

Impact of Coal Blending and SO₃ Flue Gas Conditions on Mercury Removal with Activated Carbon Injection at Mississippi Power's Plant Daniel

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ABSTRACT

While powdered activated carbon (PAC) sorbent injection has been demonstrated to reduce mercury emissions for many coal-fired power plants, multiple configuration and operating variables exist that may influence the effectiveness at a given site. Southern Company and Mississippi Power Company contracted ADA-ES, Inc., to conduct a sorbent injection demonstration program at Plant Daniel Unit 1 during Spring 2005. The test was conducted on one-quarter of the 540-MW unit.

This program exposed key variables that impacted mercury emissions and control. Plant Daniel can operate at varied bituminous/subbituminous coal blends and can fire several types of bituminous coal. The most interesting result was the dramatic influence of SO₃ injection on the mercury removal capability of both native and sorbent-based capture. The injection rate strongly dictated whether sorbent injection could be considered an option for future mercury emissions compliance at this site.

INTRODUCTION

Interest in determining viable control technologies for mercury emissions has gradually grown over the last several years. With the May 2006 reaffirmation of the federal Clean Air Mercury Rule (CAMR) and numerous aggressive state regulations being proposed and promulgated, that interest has reached a peak. Currently, there are two promising technical approaches for removing mercury from coal-derived flue gases: the capture of soluble oxidized mercury in a wet flue gas desulfurization system and the injection of PAC upstream of a baghouse or electrostatic precipitator (ESP).

In April and May of 2005, Southern Company Services and Mississippi Power Company commissioned ADA-ES to conduct a sorbent injection demonstration project at the Victor J. Daniel Plant's Unit 1 in Escatawpa, Mississippi. The demonstration was designed to assess the effectiveness of two carbon sorbents on a unit that can fire varying blends of bituminous and subbituminous coals. The typical coal blends fired at Plant Daniel result in a sulfur content below 1 wt% and consequently the electrostatic precipitators are coupled with an SO₃ flue gas conditioning (FGC) system. The initial premise of the demonstration was to conduct all testing with the flue gas conditioning system in service, according to the plant's normal operating practices.

The initial injection tests, conducted with standard PAC, yielded low mercury removal with efficiencies approaching only 40% at an injection ratio of 10 lb/MMacf. Following these first tests, an interruption to normal plant operations caused the FGC system to be taken out of service. In the absence of the SO₃ injection, the mercury removal levels nominally doubled. This dramatic performance increase caused the test team to reevaluate the original test plan and commit time and focus to better understanding and quantifying the apparent inhibiting effect of SO₃ injection on PAC sorbent effectiveness.

In the months subsequent to this discovery at Plant Daniel, similar results have been observed at other test sites within the industry. For many utilities, the issue of flue gas SO₃, either due to

native fuel sulfur content or SO₃ injection for enhanced ESP performance, inhibiting sorbent effectiveness is a key technical hurdle for meeting the new mercury emission limits. Finding a suite of solutions to this problem is a primary concern to utilities that would use PAC injection for the removal of mercury.

PLANT DESCRIPTION

Mississippi Power Company's Victor J. Daniel Plant Unit 1 is a 540-MW_G pulverized-coal unit. Although originally design to combust eastern bituminous coal, the unit now fires a blend of bituminous and subbituminous fuels. The tangentially fired furnace is equipped with overfire air ports for combustion-based NO_x control and is supplied by five coal mills. Each mill has a dedicated coal bunker, permitting coals to be blended in 20% increments. The unit typically combusts a 60% bituminous and 40% Powder River Basin (PRB) subbituminous blend.

The unit's flue gases are cooled by two parallel regenerative air preheaters, each of which discharges to a pair of cold-side ESPs. The flue gases are conditioned with gaseous SO₃ prior to treatment in the ESPs and ultimately discharged through a common stack.

The FGC system is in service continuously during typical operation, and injects SO₃ downstream of the air preheaters. The system normally injects SO₃ at such a rate to achieve nominally 6 ppm at full unit load. This injection rate can be modulated, and for the purposes of this test program, was operated at half-injection—3 ppm—for some periods.

