DELVELOMENT AND EVALUATION OF NON-CARBON SORBENTS

WESTERN RESEARCH INSTITUTE AND NOVINDA CORPORATION

Executive Summary

Western Research Institute (WRI) and its cosponsor Novinda Corporation (the Company was originally known as Amended Silicates, Inc.) proposed the development, characterization and testing of sorbents based on clay deposits abundant in Wyoming for the in-flight capture of mercury in pulverized coal derived flue gasses. As a part of the State of Wyoming's Clean Coal Technologies Research Program, a two-year sorbent development and testing program was successfully concluded such that Amended Silicates® is now a patented, commercially available mercury removal sorbent. Amended Silicates® is the first non-carbon reagent which preserves fly ash use in concrete. Amended Silicates® offers economic and environmental advantages not available with other mercury removal products.

Background

Because of escalating concern over mercury emissions from coal combustion the US Environmental Protection Agency (EPA) has issued stringent mercury emissions standards. The EPA's Maximum Achievable Control Technology (MACT) standards and new Mercury and Air Toxic Standards (MATS) apply to every coal-fired power plant in the country, including the concrete industry and industrial power plants, as well as utilities. The EPA has established an aggressive timeline for compliance with the federal standards:

- Utility MATS: April 16, 2015
- Portland Cement MACT: September 9, 2015
- Industrial Boiler MACT

Compliance deadlines for major boilers and Commercial/Industrial Solid Waste Incinerators units will be in 2016 and 2018, respectively.

The most effective method for removing mercury from coal combustion gases is the introduction of a fine powder material (sorbent) into the gas stream. The sorbent interacts with gaseous mercury, removing it from coal combustion gases. Sorbent particles containing the mercury are then captured in the power plant's particulate capture systems. Currently, brominated powder activated carbon (PAC) is the best available control technology (BACT) for in-flight elemental mercury capture in pulverized coal combustion units. With proper installation and operation it is capable of capturing about 90% of the elemental mercury in the flue gas. However, PAC injection for mercury emissions control has several drawbacks:

- Injected carbon increases the "unburnt" carbon content of the flyash. This mingling of activated carbon with the fly ash adversely impacts the use of captured fly ash as an additive in concrete production
- Activated carbon is flammable and stored quantities at a power plant pose a safety risk
- Activated carbons can suffer from poor performance when used with high sulfur coals. Firing high sulfur coals can result in sulfur trioxide (SO_3) vapor in the flue gas stream. The SO_3 competes with mercury for binding sites on the surface of the PAC (or unburned carbon) and limits the effectiveness of the injected carbon.
- Activated carbon is expensive (approx. $1500/ton).

Project Description

The goal of the proposed project was to test various non-carbon reagents for the in-flight capture of elemental mercury against the benchmark performance of brominated PAC in various power plant back-pass configurations. Novinda were to develop sorbent chemistries and test them using bench-scale equipment. Once the most promising reagents were identified at bench-scale, they were then tested in the WRI's combustion test facility (CTF). In an iterative manner the reagent chemistries were optimized for activity and downstream capture, and tested comparatively against commercially available PAC. Specific objectives of the proposed work were:

- Determine the impact of relevant variables on the sorbent performance
  - coal types (mainly PRB from Eagle Butte coal mine (Ronald Seam) with 2-3 runs with PRB from Eagle Butte mine (Smith Seam). The difference if sulfur and Hg content.
  - injection rates
  - reaction times
  - injection locations
  - temperature
- Study product formulation differences
- Measure impact of different chemical environmental constituents such as SO_3, NOx, ammonia
- Analyze the behavior in different particulate collection devices (Baghouse (fabric filter), Electrostatic Precipitator (ESP) , Spray Dryer Absorber (SDA)/Baghouse)

The target goal was to meet or exceed 90% mercury capture with a material that is cheaper than the PAC-based sorbents.

