

Enhancing Mercury Removal for PRB Coals

Presentation for:

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INTRODUCTION

ADA-ES, Inc., is conducting a test program to obtain the necessary information to assess the feasibility and costs of controlling mercury from five plants with configurations that together represent over 80% of the existing coal-fired generation plants and potentially a significant portion of new plants. This program is being conducted under a cooperative agreement with the Department of Energy's National Energy Technology Laboratory (NETL), and is co-funded by EPRI and industry partners. Host sites that will be tested as part of this program are shown in Table 1. The field-testing portion of this program will be completed in 2005.

Table 1. Host Sites Participating in the Sorbent Injection Demonstration Project.

	Coal / Options	APC	Capacity MW / Test Portion	Current Hg Removal (%)
Sunflower Electric's Holcomb Station	PRB and Blend	SDA – Fabric Filter	360 / 180 and 360 / 360	0–13
AmerenUE's Meramec Station	PRB	ESP	140 / 70	15–30
American Electric Power's (AEP) Conesville Station	Bituminous Blend	ESP + Wet FGD	400 / 400	56
Detroit Edison's Monroe Power Plant	PRB/Bit Blend	SCR + ESP	785 / 196	NA
Missouri Basin Power Project's Laramie River Station	PRB	SDA – ESP	550 / 140	<20

BACKGROUND: MERCURY REMOVAL ON SUBBITUMINOUS COALS

Data collected in EPA's 1999 ICR program on mercury capture across existing emission control equipment (equipment designed to capture SO₂, NO_x, and particulates) showed that the same emission control equipment at plants burning subbituminous/PRB coals captured lower amounts of mercury than plants burning bituminous coals (Sjostrom et al., 2002). Some of these trends can be seen in Table 2.

Table 2. ICR Data Comparing Native Mercury Removal Efficiencies between Bituminous and Subbituminous Coals.

Controls	Average Removal Efficiency	
	Bituminous	Subbituminous (PRB)
Cold-Side Electrostatic Precipitator (ESP)	46%	16%
Fabric Filter (FF)	83%	72%
Spray Dryer Absorber and FF	98%	25%

The average mercury removal was 16% for plants burning PRB coal and with cold-side electrostatic precipitators (ESPs) (Sjostrom et al., 2002). The mercury removal was 46% with the same configuration and bituminous coal. Even more dramatic is the comparison for plants that have a spray dryer absorber (SDA) to capture sulfur dioxide and a fabric filter (FF) for particulate matter. On PRB coals, the FF, without an SDA, averaged 72% mercury capture. However, when a spray dryer was added to the configuration, the average mercury capture dropped to 25%. On bituminous coals, the average mercury removal in this configuration was 98%. This occurred in spite of the lower temperature associated with the spray dryer units. For FFs without SDAs, mercury collection is known to increase substantially when temperatures go below 260°F (Lindau, 1983).

In 2001, sorbent-based mercury control technology was first applied to full-scale plants burning PRB coals. On units with ESPs it was discovered that while 50 to 70% mercury removal was achievable, there appeared to be a ceiling that prevented any higher levels of mercury removal (Durham et al., 2002). On the SDA-FF configuration, high levels of mercury control could be achieved, but only with significantly higher injection rates than needed for FFs alone (Sjostrom et al., 2002) and Bustard et al., 2003).

Because the overall SDA-FF mercury removal was low, it appeared that the spray dryer removed components from the flue gas that were critical to mercury removal by PRB fly ash collected in an FF. It was speculated that these components were halogens such as chlorine, bromine, and fluorine, which are also critical components for untreated activated carbon to be effective in removing elemental mercury based on fixed bed simulations and pilot-scale experiments. It was also speculated that this halogen deficiency was causing the ceiling effect seen with activated carbon injection into ESPs filtering PRB ash.

RESULTS FROM FULL-SCALE MERCURY REMOVAL TESTING ON PRB COAL/SDA-FF CONFIGURATION

The first unit tested under this program was Sunflower Electric’s 360-MW Holcomb Station (Sjostrom et al., 2004). Holcomb Station is located near Garden City, Kansas. The unit is a load-following sub-critical 360-MW pulverized coal opposed-fired Babcock & Wilcox Carolina-type radiant boiler designed to burn PRB coal. The existing unit is equipped with three SDA modules followed by two very low air/cloth ratio reverse air FFs, which is also the most likely air pollution control configuration for new units burning subbituminous coal. Holcomb primarily burns two different PRB coals, Jacobs Ranch and Black Thunder.

This test program was designed to provide a full-scale evaluation of new technologies that can overcome the limited mercury removal achievable at these sites. Each technology was based on supplementing certain halogens that are not available in sufficient quantities in these coals. The program was very successful in that three different technologies were found that have the potential to produce high levels (>80%) of mercury removal in this difficult application (Starns et al., 2004). These technologies are:

1. Halogen Enhanced Activated Carbon: A proprietary product of NORIT Americas, Inc. DARCO[®] FGD-E3, produced mercury removal in excess of 90%. (Note: DARCO[®] FGD-E3 has been renamed to DARCO[®] Hg-LH and DARCO[®] FGD has been renamed to DARCO[®] Hg.)
2. Coal Blending: By blending western bituminous coal with PRB coal, the mercury removal across the system increased to almost 80% even without injecting another sorbent. It is highly likely that firing a blend of Black Thunder and West Elk coals with ACI could result in greater than 90% mercury removal. Results with other coal blends must be evaluated.
3. Chemical Addition to the Coal: KNX, a proprietary chemical developed by ALSTOM Power, was found to enhance the performance of a standard activated carbon. Mercury removal of 86% was measured at a carbon feed rate of just 1.0 lb/MMacf.

