

# Removal and Recovery of Vapor-Phase Mercury from Flue Gas Using Regenerable Sorbents

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## Introduction

Mercury and its compounds are a group of chemicals identified in Title III of the 1990 Clean Air Act (CAA) Amendments as air toxic pollutants. Mercury forms several volatile compounds that are emitted from stationary sources. Municipal and hazardous waste incinerators together comprise an estimated one-third (52 tons/yr) of the emissions of mercury in the U.S. and are now regulated by the Environmental Protection Agency (EPA, 1997). The EPA estimates that coal-fired power plants emit an additional 52 tons of mercury per year to the environment, making electric power utilities the only major industrial source of mercury that is unregulated. EPA recently released the Mercury Study Report to Congress but delayed regulation of mercury emissions from utilities to provide additional time for study and the development of suitable treatment technologies.

A coal-fired utility boiler emits several mercury compounds, primarily elemental mercury ( $\text{Hg}^0$ ), mercuric chloride ( $\text{HgCl}_2$ ), and mercuric oxide ( $\text{HgO}$ ), each in different proportions depending on the characteristics of the fuel being burned and on the method of combustion. The concentration of mercury in the flue gas is typically below 1 ppb by volume, that is, below  $10 \mu\text{g}/\text{m}^3$ . At these low concentrations, the efficacy of carbon-based sorbents is severely compromised. Not only is the thermodynamic capacity of carbon reduced at the high temperature and low mercury concentration of flue gas, but the rate at which the mercury gets to the carbon can be limited by gas-phase mass transfer rates (e.g. Carey, et al., 1997). As a consequence, 10,000 to 50,000 pounds of injected carbon is required per pound of mercury removed (EPA, 1997).

Tests of carbon injection, both activated and chemically-impregnated, have been reported by Miller, et al., (1994), by Sjoström, et al., (1997), and by Bustard and Chang (1994). Results are widely variable and are explained by the dependence of the sorption process on temperature, mercury speciation, and fly ash chemistry. Chang and Offen (1995) state that based on combined operating and annualized capital costs, carbon injection will cost between \$14,000 and \$38,000 per pound of mercury removed or over \$4 million per year in a 250 MW power plant. In the Mercury Study Report to Congress, carbon injection costs ranged from \$5000 to \$70,000 per pound of mercury removed.

Currently, there is no single control method that will reliably collect different mercury species. Further, existing control systems vary in efficiency as the flue gas temperature varies, and they generate secondary hazardous wastes because they capture mercury using sorbents or reagents that are used only once. Wet scrubbing, for example, is efficient only for water-soluble mercury species such as  $\text{HgCl}_2$  (Hargrove, et al., 1997). Elemental mercury is not captured by wet scrubbers. Further, less than 20% of coal-fired utilities employ wet scrubbers, and it is not economically feasible to install a wet scrubber solely for mercury control. Wet scrubbing is therefore not a prime option for mercury control.

