

**EVALUATION OF SORBENT INJECTION  
FOR MERCURY CONTROL**

**Topical Report for:  
Basin Electric Power Cooperative's  
Laramie River Station  
Reporting Period: October 1, 2003 – December 31, 2005**

**Principal Author:  
Sharon Sjostrom**

**January 16, 2006**

**U.S. DOE Cooperative Agreement No. DE-FC26-03NT41986  
Topical Report No. 41986R11**

**Submitted by:  
ADA-ES, Inc.  
8100 SouthPark Way, Unit B  
Littleton, CO 80120  
(303) 734-1727**

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## ACKNOWLEDGMENTS

This project was made possible through the generous funding of the Department of Energy's National Energy Technology Laboratory and industry partners including ADA-ES, Inc., Arch Coal, Associated Electric Coop, City of Sikeston, Empire District Electric Company, EPRI, Kansas City Board of Public Utilities (KCKBPU), Kansas City Power and Light, Missouri Basin Power Project, Nebraska Public Power District, NORIT Americas, PacifiCorp, Southern Minnesota Municipal Power Agency, Sunflower Electric Power Corporation, Tri-State Generation and Transmission Association, Inc., TransAlta Utilities, TransAlta Energy, Westar Energy, Western Fuels Association, and Wisconsin Public Service.

Andrew O'Palko was the project manager for DOE/NETL. Bob Boettcher provided project management for Missouri Basin Power Project and Myron Singleton was the project engineer for Laramie River Station. The team gratefully acknowledges their efforts and the support of the staff at Laramie River Station. Ramsay Chang was a key technical advisor and provided project management for EPRI. The project manager for ADA-ES was Sharon Sjostrom. The on-site test team was led by Travis Starns, the site manager for ADA-ES. Jerry Amrhein provided quality control and oversight for mercury measurements. Cody Wilson was the Project Engineer for ADA-ES. The test team included Brian Donnelly, Chad Sapp, and Erik Zipp from ADA-ES. Apogee Scientific provided mercury measurements using their SCEMS operated by Rick Slye, Trevor Ley, Kevin Fisher, Tim Ebner, and Ben Ecktenkamp. Connie Senior from Reaction Engineering International led the coal and byproduct analysis effort. Jean Bustard, Mike Durham, and Cam Martin from ADA-ES provided key technical input into the project. Richard Schlager managed the contracts and Cindy Larson edited and assembled all technical reports.

## ABSTRACT

The power industry in the U.S. is faced with meeting new regulations to reduce the emissions of mercury compounds from coal-fired plants. These regulations are directed at the existing fleet of nearly 1,100 boilers. These plants are relatively old with an average age of over 40 years. Although most of these units are capable of operating for many additional years, there is a desire to minimize large capital expenditures because of the reduced (and unknown) remaining life of the plant to amortize the project. Injecting a sorbent such as powdered activated carbon into the flue gas represents one of the simplest and most mature approaches to controlling mercury emissions from coal-fired boilers.

This is the final site report for tests conducted at Laramie River Station Unit 3, one of five sites evaluated in this DOE/NETL program. The overall objective of the test program is to evaluate the capabilities of activated carbon injection at five plants: Sunflower Electric's Holcomb Station Unit 1, AmerenUE's Meramec Station Unit 2, Missouri Basin Power Project's Laramie River Station Unit 3, Detroit Edison's Monroe Power Plant Unit 4, and AEP's Conesville Station Unit 6. These plants have configurations that together represent 78% of the existing coal-fired generation plants.

The goals for the program established by DOE/NETL are to reduce the uncontrolled mercury emissions by 50 to 70% at a cost 25 to 50% lower than the benchmark established by DOE of \$60,000/lb mercury removed. The goals of the program were exceeded at Laramie River Station by achieving over 90% mercury removal at a sorbent cost of \$3,980/lb (\$660/oz) mercury removed for a coal mercury content of 7.9 lb/TBtu.

# TABLE OF CONTENTS

<b>DISCLAIMER</b> .....	<b>i</b>
<b>ACKNOWLEDGMENTS</b> .....	<b>ii</b>
<b>ABSTRACT</b> .....	<b>iii</b>
<b>INTRODUCTION</b> .....	<b>1</b>
<b>EXECUTIVE SUMMARY</b> .....	<b>2</b>
<b>DESCRIPTION OF OVERALL PROGRAM</b> .....	<b>3</b>
<b>LARAMIE RIVER PROJECT OBJECTIVES AND TECHNICAL APPROACH</b> .....	<b>6</b>
<b>Importance of Testing at Laramie River Station</b> .....	<b>6</b>
<b>Laramie River Station Unit 3 Site Description</b> .....	<b>7</b>
<b>Equipment Descriptions</b> .....	<b>9</b>
<b>Portable Sorbent Injection System</b> .....	<b>9</b>
<b>Mercury Monitoring</b> .....	<b>10</b>
<b>In-Situ Fly Ash Sampling Device</b> .....	<b>13</b>
<b>Description of Field Testing Tasks</b> .....	<b>14</b>
<b>Sorbent Selection</b> .....	<b>14</b>
<b>Sample and Data Coordination</b> .....	<b>15</b>
<b>Baseline Testing</b> .....	<b>18</b>
<b>Parametric Testing</b> .....	<b>18</b>
<b>RESULTS</b> .....	<b>20</b>
<b>Baseline Testing</b> .....	<b>20</b>
<b>Parametric Test Results</b> .....	<b>21</b>
<b>Coal Blending Results</b> .....	<b>21</b>
<b>Activated Carbon Injection</b> .....	<b>23</b>
<b>Coal Additive With and Without Activated Carbon Injection</b> .....	<b>27</b>
<b>BALANCE-OF-PLANT IMPACTS</b> .....	<b>30</b>
<b>COAL AND BYPRODUCT EVALUATION</b> .....	<b>32</b>
<b>Stability of Mercury on Ash</b> .....	<b>35</b>
<b>ECONOMICS</b> .....	<b>39</b>
<b>CONCLUSIONS</b> .....	<b>40</b>
<b>REFERENCES</b> .....	<b>41</b>
<b>ACRONYMS AND ABBREVIATIONS</b> .....	<b>42</b>

## LIST OF TABLES

<b>Table 1. Host Site Key Descriptive Information.</b>	<b>4</b>
<b>Table 2. Field-Testing Schedule.</b>	<b>4</b>
<b>Table 3. Laramie River Key Operating Parameters.</b>	<b>8</b>
<b>Table 4. Ontario Hydro Mercury Measurements 02/11/03.</b>	<b>8</b>
<b>Table 5. Data Collected during Field Testing.</b>	<b>16</b>
<b>Table 6. Sample Collection Schedule.</b>	<b>17</b>
<b>Table 7. Full-Scale Test Sequence Completed at Laramie River Station Unit 3.</b>	<b>19</b>
<b>Table 8. Mercury Measurements during Baseline Testing (corrected to 3% O<sub>2</sub>).</b>	<b>20</b>
<b>Table 9. Results from Coal Blend #1 Test on 02/26/2005 (corrected to 3% O<sub>2</sub>).</b>	<b>21</b>
<b>Table 10. Results from Western Bituminous #1 Coal Analysis (dry basis).</b>	<b>22</b>
<b>Table 11. Results from Coal Blend #2 Test on 03/07/2005 (corrected to 3% O<sub>2</sub>).</b>	<b>22</b>
<b>Table 12. Results from Western Bituminous #2 Coal Analysis.</b>	<b>23</b>
<b>Table 13. Mercury Concentrations during Sorbent Injection Testing at Laramie River (corrected to 3% O<sub>2</sub>).</b>	<b>26</b>
<b>Table 14. Comparison of SCEM and STM Measurements.</b>	<b>27</b>
<b>Table 15. Mercury Results for In-Situ and Inlet Hopper Ash Samples Collected during Mercury Control Evaluation Upstream of the SDA</b>	<b>34</b>
<b>Table 16. LOI Measured in In-Situ Ash Samples.</b>	<b>35</b>
<b>Table 17. Results of Sequential Extraction tests on Laramie River and Holcomb Fly Ash Samples.</b>	<b>38</b>

