FIELD TRIALS OF A MINERAL-BASED REAGENT FOR MERCURY CONTROL IN COAL-FIRED BOILERS

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ABSTRACT

Novinda Corporation's novel Amended Silicates® is a patented reagent product for the capture of vapor-phase mercury from coal-fired flue gas streams at utility power plants. The material contains no activated carbon, is noncombustible, and has been shown to be completely compatible with the continued sale of captured fly ash as a portland cement replacement. As part of its product roll-out, a series of field trials have been completed at power plants burning a range of coals and equipped with a variety of emissions control devices. Results from 5 full-scale coal-fired plants where Novinda has completed field trials for periods of days to months are presented. Objectives of these tests have been to characterize the performance of Amended Silicates in specific plant configurations and to optimize the injection configuration to improve the efficiency and cost-effectiveness of the technology. Balance of plant impact has also been investigated. Amended Silicates has proven to be a cost-effective option for mercury control across a broad range of plant configurations.

INTRODUCTION

Novinda Corporation manufactures 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]. Amended Silicates is the only commercial non-carbon mercury capture sorbent available in the market. 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. Laboratory testing of admixture samples of Amended Silicates and fly ash as well as samples extracted from ESP hoppers at full-scale field trials has shown that the Novinda material lowers bulk resistivity of PRB fly ash, and thus may improve performance of cold-side ESPs.

Amended Silicates captures mercury via a chemical reaction that forms mercuric sulfide on the reaction sites of the particle. Mercuric sulfide is extremely insoluble, the mineral form in which mercury is found in nature. The mercury capture reaction of Amended Silicates first results in oxidation of most of the elemental mercury vapor present in the flue gas. In multiple tests the product has also been shown to easily pass the EPA TCLP test for mercury leaching. Amended Silicates has a higher density than activated carbon products which means that slight modifications must be made to material handling equipment to reliably inject Amended Silicates into flue gas. These include provision for aeration to adequately fluidize the material in the storage silo as well as injection lance designs to more uniformly disperse the material in the flue gas cross-section. Novinda has commissioned the preparation of a generic specification for a bulk storage and material feed system to facilitate continuous, reliable metering of Amended Silicates into the flue gas of a coal-fired power plant. This specification is available to utilities and engineering companies working on design of mercury control systems.

The first dedicated commercial production facility for Amended Silicates was brought on-line in the 3rd quarter of 2012, so Novinda now has capacity to manufacture 20 million pounds per year of the product. It is readily available for full-scale field trials and long-term supply contracts. Additional capacity is easily added via modules that can be situated near utility customers to minimize shipping costs.

Full-scale trial results with Amended Silicates at utilities burning PRB or eastern bituminous coals have demonstrated success in capturing mercury sufficient to meet the EPA MATS standard. In a typical trial, Novinda prepares a test plan that outlines objectives and presents a test matrix for the period of performance. This becomes a guiding document for the on-site trial director and crew during the trial. Evaluation parameters include stack mercury measurements, injection rate for the Amended Silicates, plant load, and injection location. Amended Silicates has been found to capture mercury more efficiently when injected upstream of the air heater, due to the added contact time in the flue gas and dispersion with mixing that occurs across the air heater.

EXPERIMENTAL

In the past 2 years, Novinda Corporation has completed over 30 full-scale field trials of its Amended Silicates product at full-scale coal-fired power plants. These tests have been conducted using permanent injection equipment previously installed on host units as well as temporary installations of portable injection skids with transport lines and injection lance arrays. Trial periods have ranged from a few days to over 30 days. Novinda has employed a variety of contractors to supply temporary injection equipment for field trials.

Mercury measurements are most often collected with mercury CEMs installed specifically for the Novinda trial. At a few site, utilities have previously installed stack mercury CEMs which are maintained and calibrated routinely and thus are suitable for mercury measurements. At most sites EPA Method 30(b) sorbent traps are used to validate the CEMs measurements. Continuous measurements are preferred as they provide trending data that is valuable in making real-time adjustments to injection rates to better satisfy trial objectives. Novinda uses contractors for mercury CEMs when plant instruments are not available. Contractors are required to have calibration and QA/QC protocols in place to assure that results are high quality and technically defendable.

