EVALUATION OF ACTIVATED CARBON FOR CONTROL OF MERCURY FROM COAL-FIRED BOILERS

Grant E.Dunham, Research Engineer, and Stanley J. Miller, Senior Research Manager
Energy & Environmental Research Center
University of North Dakota
PO Box 9018
Grand Forks, ND 58202-9018

INTRODUCTION

The ability to remove mercury from power plant flue gas may become important because of the Clean Air Act Amendments requirement that the U.S. Environmental Protection Agency (EPA) assess the health risks associated with these emissions. One approach for mercury removal that may be relatively simple to retrofit is the injection of sorbents, such as activated carbon, upstream of existing particulate control devices. Activated carbon has been reported to capture mercury when injected into flue gas upstream of a spray dryer baghouse system applied to waste incinerators and coal-fired boilers.[1,2] However, the mercury capture ability of activated carbon injected upstream of an electrostatic precipitator (ESP) or a baghouse operated at temperatures between 200E and 400EF is not well known.

A study sponsored by the U.S. Department of Energy and the Electric Power Research Institute is being conducted at the University of North Dakota Energy & Environmental Research Center (EERC) to evaluate whether mercury control with sorbents can be a cost-effective approach for large power plants. Pilot-scale results have been reported over the last two years.[3,4] This paper presents a summary of the pilot- and bench-scale results.

EXPERIMENTAL APPROACH

Pilot-scale baseline and sorbent injection tests were conducted at the EERC with a pulverized coal-fired combustor known as the particulate test combustor (PTC) and a pulse-jet baghouse. The tests were conducted with two subbituminous coals and one bituminous coal. Four simultaneous EPA Method 29 inlet and outlet mercury samples were collected for each test condition. Although Method 29 does not claim to speciate between oxidized and elemental mercury, bench- and pilot-scale results indicate that primarily oxidized mercury will be trapped in the peroxide impingers and primarily elemental mercury in the permanganate impingers.[3,5,6,7] For consistency in this paper, the fraction of mercury captured in the peroxide impingers will be referred to as oxidized mercury, and the fraction captured in the permanganate impingers will be referred to as elemental mercury. The experimental approach for the pilot-scale tests and the facilities used have been described in a previous report.[8]

The bench-scale tests were completed with a fixed-bed system, which consists of a heated simulated flue gas and mercury delivery system, a heated filter holder, and an on-line mercury analyzer manufactured by Semtech. The simulated flue gas composition is presented in Table 1. The fixed-bed design involves loading a 22-inch-diameter EPA Method 5 dust-loading filter (quartz) with sorbent by pulling a vacuum on the outlet side and feeding the sorbent at the inlet side. The filters are uniformly coated with sorbent, and the process is very repeatable. The

TABLE 1

Bench-Scale Flue Gas Composition

Component	Concentration (dry basis)
O_2	6%
CO_2	12%
SO_2	1600 ppm
HCl	50 ppm
Hg (or $HgCl_2$), high value	60 :g/Nm^3
Hg (or $HgCl_2$), low value	20 :g/Nm^3
N_2	Balance
H_2O	8%

resulting bed thickness for this configuration is roughly 0.06 mm for 10 mg of sorbent, and gas channeling is not a problem. This design also eliminates the need for a diluting material to be mixed with the sorbent and provides a uniform bed and sufficient flow for EPA Method 29 sampling. This configuration allows for precise weight determinations for the activated carbon on the filter. Filters were loaded with roughly 10 to 20 mg of an iodine-impregnated activated carbon (IAC), depending on the test conditions. A full factorial test matrix was performed with the filter temperature at three levels (225E, 275E, and 325EF) and the elemental mercury concentration at two levels (20 and 60 :g/Nm^3). The test matrix will be repeated with the injection of mercuric chloride.

RESULTS AND DISCUSSION

Before discussing results and the effects of variables, an overview of the precision of the data will be given. Since the concentration of mercury in coal is very low (about 0.05 to 0.1 :g/g), mercury concentration in flue gas produced from coal combustion typically ranges from 2 to 10 :g/Nm^3. Accurate measurement of mercury at this low level is difficult, so it is important to establish the confidence intervals of the results. Each pilot-scale test normally included four pairs of simultaneous inlet and outlet EPA Method 29 mercury measurements and four baghouse ash samples. This allowed for determination of the mercury removal by two independent methods as well as calculation of the mercury mass balance. The two methods for calculating mercury removal are based on inlet and outlet mercury concentrations or inlet and baghouse ash mercury concentrations. Calculation of a mercury removal confidence interval for each of the runs is possible, based on the standard deviation and number of repeat samples. However, a more realistic view of the overall experimental precision would be to pool the sample standard deviations. The method used to pool the standard deviations has been presented in a previous paper.[9]

The inlet and outlet values were considered separately because they represent different aspects of the process variability. The inlet variance includes both the process variability and sampling and analytical variability.

