



**Novinda**

Innovative Solutions for Industry

**Amended Silicates™**

# **Miami Fort Trial 2006**

# **Demonstration of Amended Silicates™ for Mercury Control at Miami Fort Station**

**Paper #84**

**Mega Symposium, Baltimore, MD, August 28-31, 2006**

James R. Butz and Thomas E. Broderick  
ADA Technologies, Inc., 8100 Shaffer Parkway, #130, Littleton, CO 80127 USA

J. Michael Geers  
Duke Energy, PO Box 960, Mail Drop EX552, Cincinnati, OH 45201

## **ABSTRACT**

During the first quarter of 2006, Amended Silicates LLC and consortium of partners completed approximately 60 days of sorbent injection testing for mercury control at Duke Energy's Miami Fort Station. The testing included baseline measurements with no sorbent injection followed by injection of Amended Silicates sorbent and finally powdered activated carbon (PAC).

The patented Amended Silicates™ sorbent uses silicate minerals as substrate particles on which a chemical reagent with a strong affinity for mercury and mercury compounds is impregnated. The powdered sorbent is used in a fashion identical to that for PAC, and can be considered a drop-in substitute for that more common media. This was confirmed in the trial, as the same feeder and injection system was used to deliver both sorbents. Because of its silicate content, Amended Silicates sorbent does not degrade fly ash quality and allows continued sale of fly ash as a pozzolan material.

Miami Fort's Unit 6 burns run-of-the-river eastern bituminous coal and has a cold-side ESP for particulate control. During the test period the coal averaged 0.11 ppm mercury and 2.3% sulfur. The native fly ash exhibited very little capacity for mercury. Changes observed during the trial period were believed to be due to changing coal supply.

Approximately 40% mercury control was achieved with either Amended Silicates™ or PAC sorbent injection at injection rates of 5-6 lbs/MMacf. Higher injection rates did not achieve significantly increased removal. ESP operating parameters and stack opacity were not affected by sorbent injection. Lastly, the presence of PAC in fly ash from Miami Fort rendered the ash unusable as a concrete additive. The presence of Amended Silicate sorbent had no affect on fly ash quality, confirming the significant advantage of Amended Silicates when fly ash sales factor into the cost of mercury control.

## **INTRODUCTION**

In 2006, Amended Silicates, LLC, completed a cost-shared demonstration of its Amended Silicates™ mercury removal sorbent technology in a full-scale trial at a coal-fired power plant. The trial was hosted by Cinergy (now part of Duke Energy) at Miami Fort Station in southwest Ohio and funded in part by US Department of Energy's National Energy Technology Laboratory (NETL). The NETL demonstration program is designed to support

EPA's announced emissions regulations for mercury from coal-fired power plants. The objective of the program is to gather data to document the performance of mercury control technology alternatives when installed and operated at full-scale (100-MW or greater) generating units. The Amended Silicates team was selected as one of eight cost-shared projects to demonstrate mercury control concepts on a commercial scale.

The Amended Silicate™ sorbent technology is a powdered sorbent designed to be injected upstream of existing particulate control equipment for rapid and effective capture of vapor-phase mercury in the flue gas stream. The method of use is identical to that for powdered activated carbon (PAC), and the Amended Silicates sorbent can be considered a drop-in substitute for that more common media. The Amended Silicates sorbent is a non-carbon-based material and does not degrade the quality of fly ash by-products. This technology has been under development with funding from the EPA and DOE, with previous demonstrations at a pilot scale on a slipstream from a Colorado power plant and in a short-term trial at a coal-fired unit of Xcel Energy.

## **Objectives and Approach**

The trial demonstration project is intended to show the effectiveness of Amended Silicate™ sorbent as a mercury control technology, including the ability to maintain fly ash sales from plants implementing its use. Overall project objectives include the following:

- Demonstrate the ability of Amended Silicate™ sorbent to control emissions of mercury from commercial coal-fired power plants over a typical range of operating conditions for an extended period of time.
- Show that fly ash mixed with Amended Silicate sorbent is compatible with its use as a pozzolan replacement in concrete.
- Confirm that the use of Amended Silicate sorbents has no detrimental impacts on balance of plant operations.
- Estimate the cost to implement Amended Silicate mercury control at full scale specific to the Miami Fort Unit 6 power generating station.

The project incorporated three sorbent injection campaigns: one where Amended Silicates sorbent was injected over a range of ratios to establish process parameters required to meet mercury control targets, a second campaign where Amended Silicate sorbent was injected for a contiguous period of 30 days to validate long-term performance and to discover any impact on balance-of-plant operation, and a final period where PAC was injected for performance comparison. Results from these trial periods were analyzed by the team to quantify system performance with respect to the objectives outlined above.

## **Team Members & Roles**

The project included a consortium of team members to support the technical and financial requirements necessary for an extended, full-scale test of this technology. The prime contractor, **Amended Silicates, LLC**, maintained overall responsibility for the planning and implementation of the work. Amended Silicates, LLC, is a joint venture company formed by ADA Technologies

(ADA) and CH2M HILL that is focused on the commercialization of the Amended Silicates™ sorbent.

ADA staff served as the technical supervisors for the execution of the sorbent injection trial at the host site. Prior to the trial at Miami Fort, ADA personnel had completed smaller Amended Silicates studies at two Xcel Energy power plants in Colorado. ADA staff performed most of the planning, provided on-site management throughout the sorbent injection periods, and carried out the analyses of the experimental data.

Amended Silicates, LLC negotiated with **Engelhard Corporation** (Iselin, NJ) to manufacture the sorbent needed for the demonstration under a joint development agreement. This project leverages the mercury-specific expertise of Amended Silicates with the broad sorbent and catalyst manufacturing and sales experience of Engelhard. A *Fortune 500* chemicals company, Engelhard is capable of providing the logistics and infrastructure to produce and supply the Amended Silicates sorbent to the utility industry. Engelhard provided 75 tons of sorbent to the project as a cost-share contribution.

The original proposal listed Cinergy Corp. as the utility partner and host. During the project period, Cinergy merged with **Duke Energy** (Charlotte, NC). The host site was Unit 6 at Miami Fort Station. Miami Fort staff assisted with the installation of the test equipment and the sorbent injection testing. Duke Energy was responsible for coal and fly ash analyses and provided access to plant monitors and operational data. The host site also paid for and installed the injection and sorbent feeder systems. Planning, preparation, and operational support work were performed by Duke Energy as cost-share contributions to the project.