## LIST OF FIGURES

Figure 1. Plan Sketch of Laramie River Unit 3.....	7
Figure 2. Sketch of Flue Gas Flow from APH to Stack at Laramie River Unit 3.....	8
Figure 3. PortaPAC™ Injection System Installed at Laramie River. ....	9
Figure 4. Sorbent Injection Grid.....	10
Figure 5. Mercury Monitor Installed at the Air Preheater Outlet.....	11
Figure 6. Sketch of Sorbent Trap.....	12
Figure 7. Sketch of STM Sampling Console.....	13
Figure 8. In-Situ Fly Ash Sampling Device. ....	14
Figure 9. Full-Scale Mercury Control Results for DARCO® Hg-LH. ....	15
Figure 10. Sketch showing One-Half of Unit 3 ESP Hoppers.....	18
Figure 11. Summary of DARCO® Hg Results on Cold-Side ESPs.....	24
Figure 12. Results from Sorbent Injection Tests at Laramie River.....	25
Figure 13. Mercury Speciation Results during KNX Testing.....	28
Figure 14. Impact of KNX Coal Additive on DARCO® Hg Performance.....	29
Figure 15. Stack Emissions during Mercury Control Testing at Laramie River. ....	30
Figure 16. ESP Electrical Conditions (Test-Side) during Mercury Control Tests. ....	31
Figure 17. Mercury Concentrations in Test-Side (Hopper 3A1C) and Control-Side (Hopper 3A1B) Inlet Hoppers.....	32
Figure 18. Comparison of Mercury Removal based on Ash Samples and SCEM Measurements .....	33
Figure 19. Mercury Concentration in Ash across Unit 3 ESP (Test Lane). ....	35
Figure 20. Thermal Desorption Profiles of Laramie River and Holcomb Baseline Ash Samples.....	36
Figure 21. Reference Thermal Desorption Profiles for HgCl <sub>2</sub> and HgS .....	37
Figure 22. Thermal Desorption Profiles of Laramie River and Holcomb Ash Samples.....	37
Figure 23. Mercury Leaching Characteristics of Select Ash Samples.....	38

## **INTRODUCTION**

Mercury control on a unit configured with a spray dryer absorber (SDA) followed by an electrostatic precipitator (ESP) has not been evaluated at full-scale by DOE or EPRI. Available data indicate that this configuration demonstrates particularly low native mercury removal and, based upon performance at units with SDAs and fabric filters (FF), the effectiveness of non-chemically treated activated carbon is expected to be limited.

ADA-ES, Inc., with support from the Department of Energy's National Energy Technology Laboratory (DOE/NETL) and industry partners, conducted a full-scale field test of mercury control using sorbent injection into the SDA + ESP at Basin Electric Power Cooperative's 550-MW Laramie River Station. This report presents results from testing including the effect on mercury emissions of 1) blending PRB coal with western bituminous coal, 2) injecting chemical additives onto the coal, and 3) injecting alternative sorbents specifically designed to operate in a halogen-deficient flue gas.

## EXECUTIVE SUMMARY

The test program at Laramie River Station was designed to provide a full-scale evaluation of different technologies that can overcome the limited mercury removal achievable with native fly ash or standard activated carbon at units configured with spray dryers and electrostatic precipitators. Each technology was based on supplementing certain halogens that were not available in sufficient quantities in Powder River Basin coals.

The program was very successful in that two different technologies were identified that have the potential to produce high levels (>80%) of mercury removal in this difficult application. These technologies are as follows:

1. Chemical Addition to the Coal: KNX, a proprietary bromine-containing chemical developed by ALSTOM Power, was found to enhance the performance of a standard activated carbon. 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 (0.005 gal/ton coal) during short-term parametric testing. Baseline mercury removal prior to KNX addition was 0%.
2. Chemically Enhanced Sorbent: A bromine-treated activated carbon available through NORIT Americas, DARCO® Hg-LH, resulted in mercury removal in excess of 90% at injection concentrations of 4.5 lb/MMacf during short-term parametric tests. Baseline mercury removal prior to DARCO® Hg-LH injection was 0%. For coal with a mercury content of 7.9 lb/TBtu, 90% removal would result in mass emissions of 0.8 lb/TBtu (805 oz/yr).

Because the Laramie River Station has the capability to fire a blended coal, two western bituminous coals were tested to evaluate their effectiveness in altering native mercury behavior. During both tests, adjusting the blend ratio did not appear to alter mercury speciation at any point in the system and mercury removal efficiencies were at or near their respective baseline levels. The goals for the program established by DOE/NETL were to reduce the uncontrolled mercury emissions by 50 to 70% at a cost 25 to 50% below the target of \$60,000/lb mercury removed. The goals of the program were exceeded by achieving 90+% mercury removal at a sorbent cost of \$3,980/lb (\$660/oz) mercury removed for coal with a mercury concentration of 7.9 lb/TBtu.

## DESCRIPTION OF OVERALL PROGRAM

This test program is part of a five-site program to obtain the necessary information to assess the feasibility and costs of controlling mercury from coal-fired utility plants. Sorbent injection for mercury control was successfully evaluated in DOE/NETL's Phase I tests at scales up to 150 MW, on plants burning subbituminous and bituminous coals and with electrostatic precipitators (ESPs) and fabric filters (FFs). During the Phase I project, several issues were identified that still needed to be addressed, such as evaluating performance on other configurations, optimizing sorbent usage (costs), and gathering longer-term operating data to address concerns about the impact of activated carbon on plant equipment and operations.

The overall objective of this test program is to evaluate the capabilities of activated carbon injection (ACI) at five plants with configurations that together represent 78% of the existing coal-fired generation plants in the U.S. Host sites that will be tested as part of this program are shown in Table 1. Table 2 shows the schedule for testing at the five sites.

The technical approach followed during this program allows the team to 1) effectively evaluate activated carbon and other viable sorbents on a variety of coals and plant configurations, and 2) perform long-term testing at the optimum conditions for at least one month at four of the five test sites. These technical objectives are accomplished by following the series of technical tasks listed below. These tasks are repeated for each test site.