Procedures/Facilities

WRI's coal combustion test facility (CTF) is a nominal 250,000 Btu/hr balanced-draft system designed to replicate a pulverized coal-fired utility boiler. In its present configuration, the unit is set up to simulate a tangential-fired boiler, but may be easily adapted to wall-fired or other configurations. The fuel feed system consists of screw-based feeders and pneumatic transport to four burners inserted in the corners of a refractory-lined firebox. The burners can be angled to attain different tangential flow characteristics in the firebox. The unit is equipped with appropriately sized heat-recovery surfaces such that the time/temperature profile of a utility boiler is replicated. These surfaces comprise water-cooled panels that simulate the waterwall, an air-cooled superheater, reheater, two economizers and preheater. CTF includes provisions for preheating the combustion air to mimic a utility air preheater. The system also includes over-fire air injection ports for combustion staging. The unit is equipped with two baghouses for continuous fly ash removal and for "clean" sampling under different steady-state operations.

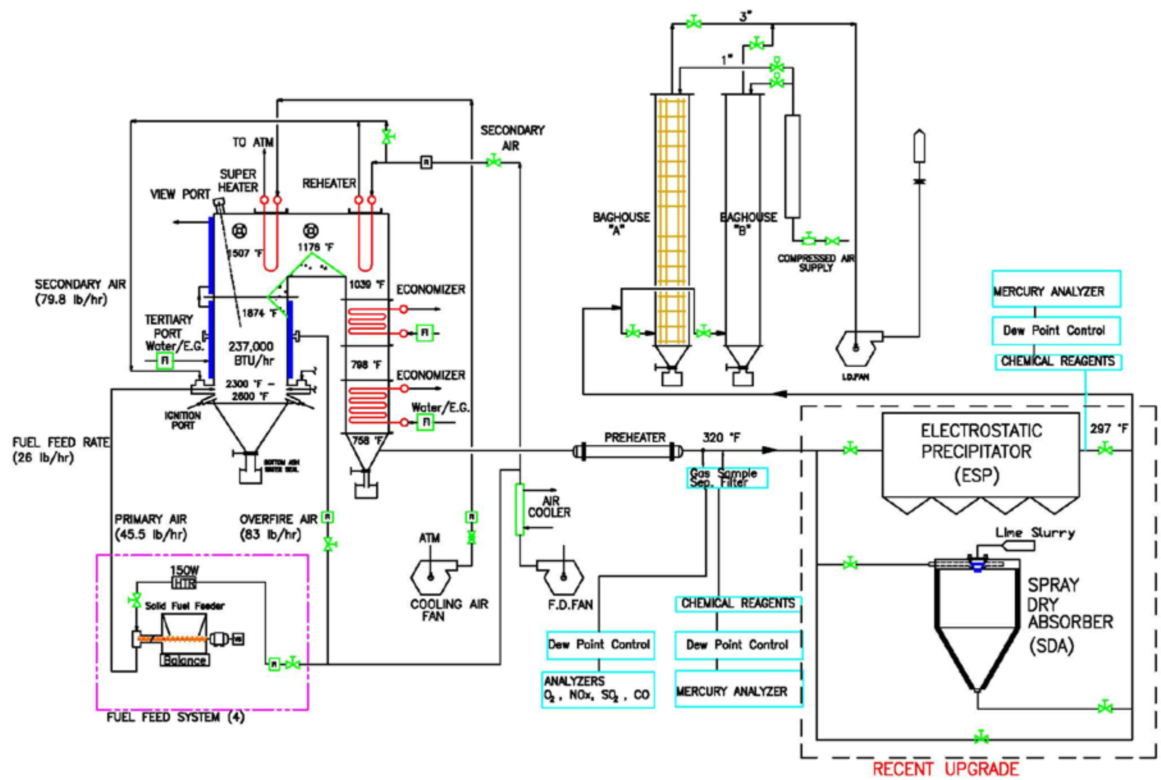

Figure 1. Schematic of the Coal Combustion Test Facility with the ESP and the SDA (Recent Upgrades)

As a part of this proposal, CTF was modified to allow sorbent testing in various back-end plant configurations such as with baghouse, with ESP, and with SDA/baghouse. As shown in Figure 1, a spray dry absorber and an ESP were added to the existing CTF layout. These modifications of the CTF allowed for flexibility in configuring the Air Pollution Control Devices (APCD) to mimic as they are typically set in a majority of the PRB coal-fired power plants. This is a very important factor, since mercury reduction levels are known to be highly dependent on the APCD installed at the plant.