**Boral Material Technologies** (San Antonio, TX) and **Separations Technologies, LLC** tested the collected sorbent plus fly ash to assess the impact of the presence of sorbent on the use of fly ash as a concrete additive. The ability to continue to sell fly ash is one of the significant advantages of Amended Silicate™ sorbents in comparison to activated carbon and can be the deciding economic factor when utilities consider mercury control options.

**Western Kentucky University** (WKU) was contracted to provide Ontario-Hydro sampling at several dates during the demonstration period. **University of North Dakota Energy & Environmental Research Center** (UNDEERC) personnel were on-site at Miami Fort throughout the test campaign operating two continuous mercury monitors (CMMs); one installed upstream of the sorbent injection ports and a second unit installed downstream of the particulate control device.

## Host Plant Description

Miami Fort Station is located on the Ohio River in southwestern Ohio, about 45 minutes from Cincinnati. The plant operates four coal-fired units generating 1,300-MW of electricity. Unit 6 was chosen for this demonstration because of its combination of firing medium- to high-sulfur eastern bituminous coals with cold-side electrostatic precipitators (ESP). This configuration is representative of a large portion of the U.S. coal-fired power plant fleet. Unit 6 features an 185MW General Electric turbine-generator and a Combustion Engineering tangentially-fired boiler. During weekdays, Unit 6 is operated at near full-load (greater than 160 MWs) from approximately 5am until midnight. At other times and on weekends, the boiler operated at roughly half-load (~90 MW). Operating conditions for the boiler can be changed on a moment's notice by the request of Duke Energy dispatchers who monitor changes in power grid

demand. During the 30-day Amended Silicate sorbent injection period, Unit 6 operated at full-load 56% of the time. The week of PAC injection the plant operated at full-load 52% of the time.

Miami Fort Station purchases “run-of-the-river” coal derived from several mines in surrounding states along the Ohio River. The coal is classified as a bituminous coal with medium sulfur content. Daily coal samples were taken during the trial. Coal samples were submitted to an outside laboratory for analysis. Average properties of the coal burned in Unit 6 during the demonstration are listed in Table 1. Some aspects of the coal changed during the trial period, as will be noted.

**Table 1. Properties of Coal Burned at Miami Fort Station**

<b>Coal Properties</b>	<b>Average Content (moisture-free basis)</b>
Ash Content	11.07%
Sulfur Content	2.28%
BTU Content	13,186 BTU/lb coal
Hg Content	0.11 micrograms/gram coal

### **Amended Silicates Sorbent**

The Amended Silicates™ sorbent (Figure 1) uses silicate minerals as substrate particles on which a chemical reagent with a strong affinity for mercury and mercury compounds is impregnated. Because of their physical construction, these silicates present extended surface area on each particle combined with a particle size of a few microns. This configuration promotes maximum exposure of the chemical amendment to the mercury vapor present in the coal-fired flue gas stream. In addition, because of their silicate content, they have been shown to allow the continued sale of fly ash as a pozzolan material. Tests by Boral Material Technologies show that the presence of Amended Silicates™ sorbent does not affect the ability to use fly ash in concrete, whereas the presence of activated carbon can destroy this beneficial use<sup>[1,2]</sup>.

**Figure 1. Amended Silicates™ is a non-carbon, mercury-specific adsorbent.**



Conventional powdered activated carbon (PAC) was used for comparison with the Amended Silicates™ material. The carbon sorbent was Norit's Darco HG, formerly known as Darco FGD, a sorbent used in a number of previous trials at coal-fired utilities.

## **Modeling, Selection and Installation of Injection System**

One of the project's first activities was the modeling and design of the sorbent injection system. Amended Silicates, LLC contracted with CH2M HILL to carry out computational fluid dynamics (CFD) modeling of the proposed sorbent injection ports on the host unit at Miami Fort Station. Duke Energy supplied a description of the unit as well as drawings of the exhaust ductwork between the combustion air preheater and the ESP.

In the final configuration, four lances were positioned at one-third the depth of duct. Compressed air transported the dry sorbent to the injection lances at a maximum delivery rate of about 400 lb-per-hour, or about 10 lb/MMacf. The lances were located just downstream of the air preheaters, which offered a residence time for sorbent injected into the flue gas flow on the order of three to four seconds before entering the ESPs.

The lances were fed by a Norit PortaPAC sorbent feeder system leased for the trial period. The system was installed on Unit 6 in early January, 2006. Sorbent fed from super sacks into the throat of an eductor where motive air carried the sorbent materials to the four injection lances. This system was used to feed both the Amended Silicates™ and PAC sorbents, and was able to handle both sorbent types without modifications. For the trial period, Amended Silicate sorbent and PAC materials were delivered in 1 cubic yard super sacks.

One operational issue encountered early in the trial was clogging in the sorbent supply piping at injection rates beyond 5 lbs/MMacf. This occurred at restrictions in the piping where they branched to deliver sorbent to each of the four injection lances. This problem was corrected by a change in the piping configuration and the installation of a wire mesh screen at the feeder outlet to collect any unground sorbent particles. Because of the clogging, the actual injection rate for the trial runs targeting injection rates higher than 5 lbs/MMACF did not reach the target rate during the parametric study.

## **Mercury Sampling**

Western Kentucky University (WKU) was contracted to provide Ontario-Hydro sampling at several dates during the demonstration period. During the Ontario-Hydro tests, triplicate measurements were made at the inlet and outlet sample ports simultaneously. The first sampling period was during the baseline phase of the project to assess mercury removal by native fly ash. The WKU team returned twice in February and once in March to complete three more Ontario-Hydro sampling sessions during the parametric and 30-day Amended Silicates™ injection periods.

UNDEERC personnel were on-site at Miami Fort throughout the test campaign operating two mercury CMMs; one installed upstream of the sorbent injection ports and a second unit installed downstream of the ESP outlet. The analyzers employed for the testing utilized commercial cold vapor atomic absorption spectrometers (CVAAS) coupled with a gold amalgamation system. The CVAAS detection system of the analyzer measures elemental mercury. For total mercury measurements, oxidized mercury in the gas sample was converted to

elemental mercury by passing the gas through a reducing solution of stannous chloride in a sodium hydroxide matrix. Hence, total and elemental vapor-phase mercury was measured respectively by inserting or removing the converter solution in the sample flow path.

