Pilot Testing of Fly Ash-Derived Sorbents for Mercury Control in Coal-Fired Flue Gas

Final Report

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Abstract

Recent research into the removal of vapor-phase mercury from coal-fired flue gas streams has shown that certain native fly ash materials have an affinity for mercury, to the point where these fly ashes capture virtually all the mercury present at some generating facilities. Specific fly ashes from Colorado bituminous and Wyoming sub-bituminous coals have been measured to remove from 75% to 98% of the mercury in full-scale generating units (Butz, et. al., 2000). Investigations of the properties of these fly ashes have revealed that most of the mercury was present in the smallest size fraction. ADA Technologies, Inc. was awarded a project by the Combustion Byproducts Recycling Coalition to investigate the feasibility of employing these fly ash materials as mercury sorbents; the planned testing was performed on a slipstream from a full-scale generating unit at Xcel Energy's Comanche station in Pueblo, Colorado. Candidate fly ash materials were obtained from three other Xcel generating facilities.

The testing was performed in a pilot plant built and installed under an earlier contract with the US Department of Energy to evaluate the use of activated carbon for the removal of mercury from a slipstream from Comanche station's Unit 2. The pilot had a flow capacity of 600 actual cubic feet per minute, and was outfitted with a reverse-gas baghouse particulate control system. The sorbent under test was injected upstream of the baghouse at a location to provide a nominal one-second residence time in the gas flow before entering the baghouse. Ports in the pilot allowed measurement of mercury content upstream of the injection location and at the outlet of the baghouse. Mercury measurements were made with a commercial portable mercury analyzer for most of the tests, with one series using an impinger train to provide a more precise measurement over a one-hour test period.

Candidate fly ash-derived sorbents were manufactured from three fly ash materials supplied by Xcel Energy. Two were from plants burning a Colorado bituminuous coal, and the third was from site burning a Wyoming sub-bituminous (Powder River Basin) coal. Two of the fly ash materials contained alkali sorbents, injected at the generating sites for reduction of SO_2 emissions. The fly ash-derived sorbents were created by grinding the materials to generate a sorbent with 90% of the mass in particles less than 20 micrometers in diameter.

Fly ash-derived sorbents were injected into the pilot gas flow at two rates, 22 lb per million actual cubic feet and 7.3 lb per million actual cubic feet. The flue gas was maintained at 300°F for all of the tests. All three fly ash materials showed significant incremental removal of fly ash, from 53% to 85% at the high injection rate and about 23% at the low rate. The pilot gas flow was also monitored to determine if there was any reduction in SO_2 levels due to the alkali compound content of the test sorbent materials; no measurable change was observed.

An economic analysis showed that the use of fly ash-derived sorbents was projected to be cost-competitive with the injection of activated carbon for flue gas conditions and plant configuration of the host site. The major factor in considering the use of fly ash-derived sorbents may well be their effect on the salability of the collected native fly ash plus sorbent at plants where mercury control must be implemented. The use of fly ash-derived sorbents for mercury control is anticipated to allow the continued sale of collected particulate material for use as a pozzolan additive.

List of Graphical Materials

1. Introduction

The 1990 amendments to the Clean Air Act mandated that the EPA study the impact of mercury in the environment and prepare a report to Congress regarding effects and recommendations for mitigation. This report, issued in 1997, cited coal-fired power plants as the largest source of uncontrolled emissions of mercury into the environment in the US. The assessment of toxic emissions from coal-fired boilers, with an emphasis on mercury, has been under way since 1993 in studies funded by the DOE, EPA, and EPRI. In particular, mercury has been found to evade capture in power plant emissions control systems, as it remains predominantly in gaseous form even at stack temperatures (Brown et. al, 1999). In anticipation of pending regulation of mercury emissions from coal-fired boilers, DOE has been sponsoring a broad program of research into control technologies. The program has included in-house research at the National Energy Technology Laboratory as well as technology development efforts with a number of commercial organizations. To date, no universal control technology has been identified as being the most cost-effective and efficient for mercury removal.

For the past five years, DOE has been sponsoring research on the removal of mercury from coal combustion flue gas, targeted for implementation at coal-fired power plants. This work advanced via cost-sharing contracts that were selected from proposals submitted in response to the DOE MegaPRDA (Program Research and Development Announcement). The multiple Phase I PRDA project winners were invited to submit applications for Phase II continued development. ADA Technologies, Inc. was the prime contractor on one project selected for Phase II funding, and a major subcontractor on a second successful project. The Phase II projects were recently completed, with promising results in several technical areas. The project evaluated the injection of activated carbon upstream of the particulate control device for the removal of mercury, a technology that remains the lowest-cost option currently available for use in many power plants. Yet the projected costs for national implementation of a mercury reduction program based on carbon injection remain in the billions of dollars annually. Nonetheless, because of the potential health effects of mercury contamination to lakes and rivers, on December 14, 2000 EPA announced a rulemaking that mandated the control of mercury emissions from coal-burning power plants in the US.

From 1996 through 2000, ADA Technologies, Inc. conducted a project to evaluate the use of activated carbon as a sorbent to remove mercury from coal-fired flue gas streams under subcontract to Public Service Company of Colorado (now Xcel Energy). In the course of this work, it was discovered that some fly ashes from western coals were effective mercury sorbents (Butz, et. al., 2000) for plants equipped with baghouse particulate control systems. The intimate contact between the flue gas and fly ash afforded in the flow through the filter cake on the bag surface improved the efficiency of the mercury removal process in the fly ash material. Further investigation showed that the smallest particle size fraction of these ashes was the most efficient sorbent. Tests were run in a pilot constructed and installed at Xcel Energy's Comanche station, which burns Powder River Basin coal.

In the current project, fly ash-derived sorbents from three plants were evaluated to determine their capacity for mercury when injected into flue gas at the same Comanche pilot used for the activated carbon testing. These candidate ash materials were selected upon review of field measurements and test results from the activated carbon injection project. Tests were planned at two flue gas temperatures, 250°F and 300°F. The pilot was fitted with a reverse-gas baghouse module to simulate the particulate control equipment of full-scale coal-burning power plants. Measurements of the mercury content upstream and downstream of the sorbent injection was made to determine the removal efficiency. A real-time mercury continuous emissions monitor was used to allow adjustments in the test matrix to reflect sorbent performance. The goal was to realize a minimum of 70% mercury removal at fly ash-derived sorbent injection rates of less than 0.15 grains per actual cubic foot. This rate was specified as the maximum since it was low enough that it would not impact the performance of the particulate control equipment at a host site.

The sorbents were prepared by performing a size separation and/or grinding of the fly ash material, collecting the smallest size fraction for use in the pilot tests. Two of the sorbent fly ashes were from plants where alkali sorbents are used for SO_2 control in the flue gas. One of these was from a plant equipped with a spray dryer absorber, and the second was from a location where Xcel injected sodium sesquicarbonate. In testing these fly ash-derived sorbents, additional equipment was used to monitor acid gas concentrations in the flue gas. Measurements were intended to determine if there was some residual acid gas control in the pilot from the alkali component of the fly ash-derived sorbent. The third sorbent was derived from the fly ash of a Colorado coal that showed a particularly strong affinity for mercury in a metro Denver plant owned by Xcel Energy.

The data from the pilot tests were used in the preparation of an economic model to predict costs for the several candidate sorbents. The economic analysis results were then compared with predictions for activated carbon systems for power plants to determine the economic viability of the fly ash alternative. Activated carbon is an expensive sorbent for this application, at an estimated 50 to 55¢ per pound.

The project was a joint effort, bringing ADA's expertise and experience in the development of mercury control technologies together with the utility/fly ash experience of Xcel Energy, formerly Public Service Company of Colorado.

2. Executive Summary

Recent research into the removal of vapor-phase mercury from coal-fired flue gas streams has shown that some native fly ash materials have an affinity for mercury, to the point where these fly ashes capture virtually all the mercury present at some generating facilities. Specific fly ashes from Colorado bituminous and Wyoming sub-bituminous coals have been measured to remove from 75% to 98% of the mercury in full-scale generating units. Investigations of the properties of these fly ashes have revealed that most of the mercury was present in the smallest size fraction. ADA Technologies, Inc. was awarded a project to investigate the feasibility of employing these fly ash materials as mercury sorbents; the planned testing was performed on a slipstream from a full-scale generating unit at Xcel Energy's Comanche station in Pueblo, Colorado. Candidate fly ash materials were obtained from three other Xcel generating facilities.

The testing was performed in a pilot plant built and installed under an earlier contract with the US Department of Energy to evaluate the use of activated carbon for the removal of mercury from a slipstream from Comanche station's Unit 2. The slipstream was extracted from the host unit upstream of the plant particulate control equipment. The pilot had a flow capacity of 600 actual cubic feet per minute, and was equipped with a flow control valve and automated control system to maintain a constant gas flow as the dust cake on the filter bags built up during normal operation. The unit was outfitted with a reverse-gas baghouse particulate control system. The sorbent under test was injected upstream of the baghouse at a location to provide a nominal one-second residence time in the gas flow before entering the baghouse. Ports installed on the pilot plant ducting allowed measurement of mercury content upstream of the injection location and at the outlet of the baghouse. Mercury measurements for these tests were made with a commercial portable mercury analyzer, with the final series using an impinger train to provide a more precise measurement over a one-hour test period.