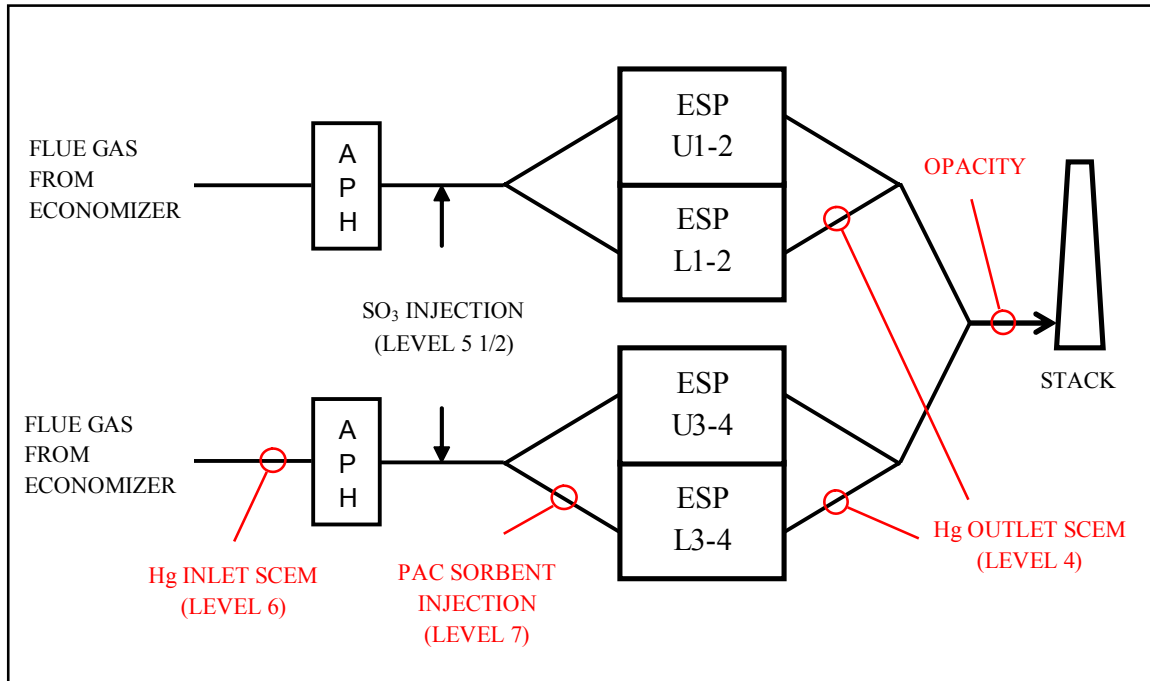
TEST SYSTEM DESCRIPTION

The sorbent injection demonstration was conducted on one of the unit's four ESPs, representing nominally one-quarter of the total flue gas. Flue gas mercury measurements were made using Semi-Continuous Emission Monitors (SCEMs) at the air preheater inlet and the test ESP outlet. The air preheater inlet was measured rather than the ESP inlet to take advantage of the higher temperature, avoiding fly ash scrubbing of mercury across the SCCEM probe filter. For quality assurance purposes, the SCCEM measurements were validated with occasional sorbent trap measurements. In addition to the test ESP outlet, a second non-treated ESP outlet was monitored to provide a control reference. During baseline testing, the two ESP outlets were shown to be consistent, validating this strategy. Figure 1 illustrates the test system.

Two carbon sorbents were evaluated during this demonstration: NORIT's DARCO[®] Hg and DARCO[®] Hg-LH, which is a brominated variant. The sorbent was injected upstream of only the test ESP.

Two fuel blends were evaluated during this program. Testing was conducted with the unit burning both 60/40% and 80/20% bituminous/subbituminous coals. The bituminous variety was typically from the Twenty Mile mine and the subbituminous varieties were from either the Black Thunder or Antelope mines.

Figure 1. Plant Daniel Unit 1 Schematic.



THEORY OF SO₃ INTERFERENCE

The physical and chemical mechanisms by which flue gas SO₃ interferes with mercury adsorption are not fully understood. The Mercury Information Clearinghouse¹ discusses a series of sorbent breakthrough curve studies, conducted by EERC, that demonstrate the impact of sulfuric acid on sorbent capacity. These laboratory experiments assessed the mercury capacity of the NORIT DARCO[®] Hg activated carbon sorbent—as expressed in mass of mercury per mass of sorbent—under varying concentrations of SO₂, as well as other typical flue gas constituents. The proposed EERC mechanism describes first the oxidation of adsorbed flue gas SO₂ followed by reaction with moisture to form sulfuric acid. The study showed a direct correlation between increased flue gas SO₂ and decreased sorbent capacity. EERC concluded that sulfuric acid and mercury compete for the same active binding sites on the sorbent surface structure and that the sulfuric acid is preferentially bound. Consequently, the concentration of sulfuric acid on the sorbent determines the number of remaining sites available for mercury capture.

While the EERC study focuses on flue gas SO₂, it is implicit from the proposed mechanism that flue gas SO₃ would have the same effect. An adsorbed SO₃ molecule would also readily react to sulfuric acid and subsequently claim potential mercury binding sites.

Another important finding of the EERC work showed that the measured breakthrough curve often peaked above the inlet mercury concentration. This phenomenon can only indicate that “captured” mercury is being desorbed, suggesting displacement by preferential flue gas species. The seemingly likely candidate would again be sulfuric acid, although that was not conclusively shown.

RESULTS FROM THE PLANT DANIEL SORBENT INJECTION DEMONSTRATION

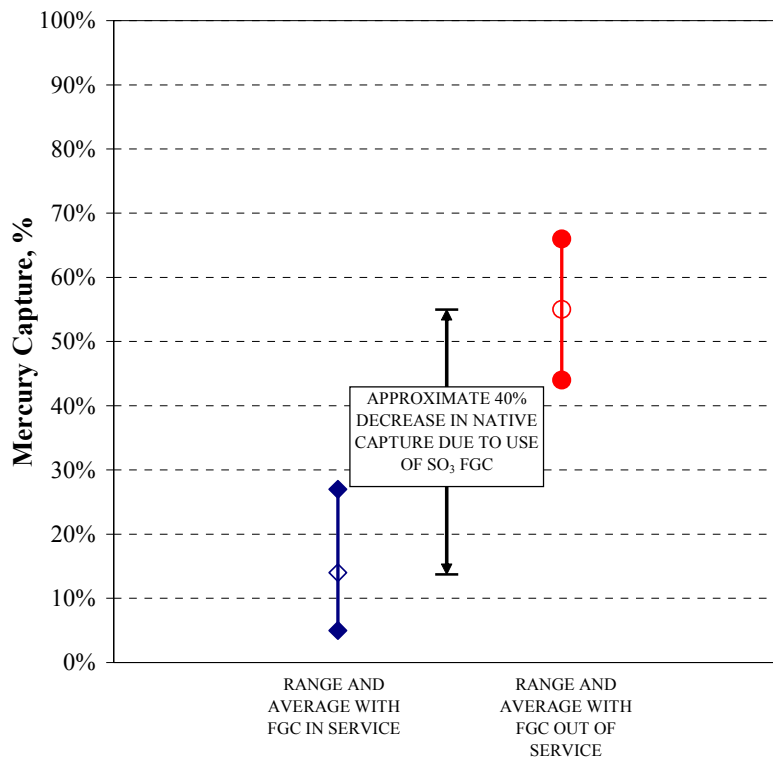
The demonstration at Plant Daniel starkly defined an installation where the success of sorbent injection as a viable control technology suitable for regulatory compliance hinges on the influences of the flue gas conditioning system. The injection of SO₃ strongly affects both the native mercury capture and sorbent-based capture across the unit's air pollution control train. These effects are presented below.

Native Capture of Mercury

Before beginning sorbent injection, and subsequently during periods where sorbent injection was shut off, the test team made mercury measurements to assess the unit's native performance. These measurements quantify how much mercury is captured by the existing unit configuration without any mercury-specific enhancements. As both the absolute concentrations and system capture of flue gas mercury vary depending on numerous fuel and combustion-related factors, measured capture rates are presented in ranges.