Early in the sampling campaign it was apparent that the CMM data show higher variation than anticipated. While the inlet samples appeared to be relatively consistent, the outlet samples suffered from frequent spikes of inordinately high mercury readings. Modifications were made to improve the insulation and temperature control of the sampling probe and gas transfer lines. Also, the particle trap in the sampling trains was monitored more closely and cleaned or replaced more often to prevent excessive accumulation of ash. These changes improved signal stability, but the outlet CMM readings continued to experience substantial perturbations. Accordingly, the data reduction protocols utilize statistical methods to assess the relevancy of each datum point so that values outside of a defined variance can be eliminated from the data set. Lastly, during a portion of the test period the team sampled the effluent gas composition for mercury using iodated carbon traps, mimicking EPA Method 324 <sup>[3]</sup>.

## Results and Analysis

The demonstration phase encompassed a series of measurement and injection campaigns at Miami Fort Station, starting in January of 2006 (see Table 2). CMMs were operated throughout the demonstration phase to collect data on mercury concentrations upstream of sorbent injection ports and at the outlet of the ESP of the host unit. At four discrete times during the demonstration, Ontario-Hydro wet chemistry sampling was performed as a check against the CMM data.

**Table 2. Test period dates at Miami Fort.**

Test Period	Dates	Sorbent injection rates
Baseline	Jan 14 – Jan 25	None
Amended Silicate Parametric tests	Jan 26 – Feb 12	2-8 lbs/MMACF
Amended Silicate 30-day trial	Feb 13 – Mar 14	4-10 lbs/MMACF
PAC comparison tests	Mar 15 – Mar 21	2-10 lbs/MMACF

### *Data Reduction and Smoothing*

For various reasons, the mercury levels recorded by the CMMs were extremely noisy and contained frequent values that appeared inordinately high or low. Consequently a systematic, statistical data processing method was necessary to reduce the raw data into a form that could be used for calculations. The utilized method was objective and unbiased, so that the resulting dataset was not favored to eliminate low or high mercury measurements, but instead identified the natural trends in the data.

The primary assumptions for the data reduction were that (1) the mercury measurements were truly well behaved, (2) the variation between sequential data points was within statistical variance, and (3) allowable variance between sequential data points was independent of time. On the basis of these assumptions, a data reduction routine was developed and applied to the raw

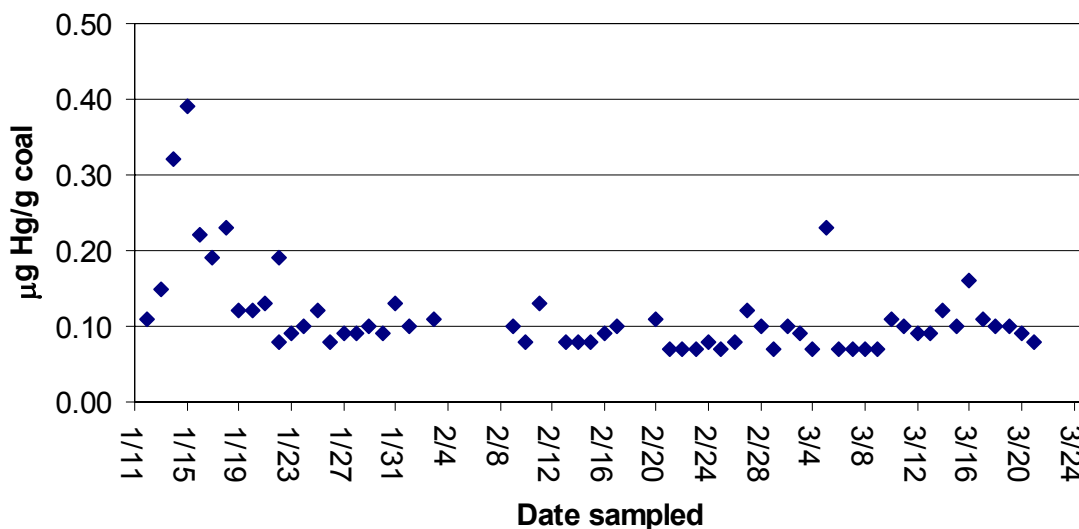
data sets. The objective function for the statistical analysis was derived as a linear “distance variable,” with the acceptance criterion for any datum point set at the mean plus three standard deviations. This constraint encompassed 95% of the total dataset.

Since Unit 6 operates in an on-demand mode, unit load can change at anytime throughout the day. Typically, Unit 6 load increased around 5 to 7 am and decreased to lower loads in the late evening. After a load change, flue gas temperatures tend to stabilize within 3.5 hours. In turn, vapor-phase mercury concentrations followed gas temperature; mercury concentrations increased with rising gas temperatures and decreased as gas temperatures cooled. Because variations in plant operating conditions had a noticeable affect on mercury concentrations, comparison data were selected from when Unit 6 was operating at full-load (>160MW) and at least 3.5 hours after a load change had occurred. Consequently, the majority of the data used in the mercury removal calculations were taken between noon and 8 pm over a minimum of three continuous hours.

### ***Coal Mercury Content***

Mercury concentration in the coal changed drastically after the first weeks of the demonstration project then leveled. Early in the baseline phase of the project, mercury levels in the coal supply ranged from 0.11 to 0.39 micrograms/gram of moisture-free coal with corresponding vapor-phase mercury concentrations 20 to 60 micrograms Hg/Nm<sup>3</sup> (corrected to 3% oxygen). Two weeks into the project, the average mercury levels in the coal dropped to 0.10 micrograms/ gram of moisture-free coal. From that point on, the mercury levels were fairly consistent with inlet mercury concentrations ranging between 10 and 15 micrograms Hg/Nm<sup>3</sup> (corrected to 3% oxygen). Variation in the coal mercury content is shown in Figure 2 below.