Halogen-Enhanced Activated Carbon

Short-term parametric tests showed that NORIT's halogen-treated sorbent DARCO[®] FGD-E3 outperformed the non-treated sorbent DARCO[®] FGD. These sorbents were injected upstream of the SDA. Based on these results, DARCO[®] FGD-E3 was selected and used for a four-week, continuous test. Figure 1 presents data collected during the four-week test. The results show that very high levels of mercury removal were obtained, average of 93%, at an injection rate of 1.2 lb/MMacf. During this test period mercury emissions averaged 0.8 lb/TBTU.

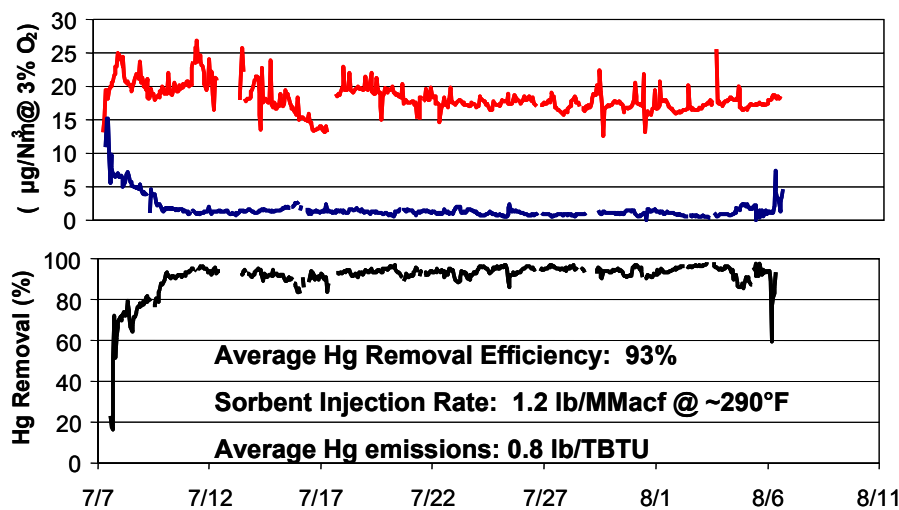


Figure 1. Results of Four Weeks of Injecting NORIT's DARCO[®] FGD Upstream of a Spray Dryer/Fabric Filter on PRB Coal.

Coal Blending

One week of coal blending tests were conducted at Holcomb. The baseline PRB coal was from the Jacobs Ranch mine. During blending tests, PRB coal from the Black Thunder mine was co-fired with western bituminous coal from the West Elk mine. Two different blend ratios of Black Thunder and West Elk were evaluated. The vapor-phase mercury removal during the first blend test was an average of 50% compared to no removal with 100% Jacobs Ranch PRB during this test period. The removal across the SDA-FF during the second blend test increased to 76% (81% based upon M324 samples). These results are summarized in Figure 2.

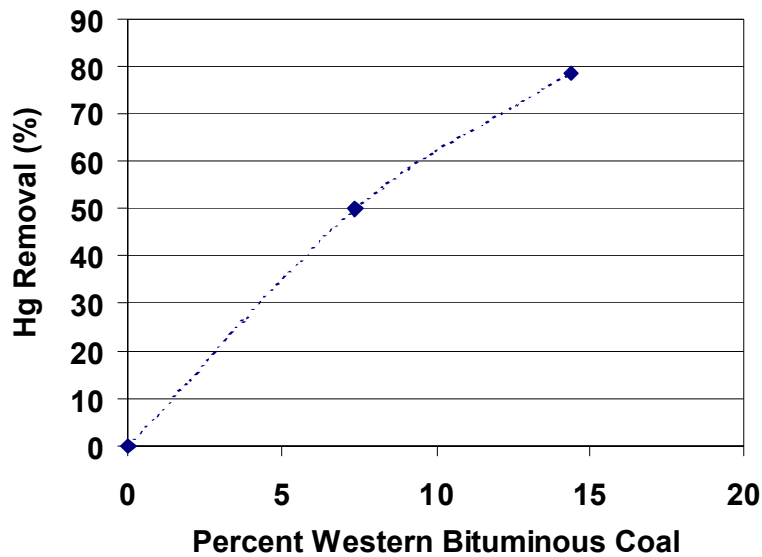


Figure 2. Summary of Coal Blending Tests Conducted at Sunflower Electric's Holcomb Station, 2004.

Coal Additive With/Without Sorbent Injection

Another option for introducing halogens is by adding them to the coal. The additive tested at this site was KNX, a proprietary ALSTOM Power mercury control technology. KNX was applied to the coal at the crusher house prior to entering the transfer house and coalbunkers.

During this period of testing, the unit was burning coal from the Jacobs Ranch mine. At normal operating conditions this coal yielded a total vapor-phase mercury concentration of 18 to 22 $\mu\text{g}/\text{Nm}^3$ at the outlet of the air preheater with 70 to 90% in the elemental form. During the chemical additive tests, the fraction of elemental mercury at the air preheater outlet decreased to 20 to 30%. Although the fraction of oxidized mercury increased substantially, no increase in mercury removal was measured across the SDA or across the SDA-FF. This suggests that either the KNX addition resulted in a sampling artifact that biased the elemental mercury measurement of the mercury monitor, or the SDA-FF was reducing oxidized mercury back to the elemental form.

The final day of coal additive testing included the injection of the DARCO[®] FGD sorbent at the SDA inlet location. The sorbent injection concentration at the inlet to the SDA was 1.1 lb/MMacf, while the chemical additive flowrate was held steady. Combining the coal additive and the non-treated activated carbon showed a total mercury capture across the system of 86%, compared to 54% with DARCO[®] FGD alone (no KNX). These data, plotted in Figure 3, clearly indicate that there was improved performance of DARCO[®] FGD when halogens were added.