With the FGC system operating at 6 ppm injection, the native mercury capture was approximately 5% to 30%, and averaged approximately 14%. When reevaluated during periods where the FGC was shut off, the native capture jumped to 44% to 66%, averaging 55%. As Figure 2 illustrates, the use of SO₃ FGC results in a loss of nominally 40% native mercury capture.

Figure 2. Impact of FGC on Native Capture.

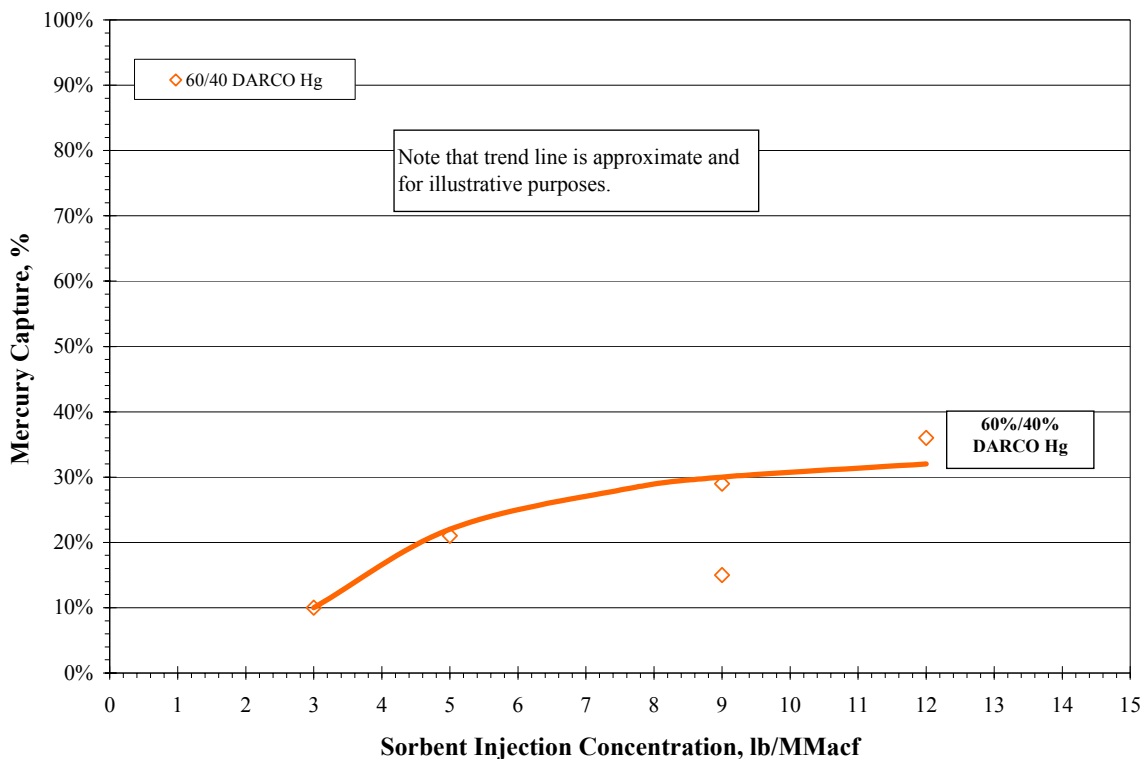


These results affirm that the presence of flue gas SO₃ affects the native mercury capture mechanisms, which depend on ash minerals and unburned carbon content.

Sorbent-Based Mercury Capture

The first sorbent injection test runs occurred using the non-brominated NORIT DARCO[®] Hg with the FGC system in service. These initial trials produced only modest mercury removals even at high injection ratios, as illustrated in Figure 3. This test was conducted while firing a 60/40% bituminous/subbituminous coal blend.

Figure 3. Initial DARCO[®] Hg Sorbent Performance With FGC In Service.



After this initial period, testing was suspended for a weekend break during which the SO₃ FGC system was taken out of service. Even without conditioning, opacity was safely below the unit limit and so the FGC system was not immediately returned to service. Unaware of this, the team resumed sorbent injection testing using the brominated PAC. The mercury removal rates were dramatically improved, well beyond what would normally be attributed to the difference between the brominated NORIT DARCO[®] Hg-LH and non-brominated NORIT DARCO[®] Hg PACs. At the end of the initial day of testing with the brominated carbon, a plant operator requested permission to return the FGC system to service. The team quickly realized the importance of the FGC system impacts to PAC performance at Daniel and toggled it on and off to informally verify its contribution to the improved mercury capture. The influence was unmistakable and the subsequent test sequences were modified to incorporate periods with and without FGC. The bulk of the subsequent testing was conducted with the FGC system turned off.

Figure 4 illustrates a typical parametric test where the effects of both sorbent injection and SO₃ injection can be discriminated. The different events of interest have been labeled alphabetically for clarity and the corresponding snapshot data from those events are summarized in Table 1. This test was conducted with DARCO[®] Hg-LH, the brominated PAC.

Figure 4. Variable SO₃ and Sorbent Injection Test. DARCO[®] Hg-LH.