**Figure 2. Mercury content in coal burned in Miami Fort Unit 6 during the trial period.**

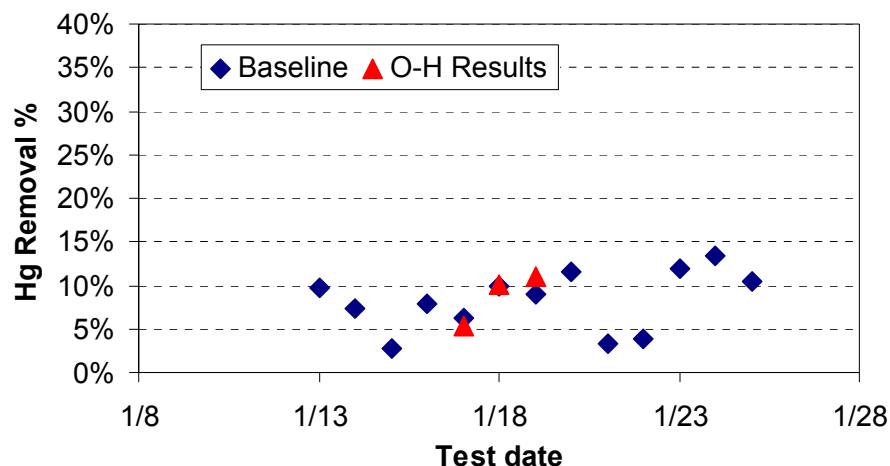


### ***Baseline Measurements***

Baseline measurement of the mercury concentration in coal, fly ash, and flue gas began on January 14<sup>th</sup>. Operational parameters of the ESP and other plant equipment were also recorded during this period so that the impact of sorbent injection on balance-of-plant operations could be assessed.

For the baseline tests, CMM and Ontario-Hydro methods were used to make mercury measurements. Inlet and outlet CMM data integrated over the baseline period from January 18<sup>th</sup> to January 24<sup>th</sup> indicated mercury removal by fly ash was about 19%. However, Ontario-Hydro tests conducted January 17<sup>th</sup>, 18<sup>th</sup> and 19<sup>th</sup> showed that the baseline mercury removal by fly ash was on the order of 10%. Similar results were obtained by a mercury balance using mercury data from coal and fly ash samples taken on those same days (Figure 3). Mercury removal by fly ash calculated by a mercury mass balance was 8%. These data and later analysis led to the conclusion that mercury capture by the native fly ash was generally 5-10% during the majority of the test period.

**Figure 3. Calculated baseline mercury capture by native fly ash as a percentage of the mercury present in the incoming coal. Data on particle-bound mercury measured by the Ontario-Hydro (O-H) sampling is also shown.**



Mercury speciation also appeared to change over the course of the demonstration. Speciation as determined by the Ontario-Hydro sampling is depicted in Figure 4. In the first couple weeks of testing the mercury appeared to be approximately 2/3 elemental; however, by the end of the trial period only about 1/3 of the total was attributed to elemental mercury.

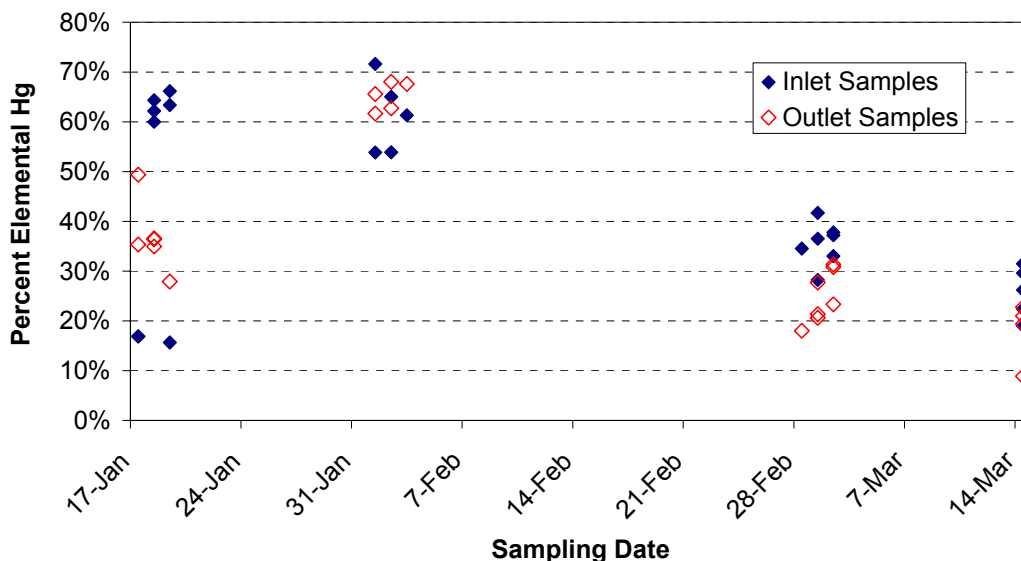
### ***Parametric Tests with Amended Silicates™ Sorbent***

The parametric tests investigated the incremental mercury removal as a function of sorbent injection rate. Only Amended Silicates sorbent was injected during this phase of the project. Sorbent was injected into flue gas for a period of 5 to 6 hours at a given injection rate, an adequate time period for the plant to reach steady-state operation. Performance of the Amended Silicates sorbent was monitored with UNDEERC’s mercury monitors and by the Ontario-Hydro wet chemistry method conducted by WKU. Ontario-Hydro mercury measurements were performed three days during the parametric tests – February 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup>. A period of 90 minutes of sorbent injection was completed before the start of O-H mercury measurements to allow steady-state operation of the mercury removal to be established.

During the first week of parametric tests sorbent was injected into the flue gas at fairly low injection rates ranging from 1 to 5 lb/MMacf. Within this sorbent injection range, the Norit feed system and downstream sorbent distribution piping and lances performed well. During the second week of the parametric tests the feed system was operated at higher injection rates of 6 to 9 lb/MMacf. As noted previously, plugging occurred at transition pieces in the piping network

and inside the sorbent injection lances. Several modifications were made to the sorbent feed system so that the feed system would function at higher injection rates. Unfortunately, the plugging meant that reliable mercury removal data at high sorbent injection rates was not obtained during the parametric trials.