1. Host site kickoff meeting, test plan, and sorbent selection
2. Design and installation of site-specific equipment
3. Field tests
4. Data analysis
5. Sample evaluation
6. Economic analysis
7. Reporting and technology transfer

**Table 1. Host Site Key Descriptive Information.**

	<b>Holcomb</b>	<b>Meramec</b>	<b>Laramie River</b>	<b>Monroe</b>	<b>Conesville</b>
Test Period	3/04–8/04	8/04–11/04	2/05–3/05	3/05–6/05	3/06–6/06
Unit	1	2	3	4	6
Size (MW)	360	140	550	785	400
Coal	PRB	PRB	PRB	PRB/Bit blend	Bituminous
Particulate Control	Joy Western Fabric Filter	American Air Filter ESP	ESP	ESP	Research-Cottrell ESP
SCA (ft <sup>2</sup> /kacfm)	NA	320	599	258	301
Sulfur Control	Spray Dryer Niro Joy Western	Compliance Coal	Spray Dryer	Coal Blending	Wet Lime FGD
Ash Reuse	Disposal	Sold for concrete	Disposal	Disposal	FGD Sludge Stabilization
Test Portion (MWe)	180 and 360	70	140	196	400
Typical Inlet Mercury (µg/dNm <sup>3</sup> )	10–12	10–12	10–12	8–10	15.8
Typical Mercury Removal	0–13%	0–30%	<20%	10–35%	50%

**Table 2. Field-Testing Schedule.**

Site	2004				2005					
	May	Jul	Sep	Nov	Jan	Mar	May	Jul	Sep	Nov
Holcomb	█									
Meramec			█							
Laramie River						█				
Monroe							█			
Conesville Spring '06										

There are more than 100 individual team members from 33 organizations participating in this five-site program. Co-funding for testing at Sunflower's Holcomb Station was provided by a subset of the participants. The organizations providing co-funding for tests at Laramie River include:

- ADA-ES, Inc.
- Arch Coal
- Associated Electric Coop
- City of Sikeston
- Empire District Electric Company
- EPRI
- Kansas City Board of Public Utilities (KCKBPU)
- Kansas City Power and Light
- Kennecott Coal
- Missouri Basin Power Project
- Nebraska Public Power District
- NORIT Americas Inc.
- PacifiCorp
- Peabody Coal
- Southern Minnesota Municipal Power Agency
- Sunflower Electric Power Corporation
- Tri-State Generation and Transmission Association, Inc.
- TransAlta Utilities
- TransAlta Energy
- Westar Energy
- Western Fuels Association
- Wisconsin Public Service

Key members of the test team include:

- Laramie River Station
  - Bob Boetcher
  - Myron Singleton
- ADA-ES, Inc.
  - Project Manager: Sharon Sjostrom
  - Site Manager: Travis Starns
  - Project Engineer: Cody Wilson
  - SCEM Lead: Jerry Amrhein
- Apogee Scientific
  - SCEM Measurements
- EPRI
  - Project Manager: Ramsay Chang
- Reaction Engineering International
  - Coal and Byproduct Analysis Interpretation: Connie Senior
- Others
  - Analytical laboratories
  - (SGS, Microbeam, Hawk Mountain Lab, Frontier GeoSciences Inc.)

# LARAMIE RIVER PROJECT OBJECTIVES AND TECHNICAL APPROACH

The primary objective of this project was to determine the cost and effects of sorbent injection for control of mercury in stack emissions at Missouri Basin Power Project's Laramie River Station Unit 3. The general technical approach to meet the objective is defined by a series of field tasks, as listed below.

1. Sorbent selection
2. Sample and data coordination
3. Baseline tests
4. Parametric tests

Parametric test conditions were chosen to meet an overall objective of identifying options to enhance mercury removal for units firing subbituminous PRB coal and configured with SDA and ESP. Options included coal blending with western bituminous coal, injecting activated carbon into the SDA, and introducing chemical additives onto the coal. The evaluation was conducted on one-quarter of the 550-MW flue gas stream.

## Importance of Testing at Laramie River Station

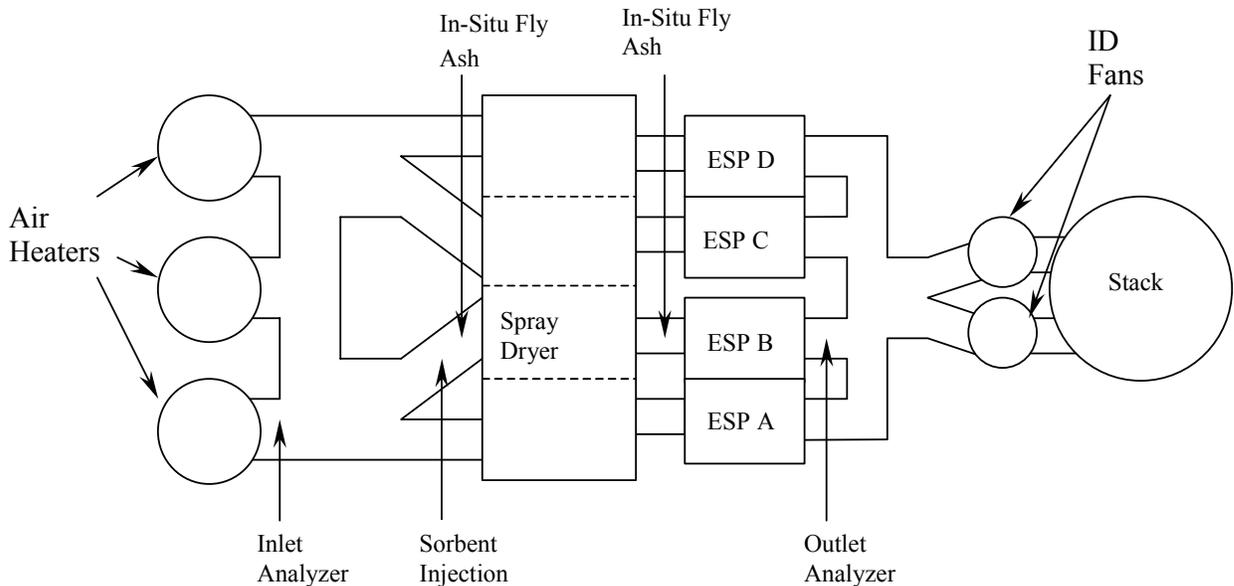
Mercury control on a unit configured with an SDA + ESP has not been evaluated at full-scale by DOE or EPRI. Because of interest in test results by industry partners on this project and support from DOE and EPRI, the effectiveness of ACI, coal blending, and coal additives for mercury control were evaluated at Laramie River Station Unit 3. Results from other sites, including Holcomb Station and Meramec Station, which were tested under this DOE program, provided insight into the potential of three technologies at Laramie River. Both Holcomb and Meramec fire PRB coal. Holcomb is configured with an SDA and FF and Meramec is configured with a cold-side ESP. Key results from Holcomb and Meramec included<sup>1,2</sup>:

- Coal Blending:
  - By blending western bituminous coal with PRB coal at Holcomb Station, the mercury removal was 50% when firing a 7.5% western bituminous PRB blend, and 80% when firing a 15% western bituminous PRB blend.
- Chemical Addition to the Coal:
  - KNX, a proprietary bromine-containing chemical developed by ALSTOM Power, was found to enhance the performance of a standard activated carbon. Mercury removal of >80% was measured at Holcomb with a carbon injection concentration of just 1.0 lb/MMacf.
  - Using either KNX or SEA2, a proprietary chemical being developed by the University of North Dakota Energy and Environmental Research Center (EERC), >80% removal was achieved at Meramec without carbon injection.