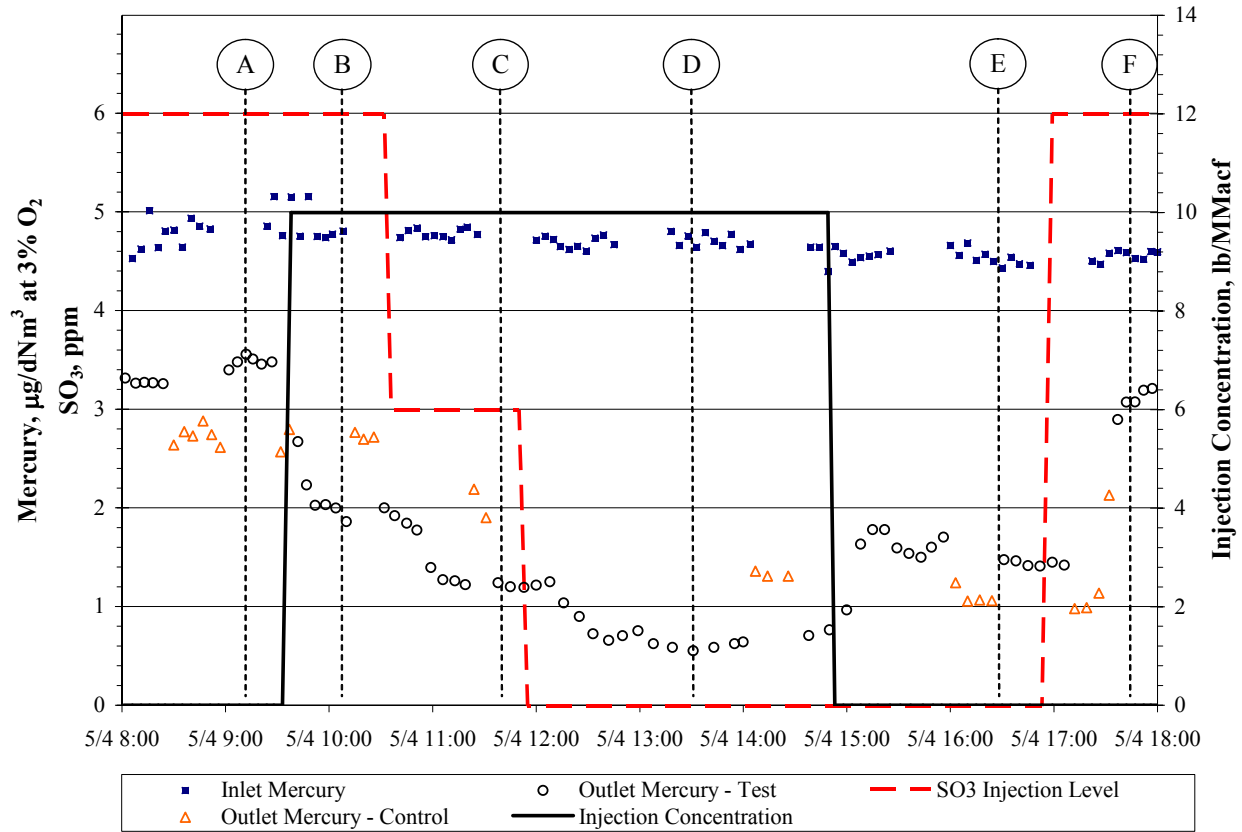


Table 1. Snapshot Data for Variable SO₃ and Sorbent Injection Test.

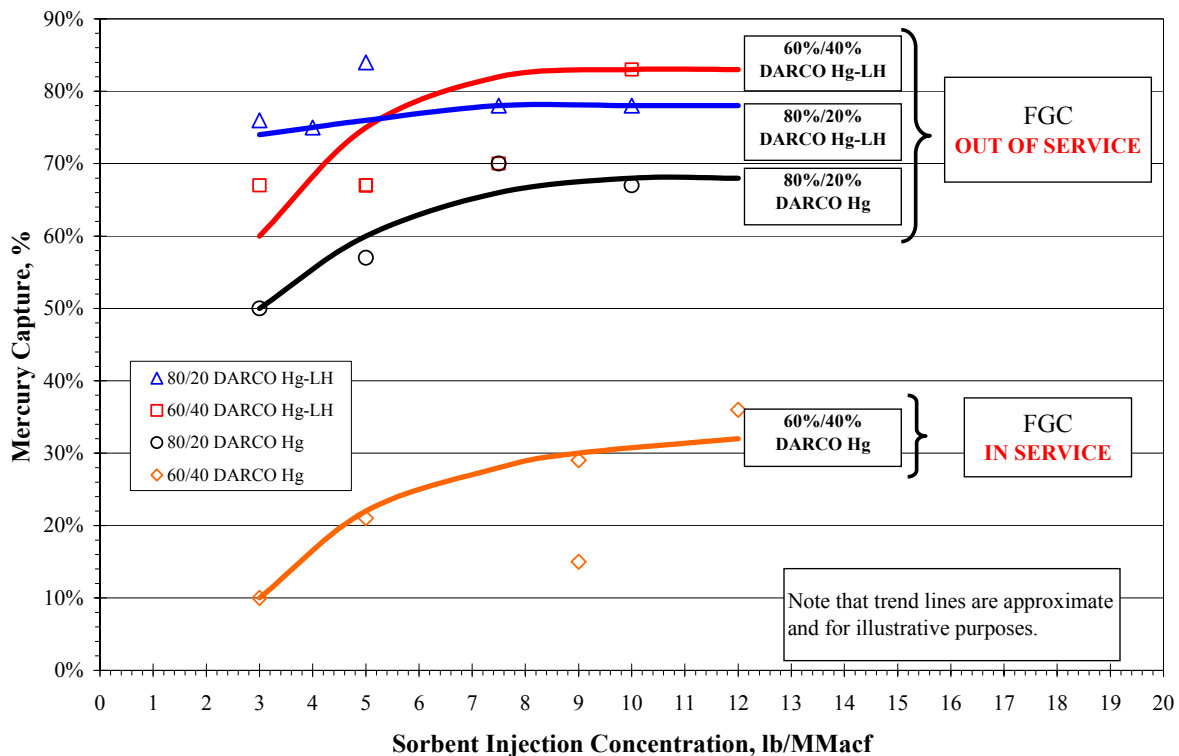
Event	Sorbent Injection Ratio lb/MMacf	SO ₃ Injection Concentration ppm	Inlet Mercury µg/dNm ³	Outlet Mercury µg/dNm ³	Mercury Capture %
A	0	6	4.9	3.5	29
B	10	6	4.8	1.9	60
C	10	3	4.8	1.2	75
D	10	0	4.8	0.6	88
E	0	0	4.7	1.5	68
F	0	6	4.6	3.1	33

The test in Figure 4 begins at Event A, where the FGC system is in normal operation at full SO₃ injection without any sorbent injection. In that condition, native mercury capture measured at the outlet of the test ESP was approximately 29%. The control ESP outlet mercury concentration was similar to the outlet mercury concentration on test ESP. Event B shows the impact of a high ratio of sorbent injection in conjunction with the FGC. This combination improved mercury capture to about 60%. Event C then shows a further improvement to 75% capture when the SO₃ injection reduced to half rate, or 3 ppm. When SO₃ injection is fully stopped, as shown by Event D, mercury capture peaks at 88%. Event E shows the potential native capture available without FGC or sorbent injection. At 68%, this is more than double the native capture achieved with FGC in service. The final snapshot, Event F, shows the system recovering to the initial condition—full SO₃ injection without sorbent injection—and the final native capture of 33% closely mirrors the 29% seen at the beginning of the day.