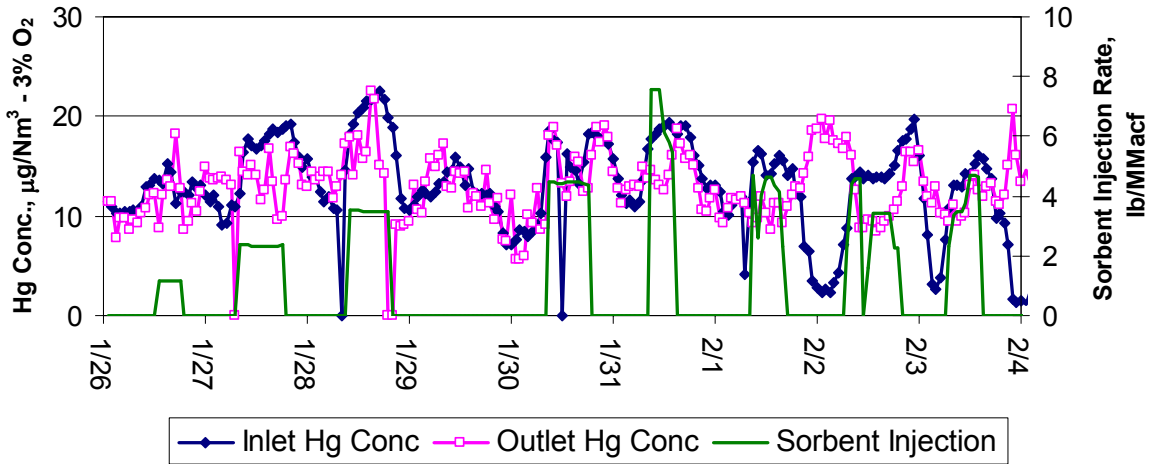
**Figure 4. Elemental mercury as a percentage of total mercury as measured by the Ontario-Hydro sampling.**



An example of the data from the CMMs during the parametric trials is shown in Figure 5. During periods of no sorbent injection, there was little difference between the inlet and outlet mercury signals; this suggests that the baseline mercury capture by fly ash during the parametric tests is even less than the 8 to 10% baseline mercury removals determined in the baseline phase of the project. At times the indicated inlet mercury concentration decreased to almost zero. This was a CMM instrument problem caused by crystals forming in the chemical conversion tubing. Eventually, the crystals choked off the flow of sample gas flow to the CMM. The problem usually occurred in the early morning hours. Gas flow to the CMM was reestablished in the morning by disassembling and cleaning the chemical conversion glassware.

Summary results for removal efficiency as a function of sorbent injection rate are presented in the **Carbon Injection** section below along with the PAC injection data for comparison. The data display a trend of increasing mercury removal as a function of sorbent injection rate up to rates of 5 lb/MMacf when the mercury removals leveled off between 35 to 42%. Sorbent injection rates greater than 5 lb/MMacf did not yield higher mercury removal.

**Figure 5. Mercury measurement during the parametric test period.**

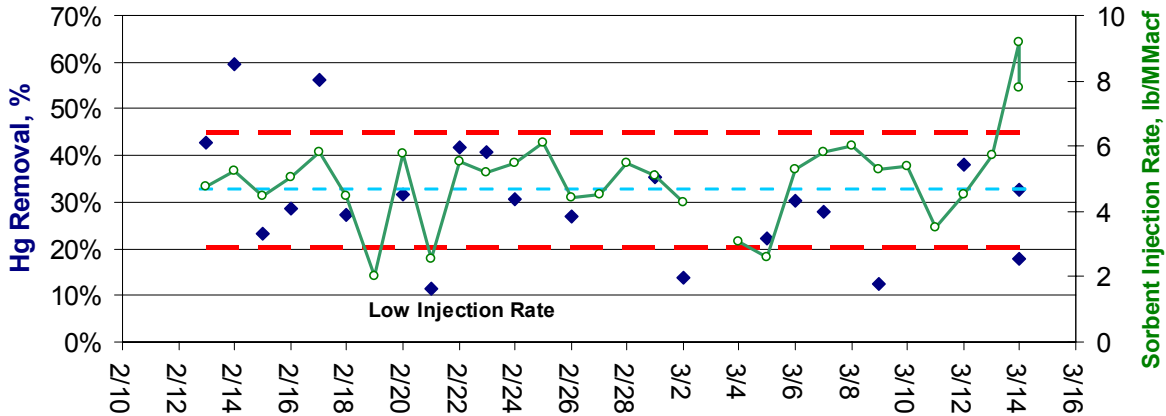


**30-Day Injection Trial with Amended Silicates™ Sorbent**

The 30-day Amended Silicates sorbent injection trial started Feb 13<sup>th</sup> and ran through March 14<sup>th</sup>. Most days during the sorbent injection demonstration the sorbent injection rate was held between 4 and 5  $\text{lb}/\text{MMacf}$ . During those days mercury removal averaged around 32% with some days attaining removals as high as 40 to 60%. The daily average mercury removal along with standard deviation and relative standard deviation were calculated for the dataset and are plotted in Figure 6. Upper and lower dashed lines in Figure 6 represent plus / minus one standard deviation about the average mercury removal.

In general, the IC trap data were within 1  $\mu\text{g Hg}/\text{Nm}^3$  of the reported Ontario-Hydro data with the exception of two samples that were differed by 3-4  $\mu\text{g Hg}/\text{Nm}^3$ . On average, the CMM data were 10% higher than the Ontario-Hydro data.

**Figure 6. Mercury removal (♦) and sorbent injection ratio (line) during the 30-day trial. Average removal and plus/minus one standard deviation are shown by the dashed lines.**



### Carbon Injection

PAC sorbent injection trial started Feb 14<sup>th</sup> and ran through March 21<sup>st</sup>. Parametric tests were conducted for the first four days to investigate incremental mercury removal for activated carbon as a function of injection rate. Figure 7 shows the mercury concentrations and sorbent injection rates during the injection trial. The performance curve for activated carbon is presented in Figure 8, along with summary data for the Amended Silicate sorbent. For both media the data followed the same trend – mercury removal reached a plateau at sorbent injection rates above about 5 lb/MMacf.

Figure 7. Mercury measurements during PAC injection period.

