

Evaluation of Amended Silicate™ Sorbents for Mercury Control

James R. Butz; John S. Lovell, PhD; Thomas E. Broderick; Rod W. Sidwell, Craig S. Turchi, PhD

ADA Technologies, Inc., 8100 Shaffer Parkway, Suite 130, Littleton, CO 80127-4107

Alfred K. Kuhn

CH2M Hill, 9191 South Jamaica St., Englewood, CO 80112

ABSTRACT

A novel sorbent for the capture of mercury from combustion gas streams has been discovered and developed by ADA Technologies, Inc. with funding from EPA and DOE. The new Amended Silicate™ sorbents employ a commodity substrate material impregnated with a chemical amendment that binds mercury to the surface of the particles. The Amended Silicate material is cost-competitive with activated carbon, and does not affect the ability of the fly ash to be sold as a concrete additive.

In packed-bed tests these sorbents showed mercury capacity of several times that of activated carbon. Pilot plant tests were recently run to quantify mercury capture in a flue gas slipstream at an operating power plant burning Powder River Basin sub-bituminous coal. Amended Silicate™ sorbents provided 70%-96% mercury capture at injection rates of 1.6-9 lb/MMACF. Samples of sorbent mixed with fly ash were collected from the pilot baghouse hopper and subjected to TCLP tests; the leachate mercury levels were below the method limit of detection. Process design and analysis for a commercial-scale manufacturing plant indicate that Amended Silicates can be cost-competitive with activated carbon for mercury control.

Several Amended Silicates formulations have also been tested at elevated temperatures and pressures as a possible mercury control technology for next-generation coal gasifiers. Laboratory experiments have shown one variant to effectively capture mercury at a temperature of 770°F and 200 psig, with sorbent mercury capacity in excess of 3% by weight. Such a technology could offer significant cost advantages in future coal gasification systems. In this application, the Amended Silicate sorbent can be disposable or used in a pressure-swing mode where a significant fraction of the captured mercury is liberated when the pressure is released at operating temperature.

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 underway 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 temperatures¹. 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. 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 by 2007.

For the past eight 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. One 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. Recent demonstrations of the use of activated carbon for mercury control at several operating power plants have produced decidedly mixed results. At one location injection of activated carbon at rates as high as 30 lb per million actual cubic feet of flue gas removed only 65% of the mercury².

ADA Technologies has conducted an extensive program to develop new technologies for the removal of trace levels of mercury from gas, liquid, solid waste streams for the past ten years. Projects totaling over \$6 million have been funded by the Department of Energy, the US EPA, and by DOE's national laboratories. Efforts have also included evaluations of several applications to reduce mercury emissions from industrial processes, undertaken with corporate sponsorship. ADA has recently delivered a commercial reactive scrubber system to a minerals processing facility for the control of mercury emissions from a process gas stream. Two processes were also licensed to an environmental cleanup firm for the stabilization of mercury in soils and sludges, and for the treatment of radioactive elemental mercury for disposal as a nonhazardous waste. ADA has also developed a mercury control system for use in dental offices, funded by the National Institutes of Health.

ADA Technologies, Inc. has in place an alliance agreement with CH2M-Hill (Denver, CO), a major environmental engineering firm, to commercialize the Amended Silicate technology through the creation of a new joint-venture company to manufacture and sell sorbent. CH2M-Hill brings to the joint venture broad expertise in the design and construction of chemical

process facilities as well as experience in the delivery of environmental control technologies to a wide range of commercial, industrial, and government clients.

AMENDED SILICATE™ SORBENT

ADA Technologies has been awarded contracts from the Environmental Protection Agency and Department of Energy for the development of a new mercury sorbent for the capture of mercury from coal-fired flue gases. These Amended Silicate sorbents use silicate materials as substrate particles on which chemicals with a strong affinity for mercury and mercury compounds are impregnated. Because of their physical structure, the silicates present extended surface area on each particle combined with an easily-generated 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. The base silicate materials typically sell for *4-8¢ per pound*, so they represent a very cost-effective sorbent material. In addition, because of their silicate content, they have been shown to allow the continued sale of fly ash as a pozzolan material. Tests completed by Boral Materials Technologies have indicated that there is no effect on fly ash use in concrete due to the addition of Amended Silicate sorbents.

The development of Amended Silicate sorbents has followed a carefully developed plan to address several key issues, including the process and conditions for preparation of the sorbent material, and evaluation of its ability to capture mercury from simulated and actual flue gas streams. In the laboratory work, ADA Technologies has identified several top-performing sorbent formulations³, which have been carried forward to pilot-scale testing. The pilot tests have been run to gather quantitative data on the ability of Amended Silicate sorbents to remove mercury from a slipstream of flue gas at an operating power plant. Results have shown very effective and efficient capture of mercury with the Amended Silicate sorbent, and are summarized in this paper. An ADA-led team has also submitted a proposal to conduct a commercial-scale demonstration of the injection of Amended Silicates for mercury control at an operating power plant in Ohio. This project would require the manufacture of 70 tons of sorbent, to validate the manufacturing process design, and the subsequent injection of the material for a total duration of six weeks to show performance in a commercial power plant. Samples of fly ash plus spent sorbent would be collected for the preparation of concrete to show that Amended Silicates do not affect the use of fly ash as a cement substitute.

Because the mercury capture by the Amended Silicates is via chemisorption, there was a possibility that mercury capacity could be substantial at elevated pressure and temperature. In 2002 ADA performed a simple test where mercury was loaded onto a sample of Amended Silicate which was subsequently pressurized and heated. Mercury was retained in the bed until the pressurization of the fixed bed was released, at which point the mercury was desorbed from the bed. This is the classic action of a pressure-swing sorption mechanism, and so a project was initiated to investigate further the performance of Amended Silicate in this mode.