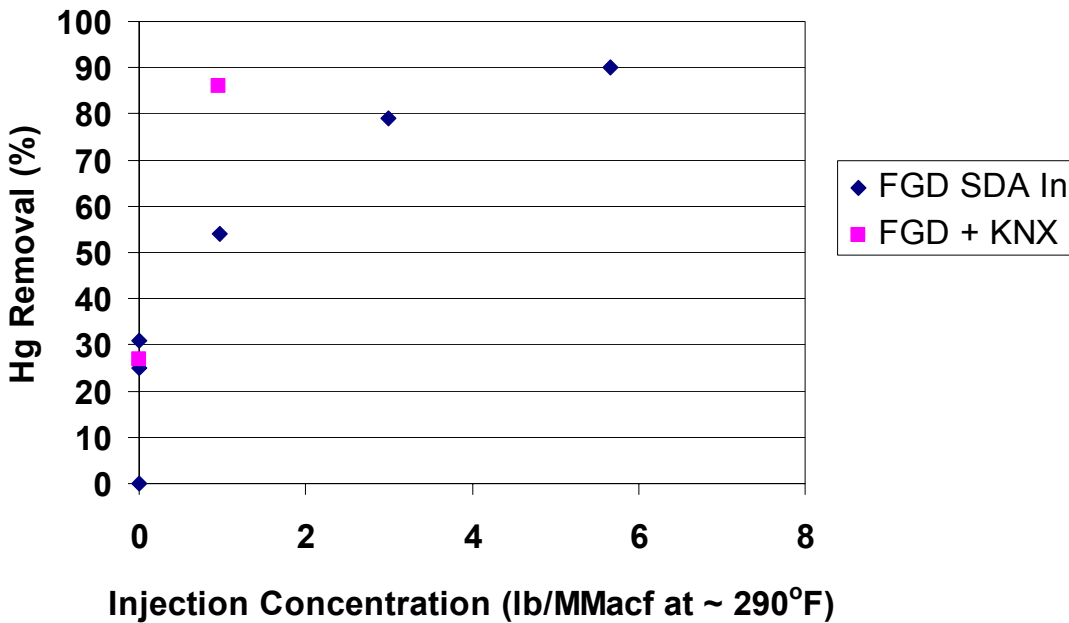


Figure 3. Impact of the Coal Additive (ALSTOM’s KNX) on Mercury Removal With and Without Injection of Non-Chemically Treated Activated Carbon (DARCO[®] FGD).

In addition to the Holcomb tests, URS conducted a DOE/NETL sponsored program at Great River Energy’s Stanton Station Unit 10 (Machalek et al., 2004). This unit fires North Dakota lignite, which has similar coal characteristics to PRB coals (Sjostrom et al., 2002), and has the identical configuration of a spray dryer/baghouse as Holcomb. During this test program two halogenated sorbents were tested, NORIT’s DARCO[®] FGD-E3 and Sorbent Technologies B-PAC. Mercury removal levels greater than 90% were achieved at an injection rate of 1.5 lb/MMacf with both of these sorbents. Figure 4 is a plot of data from both Holcomb and Stanton showing results for halogenated sorbents and the ALSTOM KNX process compared to results with standard, untreated activated carbons.

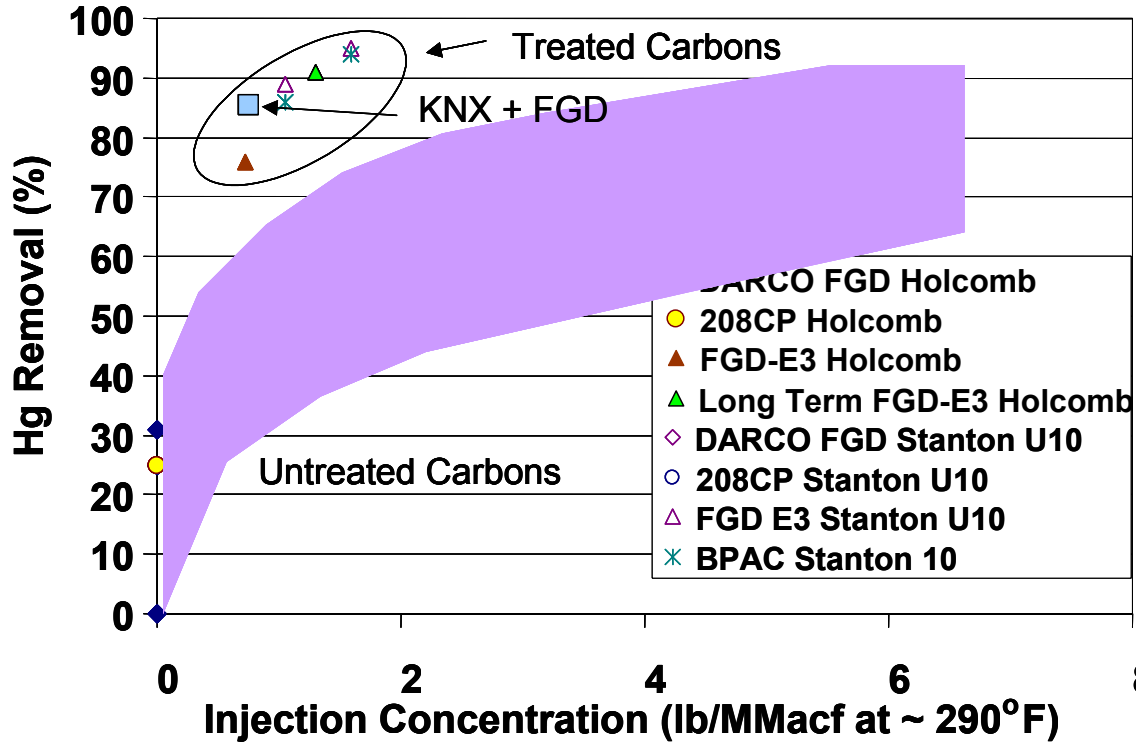


Figure 4. Performance of Halogen Enhancements on Units with Spray Dryer/Fabric Filters Burning Subbituminous and Lignite Coals.