Candidate fly ash-derived sorbents were manufactured from three fly ash materials supplied by Xcel Energy. Two were from plants burning a Colorado bituminuous coal, and the third was from site burning a Wyoming sub-bituminous (Powder River Basin) coal. Two of the fly ash materials contained alkali sorbents, injected at the generating sites for reduction of SO_2 emissions; one alkali material was lime from a spray dryer absorber, and the second was sodium sesquicarbonate injected directly into the flue gas for SO_2 control. The fly ash-derived sorbents were created by grinding to generate materials with 90% of the mass in particles less than 20 micrometers in diameter. A few hundred pounds of each candidate material were processed for the planned testing.

Fly ash-derived sorbents were injected into the pilot gas flow at two rates, 22 lb per million actual cubic feet and 7.3 lb per million actual cubic feet. These rates were selected to represent the maximum practical rate and a reduced rate at which the test sorbents could be injected. The maximum rate represented a nominal 10% increase in mass loading for the host site, a level at which the performance of the existing particulate control equipment would not be substantially affected. The flue gas was maintained at 300°F for all of the tests. The test plan had called for tests at a cooler temperature of 250°F as well, but baseline tests at the cooler temperature showed that the native fly ash removed the existing mercury to an outlet level of about one microgram per cubic meter, which would leave very little mercury to be captured by the injected sorbent material. For this reason the low-temperature tests were replaced with additional high temperature cases. All three fly ash materials showed significant incremental removal of fly ash, from 53% to 85% at the high injection rate and about 23% at the low rate. The pilot gas flow was also monitored to determine if there was any reduction in SO_2 levels due to the alkali compound content of the test sorbent materials; no measurable change was observed.

An economic analysis was completed to compare the estimated cost of fly ash-dervied sorbents with the projected use of activated carbon for control of mercury emissions from a 100-MW generating facility. The cost model used was based on an analysis originally presented in the EPA's 1997 ***Mercury Study Report to Congress***. The modeling showed that the use of fly ash-derived sorbents was projected to be cost-competitive with the injection of activated carbon for flue gas conditions and plant configuration of the host site. The fly ash-derived sorbents were assumed to be available in quantity at a price of $50 per ton, although the analysis showed that there was only a minor sensitivity of the unit cost for mercury removal as a function of the price of the processed fly ash sorbent. The major factor in considering the use of fly ash-derived sorbents may well be their effect on the salability of the collected native fly ash plus sorbent at plants where mercury control must be implemented. The injection of activated carbon could result in a collected fly ash plus sorbent product that must be landfilled rather than sold as a pozzolan. On the other hand, the use of a fly ash-derived sorbent that is mostly a silicate or alumina product could mean that the carbon content of the collected matter is low, and it remains salable on the open market. This aspect of the use of fly ash-derived sorbents merits further investigation.

3. Experimental

3.1. Objective

The overall objective of this project was to characterize the mercury removal performance of fly ash–derived sorbents injected into coal-fired flue gas streams. The evaluation were conducted in a pilot plant on a flue gas slipstream extracted from an operating coal-fired power plant. Three different candidate fly ash-derived sorbents were included in the test matrix, all derived from fly ash generated in the combustion of western coals.

The project addressed the following significant issues regarding the use of fly ash constituents as mercury sorbents:

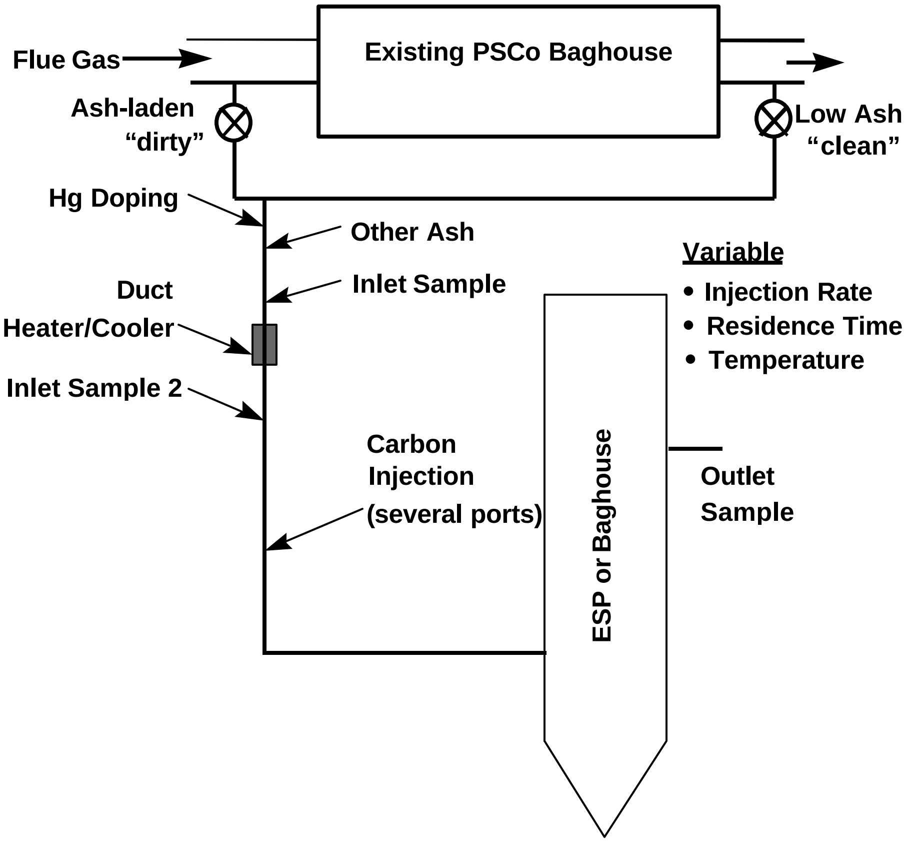
- Mercury removal efficiencies realized when size or concentrated carbon fractions from high-mercury capacity fly ashes are injected.
- The comparative mercury removal performance of fractions from three different fly ash-derived sorbents.
- The ability of the candidate fly ash-derived sorbents to remove other gaseous pollutants of interest, namely SO_2.
- The economic advantage of the use of fly ash-derived mercury sorbents over activated carbon sorbents.

The testing added to the growing database and understanding of sorbent injection for mercury control at coal fired utilities. Project team member Xcel Energy supplied candidate fly ash materials for use in the testing as part of their cost-share. The project provided valuable information on the use of fly ash-derived materials as mercury control sorbents by evaluating their performance *in an actual flue gas environment*. The testing exploited the availability of a fully-operational pilot test facility and ADA's experience in operating this facility. Testing in an existing facility was the most cost effective and efficient method to obtain quality data concerning the above-listed topics.

3.2. Pilot Plant Test Fixture and Instrumentation

The testing was conducted in a pilot plant that treated a 600 acfm slipstream extracted from Xcel Energy's Comanche station Unit 2. This 275-MW generating unit burns Powder River Basin coal, and is equipped with a reverse-gas baghouse for particulate control. The pilot plant was designed and built to offer a variety of particulate control configurations for mercury sorbent testing and is shown in schematic in Figure 2; a photo of the pilot plant is presented in Figure 2. For these tests, the pilot was configured with a reverse-gas baghouse particulate control module. The pilot is equipped with sampling ports upstream of the sorbent injection location and downstream of the baghouse. Flue gas is removed from these locations and analyzed to determine its mercury content, so that the performance of mercury sorbents can be quantified. Sorbent is injected by a screw feeder into a compressed air carrier stream to provide a consistent supply of sorbent to the flue gas slipstream.

Figure 2. Schematic of the Mercury Control Pilot Facility



The tests in the pilot facility were run at two target flue gas temperatures, 250°F and 300°F. The facility is equipped with a heater coil to allow tests to be conducted at temperatures above those typically encountered in the host flue gas, 270° to 280°F. The facility is also fitted with a fine water mist injection system to provide cooling to the extracted flue gas. This subsystem can cool the gas stream down to as low as 230°F, and was used extensively in the earlier tests of activated carbon injection for mercury control. The use of spray cooling in the testing was extremely limited, as the inlet mercury loadings under the spray-cooled test condition proved to be so low as to make calculation of removal efficiencies quite difficult and the precision of such measurements very poor.

Operation of the pilot was monitored via an installed set of sensors that characterized the flue gas and particulate control module performance. Pressures, temperatures, and flows were measured and recorded at one-minute intervals. These data were transferred to computer files for analysis and interpretation, so that test conditions and pilot operating response were fully documented for all tests.

