Enhanced Control of Mercury and Other HAPs by Innovative Modifications to Wet FGD Processes

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Introduction

This project is funded by the U.S. Department of Energy's Federal Energy Technology Center (DOE/FETC) under a cost-sharing PRDA with Radian International. The Electric Power Research Institute (EPRI) is providing cofunding and technical oversight. The project is part of FETC's Advanced Power Systems Program, whose mission is to accelerate the commercialization of affordable, high-efficiency, low emission, coal-fueled electric generating technologies.

The 1990 Clean Air Act Amendments mandated the Environmental Protection Agency to study the health effects caused by hazardous air pollutants (HAPs) from electric utility plants. The act also mandated a separate study on the effect of mercury emissions. Most of the HAPs in power plants occur in the particulate phase at flue gas exit temperatures. However, mercury, while emitted in extremely low concentrations, is primarily in the vapor phase at most plants. The goal of this PRDA research was to explore the development of advanced concepts for removing toxic substances from flue gases using wet flue gas desulfurization (FGD) systems.

Objective

The overall objective of this project was to learn more about controlling emissions of hazardous air pollutants (HAPs) from coal-fired power plants that are equipped with wet flue gas desulfurization (FGD) systems. The project was included by FETC as a Phase I project in its Mega-PRDA program. Phase I of this project focused on three research areas. These areas in order of priority were:

- Catalytic oxidation of vapor-phase elemental mercury;
- Enhanced particulate-phase HAPs removal by electrostatic charging of liquid droplets; and
- Enhanced mercury removal by addition of additives to FGD process liquor.

Mercury can exist in two forms in utility flue gas—as elemental mercury and as oxidized mercury (predominant form believed to be $HgCl_2$). Previous test results have shown that wet scrubbers effectively remove the oxidized mercury from the gas but are ineffective in removing elemental mercury. Recent improvements in mercury speciation techniques confirm this finding.

Catalytic oxidation of vapor-phase elemental mercury is of interest in cases where a wet scrubber exists or is planned for SO_2 control. If a low-cost process could be developed to oxidize all of the elemental mercury in the flue gas, then the maximum achievable mercury removal across the existing or planned wet scrubber would increase. Other approaches for improving control of HAPs included a method for improving particulate removal across the FGD process and the use of additives to increase mercury solubility. This paper discusses results related only to catalytic oxidation of elemental mercury.

Approach

During this program, catalytic oxidation of vapor-phase elemental mercury was investigated in three phases. During the first phase, bench-scale tests were conducted to screen potential catalyst and fly ash types for catalytic activity[1]. Based on the results from these tests, the most promising catalysts were tested at EPRI’s Environmental Control Technology Center (ECTC) in Barker, New York, using a 4-MW pilot FGD system. Following the pilot tests, a catalyst field test unit was developed, and additional catalyst testing was conducted at a utility power plant which burns lignite coal. Results from tests conducted at the full-scale facility were still being reduced and evaluated at the time of this paper’s preparation.

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[1] Tested materials are referred to throughout this paper as “catalyst” or fly ash samples. Testing of these materials has not been performed long enough to determine whether the material reacts directly with elemental mercury or instead catalyzes the oxidation of elemental mercury. The term “catalyst” is used for convenience.

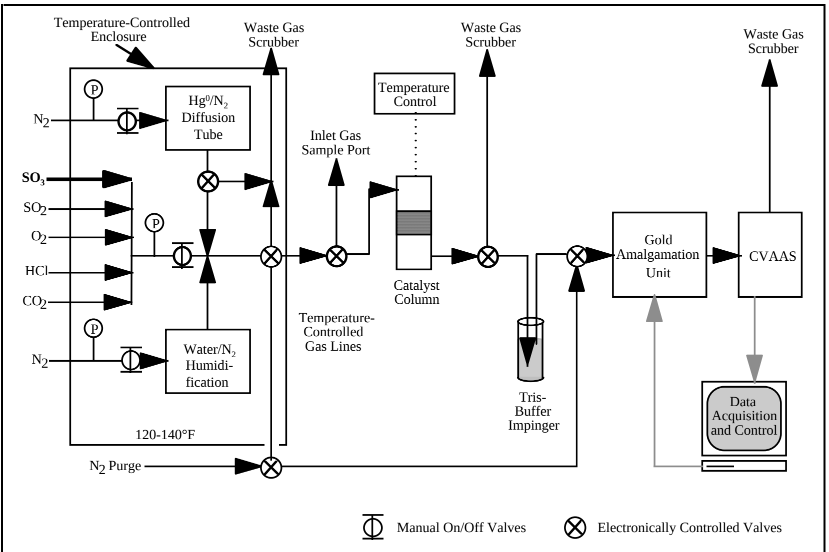

Figure 1. Elemental mercury conversion bench-scale test apparatus.

The bench-scale unit used to test the reactions of gas-phase elemental mercury with potential catalysts is shown in Figure 1. The general test approach consisted of passing a simulated flue gas containing elemental mercury across a fixed-bed reactor containing a mixture of catalyst material and sand. The gas exiting the fixed bed was analyzed semi-continuously to determine the fraction of inlet elemental mercury oxidized across the bed.

The simulated flue gas was prepared using reagent gases and calibrated flow meters. Elemental mercury was added to the simulated flue gas by passing nitrogen carrier gas across a mercury diffusion cell which contained a Hg^0 permeation tube. The amount of diffused mercury was controlled by controlling the flow of nitrogen through the diffusion cell and the temperature of the diffusion cell. The mercury-containing nitrogen was then mixed with other flue gas components (SO_2, HCl, O_2, CO_2, and H_2O) at constant temperature before the gas entered the fixed-bed reactor.