RESULTS FROM FULL-SCALE MERCURY REMOVAL TESTING ON PRB COAL – COLD-SIDE ESP

Following the success of the halogenated sorbents on the SDA-FF, the next test site was AmerenUE’s Meramec Unit 2, located south of St. Louis, Missouri. Meramec Unit 2 is 140 MWs and fires 100% PRB coal obtained from several different mines. The unit is equipped with cold-side ESPs for particulate control (Starns et al., 2004). This configuration represents the majority of existing plants that burn subbituminous coals.

Halogen-Enhanced Activated Carbon

During this program, the performance of NORIT’s standard carbon, DARCO® FGD, was compared to the halogenated version, DARCO® FGD-E3, in short-term, parametric tests. The results are shown in Figure 5. With the standard carbon, the “ceiling effect” is observed in that a maximum of about 70% mercury removal is achieved at a feed rate of 3 to 5 lb/MMacf. No additional mercury removal was obtained even if the carbon feed rate was double and tripled. In contrast, DARCO FGD-E3 overcomes this effect and greater than 90% mercury removal is achieved at a feed rate of 3 lb/MMacf (Starns et al., 2004).

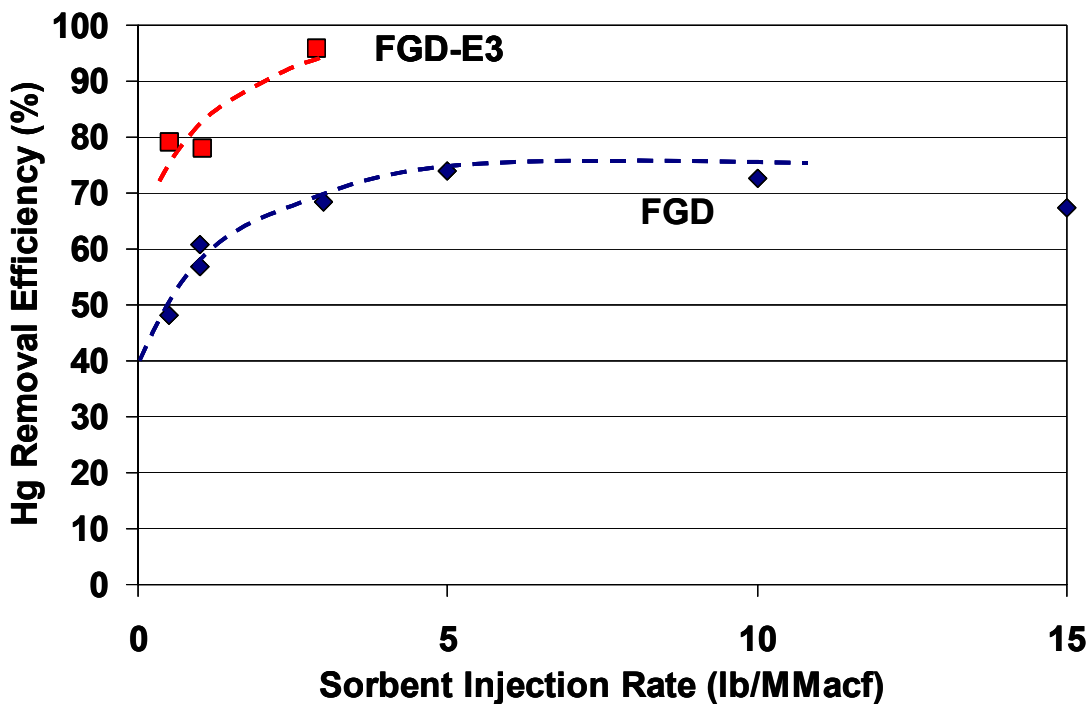


Figure 5. Mercury Removal on PRB Coal with NORIT’s Halogenated Activated Carbon DARCO[®] FGD-E3 Injected Upstream of a Cold-Side ESP.

In a longer-term test, DARCO[®] FGD-E3 was continuously injected over a 30-day period. A trend graph showing mercury concentrations at the inlet and outlet of the ESP during long-term testing is presented in Figure 6. During this test period the average mercury removal was 93%, with an average outlet emission of 0.44 lb/TBtu (Sjostrom, 2005).

Coal Additive With/Without Sorbent Injection

Similar to the tests with the SDA-FF at Holcomb, it was of interest to see the effect of a coal additive on native mercury removal and if the coal additive enhanced performance of an untreated activated carbon. In one of the parametric test series, ALSTOM’s KNX material was evaluated. With KNX, removal ranged from 57 to 64% compared to 22 to 34% with no KNX. No boiler operational changes were made during this time. These data suggest the KNX alone can enhance the effectiveness of native fly ash containing LOI.

During one day of KNX injection with DARCO[®] FGD, the maximum vapor-phase mercury removal was 87% at an injection concentration of 5 lb/MMacf, compared to 73% in the absence of KNX.

