Demonstrations of Amended Silicates for Mercury Control in Coal Fired Generating Units

James R Butz, Clifton H Brown, Jr, and Benjamin N Bernardo
Novinda Corporation, 2000 S Colorado Blvd Suite A-315, Denver CO 80222

Thomas N Henderson, PE
Santee-Cooper, 1 Riverwood Drive, Monck’s Corner, SC 29461

INTRODUCTION

Novinda Corporation is introducing a novel mercury removal reagent that features a mineral substrate as its base, with a proprietary chemical amendment to efficiently and effectively capture mercury from coal-fired power plant flue gas\(^1,2,3\). Early development of Amended Silicates was funded by U.S. EPA, DOE as well as private sources. Because of its unique formulation, Amended Silicates is compatible with the continued sale of fly ash as a replacement for portland cement in concrete\(^4\). The particular components of Amended Silicates also render it a nonflammable product.

Full-scale trial results with Amended Silicates at a utility burning PRB coal have demonstrated success in multiple boilers. As previously reported, Novinda has conducted intermittent testing of Amended Silicates in several units at the Gillette Energy Complex of Black Hills Power\(^5\). Trials were run in the Wygen 1, 2 and 3 units, each burning Powder River Basin (PRB) coal and equipped with a pulse jet baghouse for collection of particulate and sorbent from the flue gas, Selective Catalytic Reduction (SCR) for NOx reduction, and a Spray Dryer Absorber (SDA) for SO\(_2\) removal. Amended Silicates was injected into the flue gas downstream of the air heater and upstream of the SDA using existing dry sorbent injection systems which were permanently installed on the host units. Additional trials were conducted in a neighboring 80-MW unit firing PRB coal (Neil Simpson 2) equipped with a Circulating Dry Scrubber and ESP for environmental controls.

This paper focuses on another trial of Amended Silicates, conducted on Santee-Cooper’s Winyah Station Unit 4. The 300-MW host unit burned a medium sulfur Eastern bituminous coal, and is equipped with an SCR for NOx abatement, ESP for particulate control and a wet flue gas desulfurization unit (wet FGD) for SO\(_2\) capture. The wet FGD reaction product, gypsum, is sold for the manufacture of wallboard in a nearby plant.

For the trials reported here, Novinda contracted with vendors to provide temporary injection equipment to add Amended Silicates reagent for mercury control and hydrated lime for removal of SO\(_3\) from the flue gas stream. In addition, other suppliers provided real-time mercury continuous emissions monitors for measurements of mercury at multiple locations in the flue gas stream. Novinda also compiled data from the plant computer data acquisition system for use in analysis of the mercury measurements. Samples of coal and fly ash were also obtained during most trials for additional data collection and analysis.
PLANT CONFIGURATION

Santee Cooper Winyah Station houses four 300 MW generating units firing bituminous coal; Unit 4 was tested during the subject trial. Winyah Unit 4 consists of a boiler / economizer, an SCR for NOx control, air preheater, a Cold Side ESP for particulate control, and a wet flue gas desulfurization (FGD) module for SO2 control as shown in Figure 1.

**Figure 1. Winyah Unit 4 Layout**

Novinda conducted a full scale trial at Winyah Unit 4 from June 18-27, 2012. During the test period Industrial Accessories Company (IAC) supplied and operated two portable sorbent injection systems: one for Amended Silicates and one for hydrated lime. Ohio Lumex provided three Mercury Continuous Emission Monitors (CEM) located at the SCR outlet (Train B) and at the FGD Inlet on both trains. Apogee Scientific provided two CEMs which were located at the FGD outlet on both trains. Data from the CEMs permitted calculation of mercury removal across the ESP and across the wet FGD during multiple trial periods. Stack testing was performed by Shaw Environmental and Southern Air Solutions. Stack testing included mercury sorbent traps (EPA Method 30(b)) and filterable particulate matter (Method 5). Several variables were evaluated throughout the trial including material injection rate, injection location, and impacts of hydrated lime with respect to AS-022 performance.

**TRIAL SET-UP**

Industrial Accessories Company (IAC) provided the portable injection system employed for the Novinda reagent and the portable injection system for hydrated lime in the trial at Santee Cooper Winyah Station. The Novinda reagent system consisted of a bulk-bag unloader into a loss-of-weight feeder, eductor, and a regenerative blower subsystem to provide transport air. The loss-
of-weight feeder was installed on an electronic scale which was equipped with a real-time digital output subsequently transmitted to a computer with an associated analysis spreadsheet.