- Chemically Enhanced Sorbent:
  - Bromine-treated activated carbon available through NORIT Americas Inc., DARCO<sup>®</sup> Hg-LH, resulted in mercury removal in excess of 90% during long-term tests at Holcomb with a carbon injection concentration of 1.2 lb/MMacf. Throughout long-term testing, the average outlet mercury emission was less than 1 lb/TBtu.
  - High removal (>90%) achieved at Meramec during the long-term test periods with DARCO<sup>®</sup> Hg-LH. The average outlet mercury emission was 0.44 lb/TBtu at an average sorbent injection concentration of 3.3 lb/MMacf.

## Laramie River Station Unit 3 Site Description

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 U.S. Laramie River Station, which is operated by Basin Electric Power Cooperative, has three units, each with 550 MW of generating capacity. The test unit (Unit 3) utilizes an SDA + ESP for air pollution control. During sorbent injection testing with injection upstream of the SDA, only one-quarter of the 550-MW flue gas stream was treated, nominally 138 MW. Figure 1 is a plan sketch of the plant showing the portion of the unit that was tested. An elevation sketch showing flue gas flow from the air preheater (APH) to the stack on Unit 3 is shown in Figure 2. Key operating parameters for Laramie River Unit 3 are shown in Table 3. As shown in Table 4, results from Ontario Hydro (OH) measurements collected in 2003 demonstrate that the native mercury removal was essentially zero.



**Figure 1. Plan Sketch of Laramie River Unit 3.**

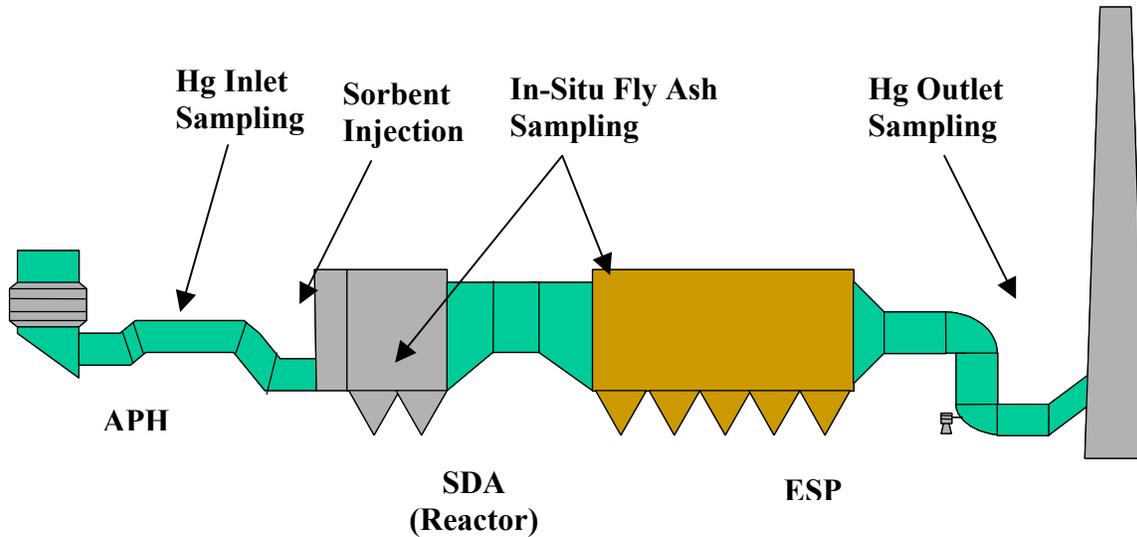


Figure 2. Sketch of Flue Gas Flow from APH to Stack at Laramie River Unit 3.

Table 3. Laramie River Key Operating Parameters.

Unit	3
Size (MW)	550
Test Portion (MWe)	~138
Coal	PRB Coal blending facilities available
Heating Value (as received)	8,467 Btu/lb
Sulfur (% by weight)	0.3-0.5
Chlorine ( $\mu\text{g/g}$ )	<35
Mercury ( $\mu\text{g/g}$ )	0.04 – 0.1
Particulate Control	Cold-Side ESP SCA = 599 ft <sup>2</sup> /kacfm
Sulfur Control	Spray Dryer
Ash Reuse	Disposed

Table 4. Ontario Hydro Mercury Measurements 02/11/03\*.

Location	Hg <sub>p</sub>	Hg <sup>++</sup>	Hg <sup>0</sup>	Total
SDA Inlet ( $\mu\text{g/Nm}^3$ )	1.0	1.1	7.4	9.5
ESP Outlet ( $\mu\text{g/Nm}^3$ )	0.2	0.2	9.2	9.6
% Removal				-1.1

\* Ontario Hydro measurements conducted by Western Research Institute.

## Equipment Descriptions

### Portable Sorbent Injection System

The NORIT PortaPAC™ is a dry injection system, which pneumatically conveys a predetermined and adjustable amount of powdered activated carbon (PAC) from bulk bags into the flue gas stream. The unit is portable, consisting of two eight-foot-tall sections, making shipping, set-up, and movement easy. PAC is metered into an eductor from a volumetric feeder. Air from an on-board blower transfers the carbon from the eductor to the final injection point. A series of interlocks control the operation of the unit and allow local and/or remote operation/monitoring of the system. The PortaPAC™ injection system, shown installed at Laramie River in Figure 3, has the capability of delivering up to 350 lb/hr of activated carbon to the injection location. Flexible hose carries the sorbent from the feeders to distribution manifolds located at the injection location. Each manifold supplies up to six injectors.

The sorbent injection grid was installed approximately 65 feet upstream of the “B” reactor on the Unit 3 SDA at Laramie River. Six sorbent injection lances, shown in Figure 4, penetrated into the flue gas stream to deliver sorbent at various elevations in the duct.



**Figure 3. PortaPAC™ Injection System Installed at Laramie River.**



**Figure 4. Sorbent Injection Grid.**

### **Mercury Monitoring**

Two techniques were used to measure mercury during the program at Laramie River: semi-continuous mercury emission monitors (SCEM) and the sorbent trap method (STM). These techniques and the equipment required are presented below.

#### **Mercury Analyzers**

Two SCEMs, one at the air preheater outlet and one at the ESP outlet, were used to monitor the flue gas mercury concentrations and provided real-time feedback during baseline and sorbent injection testing. The mercury analyzers consisted of a cold-vapor atomic absorption spectrometer coupled with a gold amalgamation system. The system is calibrated using vapor-phase elemental mercury. An inertial separation probe was used to separate the particulate matter from the sample stream with minimal sampling artifacts from fly ash or injected sorbent. The SCEMs and probes used on this project were fabricated and provided by Apogee Scientific, Inc. A photograph of the mercury monitor installed at the air preheater outlet is shown in Figure 5.