The fixed-bed reactor consisted of a mixture of catalyst or fly ash material and sand placed in a temperature-controlled, vertical Pyrex column (typically yielding a bed length of about 1.75 inches). Gas exiting the fixed-bed was analyzed to determine the percentage of inlet elemental mercury that was either removed or oxidized across the bed. Oxidized forms of mercury exiting the bed were captured in a 1M Tris buffer solution. This impinger solution has been shown in other studies to effectively capture oxidized mercury while allowing elemental mercury to pass through the solution. Elemental mercury passing through the Tris solution was measured semi-continuously using a gold amalgamation unit and cold vapor atomic absorption (CVAA) unit. The inlet Hg^0 concentration was also measured using the gold amalgamation/CVAA unit at the beginning and end of each test.

Ideally, the total mercury concentration (oxidized plus elemental) exiting the fixed-bed reactor should be equal to the inlet concentration. The outlet oxidized mercury concentration was determined by analyzing the Tris buffer solutions. By comparing this concentration to the inlet mercury concentration, the fraction of mercury oxidized across the fixed-bed could be determined. The outlet elemental mercury concentration was determined based on the gold amalgamation/CVAA analyses to provide the fraction of mercury that passed through the bed unchanged. The sum of these two analyses was compared to the inlet concentration to determine the total fraction of inlet mercury that was detected at the outlet. In many cases, the total outlet concentration was lower than the inlet concentration. These differences were attributed to adsorption of mercury by the catalyst material.

During the bench-scale tests, fourteen different catalyst and eleven different fly ash samples were tested to determine their ability to oxidize elemental mercury. Each sample was tested at the baseline conditions shown in Table 1. In addition, several parametric tests were conducted which evaluated the effect of temperature, SO_2 concentration, HCl concentration, and NO_x concentration on the oxidation of elemental mercury. The materials tested are shown in Table 2. During each test, a ten gram mixture of sand and catalyst was placed in the fixed-bed reactor. Most materials were tested using a bed loading of 100 mg/g. Lower loadings, shown in Table 2, were used for some catalysts thought to be more reactive.

Most of the laboratory tests were conducted for only a few hours, not long enough for the adsorption capacity of the catalyst to be depleted. Therefore, elemental mercury oxidation was not measured at steady-state. These short tests were intended to be catalyst screening tests to indicate relative differences in performance between catalysts. A few long-term tests were conducted until steady-state was obtained. Elemental mercury oxidation measured during these tests provides a better estimate of catalyst performance.

The catalyst samples shown in Table 2 can be classified as either commercial catalysts, laboratory-prepared catalysts, or fly ashes. Several commercial catalysts were obtained from a catalyst supplier. These included samples consisting of both palladium and nickel on an alumina (Al_2O_3) substrate. Other samples included a zinc catalyst, alumina powder, a SCR catalyst, and a carbon-based catalyst. Seven of the fourteen catalysts were iron-based. Some of these iron-based catalysts were obtained commercially while others were generated in the laboratory.

Table 1. Baseline Gas Conditions for Catalyst Screening Tests

Parameter	Baseline Condition(s)
Fixed-Bed Temperature	300 and 700°F
$[Hg^0]$	45 - 60 mg/Nm^3
O_2	7%
CO_2	12%
H_2O	7%
SO_2	1600 ppm
HCl	50 ppm
Gas Flow Rate	1 L/min

Table 2. Catalyst and Fly Ashes Tested in Bench-Scale Reactor

Catalyst Samples	Fly Ash Samples
Alumina	Subbituminous Ash #1
NiO	Subbituminous Ash #2
ZnO	Bituminous Ash #1
Pd #1	Bituminous Ash #2 - Cyclone
Pd #2 (20 mg/g)	Bituminous Ash #2 - ESP Field 1
NOx Catalyst	Bituminous Ash #2 - ESP Field 5
Carbon (2 mg/g)	Bituminous Ash #3
Fe #1 (100, 20 mg/g)	Lignite Ash #1
Fe #2 (20 mg/g)	Lignite Ash #2
Fe #3 (20 mg/g)	Lignite Ash #3
Fe #4	Oil-Fired Ash
Fe #5	
Fe #6	
Fe #7	

Previous testing has shown that fly ash at the ECTC is capable of oxidizing Hg^0 in flue gas. To determine if this property is shared by other fly ashes, several fly ash samples generated from different coal sources were obtained for bench-scale testing. The goal was to determine if particular fly ash sources are more effective at oxidizing mercury. Ash samples from bituminous, subbituminous, and lignite coals were obtained. An additional sample from an oil-fired system was also obtained for comparison. Three different samples of Bituminous #2 ash, each collected from a different process location, were obtained. The locations included the first and fifth fields of the ESP as well as a cyclone connected upstream of a gas sampling train.

Subsequent to testing at the ECTC, some additional bench-scale tests were run to determine the effect of SO_3 and HCl on the oxidation of the catalyst samples. Results from the ECTC had indicated that SO_3 could be deactivating or inhibiting catalyst activity. SO_3 was added to the gas by purging a solution of fuming sulfuric acid (30% free SO_3) with a nitrogen stream. The HCl bench-scale tests were repeated as long-term tests since the initial, short-term bench tests were inconclusive.