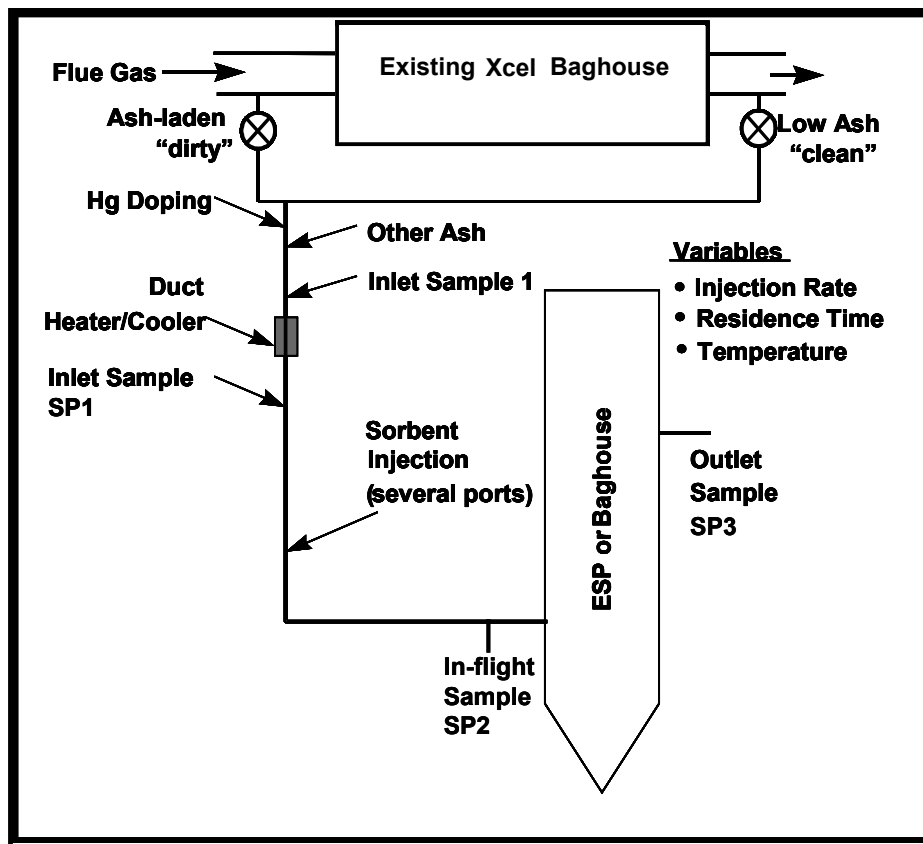
TEST EQUIPMENT

Pilot Test Fixture

Testing of the Amended Silicate sorbents on a coal-fired flue gas was conducted in a pilot plant that treats a nominal 500-1,000 acfm slipstream extracted from Xcel Energy's Comanche station Unit 2. This 275-MW generating unit burns Powder River Basin (PRB) coal, and is equipped with a reverse-gas baghouse for particulate control. PRB coals are low in chloride content, which results in most of the vapor-phase mercury in the flue gas being elemental rather than in an oxidized form. Activated carbon has greater difficulty in capturing elemental mercury as compared to oxidized mercury.

The pilot plant was designed and built by ADA to offer a variety of particulate control configurations for mercury sorbent testing⁴ and is shown in schematic in Figure 1. For these tests, the pilot was configured with a reverse-gas baghouse particulate control module. The pilot is also equipped with sampling ports upstream of the sorbent injection location and at the entrance and exit 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 special low-rate feed device into an air carrier stream to provide a consistent supply of sorbent to the flue gas slipstream.

Figure 1. Schematic of the Mercury Control Pilot Facility



The pilot facility is configured to allow control of the flue gas temperature over a range of 200°F to 325°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 earlier tests of activated carbon injection for mercury control. Target temperature range for the Amended Silicate™ sorbent tests was from 280° to 300°F.

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

The test procedure in the pilot facility at Comanche station is straightforward, and has been refined through the extensive testing done over the past five years with activated carbon and fly ash injection for mercury control. The pilot unit was operated by at least one ADA technician and an ADA engineer using a standard operating procedure for the facility. Run conditions for the pilot including temperature set points and flue gas flow rate were taken from the test matrix. The pilot unit was at steady state operating conditions prior to the start of each test, and a cleaning cycle was initiated to dislodge ash and sorbent materials accumulated on the particulate control module (PCM) bags. The ash hopper was emptied prior to any sorbent injection.

During a test, flue gas was sampled at three different locations in the pilot unit as identified in Figure 1: upstream of the sorbent injection port (SP1), downstream of the sorbent injection port corresponding to a 1.0 second residence time (SP2), and at the outlet of the PCM (SP3). Vapor-phase mercury measurements were made using the modified Ontario-Hydro technique described later. Operators filled out a Mercury Sampling Data Run Sheet for each sample to document sampling times, gas volumes and glassware weights. Data from this sheet were used to calculate ash loading in the gas stream and volume of gas extracted from the pilot.