The key measurement to quantify performance of the fly ash-derived mercury sorbents was determination of the mercury content of the flue gas upstream of sorbent injection and downstream of sorbent removal in the pilot baghouse. Three methods were employed in the measurement of mercury concentration. The mercury exists in two phases in the gas stream, deposited on the fly ash native to the flue gas (solid phase) and as vapor in the gas. Downstream of the baghouse, the flue gas is essentially free of particulates, so that the only phase in which mercury is present is vapor. Thus, the ADA mercury CEM was appropriately used as the downstream measurement technology (it measures only the vapor-phase mercury in the sampled gas stream). The CEM uses atomic absorption to measure the mercury concentration in real time. The most significant advantage to the use of the CEM was that results were immediately available, which allowed "real-time" adjustments to be made in the test matrix and improved the efficiency of the test program in evaluating sorbent performance. The CEM was used to obtain upstream measurements of the vapor fraction of the mercury as well.

Figure 2. Photo of Comanche Pilot

When performance of the ADA CEM became an issue, an alternate instrument was identified and obtained for use in the testing. Ohio Lumex offers a compact, commercial instrument for the real-time monitoring of elemental mercury vapor levels in gaseous media. The Lumex model RA-915+ offers advantages over the ADA CEM, including much smaller size and a mercury pen lamp that generates a more consistent light source. The small size allowed installation of the mercury instrument at the sampling location on the pilot, eliminating the need for heated sampling lines with runs of 50 to 100 ft. The overall effect was a greater precision in the mercury measurement and dramatic reduction in the drift experienced in measurements with the ADA CEM.

In order to characterize the total removal of mercury from the flue gas, another measurement will be made as well. In the upstream location, a sampling train was operated in an isokinetic mode and equipped with a prefilter on which a representative fly ash sample was collected. The real-time vapor-phase mercury measurement was then made downstream of the isokinetic measurement, using a cross-flow filter to remove and minimize the effect of particulate material on the measured mercury content of the flue gas upstream of the fly ash-derived sorbent injection in the pilot. Because of this the upstream sample is accurate only in determining total mercury present in the flue gas, and not in characterizing the partitioning of total mercury.

Two of the candidate fly ash-derived sorbents contained alkali reagents originally injected for removal of SO_2 from the flue gas at the generating units in which these fly ashes were produced. It was speculated that there may have been sufficient unreacted reagent to provide some incremental removal of SO_2 from the flue gas into which the sorbent material was injected. To evaluate its ability to remove SO_2, a portable instrument was used to sample the flue gas feed to the pilot upstream and downstream of the sorbent injection location, measuring SO_2, NOx, and CO. The multigas analyzer output was recorded to provide data for evaluation of the fly ash-derived sorbents as SO_2 control agents. Multipollutant control from the fly ash-derived sorbents would provide added value to the process, and increase the price that could be obtained for fly ash sorbents.

3.3. Fly Ash-Derived Sorbent Acquisition and Preparation

Fly ash samples from three different generating stations were provided by Xcel Energy, formerly Public Service Company of Colorado for processing to create the fly ash-derived sorbents. One fly ash sample was collected from the Hayden station; and another was from the Arapahoe station unit 4. To provide a third material for testing, Xcel Energy agreed to supply several hundred pounds of fly ash from the Cherokee generating station Units 3 and 4 ash silo.

There were specific reasons for the selection of the candidate ashes from the Xcel generating plants. In previous testing, the fly ashes from all three sites showed a significant affinity for mercury. This is of particular interest since the plants burn coal from very different sources. The Arapahoe plant burns a Powder River Basin sub-bituminous coal, while the Hayden and Cherokee station burn a Colorado bituminous coal. At the Arapahoe and Hayden sites alkali sorbents are injected to reduce emissions of SO_2. These alkali sorbents are subsequently collected in the baghouses at both facilities, and so are present in the fly ash samples obtained for use in the pilot investigation.

The candidate fly ash materials were processed to reduce their particulate size, as earlier work had shown that the most effective size fraction in removing mercury from coal-fired flue gas streams was the smallest in diameter. ADA had established a target cutoff size of about 20 microns for the fly ash-derived sorbent materials to be used in the pilot tests. Two vendors were identified in the Denver metropolitan area with the capability to separate and/or grind the fly ash material to generate the size distribution of interest, and selected one to process the sample ash materials to the target particle size class. The goal was to generate approximately 300 lbs. of processed material, where the mean particle diameter was less than 10 microns, and more than

80% of the volume consisted of particles less than 20 microns. The Hayden ash sample was processed in two ways: first, a simple size separation was completed at an approximate cutoff diameter of 20 µm; then a second process was applied to the over-20 µm fraction where it was ground to reduce its size. There was a slight difference in the size distributions generated in these two approaches to processing of the Hayden ash. The size-separated material was measured to have a volumetric mean particle size of 8.4 µm, while the ground material exhibited a mean particle size of 11.5 µm. The Cherokee and Arapahoe fly ashes were also processed by grinding, similar to the Hayden oversize material. The processed Cherokee material showed a volumetric mean diameter (VMD) of 9.4 µm, while the Arapahoe material was found to have a VMD of 8.7 µm.

The first step in the treatment process was to feed the fly ash to an air classifier, with a nominal cutoff of about 20 microns. The undersize product was immediately stored for use in the testing. The oversize material was routed to a vibra-drum mill for size reduction. The milled material was then sent to the air classifier, with the undersize material sent to product storage, and the oversize material recycled to the mill. The final treated product was run through a cyclone, with one stream sent directly to a storage container, and the lightest fraction carried to a baghouse collector through which the transport air was filtered before exhaust to the environment. The baghouse capture material was then added to the storage container, to generate a blended product consisting of fly ash that was initially smaller than 20 microns plus the ground-and-classified material.

The size reduction process was applied to three samples of fly ash from different Xcel plants. Two of the plants burned a Colorado bituminous coal, and the third burned a PRB sub-bituminous coal. After processing, samples of the treated ash material were withdrawn from the containers and subjected to a laser particle analysis. Typical results are presented in Figure 3 and

Figure 4 below.

Figure 3. Laser Analyzer Size Distribution for Hayden Fly Ash Product

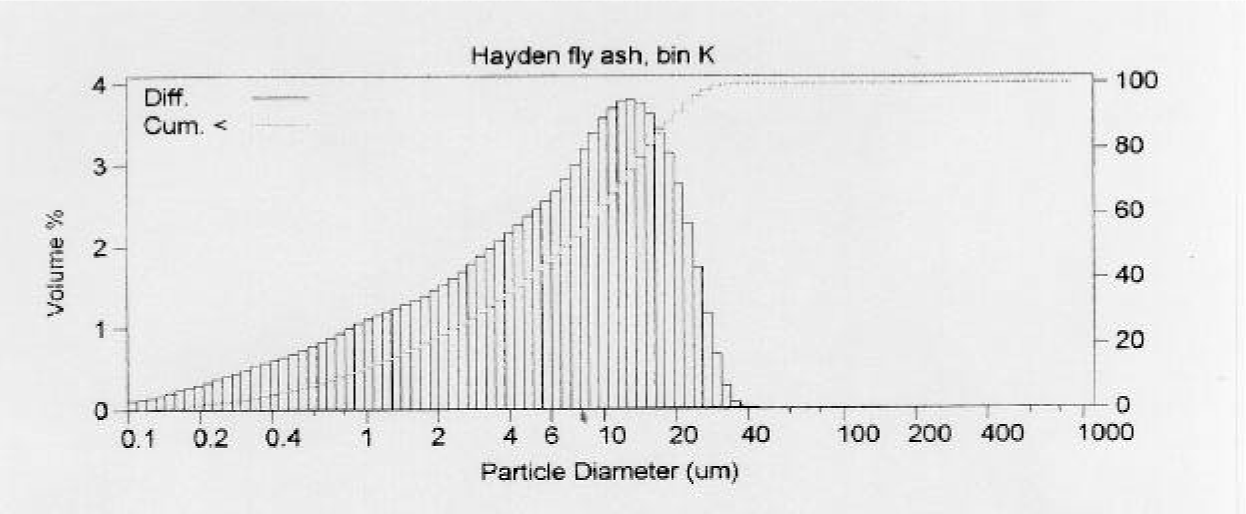
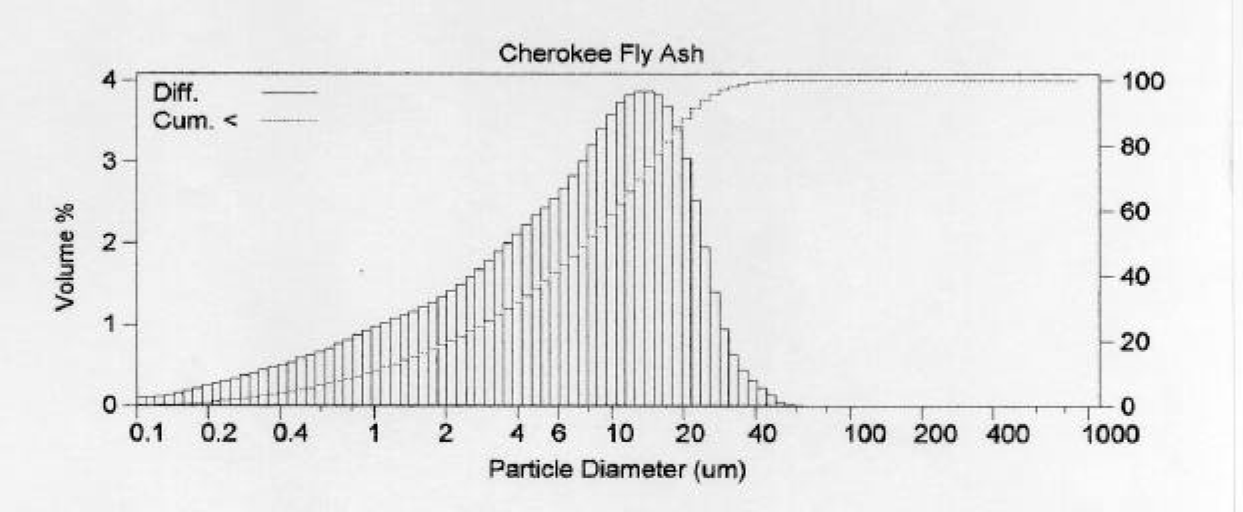