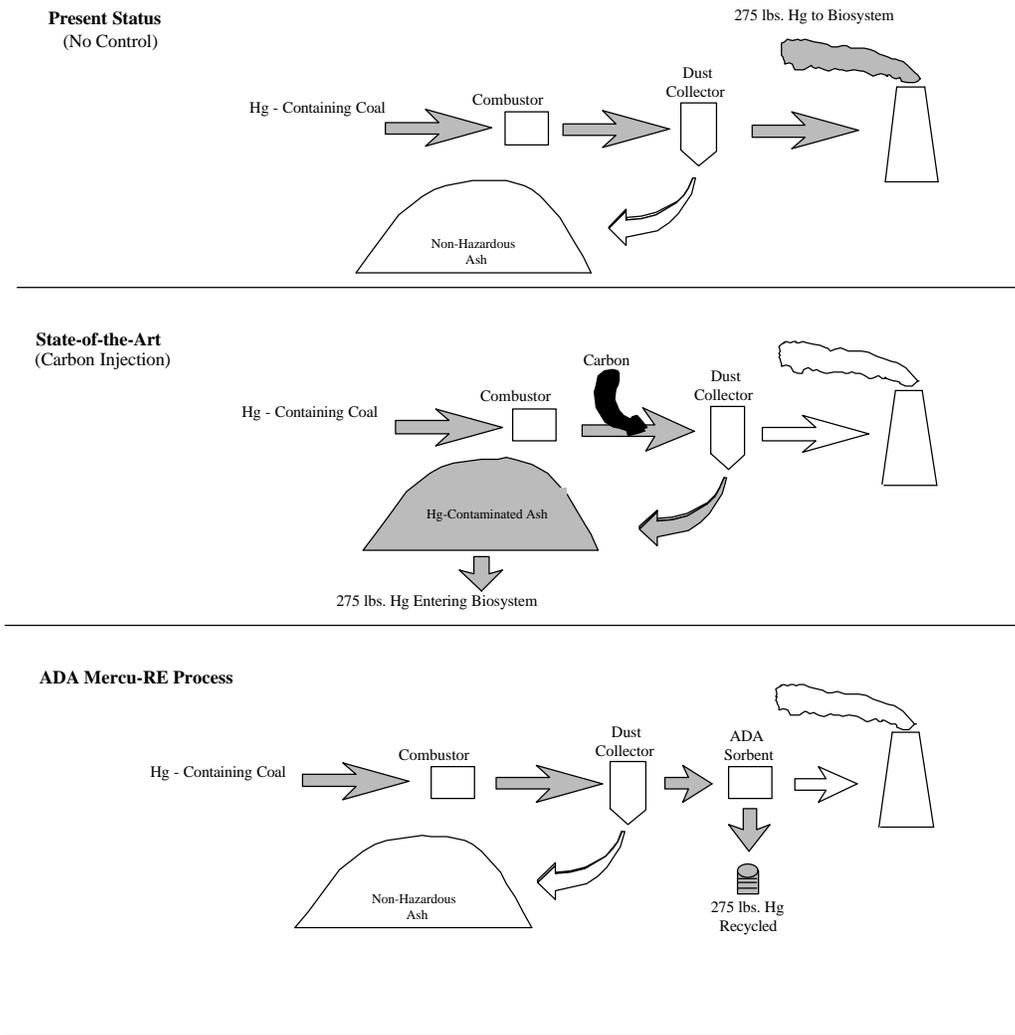
The technology being developed by ADA uses a regenerable sorbent that allows for recovery and recycling of mercury from the flue gas. For these reasons, we call our technology the “Mercur-RE process.” The Mercur-RE process is based on the ability of noble metals to repeatedly sorb large quantities of mercury and related mercury compounds at flue-gas conditions and to desorb the mercury when heated to several hundred degrees above flue-gas temperatures. If condensation is employed, liquid mercury can be recovered for recycle and re-use. Over 50% of commercially-sold mercury is made by companies that triple distill crude mercury (e.g. Bethlehem Apparatus Company, Hellertown, PA), and therefore existing companies are ready to accept the crude mercury recovered via ADA’s Mercur-RE process. Alternately, mercury vapors can be combined with a source of sulfur to form a stable mercuric sulfide - a feed stock for mercury retorters. The Mercur-RE process has the following advantages:

- mercury removal efficiencies exceeding 95% regardless of the chemical form of the mercury
- a substantial reduction in the cost of mercury control compared with alternative approaches
- minimal mercury-contaminated solid or liquid wastes, and
- removal of mercury from the biosystem.

Figure 1 contrasts the fate of mercury in the Mercur-RE process with the fate of mercury in an uncontrolled coal-fired combustor and in a system using carbon injection for mercury control. The quantities of ash and mercury in Figure 1 are those generated annually by a 500 MW coal-fired utility running at 60% capacity for the year. The end product of the Mercur-RE process is a small volume of mercury or mercuric sulfide, suitable for recycle.

Conceptually, the Mercur-RE process would involve multiple sorbent modules treating approximately 100,000 ACFM each and would encompass the following steps:

- 1) capturing approximately  $10 \mu\text{g}/\text{m}^3$  of Hg for twenty-four hours from 100,000 ACFM of flue gas at 300°F to 400°F;
- 2) taking one sorbent module off-line;
- 3) regenerating the offline sorbent module for eight hours at 600°F to 700°F by passing a hot purge gas through the module, thereby creating a highly concentrated mercury stream;
- 4) capturing the mercury contained in the purge gas;
- 5) putting the sorbent module back on-line; and
- 6) shipping the recovered mercury for recycle or disposal.