Over the course of the project, fifty-four test runs were completed with non-carbon based mercury sorbents prepared by Novinda. A total of nineteen test runs were conducted with baghouse, twenty-eight runs with ESP (both in energized and de-energized modes), and five runs with SDA/baghouse. Tests investigated the effect of flue gas temperature, sorbent composition, and sorbent injection rate on the mercury emission reduction. In addition variables specific to the APCD in use were also investigated. A typical test included starting the CTF on an auxiliary fuel to warm-up the furnace. It is extremely important that carbon monoxide level during start up and during the test were kept at the lowest possible level. During coal firing, a high level of carbon monoxide is a sign of formation of unburned carbon. To minimize the formation of unburned carbon in the fly ash, high temperature in the lower furnace and sufficient excess oxygen are required. After a sufficient warm-up, and when the desired exit temperature from the APCD was satisfied, coal feed was started while maintaining the excess oxygen in the lower furnace at 5% oxygen. CTF was operated on coal for four to six hours to achieve steady state. Mercury measurements were then made to establish base-line mercury concentration in the flue gas. For the PRB coal used for all the tests concluded under this project the uncontrolled mercury concentration was expected to be in the 9-10 µg/Nm3 range. Sorbent injection was started at the desired rate while continuously monitoring the mercury content of the gases leaving APCD configuration. A typical sorbent injection test was about 90 minutes long.

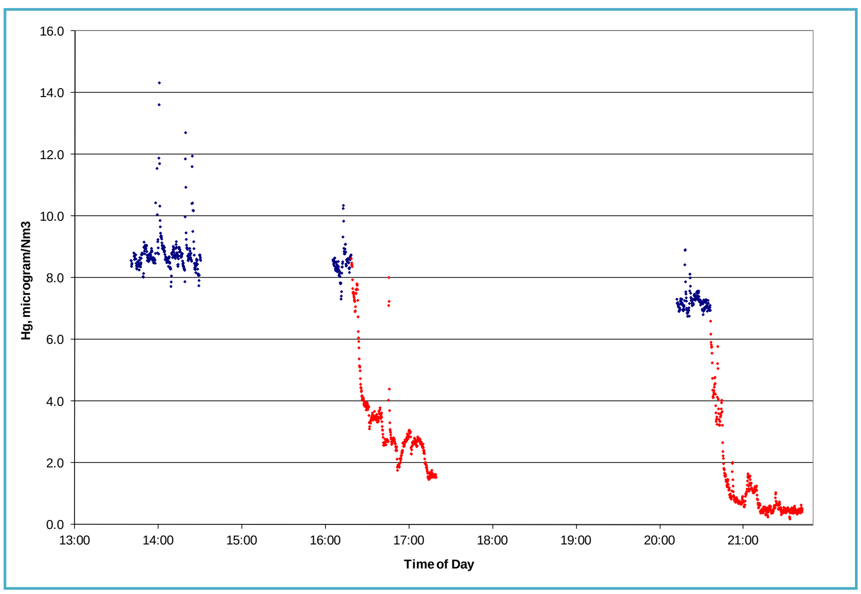

Figure 2. Typical sorbent tests run data

Figure 2 shows a typical test run data for mercury sorbent test. The figure shows the mercury concentration in the combustion gases as a function of time-of-day. Black symbols represent the mercury concentration in the combustion gases when no sorbent is being injected and thereby represent baseline mercury concentration. For example, around 2:00 PM on that test day the mercury concentration in the flue gas was just below 9 microgram/Nm3. Red symbols represent the mercury concentration when sorbent injection has been started. The figure shows two such time periods for two different sorbent injection rates. Clearly, irrespective of the injection rate, mercury concentration in the combustion gases begins to decrease as soon as the sorbent injection is started and within minutes reach a considerably lower value. In the graph displayed in Figure 2 this value around 9:00 PM is less than 0.5 microgram/Nm3, representing a better than 90% reduction in mercury concentration.

From several similar test runs with several different sorbent chemistries it was established that indeed non-carbon sorbents can achieve mercury emissions reduction comparable or better that those possible with brominated activated carbons. Figure 3 compiles data from several non-carbon sorbent tests at different injection rates, and compares them with activated carbon data. Clearly, performance of the non-carbon chemistries is quite comparable with that of conventional and treated powder activated carbons.