Figure 4. Laser Analyzer Size Distribution for Cherokee Fly Ash Product



3.4. Test Procedure

The test procedure in the pilot facility at Comanche station was simple, and has been refined in the extensive testing done under previous projects to evaluate activated carbon and fly ash reinjection for mercury control. Flue gas was drawn through the pilot by the induced-draft fan. The candidate sorbent under test was metered into a carrier air stream by a variable-speed screw feeder, which has been calibrated to deliver known rates of material. This sorbent-containing air flow was injected into the flue gas upstream of the pilot baghouse. Data taken in earlier tests has shown that equilibrium conditions in the pilot are reached quickly, in under an hour, so that a test run of a few hours provides sufficient time to reach equilibrium and to acquire a large amount of mercury data from the real-time analyzer. For a few tests, SO_2 control was evaluated for the sorbent, with inlet and outlet SO_2 measurements made with a portable multigas analyzer. Fly ash and mercury sorbent captured in the baghouse of the pilot were collected in a hopper, and returned to the host flue gas duct. This material was also be sampled for analysis to confirm the removal of mercury from the flue gas stream.

In the test plan, approximately one week was allocated for testing of each sorbent. Due to problems encountered with mercury measurements in the flue gas, acceptable data was acquired for a more limited test series. Two types of measurements were made during test operations to characterize sorbent performance. The first was measurement of vapor-phase mercury in the flue gas upstream of the sorbent injection location and downstream of the particulate control device in the pilot. The second was "spot check" measurements to characterize the flue gas composition with a portable combustion gas analyzer at the same locations to determine if the candidate fly ash-derived sorbents provide any incremental removal of acid gases due to their alkaline sorbent content.

Logistics of testing were under the control of an on-site ADA test engineer. ADA had previously operated this pilot facility for over two years, and acquired an intimate understanding of the subtle operational issues of the system hardware. The ADA test engineer coordinated delivery of the candidate sorbents with our contact at Xcel Energy. In addition, ADA technicians performed periodic maintenance to the pilot unit as well as to the instrumentation. The host site also provided informal support of testing operations as problems arose.

Real-time mercury measurements were made during the testing with two different instruments. Initially, the ADA mercury CEM was used to obtain data on the removal of mercury by the candidate sorbents. This instrument uses the principle of atomic absorption at the 253 nanometer mercury emission line to measure the concentration of mercury in a quartz sample tube. By maintaining the sample tube at a high temperature, all mercury species are reduced to their constituent elements, thus the mercury is present only in its elemental state. The ADA instrument was installed in a trailer situated at the base of the pilot plant, with heated sample lines installed to route gas from the inlet and outlet to the analyzer. Because of the location of the pilot at the site, the trailer was subjected to significant temperature changes over the course of a test day, in the shadow of the ductwork in the morning, then exposed to the afternoon summer sun. Despite of the fact that the trailer housing the analyzer was air-conditioned, the thermal environment was not constant, and the instrument showed significant drift over a day's operation. A change in the operating procedure was made to increase the frequency of zero calibrations run with the instrument, but this proved insufficient to produce credible data with the ADA analyzer.

Upon a review of alternatives, a decision was made to obtain a commercial instrument for real-time mercury measurements. ADA arranged for rental of an analyzer from Ohio Lumex. This instrument uses the same atomic absorption principle of the ADA unit engineered into a more compact design. Due to the small size of the Lumex analyzer, a sampling arrangement was implemented where the analyzer was moved to the deck of the pilot plant adjacent to the inlet and outlet sample ports. To assure that all forms of mercury were recognized by the instrument, the sample extracted from the pilot was run through a stannous chloride impinger to reduce any ionic mercury to its elemental state. Results from early tests showed some drift due to the temperature environment, although much less than that experienced with the ADA analyzer.

To allow for a greater precision in the mercury measurements, an alternate sampling technique was implemented, where the extracted gas sample was passed through an impinger filled with potassium permanganate. The permanganate solution converted any elemental mercury to an ionic state, which is soluble and therefore captured along with any mercury present as Hg^{+2}. After a sampling period on the order of an hour, the sampling train was disconnected from the sample line. A hydroxylamine solution was added to reduce any remaining permanganate to MnO_2, and eventually to Mn^{+2}. This was followed with the addition of a stannous chloride solution to convert the ionic mercury in the solution back to the elemental state, which is insoluble. A sweep gas stream was then flowed through the impinger to transport the liberated gas-phase elemental mercury to the Lumex analyzer. Total collected elemental mercury was determined by integrating the spike measured with the Lumex instrument over time. This impinger technique did not provide real-time results, but the integration over an extended sample period allowed more precision in the measurement than the real time alternative.

Measurements of the trace acid gas constituents of the flue gas were made with a portable multi-gas combustion analyzer, a model ENR-2000E Combustion Gas Analyzer obtained from Electro-Rent. Data acquired with this instrument was printed on a paper tape, and was then transferred to a spreadsheet for later analysis. Problems were encountered with the initial unit, which was subsequently exchanged for another instrument successfully used in the pilot tests.

Operational data for the pilot facility (temperatures, flows, and baghouse operating parameters) were recorded by a Campbell Scientific data logger system and periodically transferred to computer files. The data logger data files were directly input to Excel spreadsheets for further analysis. These were transmitted to the ADA Denver office on a regular schedule.

During the extensive operation of the pilot facility in previous projects, ADA developed a test protocol that has proven very efficient. Experience with the pilot has shown that equilibrium is achieved in a short period of time, on the order of one-half hour. Thus an extended set of data for a test condition can be obtained in a single day. The approach was to set injection rates at two levels, one high and one low. The high injection rate was selected as the maximum allowable so as to avoid impact on operation of the baghouse due to the presence of additional particulate matter in the form of the injected sorbent. Mercury removal at this condition would be representative of the maximum practical level achievable using a fly ash-derived sorbent. The low injection rate was included to determine if any incremental mercury removal occurred at an injection rate of about 1/3 of the maximum.

3.5. Test Matrix

The test matrix was designed to investigate three parameters: the rate at which fly ash-derived sorbent was injected into the flue gas stream, the source of the fly ash-derived sorbent, and the temperature of the flue gas into which the fly ash-derived sorbent was injected. The original intention was to use the real-time mercury measurements to adjust the fly ash-derived sorbent injection rate to achieve target mercury removal efficiencies of 70% and 90% for each combination of sorbent and flue gas temperature. This approach was modified when it became obvious that the precision of the real-time measurements were not sufficient to operate the pilot in this mode. Also during baseline testing, it became obvious that at the cooled flue gas condition, there was virtually no mercury present in the baghouse outlet. That is, the fly ash present in the flue gas stream as a product of combustion was serving as a very effective mercury sorbent. This condition made the evaluation of incremental mercury removal due to the injection of fly ash-derived sorbents not practical. The test matrix was therefore revised to include only high temperature tests (300°F target slipstream gas temperature).

With the change in mercury measurement technologies and baseline results, a revised test matrix was developed for use in evaluation of the fly ash-derived sorbents. The first test series was used to determine the approximate level of removal for the fly ash present in the flue gas slipstream from combustion of Powder River Basin subbituminous coal in Comanche Unit 2. The test series 2 through 4 evaluated the mercury removal efficiency of the three processed fly ash sorbents generated for use in this project. The high and low injection values were 6 and 2 grams per minute, respectively. The high injection rate reflects a value of 10% of the typical loading found in the feedstream to the pilot plant of about 1.5 grains per actual cubic foot.