The hydrated lime injection system consisted of a bulk silo with a rotary airlock and a regenerative blower subsystem to provide transport air. The injection rate of hydrated lime was controlled electronically by the rotational speed of the rotary airlock. Manual feedback of silo loss in weight was used to maintain a desired lime feedrate of 500 lb/hr. A regenerative blower subsystem provided transport air for the hydrated lime to the injection lances above the air preheater. The hydrated lime injection lances were located just below the SCR outlet.

Amended Silicates™ AS-022 was metered via a screw feeder which discharged into an eductor supplied with air from a transport air subsystem via a regenerative blower. The injection system was used to supply sorbent to three different/separate sorbent injection locations at Winyah Unit 4: 1) an array of 7 lances installed in each of the two air heater supply ducts upstream of the air preheater (total of 14 lances; ~50 ft below the hydrated lime lances), 2) an array of 7 lances installed in each of the two air heater supply ducts downstream of the air preheater (total of 14 lances), and 3) an array of 7 lances installed directly upstream of the “Train B” ID Fan. These injection lances were designed specifically for the Winyah test to ensure proper dispersion of the sorbent in the flue gas stream by injecting through multiple orifices spaced along their entire length. The injection lances were installed such that the sorbent was injected co-current to the flue gas.

Injection rates were controlled by a process computer integral to the dry sorbent injection system. Novinda personnel routinely inspected the DSI transfer lines and injection lances to assure integrity and consistent operation of the system while the injection of the Amended Silicates™ was in progress.

Mercury measurements were made with a semi continuous (real-time) mercury monitors provided and operated by Ohio Lumex and Apogee Scientific. The instruments are periodically cycled between measurement of total mercury and elemental (Hg⁰) mercury. The difference between these two measurements is the speciated or oxidized mercury (Hg²⁺). The instruments were calibrated daily, and subjected to routine quality control checks. All data was certified as passing Ohio Lumex and Apogee QA standards.

**TRIAL OBJECTIVES**

Novinda designed a full scale field trial that was conducted on the Santee Cooper Winyah #4 unit during the period from June 18-22, 2012. The following test objectives were set to satisfy both the requirements of the client as well as meet Novinda’s technical needs.

1. **Conduct pre-trial characterization.** To aid in trial design and planning, pre-trial sampling and analysis was performed. These data were utilized to facilitate final test planning in terms of injection rates and lance placement. The measurements consisted of the following:
a. Total mercury and mercury speciation (Method 30b)
b. SO$_3$ characterization (Method 8a)
c. PM (Quasi Method 5)

2. **Demonstrate the ability to remove mercury to EPA MATS levels utilizing AS-022.**
   a. Evaluate relative merit of 3 different Novinda product injection locations.
      i. Run AS-022 injection above the air heater with and without hydrated lime Injection.
      ii. Run AS-022 injection below the air heater to eliminate SO$_3$ condensation potential.
      iii. Run AS-022 injection downstream of the ESP and upstream of the ID fan to provide extended contact time and mixing to improve efficiency of mercury capture.

3. **Characterize scrubber gypsum product** under a stabilized / extended period of operation, nominally a 5 day X 24-hr trial. The key criteria for evaluating gypsum quality are:
   a. Gypsum purity (>93%) as measured by Acid Insoluble Matter
   b. Total organic carbon concentration (<1000 ppm)

**TEST PLAN**

Amended Silicates’ AS-022 was delivered to the site in super sacks that were then mounted on the sorbent injection skid to feed the material to the system at one of three injection locations noted above. Hydrated lime was supplied via bulk pneumatic truck and supplied to the lime injection (DSI) system from a storage silo. The testing conducted is summarized in Table 1 provided below.