Once the baseline measurements were completed, the sorbent injection tests began. The candidate sorbent being tested was fed into the flue gas slipstream using a customized vibratory feeder. The feeder was calibrated to deliver known rates of material. Sorbent injection rates for these tests varied from about 0.75 to 3.5 grams/minute depending on the test conditions. This range of injection rates correspond to full-scale sorbent injection rates of 1.6 to 9 pounds/million actual cubic feed (MMACF). Mercury sampling was initiated about one hour after the start of sorbent injection to allow time for the pilot system to equilibrate with respect to mercury removal. Data taken in earlier tests has shown that equilibrium conditions in the pilot are reached in under an hour, so that a test run of a few hours provided sufficient time to achieve equilibrium and allow for a one-hour impinger sampling period. Impinger samples were immediately transferred to an analytical trailer on-site and analyzer per the protocol described later.

At the end of the test, the operators initiated a clean cycle in the PCM to collect in the pilot hopper the fly ash and sorbent materials deposited on the bags during the test. Several samples

of fly ash mixed with spent sorbent were retrieved from the hopper for analysis of mercury content. Samples were also subjected to an acid leach following the Toxic Characteristic Leaching Procedure (TCLP) to evaluate the potential for leaching of mercury from the fly ash and spent sorbent mixture.

High-Temperature, High-Pressure Test Fixture

The Amended Silicate sorbent has also been tested to determine its suitability to capture mercury at conditions representative of coal gasifier systems. As part of a Phase I SBIR research grant, a test apparatus was constructed to investigate the capacity and behavior of Amended Silicates at high pressures and temperatures.

The test fixture was designed to simulate conditions inside a coal fired gasifier by passing mercury-laden nitrogen at high temperature and pressure through a ½” tubular packed bed filled with Amended Silicate sorbent mixed with 20 g of quartz sand; typically 0.5 g of sorbent was used. A thermocouple was inserted into the bed to measure its temperature and glass wool plugs were used to contain the bed. A mercury source and by-pass lines allowed known concentrations of vapor-phase mercury to be entrained in the gas stream. During experiments both pressure and temperature of the sorbent bed were controlled and loading of the bed occurred over a period of days. In one recent experiment, a one standard liter per minute (slpm) gas flow doped with 700 µg/m³ mercury was used to load 42 µg/hour Hg onto the sorbent, held at 600° F and 200 psi (315 C and 13.6 atm) until breakthrough occurred. A portable atomic absorption mercury analyzer (Lumex) was used to measure in-line mercury concentrations directly from the mercury source or after flow through the sorbent bed.

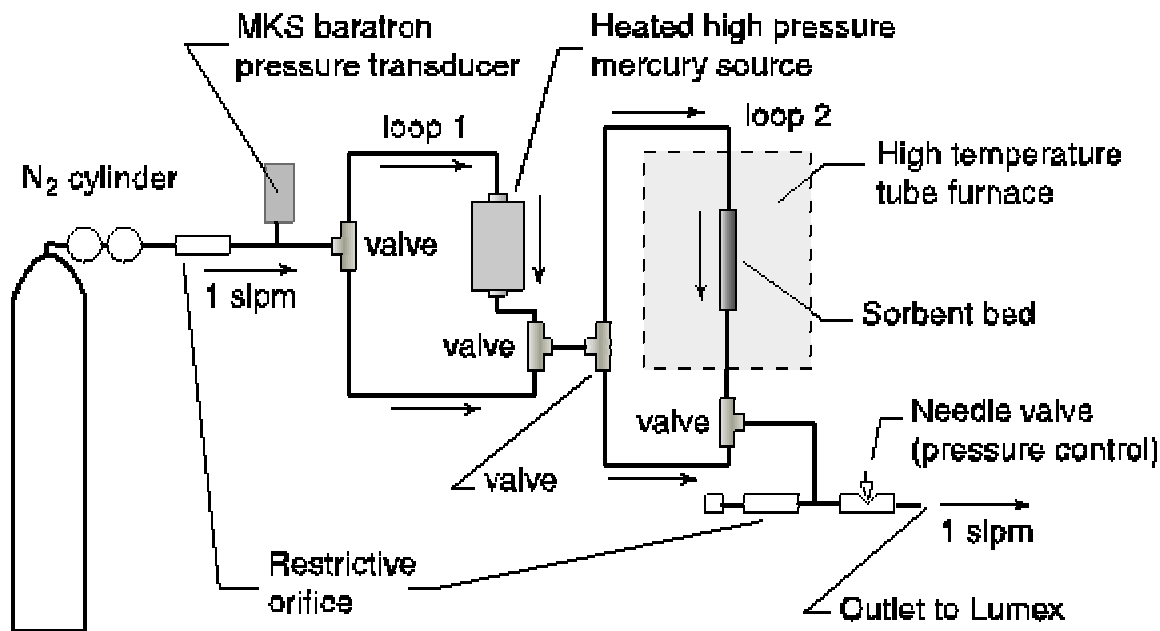
Figure 2 illustrates the high pressure high temperature test apparatus used during the Phase I investigation. Flow of nitrogen into the apparatus was maintained by a restrictive orifice and pressure regulator. Once the pressure drop across the restricting orifice exceeded a critical pressure ratio, the mass flow at the inlet became constant. Pressure in the apparatus was adjusted with a pressure transducer and a needle valve at the exit.

As gas flowed into the apparatus it encountered two loops in series. The first loop contained a mercury source and a bypass line. Vapor-phase mercury was entrained in the flow by heating a small amount of elemental mercury held in an open flask. The flask was positioned inside a vertical 6” length of ½” diameter stainless-steel tubing. Mercury concentration in the gas stream was adjusted by changing the temperature of the mercury source and measuring the downstream concentration with the analyzer. To heat the mercury source, an aluminum fixture with cartridge heaters clamps onto the outside of the tubing containing the mercury flask. Thermocouples located in the mercury source and aluminum fixture are for feedback control of the mercury source temperature. All lines downstream of the mercury source are heat traced to reduce Hg holdup in the lines, fittings and valves.

