution. EPA-600 S7-84-089, U.S. EPA, Washington, DC., 1984.
2. APHA-AWWA-WPCF Standard Methods for the Examination of Water and Wastewater, 17th ed., Port City Press, Baltimore, MD, 1989.
3. Hall, B, Schager, P., and Lindqvist, O. (1991) "Chemical Reactions of Mercury in Combustion Flue Gases." *Water, Air, and Soil Pollut.*, 56, 3.

### For More Information:

Luis Garcia  
Risk Reduction Engineering Laboratory  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268  
513-569-7932

**APPLICATION OF AMBERSORB 563 ADSORBENT TECHNOLOGY  
FOR TREATMENT OF CHLORINATED ORGANICS IN GROUNDWATER**

Russell W. Frye, Joseph F. Martino, and Russell E. Turner  
Roy F. Weston, Inc.  
1 Weston Way  
West Chester, PA 19380  
610-701-6173

Eric G. Isacoff and Deborah A. Plantz  
Rohm and Haas Company  
Research Laboratories  
Spring House, PA 19477  
215-641-7255

**INTRODUCTION**

Roy F. Weston, Inc. (WESTON), in conjunction with Rohm and Haas Company (Rohm and Haas), conducted a field pilot study to demonstrate the technical feasibility and cost-effectiveness of Ambersorb 563 (A-563) carbonaceous adsorbent for the remediation of groundwater contaminated with volatile organic compounds (VOCs). The project was conducted under the Emerging Technology Program of the EPA Superfund Innovative Technology Evaluation (SITE) program.

Ambersorb adsorbents are a family of patented, synthetic, tailorable carbonaceous adsorbents that were developed by Rohm and Haas in the 1970's for the treatment of contaminated water. In specific applications, Ambersorb adsorbent technology may offer a cost-effective alternative to air stripping or granular activated carbon (GAC), which are typically used in pump and treat systems for remediating groundwater contaminated with organic compounds.

Ambersorb adsorbents have been found to be effective in the removal of low levels of VOCs and other synthetic organic compounds from contaminated water (1). Previous applications using Ambersorb adsorbents have demonstrated several key performance benefits over GAC (2,3,4,5). Ambersorb 563 adsorbent can be regenerated onsite using steam, solvents, or other techniques, permitting the recovery of a concentrated organic stream which can be disposed of or reclaimed. Ambersorb 563 adsorbent has a significantly greater adsorption capacity than GAC for chlorinated hydrocarbons when the contaminants are present at low concentrations. Ambersorb 563 adsorbent systems can operate at higher flow rates than GAC systems, while maintaining effluent water quality below drinking water standards.

**METHODOLOGY**

The Ambersorb technology demonstration was conducted at Pease Air Force Base (AFB) in Newington, New Hampshire. The base has been included on the National Priorities List (NPL) and WESTON has been conducting an Installation Restoration Program (IRP) Stage 3 Remedial Investigation (RI) at Pease AFB over the past several years. Based on a review of groundwater data for various sites at Pease AFB, Site 32/36 was selected for the Ambersorb 536 adsorbent field trial. The groundwater in this area is contaminated with a number of chlorinated organics including vinyl chloride (VC), 1,1-dichloroethene (1,1-DCE), cis-1,2-dichloroethene (cis-1,2-DCE), trans-1,2-dichloroethene (trans-1,2-DCE), and trichloroethene (TCE).

The Ambersorb technology demonstration project under the SITE program used a 1-gallon-per-minute (gpm) continuous pilot system, consisting of two adsorbent columns, to evaluate the treatment of groundwater from Site 32/36 at Pease AFB. The field study was performed over a 12 week period during the spring/summer of 1994. The testing program included four service cycles and three steam regenerations. A summary of the conditions for the service cycles and steam regenerations is provided in Tables 1 and 2, respectively.