Once injection of Amended Silicates has begun in a field trial, the recommended protocol is to inject the material continuously throughout the trial period. Experience has shown that the Novinda product sometimes requires an extended period of injection – four to eight hours or more- to achieve steady-state operation at full-scale. When changes in injection rates are made on a continuous injection protocol, response to these changes is seen more quickly, and steady-state operation is achieved sooner.

In addition to CEMs measurements, Novinda collects an array of plant operating data for use in analysis of the stack mercury emissions data. Parameters include temperature at the injection location as well as the stack, plant load, stack trace gas concentrations and flows, and characteristics of the particulate control device (PCD) in use. Samples of coal from the mills and fly ash from the PCD are also collected and analyzed. Coal mercury content

data provide a means to confirm that vapor-phase mercury measurements in the flue gas are credible, as these are used as a basis for comparison with stack mercury measurements.

Descriptions of plant configurations and test objectives for the multiple tests are presented below. The host units burned either PRB or eastern bituminous coal, and were fitted with a variety of flue gas treatment technologies for NOx, SO_2, and particulate control.

Wygen 2

Novinda has completed numerous trials at Black Hills Energy's Gillette Energy Complex (GEC) near Gillette, WY. These have encompassed product development trials, mercury capture demonstration trials, and extended term performance trials. The GEC is home to five coal-fired generating units, all burning PRB coal from an adjacent mine. Four of the five units are equipped with dry scrubbers, and Novinda products have been injected into each of these. Typical data from two of the units are included in this paper.

Novinda conducted two trials at Wygen 2 to compare the performance of successive generations of Amended Silicates. Wygen 2 is a 100 MW boiler that features a selective catalytic reactor (SCR) for NO_x control, spray dryer absorber (SDA) to capture SO_2, and pulse-jet baghouse for particulate collection. The unit is also equipped with a sorbent injection system to add a mercury control reagent to the flue gas downstream of the air heater and upstream of the SDA via four injection lances. The unit is also fitted with a mercury CEMS at the stack that is operated and maintained by plant personnel.

The objective of the trials on Wygen 2 were twofold: 1) to determine an injection rate that provided sufficient mercury capture to meet the EPA MATS emissions limit, and 2) to compare the performance of the commercial AS-022 material to the second generation Amended Silicates product known as AS-HgX. The trial of AS-022 product was conducted in September of 2012 and the follow-on trial of AS-HgX was completed in early 2013. For the trials reported here, the stack CEMS data were consolidated into daily averages, and those daily averages were incorporated each day into a cumulative average for the entire trial to date. Minor issues with the materials handling system were encountered early in the September trial, resulting in short-term feed interruptions. The issue was addressed with changes to the PLC logic that improved the injection of air into the silo cone to maintain better fluidization and particle flow.

Neil Simpson 2

Neil Simpson 2 is another PRB-fired unit at Black Hills' GEC. It is an 80-MW unit typically base-loaded, and incorporates a circulating dry scrubber (CDS) for SO_2 removal followed by a cold-side ESP for particulate control. A fraction of the particulate captured in the ESP is recycled to the CDS for improved utilization of the lime reagent. A dedicated silo for mercury sorbent feeds Neil Simpson 2 as well as another BH unit located next door. Mercury sorbent is injected downstream of the air heater and upstream of the CDS via four injection lances. An automated control system operated a gravimetric feeder that supplied material to the transfer lines and injection lance array. This feeder was unable to reliably control continuous metering of AS-HgX into the host unit at the low rate so programming changes were made to inject the Novinda material intermittently in a batch mode. This change proved successful in metering HgX at a very low average rate into the host unit. The 30-day trial reported here featured injection at an average ratio of 0.3 lb/mmacf.