The second loop allowed mercury-laden gas to be passed through a sorbent bed or routed directly to downstream instrumentation. With the by-pass line in loop 2 closed, gas flowed from the mercury source to the top of the sorbent bed, through the bed, and then out via the needle valve and analyzer. Alternatively, the sorbent bed could be purged with nitrogen via the by-pass

leg of loop 1. The sorbent bed was positioned inside a tube furnace for temperature control. This configuration allowed measurement of both the mercury burden being delivered to the sorbent bed as well as any mercury breakthrough from the bed.

Figure 2. Schematic of HTHP Mercury Test Fixture



Once breakthrough occurred, the mercury source was cooled and by-passed. Next, the sorbent bed is held at the test temperature and purged with a constant flow of low-pressure nitrogen while measuring the Hg concentration, i.e. a pressure swing of the sorbent is performed. Mercury released by the sorbent is captured by passing the purge flow through a potassium permanganate impinger. Once the mercury release from the sorbent has fallen to low concentrations, the sorbent is cooled, removed from the bed, and analyzed to determine the total Hg burden per gram sorbent ($\mu\text{g/g}$). The impinger is analyzed as well per the protocol described below. The total loading of mercury on the sorbent is determined as the sum of the residual mercury on the sorbent plus the released mercury captured in the impinger solution.

Preparation of a suitable packed bed was the first step in the experiment. The sorbent bed was removed from the test rig and cleaned. The Amended Silicate sorbent was prepared in an appropriate particle size for the dimensions of the packed bed, with sand used to dilute the sorbent and provide additional volume in the bed. For most experiments 20 g of quartz sand was mixed with 0.5 g of sorbent, then loaded into a $\frac{1}{2}$ " diameter stainless-steel tube about 10" in length. A glass wool plug was inserted into the empty tube to contain the sand/sorbent mixture during loading. A second glass wool plug was inserted into the top of the tube after loading the sand/sorbent mixture. A stainless-steel sheathed thermocouple was inserted into the top of the bed and fittings were tightened to complete assembly of the packed bed.

Individual component of the test apparatus were then assembled. Mercury was added to the flask inside the mercury source as needed. Weights of the elemental mercury in the mercury source were recorded before and after each test run. This allowed a mass balance to be made with mercury captured downstream of the mercury source, i.e. by the sorbent or in the potassium permanganate impingers. The packed bed assembly and all fittings in the test apparatus were tightened and leak checked at pressure. Once the test fixture was confirmed as leak-tight, a bubble flow meter was used to calibrate the flow rate of nitrogen through the test apparatus. A Dwyer flow meter was used during the experiment to verify the flow. Pressure at the inlet restricting orifice was maintained at a constant value throughout the experiment, thereby generating a constant flow rate.

Tests began by monitoring for residual mercury in the heated bypass lines. Gas was flowed through the bypass line of each loop (as shown in Fig. 2) at full pressure. Monitoring continued while the sorbent bed was brought up to operating temperature. Gas flow was then switched to pass through the sorbent bed and the discharge gas stream checked for mercury contamination. Once the flow through the fixed bed was shown to be clear of mercury, nitrogen flow was diverted around the packed bed and through the mercury source. Temperature of the mercury source was increased from room temperature until the desired concentration of mercury was entrained in the gas, as measured by the Lumex atomic absorption analyzer at the gas discharge. Finally, the gas flow was switched to so that it passed through the mercury source, then the test sorbent bed.

Potassium permanganate traps were used to capture mercury not removed by the sorbent. Gas at the outlet of the test apparatus was monitored with the Lumex instrument upstream of the potassium permanganate traps. Periodically, gas flow through the sorbent bed was bypassed to measure mercury concentration from the mercury source. Temperature of the mercury source was iteratively adjusted to maintain the desired loading rate ($\mu\text{g}/\text{hour}$).

High mercury concentrations at the sorbent bed outlet indicated breakthrough, and signaled the end of the sorption phase of the test. Gas flow was then switched to bypass the mercury source. After a short while mercury concentrations were seen to reach steady state. Once this happened, the pressure in the test fixture was reduced while maintaining a purge flow of nitrogen. Due to the pressure-swing sorption effect, some fraction of the mercury captured by the sorbent was released. Following the pressure swing release of mercury, gas flow through the bed was maintained while the sorbent bed was cooled to room temperature. As the final step the sorbent bed was removed and the sorbent was analyzed for residual mercury content.

Mercury concentration in the test gas was monitored using a mercury analyzer manufactured by Ohio Lumex. The analyzer operates on the principle of cold vapor atomic absorption (CVAA) of ultraviolet (UV) light by vapor-phase elemental mercury, where the amount of UV absorption was proportional to the mercury concentration in the gas stream. The Lumex instrument was operated in a mode where its limit of mercury detection was about one microgram per cubic meter.

WET CHEMISTRY MERCURY MEASUREMENTS (COMANCHE PILOT)

Mercury measurements were made using a wet chemistry approach. This method was an adaptation of the Ontario-Hydro Method or U.S. EPA Method 29. However, the ADA adaptation was simplified in that it did not attempt to quantify particulate mercury or determine the mercury apportionment between oxidized and elemental mercury in the gas stream. Instead, total vapor-phase mercury was the measurement of interest. Many factors can affect the data produced from this analytical procedure and these factors must be taken into account to provide meaningful results. Cross flow filters were used when sampling a particulate-laden flue gas stream to eliminate the capture of mercury in particulate filter cake. A heated Teflon sample line was installed to transport sample gas to the permanganate impinger to minimize line losses of vapor-phase mercury.