Based on the bench-scale results, the most promising catalyst samples were to be tested on the 4-MW pilot system at EPRI’s ECTC. The configuration used for testing catalysts on the pilot-scale at the ECTC is shown in Figure 2. Gas containing fly ash passed through the dirty raw gas (DRG) duct to the pilot-scale electrostatic precipitator (ESP). After removing over 99% of the fly ash, the gas passed through the clean raw gas (CRG) duct to the spray-dryer absorber (SDA) and pulse-jet fabric filter (PJFF). The SDA is used only as a means to convey gas to the PJFF (i.e., the atomizer wheel is not in service). After passing through the PJFF, the gas was returned to the Kintigh stack through the treated gas return (TGR) duct.

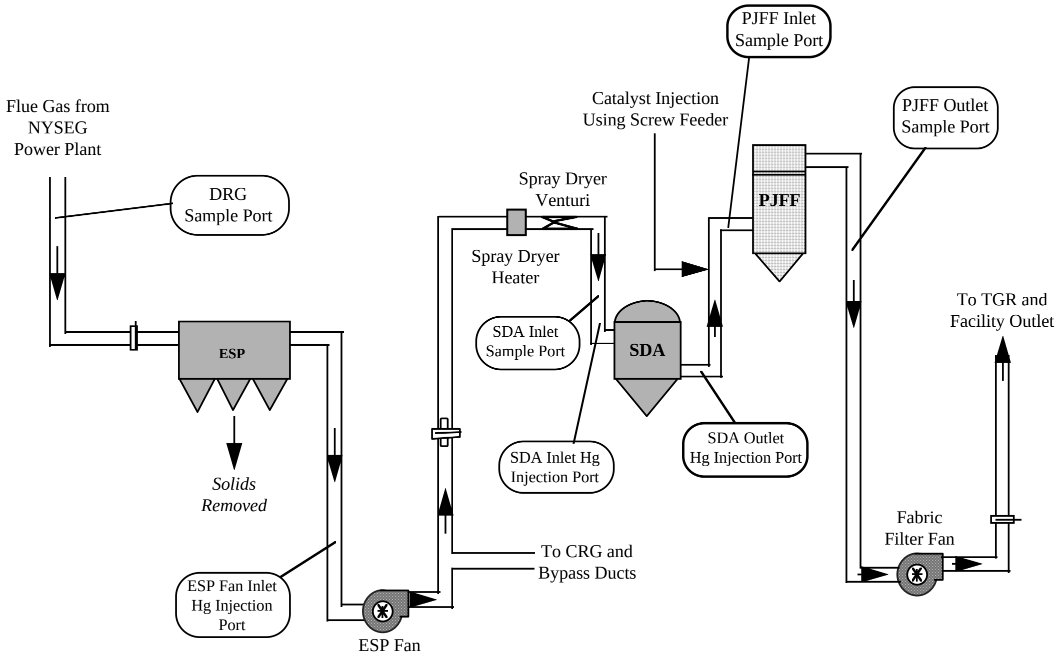

Figure 2. Simplified flow diagram for pilot-plant Hg^0 oxidation testing

Flue gas for the pilot system was drawn from New York State Electric and Gas' Kintigh Station. The Kintigh flue gas contained about 90% oxidized mercury. In order to test the oxidation of elemental mercury, the elemental mercury concentration had to be artificially increased by injecting elemental mercury into the duct. Mercury was injected at several different locations. To determine the concentrations of both oxidized and elemental mercury in the flue gas, a modified Method 29 gas sampling train was used. In this train, the Method 29 peroxide/nitric acid impingers were replaced with Tris impingers (M29T). The Tris solution effectively captures oxidized forms of mercury while allowing elemental mercury to pass through the solution to the permanganate impingers. The M29T train is shown in Figure 3.

Using the configuration shown in Figure 2, the ability of various catalyst samples to oxidize elemental mercury was determined by coating the catalyst material on the PJFF bags. The bags were pulsed clean before adding the desired mass of catalyst and then were not cleaned again until testing of the given sample was complete. By injecting elemental mercury upstream of the PJFF, elevated concentrations of elemental mercury contacted the catalyst material as the gas passed through the PJFF. Mercury samples were collected upstream of mercury injection, at the PJFF inlet, and PJFF outlet. By comparing the PJFF inlet and outlet elemental mercury concentrations, the fraction of inlet elemental mercury oxidized was determined. By collecting the prespike sample, the actual amount of elemental mercury spiked into the duct was determined (this sample is not absolutely necessary to determine the oxidation fraction across the PJFF).

