LATEST DEVELOPMENTS OF THE
PLASMA-ENHANCED ELECTROSTATIC
PRECIPITATOR FOR MERCURY REMOVAL
IN COAL-FIRED BOILER FLUE GAS

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ABSTRACT

The plasma-enhanced electrostatic precipitator (PEESP) is an innovative coal-fired boiler flue
gas mercury removal system that combines existing electrostatic precipitator technology with
low-energy plasma technology. This new technology is energy efficient and produces very little
secondary waste as compared to baseline absorbent mercury removal technologies. In April
2002, MSE Technology Applications, Inc. (MSE), and Croll-Reynolds Clean Air Technologies
(CRCAT) were awarded a joint patent on the PEESP technology based on bench-scale
experimental work conducted by MSE in February 2000. The original PEESP bench-scale
qualitative experiments performed at MSE during the summer of 2000 indicated high mercury
removal efficiencies while treating a simulated coal-fired boiler gas stream containing 250
micrograms per dry standard cubic meter (µg/dscm) of elemental mercury. Steam plus oxygen
were used as the reagent gas while applying a constant negative high-voltage source to the
electrode in a single-element reactor. Bench-scale testing results were reported at AQ3 last.
This paper will provide an update on laboratory scale testing in a multiple electrode tubular wet
ESP.
1. INTRODUCTION

Coal is the United States' most abundant source of fossil fuel; however, drawbacks to burning coal include emissions of oxides of sulfur (SO\textsubscript{x}), oxides of nitrogen (NO\textsubscript{x}), and trace metals. Mercury, a toxic metal regulated under the Resource Conservation and Recovery Act, exists naturally in coal, and during combustion, mercury compounds within the coal are volatilized and become part of the flue gas exiting the boiler. In contrast to most trace metals in coal, mercury is highly volatile and therefore exists exclusively in the vapor phase within the combustion flue gas. At combustion temperatures, elemental mercury is the thermodynamically stable form, even within an oxidizing environment. However, as the flue gas cools, a significant fraction of the vaporized mercury adsorbs onto residual carbon particles and other particles with a large surface area-to-volume ratio. Also, oxidizing compounds within the flue gas react with the mercury vapor at these lower temperatures to form mercury compounds. Consequently, the forms of mercury in flue gas includes both gaseous and solid phases. The physicochemical forms of the elemental and inorganic phases have been predicted as functions of temperature, pressure, and flue gas composition based on thermochemical equilibrium calculations. The predictions indicate that elemental mercury vapor, mercuric chloride, mercuric oxide (HgO), and mercuric sulfide (HgS) are the predominant forms (Ref. 1). Measurements indicate that the proportions of the different mercury species in flue gas vary widely. This variability in speciation is attributable to a number of factors, which include the concentration of mercury and its mode of occurrence in the feed coal, flue gas temperature and composition, concentration and physical characteristics of the entrained ash, and the length of time that mercury and its compounds are entrained in the flue gas.

A major problem in controlling mercury emissions is the low ratio of oxidized mercury to elemental mercury within the flue gas. Existing air pollution control systems, such as wet flue gas desulfurization (FGD) systems used to abate acid gas emissions, can efficiently remove water-soluble mercury compounds and mercury adsorbed onto particulate matter; however, the elemental mercury removal efficiency of these systems is typically less than 1%. Power plant studies have shown mercury emissions average a 60/40 split in elemental versus oxidized mercury and is largely dependent on the type of coal being burned in the process. Typically, mercury emissions generated by burning bituminous coal from the eastern United States are 60% to 80% in the oxidized state. Comparably, emissions from lignite coals from the western regions of the U.S., because of their inherent low sulfur and chlorine content, are only 10% to 20% in the oxidized state (Ref. 2).

In December 2000, under the authority of the 1990 Clean Air Act Amendments, the U.S. Environmental Protection Agency (EPA) announced plans to regulate mercury emissions from coal-fired power plants. Although the proposed regulatory limits are still in debate, the utility industry is anticipating a final compliance date of December 2008. If a Maximum Achievable Control Technology rule is imposed, anticipated regulations are expected to require a 70% to 90% reduction in the current mercury emission rate, which is estimated to be 48 tons/yr. Under President Bush's Clear Skies Initiative, a two-phase mercury reduction process would occur over the next several years. In Phase I, the current mercury emissions would be reduced to 26 tons/yr by 2010. Phase II would require an additional reduction to 15 tons/yr by 2018.