Confidential Plant 1

A short trial was conducted at a >700MW unit in late 2012 burning medium-sulfur eastern bituminous coal and equipped with a cold-side ESP and wet flue gas desulfurization (FGD) for SO_2 control. Measurements in the flue gas downstream of the air heater revealed that SO_3 levels were in the range of 7 to 13 ppm for the test period reported here. A portable injection skid, transport hoses, and injection lances were brought on-site and set up for injection of the Amended Silicates. AS-HgX was injected over a range of about 3 to 4 lb/mmacf into the flue gas downstream of the air heater/upstream of the cold-side ESP. A lengthy duct run of over 200 ft with multiple turns between the injection location and entry into the ESP facilitated dispersion of the material in the flue gas. Target injection rates included higher ratios due to the coal sulfur content, but issues with the injection equipment were encountered during the trial that limited maximum injection rates. There was also significant variability in the mercury content of the coal burned during this trial. Tests were conducted with and without the

use of hydrated lime injection for SO_3 mitigation upstream of the wet FGD. Objectives of the trial were to demonstrate ability to meet the MATS mercury emissions standard with the use of Amended Silicates and to determine if the simultaneous injection of hydrated lime affected the performance of the Novinda material.

Confidential Plant 2

Another trial was conducted at unit burning PRB coal and equipped with an SCR, SDA, and pulse-jet baghouse. The unit is >600MW and was operated at full-load throughout the four-day trial. The unit is equipped with a permanent sorbent injection system, which was used in part by tapping into the transfer lines just downstream of the installed gravimetric feeders. The Novinda material was fed from a temporary supersack injection skid. Custom Novinda lances were installed upstream of the SDA (downstream of the air heater) for the trial, and connected to the existing splitters via flexible hoses. Mercury measurements were obtained from a permanently installed stack mercury CEMs, and were validated via Method 30B traps run during the trial. All mercury data was reported in lb/GWhr as the plant permit limits are expressed in those units. The objective of this trial was to demonstrate the ability of Amended Silicates to achieve a stack mercury concentration below the MATS limit to provide performance assurance to the host utility that consistent compliance can be met with the Novinda product.

Confidential Plant 3

A trial of Amended Silicates was completed in late 2012 at a site where the host unit was conducting a trial burn of a blend of PRB and western bituminous coals. Amended Silicates was injected downstream of the air heater for mercury capture using a temporary supersack injection skid. The >150 MW host unit was also evaluating the use of hydrated lime for HCl control to meet upcoming MATS standards. Due to confidentiality with the host utility, details of the mercury testing results are not available, other than to note that the test was successful in meeting the MATS standard. In this trial fly ash samples were obtained from the ESP hoppers before the start of injection of Amended Silicates, during injection of Amended Silicates (both AS-022 and AS-HgX), and during simultaneous injection of Amended Silicates and hydrated lime. These samples were subjected to laboratory tests to determine the resistivity of the neat fly ash and of the fly ash/Amended Silicates admixtures. One sample was obtained during the simultaneous injection of hydrated lime. Both the original AS-022 product and the second-generation AS-HgX were injected at this site at different times, and each was sampled from the ESP hoppers mixed with fly ash.

RESULTS AND DISCUSSION

Wygen 2

Results from the two test series at Wygen 2 are plotted in Figure 1 below. The graph presents stack mercury measurements as a cumulative daily average value. That is, 24 hours of CEMs data is averaged for each operating day and used to compute a cumulative average by adding the daily averages from the start of injection and dividing by the number of days accumulated for each data point. The graph is marked with a dotted horizontal line to indicate the 2012 EPA MATS standard. The uncontrolled stack mercury emissions for this plant are seen to be less than 7 lb/TBTU. When injection of Amended Silicates is started, the daily average drops quickly and dramatically to reflect the mercury capture seen across the SDA and pulse-jet baghouse.

Performance of two different Amended Silicates products is documented in Figure 1, AS-022 (the original product) and AS-HgX, the second-generation product manufactured in the 20-million lb per year facility now on-line. The AS-022 was injected at a rate of 2.2 lb/mmacf, while the AS-HgX was injected at a lower rate of 1.3 lb/mmacf. A short interruption in the feed of AS-022 is reflected in the slight rise in the cumulative average around September 4th. Feed was re-established, and the ability of the Novinda product to meet and exceed the mercury capture requirement of the EPA MATS standard on a consistent basis was demonstrated for the following two weeks. Data collected during injection of AS-HgX is shown in comparison via the open squares of the plot. The superior performance of the AS-HgX at a substantially lower injection rate is seen in the data. After 10 days of injection the cumulative average is around 0.7 lb/TBTU, well below the MATS standard.