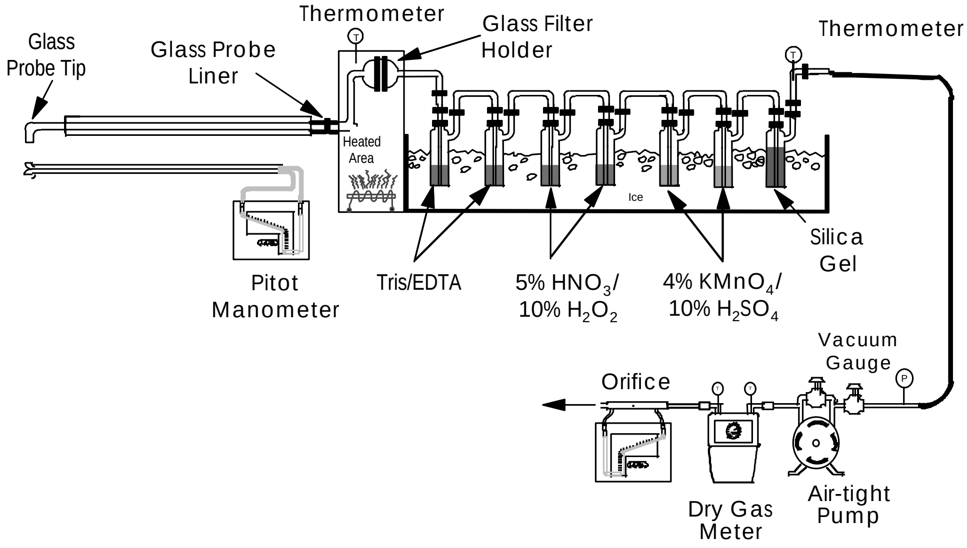

Figure 3. Schematic of Method 29–Tris Sampling Train

The above method of testing catalysts was generally effective at the ECTC. However, operational difficulties caused by unexpectedly high oxidation across the original Ryton™ bags and failure of acrylic bag material (already available on site) limited catalyst testing on the pilot equipment. During periods when the PJFF was out of service, testing was conducted by placing catalysts or bag materials in the filter holder location of a Method 29–Tris (M29T) sampling train to maximize data collection.

Results

Lab Results. Figure 4 shows results from the 300°F (baseline) and 700°F catalyst tests for the most active of the catalyst materials. The percentages of inlet elemental mercury oxidized and adsorbed by the catalyst samples are shown. As shown in Table 2, most of the catalysts were tested using 1000 mg of catalyst in a 10 gram mixture of catalyst and sand. Materials tested using a smaller mass were carbon (20 mg) and Fe #2 and #3 (200 mg).

Catalysts with the greatest combined adsorption and oxidation in the baseline tests were the two Pd-based catalysts, Fe #1, Fe #2, Fe #3, Fe #4, and carbon. The activity of carbon was considered high since a small mass was used relative to the other catalysts. Generally, both oxidation and adsorption across the catalysts were higher at 300°F than at 700°F. These data suggest that elemental mercury is first adsorbed to the catalyst surface and then reacts. Since physical adsorption generally decreases as temperature increases, less of the mercury is also oxidized.

Results from the baseline tests (300°F) with fly ash samples are summarized in Figure 5. (The effect of temperature is similar to that with the catalysts—the fly ash activity at 300°F is generally greater than at 700°F so 700°F results are not shown.) Both subbituminous ashes and Bituminous #1 showed greater oxidation than any of the lignite ashes. Lignite #1 showed greater oxidation than the other two lignites which exhibited greater adsorption than oxidation at 300°F.