To address the problem of controlling mercury emissions, MSE Technology Applications, Inc. (MSE) and C-R Clean Air Technologies, Inc. (CRCAT) teamed to develop an innovative technology that applies plasma physics to a wet electrostatic precipitator (WESP), creating a plasma-enhanced electrostatic precipitator (PEESP). The PEESP technology uses the central electrode of the WESP to inject a reagent gas directly into the flue gas stream. At a corona power ratio of 3 W/cfm, a visible discharge is generated around the central electrode. As the reagent gas passes through the corona discharge, reactive species are formed, which subsequently oxidize the elemental mercury vapor within the flue gas. In its oxidized state, mercury takes the form of fine particulate that becomes charged in the electrical field of the precipitator. The charged mercury particles are attracted to the collection electrode where they are absorbed into the liquid layer of the WESP and are removed from the process in the normal wash-down sequence.

In addition to controlling mercury emissions, MSE and CRCAT have observed that the PEESP technology is also capable of reducing both NO\textsubscript{x} and sulfur dioxide (SO\textsubscript{2}) emissions, making the technology a multipollutant control devise. The results from a series of bench-scale experiments conducted last year are the subject of this paper.
2. DESCRIPTION OF THE 1-SCFM BENCH-SCALE TEST BED

A photograph of the PEESP 1-scfm test bed used in the following experiments is shown in Figure 1; Figure 2 is a process flow diagram (PFD) of the test bed. Process streams supplying the test bed include oxygen, nitrogen, plant air, and plant service water. Bottled pollutant gases were mixed with the oxygen, nitrogen, and water vapor in a heated manifold to produce a simulated flue gas with a nominal stream composition of 71% nitrogen, 5% oxygen, 12% water (H₂O), 12% carbon dioxide (CO₂), 20 ppmv carbon monoxide (CO), 70 ppmv nitrogen oxide (NO), and 100 ppmv SO₂. The temperature of the simulated flue gas entering the 1-scfm PEESP test cell (Figure 3) was maintained at 300 °F (150 °C), and the temperature at the test cell outlet averaged between 90 °F (32 °C) and 100 °F (38 °C). Plant water, which was circulated through the precipitator cooling jacket, created a wet wall within the precipitator for improving the scrubbing efficiency of the 1-scfm PEESP test cell.

Figure 1. 1-scfm precipitator test bed.

To model residence times typical of a full-scale WESP system, the process gas flow rate was maintained at 1-scfm. At the inlet temperature of 300 °F (150 °C), the actual flow rate through the 1-scfm PEESP test cell was approximately 1.5 acfm with a residence time in the active zone of 1 s. A vane pump provided the motive force to draw the process gases through the test bed and to maintain the test bed under a slight vacuum during testing. To protect the pump from condensation and fugitive mercury emissions, a knockout trap and desiccant/carbon traps were installed downstream of the 1-scfm PEESP test cell. The reagent gas flow rate to the PEESP central electrode (Figure 4) was varied for each test condition but never exceeded 3.5% of the process gas flow rate or 1 L/min.
Figure 2. 1-scfm precipitator test bed PFD.

Figure 3. 1-scfm PEESP test cell.
The mercury concentration entering the 1-scfm PEESP test cell was measured at Sampling Port (see Figure 2) using an online mercury analyzer developed by Ohio Lumex. The analyzer uses ultraviolet light adsorption to determine the mercury concentration in the gas sample. A Zeeman correction is applied to the analyzer output signal to adjust for adsorption interferences caused by ozone, NO, SO$_2$, and water vapor. Two other sample ports were installed in the test bed to measure the mercury concentration at the outlet of the precipitator, SP-2 and at the outlet of the knockout trap, SP-3 (see Figure 2). By comparing elemental mercury concentrations measured at the outlet sample ports to the precipitator inlet, the mercury removal efficiency of the 1-scfm PEESP test cell was determined.

3. TEST OBJECTIVES

The concept of the PEESP technology was conceived in December 1999. To evaluate the feasibility of the technology and to establish proof of concept (POC), a series of bench-scale experiments were conducted in February 2000. Based on the initial results, MSE and CRCAT were awarded a joint patent on the PEESP technology in April 2002. With the EPA's announcement to regulate mercury emissions from coal-fired generators, MSE approached the Electric Power Research Institute, Inc. (EPRI) to fund a follow-on test campaign designed to repeat the initial POC tests and to generate test data to support the development of a scale-up test cell.