**Figure 1 – Fate of Mercury in Various Control Schemes (assumes  $2 \times 10^6$  ACFM at  $10 \mu\text{g Hg}/\text{Nm}^3$  and 60% capacity over one year)**

## Approach

This technology development project is following a multi-phase path. The Phase I work comprised laboratory development of a favorable form of the sorbent, field testing of a skid-mounted unit at a coal-combustion pilot plant, and initial assessment of the economics of the process. These activities were completed in Fall, 1997, and are documented in the Phase I Final Report (Roberts et al., 1998)

The current, Phase II program is designed to advance ADA's mercury control technology to small-scale demonstration. A key part of the Phase II work is testing at a utility site. A test of at least nine months duration is planned to determine the field performance of the system. Phase II will conclude with a preliminary design and economic assessment of a mercury removal system suitable for a 500 MW plant, carried out by a major engineering firm.

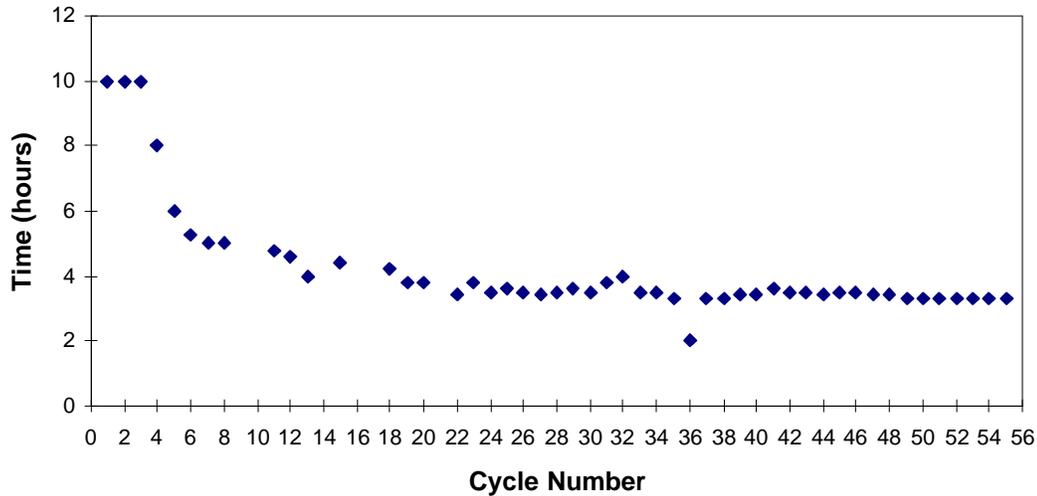
## Results - Phase I

Through laboratory testing, we found a sorbent formulation that was thermally durable, would take up mercury and desorb it repeatedly (tested through 55 cycles), and could be dispersed onto support materials that had extremely low pressure drop at high throughputs (less than one second residence time required). Eighteen different sorbent blends were examined during Phase I.

The thermal endurance of the each sorbent was tested by placing samples of sorbent in an oven held at 700°F. Periodically, one-gram portions of the sorbent were taken from the oven and examined by X-ray diffraction. This technique allowed us to see the size of the noble metal crystallites on the surface of the sorbent. Degradation of the sorbent would be indicated by coalescence and growth of the noble metal crystallites. We found several formulations of sorbent that had remained completely stable after 180 days of testing and others that came to a stable size after 120 days of testing. Several formulation were obtained that had acceptable thermal stability and were selected for further testing. This thermal stability testing is continuing and has currently exceeded one-year. Because the samples are held at 700 °F, the one-year findings represent two to four years of service life. No significant crystal growth has been seen with the best sorbent formulations

We next examined the ability of the sorbent to repeatedly take up mercury at typical flue gas temperatures and to desorb the mercury at temperatures not exceeding 700°F. For our longest duration test, we chose a mercury concentration much higher than that found in typical flue gases so as to accelerate any mercury-related degradation processes. After an initial decline, we found repeatable sorption and desorption through 55 cycles (Figure 2). We then treated a metallic monolith with the sorbent and exposed it to 21 cycles of sorption and desorption in a synthetic flue gas with 18  $\mu\text{g}/\text{m}^3$  of mercury. This monolith was fully regenerable and at face velocities up to 1.5 ft/sec had a pressure drop of only 0.05" of water. This same monolith was tested for simultaneous uptake of mercury and mercuric chloride and was found to sorb both effectively. Our laboratory tests indicated that the sorbent would repeatedly sorb and desorb

mercury and that we were ready for the pilot testing.