**Table 1. Winyah Unit 4 Test Plan**

<table>
<thead>
<tr>
<th>Day</th>
<th>Test ID</th>
<th>Duration (Hours)</th>
<th>AS-022 Injection Rate (lb/hr)</th>
<th>Lime Injection Rate (lb/hr)</th>
<th>Unit Load</th>
<th>AS-022 Injection Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1</td>
<td>5</td>
<td>450</td>
<td>0</td>
<td>Full Load (300 MW Gross)</td>
<td>Above Air Heater</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>0.75</td>
<td>450</td>
<td>500</td>
<td>Full Load (300 MW Gross)</td>
<td>Above Air Heater</td>
</tr>
<tr>
<td>2</td>
<td>2.1</td>
<td>4</td>
<td>450</td>
<td>0</td>
<td>Full Load (300 MW Gross)</td>
<td>Above Air Heater</td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>3</td>
<td>450</td>
<td>500</td>
<td>Full Load (300 MW Gross)</td>
<td>Above Air Heater</td>
</tr>
<tr>
<td>3</td>
<td>3.1</td>
<td>2</td>
<td>450</td>
<td>500</td>
<td>Full Load (300 MW Gross)</td>
<td>Below Air Heater</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>3</td>
<td>450</td>
<td>0</td>
<td>Full Load (300 MW Gross)</td>
<td>Below Air Heater</td>
</tr>
<tr>
<td>3</td>
<td>3.3</td>
<td>3</td>
<td>450</td>
<td>0</td>
<td>Full Load (300 MW Gross)</td>
<td>Upstream of ID Fan</td>
</tr>
<tr>
<td>4-8</td>
<td>4.1</td>
<td>100</td>
<td>450</td>
<td>500</td>
<td>Varying Plant Load</td>
<td>Above Air Heater</td>
</tr>
<tr>
<td>8-9</td>
<td>8.1</td>
<td>32</td>
<td>220</td>
<td>500</td>
<td>Varying Plant Load</td>
<td>Above Air Heater</td>
</tr>
<tr>
<td>9</td>
<td>9.1</td>
<td>17</td>
<td>220</td>
<td>0</td>
<td>Varying Plant Load</td>
<td>Above Air Heater</td>
</tr>
</tbody>
</table>

1. Hydrated Lime Injection Only above the air heater
A total of ten tests were conducted during a nine day period. The first three days were utilized to conduct parametric testing during which the AS-022 injection rate was held constant, hydrated lime injection was either on at 500 lb/hr or off; further AS-022 was injected at three different locations. Unit load was 300 MW during all of the parametric tests.

Based on the results of the parametric tests the trial was operated for five consecutive 24 hour periods. For this extended test, hydrated lime was injected just below the economizer and AS-022 was injected into two parallel ducts just above the air heater inlet at a total injection rate of 450 lb/hr. During this period plant load varied from 300 MW to a low of approximately 200 MW. A significant goal of this extended trial was to allow the FGD to reach chemical equilibrium and to evaluate the impact (if any) of AS-022 injection on gypsum quality.

Following the five day trial the system was operated for 32 hrs with the AS-022 injection rate cut in half to 220 lb/hr keeping all other variables constant. This was followed by a 17 hr period during which the hydrated lime injection was turned off and the AS-022 remained at the 220 lb/hr rate.

**DISCUSSION OF RESULTS**

About two weeks prior to performance of the extended Novinda trials a baseline characterization was completed for the host unit. Measurements included vapor-phase mercury at three locations, SO₃ levels, and Particulate Matter at the stack. Mercury measurements were made via EPA Method 30(b) sorbent traps, and are summarized in Figure 2 below. Samples were obtained downstream of the unit SCR, at the inlet to the unit wet flue gas desulfurization (wet FGD) and at the stack, downstream of the wet FGD systems. The three leftmost stacked bars in Figure 2 show the speciation of the mercury as measured with the M30(b) traps. As can be seen in the graph, the combination of medium sulfur Eastern bituminous coal and the presence of an SCR resulted in very high oxidation of the vapor-phase mercury at both locations upstream of the wet FGD. The wet scrubber captures virtually all the oxidized mercury due to its solubility in water, an effect commonly seen in wet FGD systems. In addition, these samples showed very low native capture of mercury across the ESP in the host unit. The stacked bar on the right side of Figure 2 shows the locations where mercury is removed from the flue gas in a simple color-code; this presentation of data is used throughout the paper where green indicates mercury capture across the ESP, red indicates capture in the wet FGD, and blue indicates mercury emitted from the stack. The total height of the bar represents the measured vapor-phase mercury present in the flue gas at the outlet of the SCR.

As noted earlier, there were two series of trials completed at Winyah station with injection of the Novinda reagent for mercury control. In the first, parametric tests were run to determine the optimum injection configuration for the Novinda reagent and in the second, trials were run at a fixed operating condition for an extended period of time to allow steady-state operation of the wet FGD to be achieved during injection of AS-022.
In the parametric tests, three different injection locations for the Novinda material were evaluated: (1) at the inlet to the air heater, (2) at the inlet to the ESP, and (3) at the inlet to the induced draft fan downstream of the ESP and upstream of the wet FGD. Parametric tests were also completed with and without the simultaneous injection of hydrated lime to reduce the potential for SO$_3$ condensation on flue gas particulate.

