ENHANCED CONTROL OF MERCURY IN WET FGD SYSTEMS

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The U.S. Department of Energy's Pittsburgh Energy Technology Center (DOE/PETC) is cofunding this project 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 is being conducted under a cost-sharing PRDA agreement between DOE/PETC, Radian International, and the Electric Power Research Institute (EPRI). This HAP project will focus on three research areas. These areas in order of priority are:

- 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.

This paper presents work related to the catalytic oxidation of vapor-phase elemental mercury. Catalytic oxidation of vapor phase elemental mercury is of interest because previous investigations have shown that elemental mercury (Hg^0) is not removed effectively from flue gas in wet FGD systems but oxidized forms of mercury are effectively removed. Therefore, if a process could be developed to oxidize all of the Hg^0 in the flue gas, a highly efficient wet scrubber could then remove a very high percentage of the total mercury. This program is evaluating catalytic oxidation of vapor phase elemental mercury in two phases.

The first subject for discussion is measurement of elemental and oxidized mercury species. Without a method, understanding removal mechanisms and methods of improving mercury removal is extremely difficult. On a separate project, EPRI has recently developed a method at the ECTC which apparently can separate vapor-phase mercury into its elemental and oxidized components. This method will be discussed, but it is emphasized that the method has not under-gone vigorous verification and validation procedures. EPRI continues to work in the mercury speciation methods development and validation area.

The first phase of testing was recently completed and consisted of bench-scale tests conducted to screen potential catalyst and fly ash types for oxidation activity. Fourteen different catalysts and eleven different fly ashes were tested at various conditions to determine their ability to oxidize elemental mercury. The effect of flue gas temperature, SO_2 concentration, HCl concentration, and NO_X concentration were investigated.

Based on the bench-scale results, the most promising catalysts are being tested in a second phase being

conducted at EPRI's Environmental Control Technology Center (ECTC) in Barker, New York, using a 4-MW pilot FGD system. The pilot-scale system is being used to determine oxidation activity with actual (rather than simulated) flue gas.

Mercury Speciation Method

Some initial full-scale and pilot-scale results seemed to indicate that EPA Method 29 adequately speciated oxidized and elemental mercury. Further testing, however, showed that essentially all oxidized mercury was captured in the two peroxide/nitric acid impingers, but that some elemental mercury was also captured in the peroxide impingers. After testing numerous different impinger solutions, tris(hydroxymethyl)aminomethane (Tris) buffer, in combination with ethylenediaminetetraacetic acid (EDTA), was found to be a solution which captured oxidized mercury but allowed elemental mercury to pass to the permanganate impingers. A schematic of this train is shown in Figure 1 and is referred to as Method 29 Tris or M29T.

Figure 2 compares the Hg^0 capture efficiency of the Method 29 and M29T trains with Hg^0 spiked into the sampling trains upstream of the first impingers. The peroxide solution capture Hg^0 spiked in air. However, two peroxide impingers capture 44% of the Hg^0 spiked into flue gas, indicating an interaction between some flue gas constituent, the impinger solution, and vapor-phase Hg^0. By comparison, the Hg^0 spiked in flue gas passed the Tris solution and was captured by the permanganate solution. Thus, the M29T train appears to separate elemental mercury and oxidized mercury as desired. Other test results indicated that the total mercury captured in the M29 and M29T trains are essentially the same and that the oxidized mercury (captured in the Tris solution) at the wet scrubber inlet is removed with approximately the same efficiency as the SO_2 across the absorber. (Oxidized mercury is constrained by the gas-film mass transfer limit of the absorber.) However, more formal verification and validation tests are still planned at the Uni-versity of North Dakota's Energy Environmental Research Center.

<u>Summary of Bench-Scale Testing</u>

The bench-scale unit used to test the reactions of gas-phase elemental mercury with po-tential catalysts is shown in Figure 3. 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 oxidized across the bed. Oxidized forms of mercury exiting the bed were captured in a 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. 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 concen-tration, HCl concentration, and NO_x concentration on the oxidation of elemental mercury. Table 2 lists all of the samples tested and the various parametric conditions tested. During each test, a ten gram mixture of sand and catalyst was placed in the fixed-bed reactor. Table 2 shows the catalyst loading (mass of catalyst per total mass of solids in the reactor) used for each catalyst. Lower loadings were used for some catalysts thought to be more reactive.

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

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. The main difference between the samples was the particle size distribution.

Results from the baseline catalyst tests (300°F) and 700°F tests using various catalyst samples are summarized in Figures 4 and 5. The percentage of inlet elemental mercury oxidized and adsorbed by the catalyst samples is shown. Figure 4 includes catalyst results in which the combined adsorption and oxidation were generally in the lower half of those tested. Alumina is a substrate used for some catalyst coatings and is included here for reference. As shown in Table 2, most of the catalysts were loaded at 1 gram (1000 mg) in a total mixture of 10 grams of catalyst and sand. Exceptions were carbon (20 mg) in Figure 4 and Fe #2 and #3 (200 mg) in Figure 5.

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 oxi-dation and adsorption across the catalysts were higher at 300°F than at 700°F. Exceptions in-cluded alumina and NiO.