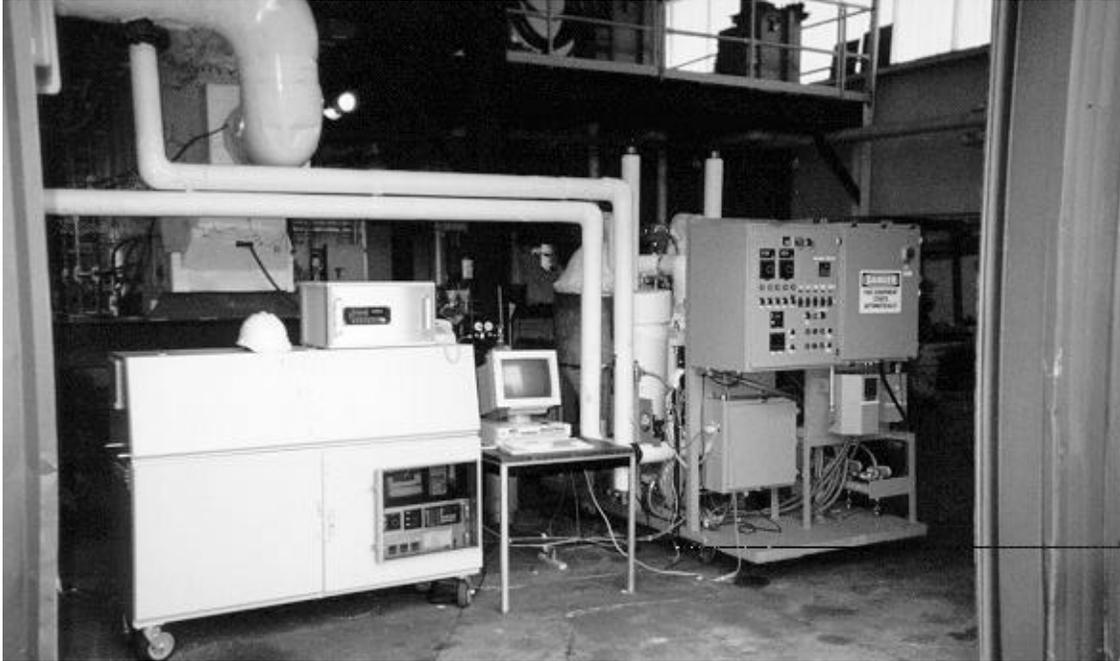


**Figure 2 - Mercury Uptake by Sorbent BVI under Repeated Sorption/Desorption Cycles.**

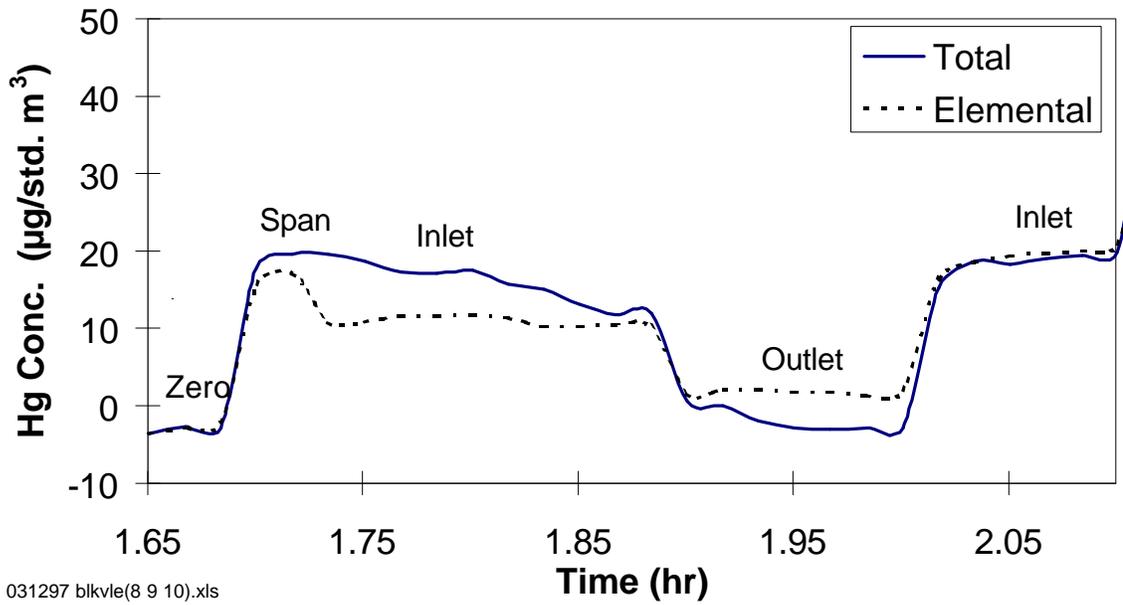
### Field Testing of 20 ACFM Unit

On the basis of the laboratory work, we designed and built a 20-ACFM test unit – a factor of 280 scale-up from the laboratory work. The unit incorporated two sorbent vessels that were physically similar to shell-and-tube heat exchangers. There were 17 tubes in each vessel; each tube was 18" long and held three 6"-long sorbent-coated monoliths.

The 20 ACFM skid unit was shipped to CONSOL, Inc. (Library, PA) where it was tested on a slipstream from CONSOL's 100-lb/hr pilot coal-combustor (Figure 3). Testing was done with four coals between January and June, 1997 – an example trace is shown in Figure 4. Several important results were found in the field. First, the sorbent modules took up elemental mercury and non-elemental mercury at over 95% removal efficiency. Second, the sorbent modules gave off nearly quantitatively the amount of mercury expected during regeneration. Third, each module recorded over 180 hours of sorption and 250 hours of regeneration during exposure to four coals, with no discernible decrease in performance. Finally, a monolith from each sorbent module was returned to the laboratory after the pilot testing and performed as well as before going to the field. Complete details on this work are found in Roberts et al., 1998.



**Figure 3 - ADA's pilot Mercur-RE Skid in Operation at CONSOL during Phase I.**



**Figure 4 - Field Test Data for low-sulfur Pittsburgh coal. Trace shows analyzer calibration data as well as process inlet and process outlet samples.**

The major inefficiency found in the pilot testing was heating the sorbent to the desired regeneration temperature of 700°F. This difficulty was attributed to the stagnant air gap that existed between the outer diameter of the monoliths (1.75”) and the inner diameter of the sorbent vessel tubes (1.87”). We were able to desorb in the Phase I field work, but improving the heat transfer efficiency is our first priority in the Phase II work.