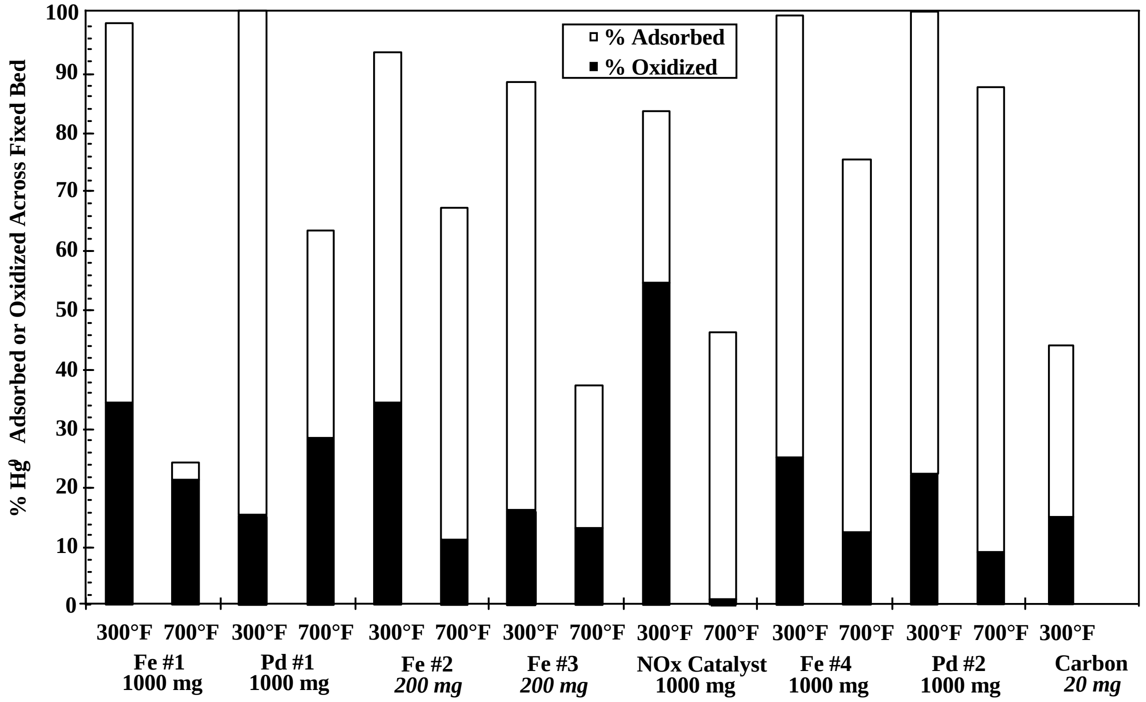

Figure 4. Catalyst Activity at Baseline Conditions

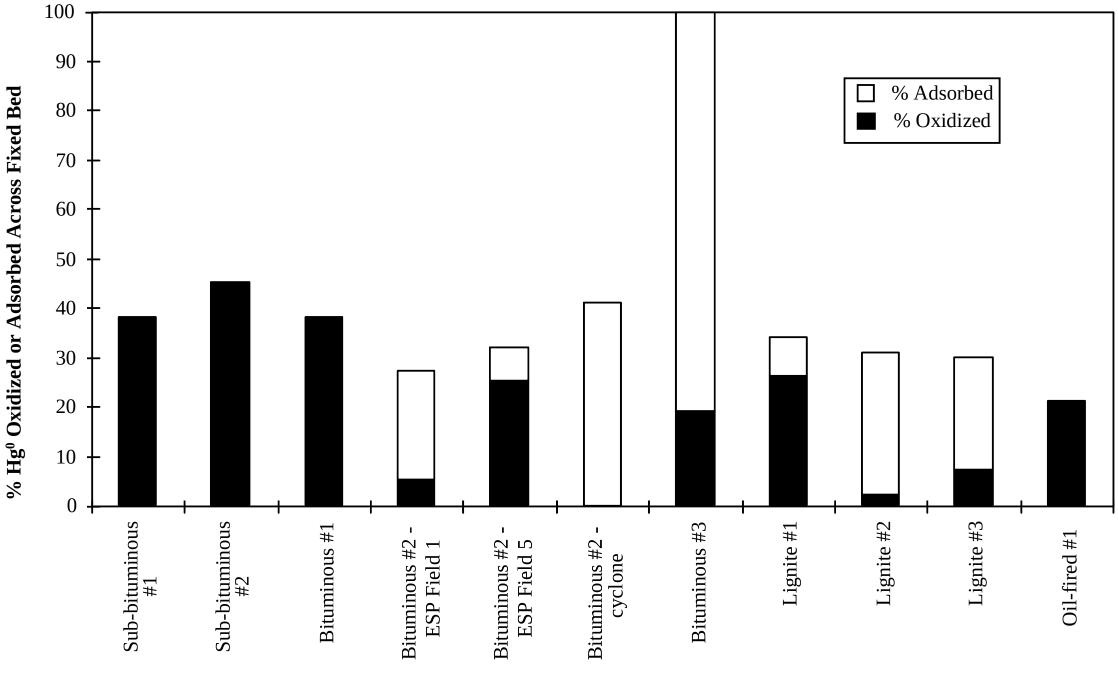

Figure 5. Fly Ash Activity at Baseline Conditions

Three different samples of Bituminous #2 fly ash were tested. These samples were collected from ESP Field 1, ESP Field 5, and a cyclone pre-cutter in a sampling train. The highest oxidation observed was from the Hopper E ash, the smallest-sized material. The lowest oxidation observed was from the cyclone catch. Since all of these samples were tested at the same loading (1 gram), the effect may be due to size differences or to surface chemistry differences.

The effects of SO_2, HCl, and NO_x concentration on oxidation activity were also tested during the bench-scale tests. Variability in the data resulted in no distinct trends being identified during the first series of tests. Because of the perceived importance of HCl in the oxidation step and because catalyst testing at the ECTC indicated that some of the materials were being deactivated by SO_3, additional laboratory parametric tests were conducted at the conclusion of the pilot program to determine the effect of these flue gas constituents on oxidation.

Testing of the metal-based catalysts at the ECTC indicated that oxidation quickly decreased as exposure to flue gas increased. These observations suggested that a flue gas component present at the ECTC was deactivating the catalysts. This component was suspected to be SO_3.

To confirm the suspected effect of SO_3, SO_3 was added to the matrix gas during tests with fresh Fe Catalyst #1 samples. The sample size was reduced to 0.02 grams (in 0.98 g of sand) so that effects could be observed over a reasonably short time period. These results are summarized in Figure 6. After adding about 10 ppm SO_3 to the gas, Hg^0 oxidation decreased from 29% to 4% and the percentage of Hg^0 passing through the column unchanged increased from 8% to 96%. Apparently, the SO_3 reacts with the metal oxide-based catalyst in some manner, thereby preventing mercury reactions from occurring. The deactivation mechanism, however, is unknown.

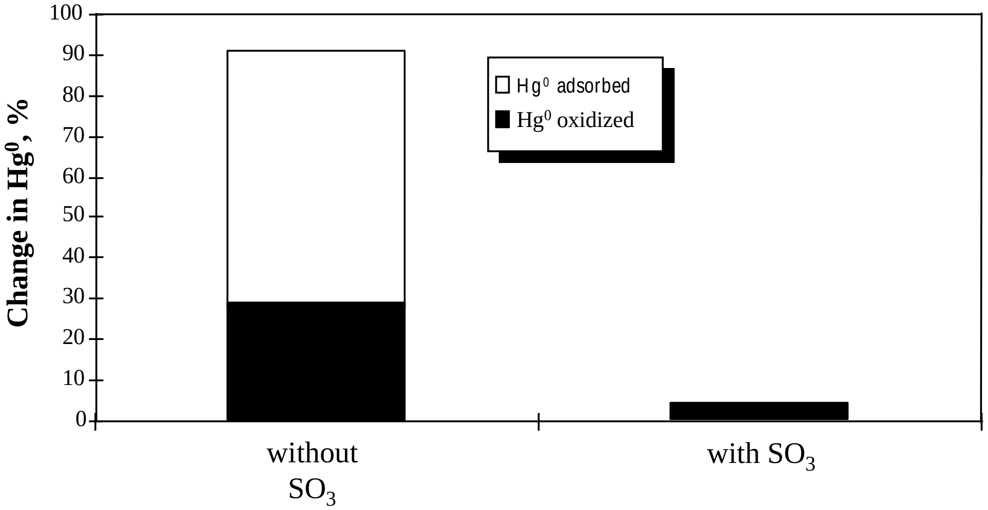

Figure 6. Effect of SO_3 on Catalyst Fe #1–Lab Results

The effect of HCl on Hg^0 oxidation with a carbon-based catalyst in the laboratory reactor is shown in Figure 7. These results show that Hg^0 oxidation is essentially zero at HCl concentrations below 10 ppm. It is emphasized that these results are valid for the simulated flue gas used in these tests. Interaction with other flue gas constituents such as NO_x may have important effects as well. However, the fact that the HCl concentration is 50 ppm at the ECTC may be one reason that high Hg^0 oxidation occurs naturally there.