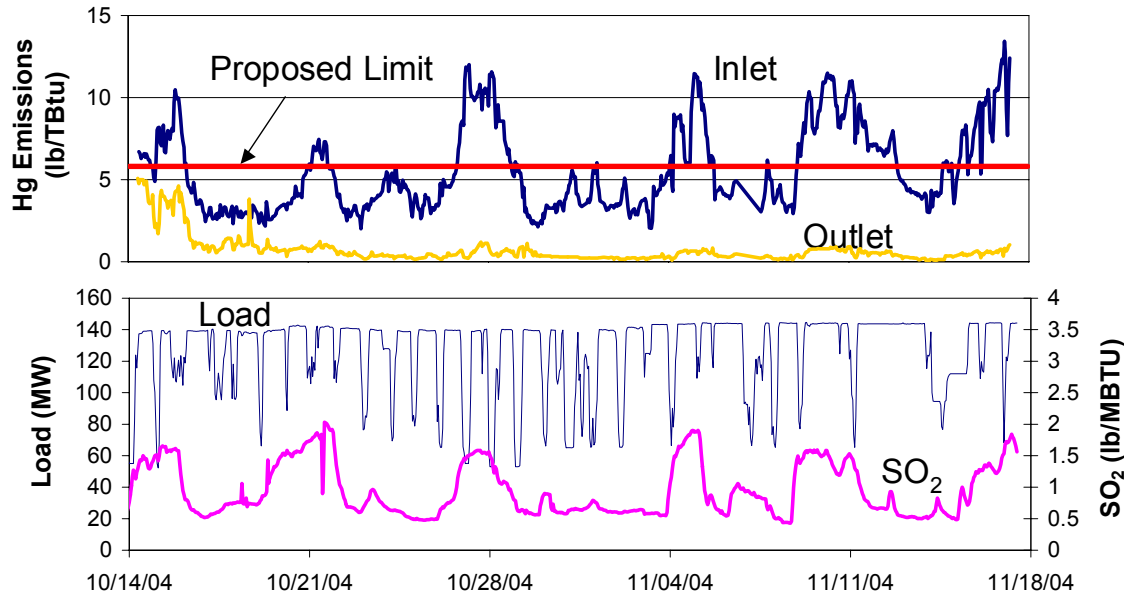


Figure 6. Mercury and SO₂ Trends During Long-Term Activated Carbon Testing at AmerenUE's Meramec Unit 2.

RESULTS ON A FULL-SCALE EVALUATION AT A PLANT BURNING PRB COAL WITH A SPRAY DRYER AND ESP

Missouri Basin Power Project's Laramie River Station, located near Wheatland, Wyoming, is one of the largest consumer-operated, regional, joint power supply ventures in the United States. Laramie River Station, which is operated by Basin Electric's Power Cooperation, has three units, each with 550 MW of generating capacity. The test unit (Unit 3) utilizes an SDA + ESP for their air pollution control. For sorbent injection testing with injection upstream of the SDA, only one-quarter of the 550-MW flue gas stream was treated, nominally 138 MW. A sketch showing flue gas flow from the air preheater (APH) to the stack on Unit 3 is shown in Figure 7.

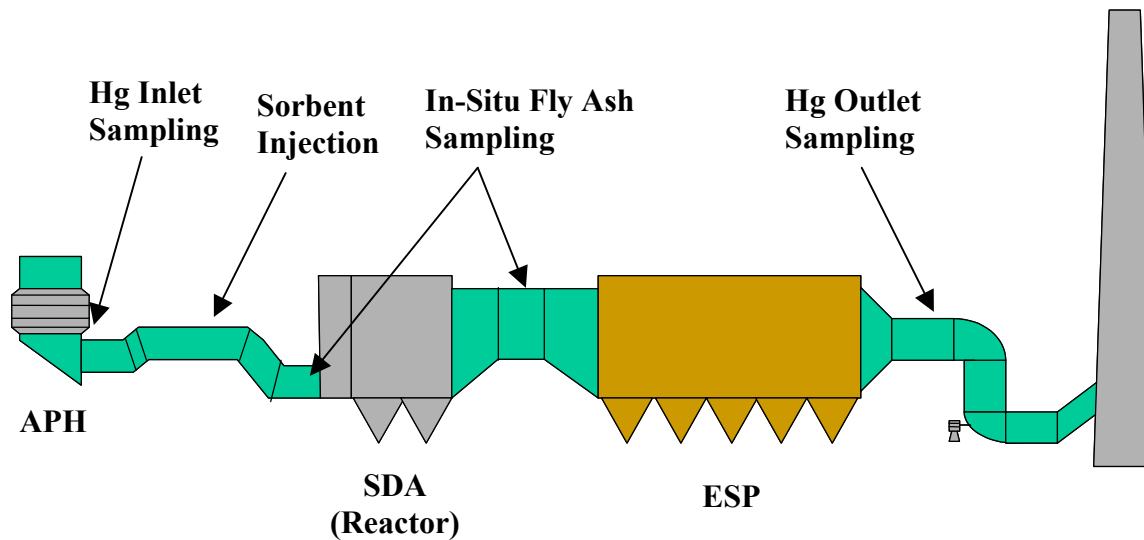


Figure 7. Sketch of Flue Gas Flow from APH to Stack (LRS3).

Baseline Testing – Laramie River Station

Field-testing at Laramie River Station began February 24, 2005. Baseline mercury measurements were made during the first two days of testing. During this period, Unit 3 was held steady at full-load conditions firing 100% PRB coal. The average vapor-phase mercury removal efficiency was approximately 12%. Average total mercury concentrations at the inlet to the spray dryer and the outlet of the ESP were 9.9 and 8.7 $\mu\text{g}/\text{Nm}^3$ respectively. The vapor-phase mercury was >90% elemental mercury at both the inlet of the SDA and the outlet of the ESP. The average particulate mercury concentration at the SDA inlet during baseline testing was low at 0.3 $\mu\text{g}/\text{Nm}^3$. To measure the particulate fraction of mercury at the SDA inlet, an in-situ particulate sample was collected just upstream of the Unit 3 “B” Reactor. The particulate sample was analyzed for mercury content, and the particulate-phase fraction of mercury present at the inlet to the SDA was calculated.

Parametric Testing

Following the baseline test period, a series of parametric tests were conducted to evaluate various mercury control technologies. The parametric tests were conducted at full-load conditions to document performance of coal blending, sorbent injection, and coal additive addition (with and without ACI) for control of mercury in stack emissions.

Coal Blending

During the coal blending tests, two types of western bituminous coals were evaluated. The plant typically fires 100% PRB coal; however, during the coal blend tests, a blend of approximately 80% PRB and 20% western bituminous was used.