**Process Economics**

With capital and operating costs estimated from the results of Phase I, we expect our system to cost about \$866,000 per year on an annualized basis for a 250 MW plant. Carbon injection is the only available technology for mercury control for flue gas treatment today. Annualized capital and operating costs for carbon injection are in the range \$14,400 to \$38,200 per pound of mercury removed, or \$4.25 million to \$11.3 million for a typical 250 MW plant that emits about 295 pounds of mercury per year (Chang and Offen, 1995). More recent data puts the cost at \$5000 to \$70,000 per pound of mercury, depending on conditions (Mercury Study Report, 1997).

We found that the cost of the active ingredient, namely the noble metal, is insignificant to the overall process economics. We estimate that \$90,000 of active ingredient added to the metallic monoliths will treat 1,000,000 ACFM (250 MW<sub>e</sub>) of flue gas with 10 µg/m<sup>3</sup> of mercury. This estimate is based on the actual amount of active ingredient used in the 20 ACFM unit.

**Table 1. Estimated Cost of ADA Sorbent Process vs. Carbon Injection**

Cost Basis: 250 MW <sub>e</sub> plant 10 µg/m <sup>3</sup> of mercury in the flue gas 95% removal of mercury	
<b>Mercury Removal Process</b>	<b>Estimated Average Cost (\$/lb Hg)</b>
Injection of disposable carbon	
1. Chang and Offen, 1995	\$26,000
2. Mercury Study Report, 1997	\$32,000
ADA regenerable sorbent	\$4,300

Considering the ability of the Mercur-RE process to collect all chemical forms of mercury, to generate minimal secondary wastes, and to remove over 95% of the mercury, the Mercur-RE process has clear technical and economic advantages over available technologies. The Phase II work is aimed at bringing these performance and cost benefits closer to reality for the electric power industry.