Test results, from the follow-on test campaign (Ref. 3), clearly showed the PEESP technology was capable of oxidizing elemental mercury vapor in a process gas comprised of dry air and trace quantities of elemental mercury. However, results from tests using a simulated flue gas containing CO, NO, SO$_2$, as well as trace amounts of elemental mercury showed a significant reduction in the mercury removal efficiency. Upon further investigation, it was concluded that NO (and to a lesser extent SO$_2$) were reducing the effective ozone concentration through competing reactions, thus reducing the mercury removal efficiency of the process. Because NO and SO$_2$ are always present in flue gas and in much higher concentrations than elemental mercury, it may prove difficult to achieve a high degree of
mercury removal without either first removing most of the NO and SO₂ from the flue gas or identifying a mercury-selective reagent gas.

For the experimental work presented in this paper, the primary test objectives were to identify and demonstrate various reagent gases that, when passed through a corona discharge, would produce selective chemical reactions in the flue gas. In particular, reagent gases were sought that would:

- oxidize elemental mercury without affecting the oxidation states of NO and SO₂;
- oxidize NO to nitrogen dioxide (NO₂) without affecting the oxidation states of SO₂ and elemental mercury; and
- oxidize SO₂ to sulfur trioxide (SO₃) without affecting the oxidation states of NO and elemental mercury.

4. TEST RESULTS

4.1 MERCURY-SELECTIVE REAGENT GAS DEMONSTRATION TESTS

As a starting point in determining a mercury-selective reagent gas, the chemistry of mercury (in particular Hg²⁺) was reviewed to determine what mercury compounds were readily formed in a flue gas environment and could be charged by an electrical field and absorbed into a wash-down liquid. It is well known that mercury compounds formed with halides, acetate, and cyanide are soluble in water. Interestingly, many of these compounds are also weak electrolytes, which mean they are only slightly ionized in neutral solutions (i.e., pH = 7). Other compounds (e.g., HgO and HgS) are insoluble in water and exist as fine particulate in the flue gas. The study led to the selection of several reagent gases that were tested in the 1-scfm cell.

For the following test condition, a simulated flue gas of 71% nitrogen, 5% oxygen, 12% H₂O, 12% CO₂, 20 ppmv CO, 70 ppmv NO, and 100 ppmv SO₂ and containing trace quantities of elemental mercury was introduced to the 1-scfm PEESP test cell. With the ability to add individual pollutants (CO, NO, and SO₂) to the process gas, competitive reactions were identified, providing additional information on the gas chemistry within the PEESP test cell. Finally, a comparison of inlet concentrations to outlet concentrations determined the average mercury removal efficiency on the 1-scfm test cell.

To determine what affects (if any) pollution gases have on the mercury oxidation efficiency of the PEESP technology, pollutant gases were added individually to the process gas while monitoring the outlet element mercury concentration. The concentrations of each pollutant were based on typical flue gas emissions and were held constant throughout the test sequence. The results of these tests are shown in Figure 5 for one of the more promising reagent gasses.
Figure 5. Competitive reactions between injected reagent gas and flue gas constituents (real-time data plot).

In the absence of pollutant gases (CO, NO, and SO$_2$), the mercury oxidation efficiency of the PEESP technology averaged 77%. The addition of CO, NO, and SO$_2$ to the flue gas had no significant affect on the mercury oxidation efficiency of the technology. One interesting observation was that the addition of NO and SO$_2$ to the process gas improved the mercury oxidation efficiency of the system.

To determine the mercury removal efficiency of the 1-scfm PEESP test cell, three test runs were completed at this test condition. Each run consisted of three 15-min sampling events to determine the inlet elemental mercury concentration (SP-1) and the outlet elemental mercury concentration (SP-3) with the precipitator electrode energized to 3 W/cfm. Results for the three test runs are shown in Figure 6.
Based on the measured inlet and outlet elemental mercury concentrations, the mercury removal efficiency of the 1-scfm test cell averaged 79% with an effective reagent concentration of 70 ppmv. Decreasing the effective reagent concentration to 18 ppmv lowered the mercury removal efficiency of the system to an average value of 63%. Results for the three test runs are shown in Figure 7.