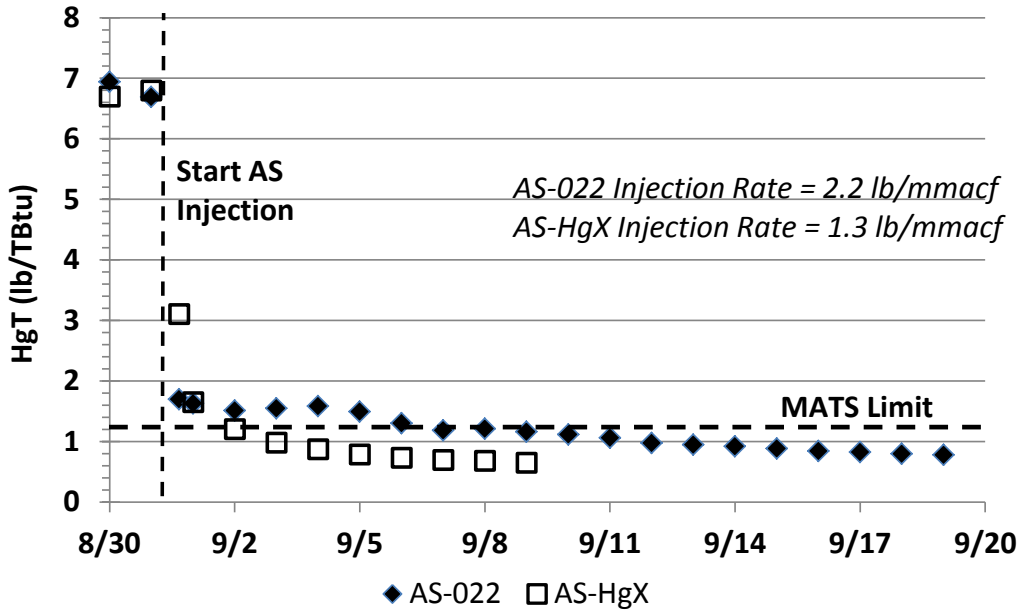

Figure 1. Results from Wygen 2 injection trials of Amended Silicates.

Neil Simpson 2

Success in meeting the EPA MATS standard at low Amended Silicates injection rates for Wygen 2 resulted in a decision by Black Hills Energy to conduct a 30-day trial in their Neil Simpson 2 unit. Amended Silicates HgX was injected downstream of the air heater and upstream of the circulating dry scrubber installed for SO_2 control. Results from this trial are presented in Figure **2** below. Data is again plotted as a cumulative daily average computed as described earlier, and the EPA MATS standard is indicated by the dotted line on the graph. Recall that due to the very low injection rate at which MATS was met in this unit, the gravimetric feeder was operated in a batch mode for the final 70% of the trial. The initial injection rate was reduced several times early in the trial, with adjustments resulting in a short-term loss of feed around the end of the first week. Once the batch mode operation was refined, injection on a long-term basis was consistently maintained, and response at the stack showed mercury emissions below MATS for the final three weeks. This low injection rate matched the best performance of Amended Silicates seen to date in field trials. The extended contact time and intimate interaction between the Novinda material and the flue gas in the fluidized bed of the circulating dry scrubber is believed to contribute to the high efficiency of mercury capture by the AS-HgX in this unit.