In this method the sampled flue gas was drawn through two liquid impingers in series each filled with acidified potassium permanganate (KMnO_4) to oxidize and capture all vapor-phase mercury in the gas stream. The impingers were 250 ml gas washing bottles and were filled with 100 ml of the potassium permanganate solution. The impinger train was connected to the sample port with thin walled Teflon tubing and plastic elbows. The impinger train was placed in an ice bath to regulate the temperature of the oxidizing solution and to condense moisture present in the gas stream. Sample gas was pulled through the sample train for approximately one hour at a rate of 300 scfm. Mercury content of the impingers was determined in the field.

For the field samples, the impingers and tubing were disconnected and analyzed individually. The permanganate solutions contained both oxidized elemental mercury and ionic mercury removed from the sample gas. A sufficient amount of 10% hydroxylamine solution was added to the impinger to convert the purple solution to a clear solution, reducing any remaining permanganate to MnO_2 , and eventually to Mn^{+2} . This was followed with a 5 ml addition of a 10% stannous chloride solution to reduce any ionic mercury in solution to elemental mercury, which is insoluble. A nitrogen sweep gas stream at a known flow rate was passed through the impinger to transfer the elemental mercury to a Lumex Model RA-915+ analyzer. Total elemental mercury in the transport gas was determined by integrating the continuous mercury measurements of the Lumex instrument over time until the mercury in the sweep gas dropped to zero.

RESULTS

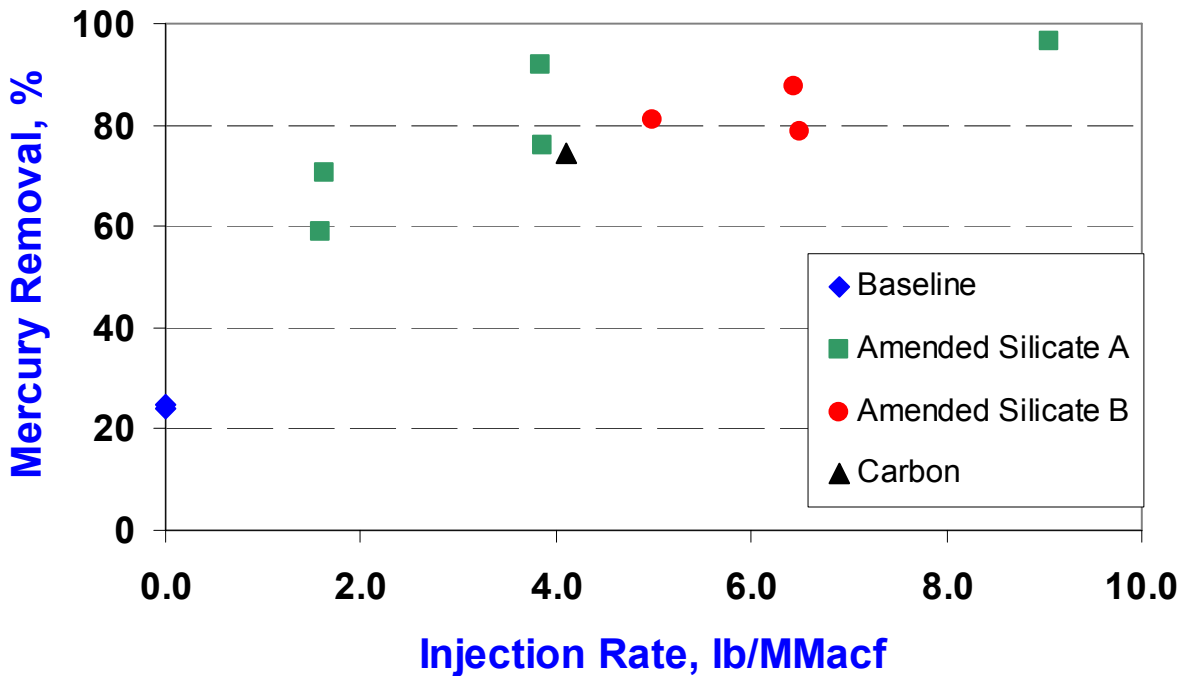
Pilot Testing

ADA Technologies has run tests in the Comanche pilot for three different Amended Silicate™ sorbent formulations. One variant produced superior results, and a second showed promise, as it easily matched the performance of carbon, and was a lower-cost formulation. Tests were conducted in several campaigns between November 2002 and March 2003. For these tests, Total mercury concentrations in the flue gas stream ranged from about 4 to 8 $\mu\text{g}/\text{Nm}^3$, with the particulate-bound fraction well under 20%. Mercury analyses were run for samples collected upstream of the sorbent injection location in the pilot.

Mercury measurements were made at several locations in the pilot, upstream of sorbent injection, immediately upstream of the inlet to the baghouse, and at the outlet from the pilot baghouse.. Samples obtained at baghouse inlet were used to quantify the “in-flight” capture of mercury by the sorbent, which occurs in the 1.0 seconds of contact time between the injection point and the location of the baghouse inlet sampling port.

Results from the pilot tests are presented in Figure 3, which plots mercury removal as a function of sorbent injection rate. The baseline data show a mercury removal across the pilot baghouse by the native fly ash of about 24%. When Amended Silicate A sorbent is injected, the mercury removal rises dramatically. At an injection rate of 1.6 lb per million actual cubic feet of flue gas, the mercury removal increases to 70% in one test and 60% in another. The rate of mercury removal continued to increase as the injection rate of Amended Silicate A was increased, rising to almost 92% at a rate of 3.8lb/MMACF, and finally reaching 96.7% for the injection of 9.1 lb/MMACF. The alternate Amended Silicate sorbent (labeled ‘B’ in Figure 3) also showed significant mercury removal levels. At an injection rate of 5 lb/MMACF, the B sorbent removed 81% of the mercury, and at a rate of 6.4 lb/MMACF the mercury removal reached 87%. For comparison, tests run several years ago in this same facility with activated carbon showed a mercury removal rate of 74% at a sorbent injection rate of 4.1 lb/MMACF. Thus, the Amended Silicate™ sorbent is seen to easily match the performance of activated carbon in this pilot test.