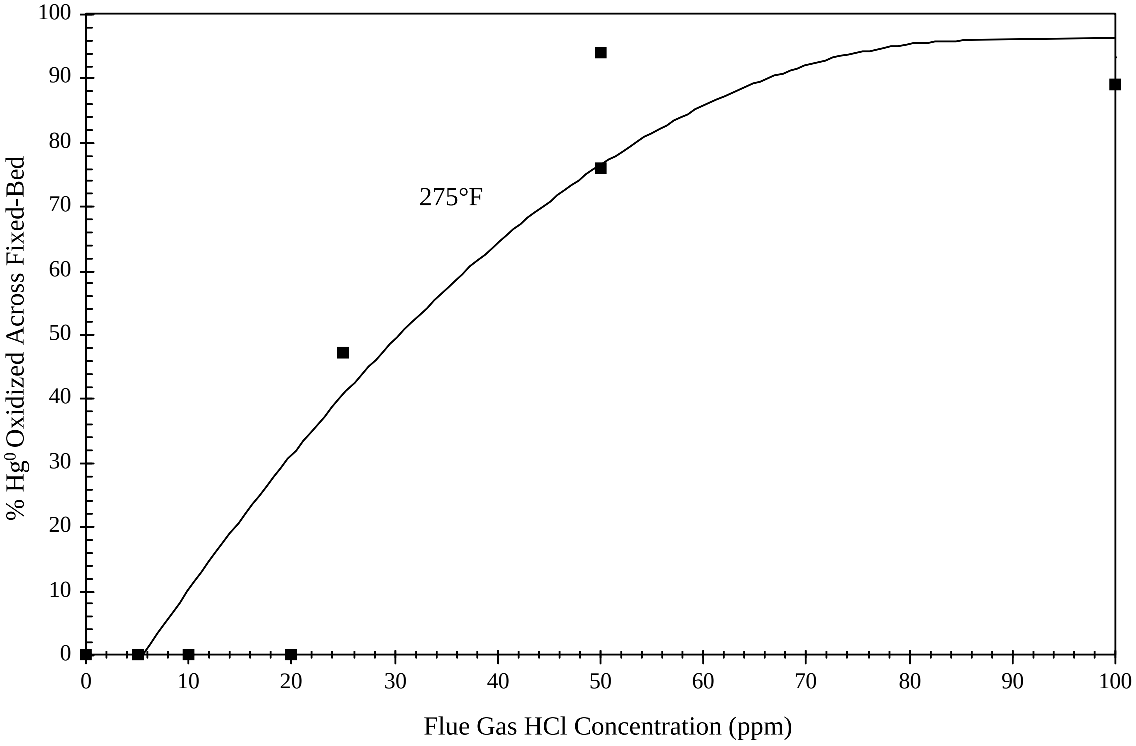

Figure 7. Effect of HCl Concentration on Oxidation of Hg^0

Based on the baseline test results and anticipated catalyst material costs for full-scale application, the following samples were recommended for pilot-scale testing: Fe #1, Fe #2, Fe #4, carbon, bituminous #2 fly ash, and lignite #3 fly ash.

Pilot Results. Initial testing using the configuration shown in Figure 2 indicated that the elemental mercury spike was nearly 100% oxidized at the PJFF outlet even with no catalyst material added to the PJFF. Previous testing at the ECTC has shown that elemental mercury oxidation in the duct is a strong function of the residence time. Several changes were made in order to decrease the duct residence time of the mercury spike; however, after decreasing the residence time from the spike location to the post-PJFF sampling location from 51 seconds to 12 seconds, a significant fraction of the elemental mercury spike was still oxidized.

Ryton bags were used in the PJFF for the residence time testing described above. Several tests, including those at short residence times, indicated that these bags were responsible for oxidizing a significant fraction of the elemental mercury (20-30%). These results indicated the need to study the oxidation of elemental mercury across different bag materials. For these tests, different bag materials (some new and some previously contacted with fly ash) were placed on filters in a Method 29T gas sampling train, and the oxidation of mercury across these materials was compared to a baseline Method 29T train sampling along side the test train. Based on the bag materials tests, Gore-Tex™ on fiberglass bags resulted in very little oxidation of elemental mercury; therefore, a set of these bags was ordered to rebag the PJFF.

To continue testing catalyst samples while the new bags were being purchased, Method 29T sampling trains were used to test various catalyst samples. Catalyst samples tested on the Method 29T sampling filters included Fe #1, Fe #2, Fe #4, Pd #1, carbon-based material, and the SCR catalyst. The results from these tests are shown in Figure 8. A decrease in $KMnO_4$ capture indicates the amount of elemental mercury oxidized and/or adsorbed. An increase in Tris capture indicates the amount of elemental mercury oxidized.