![Figure 6. Summary of mercury test results with an effective reagent concentration of 70 ppmv.](image)

![Figure 7. Summary of mercury test results with an effective reagent concentration of 18 ppmv.](image)

### 4.2 NOx/SOx REDUCTION TESTS

In addition to the mercury reduction testing, part of the EPRI work scope was to evaluate the capability of the PEESP technology to remove NOx and SOx emissions, making the PEESP technology a multipollutant control system. Based on previous experience and information gained in a literature review, it is well known that NO reacts with ozone to produce NO2. To form a water-soluble salt that can be readily removed from the process using a WESP, aqueous ammonia (30% solution by volume) was added to the process gas upstream of the precipitator test cell.
In addition to removing NO, it is possible to also reduce SO\textsubscript{2} emissions by using a steam-oxygen reagent gas mixture. Theoretically, as water vapor passes through the corona discharge, hydroxyl radicals in addition to ozone are formed, which, according to the researched literature, play an important role in the oxidation of SO\textsubscript{2} to SO\textsubscript{3}. In a saturated gas stream, SO\textsubscript{2} and SO\textsubscript{3} are absorbed by condensing water droplets, forming sulfurous and sulfuric acid, respectively. The ammonia addition neutralizes these acids, forming water-soluble ammonium salts that are also readily removed using a WESP.

In this test condition, the simulated flue gas with a nominal stream composition of 71% nitrogen, 7% oxygen, 12% CO\textsubscript{2}, 12% H\textsubscript{2}O, 20 ppmv CO, 70 ppmv NO, and 100 ppmv SO\textsubscript{2} was introduced to the PEESP test cell at a flow rate of 1 scfm. The reagent gas was an 80% steam-20% oxygen mixture at a total flow rate of 0.6 slpm. An aqueous ammonia solution was added to the process gas upstream of the precipitator at a nominal flow rate of 0.1 mL/min, which yielded an ammonia concentration of approximately 1,200 ppmv in the process gas.

The results from the NO\textsubscript{x} reduction experiments (Figure 8) showed that ozone generated by the PEESP electrode effectively oxidized NO to NO\textsubscript{2}. Once at the higher oxidization state, NO\textsubscript{2} was partially water soluble and could be removed through absorption. The addition of ammonia to the process gas upstream of the precipitator decreased the NO\textsubscript{2} concentration within the process gas, thereby increasing the NO\textsubscript{x} removal efficiency of the PEESP technology. With a nominal stream composition of 75 ppmv and operating the central electrode at a nominal power density of 10 W/cfm, the NO\textsubscript{x} removal efficiency averaged 17%. The addition of ammonia to the process gas further increased the NO\textsubscript{x} removal efficiency to 22%.

By substituting oxygen with propane as a reagent gas, the reaction mechanism for NO\textsubscript{x} reduction was changed from an oxidation process to a reducing process. In this configuration, NO is reduced to nitrogen and oxygen. The NO\textsubscript{x} removal efficiency of the PEESP system using propane as a reagent gas was determined to be 20% at a power density of 10 W/cfm. The addition of ammonia to the flue gas increased the NO\textsubscript{x} removal efficiency to 36%. By increasing the residence time of the flue gas through the PEESP system, it may be possible to achieve high reduction efficiencies.

### 4.3 SO\textsubscript{2} REDUCTION

The SO\textsubscript{2} reduction experiments showed that in a saturated process gas approximately 8% of the total SO\textsubscript{2} was absorbed by the condensing vapor. The addition of 1,200 ppmv ammonia to the process gas reduced 99.8% of the SO\textsubscript{2} to either ammonium sulfite or ammonium sulfate (Figure 8). In effect, the PEESP technology under these test conditions was functioning as a FGD using ammonia in place of lime as a reducing agent.
5. RECOMMENDATIONS

Based on these test results, the PEESP technology has the potential to be developed into an industrial-size mercury abatement system, and it is recommended that further demonstration testing be conducted on an actual coal-fired flue gas. For further development, it is recommended that a 5,000-scfm test cell be fabricated and demonstrated on an operating power plant burning western or Powder River Basin coal. In a test cell of this magnitude, a commercial-size PEESP electrode could be demonstrated, and reagent gas flows could be refined.

Key test objectives, which should be investigated on any scale, include those given below.

- Evaluate how the flue gas saturation temperature and condensing water droplets affect the mercury oxidation efficiency of the dry chlorine reagent gas.
- Evaluate how the addition of a reducing agent, such as ammonia, upstream of the PEESP technology affects the mercury oxidation efficiency.
- Evaluate how the flue gas chloride concentration affects the mercury oxidation efficiency of the PEESP technology.
- Gather process data to determine how the PEESP technology performs over time.

6. REFERENCES