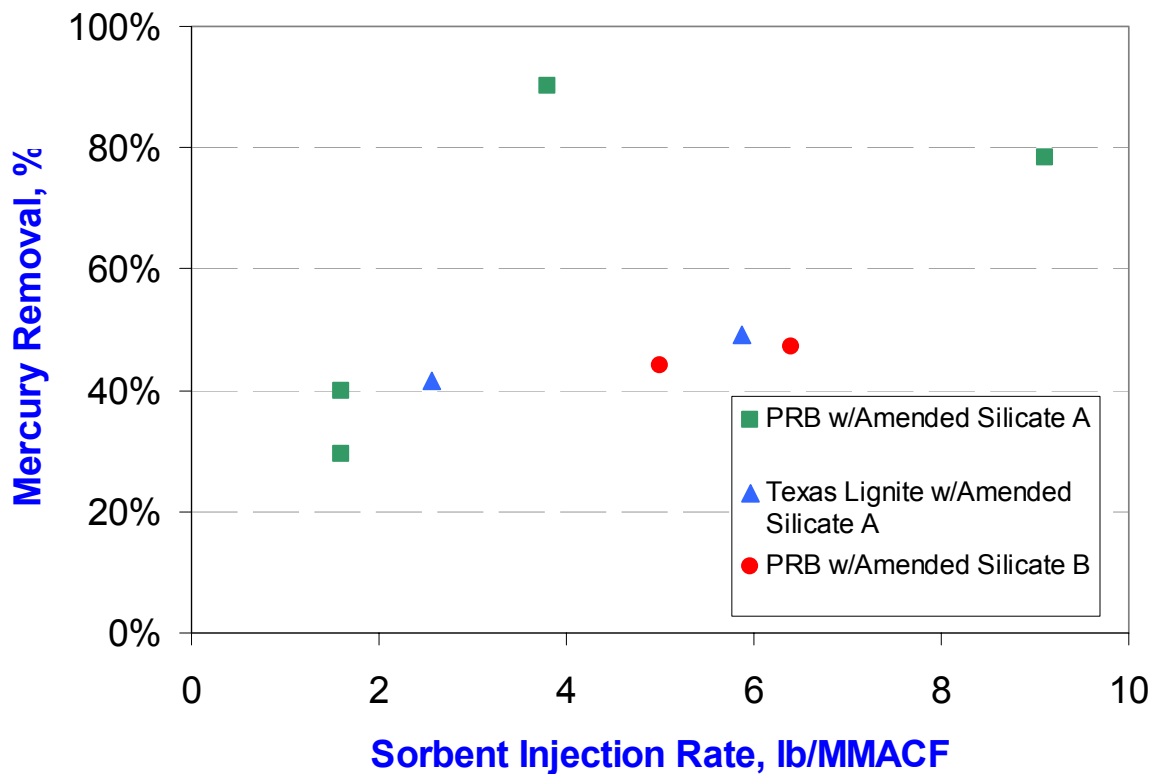
Figure 3. Mercury Removal Results from Pilot Slipstream Tests



Test results from an earlier pilot test at another facility burning Texas lignite indicated that the Amended Silicate™ sorbent rapidly captures the vapor-phase mercury in the gas stream, a factor that suggests the Amended Silicate would perform well in a plant equipped with an electrostatic precipitator, where activated carbon has shown decidedly mixed results. As a measure of the short-term performance of the Amended Silicate™ sorbent, the flue gas in the pilot was sampled to measure mercury content after a sorbent contact time of 1 to 1.4 seconds with the flue gas. Results are presented in Figure 4 below.

The data in Figure 4 show that there is significant mercury removal in the short contact time between sorbent injection the downstream measurement location. Even at low sorbent injection rates, 20 to 40% of the mercury was captured by the Amended Silicate™ sorbent. As injection rates rose, there was extensive capture of over 80% of the vapor-phase mercury in this short contact time, indicating that the kinetic performance of Amended Silicate™ sorbent for mercury capture by is quite high, even at the low mercury concentrations found in coal-fired flue gases.

Figure 4. In-Flight Mercury Removal by Amended Silicates Sorbent



Finally, a series of tests were run on samples of fly ash mixed with Amended Silicate™ sorbent collected from the hopper of the Comanche pilot facility during each of the test cases reported in

Figure 3. The samples were subjected to the EPA’s Toxic Characteristic Leaching Procedure (TCLP) test, standard for measuring the leachability of metals from waste streams. The tests revealed that for all the Amended Silicate™ samples the mercury level in the leachate solution was below the limit of detection for the method, or less than 0.2 ppb. This is a strong indication that the mercury captured by the Amended Silicate™ sorbent is tightly bound by a chemisorption process, and that the collected mixture of fly ash and sorbent can be safely disposed as a nonhazardous waste.

High-Pressure, High Temperature Testing

The objectives of the High-Temperature-High-Pressure sorbent testing were:

1. Determine sorbent adsorption at a pressure of 200 psig and temperatures (500 to 750°F) typically encountered in gasifier operations.
2. Demonstrate that pressure-swing desorption can be used to regenerate the sorbent.