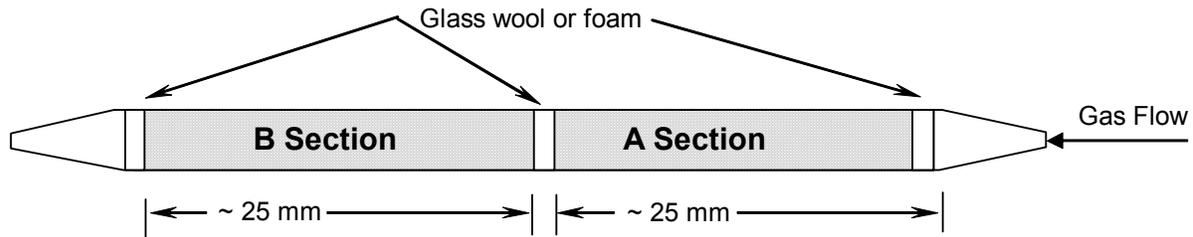
**Figure 5. Mercury Monitor Installed at the Air Preheater Outlet.**

The mercury analyzers are capable of measuring vapor-phase mercury in the elemental form. The SCEM system is configured to report both elemental and total vapor-phase mercury. Total vapor-phase mercury concentrations are determined by reducing all of the oxidized mercury to the elemental form near the extraction location. To measure elemental mercury, the oxidized mercury is removed while allowing elemental mercury to pass through without being altered.

#### **Dry Sorbent Trap Method Testing (STM)**

The dry sorbent trap method was proposed in the Utility Mercury Reduction Rule (FR January 30, 2004) as a draft EPA test method, *Method 324 Determination of Vapor Phase Flue Gas Mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling*. The method was proposed in the Utility Mercury Reduction Rule for application as either a reference method test or for continuous compliance measurement for mercury. ADA-ES has used the method in the field since the early 1990s, and conducted the validation testing for Method 324, in which it compared favorably with the OH Method. In the Clean Air Mercury Rule (CAMR) signed by the EPA Administrator on March 15, 2005, the proposed Method 324 was revised and renamed 40 CFR Part 75 Appendix K. The procedures used during these tests were consistent with the procedures used during validation testing of the new Method.

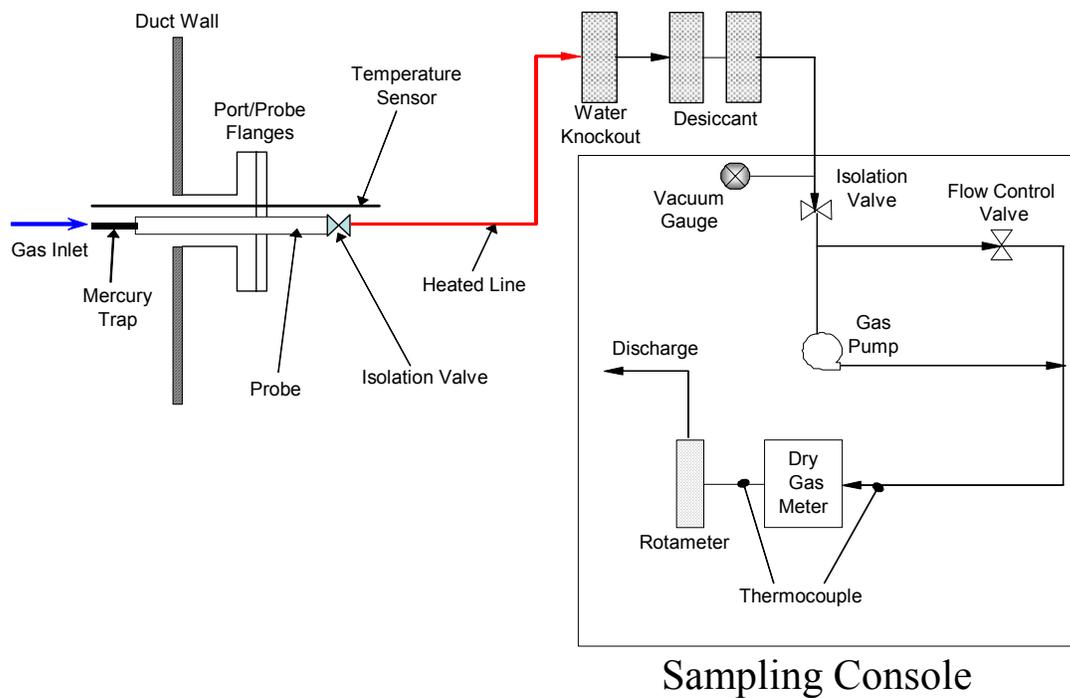
For this mercury measurement method, a known volume of flue gas is extracted from a duct through a dry sorbent trap (containing a specially treated form of activated carbon) as a single-point sample, with a nominal flow rate of about 400 cc/min at the gas meter. The dry sorbent trap, which is in the flue gas stream during testing, represents the entire mercury sample. Each trap is recovered in the field and shipped to a specialized lab such as Frontier GeoSciences Inc. for analysis. The contents of each trap are digested and the resulting solution is analyzed for mercury using cold-vapor atomic fluorescence spectrometry. A sketch of the trap is shown in Figure 6. Samples can be collected over time periods ranging from less than an hour to weeks in duration. The test result provides a time averaged total vapor-phase mercury measurement of the flue gas stream.



**Figure 6. Sketch of Sorbent Trap.**

During STM sampling, paired samples are typically collected as a quality control measure. The analysis results of the paired sample trains are compared and are typically in agreement within 5-20% relative percent difference (RPD) or about 1 lb/TBtu. Another built-in quality assurance measure is achieved through the analysis of two trap sections in series. Each trap has two separate mercury sorbent sections, as shown in the figure below, and the “B” section is analyzed to evaluate whether any mercury breakthrough occurred. Low B section mercury, in conjunction with a field blank trap, is used to confirm overall sample handling quality.

The sample train is fairly simple, as shown in Figure 7. Major components are a dry sorbent trap mounted directly on the end of a probe (usually heated), a moisture knockout outside the duct, and a sampling console that controls the sampling rate and meters the flue gas, as well as recording data in a data logger. Key temperatures, sampling volume, and barometric pressure are recorded on field sampling data sheets and/or by a data logger for each sample run.



**Figure 7. Sketch of STM Sampling Console.**

The STM directly measures mercury concentration in units of  $\mu\text{g}/\text{dNm}^3$ . Using stack gas flow rate and gaseous data from the plant's CEMs and coal Ultimate Analysis (or EPA Method 19 F-Factors if Ultimate Analysis is unavailable), results can be calculated and reported in lb/TBtu.

### **In-Situ Fly Ash Sampling Device**

In-situ fly ash samples were collected at the SDA and ESP inlets to determine the amount of mercury captured in-flight prior to entering the SDA and ESP. The in-situ fly ash sampling device consists of a PM 2.5 cyclone separator, venturi flow meter, and an eductor. The cyclone was designed to measure particulate emissions  $\geq 2.5$  microns using EPA method 201A. Operating the cyclone at higher than design flow rates, as was done at Laramie River, makes the cyclone more efficient in capturing particulate below the design cut diameter. The fly ash collected was analyzed for mercury content and used to calculate the particulate fraction of mercury in the flue gas. A photo of the cyclone used at Laramie River is shown in Figure 8.