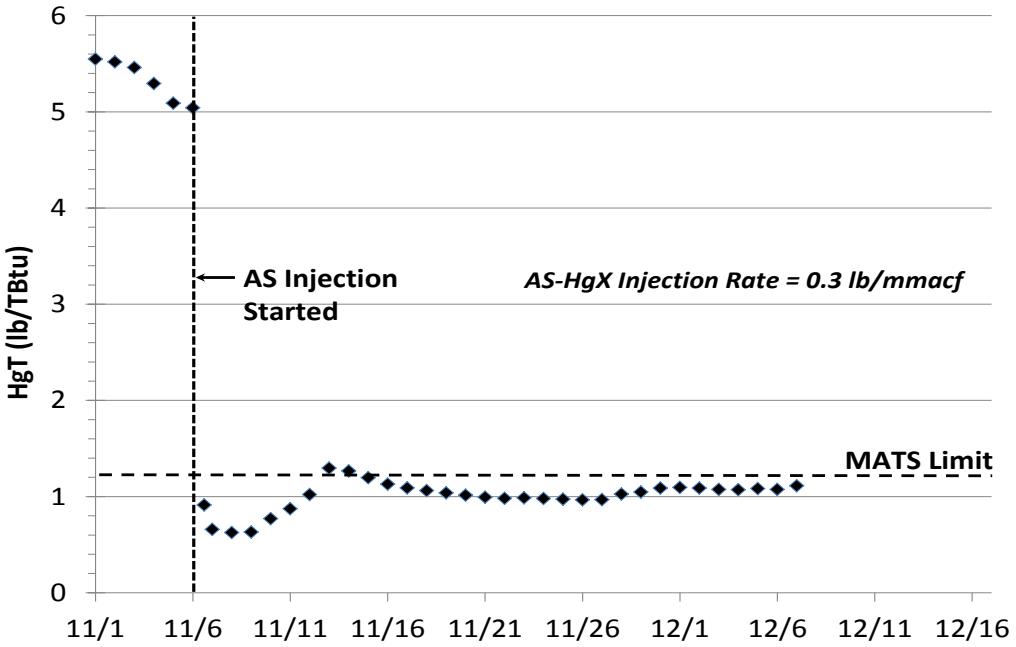

Figure 2. Results from the extended trial of AS-HgX at Neil Simpson 2.

Confidential Plant 1

In late 2012 a trial of Amended Silicates was conducted at a confidential site burning medium-sulfur eastern bituminous coal. The mercury content was variable, and CEMs mercury measurements upstream of the air heater were observed to vary by greater than a factor of two over the several-day period of the trial. Amended Silicates was injected without hydrated lime for the 24-hr period shown in Figure **3** below. Near the left side of the graph, stack data shows that uncontrolled mercury levels were around 5 lb/mmacf due to some capture of oxidized mercury in the wet FGD. Upstream vapor-phase mercury was rising early in the day, and then data was unavailable for a short time when problems were encountered with the real-time CEMs. Amended Silicates injection was initiated about 11 AM, and then halted to address feed issues with the injection skid. AS-HgX injection was restarted about 1 PM and continued throughout the night and into the next day. A target injection ratio of 4 lb/mmacf was specified, but the injection equipment was unable to maintain this ratio. A stable ratio of about 3.3 lb/mmacf was achieved for the final four hours of the test period.

Stack mercury measurements exhibited a trend where a period of hours was required to reach an equilibrium with mercury capture in the extended ductwork of this host unit. MATS compliance was achieved and maintained approximately 12 hours after the start of injection after the injection ratio had been increased first to about 3 lb/mmacf and then to 3.3 lb/mmacf.

To confirm the capture of mercury by the Amended Silicates, samples of fly ash were obtained from the ESP prior to the start of the trial with additional samples gathered during the injection of the Novinda material. Results are presented in Table **1** below. Analyses of pre-trial samples all were found to be below the limit of detection for the analytical method (0.25 ppm). Analyses of samples acquired during injection of Amended Silicates all showed substantial increase in mercury content, over three times the limit of detection. These data confirm that the Amended Silicates was indeed capturing significant quantities of mercury from the flue gas stream in the host unit, and that the reduction in stack mercury during the first 8 hours of injection is not due to reduced coal mercury content. These data are similar to fly ash analyses from one of the Black Hills units where the injection of Amended Silicates resulted in tripling the fly ash mercury content to around one ppm.