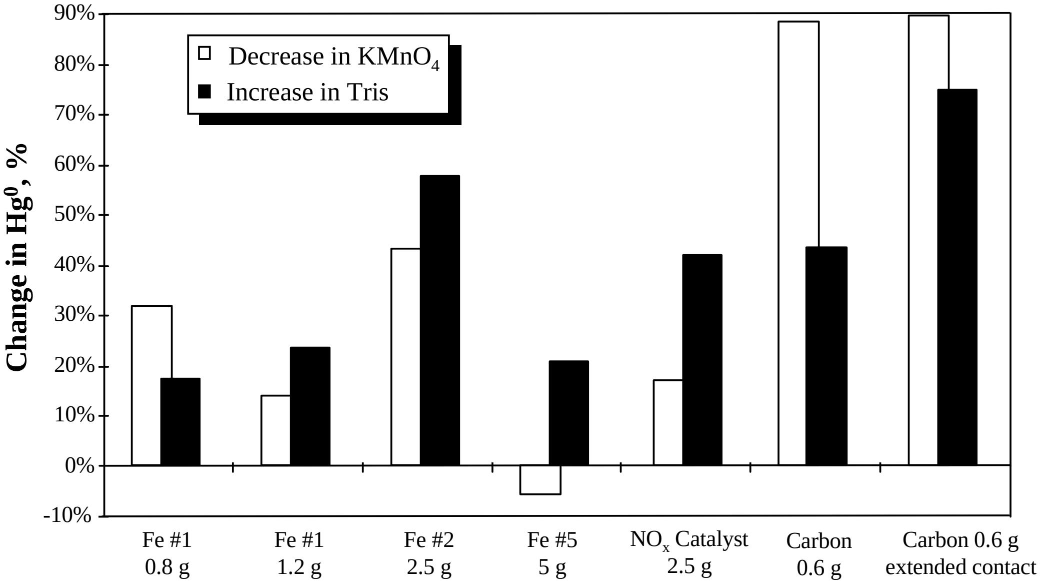

Figure 8. Effect of Hg^0 Oxidation "Catalysts" at 300°F (M29T Trains)

The results show that the carbon-based catalyst was the most active by a significant margin, even though only 0.6 g of carbon was used compared to 2.5 g of the next most reactive material (Fe #2). It is also important to note that the carbon-based material oxidized a greater fraction of the mercury (measured as increase in Tris) as the run time was extended and adsorption decreased. This could indicate that the carbon-based catalyst may oxidize a high percentage of Hg^0 after steady state is reached.

During the Method 29T tests, most of the catalyst materials appeared to be deactivated during continued exposure to flue gas. As exposure time to flue gas increased, Hg^0 oxidation decreased. One of the major differences between the ECTC flue gas and the simulated laboratory flue gas was the presence of SO_3 at the ECTC. These observations led to the laboratory testing of SO_3 as discussed previously.

Once the new Gore-Tex™ on fiberglass bags were installed in the PJFF, catalyst CT-9 (a carbon-based catalyst) was coated on the PJFF bags to determine its ability to oxidize mercury. The catalyst was introduced to the PJFF downstream of the ESP to ensure that a minimal amount of fly ash would be present with the catalyst on the bags. (The initial test was with 20 pounds of CT-9, although subsequent tests included higher and lower catalyst loadings.) The PJFF was then operated continuously for ten days with no pulse-cleaning, and samples were taken each day to determine elemental mercury oxidation and removal. Although all ESP fields were placed in service and the fly ash loading was below 0.03 lb/MMBtu, the PJFF continued to remove fly ash. The effect was that the oxidation of Hg^0 increased over time with just the native fine fly ash accumulation. This effect of fly ash accumulation on oxidation is shown in Figure 9. The baseline oxidation increased from 30-50% immediately after bag cleaning (baseline) to 50-80% after several days. This makes it somewhat difficult to interpret the effect of catalyst materials added to the PJFF.