The outlet variance includes the same process and sampling and analytical variability of the inlet and the additional process variability attributed to the injection of the sorbents. With the large number of degrees of freedom, the pooled standard deviation can be treated as a good estimate of the population deviation, F. The overall pooled standard deviations for the inlet, outlet, and baghouse ash are 0.85, 0.97, and 0.60 :g/Nm^3, respectively. Whether this is primarily process variability or sampling and analytical variability cannot be determined from the information given, since the measurements were done sequentially. However, in other research at the EERC, an EPA Method 301 self-validation test was conducted to evaluate the precision and bias of Method 29 for determination of mercury.[10] In these tests, twelve pairs of simultaneous Method 29 samples resulted in a standard deviation for Method 29 of 0.58 :g/Nm^3. Therefore, the values of 0.85 and 0.97 :g/m^3 appear to be reasonable, indicating that about 60% of the variability is due to the sampling and analysis and 40% of the variability is due to the process. To improve the resolution of possible differences caused by a variable would require significantly improved precision of the experiments or significantly more tests.

Figure 1, which plots the 95% confidence interval of the removal efficiency as a function of the number of samples, illustrates the point. Each curve represents a hypothetical case where the inlet and outlet mercury concentrations are 8 and 4 :g/Nm^3, respectively. The curves are based on the pooled standard deviations of the inlet and outlet concentrations, F, which are varied from 0.25 to 2.0 :g/Nm^3. For simplicity, the pooled standard deviations of the inlet and outlet concentrations are assumed to be the same. The confidence intervals can be determined based on the number of samples and the pooled standard deviations. From the curves, it can be seen that to cut the confidence intervals by a factor of two would require increasing the number of replicate tests from four to sixteen.

Based on statistical evaluation of the data, the following preliminary conclusions have been drawn about the pilot-scale tests[11]:

- Inlet mercury speciation for the three coals was significantly different and highly dependent on the Method 29 filter temperature.
- The highest level of natural mercury capture (by the fly ash) was observed with the Absaloka coal, but some natural mercury capture occurred for all three coals. The level of capture was highly temperature-dependent.

- Lignite-based activated carbon provided good mercury control at temperatures of 250EF and lower for all three coals, but at 300EF, the best removal was observed for the Comanche coal.

- IAC provided effective mercury control at 300E and 400EF with the Absaloka subbituminous coal but was ineffective for Comanche subbituminous coal.

- IAC was highly effective at reducing the outlet elemental mercury concentration for all three coals; however, in some cases, the elemental mercury was apparently converted to oxidized mercury and was not captured.

In the past year, the focus of the project has been on developing a reliable bench-scale system and sorbent-screening protocol. The purposes of the bench-scale tests are to screen potential sorbents, develop breakthrough curves for these sorbents, and determine the effects of process conditions on the effectiveness of sorbents for mercury control. Figure 2 is a set of typical breakthrough curves and plots the outlet mercury concentration for 4 runs with the IAC sorbent at 325EF and a nominal inlet elemental mercury concentration of 55 :g/Nm^3. The mercury concentration is plotted as a percent of the inlet mercury concentration. This plot represents the excellent repeatability achieved with the fixed-bed configuration. There are two mechanisms for mercury capture with the IAC sorbent, physical adsorption and chemical adsorption. The change from physical to chemical adsorption is represented by the change in slope of the plot. Recent

results with the IAC sorbent are presented in Figure 3. Each data point represents at least two tests at the same conditions, and the error bars represent " 1 standard deviation. As expected, the sorbent capacity shows a strong dependence on temperature, decreasing with increasing temperature. The ratio of the capacities at an inlet mercury concentration of 60 :g/Nm^3 to the capacities at an inlet concentration of 20 :g/Nm^3 is roughly 2.0. This may be checked with future tests at different inlet concentrations. If these relationships hold true, the data can be used to model isotherms for each sorbent. Adsorption isotherms

express the variation of adsorption with concentration at a constant temperature.