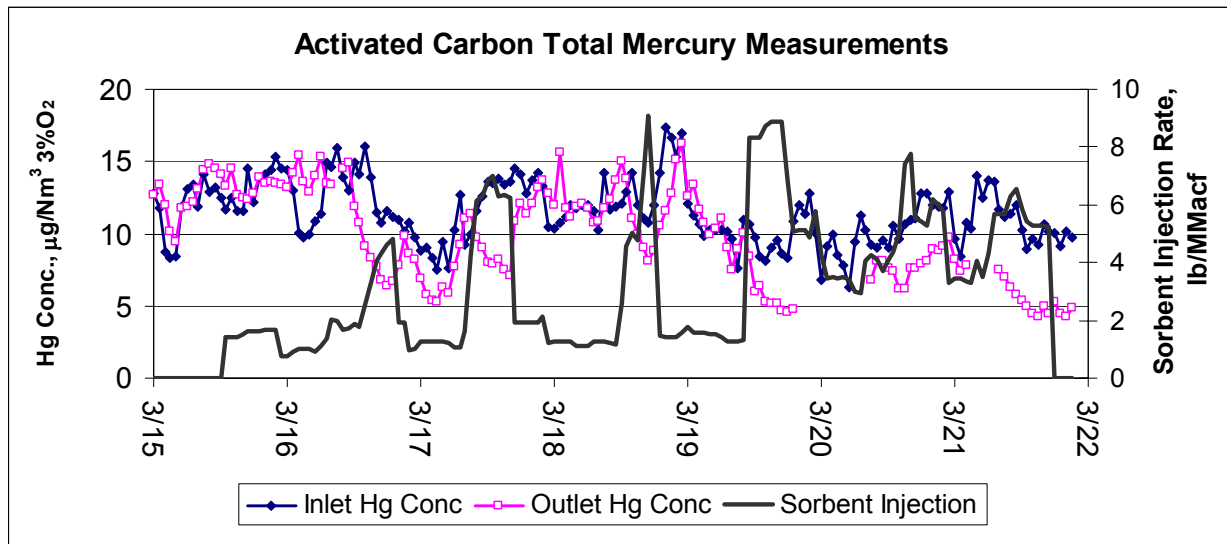
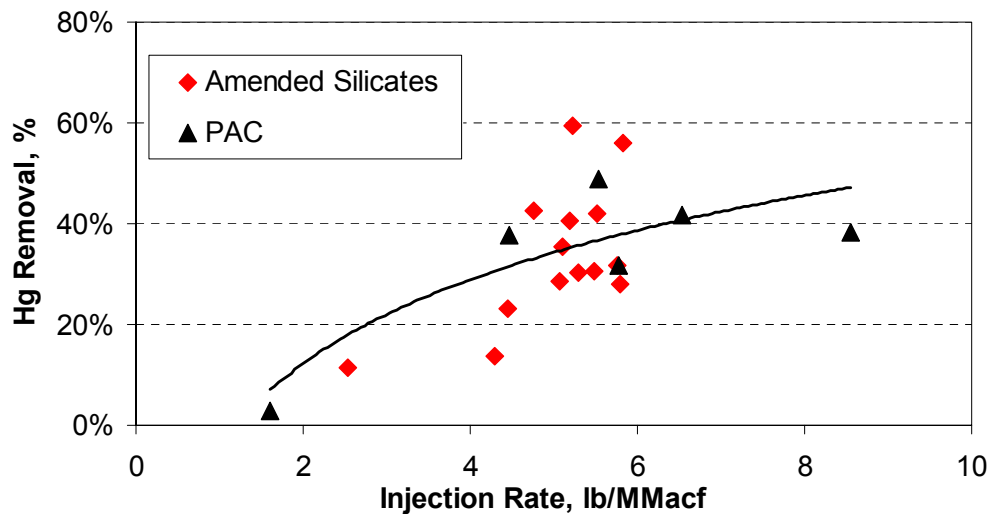


Figure 8. A comparison of capture efficiency by PAC and Amended Silicates sorbent shows the two sorbents performed similarly.



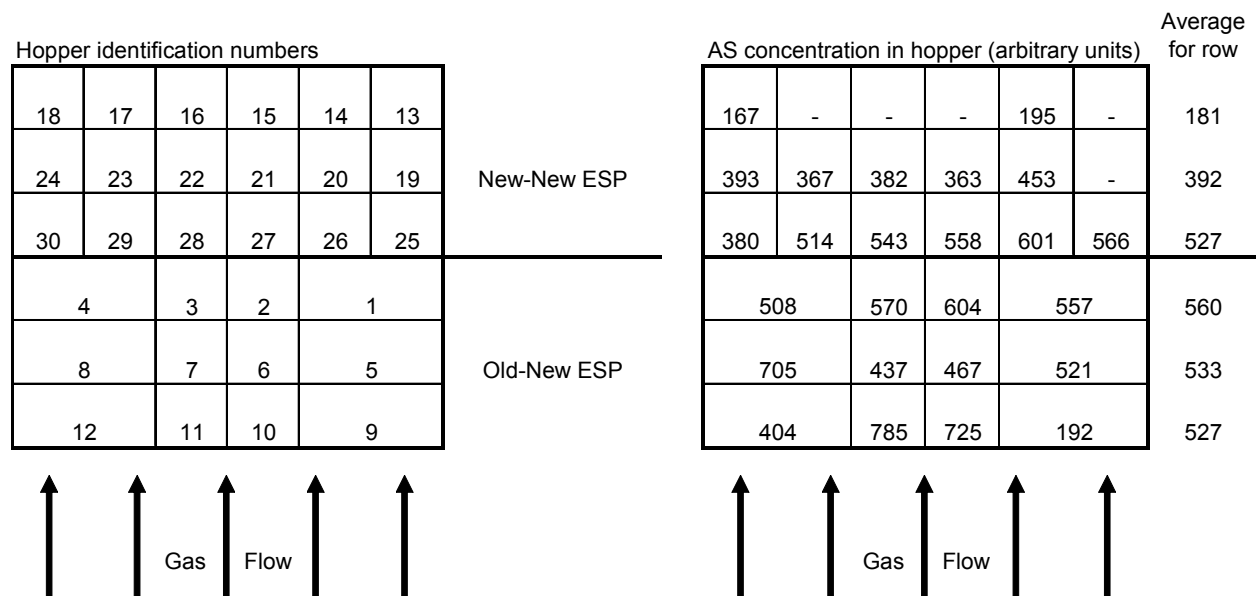
### Fly Ash & Sorbent Collection

Fly ash at Unit 6 is separated from the flue gas in a series of three ESPs designated by plant personnel as “old-new”, “new-new”, and “old”. These units were installed at different times over the operation history of Unit 6; the old ESP was not included in the demonstration. The hopper configuration for the close-coupled old-new and new-new ESPs in Unit 6 is shown in Figure 9. The ash-laden flue gas enters from the bottom in the figure. Most of the ash is collected in the first few rows of hoppers of these units. Currently, Miami Fort does not market the fly ash generated in Unit 6. Rather, the plant uses a combination of dry and wet ash-pull systems for transferring fly ash to one of two ash ponds.