Note that the inlet mercury concentration was nominally steady throughout this test sequence. The unit was also held at a constant full load and the coal supply was unchanged. This stepwise examination clearly delineates the positive effects of sorbent injection and negative effects of SO₃ injection on mercury capture.

A series of such parametric tests were conducted over the balance of the demonstration. The summary performance curves are shown in Figure 5, which includes the data shown in Figure 3 above. As the figure is notated, the curve lines are approximations for illustrative purposes and not statistical data fits. The actual data points are also shown.

Figure 5. Sorbent Performance Curves With and Without FGC.



These curves require some explanation, given the combinations of coal blend, sorbent type, and FGC operation that are included. The only data set that reflects the FGC system in operation is the bottom curve, which represents DARCO[®] Hg with the 60/40% fuel blend. Given how suppressed the control levels are in that bottom curve, it is easy to superficially conclude that SO₃ injection inhibits control by 30% to 40%. Given the number of variables, however, some further consideration is prudent. Firstly, the best curve to compare against the bottom, FGC in service, curve is the 80/20% DARCO[®] Hg. The confounding factor is that the fuel blend does differ. Examination of the two DARCO[®] Hg-LH curves, however, strongly suggests that the difference in the two fuel blends has only a minor effect on mercury capture, perhaps a 5% impact. Consequently, if direct comparison of the two DARCO[®] Hg curves shows a 30% to 40% difference, only 5% is likely attributable to the difference in fuel blend. This leaves approximately a 25% to 35% impact solely due to the impact of the FGC system.

Another compelling presentation of the project data is shown in Figure 6. This figure summarizes the data sets where sorbent type, fuel blend, and injection ratio are held constant and only the SO₃ injection rate is varied. These seven curves consistently and without exception show a steady decrease in mercury capture with increased SO₃ injection rate.

Figure 6. Impact of SO₃ Injection Level on Mercury Performance.

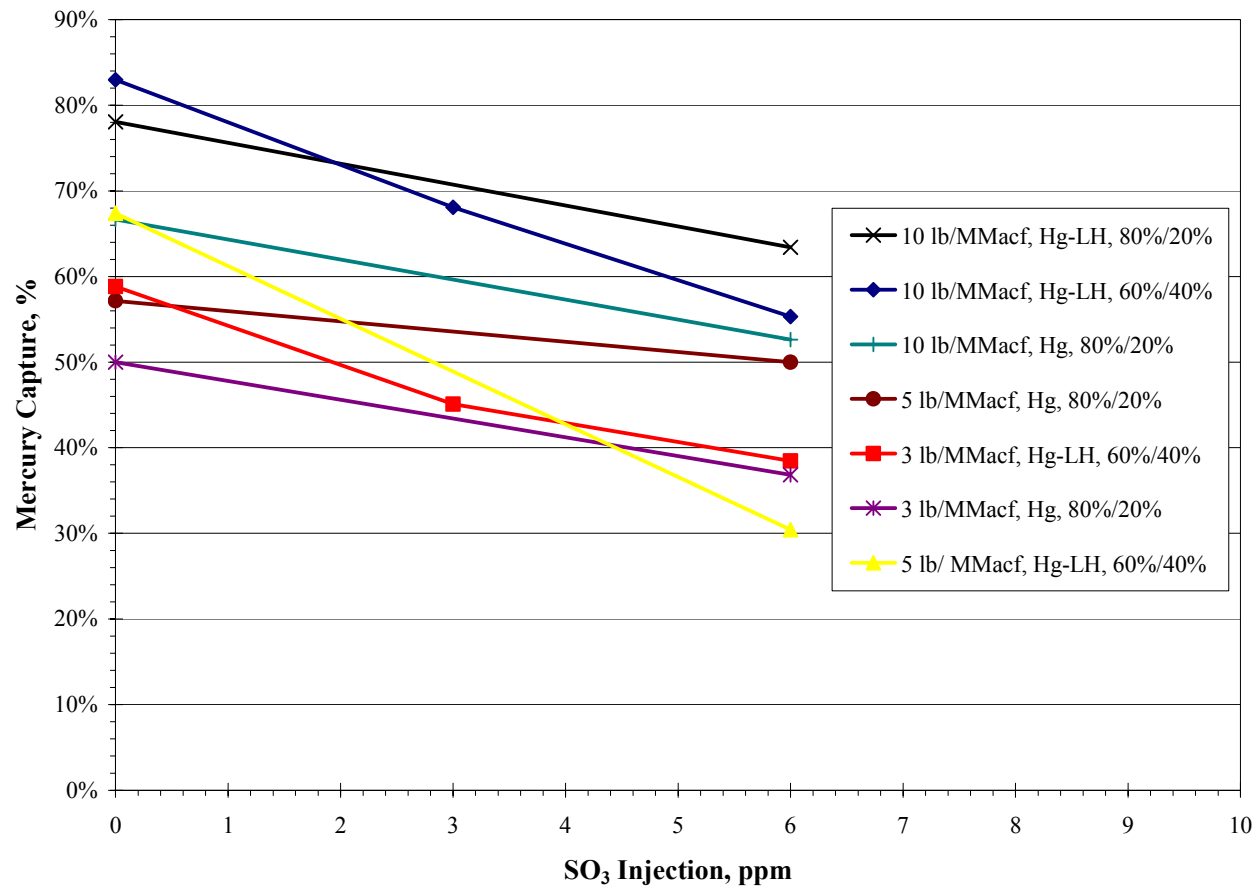


Table 2 then summarizes the data from Figure 6, showing for each of the seven conditions the maximum and minimum mercury captures, as well as the impact per ppm of SO₃ injected.