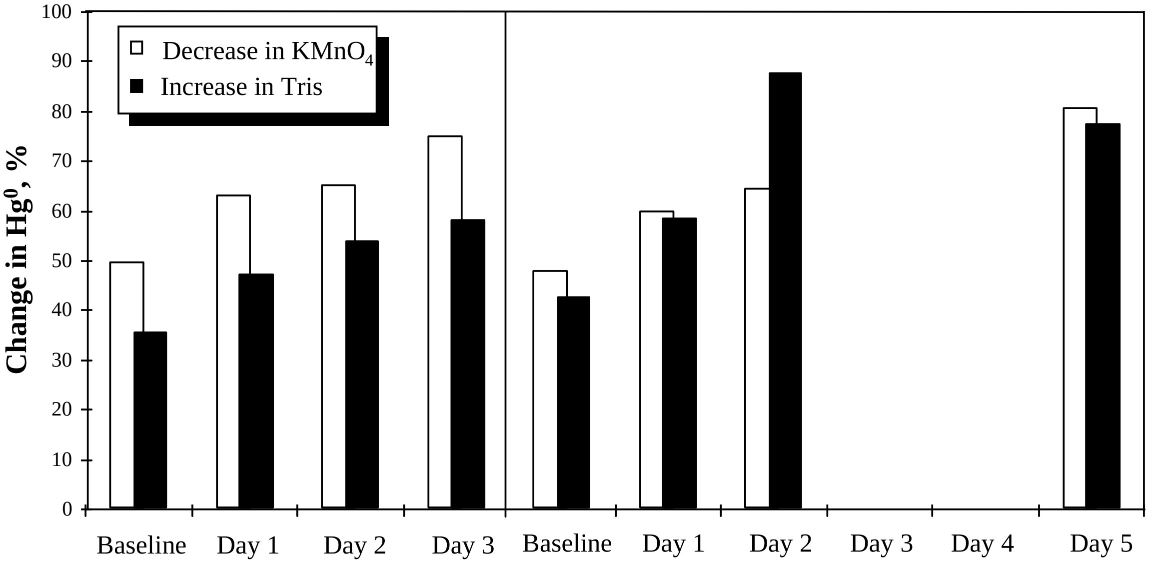

Figure 9. Effect of Fine Ash Accumulation on PJFF Bags

The effect of CT-9 was estimated by using the data in Figure 9 to "correct" for the background oxidation due to the fine ash accumulation. The results of this analysis are shown in Figure 10. The results indicate that 20 pounds of CT-9 accounted for about an 85 % decrease in the outlet Hg^0 concentration after correcting for fine ash oxidation. Ten and 5 pounds of carbon accounted for about 65 and 35% oxidation. It should be noted that average values over several days of operation were used to generate Figure 10. With the difficulty in measuring very low mercury concentrations and the daily variations in oxidation values, the uncertainty in Figure 10 data is quite large despite the smooth curves shown.

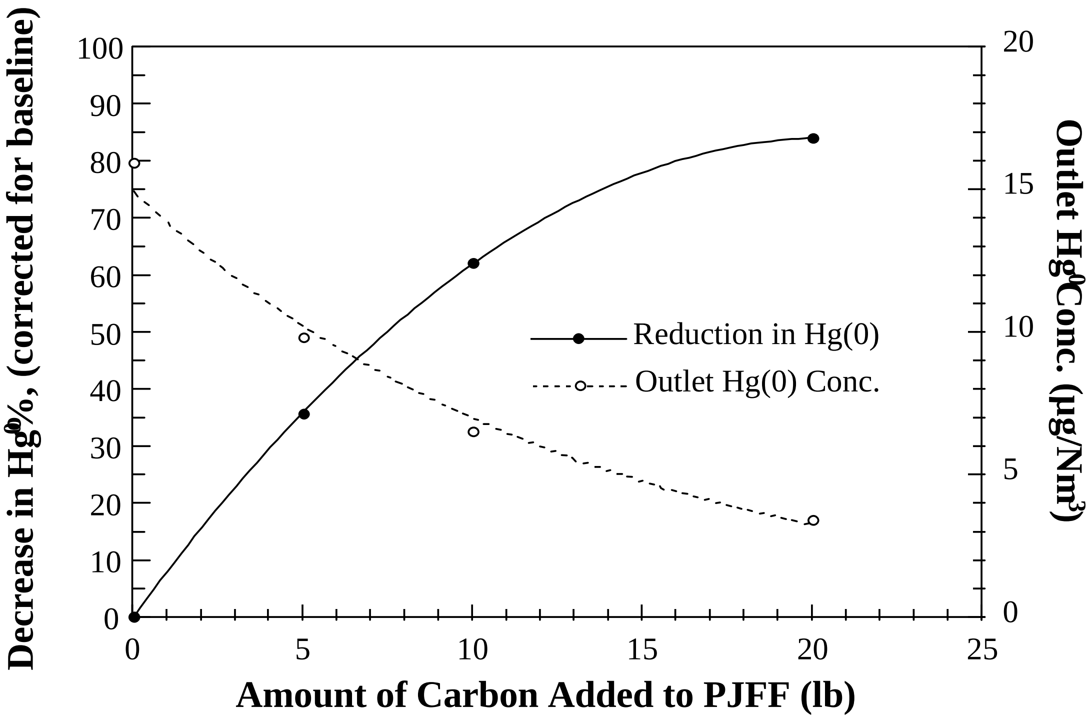

Figure 10. Effect of Carbon on Hg^0 Decrease and Hg^0 Outlet Concentration

Extended Catalyst Testing at Other Sites. While results from the ECTC indicate that a carbon-based catalyst can be used to oxidize elemental mercury, there are several issues that limit the usefulness of further Hg^0 oxidation test work there. First, the naturally-occurring mercury consists of 90% oxidized mercury with only about 1 µg/Nm^3 Hg^0 in the flue gas. This limitation requires that Hg^0 be spiked into the flue gas to increase the accuracy of the Hg^0 determinations. However, even with no catalyst, the injected Hg^0 is easily oxidized which complicates the determination of catalyst material performance.

A second limitation is the amount of catalyst material that can be coated on the PJFF without exceeding the allowable pressure drop. For the carbon-based catalyst, the maximum amount was about 30 pounds for a 5-10 day run. The pressure drop continues to increase with time of operation because most of the fine ash exiting the ESP is collected by the PJFF. This limits the maximum length of a test to about 10 days. For a catalyst to be economically attractive, it must stay active for considerably longer than 10 days. Therefore, more useful results could be generated at different utility sites with higher concentrations of Hg^0 in the flue gas using a device designed to expose the catalyst to flue gas for long periods of time.

Future Activities

Initial short-term tests have been conducted at a power plant that burns lignite coal. While preliminary data indicate that the carbon-based catalyst oxidized the Hg^0 fairly efficiently, the data from this test are still being interpreted. A test unit has been designed and will be built to allow extended catalyst testing. This extended catalyst testing will be part of the proposed Phase II PRDA activities.

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