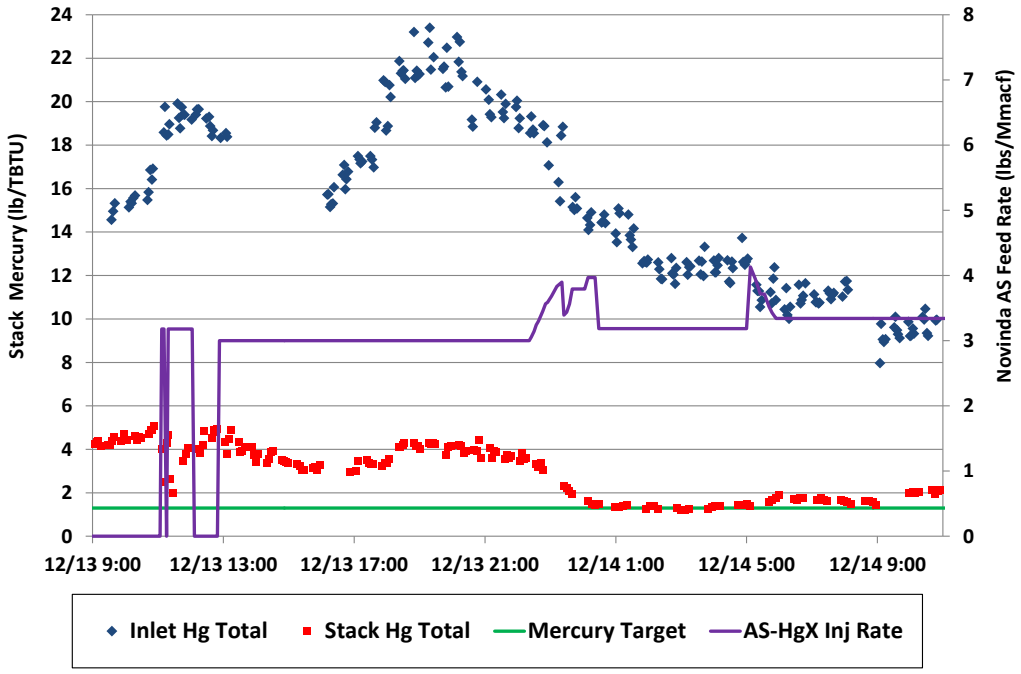

Figure 3. Stack mercury measurements from Confidential Plant 1.

Table 1. Fly ash mercury measurements from Confidential Plant 1.

Sample Date	AS-HgX Injection Rate (lb/MMacf)	Mercury (ppm)
12/4/2012	0	<0.25
12/5/2012	0	<0.25
12/5/2012	0	<0.25
12/13/2012	3.0	0.861
12/13/2012	3.0	0.928
12/14/2012	2.9 - 3.3	0.928

Confidential Plant 2

A trial of Amended Silicates was completed in the summer of 2013 at a confidential plant burning PRB coal and equipped with an SDA and pulse-jet baghouse. The trial was run for a period of four days, where AS-HgX was injected over a range of rates to demonstrate the ability of Amended Silicates to capture sufficient mercury to maintain stack emissions below the EPA MATS level. The Amended Silicates material was fed via temporary injection skid with output tapped into existing transfer lines. Novinda supplied and installed custom lances in alternate ports upstream of the SDA/downstream of the air heater.

Results of the trial are plotted in Figure 4 below. Continuous injection of PAC for mercury control at the host site was shut off 24 hours in advance of the start of the AS-HgX trial. Mercury at the stack (small circles) was seen to rise above 0.030 lb/GWhr, followed by a dramatic drop to below the MATS level (indicated by the solid black line) within a few hours after the start of AS-HgX injection. Injection ratio of Amended Silicates was controlled manually, and is shown in the graph of Figure 4 as triangles. Feed interruptions with the temporary injection skid were encountered overnight on several days, which in turn resulted in short-term mercury spikes

as plotted in the graph. Daily averages for the stack mercury were computed for each of the four trial days, and are indicated as large open circles. Once continuous injection was initiated, the mercury levels were consistently below MATS. The average stack mercury for the trial was 0.011 lb/GWhr at an injection rate of 0.9 lb/mmacf.