Table 2. Impact to Mercury Capture by SO₃ Injection.

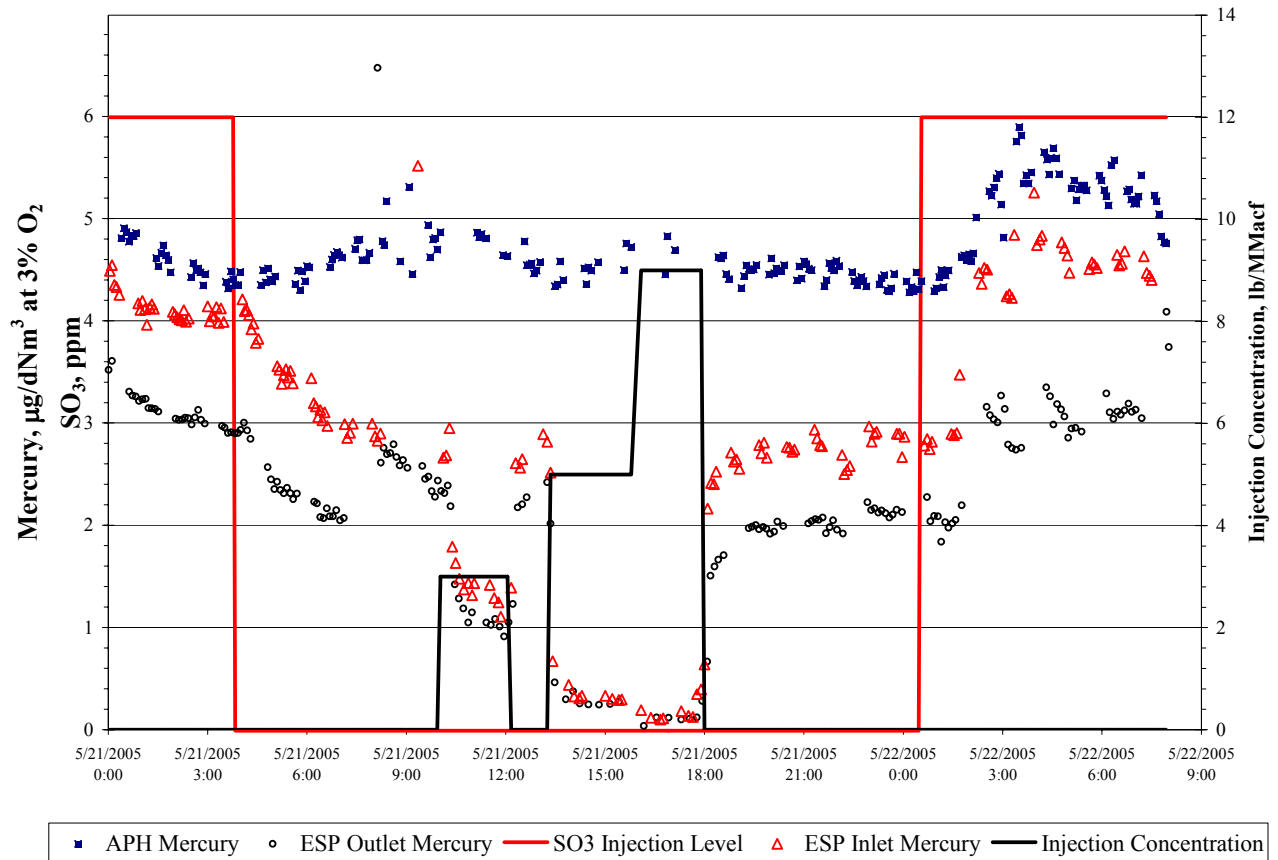
Sorbent	Sorbent Injection Ratio lb/MMacf	Fuel Blend	Maximum Capture % at 0 ppm SO₃	Minimum Capture % at 6 ppm SO₃	Total Impact to Mercury Capture %
DARCO [®] Hg-LH	5	60/40%	67	30	37
DARCO [®] Hg-LH	10	60/40%	83	55	28
DARCO [®] Hg-LH	3	60/40%	59	38	21
DARCO [®] Hg-LH	10	80/20%	78	63	15
DARCO [®] Hg	10	80/20%	67	53	14
DARCO [®] Hg	3	80/20%	50	37	13
DARCO [®] Hg	5	80/20%	57	50	7

MODIFIED INJECTION STRATEGY SORBENT INJECTION TEST

Based on the test program results with the FGC system in service, sorbent injection for mercury control would require higher than usual injection rates. This would significantly reduce the cost-effectiveness of the technology. A test was therefore devised to determine if sorbent injection could be successfully installed upstream of SO₃ injection, such that both technologies could successfully operate together. In this test, the FGC system injection location would be simulated downstream of the PAC injection location. The mercury scrubbing would be done in the duct before encountering the SO₃ from the FGC system. To simulate this future configuration, the sorbent injection lances were relocated from Level 7 to Level 5½, just downstream of the existing SO₃ lances. For the purpose of this test, the SO₃ injection was turned off, and mercury measurements were taken upstream of the air preheater and just upstream of ESP inlet, where the SO₃ lances would be moved to in the future. Comparison of these two measurements is a prediction of the potential in-flight mercury capture that could be achieved by the future retrofit. ESP outlet measurements were also taken for comparison to in-duct removals.

As a note of caution, the SO₃ interference mechanism is not fully understood. Presumably, SO₃ either preferentially occupies sorbent sites such that mercury cannot be adsorbed or bonds with the mercury in such a way that it cannot be adsorbed. An alternative possibility, proposed by the EERC, is that the SO₃ actually displaces mercury that has already been captured by the sorbent. If this last scenario is true, the modified test configuration would not assess it.

Figure 7. Modified Injection Strategy Sorbent Performance Curves.