Western Bituminous Blend 1

The first western bituminous coal was tested at two different blend ratios: 80/20 and 75/25. While testing at the 80/20 ratio, the average total vapor-phase mercury concentrations at the SDA inlet and ESP outlet were 9.2 and 9.3 $\mu\text{g}/\text{Nm}^3$ respectively. Mercury speciation at both locations was consistent with baseline measurements, where approximately 2% of the vapor-phase mercury at the SDA inlet and 8% at the ESP outlet was oxidized.

Coal samples were collected at the mine and sent to ADA-ES. A composite sample was sent to an outside lab for analysis.

Immediately following the 80/20 blend test, the amount of western bituminous coal added to the Unit 3 boiler was increased to 25%. Average vapor-phase mercury concentrations at the SDA inlet and ESP outlet for this blend were 8.6 and 8.2 $\mu\text{g}/\text{Nm}^3$ respectively. During both blends, total vapor-phase mercury removal was less than 10%.

Western Bituminous Blend 2

On March 7, 2005, a second coal blend test was conducted with a different western bituminous coal, at a coal blend ratio of approximately 84% PRB and 16% western bituminous. The new western bituminous coal appeared to enter the boiler around 7:00 a.m. on March 7. During this transition, total coal flow into the boiler decreased while the gross generation increased. This is likely due to the higher heating value of the western bituminous coal.

Coal samples were collected at the mine and sent to ADA-ES. A composite sample was sent to an outside lab for analysis and to help calculate an expected coal quality for the blended coal.

A few hours prior to the second coal blend test, the total vapor-phase mercury removal across the system was approximately 22%. This is higher than during baseline testing and may be attributed to the residual effects of sorbent injection conducted before the coal blending tests. During coal blend tests, total vapor-phase mercury removal efficiency increased up to 30%, indicating a slight improvement in mercury removal with coal blending.

Sorbent Injection Testing

Sorbent injection tests began on February 28, 2005. Two sorbents were evaluated at Laramie River: the non-treated benchmark sorbent, DARCO[®] Hg, and the bromine-treated sorbent, DARCO[®] Hg-LH.

The vapor-phase mercury removal efficiency with DARCO[®] Hg appeared to be limited to nominally 50% at injection concentrations up to 6.2 lb/MMacf. Data from other cold-side ESP sites burning low-rank coals (PRB or North Dakota lignite) also show limitations in mercury capture when injecting DARCO[®] Hg, as shown in Figure 8. Halogens, such as HCl, must be present for effective mercury capture by untreated activated carbon. It is speculated that activated carbon injection rates of 3 to 10 lb/MMacf are sufficient to absorb the available halogens so that subsequent increases in injection rates are ineffective.

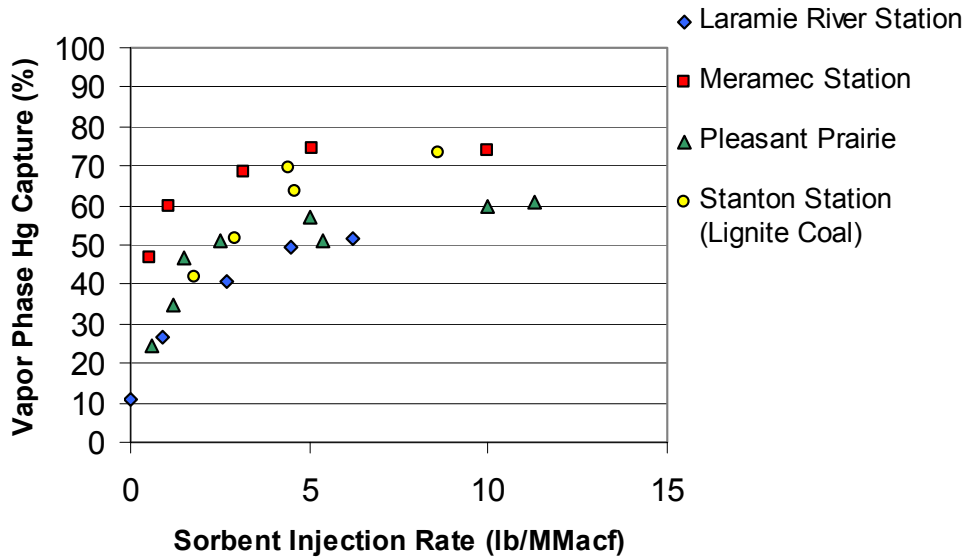


Figure 8. Summary of DARCO[®] Hg Results on Cold-Side ESPs.

When the halogen concentration in the flue gas is low, an activated carbon treated with a halogen can be used for higher mercury capture. When DARCO[®] Hg-LH sorbent was injected upstream of the SDA, 79% mercury removal was achieved at an injection concentration of 2.7 lb/MMacf, and 92% removal was achieved at 4.5 lb/MMacf. The results of DARCO[®] Hg and DARCO[®] Hg-LH sorbent injection are presented in Figure 9.