**Figure 8. In-Situ Fly Ash Sampling Device.**

## **Description of Field Testing Tasks**

The field tests were accomplished through a series of four subtasks: 1) sorbent selection, 2) sample and data coordination, 3) baseline testing, and 4) parametric testing. The subtasks are independent from each other in that they each have specific goals and tests associated with them. A summary of each subtask is presented.

### **Sorbent Selection**

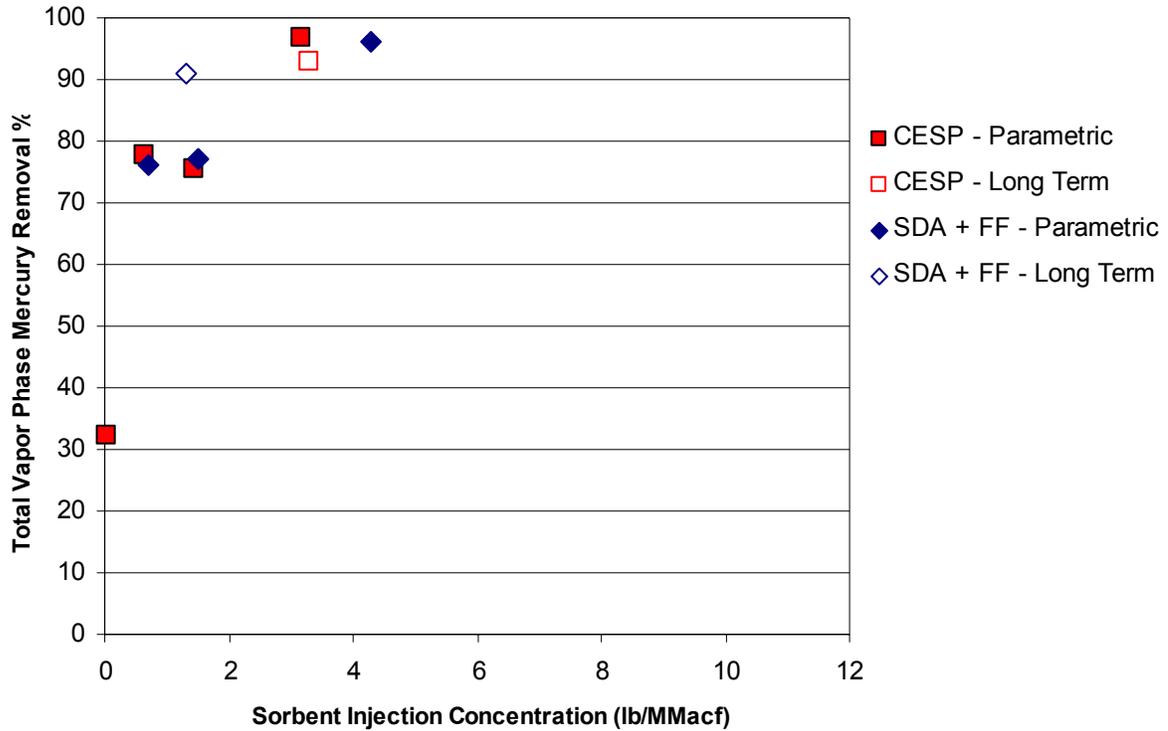
A key component of the planning process for this program is identifying potential sorbents for testing. At the onset of the testing period at Laramie River, the test team determined that no sorbents that were substantially different from materials tested at other PRB sites were available in quantities large enough for full-scale testing. Therefore, the sorbent selection process for full-scale parametric testing did not include sorbent screening.

Two sorbents were selected for testing at Laramie River Station, DARCO<sup>®</sup> Hg and DARCO<sup>®</sup> Hg-LH, both manufactured by NORIT Americas. Brief descriptions are shown below:

- DARCO<sup>®</sup> Hg
  - Derived from Texas lignite coal
  - Bulk density of 25–30 lb/ft<sup>3</sup>
  - *This sorbent has been tested in various lab, pilot, and full-scale mercury control demonstrations and is considered the benchmark for performance comparisons.*
- DARCO<sup>®</sup> Hg-LH
  - Derived from Texas lignite coal
  - Treated with bromine to improve effectiveness in low-halide environments

- Bulk density of 25–30 lb/ft<sup>3</sup>
- *This sorbent has shown mercury removal efficiencies greater than 90% at Holcomb Station (PRB fuel equipped with an SDA + FF) and Meramec (PRB fuel equipped with cold-side ESP).*

Results of DARCO<sup>®</sup> Hg and DARCO<sup>®</sup> Hg-LH testing from Holcomb and Meramec are shown in Figure 9.



**Figure 9. Full-Scale Mercury Control Results for DARCO<sup>®</sup> Hg-LH.**

### Sample and Data Coordination

Collecting, analyzing, and archiving samples and plant operating data is a key aspect of any field test program. An example of the data collected during testing at Laramie River is presented in Table 5. An example of samples and the data collection schedule is presented in Table 6.

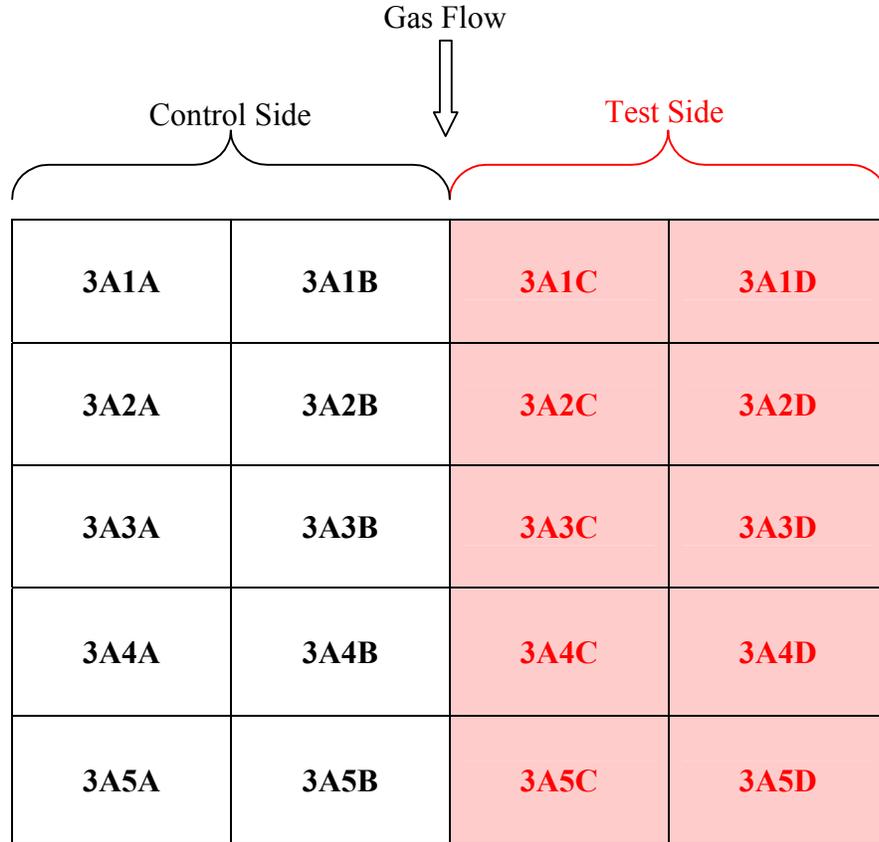
Grab samples of ash were collected from the ESP hoppers each day of testing and analyzed for mercury. A sketch of one of the ESPs with the row numbers is presented in Figure 10.