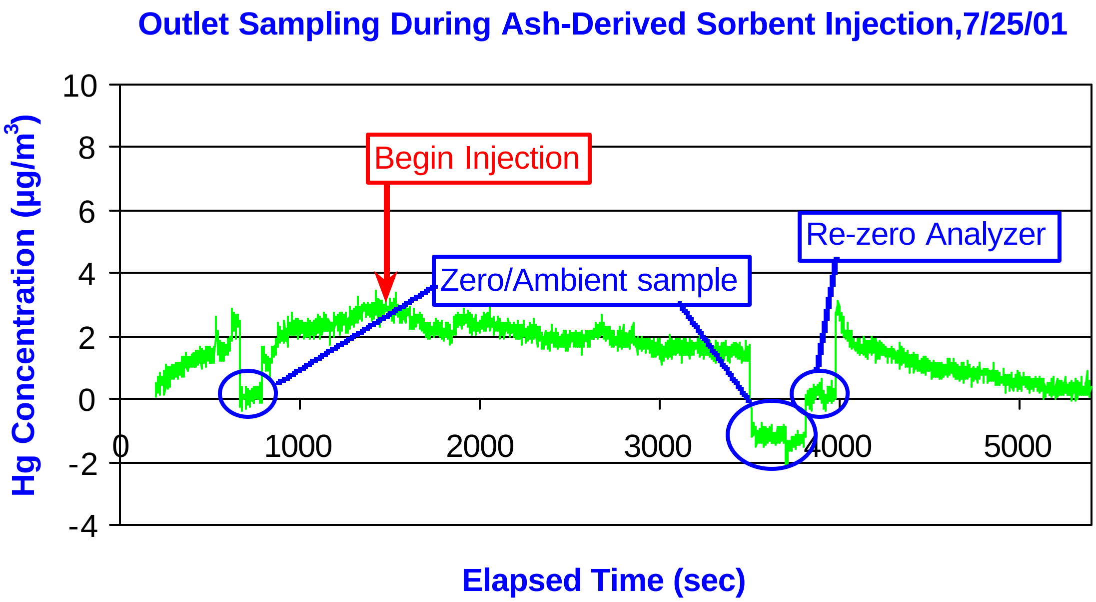
3.6. Data Analysis

During operation of the pilot for evaluation of the injection of fly ash-derived sorbents, data were collected to computer files with the ADA mercury analyzer, the Lumex analyzer, and the automated Campbell Scientific data logger for operational performance of the pilot baghouse unit. All files were transferred to the ADA corporate network file server for storage and backup. In addition, detailed logbooks were maintained during the testing in order to carefully document the conditions under which every test was run. These logbooks were later used to annotate the data plots after they had been prepared.

Analyses of data sets was done in Microsoft Excel spreadsheets. The main source of data was the Lumex analyzer, which output its data sets to a personal computer running a proprietary software program. The Lumex software generated an ASCII text file, comma-delimited that was suitable for immediate transfer into an Excel spreadsheet. The files consisted of an elapsed time, followed by a value for the mercury content of the sampled gas stream as determined by the analyzer. Data were written to the file at one-second intervals during normal analyzer operation. Because of the low levels of mercury in the Comanche flue gas under study, the signal from the analyzer was somewhat noisy. This was minimized via the application of a low-pass filter to the data sets. As noted earlier, there was an obvious drift to several of the Lumex data sets, which appeared to be quite linear and an effect of exposure of the instrument to increasing ambient temperatures throughout the day. An example of this drift is shown in the Lumex analyzer data plot of Figure 5. The drift was quantified by periodically halting the sampling from the pilot plant and acquiring a zero-mercury (baseline) sample by flowing ambient air through the instrument, as indicated in the example data graph. In data segments where drift was an issue, the Excel linear regression tool was applied to develop a quantitative adjustment that could be used to remove the drift effect from the data set.

In an effort to eliminate the drift problem, an alternate sampling technique was employed for the last test series. As described earlier, this measurement technique featured an impinger train that was used to sorb mercury from the sample gas flow for periods of one to two hours. The impinger was then chemically treated to release the mercury from solution, and a sweep gas flow was used to carry the mercury to the Lumex analyzer. The data file recorded a spike as the sweep gas moved the released mercury to the instrument. By integrating the measurement over the time period of the release spike, the total mercury captured in the impinger was quantified. A mass flow controller had been used to maintain the flow from the pilot sample port through the impinger, so that the total volume of the gas sample was known. The average mercury concentration over the sampling period could thus be easily calculated.

Figure 5. Example of Drift in Lumex Analyzer Measurements



3.7. Cost Modeling

To facilitate use of the results of this project in the estimation of full-scale costs for mercury removal by the injection of fly ash-derived sorbents, an economic model developed by ADA in an earlier mercury control testing project was used. The approach taken to the modeling effort was to utilize a cost prediction model first proposed by EPA in the ***Mercury Study Report to Congress*** (1997), and to modify that model to account for size changes in the equipment cited in the configurations of interest. This same approach had been used in a previous ADA analysis of the economics of activated carbon injection for the removal of mercury. By using the same model to generate estimates of the costs for mercury removal with fly ash-derived sorbents, a direct comparison could be made with the activated carbon costing results.

The economic model used data from ADA testing of activated carbon injection as a mercury control technology in the Comanche pilot facility used in the testing reported here. Cost projections were developed for three particulate control configurations in the pilot as well as for two levels of mercury control in the earlier study. Multiple linear regression equations were generated from the test data, and used to predict the injection ratios for activated carbon needed to achieve specified mercury control targets. These baseline technology data were compared with cost projections for the use of fly ash-derived sorbents in the analysis presented later in this report.

Economic Model

The cost of installing and operating a carbon injection system to remove mercury from coal-fired flue gas has been estimated and presented in EPA's ***Mercury Study Report to***

Congress (1997). The EPA report developed costs for 90% mercury control at a 975-MW(e) and a 100-MW(e) power plant. Annual costs were based on total capital costs, operating labor and materials, maintenance labor and materials, power consumption, carbon cost, disposal costs, overhead, taxes and insurance. Capital costs were amortized over a 20-year period at an interest rate of 7%.

For this analysis, the EPA cost model was adjusted to estimate the annual total capital and operating costs for mercury control using injection of fly ash-derived sorbents at power plants burning Powder River Basin (PRB) coal. The approach was to use a logarithmic relationship to scale costs similar to the “sixth-tenths factor” from the **Chemical Engineer’s Handbook** (Perry, 1973), developed for scaling of hardware costs for identical systems of different capacities. The basic form of the sixth-tenths factor equation is:

$$\textbf{New Cost = Old Cost (New Capacity/Old Capacity)}^{0.6}$$

The Perry scaling equation was adapted for use in ADA’s earlier activated carbon study by replacing the 0.6 exponent with exponents suitable for the dry carbon injection and spray cooling systems. This was done by substituting listed cost and capacity values from the EPA analysis, and determining exponents needed to satisfy an equation of the form shown above. These exponent values are then substituted for the 0.6 value in the Perry equation, and used to scale cost estimates for capital, operations and maintenance, and for power and carbon disposal. The “capacity” variable in the Perry equation was the amount of activated carbon injected into the flue gas stream. It was found that the exponent for capital costs adjustments had a value of 0.68. The same approach was used to estimate operating and maintenance cost adjustments as well as power and disposal cost adjustments. The exponents for operating and maintenance costs was 0.33 and nearly 1.0 for power and carbon disposal costs.

Annual carbon consumption values for target mercury control levels in power plants burning PRB coal were determined from the mercury removal models developed in the activated carbon final report. The same plant availability factor of 65% used in the EPA cost estimate was used in calculating the annual carbon consumption for this economic analysis.

Cost estimates for these coal- and configuration-specific cases were then made using adjustments to the capital, operating and maintenance, and power and disposal costs computed with the Perry equation modified with the previously-noted exponents. The old cost and old capacity values were those from the EPA study, and the new capacity was that predicted by a mercury removal model that ADA developed from the pilot test data of the earlier activated carbon evaluation. The new cost was then calculated from the modified Perry scaling equation.

Basic Assumptions for the Cost Estimate

Table 1 below presents the factors included in the cost estimate model and the basis used in the estimating process.

Two new cases were defined for input to the cost model to calculate mercury removal cost estimates for the fly ash-derived sorbents. The cases addressed the two injection ratios evaluated in the pilot tests, scaled to a plant size of 100 MW(e). Cost were computed in two categories, total capital costs and annual operating costs. The capital costs were amortized over a 20 year period at 7% interest to compute an annual capital recovery cost. The operating costs and capital recovery costs were summed to arrive at total annual costs for mercury removal. To provide a basis of comparison, the total annual costs were divided by the amount of mercury removed from the flue gas stream to calculate a specific cost per pound of mercury. These specific mercury removal cost estimates were then compared to similar data for activated carbon, developed with the same cost model.

Table 1. Factors Considered in the Cost Model and Their Basis

Model Factor	Basis
Plant generating capacity	100-MW
Plant annual availability	65%
Mercury concentration in flue gas	12.5 μg/dscm
Desired mercury removal efficiency	70% and 90%
Duct residence time of carbon sorbent	1 second
Gas flow rate	411,000 dscm/hr
Gas temperature without gas cooling	300°F
Coal type	Low-sulfur PRB
Operating labor hourly rate	$12/hr
Supervision labor	15% of operating labor costs
Maintenance labor hourly rate	$13.20/hr
Maintenance materials	Equal to maintenance labor
Carbon cost	$0.55/pound
Nonhazardous waste disposal cost	$36/ton
Power cost	$0.046/kW-hr
Overhead rate	60% of labor and maintenance costs
Taxes, Insurance and Administration	4% of the total capital cost
Capital recovery factor	7% interest rate for 20 years

4. Results and Discussion

A total of eleven tests were run to evaluate the ability of fly ash-derived sorbents to remove mercury from a coal-fired flue gas slipstream in the ADA pilot baghouse at Comanche station. Four of the tests were baseline runs, performed to determine the mercury removal efficiency of the native fly ash in the Comanche flue gas. This is important, as the fly ash at Comanche has been seen in past tests to remove a significant fraction of the mercury present, from 25 to 60%, depending on the temperature of the gas stream and the particulate control module installed in the pilot (Haythornthwaite, et. al., 1999). One of the baseline tests was run with the spray cooling injection system in operation to drop the temperature of the flue gas to 250°F. Four tests were run with injection of the modified Arapahoe fly ash material, one with the Hayden material, and two with the Cherokee material. Injection rates were 6 g/min and 2 g/min into a nominal 600 acfm gas stream. The pilot baghouse was operated in an automated mode where the flow was maintained at a constant level as the pressure drop across the collector bags increased during build-up of the dust cake. A cleaning cycle for the baghouse was run before the start of each test. A flow control valve operated by the system data logger was modulated to maintain the constant flow. As the dust cake depth on the bags increased, the control valve was adjusted by the control algorithm to accommodate the increased pressure drop across the baghouse tubesheet.