Table 1 summarizes the test conditions for a series of tests using two different chemical amendments of the silicate substrate.

Table 1. Summary of Sorbent Test Conditions

Test ID	Formulation	Sorbent Pressure	Sorbent Temperature	Average Hg Addition Rate µg/min	Nominal Gas Flow Rate
CAP-1	A	200 psig	770°F	3.4	1 l/min
CAP-2	B	200 psig	510°F	5.47	1 l/min
CAP-3	A	200 psig	752°F	5.3	1 l/min

As discussed earlier, the total mercury capacity of the sorbents was determined as the sum of two distinct measures of absorbed mercury. These measures were the quantity of mercury desorbed from the sorbent as the pressure was lowered (the pressure swing fraction) plus the mercury that remained bound to the sorbent at atmospheric pressure and the desorption temperature of 510-752°F, as determined by digestion and chemical analysis. It was observed that there was no steady increase in desorbed mercury as the pressure was released, and desorption only occurred at a significant rate after the pressure had been lowered to less than 50 psig. These data are summarized in Table 2.

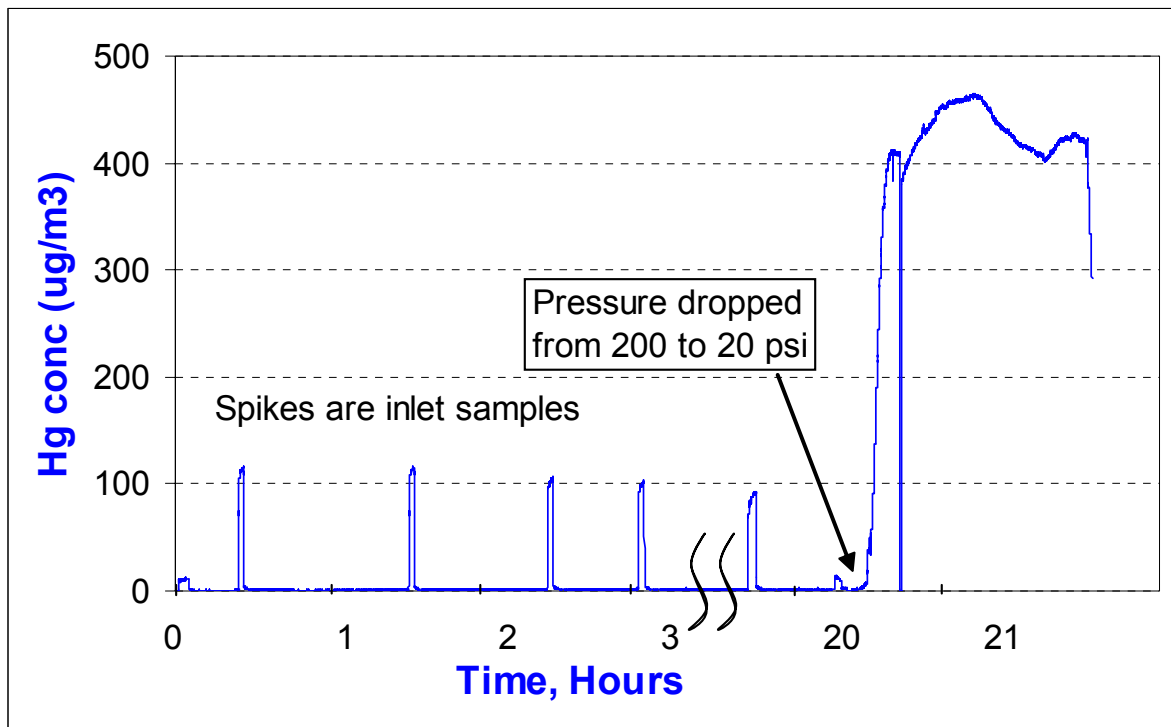
These tests demonstrated that the mercury capacities of these sorbents at elevated pressures are extraordinarily high (up to 3% Hg), even at temperatures as high as 770°F. Furthermore, the major proportion of mercury remained within the sorbent bed even when the pressure was dropped to only 20 psig. In fact, this mercury was so strongly sorbed into the sorbent that it could only be recovered by chemical digestion.

Table 2. Summary of Sorbent Mercury Capacities

Test ID	Desorbed Mercury (µg/g)	Digested Mercury (µg/g)	% mercury desorbed	Total Mercury Capacity (µg/g)
Formula A	7,948	22,600	26%	30,548
Formula-B	1,620	3,680	30.6%	5,300
Formula-A	1,037	20,800	4.7%	21,837

The results of a typical pressure swing test are shown in Figure 5. Here the mercury concentration in the purge gas is plotted, showing that no mercury is released from the sorbent bed until the pressurization is dropped from 200 psig down to 20 psig.

Figure 5. Mercury release from an amended silicate sorbent with a pressure swing.



At the outset of this program it was assumed that at typical gasifier temperatures of >500°F, it would be relatively easy to release the mercury from the absorbent, by simply lowering the pressure. Unexpectedly, the elevated pressures appear to bind the mercury so strongly to the sorbent that it remains attached to the sorbent, even at pressures close to atmospheric. Furthermore, at the higher pressure, the total mercury capacity increases by a factor of at least five-fold, compared to the same sorbents at atmospheric pressure.

These results suggest that, rather than regenerating the sorbents, a more attractive method of deployment may be to use them as a disposable sorbent bed. The very high capacity of the sorbents implies that all of the mercury from 1 million tons of coal, containing 100 ppb Hg, could be captured from a gasifier by as little as 3.5 tons of sorbent in a fixed-bed, giving a system cost of less than \$1,000/lb Hg captured, as compared to EPA estimates of \$25,000-50,000/lb Hg from conventional coal-fired power plants.