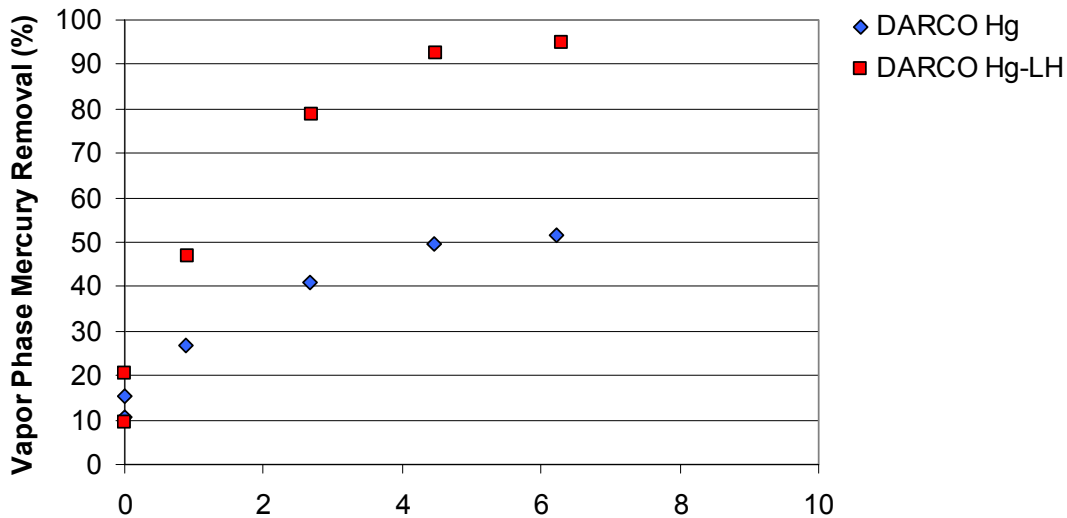


Figure 9. Results from Sorbent Injection Tests at Laramie River.

The in-situ fly ash sampler was used to evaluate in-flight mercury capture (by measuring mercury that ended up in the particulate phase). At baseline conditions (no sorbent injection), the particulate-phase mercury was found to be less than 10% of the total mercury present at the inlet of the SDA. At sorbent injection concentrations of up to 6.3 lb/MMacf, a vapor-phase mercury removal rate of up to 40% was measured for DARCO[®] Hg and DARCO[®] Hg-LH.

Coal Additive Testing

Another option for introducing halogens into the flue gas stream is to treat the coal before it enters the boiler rather than injecting treated carbons. The coal additive tested was KNX, a proprietary mercury control technology from ALSTOM Power.

Unit 3 is equipped with a wall-fired boiler fed by seven coal feeders. KNX was applied to the coal at feeders 3B and 3C, which supply the lower burner elevations on each side of the boiler. At this chemical injection location, the treated coal reached the burner within seconds. The KNX additive was applied to the coal at injection rates up to 2.7 gph.

Prior to the start of KNX testing, the fraction of oxidized mercury at the SDA inlet was 2.4%. Injecting the KNX additive onto the coal at a rate of 0.7 gph resulted in a 2% increase in oxidized mercury at the SDA inlet. It should be noted that due to the pump's flow capacity, chemical flow less than 1 gph was unsteady and may have slightly deviated from the target set point. Increasing the KNX flow rate to 2.7 gph resulted in a 14% increase in speciation from baseline levels at the SDA inlet. Mercury speciation data from KNX testing are presented in Figure 10.

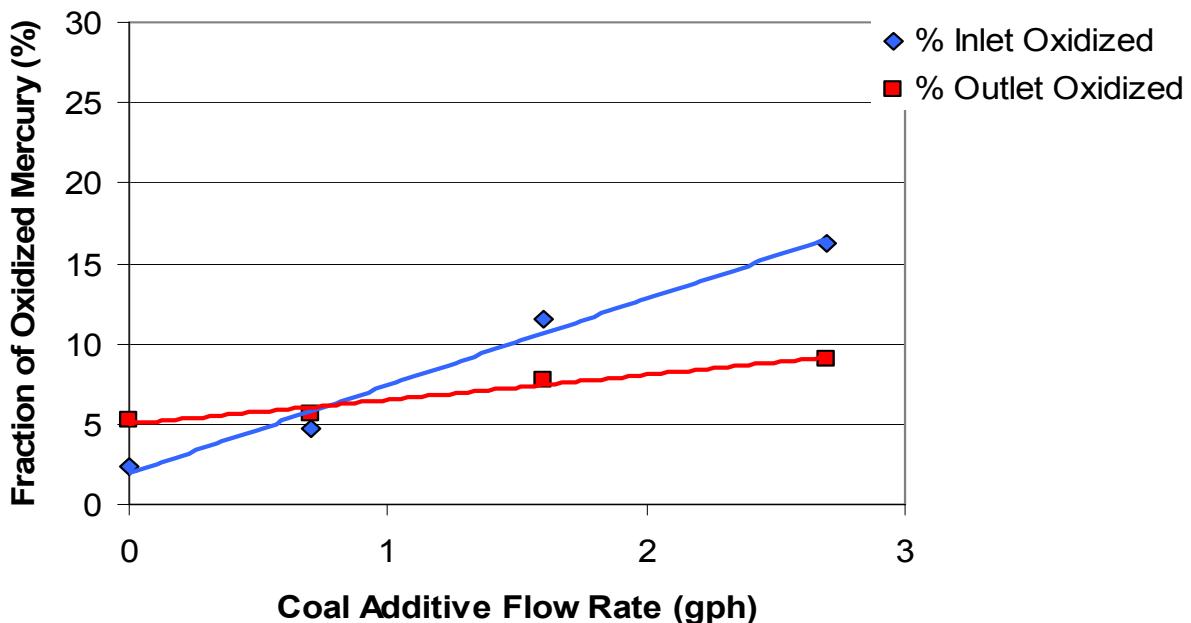


Figure 10. Mercury Speciation Results during KNX Testing.

Although the fraction of oxidized mercury at the inlet of the SDA increased, mercury removal across the system was limited to less than 20%, and the fraction of oxidized mercury at the outlet of the ESP was lower than at the SDA inlet. These data suggest that either the KNX addition resulted in a sampling artifact that biased the elemental mercury measurement at the SDA inlet, or the SDA-ESP configuration was reducing oxidized mercury back to the elemental form. This same phenomenon has been seen on other PRB/SDA units during KNX testing.