Ash samples from individual ESP hoppers were retrieved during the demonstration. On several occasions during the trial samples were obtained from each hopper; on a daily basis, samples were pulled from six hoppers in the first few rows that were found to be representative of the entire array. Hopper samples were analyzed for a tracer metal that was present in very low levels in the native fly ash. The tracer thus offered a means to assess the distribution of Amended Silicates sorbent in the flue gas stream. The relatively uniform distribution of tracer in the various ESP hoppers indicates that the sorbent was uniformly distributed by the injection system into the flue gas duct cross-section (see Figure 9, at right). The first four rows within the ESP show a consistent collection of Amended Silicate sorbent and the sorbent concentration from left to right across duct also appears fairly uniform. As seen in the right panel of Figure 9, sorbent concentration drops in the later hopper rows, demonstrating that the ESP is effectively collecting the injected sorbent along with fly ash from the flue gas.

Larger samples from the fly ash hoppers were recovered and sent to Boral Material Technologies for assessment of the suitability of the fly ash and sorbent / fly ash mixture for use as a pozzolan additive in concrete. Additional samples were analyzed by ADA to quantify mercury leachability from samples.

**Figure 9. Miami Fort Unit 6 ESP hopper configuration and identification numbers (left) and the relative amounts of Amended Silicate (AS) sorbent collected in each hopper (right) during sorbent injection tests on February 1<sup>st</sup>.**

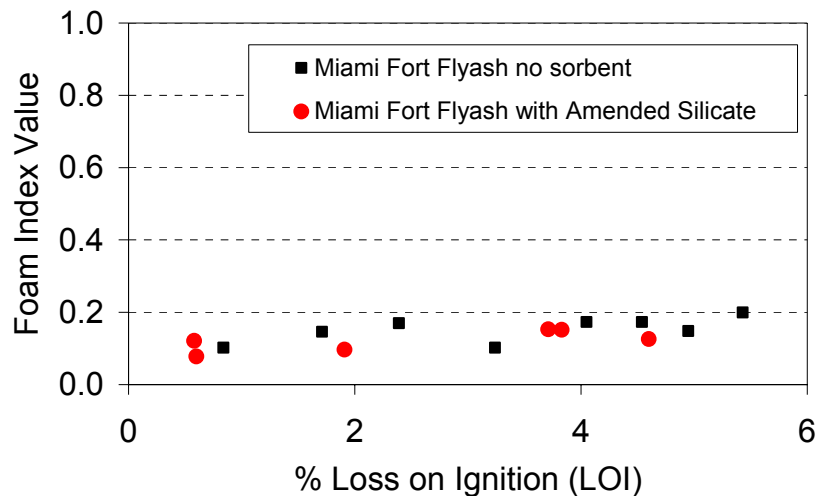


### ***Fly Ash By-Product Assessment***

Prior work has demonstrated that the presence of PAC in fly ash can render that fly ash unusable as a pozzolan additive in concrete <sup>[2]</sup>. The inability to sell fly ash as a by-product can have an enormous impact on the economics of mercury removal in coal-fired power plants, effectively multiplying the cost of mercury control by several-fold <sup>[1]</sup>. A driving factor behind the development of the Amended Silicates sorbent is the fact that it does not impact the quality of fly ash nor the ability to use that fly ash in concrete.

To verify this attribute, the team submitted samples of fly ash for characteristic testing by Separation Technologies LLC (STL), a reseller of coal combustion fly ash. Figure 10 shows the results for Foam Index testing of concrete mix made with Miami Fort fly ash with and without the presence of Amended Silicate sorbent. STL also processed the fly ash sample to reduce the unburned carbon content (measured as Loss On Ignition, or LOI); this allowed the Foam Index tests to be run over a range of LOI. The Foam Index test is a standardized method of determining the amount of air-entraining agent required for producing concrete. Because this agent is costly, an increase in the amount required can greatly impact the cost of making the concrete. Over a significant range of unburned carbon levels the addition of the Amended Silicate sorbent had no effect on Foam Index Value. In contrast PAC will adsorb air-entraining agent, necessitating the use of much more agent, and making the process uneconomical.