Inspection of Figure 7 again confirms that SO_3 injection inhibits mercury capture. When the SO_3 system was shut down at 0345, both the ESP inlet and outlet mercury levels immediately started to decrease, even though inlet mercury held steady and even started to rise. It took more than two hours for the effect of the SO_3 to wear off after the system was stopped, finally showing a decline from $3.1 \mu\text{g}/\text{Nm}^3$ to $2.1 \mu\text{g}/\text{Nm}^3$, a decrease of $1.0 \mu\text{g}/\text{Nm}^3$. At the end of this test sequence, when SO_3 injection was restarted, mercury jumped from $2.0 \mu\text{g}/\text{Nm}^3$ to $2.9 \mu\text{g}/\text{Nm}^3$, an increase of $0.9 \mu\text{g}/\text{Nm}^3$. Note that magnitudes of the impact and recovery due only to SO_3 injection are very similar, $1.0 \mu\text{g}/\text{Nm}^3$ versus $0.9 \mu\text{g}/\text{Nm}^3$.

In the period before SO_3 injection was stopped, total system mercury capture was only 33%, of which only 11% occurred in-flight, i.e., upstream of the precipitator. After SO_3 injection was stopped, the in-flight contribution to overall capture started to increase. This trend continued when sorbent injection commenced. With sorbent injection in service, ESP capture fell to only a few percent. This is much less a commentary on the performance of the ESP than on the in-flight performance. With sorbent injection in service, the in-flight removal jumped up dramatically, such that there was very little mercury left for the ESP to capture. Note that the ESP capture values are based on APH inlet levels. When recalculated based on ESP inlet values, the performance appears much steadier, in the range of 15% to 30%.

Table 3 then summarizes the data from the modified sorbent injection test.

Table 3. Summary of Modified Injection Strategy.

Time	SO ₃ Injection	Sorbent Injection	APH Inlet Mercury	ESP Inlet Mercury	ESP Outlet Mercury	In-Flight Capture	ESP Capture	Overall Capture
	ppm	lb/MMacf	µg/Nm ³	µg/Nm ³	µg/Nm ³	%	%	%
0000–0345	6	0	4.6	4.1	3.1	11	22	33
0345–1012	0	0	4.1	3.5	2.6	15	22	37
1012–1205	0	3	4.8	1.4	1.3	71	2	73
1205–1315	0	0	4.6	2.5	2.1	46	9	55
1315–1554	0	5	4.5	0.6	0.5	87	2	89
1554–1755	0	9	4.7	0.2	0.1	96	2	98
1755–1230	0	0	4.5	2.7	2.0	40	16	56
1230–0900	6	0	5.2	4.2	2.9	19	25	44

In this test arrangement, it was estimated that the sorbent had approximately one second of residence time prior to in-flight measurement. Excellent removal rates have been estimated to occur in the one-second timeframe provided that good flue gas mixing and proper distribution is occurring. At Plant Daniel, the carbon injection occurred downstream of a 90° bend and had two more 90° bends in the ducting downstream of the injection location prior to measurement. This configuration provides substantial turbulence to aid sorbent/gas mixing.

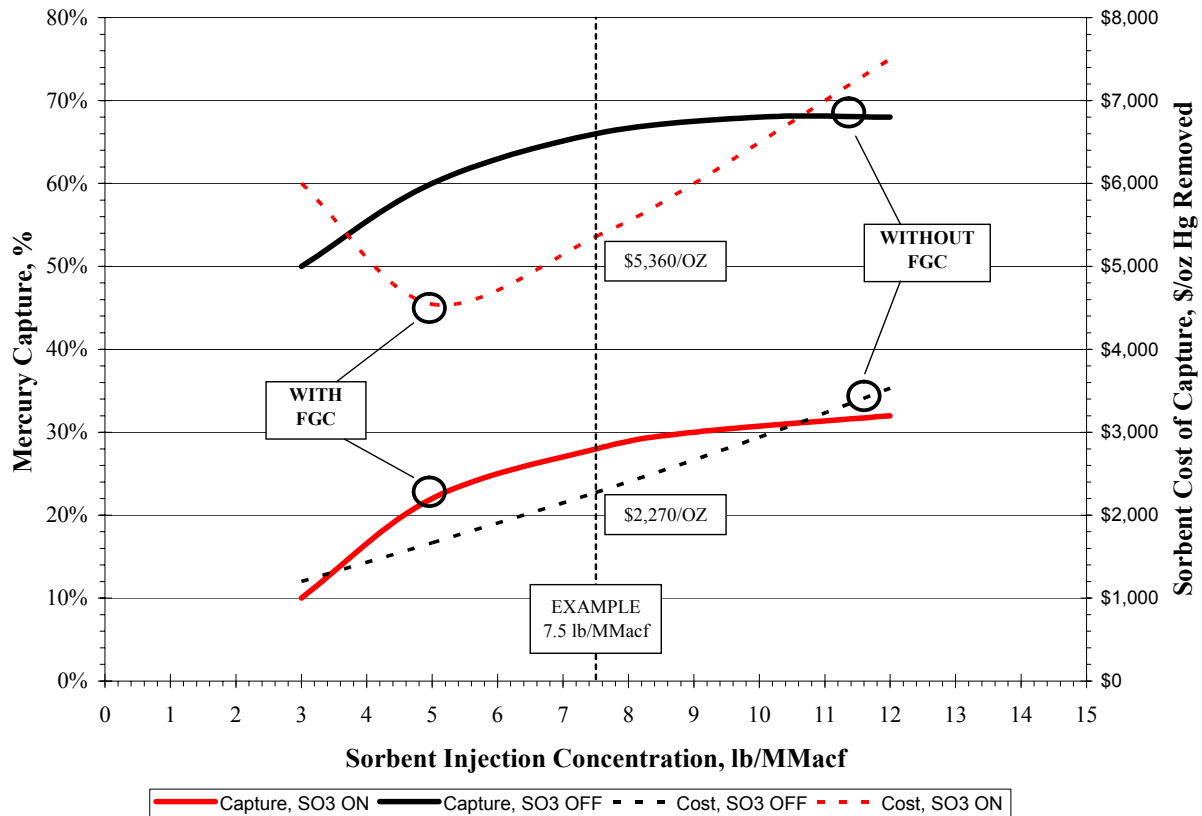
SIGNIFICANCE TO INDUSTRY

The inhibiting effect of flue gas SO₃ on sorbent-based mercury capture is for many units the major obstacle to economical compliance with the impending mercury regulations. SO₃ can be present either from an installed FGC system or naturally in the flue gas. The suppressed effectiveness of the common PAC sorbents may prevent some units from meeting the new regulatory emissions limits with a simple sorbent injection system. Other units may be able to achieve the required reductions but only with significantly greater sorbent expenditures.