## Future Activities - Phase II Work Plan

Phase II encompasses six tasks in 24 months. The numbering of the tasks continues from the five tasks of the Phase I work. The following sections describe the Phase II work.

**Table 2. Summary of Tasks for Phase II**

<b>Task</b>	<b>Task Description</b>	<b>Duration</b>
II-6	Modify 20-acfm Skid	1/09/98 - 7/31/98
II-7	Establish Routine Operation at Pilot Coal-Combustor	6/01/98 - 12/31/98
II-8	Install and Shakedown Skid at Utility Site	1/01/99 - 2/28/99
II-9	Test Long-term Performance at Utility Site	3/01/99 - 1/31/00
II-10	Prepare Economic Assessment for Full-Scale System	8/01/99 - 12/31/99
II-11	Prepare Documents	1/09/98 - 1/31/00

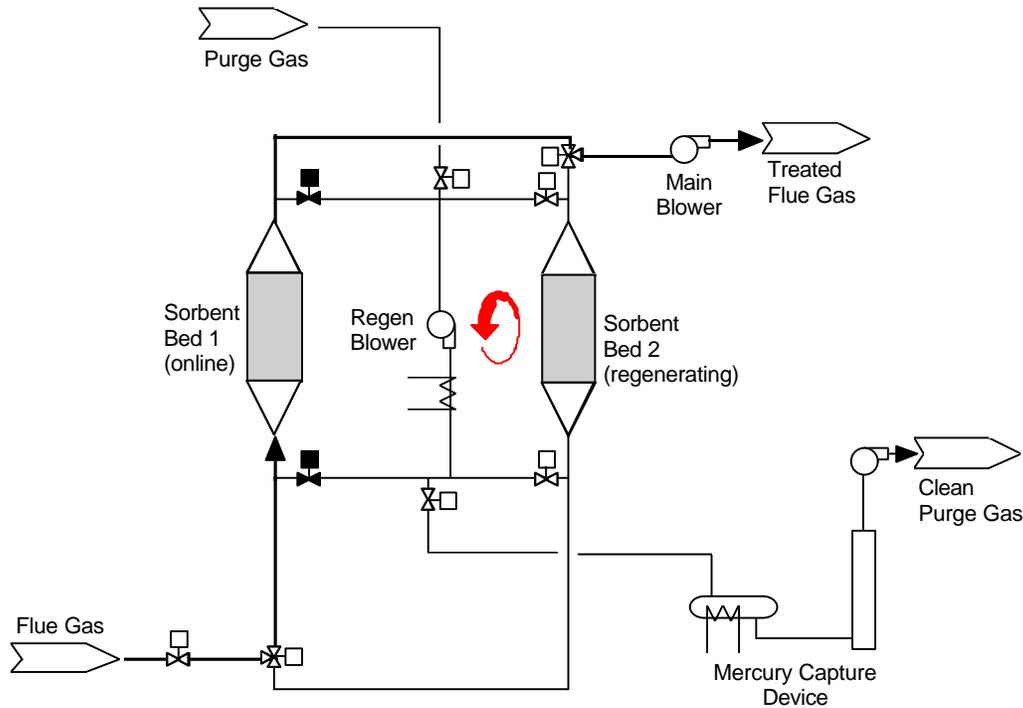
### Modifications to 20-acfm Skid

In Phase I, ADA used a shell-and-tube configuration for the sorbent bed, with sorbent-coated monoliths installed on the tube-side. Hot gas was applied to the shell-side in order to heat the sorbent to the required regeneration temperature. Following the completion of Phase I, ADA considered three options for enhancing the rate of heating the sorbent during regeneration: continuing with shell-side hot gas, using electric heaters on the shell-side, or direct tube-side hot gas heating. The third option was selected for implementation in Phase II because it was well suited for use in full-scale applications.

By applying the hot gas directly to the sorbent on the tube-side we will be able to achieve rapid heating and close packing of the vessels. However, a high gas flow rate is required to supply enough energy to heat the monolith to the regeneration temperature. To achieve this flow rate and maintain thermal efficiency, the regeneration blower will recirculate hot gas through the sorbent bed until the required regeneration temperature is reached. After the bed has stabilized at the regeneration temperature, a slow purge gas will drive the mercury-laden gas to the mercury recovery device (Figure 5). A valuable benefit of this technique is the lack of any shell-side contact. Thus the sorbent can be packed closer together, further aiding the heating process. Packing density becomes very important on larger systems where high flow rates will necessitate large sorbent beds.