4.1. Baseline Mercury Concentrations

In preparation for the pilot-scale testing, some predictions were made for the anticipated mercury concentration in the slipstream flue gas. Combustion calculations were based in an ultimate composition for the Bell Ayr PRB coal burned at Comanche, as supplied by Xcel Energy. The calculations were corrected to a 3% O_2 concentration in the flue gas. As part of the EPA Information Collection Request, Xcel sampled coal shipments over the course of 1999 and subjected a sample from each shipment to analysis for mercury content. These data are available on-line from the EPA and were transferred to a spreadsheet, where an average mercury content was computed for a total of 41 shipments. The mean value of the Bell Ayr coal was 0.0767 parts per million (76.7 parts per billion). There was considerable range in the measurements, with a high value of 0.156 ppm and a minimum value of 0.039 ppm; the standard deviation was 0.02234 ppm. The combustion model was applied to these data, and the calculated flue gas mercury concentrations are shown in Table 2 below. These values represent total mercury in the flue gas, which may be present as particulate-bound mercury, vapor-phase elemental mercury, or vapor-phase ionic mercury. The results show that typical total mercury content was expected to be well over 10 $\mu g/m^3$. Using the results from earlier tests where 25-60% of the total mercury at Comanche was removed by the native fly ash, the gas-phase mercury content in the slipstream flue gas was anticipated to be between 5 and 10 $\mu g/m^3$.

Table 2. Calculated Flue Gas Mercury Content for Comanche Unit 2

Case Definition	Coal Hg Content (parts per million)	Calculated Mercury Content in Flue Gas ($\mu g/m^3$)
Average for 1999 coal shipments	0.0767	12.5
Plus standard deviation	0.0990	16.1
Minus standard deviation	0.0544	8.8
Maximum Hg shipment	0.159	25.3
Minimum Hg shipment	0.039	6.3

Baseline mercury concentration levels were measured at two different temperatures, 300°F and 250°F, to quantify the capacity of the native fly ash present in the Comanche flue gas to sorb mercury. The typical slipstream flue gas temperature at the extraction point for these tests was between 270°F and 290°F, depending on the time of day and unit load condition. The tests were run during the months of July and August, when the Comanche units are often at full load, especially on hot afternoons. To maintain the 300°F condition, an in-duct heater was operated by a feedback controller. As noted earlier, the lower target temperature required the use of a spray cooling system where a fine mist of water was injected at very low flow rates using a dual-fluid atomizing nozzle. Several tests were intended as baseline-only runs, and inlet and outlet baseline (no injection) measurements were made in conjunction with most fly ash-derived sorbent injection tests. In some cases, only inlet or outlet baseline data was available due to sampling problems with the mercury measurement equipment.

A summary of baseline data is presented in Table 3 below. Several aspects of the baseline data set are noteworthy. The first is that the inlet vapor-phase mercury levels are quite low, which leads to a major concern with the testing performed as the main activity of this project. When the inlet mercury levels are low, it becomes quite difficult to make accurate outlet mercury measurements during injection of candidate sorbent materials, as high removal rates result in mercury concentrations at or below one microgram per cubic meter for well-performing sorbents. This was the case for several of the test runs to be discussed here. Also, the baseline measurement under the spray-cooling condition was seen to result in a baseline outlet vapor-phase mercury concentration that was so low as to preclude any precise measurement of the impact of fly ash-derived sorbent on overall mercury removal. As a consequence of this measurement, the planned low-temperature tests were abandoned in favor of additional high-temperature cases.

There was also a relatively high standard deviation in the measurements. This could have been due to variations in the temperature of the flue gas at the extraction location in the main Unit 2 ductwork. For all the fly ash-derived sorbent injection tests, the gas feed to the pilot was heated to a uniform temperature of 300°F, but the flue gas temperature at the extraction point varied between 270° and about 300°F. Since inlet measurements of vapor-phase mercury concentration were made for most of the test runs at a location just upstream of the injection port, these values are included in the table. These multiple measurements allow computation of an average value, seen to be 4.0 $\mu g/m^3$, with a standard deviation of 1.89 $\mu g/m^3$, or 47% of the average. In the context of the calculated values of expected mercury content noted earlier, the inlet measurements reflect a condition where either the mercury content of the coal burned during the testing was lower than the average over the 1999 measurements, or the native fly ash was very effective in removing mercury from the flue gas. In either case, the resultant low inlet vapor-phase mercury levels made precise quantification of sorbent performance a challenge.

Table 3. Summary of Mercury Measurements at Baseline Conditions

Test ID	Test Condition	Inlet <Hg>	Baseline Outlet <Hg>	Native Ash Removal (%)
71201A	Base-300°F	7.2	5.2	27.8%
71901	Hayden	4.1		
72001A	Arapahoe		1.85	
72401A	Baseline	3.6		
72501	Arapahoe		2.9	
72601	Arapahoe	2.7		
8601	Baseline	2.5	0.7	72.0%
8701	Cherokee		4.5	
8801	Cherokee		2.2	
71301A	Base-250°F	2.4	1.0	58.3%
Average Value		4.0	2.9	28.1%
Standard Deviation		1.89	1.69	

<Hg> indicates vapor-phase mercury concentration in µg/m^3

There were multiple measurements of vapor-phase mercury concentration at the outlet sampling port as well, where a baseline value was measured before the start of injection for the test runs. The outlet average is seen to be 2.9 µg/m^3, with a standard deviation of 1.69 µg/m^3, or 58% of the average. Note that the native ash removal listed in the final column of Table 3 is for individual runs, and reflects the change in vapor-phase mercury measurements across the baghouse tubesheet. It can be readily postulated that some fraction of the total mercury sorbed by the native fly ash occurred in the ductwork upstream of the baghouse; the reduction shown was the increment sorbed in the fly ash dustcake of the pilot baghouse. The average removal by the native fly ash is shown at the bottom of the table, and was computed using the average values for inlet and outlet mercury concentrations. The calculated value of 28% fell well within the range of results from earlier testing conducted on the pilot during evaluation of activated carbon sorbents for mercury removal. This result served as a qualitative check on the mercury measurements made in the current test series.

4.2. Injection of Fly Ash-Derived Sorbents

The fly ash-derived sorbent tests were performed in three different series, with modifications to the mercury measurement method implemented between each series. In the first series, a gas sample was extracted continuously from the pilot, and was passed through an empty impinger to remove any condensed moisture in the gas followed by a second impinger filled with stannous chloride solution. The stannous chloride served as a reducing agent, to return any ionic mercury in the gas flow to its elemental state. These test results showed instrument output drift over the course of a day of sampling, such that the procedure was modified somewhat for the second series, where on a regular basis the analyzer inlet was switched from the pilot sampling ports to an ambient air feed. This allowed a zero mercury condition to be added to the data set. As a further correction to the previously-observed ambient temperature-induced drift, the analyzer zero was also reset hourly via a menu option in the data collection software.

As the early test data were subjected to preliminary analysis, it became obvious that the mercury levels at the inlet and outlet of the pilot plant were quite low, and that to obtain a more precise measurement of the mercury content, a more rigorous measurement technique was needed. A wet-chemistry sampling method was therefore initiated as described earlier. The flue gas was sampled through an impinger train where the mercury was converted to an ionic form and subsequently captured in a potassium permanganate solution. After a specified sampling time, the impinger was disconnected from the train and treated with a series of reagents to release the mercury as an elemental vapor. A flow of sweep gas was used to transport the vapor to the Lumex analyzer, where the concentration was recorded as a function of time. A characteristic peak was seen in the resulting data, which was integrated to obtain a total quantity of mercury captured in the permanganate impinger. Since the flue gas was sampled at a known fixed rate, it was simple to compute the average mercury concentration in the gas stream over the sampling period.