Mercury measurements were made with CEMS at multiple locations as described earlier. Typical mercury results at the outlet of the SCR are shown in Figure 3 below. Several features of this graph are noteworthy. The green trace shows the variation in plant load (right vertical axis) for the 7-day period reported on the graph. The blue trace shows vapor phase mercury at the SCR outlet for the reporting period. There is an obvious effect of plant load changes on the mercury content of the gas stream which in turn affects the performance of the mercury reagent injected downstream of the measurement location.
Typical stack mercury CEMS data are plotted in Figure 4. The shaded areas of the graph indicate times during which Amended Silicates was injected into the flue gas. The green trace shows daily load cycling of the host unit, with low loads observed overnight and on a weekend. Two mercury concentrations are shown: total mercury in red and elemental mercury in blue. The mercury emitted from the stack is almost all elemental. There is an obvious correlation between stack mercury and plant load, with excursions often seen with load changes. The graph also marks the EPA MATS emissions limit for mercury as a blue dotted line. One other feature to note on this graph is that an equilibrium stack mercury level was reached only after four days of continuous injection.

The parametric tests resulted in the selection of the air heater inlet location as preferred for the injection of Amended Silicates, with simultaneous injection of hydrated lime about 50 ft upstream of the AS-022 location. Injection rates for the extended trial of Amended Silicates were 440 lb per hour for the AS-022 and 500 lb per hour for hydrated lime.

The host unit was configured such that the flue gas split into two trains downstream of the economizer. Mercury measurements were made in both trains at the ESP outlet/wet FGD inlet location and at the outlet of the parallel wet FGD units. These two trains are labeled A and B in the data presentations to follow. Before the start of parametric trials, a baseline data set was collected for about a four-hour period. This data set is included on the following graphs with the label ‘Baseline’.
Consolidated results for the extended trial at fixed injection of 440 lb/hr of AS-022 plus 500 lb/hr of hydrated lime are presented in Figure 5. Here, a substantial increase in baseline mercury capture across the ESP is seen in comparing the baseline data with the pre-trial samples taken two weeks earlier. Most significantly, the averages computed from the CEMS data for the entire 100-hr extended trial (two rightmost stacked bars) showed a fundamental shift in the capture of mercury to a condition where about 80% of the mercury capture took place in the ESP with less than 20% removed across the wet FGD. This transformation allowed the utility to better control mercury emissions by shifting from a passive mechanism (wet FGD capture) to an active mechanism in mercury capture via the addition of Novinda’s AS-022 mercury reagent to the flue gas. It is also important to note that the average mercury emissions for the trial period were well below the EPA MATS level as marked by the dotted line on the graph (1.2 lb total mercury/TBtu).
Further insight into the performance of Amended Silicates AS-022 in the Winyah 4 host unit is presented in Figure 6. Here, daily averages have been computed from the CEMS data on both the A and B trains. Several observations are significant. First, all daily averages for stack emissions from both trains met the EPA MATS emissions limit. Second, there was day-to-day variation in the performance, due in part to the variation in inlet mercury concentration and the impact of load changes as illustrated earlier in the sample CEMS graph (Figure 4). Third, there is a consistent downward trend in the stack mercury emissions (blue segment of the stacked bar in Figure 6) as the trial continued. This trend further confirms the earlier note that it took four days to reach an equilibrium condition for mercury content in the flue gas at the outlet of the wet FGD. This is attributed, at least in part, to the presence of a very large mass of circulating liquid scrubber solution that serves as a sink for soluble mercury in the system.
Further tests were conducted at the conclusion of the 100-hr trial to investigate the impact of (1) reduced injection rate of AS-022 to 220 lb/hr and (2) reduced injection rate of AS-022 to 220 lb/hr without injection of hydrated lime. These results are summarized in Table 2. Details of CEMS averages for these two cases are presented in the bottom two rows of the table. In these trials the stack mercury emissions continued to fall below the EPA MATS level. There continued to be substantial capture of mercury across the ESP, although quantities were slightly smaller than those observed during the 100-hr trial.

During the entire trial period consisting of both parametric trials as well as the extended injection trials, multiple samples were extracted each day from the wet FGD slurry for mercury analysis. Results of these analyses are presented in Figure 7. Parametric testing was conducted from June 18th through June 20th, and the extended trial began on June 21st. During parametric testing AS-022 reagent was injected into the flue gas for only part of the day. The mercury content of the slurry samples reflects the change in mercury loading as the extended trial gets under way and most of the vapor-phase mercury is captured across the ESP and removed from the flue gas upstream of the wet FGD. Mercury concentration in the FGD slurry is reduced by a factor of two or more in samples taken after June 21st. Mercury levels start to rise again after the completion of trials on June 27th.
Table 2. Summary of Results for Extended Trial Testing