The following scenario explores the economic impact of the SO₃ inhibition effect on sorbent operating costs. This scenario applies the DARCO[®] Hg PAC performance demonstrated at Plant Daniel to a hypothetical unit. Figure 8 again presents the DARCO[®] Hg sorbent performance curves with and without FGC. The figure also includes the equivalent mercury removal costs, expressed on a per ounce basis. The equivalent cost calculation is based on the following assumptions:

- Technical
 - ESP inlet mercury is 5 µg/dNm³ (approximately 4 lb/TBtu coal equivalent)
 - 1 MMacfm flue gas flow
 - 10% moisture
 - 330 °F
- Economic
 - DARCO[®] Hg sorbent cost, \$0.60/lb delivered.

Figure 8. DARCO[®] Hg Sorbent Performance and Hypothetical Removal Costs With and Without SO₃ FGC.



Perhaps the most striking point to take away from Figure 8 is that the two sorbent performance curves (solid lines) do not even cross in capture efficiency for the PAC injection rates analyzed. The maximum removal achieved with the FGC system in service was less than the minimum achieved without FGC.

To take a mid-injection ratio example, at 7.5 lb/MMacf the removal costs are approximately \$5,360/oz and \$2,270/oz. In other words, the use of FGC results in more than a doubling of the unit cost of removing mercury.

The reader should understand the unit removal costs presented above are specific to the example cited and are not broadly applicable. One factor that strongly influences the unit cost is the coal mercury content. Because a given sorbent injection ratio yields a fixed mercury removal *efficiency*, a higher coal mercury content results in more mercury mass being captured for a given injection ratio. To extend the example above, Table 4 shows the unit removal costs for varying coal mercury contents. Again, these results assume the sorbent performance demonstrated at Plant Daniel and shown in Figure 8.

Table 4. Unit Cost of Removal for Varying Coal Mercury Content at 7.5 lb/MMacf.

Coal Mercury Content lb/TBtu	With FGC		Without FGC		Cost Ratio Due to FGC
	Mercury Capture %	Capture Cost \$/oz	Mercury Capture %	Capture Cost \$/oz	
4	28	5,360	66	2,270	2.35
8	28	2,680	66	1,140	2.35
12	28	1,790	66	760	2.35

POTENTIAL SOLUTIONS

With federal and state regulations looming, and sorbent injection remaining arguably the best mercury-specific control technology, the industry is urgently trying to identify a means to avoid the substantial SO₃ inhibition effect. For many units, such a solution is the difference between achieving economical compliance or expending a large capital investment. Several promising possibilities are being explored and are summarized here.

SO₃-Friendly Sorbents

The various sorbent manufacturers are actively trying to develop mercury sorbents that will be immune to the inhibition effect experienced by currently available materials. Both carbon- and mineral-based materials are being evaluated, but to date no material has been demonstrated effective.

Alternate ESP Enhancement Approaches

Currently, SO₃-based FGC systems are the most economical choice in enhancing the performance of electrostatic precipitators. If other technologies are employed to replace SO₃ conditioning, ESP performance could be enhanced while effects on sorbent performance could be mitigated. One such approach could be the use of alternate flue gas treatment methods such as ammonia conditioning or water humidification. While both approaches could be successful, one must note that there are severe disadvantages. The use of pulsing technology (such as the rapid onset pulse energization (ROPE) approach) would be ideal when a replacement to SO₃ is needed.

Sorbent Injection Upstream of FGC

SO₃ and mercury sorbent often compete for the ideal injection locations. In each case, the conventional wisdom is to locate the point of injection as close to the air preheater outlet as practical. For a typical retrofit application, the FGC system already exists, relegating the mercury sorbent to a second-best location after the point of SO₃ injection. It is this configuration that has been tested and proven to be ineffective. It may be that reversing the order of injection will significantly improve total mercury capture, particularly for installations where appreciable in-flight residence time exists between the sorbent injection point and the subsequent SO₃ injection point. It has not yet been demonstrated whether SO₃ and the subsequent sulfuric acid will displace mercury after it has been successfully adsorbed onto the sorbent. If this configuration can be proven effective, some existing plants could relocate their SO₃ injection closer to the ESP inlet and improve their mercury capture and sorbent utilization. While such relocation is far from trivial, the potential sorbent cost savings could be very significant.

Co-Inject Alkali Minerals

For applications where the SO₃ is derived from high coal sulfur content instead of FGC, alkaline mineral injection may be used to mitigate the free SO₃ in the flue gas upstream of the point of sorbent injection. This is the same principal as is used for mitigating SO₃ plumes. Viable mineral candidates include trona, lime, and magnesium oxide. Tests evaluating some of these materials' effects on sorbent injection are underway in a DOE program.

SUMMARY AND CONCLUSIONS

The sorbent injection testing at Plant Daniel and elsewhere has raised the industry's awareness to the significant challenge of SO₃ interference with sorbent-based mercury capture. The Plant Daniel test results illustrate a unit where regulatory compliance is likely a simple technical feat in the absence of SO₃ flue gas conditioning but very challenging with it. Numerous other units throughout the industry are subject to similar control limitations due either to their own conditioning systems or high-sulfur coals. For all of these units, the availability of economical compliance strategies will hinge on the successful development of low-cost solutions to this chemistry-level problem.

ACKNOWLEDGEMENTS

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KEYWORDS

Plant Daniel
mercury control
sorbent injection
SO₃ interference
flue gas conditioning
sorbent economics