Results from the fly ash-derived sorbent injection tests are presented in Table 4 below. The injection tests were all run at the 300°F flue gas temperature, as the baseline testing at 250°F indicated that the native fly ash removed virtually all the mercury at the cooled flue gas condition. Test conditions are presented in columns two and three, listing the source of the ash-derived sorbent and the injection rate, respectively. It is noted that data for all sampling locations were not available for all test cases. For example, it was not always possible to get reliable inlet mercury concentrations during the tests. And because of drift problems with the Lumex analyzer in the early tests, zero references were sometimes hard to determine. However, it was typically possible to quantify a change in the analyzer signal level after the ash-derived sorbent injection was initiated, so that the incremental mercury removal from the added sorbent could be determined. In particular, this was the case for the Hayden test and the fourth Arapahoe test (72601) shown in the table.

The Hayden test (71901) was run at an injection rate of 6 grams per minute. The baseline outlet mercury level is estimated for this test, as a zero for the Lumex analyzer was not established after the drift in the analyzer output was recognized. However, a differential between the pre-injection outlet mercury level and mercury measurements during injection were easy to measure, and as shown as the injection delta mercury concentration. An estimated baseline outlet mercury value was determined by using the average mercury removal measured in the baseline tests noted above, and applying this removal rate to the measured inlet mercury concentration. This estimated outlet baseline was in turn used to calculate a incremental mercury removal rate provided by the Hayden fly ash-derived sorbent, shown to be about 64% in the table.

For the two Arapahoe runs on July 20, 2001 (72001A and 72001B), a baseline outlet mercury level was established, and the incremental mercury removal from the fly ash-derived sorbent was seen to be about one microgram per cubic meter. This represented a 54% incremental mercury removal with the fly ash-derived sorbent. A second test run later in the day showed a similar outlet measurement, indicating good consistency in the performance of the fly ash-derived sorbent material. The next two tests once again used the Arapahoe fly ash-derived sorbent material. The July 25 test (72501) was run at the high sorbent injection rate of 6 grams per minute, with a slightly revised analyzer protocol that results in successful baseline and ash-injection mercury concentration measurements. Results from this test correlate closely with the earlier test in showing a 55% mercury removal rate for a slightly higher baseline mercury rate in the pilot flue gas. The following day a test of the Arapahoe fly ash-derived sorbent was run at a lower injection rate of two grams per minute, with a corresponding reduction in the incremental mercury removal attributable to the sorbent (23.2%).

The final set of tests were run using the impinger method for mercury measurement described earlier in this report, and used the Cherokee fly ash-derived sorbent material. With the impinger method, it was possible to obtain reliable baseline and sorbent injection outlet mercury concentration data, averaged over one to two hour sampling periods. The high-injection rate Cherokee test (at 6 grams per minute) resulted in the most effective mercury removal for the fly ash-derived sorbents tested at an incremental rate of almost 88%. This was a influenced by a baseline outlet concentration above most of the values found in earlier tests, and the lowest outlet mercury concentration measured during the entire test series. The lower injection rate test of the Cherokee fly ash-derived sorbent showed a much lower incremental rate of mercury removal of about 23%, which was very similar to the rate seen with the Arapahoe sorbent at the lower injection rate. As noted earlier, these injection rates are considerably higher than typical rates for activated carbon that is considered the baseline technology for mercury control in coal-fired flue gas streams.

Table 4. Summary of Results from Fly Ash-Derived Sorbent Injection Tests

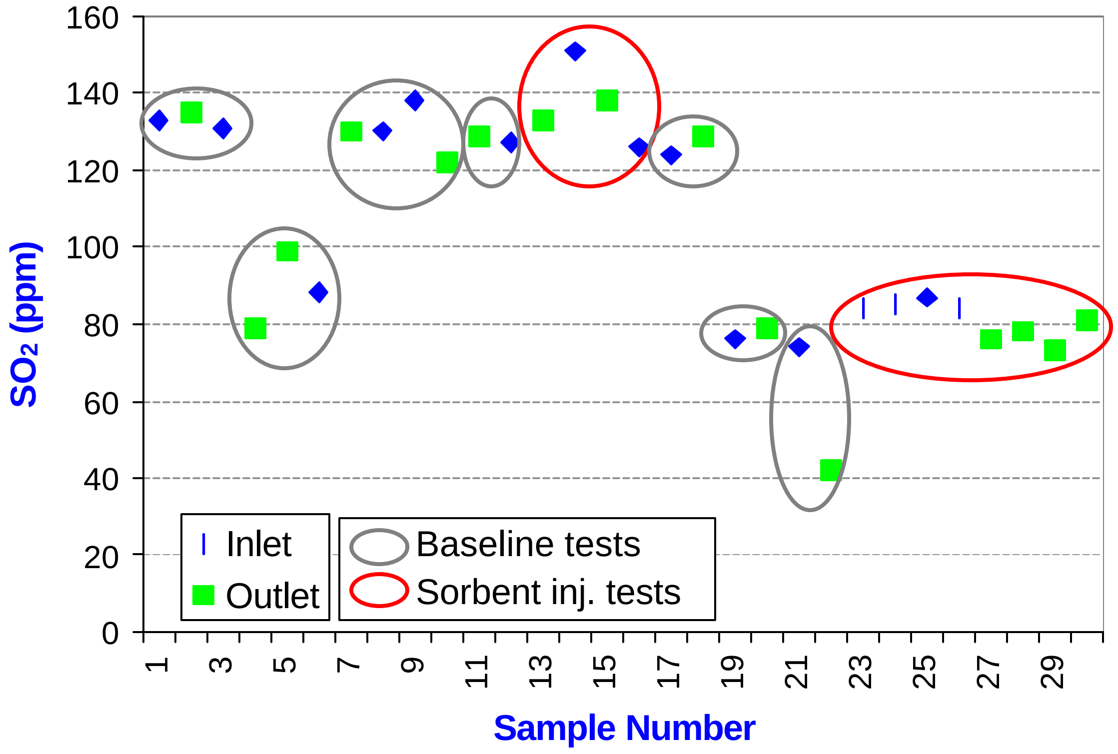
Test ID	Test Condition	Injection Rate, g/min	Inlet <Hg>	Baseline Outlet <Hg>	Injection Outlet <Hg>	Injection Delta<Hg>	Incremental Rate (%)
71201A	Base-300°F		7.2	5.2			
71301A	Base-250°F		2.4	1.0			
71901	Hayden	6	4.1	[2.95]		1.9	64.4%
72001A	Arapahoe	6		1.85	0.85	1.0	54.1%
72001B	Arapahoe				0.77		
72401A	Baseline		3.6	[2.59]			
72501	Arapahoe	6		2.9	1.3	1.6	55.2%
72601	Arapahoe	2	2.7	[1.94]		0.45	23.2%
8601	Baseline		2.5	0.7			
8701	Cherokee	6		4.5	0.55	3.95	87.8%
8801	Cherokee	2		2.2	1.7	0.5	22.7%

<Hg> indicates value is a mercury concentration measurement in the pilot flue gas.
All mercury concentration measurements in µg/m^3
Bracketed values were calculated using average baseline mercury removal rate

Two of the fly ash-derived sorbents contained additives employed at the generating plants for SO_2 control. These were the Hayden ash, where a spray dryer has been installed for SO_2 reduction, and the Arapahoe ash, where sodium sesquicarbonate is injected. To determine if fly ash-derived sorbents from these two plants had the ability to affect SO_2 levels in the pilot plant, SO_2 measurements were made at the inlet and outlet of the pilot during injection of fly ash-derived sorbents. Results of these measurements did not show any significant change in SO_2 levels wither either of the sorbents containing alkali materials.

A summary plot of the SO_2 measurement data is shown in Figure 6 below. Inlet and outlet measurements are plotted in different colors for easy identification, inlet values in blue and outlet levels in green. Typically, multiple measurements were taken at each location to obtain a sense of the variability of the measurements; data points associated with specific tests are circled to group them accordingly. Grey circles indicate baseline tests while fly ash-derived sorbent tests are circled in red. Values shown in the graph are below typical SO_2 levels at Comanche, but the oxygen levels of 8 to 10% read by the probe simultaneous to the SO_2 values indicated that there was significant dilution in the sampling probe. Since inlet and outlet measurements were taken within a few moment of one another, the data present a strong indication that there was no SO_2 removal across the pilot baghouse for either the baseline or fly ash sorbent injection cases. Especially significant is the last set of measurements, taken on July 20, 2001 during injection of Arapahoe fly ash-derived sorbent material at a rate of 6 grams per minute. There is a clear indication here that inlet and outlet SO_2 levels are within measurement variability, and there is no supplemental SO_2 removal from the injected sorbent material.

Figure 6. Results from SO2 Measurements during Sorbent Injection



4.3. Cost Modeling of Mercury Removal with Fly Ash-Derived Sorbents

The previously described cost model for the injection of activated carbon for mercury control was used to generate estimates for the cost of the use of fly ash-derived sorbents for incremental mercury control. As noted in the earlier results, the fly ash-derived sorbents showed significant removal of mercury from the pilot plant flue gas. To reach control levels that may be required to achieve a 90% level of mercury removal, the maximum rate of injection evaluated in these tests was assumed.