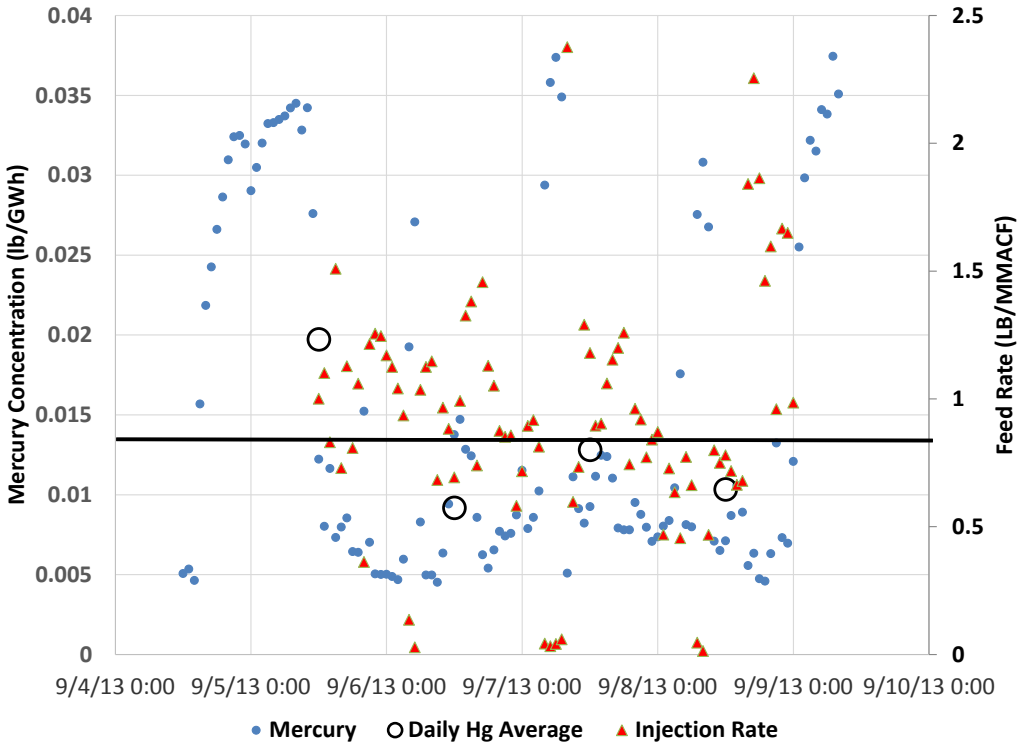

Figure 4. Results from the injection of AS-HgX at Confidential Plant 2.

Confidential Plant 3

A trial was conducted in the fourth quarter of 2012 at a plant undergoing an experimental burn of a blend of PRB and western bituminous coals. For this trial, details of the mercury results are confidential under agreement with the host utility. The plant was equipped with three cold-side ESPs in series for particulate control. Before and during the trial, samples were extracted from the ESP hoppers for measurement of resistivity. These samples were either neat fly ash, for samples taken before the start of injection, or admixtures of fly ash and other injected materials, either Amended Silicates or a combination of Amended Silicates and hydrated lime. The lime was injected to investigate feasibility of its use for HCl control in this unit. The fly ash and admixture samples were then submitted to Southern Research Institute for resistivity measurements via the protocol of IEEE 548-1984.

Results of the resistivity testing are presented in Figure 5 below. The measurements for the neat fly ash peak at just under 10^{12} ohm-cm, a value typical of PRB fly ashes. With injection of AS-HgX, the data shows a resistivity lower by an order of magnitude or more, a significant reduction that would result in improved particulate capture in a cold-side ESP with flue gas temperature around 300°F. The injection of AS-022, the original Amended Silicates product resulted in a smaller reduction of a factor of 5 to 8. When hydrated lime was injected simultaneous with the AS-022, the added calcium showed a characteristic increase in resistivity compared to the fly ash plus AS-022 admixture. The reduction in admixture resistivity afforded with the injection of Amended Silicates is substantial, and may allow units that are adding SO_3 for flue gas conditioning to reduce or eliminate the SO_3 injection. Novinda is seeking a trial site to more rigorously explore this potential co-benefit of its mercury control product.