Oxidation was also higher at 700°F than 300°F when using Pd #1. These data suggest that elemental mercury is first adsorbed to the catalyst surface and then re-acts. Since physical adsorption generally decreases as temperature increases, less of the mercury is also oxidized.

Results from the baseline tests (300°F) and 700°F tests using various fly ash samples are summarized in Figures 6 and 7. 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. 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.

Three different samples of Bituminous #2 fly ash were tested. These samples were collected from ESP Field 1 (Hopper A), ESP Field 5 (Hopper E), 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, and further testing is needed to quantify any effects. Based on the baseline test results and anticipated material costs, 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.

Summary of Pilot-Scale Testing

Pilot-scale testing is being conducted at EPRI's ECTC. Flue gas for the ECTC pilot system is drawn from New York State Gas and Electric's Kintigh Station. Naturally occuring mercury in the Kintigh flue gas is about 90% oxidized. In order to test the oxidation of elemental mercury, the elemental mercury concentration has to be artificially increased by injecting elemental mercury into the duct. Injection of this mercury can be accomplished in several different locations. To determine the concentrations of both oxidized and elemental mercury in the flue gas, a modified Method 29 gas sampling train is used. In this train, the Method 29 peroxide/nitric acid impingers are replaced with Tris impingers (Method 29T). As described previously, the Tris solution effectively captures oxidized forms of mercury while allowing elemental mercury to pass through the solution.

Figure 8 illustrates the process configuration to be used during most of the pilot-scale tests. Flue gas from the Kintigh Station containing fly ash passes through the dirty raw gas duct (DRG) to the pilot-scale electrostatic precipitator (ESP). With over 99% of the fly ash removed by the ESP, the gas passes through the clean raw gas duct (CRG) to the pilot-scale spray dryer absorber (SDA) and the 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 is returned to the Kintigh stack through the treated gas return duct (TRG).

Using the above configuration, the ability of various catalyst samples to oxidize elemental mercury can be determined by coating the catalyst material on the PJFF bags. The bags are pulsed clean before adding the desired mass of catalyst and then are not cleaned again until testing of the given sample is complete. Elemental mercury injected upstream of the PJFF contacts the catalyst material as the gas passes through the PJFF. Mercury samples are 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 can be determined. By collecting the prespike sample, the actual amount of elemental mercury spiked into the duct can be determined (this sample is not absolutely necessary to

determine the oxidation fraction across the PJFF).

Initial testing using the above configuration showed the elemental mercury spike was nearly 100% oxidized at the PJFF outlet even though no catalyst material was 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 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, and the SCR catalyst. Results from these tests are still being interpretted and are not included here. Future pilot-scale tests will consist of testing potential catalysts across the PJFF. This testing will begin after re-bagging the PJFF with relatively inert Gore-Tex™ bags and determining the baseline oxidation with no catalyst material added to the bags.

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. Parametric Test Conditionf for Bench-Scale Catalyst Tests

Catalyst Tested	Fixed-Bed Loading (mg/g)	Parametric Test Conditions (1) Temperature (°F)	SO_2 (ppm)	HCl (ppm)	NO_x (ppm)
Catalyst Samples					
Alumina	100	700	-	-	145
NiO	100	700	-	-	110
ZnO	100	700	-	-	145
Fe #1	100, 20	700	0, 500, 3000	0, 100	110
Pd #1	100	700	-	-	-
Fe #2	20	700	500, 3000	0, 100	120
Fe #3	20	700	500	-	-
NOx Catalyst	100	700	0	-	-
Carbon	2	-	500, 3000	-	-
Fe #4	100	-	-	-	-
Fe #5	100	700	-	-	110
Pd #2	20	700	-	-	145
Fe #6	100	-	-	100	-
Fe #7	100	-	-	-	-
Fly Ash Samples					
Subbituminous Ash #1	100	700	-	-	110
Subbituminous Ash #2	100	700	500	-	110
Bituminous Ash #1	100	700	-	-	-
Bituminous Ash #2 - Cyclone	100	700	-	-	-
Bituminous Ash #2 - ESP Field 1	100	700	-	-	-
Bituminous Ash #2 - ESP Field 5	100	700	500, 3000	0, 100	110
Bituminous Ash #3	100	700	-	-	-
Lignite Ash #1	100	700	-	0, 100	110
Lignite Ash #2	100	700	-	-	110
Lignite Ash #3	100	700	3000	0, 100	115
Oil-Fired Ash	100	700	-	-	110

(1) - Conditions listed represent a deviation from baseline conditions in Table 1

Remaining graphics and diagrams to be entered later

Figure 1. Method 29 Tris Schematic

Figure 2. Comparison of M29T and M29 Speciation Capability

Figure 3. Elemental mercury conversion bench-scale test apparatus.

Figure 4. Catalyst Activity at Baseline Conditions (Lesser activity)

Figure 5. Catalyst Activity at Baseline Conditions (Greater activity)

Figure 6. Subbituminous, Lignite, and Oil-Fired Fly Ash Activity at Baseline

Figure 7. Bituminous Fly Ash Activity at Baseline Conditions

Figure 8. ECTC Hg0 Oxidation Catalyst Testing Configuration