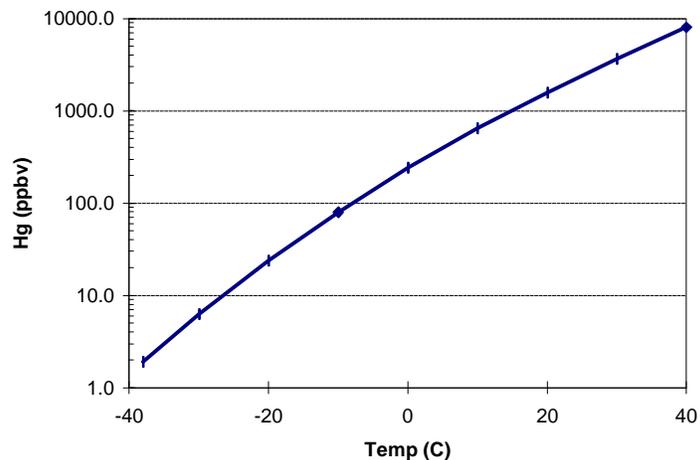
The dual-vessel design of the 20-ACFM skid will allow ADA to examine two different bed configurations. The first sorbent vessel will contain a monolith as described above. In the second vessel ADA will explore the use of a shallow bed of sorbent pellets. ADA has used this design in other mercury-removal applications. Compared with monoliths, the pellets allow for a higher

loading of noble-metal sorbent per mass of support material – thereby reducing bed size and simplifying regeneration. The drawback of a packed bed is the slightly higher pressure drop.



**Figure 5 - Simplified Process Flow Diagram of 20-cfm Pilot Unit.**

The method used for heating the sorbent bed during regeneration is coupled to the technique used for recovery of the mercury, because the regeneration method will fix the temperature and flow rate of the regeneration gas. Thus, selection of the heating method and mercury recovery method must be made in concert. Condensation is straightforward, but may not be the most efficient means of capturing the mercury. As shown in Figure 6, even at 0°C (32°F) mercury's vapor pressure is 240 ppbv (2000 µg/m<sup>3</sup>), indicating that a substantial amount of mercury would escape a condenser operating at that temperature. Offgas from the condenser can be routed back into the sorbent beds, although this will shorten the sorption cycle time for the bed.



**Figure 6 - Vapor Pressure of Mercury as a Function of Temperature.**

As an alternative to a chilled condenser, ADA will investigate the conversion of mercury into stable mercuric sulfide (HgS). Conversion of mercury vapors to HgS by contact with an aqueous sulfide solution is a novel technique that was recently demonstrated in ADA’s laboratory. This method bubbles the regeneration gas through a solution which converts the mercury into solid HgS. The HgS is periodically (or continuously) filtered from solution and make-up sulfide reagent added as necessary. ADA will explore the efficiency of the process and develop designs for a larger scale contactor.

### **Operation at Pilot Coal-Combustor**

With the modifications incorporated into the skid, we will re-install the skid along with ADA’s mercury analyzer in the same location where they operated in Phase I, namely CONSOL’s pilot coal-combustor. The unit will be run in a dual-bed mode where one sorbent bed is online while the second bed is being regenerated. Overnight, on weekends, holidays and other extended periods when the combustor is not operating, the Mercu-RE skid will run in a “hot-standby” mode. In this configuration, ambient air will pass through the online sorbent bed. The system will cycle through its regeneration cycle as if it were online with flue gas, and the mercury analyzer will run as if the skid were on flue gas. This procedure will facilitate smooth operation of the equipment by avoiding frequent start-up and shut-down. This mode also supplies a greater challenge to the skid by maximizing the unit’s total operating time.

The testing at CONSOL will begin with verification that all skid systems (electrical, controls, analytical, and process) are functioning. Operators will then run a series of tests to determine the breakthrough time. Breakthrough is defined as the point where less than 90% removal of mercury is achieved. If the inlet flue gas is found to contain too little mercury to challenge the skid (e.g., less than  $2 \mu\text{g}/\text{m}^3$ ), we will include tests where we spike mercury into the gas stream. Initial values for the regeneration cycle times and temperatures that were determined at ADA will be fined-tuned to the conditions present at the coal-combustor. Finally, the system controls will be set for the optimized values and the unit allowed to run continuously.