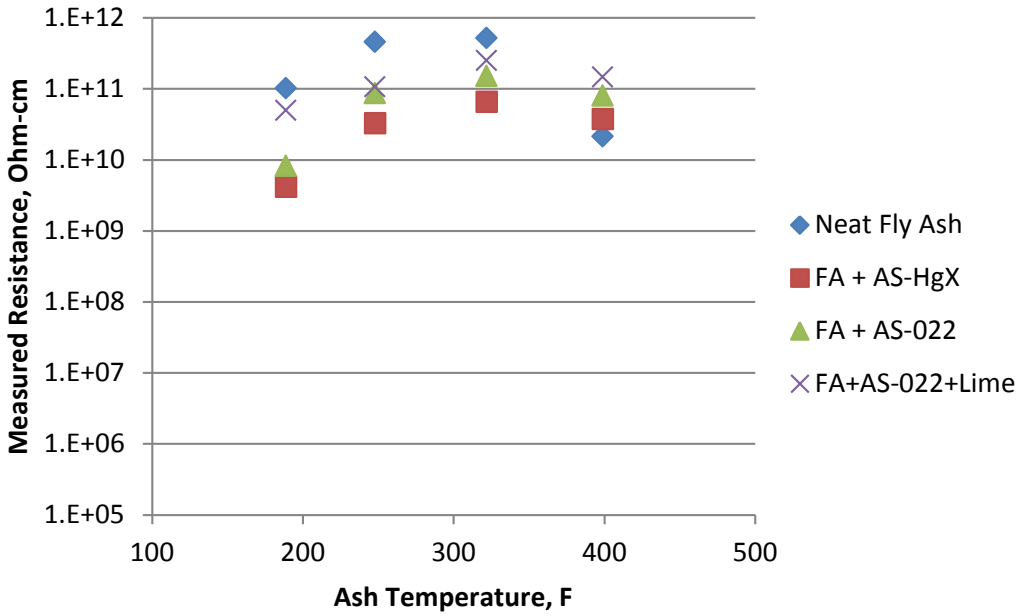

Figure 5. Resistivity test results from Confidential Plant 3.

CONCLUSIONS

Novinda Corporation has conducted more than 30 full-scale trials of its Amended Silicates non-carbon product for mercury capture in coal-fired power plants. Results from five plants are presented in this paper, with conclusions as follows:

- Amended Silicates has consistently demonstrated the capacity to reduce mercury emissions to levels well below the pending mercury MATS in plants burning PRB coal and equipped with dry scrubber systems.
- AS-HgX, the second-generation Novinda product, has shown more than 40% improvement in mercury capture when injected at a 100-MW PRB fired unit in Wyoming. Stack mercury was well below the EPA MATS standard by a substantial margin at an injection rate of 1.3 lb/mmacf at this host site.
- In a 30-day trial at another Wyoming PRB unit, the MATS standard was consistently met at an injection ratio of 0.3 lb/mmacf. This represents to best performance to date for Amended Silicates in a dry-scrubbed plant.
- When injected into the flue gas of a large confidential plant (>700 MWe) burning eastern bituminous coal, Amended Silicates was able to meet MATS despite limitations on feedrate from the temporary injection equipment. Maximum injection rate at this site was 3.3 lb/mmacf.
- Substantial mercury capture by Amended Silicates HgX at Confidential Plant 1 was confirmed via analyses of fly ash samples that showed an increase in mercury content in the fly ash by a factor greater than 3 times the uncontrolled baseline value.
- Another recent trial was completed at a large (>600 MWe) PRB combustor equipped with a spray dryer absorber and pulse-jet baghouse. In a four-day test, Amended Silicates AS-HgX reduced stack mercury to an average of 0.011 lb/GWhr at an average injection rate of 0.9 lb/mmacf.
- In a trial at a plant burning a blend of PRB and western bituminous coal, injection of Amended Silicates resulted in the reduction of fly ash resistivity by an order of magnitude as measured in the lab via IEEE protocol 548-1984. This represents a reduction substantial enough to improve the capture

efficiency of a cold-side ESP operating on PRB fly ash. This resistivity reduction is a co-benefit that could lead to the reduction or elimination of SO_3 as a flue gas conditioning agent.

Novinda Corporation is pursuing additional full-scale trials to demonstrate the performance of Amended Silicates across a broad range of plant configurations. A 20-million lb per year production facility was commissioned in late 2012, and now manufactures commercial quantities of Amended Silicates for full-scale trials and long-term utility supply contracts.

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