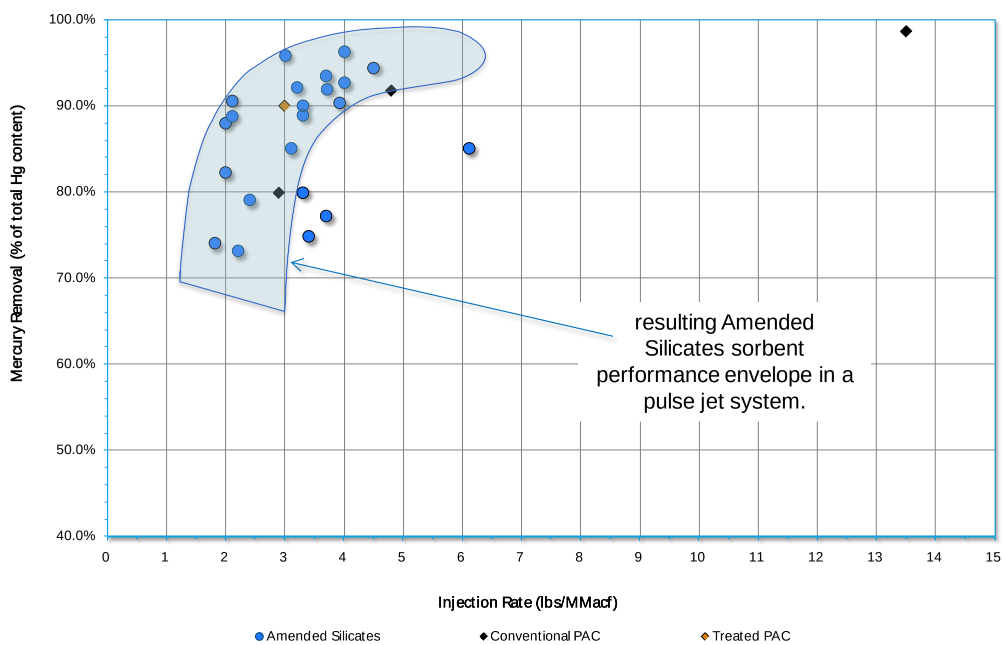

Figure 3. Mercury removal as a function of sorbent injection rate for baghouse plant configuration

Please note that the data presented in figure 3 are for the plant configuration employing a baghouse. Similar results were also obtained in plant configurations with spray dryer absorber with a baghouse. The performance of the non-carbon sorbent was similarly comparable to conventional PAC in an ESP set-up.

Flyash samples collected during these tests were subjected to Toxicity Characteristic Leaching Procedure (TCLP). TCLP is designed to determine the mobility of elements and compounds in liquid and solid waste byproducts. Tests have shown the mercury captured by Amended Silicates to be extremely stable.

Testing conducted elsewhere have shown that Amended Silicates® is 100% compatible with fly ash use in concrete products. By using Amended Silicates for mercury control, utilities enjoy the dual benefits of preserving the beneficial use and value of fly ash as a portland cement replacement, while avoiding costs associated with landfill disposal. The U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL) estimates the beneficial use value of coal fly ash to be $18/ton, while landfill costs are estimated to be $17/ton. This indicates a net benefit of $35/ton of fly ash to a plant selling its ash as a portland cement replacement simply by adopting Amended Silicates for mercury emission control.

Conclusions

As a part of the State of Wyoming's Clean Coal Technologies Research Program, a two-year sorbent development and testing program was successfully concluded. Novinda Corporation has developed non-carbon mercury sorbent for the in-flight capture of mercury in pulverized coal derived flue gasses.

- Amended Silicates® is the first non-carbon reagent which preserves fly ash use in concrete.
- Amended Silicates® offers economic and environmental advantages not available with other mercury removal products.
- In tests concluded under this project, Amended Silicates® achieved mercury removal comparable to conventional PAC
- With respect to impact of flue gas chemical environment, Amended Silicates® performance was similar to conventional PAC with respect to not affected by flue gas chemical environment