The final day of KNX testing included the injection of the DARCO[®] Hg sorbent at the SDA inlet at 4.5 lb/MMacf in conjunction with KNX addition at 1.6 gph. The resulting total mercury capture across the system was 94% compared to 50% with DARCO[®] Hg alone (no KNX). These data, shown in Figure 11, clearly indicate the improved performance of DARCO[®] Hg when halogens are added to the flue gas stream.

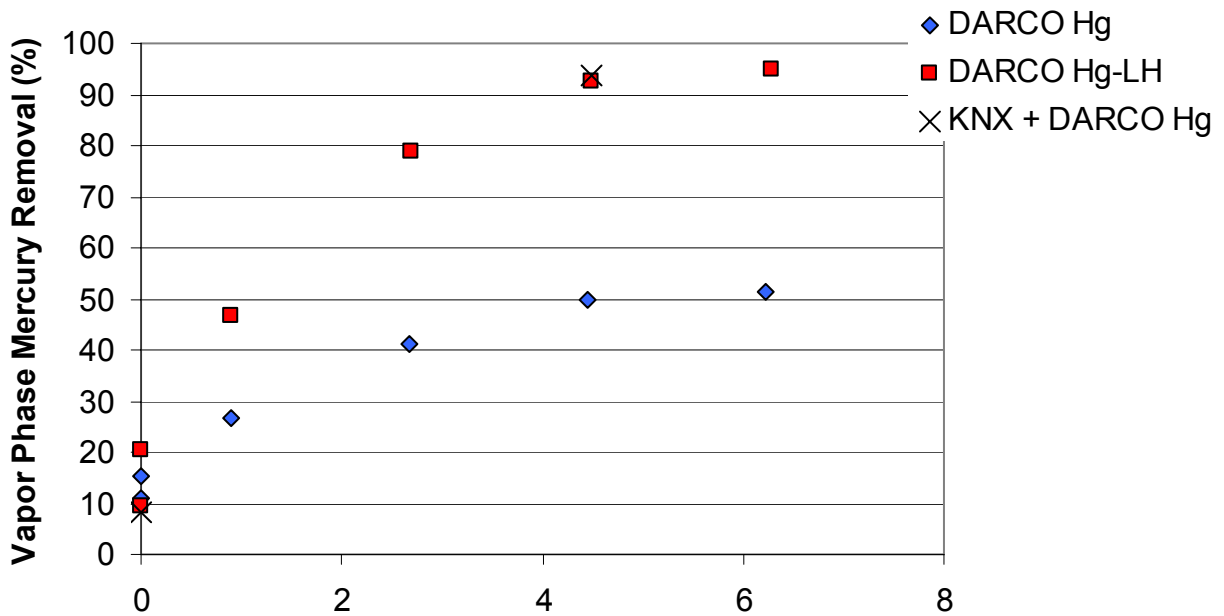


Figure 11. Impact of Coal Additive on DARCO[®] Hg Performance.

CONCLUSIONS

Field-testing has been completed at Holcomb, Meramec, and Laramie River Station. Results from Holcomb, Meramec, and Laramie River provide information about options for mercury control at plants firing PRB coals. Options evaluated include coal-blending, introduction of additives onto the coal, and sorbent injection. General conclusions and observations from these tests include:

Coal Blending

- Testing at Laramie River Station (SDA + ESP) indicates no significant increase in mercury removal was achieved with two different western bituminous coals at blend ratios up to 80/20 (PRB/bituminous).
- Up to 80% mercury removal was achieved during short-term testing at Holcomb (SDA + FF) at blend ratios up to 76/14 (PRB/bituminous).
- Additional tests are required to confirm this result.
- Blending tests are planned at Monroe (ESP).

Coal Additives

- >80% mercury removal was achieved at Holcomb and Laramie River using a combination of DARCO[®] Hg injection and coal additive.
- >80% removal was achieved at Meramec without carbon injection (plant configuration and high LOI may have contributed to removal).

Treated Activated Carbon Injection (DARCO[®] Hg-LH)

- High removal (>90%) was achieved at Holcomb and Meramec during the long-term test periods and at Holcomb, Meramec, and Laramie River during parametric testing (no long-term tests were conducted at Laramie River).
- No adverse balance-of-plant impacts were noted at either site.
- Treated sorbents will be considered for testing at the remaining test sites.

Other Balance-of-Plant Concerns

- SGLP analyses from ash collected during the long-term test periods at Holcomb and Meramec were below the detection limit for mercury. Historical data suggest that no measurable mercury will leach from collected ash.
- Flue-gas bromine measurements were made at Holcomb and Meramec during long-term testing of DARCO[®] Hg-LH. No levels of bromine in excess of those expected for plants firing PRB coals were measured.

- Trace amounts of activated carbon can be detrimental to ash quality for cement use. Options to protect ash for sales include TOXECON™ and TOXECON II™. TOXECON II™ tests are scheduled to begin in the fall of 2005 on a separate DOE contract.

Specific Conclusions and Observations from Testing at Laramie River include:

- Two technologies were demonstrated to enhance the performance of standard activated carbon:
 1. Chemical Addition to the Coal: Mercury removal of 94% was measured at a carbon feed rate of 4.5 lb/MMacf and a KNX injection rate of 1.6 gph. (KNX is a proprietary chemical developed by ALSTOM Power.)
 2. Chemically Enhanced Sorbent: Mercury removal in excess of 90% was achieved at DARCO® Hg-LH injection concentrations of 4.5 lb/MMacf. (DARCO® Hg-LH is a proprietary product of NORIT Americas.)
- Co-firing PRB and up to 20% western bituminous coals was ineffective at significantly increasing the native mercury capture. Two different western bituminous coals were evaluated. No change in the baseline mercury removal was noted with the first western bituminous coal tested, and the increase in mercury capture was limited to 10% with the second western bituminous coal.
- No measurable increase in stack opacity was observed during parametric testing.
- No change in ESP operating performance was noted as a result of parametric testing.

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