SUMMARY

Statistical analysis was used to determine the overall precision of the pilot-scale data. The overall pooled standard deviations for the inlet, outlet, and baghouse ash are 0.85, 0.97, and 0.60 :g/Nm^3, respectively. Based on other research at the EERC, about 60% of the variability is due to sampling and analysis and 40% of the variability is due to the process. To improve the resolution of possible differences caused by a variable would require significantly improved precision of the experiments or increasing the number of replicate tests.

Based on the statistical evaluation of the data, several preliminary conclusions have been drawn about the pilot-scale tests, the most significant being the following:

$Inlet mercury speciation for the three coals was significantly different and highly dependent on the Method 29 filter temperature.

$The level of natural mercury capture (by the fly ash) was highly temperature-dependent.

$The effectiveness of the mercury sorbents was also highly temperature-dependent.

The focus of the work has been shifted to bench-scale testing. Excellent repeatability has been demonstrated with the fixed-bed configuration and simulated flue gas. Initial results with the sorbent indicate two mechanisms for mercury capture, physical adsorption and chemical adsorption. From the results, the sorbent capacity shows a strong dependence on temperature, decreasing with increasing temperature. The sorbent capacity at initial breakthrough increases with increasing inlet mercury concentration.

REFERENCES

1. Felsvang, K. et al. "Air Toxics Control by Spray Dryer Absorption Systems," Presented at the 2nd International Conference on Managing Hazardous Air Pollutants, Washington, DC, 1993.

2. White, D.M. et al. "Parametric Evaluation of Powdered Activated Carbon Injection for Control of Mercury Emissions from a Municipal Waste Combustor," Presented at the 85th Annual Meeting of the Air & Waste Management Association, Kansas City, MO, 1992; Paper No. 92-40.06.

3. Laudal, D.L.; Miller, S.J. "Evaluation of Sorbents for Enhanced Mercury Control," *In* Proceedings of the 10th Annual Coal Preparation, Utilization, and Environmental Control Contractors Conference; Pittsburgh, PA, July 1994.

4. Miller, S.J.; Laudal, D.L.; Dunham, G.E. "Evaluation of Activated Carbon for Control of Mercury from Coal-Fired Boilers," *In* Proceedings of the 11th Annual Coal Preparation, Utilization, and Environmental Control Contractors Conference; Pittsburgh, PA, July 1995.

5. Biscan, D.A.; Gebhard, R.S.; Matviya, T.M. "Impact of Process Conditions on Mercury Removal from Natural Gas Using Activated Carbon," *In* Proceedings of the 8th International Conference on Liquefied Natural Gas; 1986; pp 1B12.

6. Tumati, P.R.; DeVito, M.S. "Partitioning Behavior During Coal Combustion," Presented at the Joint ASME/IEEE Power Generation Conference, Kansas City, MO 1993; Paper No. JPGC-EC-8.

7. Chang, R. et al. "Pilot-Scale Evaluation of Activated Carbon for the Removal of Mercury at Coal-Fired Utility Power Plants," Presented at the 2nd International Conference on Managing Hazardous Air Pollutants, Washington, DC, 1993.

8. Miller, S.J.; Laudal, D.L. "Pulse-Jet Baghouse Performance Improvement with Flue Gas Conditioning," final project report for Project No. RP-38083-9 for Electric Power Research Institute, U.S. Department of Energy, and Canadian Electric Association; Oct. 1992.

9. Dunham, G.E.; Miller, S.J.; Chang, R.; Bergman, P.D. "Investigation of Mercury Control in Baghouses with Sorbents," Presented at the 89th Annual Meeting of the Air and Waste Management Association, Nashville, TN, June 1996.

10. Heidt, M.K.; Laudal, D.L. "EPA (Draft) Method 29: An Evaluation of Its Ability to Speciate Mercury," *In* Proceedings of the EPRI/DOE International Conference on Managing Hazardous and Particulate Air Pollutants; Toronto, Canada, Aug. 15B17, 1995.

11. Miller, S.J.; Laudal, D.L.; Dunham, G.E.; Chang, R.; Bergman, P.D. "Pilot-Scale Investigation of Mercury Control in Baghouses," *In* Proceedings of the EPRI/DOE International Conference on Managing Hazardous and Particulate Pollutants; Toronto, Canada, Aug. 15B17, 1995.