<table>
<thead>
<tr>
<th>Case</th>
<th>SCR Outlet</th>
<th>ESP Removal</th>
<th>WFGD Removal</th>
<th>Stack Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Trial Characterization (Method 30B)</td>
<td>9.42</td>
<td>0.56</td>
<td>8.31</td>
<td>0.55</td>
</tr>
<tr>
<td>Baseline: No Injection</td>
<td>8.21</td>
<td>3.30</td>
<td>3.66</td>
<td>1.26</td>
</tr>
<tr>
<td>AS-022 @ 400 lb/hr</td>
<td>8.70</td>
<td>7.13</td>
<td>1.08</td>
<td>0.49</td>
</tr>
<tr>
<td>Hydrated Lime @ 500 lb/hr</td>
<td>8.99</td>
<td>6.75</td>
<td>1.29</td>
<td>0.95</td>
</tr>
<tr>
<td>AS-022 @ 220 lb/hr</td>
<td>9.04</td>
<td>5.79</td>
<td>2.51</td>
<td>0.74</td>
</tr>
<tr>
<td>Hydrated Lime Off</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: All Hg Concentrations in lb/TBtu
Green Indicates Hg level below MATS limit of 1.2 lb/TBtu

Figure 7. Mercury Content of Slurry Samples from Wet FGD Units
Stack measurements were made via EPA Method 5 to confirm that the injection of AS-022 and hydrated lime did not impact particulate emissions from the host unit. Results are presented in Table 3, and show that the stack measurements obtained during the long-term injection trial actually showed lower particulate levels than the baseline measurements made two weeks in advance of the trial.

<table>
<thead>
<tr>
<th></th>
<th>EPA Method 5</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Trial</td>
<td>0.028</td>
<td>0.030</td>
</tr>
<tr>
<td>During AS Injection</td>
<td>0.010</td>
<td>0.030</td>
</tr>
</tbody>
</table>

### CONCLUSIONS

Novinda’s Amended Silicates® AS-022, a mineral-based reagent developed for mercury capture, was successfully demonstrated in a host unit burning Eastern bituminous coal. Winyah Unit 4 was configured with a Selective Catalytic Reduction system (SCR) for NOx control, an Electrostatic Precipitator (ESP) for particulate control, and a wet Flue Gas Desulfurization unit (wet FGD) for SO₂ capture. In the extended trial, Novinda’s AS-022 reagent was injected upstream of the host unit air heater simultaneous with hydrated lime to capture mercury before the flue gas entered the wet FGD.

Parametric runs were completed on the host unit to determine the optimum injection location as well as to evaluate the use of hydrated lime to mitigate the effect of SO₃ on the performance of Amended Silicates. Analysis of data from the parametric trials resulted in a decision to inject hydrated lime during the extended trial of Amended Silicates and inject AS-022 at the inlet of the air heater. Since one objective of the extended trial was to characterize the impact of Amended Silicates on scrubber slurry and gypsum reaction product from the wet FGD, the AS-022 was added at a maximum practical rate of 440 lb/hr. The hydrated lime injection rate was 500 lb/hr.

AS-022 delivered substantial mercury removal during the extended trial, including:

- Mercury emissions measured at the stack of about 0.5 lb/TBtu, well below the EPA mercury MATS standard of 1.2 lb/TBtu.
- Mercury capture across the ESP of about 80% of total mercury removal in the flue gas treatment system, increasing from 3.3 lb/TBtu in the baseline measurement to 7.1 lb/TBtu for the trial.
- A dramatic reduction in the mercury capture across the wet FGD, from a baseline value of 3.7 lb/TBtu to less than 1.1 lb/TBtu.

Analysis of multiple samples extracted from the wet FGD units showed that the use of Amended Silicates reduced the mercury content of scrubber slurry and did not impact the quality of gypsum for sale to a nearby wallboard facility.
In further trials at a lower AS-022 injection rate, stack mercury emissions were maintained at levels less than 1.0 lb/TBtu, comfortably below the EPA MATS limit. This low mercury emission rate was maintained even when the injection of hydrated lime was halted.

Stack PM measurements made via EPA Method 5 showed that there was no impact from the injection of AS-022 plus hydrated lime on particulate emissions from the host unit.

Novinda has available commercial quantities of AS-022 and is now working with utilities to schedule full-scale trials in a range of coal-fired power plants. AS-022 has a market cost equivalent to brominated PAC products.

REFERENCES

2. Lovell, J.S. US Patent 7,048,781

ACKNOWLEDGMENTS

Novinda would like to acknowledge the exceptional cooperation of Santee-Cooper in the performance of the trial reported in the paper. Plant personnel were very responsive and generous in providing technical support in all phases of the project. In addition Industrial Accessories Company, Apogee Scientific, Ohio Lumex, Shaw Environmental and Southern Air Resources were key contributors that helped assure the success of the demonstration.