To model the cost of the fly ash injection, the costs of an activated carbon injection system were scaled using the *Perry's* exponential scaling rule described earlier. In addition, the operations and maintenance costs were also scaled to account for higher injection rates required with the fly ash-derived sorbents. A unit cost for mercury removal was calculated using an annualized cost comprising the operations and maintenance cost plus a capital recovery cost based on the total capital cost and an assumed interest rate and lifetime of the system. A total of four cases were considered in the cost modeling, two for activated carbon and two for fly ash-derived sorbents. The activated carbon cases represent injection rates for 70% and 90% mercury removal rates, determined in the earlier cost modeling effort for a full-scale activated carbon system using data from the Comanche pilot. The two fly ash-derived sorbent cases were based on the low and high injection rates used in the testing discussed here. The low rate (nominally 23% incremental removal) was compared with the activated carbon estimate for 70% control, and the high rate (54 to 88% removal) was compared to the activated carbon estimate for 90% control. All calculations were done for a 100 MW plant capacity.

Results from the application of the cost model to the use of fly ash-derived sorbents for mercury control are presented in Table 5 below.

Table 5. Cost Model Results for Activated Carbon and Fly Ash-Derived Sorbents

	AC, 70%	F-A Low	AC, 90%	F-A High
Annual Sorbent Usage (lb/yr)	328,767	913,109	450,744	2,739,328
Total Capital Costs	$ 84,987	$ 170,505	$ 105,315	$ 359,266
Operating Costs	$ 289,073	$ 197,908	$ 368,935	$ 357,591
Capital Recovery Costs	$ 8,022	$ 16,094	$ 9,941	$ 33,911
Total Annual Costs	$ 297,095	$ 214,002	$ 378,876	$ 391,502
Specific Cost ($/lb Hg)	$ 8,234	$ 5,931	$ 8,167	$ 8,439

Key to Case definitions:
AC, 70%: Activated carbon injection to achieve 70% mercury removal
F-A Low: Injection of fly ash-derived sorbent at low rate of 7 lb/MMACF
AC, 90%: Activated carbon injection to achieve 90% mercury removal
F-A High: Injection of fly ash-derived sorbent at high rate of 22 lb/MMACF

Several significant observations can be made upon review of the cost modeling results. First, the two fly ash-derived sorbent cases show unit mercury removal costs that are quite competitive with the estimates for activated carbon. This is in spite of the fact that considerably more fly ash-derived sorbent must be injected for comparable levels of mercury control, as indicated in the first row of the table. Because of these relatively high injection rates, the operating costs for the fly ash-derived sorbent systems are not particularly sensitive to the cost of the fly ash-derived material. The model reported in the table used a value of $50 per ton for the processed sorbent material, but doubling the processed sorbent cost only increased the unit mercury cost by about 17%. Second, there are elements of the fly ash-derived sorbent processing cost that can dramatically affect the overall economics of the use of fly ash-derived sorbents.

These are the distance over which the fly ash-derived sorbent must be transported, and the effect of sorbent injection on the salability of the collected native fly ash/sorbent mixture. The cost of the fly ash-derived sorbent would likely be increased dramatically if the material was required to be transported over great distances. Thus the likely application of this technology would be at plants located within a few hundred miles of the sources of the fly ash-derived sorbents. Perhaps the most significant impact on the economics of the use of fly ash-derived sorbents would be the salability of the collected native fly ash plus sorbent. There is a consensus concession that in many cases the addition of the activated carbon would require that the collected native fly ash plus AC mixture be landfilled, rather than sold as a pozzolan material. Such may well not be the case with the fly ash-derived sorbent, as it is primarily fly ash, with the presence of unburned carbon from the source boiler.

The salability of the fly ash from the sorbent application site is a significant cost element that was not included in the analysis. This single factor could easily alter the economics in favor of the fly ash-derived sorbent. A quick calculation illustrates the magnitude of the issue: the 100 MW capacity plant that is the basis of the estimate would generate on the order of 15,000 tons of fly ash per year. If the fly ash must be landfilled rather than sold, the cost of landfilling could be $10 per ton, as compared to a $20 per ton revenue for material sold as a pozzolan. This $30 per ton delta represents a $450,000 shift that totally overwhelms the total annual costs for even the high mercury removal cases as shown in the table.

5. Conclusions

For this project, mercury sorbents were generated by the grinding and classifying of fly ash materials obtained from three Xcel Energy plants in Colorado. These fly ash materials had all been shown previously to sorb mercury from flue gas streams. Two of the fly ash materials also contained alkali sorbents used for the removal of SO_2 from flue gas at the generating plants of their origin. The modified fly ash sorbents were injected into a coal-fired flue gas slipstream in a pilot plant located at the Xcel Energy Comanche station in Pueblo, Colorado. The fly ash-derived sorbents were injected at two different ratios, 22 lbs per million actual cubic feet and seven lbs per million actual cubic feet. Tests were planned at two flue gas temperatures, 250°F and 300°F, but baseline tests at the lower temperature indicated that virtually all the mercury in the flue gas slipstream was being removed by the native fly ash present from the host boiler. Therefore, fly ash-derived sorbent injection tests were run only at the 300°F pilot temperature.

During injection of the modified fly ash sorbents, measurements were made of the mercury content of the flue gas upstream of the injection location and at the outlet of the baghouse that served as the particulate collection device of the pilot facility. The flue gas was also monitored with a portable multi-gas analyzer to evaluate the potential for removal of SO_2 from the flue gas slipstream by the residual alkali sorbents present in the injected fly ash-derived sorbents. During initial testing in the pilot facility, mercury concentration measurements made with the ADA mercury continuous emissions monitor showed considerable drift and problems with sample transport from the sampling locations on the pilot to the trailer in which the analyzer was housed. An alternate instrument, a Lumex RA915+ portable analyzer, was obtained and used for the remainder of the testing. The Lumex was used in two sampling configurations, one where the sample was drawn through an impinger filled with stannous chloride to reduce any ionic mercury to its elemental state before measurement in the analyzer, and a second where a sampling train was used to capture all mercury species in a potassium permanganate impinger for a one- to two-hour sampling period. The potassium permanganate solution was then processed to desorb all mercury present in the impinger to a carrier gas stream that was subsequently passed through the Lumex instrument. This method provided an integrated sample of the flue gas mercury content that was more representative and avoided the slight temperature drift encountered when the Lumex analyzer was operated in the afternoon sun.

Data obtained during the baseline tests and injection of fly ash-derived sorbents showed significant incremental removal of mercury from the flue gas stream and led to the following conclusions:

- It was straightforward to grind and classify the candidate fly ash materials to a size where more than 80% of the mass was found in particles less than 20 µm in diameter.
- This fine fly ash-derived sorbent material was easily injected into the flue gas slipstream of the pilot plant via a simple eductor operated with a low flow of compressed air.
- Baseline measurements indicated that during spray cooling of the flue gas slipstream to control the temperature to the target level of 250°F, the native fly ash removed virtually all of the mercury present, to where the outlet vapor-phase mercury content was less than one microgram per cubic meter. As a consequence of this fact, it was not practical to run tests of the fly ash-derived sorbents at the low-temperature target condition.
- Baseline measurements at 300°F showed that there was a low level of vapor-phase mercury present in the flue gas slipstream entering the pilot plant, an average of four micrograms per cubic meter. This was deemed sufficient to run tests as it would be possible to observe removal of a few micrograms per cubic meter with the available mercury measurement approach.
- At the exit from the pilot baghouse, baseline mercury levels (measured before injection of fly ash-derived sorbent materials) averaged 2.9 micrograms per cubic meter, for an average mercury removal by the native fly ash of approximately 28%.
- All three of the fly ash-derived sorbents demonstrated significant incremental removal of mercury from the host flue gas when injected into the pilot flow at a

ratio of 22 lbs per million actual cubic feet (0.15 grains per ACF). Results ranged from 55% for the Arapahoe source material to almost 88% for the Cherokee fly ash-derived sorbent.

- At the lower injection rate of 7.3 lbs per million actual cubic feet (0.05 grains per ACF), both the Arapahoe and Cherokee sorbents showed a reduction of about 23% in the vapor-phase mercury content of the flue gas in the pilot.
- The target fly ash-derived sorbent injection rates were selected to be less than 10% of typical fly ash loadings, so as not to impact the performance of a baghouse due to the incremental mass loading from the sorbent material.
- Fly ash-derived sorbents containing alkali matter for SO_2 control at their plants of origin did not show any measurable effect on the SO_2 content of the pilot plant slipstream.
- The high injection rate for the fly ash-derived sorbents was approximately six times that for activated carbon to achieve a similar level of mercury control in the Comanche pilot. This provided information to size injection equipment for an economic analysis of the fly ash-derived sorbent.
- The economic modeling results showed that the fly ash-derived sorbents can provide mercury removal at unit costs that are very competitive with those using activated carbon, in the range of $6,000 to $8,000 per pound of mercury removed.
- The single most significant element of the cost estimate is the impact of the mercury control sorbent on salability of the collected fly ash plus sorbent. If the collected material must be landfilled rather than sold due to the presence of the sorbent, the loss of the sale revenue overwhelms the mercury removal costs, and must be considered as the controlling factor in the selection of a mercury control technology. For such a situation, the use of fly ash-derived sorbents presents a cost-effective option due to the likelihood of continued salability of the collected native fly ash plus sorbent material.

6. References

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