**Table 5. Data Collected during Field Testing.**

<b>Parameter</b>	<b>Sample/Signal/Test</b>	<b>Baseline</b>	<b>Parametric</b>
Coal	Batch sample	Yes	Yes
Coal	Plant signals: burn rate (lb/hr) quality (lb/MMBtu, % ash), coal blending data (blend ratios, etc.)	Yes	Yes
Fly Ash	Batch sample	Yes	Yes
Unit Operation	Plant signals: boiler load, etc.	Yes	Yes
Temperature	Plant signal at AH inlet, SDA inlet/outlet, Stack	Yes	Yes
Mercury (total and speciated)	Hg Monitors at SDA inlet and ESP outlet M324 (Manual)	Yes Yes	Yes Yes
Sorbent Injection Rate	lb/hr	No	Yes
Plant CEM Data (NO <sub>x</sub> , O <sub>2</sub> , SO <sub>2</sub> , CO)	Plant data – stack	Yes	Yes
Stack Opacity	Plant data – stack	Yes	Yes
ESP Data	Plant data – (Sec mA, Sec. Voltage, Sparks, etc.)	Yes	Yes
SDA Data	Plant data – (Slurry flow rate, fresh lime flow, recycle rate, SO <sub>2</sub> inlet/outlet concentrations if available)	Yes	Yes

**Table 6. Sample Collection Schedule.**

<b>Test Condition</b>	<b>Type</b>	<b>Frequency</b>	<b>Comments</b>
Baseline	Coal	Daily	One liter
	ESP Ash	Daily: A1B, 3A1C	One liter
		Special Sampling: One hopper per row on test side (3A1C – 3A5C)  One hopper from front field (3A1C)	One liter  Two 5-gallon samples
SDA Scrubber Slurry	One sample collected during baseline testing	One liter	
Parametric	Coal	Daily	One liter
	ESP Ash	Daily: 3A1B, 3A1C	One liter
		Special Sampling: One hopper from front field (3A1C)	One 5-gallon sample
SDA Scrubber Slurry	One sample collected during each week of parametric testing	One liter	



**Figure 10. Sketch showing One-Half of Unit 3 ESP Hoppers.**

### **Baseline Testing**

Baseline testing (no sorbent injection) was conducted for two days. During the baseline testing series, mercury measurements were made at the inlet of the SDA and the outlet of the ESP. These data were used to characterize native mercury capture across the SDA + ESP without sorbent injection. Unit operations were set at conditions expected during the parametric tests.

### **Parametric Testing**

Following baseline testing, a series of parametric tests was conducted to evaluate the performance of various mercury control technologies. These parametric tests were conducted at full-load conditions to document performance of sorbent injection, coal additive (with and without ACI), and coal blending for control of mercury in stack emissions. Mercury measurements were made during the parametric tests to characterize mercury capture across the SDA + ESP and compare each mercury control technology. The test matrix is shown in Table 7.

**Table 7. Full-Scale Test Sequence Completed at Laramie River Station Unit 3.**

Test Description	Start Date	Parameters/Comments	Boiler Load
Setup Baseline Parametric  Week 1	2/21/05	Day 1 – Setup PortaPAC™, Hg analyzers Day 2 – Setup PortaPAC™, Hg analyzers Day 3 – Setup PortaPAC™, Hg analyzers Day 4 – Start Baseline Testing, Hg analyzers operating, normal operating conditions, no ACI. Day 5 – Hg Analyzers operating, normal operating conditions, no ACI. Day 6 – Coal Blend (western bituminous #1)	Full Load 6 AM–6 PM
Parametric  Week 2	2/28/05	Day 1 – DARCO® Hg, 1–3 lb/MMacf Day 2 – DARCO® Hg, 5–7 lb/MMacf Day 3 – DARCO® Hg-LH, 1–3 lb/MMacf Day 4 – DARCO® Hg-LH, 5–7 lb/MMacf Day 5 – Coal Additive (KNX) without ACI Day 6 – Coal Additive (KNX) with ACI, sorbent injection (DARCO® Hg) at 5 lb/MMacf	Full Load 6 AM–6 PM
Parametric Week 3	3/07/05	Day 1 – Coal Blend (western bituminous #2) Day 2 – Decommission	Full Load 6 AM–6 PM

The first series of parametric tests were used to evaluate the effects of coal blending on mercury control and mercury speciation across the system. Two western bituminous coals were used during the blend tests. The western bituminous coal was loaded into a storage silo at Laramie River that is configured with a variable speed coal belt. PRB fuel was fed from an adjacent silo that uses a fixed-speed feed belt. Western bituminous coal was metered onto the belt carrying the PRB coal into the plant. The goal for both coal blending test periods was to test at two different blend ratios.

The second series of parametric tests was used to evaluate the effects of activated carbon injection and the potential mercury removal enhancements achievable by using bromine-treated activated carbon. The two sorbents, DARCO® Hg and DARCO® Hg-LH, were tested at various rates to achieve several levels of mercury control across the SDA + ESP.

During the final parametric test, a bromine-based coal additive was evaluated for its effect on mercury removal both by native fly ash and when injecting untreated activated carbon. The coal additive, KNX, was developed by ALSTOM Power. It was applied to the coal prior to entering the boiler. The same material was tested at both Holcomb and Meramec stations and demonstrated the ability to alter the mercury speciation at the air preheater exit. The KNX coal additive combined with DARCO® Hg injection demonstrated mercury removal efficiencies greater than 80% at both previous test sites.

KNX was applied directly on the coal at the 3B and 3C coal feeders. This point-of-entry allowed the additive to enter the lower levels of the boiler and provided sufficient residence time to disperse the additive evenly throughout the flue gas stream.

## RESULTS

### Baseline Testing

It is important to note that data from the SCEMs can be reported on a raw, uncorrected basis or corrected to 3% O<sub>2</sub> to account for air inleakage between the boiler and measurement location, depending on how it is being used. For example, if SCEM data are to be used to calculate mercury removal, it is important to correct the data to 3% O<sub>2</sub> before calculating removal. On the other hand, if SCEM data are being compared to OH data or STM data, then the uncorrected data will be used. In most cases throughout this report, both values will be presented.

Field-testing 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 24 hours/day firing 100% PRB coal. Average, uncorrected total mercury concentrations at the inlet to the spray dryer and the outlet of the ESP during this test were 9.5 and 8.4 µg/Nm<sup>3</sup>, respectively. The mercury concentrations, corrected to 3% O<sub>2</sub> to account for inleakage across the system, are presented in Table 8 and yield an average vapor-phase mercury removal efficiency of about 2%. These agree well with OH results conducted in February 2003 (Table 4). Secondary mercury measurements were made using the STM at the outlet of the ESP. A duplicate, simultaneous run was conducted and the results indicated 10.4 and 10.0 µg/Nm<sup>3</sup> compared to an uncorrected SCEM value during the STM run of 8.8 µg/Nm<sup>3</sup>. This is a difference of 16%, which is within the allowable range of error (20%) for these types of comparisons.