**Figure 10. The presence of Amended Silicate sorbent in the fly ash has no effect on Foam Index test. Data from STL.**



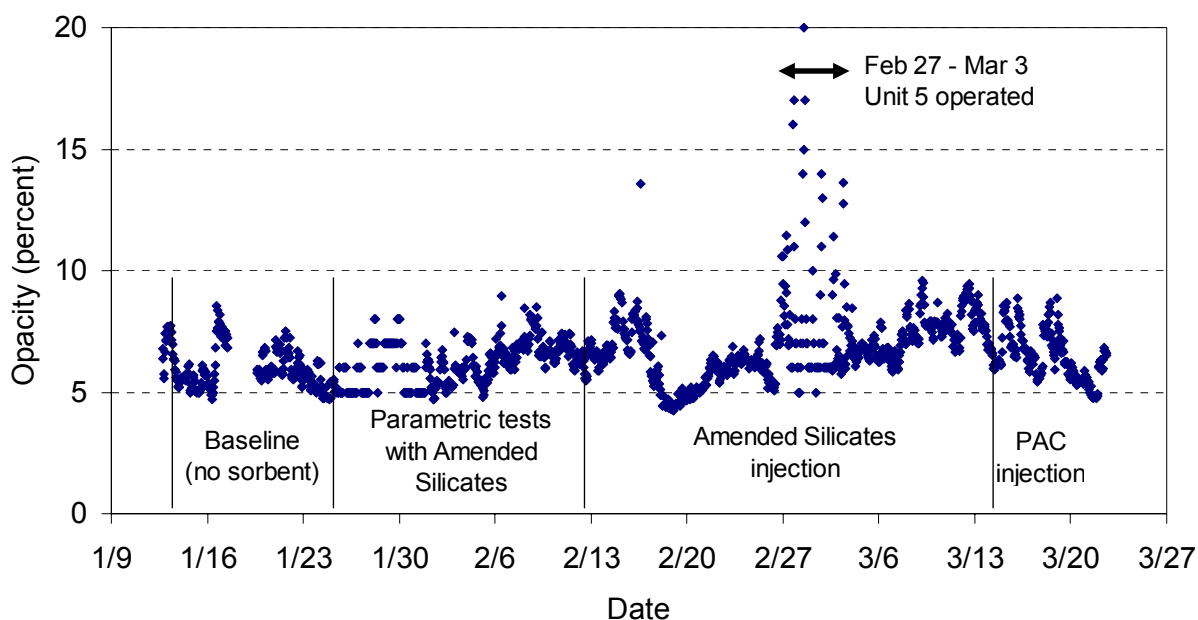
Further testing at Boral demonstrated the dramatic effect PAC has on fly ash properties. Two fly ash samples were analyzed – samples collected on March 14<sup>th</sup> during Amended Silicates injection and on March 21<sup>st</sup> during PAC injection. The two samples were very similar chemically, since the vast majority of each sample is fly ash. However, the physical properties of interest for concrete manufacturing are quite different. The PAC sample exceeded the AASHTO allowable LOI limit and achieved only 3.8% of the control for the Mortar Air Ratio (another measure of air-entraining agent consumption). Results for the Amended Silicate sample were acceptable: an LOI well under 5% and a Mortar Air Ratio of 61.5%. The data confirmed the advantage held by Amended Silicates when fly ash sales factor into mercury control economics.

## Balance-of-Plant Impacts

The voltage / current behavior of twelve transformer rectifier sets of Unit 6's ESP were monitored during the sorbent injection trials to assess the impact of sorbent injection on ESP performance via daily readings in the ESP control room. The mean values for output voltage and current for each of the T/R sets were compared during the periods of no sorbent injection, Amended Silicates injection, and PAC injection. Assuming a random variation of 3% to be within the setpoint range, there was no observed difference between the mean readings within a 95% confidence level. An inspection during an outage about four weeks following the sorbent injection trial indicated no discernable deposition or corrosion attributable to the sorbent injection on the Unit 6 ESPs.

Figure 11 displays the opacity data for the stack shared by Miami Fort's Units 5 and 6. Unit 5 is an older unit which was only operated for a few days during the sorbent injection trials. Analysis showed that the injection of Amended Silicates™ sorbent had no observed effect on stack opacity at the injection rates used during the trial. Opacity data taken during the period of PAC injection also showed PAC injection had no effect on stack opacity. The only time opacity changed by a significant amount was during the brief operation of Unit 5, from Feb. 27<sup>th</sup> through March 3<sup>rd</sup>. That increase is attributed to the contribution from Unit 5 to the common stack, and is unrelated to the sorbent injection testing at Unit 6.

**Figure 11. Stack opacity data for the shared stack of Miami Fort Units 5 and 6. Sorbent injection had no discernable effect on opacity.**



## CONCLUSIONS

During the first quarter of 2006, Amended Silicates LLC and consortium of partners completed approximately 60 days of sorbent injection testing for mercury control at Duke Energy's Miami Fort Unit 6. The testing included baseline measurements with no sorbent injection, followed by injection of Amended Silicates sorbent and finally PAC. Samples of

collected fly ash were tested to determine if fly ash quality was impacted by the presence of sorbent. The major conclusions from these tests are summarized as follows:

- Early in the project, injection rates greater than about 5-6 lbs/MMACF proved impossible to sustain with the injection system as configured. This was due to the particular plumbing of the injection system and was not an inherent limitation of the technology. Modifications to the sorbent feed system were implemented and the feed system was able to inject both sorbent materials with no issues.
- The native fly ash had very little capacity for mercury. Analysis indicated somewhere from zero to ten percent capture by the native fly ash during the trial period.
- The fraction of elemental mercury ranged from 2/3 of the total at the outset of the test period, to 1/3 of the total later during the test period. The change is believed to be due to changing coal supply.
- Approximately 40% mercury control was achieved with either Amended Silicates™ or PAC sorbent injection at injection rates of 5-6 lbs/MMacf. Higher injection rates did not achieve significantly increased removal.
- Erratic performance of the CMMs was attributed to problems with the sample transfer lines and ash accumulation within the sampling probes. The CMMs required maintenance and calibration checks on a daily basis. These issues reinforce concerns about the readiness of CMM systems for industrial monitoring.
- ESP operating parameters and stack opacity were not affected by sorbent injection. Subsequent inspection of the ESP did not show any effects of the sorbent on the ESP internal components.
- The presence of Amended Silicate sorbent had no effect on the ability to use collected fly ash plus sorbent as a cement additive.

## **ACKNOWLEDGEMENTS & DISCLAIMER**

This project was undertaken with cost-shared funding from the US Department of Energy's National Energy Technology Laboratory under DOE Award Number: DE-FC26-04NT41988. The work was also partially supported by Engelhard Corporation, Amended Silicates, LLC, and Duke Energy.

This paper was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## REFERENCES

- [1] Hoffmann, J., and J. Ratafia-Brown, “Preliminary Cost Estimate of Activated Carbon Injection for Controlling Mercury Emissions from an Un-Scrubbed 500 MW Coal-Fired Power Plant,” Final Report for U.S. Department of Energy, National Energy Technology Laboratory, Innovations for Existing Plants Program, prepared by Science Applications International Corporation, November 2003.
  
- [2] Bustard, J., M. Durham, T. Starns, C. Lindsey, C. Martin, R. Schlager, and K. Baldrey, “Full-Scale Evaluation of Sorbent Injection for Mercury Control on Coal-Fired Power Plants,” Presented at Air Quality III, Arlington, VA, September 12, 2002.
  
- [3] Frontier Geosciences, Seattle, WA, Method 342, <http://www.fgsdata.com/> viewed June 30, 2006.