## **Testing at Utility Site**

Public Service Electric & Gas (Newark, NJ) has agreed to host our unit at its Hudson Station in Jersey City, NJ. The Hudson Station already has a facility where pilot work is being undertaken by ADA; consequently, the site has slip-stream ducting, and plant personnel are familiar with having a small pilot facility on site. Hudson burns a low-sulfur, bituminous coal with documented mercury concentration levels.

On the basis of the testing at CONSOL, the sorbent unit will be reconfigured to contain two identical sorbent vessels. For the tests at Hudson Station the skid may also be configured to allow parallel flow through the two sorbent beds. This configuration will double the on-line throughput of the skid. Regeneration will occur with the system offline from the flue-gas slip stream. This configuration will result in greater overall throughput because the desorption cycle generally takes less time than the adsorption cycle.

The testing at Hudson will be undertaken with minimum operator involvement. The goal is to have the equipment run for several months without unscheduled maintenance or operator adjustments. The role of ADA visits and on-site personnel will be to monitor the performance of the equipment. All required maintenance or changes to the system operating conditions will be recorded. The sorbent will be regenerated daily, or at the optimum interval derived from the prior tests. This frequency of regeneration is much higher than that anticipated in our original proposal; however, prior results indicate that the sorbent is robust enough for frequent regeneration. Regenerating each day substantially cuts down on the capital cost of an eventual full-scale installation of this process. We plan to achieve over 100 sorption/desorption cycles in the field.

Similar to testing at the pilot combustor, the skid will be kept continuously online (or regenerating) throughout the period of the tests. If for any reason the flue gas supply is unavailable, the unit will shift into a hot-standby mode and ambient air will be processed through the sorbent bed. Continuous monitoring of the inlet and outlet flue gas will be provided by ADA's mercury analyzer. We will determine the mass of recovered mercury by periodic measurement of the amount of elemental mercury or mercuric sulfide in the mercury-capture device. Operators will occasionally check mercury concentration in the offgas from the capture device and the flue gas with iodated carbon traps.

## **Economic Assessment for Full-Scale System**

ADA will work with Burns & McDonnell (Kansas City, MO), an engineering construction contractor in the electric utility business, to develop preliminary design and cost estimates for a Mercu-RE process suitable for a 500 MW power plant. The design will be based on the field data and will consist of the following elements:

- process flow diagram(s),
- energy and material balances,
- size and cost of major equipment,
- estimated costs for ancillary equipment based on good engineering practice, and
- total capital and annual O&M costs.

The costs for the ADA process will be compared to those of the state-of-the-art mercury control technology that prevails at the time (e.g., carbon injection).

## Conclusions

The ADA mercury removal process relies on the ability of noble metals to sorb mercury and its common compounds at ordinary flue-gas temperatures and to desorb the mercury at elevated temperatures. The technology offers several potential advantages to the electric power industry. First, because different chemical forms of mercury are removed from the flue gas, the user does not need to know the form of the mercury nor be concerned that changes in the fuel, in the firing conditions, or in the flue gas temperature (either seasonally or with load swings) will alter the efficiency of mercury removal. Second, the mercury is recovered in a form that is suitable for commercial recycling, eliminating disposal costs, secondary wastes, and any associated liabilities. Finally, the technology offers significant cost savings with respect to options such as injection of activated carbon or related sorbents, at the same time eliminating possible adverse effects of these sorbents on particle control devices and fly ash properties.

In Phase I we demonstrated key attributes of the new technology for removing mercury from flue gases, namely:

- removal of greater than 95% of both elemental and oxidized forms of mercury, both in the laboratory and in the field
- regenerability and robustness of the sorbent
- ability to scale up, and
- favorable economics.

Under Phase II, we propose to implement an improved method of sorbent regeneration, one that will produce recyclable mercury. This work will be accomplished by modifying the 20 ACFM skid-mounted unit employed in the Phase I work. Phase II is targeted at accomplishing long-term operation under field conditions. Scale changes from the Phase I test will be modest and will be associated with modifications to the regeneration and recovery methods. Phase II will conclude with a preliminary design and cost analysis for a full-scale mercury-treatment system. Successful completion of Phase II will set the stage for large-scale demonstration of this promising mercury-treatment technology.

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