ADA has performed TCLP extractions on a loaded sorbent to ensure that they will pass TCLP, for disposal as a non-hazardous waste. The TCLP-extractable mercury from a sorbent loaded with 20.8mg/g Hg, was less than 2 ppb, thus not only passing the TCLP extraction limit but also passing the more stringent Universal Treatment Standard of 25 ppb.

ECONOMICS

A process flow diagram and a detailed heat and material balance model have been developed to investigate the effect of process variables on the economics of a full-scale process to manufacture Amended Silicates™ sorbent in a dedicated production facility. The heat and material balance model has been used to optimize a process flow scheme that balances high utilization of raw materials and chemicals with low capital and energy costs for manufacture. Each of the steps in the optimized process has been demonstrated at bench scale to establish appropriate confidence in the feasibility of the processing sequence.

Additional confirmation and process optimization is being obtained through a project which has been launched to manufacture demonstration-scale quantities of Amended Silicate sorbent. Three toll processors have been contacted for extensive discussions of process steps and the configuration of a pilot-scale process trial in which tons of sorbent would be manufactured. To further discuss this approach, site visits to all three vendors were made by an ADA/CH2M Hill technical team. These discussions confirmed that all vendors consider this to be a comparatively simple manufacturing process. It is envisioned to produce first one or two small-scale batches to optimize the substrate preparation step as well as to confirm the simplicity of the amendment steps. The original cost estimate was based on very conservative assumptions for process parameters such as reactor contact times. In addition, cost savings are expected for the solid/liquid separation step when larger-scale tests confirm that less expensive equipment can be used. The demonstration-scale quantity of 70 to 100 tons will utilize equipment that is in the size range of commercial production facilities. Further economic improvements will be realized in the ultimate plant since all processing steps will be carried out on a continuous basis rather than batch basis.

Based on all these considerations, an equipment list has been developed and used to prepare a capital and operating cost estimate for a complete processing facility at full production scale. Staffing needs have been based on staffing used in plants to produce similar products. Using the latest results of the engineering and economic models, the current estimated cost of manufacturing the Amended Silicates™ sorbent, including recovery of capital and operating costs and a reasonable return on investment, is in the range of \$0.45 to \$0.55 per pound.

CONCLUSIONS

ADA Technologies has discovered and developed a new class of sorbents for the removal of mercury from flue gas streams. The Amended Silicate sorbents have been prepared in a number of formulations which are custom-configured to provide economic mercury recovery in multiple applications. They have been tested in a pilot plant on a slipstream of a sub-bituminous (PRB) coal, and for potential use in coal gasification systems at elevated temperatures and pressures. Results are summarized below.

- Amended Silicate sorbent removed 70% of the mercury from the pilot at an injection ratio of 1.6 lb/MMACF, and over 96% at a ratio of 9.1 lb/MMACF.
- The injected Amended Silicate removed 40% or more of the mercury in the first one second of contact time in the pilot tests.
- When fly ash plus spent sorbent samples were subjected to TCLP tests, no measurable mercury was found in the leachate.
- Detailed engineering cost studies indicate that the Amended Silicate sorbent can be manufactured in commercial quantities at 45 to 55¢ per pound.
- Another variant of the Amended Silicate sorbent was shown to capture mercury at 770°F and 200 psig, conditions representative of coal gasification systems.
- The mercury capacity of Amended Silicate in the high-pressure, high-temperature tests was as high as 3% by weight, almost five times the capacity at ambient pressure.
- The Amended Silicate performed as a pressure-swing sorbent, releasing as much as 30% of the captured mercury upon depressurization.
- In a gasifier, it would be economic to operate a mercury removal system using Amended Silicate sorbent in either a pressure-swing or disposable sorbent bed configuration.
- The mercury captured at the high-temperature, high-pressure conditions was tightly bound to the sorbent, as indicated by a leachate mercury concentration of only 2 ppb.

ACKNOWLEDGMENTS

Funding for the discovery and development of Amended Silicate™ sorbents has been provided by the US Environmental Protection Agency and US Department of Energy under the Small Business Innovations Research program. Additional funding and in-kind technical support has been supplied by CH2M Hill. We also wish to recognize Xcel Energy for site access and support in the pilot testing of the Amended Silicate sorbent at Comanche station in Pueblo, Colorado. The ADA Mercury Group technical team has spent long hours in the field and in the laboratory advancing the development and testing of Amended Silicates, and their contributions are gratefully acknowledged.

REFERENCES

1. Brown, T.D., D.N. Smith, R.A. Hargis, Jr., and W.J. O'Dowd, "1999 Critical Review, Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate," J. Air & Waste Management Assoc., June, 1999.
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," Air Quality III Conference, Arlington, VA, September 9-12, 2002.
3. Butz, J.R., T. E. Broderick, J. S. Lovell, C. S. Turchi, G. D. Brown, and R. Pearson, "Amended Silicates: High Capacity Mercury Sorbent Unaffected by Acid Gases," Air Quality III Conference, Arlington, VA, September 9-12, 2002.
4. Butz, J., C. Turchi, T. Broderick, J. Albiston, "Options for Mercury Removal from Coal-Fired Flue Gas Streams: Pilot-Scale Research on Activated Carbon, Alternative and Regenerable Sorbents," Pittsburgh Coal Conference, Pittsburgh, PA, September 12-14, 2000.

Key Words

Mercury
Sorbents
Amended Silicate
Flue gas
Coal gasification
TCLP