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” spray dryer reactor. The particulate sample was analyzed for mercury content and the particulate loading was estimated using coal analyses. The average particulate mercury concentration at the SDA inlet was 0.3 µg/Nm<sup>3</sup>.

**Table 8. Mercury Measurements during Baseline Testing (corrected to 3% O<sub>2</sub>).**

Location	Hg <sub>P</sub>	Hg <sup>++</sup>	Hg <sup>0</sup>	Total
SDA Inlet (µg/Nm <sup>3</sup> )	0.3	0.3	10.8	11.4
ESP Outlet (µg/Nm <sup>3</sup> )	NA*	0.9	10.0	10.9
% Removal				4.4

\* No particulate samples were collected at the outlet during testing. It is expected the contribution to the mercury loading will be low because the particulate loading should be very low.

During baseline testing, the total amount of mercury exiting the boiler, assuming no mercury was being removed inside the boiler, was approximately 0.057 lb/hr based on mercury concentrations measured with the SCEMs. Fly ash samples collected from the inlet field of the ESP had an average mercury concentration of 75 ng/g, which is equivalent to a mercury collection rate of 0.0045 lb/hr or an average mercury removal efficiency of 7.9%. This agrees with the removal efficiency measured with the SCEMs of 4.4%.

## Parametric Test Results

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

### Coal Blending Results

During the coal blending tests, two types of western bituminous coals were evaluated at blend ratios of 80% PRB to 20% western bituminous and 75% PRB to 25% western bituminous.

#### **Western Bituminous Coal #1: ColoWyo Coal**

While testing at the 80/20 blend ratio, mercury speciation and mercury removal across the system were similar to baseline measurements. Approximately 2% of the vapor phase mercury at the SDA inlet was oxidized and 8% was oxidized at the ESP outlet. The total vapor-phase mercury removal was insignificant. These data are summarized in Table 9. An in-situ ash sample collected during the 80/20 blend test indicates  $0.4 \mu\text{g}/\text{Nm}^3$  was present in the particulate phase at the inlet to the SDA. This is similar to the level measured with 100% PRB during baseline testing.

Mercury concentration measurements were also made via the STM during the 80/20 blend test. The results of the duplicate simultaneous test at the ESP outlet were 7.7 and 7.6  $\mu\text{g}/\text{Nm}^3$  as compared to an uncorrected SCEM concentration of  $8.9 \mu\text{g}/\text{Nm}^3$ . The difference is within the allowable range for mercury measurements. A coal sample collected from the coal feeder during the 80/20 test also indicated an expected concentration of  $9.5 \mu\text{g}/\text{Nm}^3$ , which agrees well with the SCEM data.

**Table 9. Results from Coal Blend #1 Test on 02/26/2005 (corrected to 3% O<sub>2</sub>)**

Test	Location	Hg <sup>++</sup>	Hg <sup>0</sup>	Total Gas-Phase
<b>Baseline 05:00–07:30</b>	SDA Inlet ( $\mu\text{g}/\text{Nm}^3$ )	0.2	11.0	11.2
	ESP Outlet ( $\mu\text{g}/\text{Nm}^3$ )	1.0	10.3	11.3
<b>Blend Ratio (80/20) 08:15–17:00</b>	SDA Inlet ( $\mu\text{g}/\text{Nm}^3$ )	0.2	11.4	11.6
	ESP Outlet ( $\mu\text{g}/\text{Nm}^3$ )	0.9	11.3	12.2
<b>Blend Ratio (75/25) 18:47–22:00</b>	SDA Inlet ( $\mu\text{g}/\text{Nm}^3$ )	0.2	9.8	10.0
	ESP Outlet ( $\mu\text{g}/\text{Nm}^3$ )	1.1	10.1	11.2

Coal samples were collected at the mine and sent to ADA-ES. A composite sample was sent to the lab for analysis to help calculate an expected coal quality for the blended coal. The expected heating value of the blended coal to enter the boiler during the 80/20 blend test was 12,152 Btu/lb (dry basis). A coal sample collected during the 80/20 test period had a measured heating value of 12,128 Btu/lb which results in a 0.2% difference between the blended and expected coal quality. Results from the coal analyses are presented in Table 10.

The estimated mercury concentration calculated from the mercury concentrations measured in the PRB and western bituminous coals at a blend ratio of 80/20 is 8.3  $\mu\text{g}/\text{Nm}^3$  at 3%  $\text{O}_2$ , which is 17 to 30% lower than the measured concentration in the flue gas of 10 to 12.2  $\mu\text{g}/\text{Nm}^3$ . It is sometimes difficult to get a tight correlation between coal and flue gas values when a single coal sample is used.

**Table 10. Results from Western Bituminous #1 Coal Analysis (dry basis).**

Sample Description	Date Collected	Btu/lb	% Sulfur	Hg (ng/g)	Cl ( $\mu\text{g}/\text{g}$ )
100% PRB	02/25/05	12,051	0.39	69.8	8
100% WBIT (Coal #1)	02/18/05– 02/21/05	12,555	0.37	8.4*	11
Blended Coal – ~80/20	02/26/05	12,128	0.42	85.3	14
Expected Coal Quality for Blended Coal (80/20)		12,152	0.39	74.3	8.6
% Difference (Blended/Calculated)		<b>0.2</b>	<b>-8.8</b>	<b>-48.3</b>	<b>-62.8</b>

\* Resubmitted for analysis to verify concentration—results pending.

### Western Bituminous Coal #2

The coal blend ratio for the second blend test was approximately 84% PRB to 16% western bituminous. This coal was from a separate western bituminous mine. A few hours prior to the coal #2 blend test, the total vapor-phase mercury removal across the system was approximately 12%. Blended coal appeared to enter the boiler around 07:00 hours on March 7. During the coal blend tests, total vapor-phase mercury removal efficiency did not increase above 18%. Average mercury concentrations for the two blend periods are presented in Table 11.

Mercury concentration measurements were also made via the STM during the 84/16 blend test. The results of the duplicate simultaneous test at the ESP outlet were 5.4 and 5.3  $\mu\text{g}/\text{Nm}^3$  as compared to an uncorrected SCEM concentration of 6.3  $\mu\text{g}/\text{Nm}^3$ . The difference is within the acceptable range.

**Table 11. Results from Coal Blend #2 Test on 03/07/2005 (corrected to 3%  $\text{O}_2$ ).**

Test	Location	$\text{Hg}^{++}$	$\text{Hg}^0$	Total Gas-Phase
<b>Baseline</b> <b>05:00–07:30</b>	SDA Inlet ( $\mu\text{g}/\text{Nm}^3$ )	0.6	10.5	11.1
	ESP Outlet ( $\mu\text{g}/\text{Nm}^3$ )	0.6	9.2	9.8
<b>Blend Ratio (84/16)</b> <b>07:20–15:45</b>	SDA Inlet ( $\mu\text{g}/\text{Nm}^3$ )	0.7	9.7	10.4
	ESP Outlet ( $\mu\text{g}/\text{Nm}^3$ )	0.5	8.2	8.7
<b>Blend Ratio (84/16)</b> <b>15:45–23:30</b>	SDA Inlet ( $\mu\text{g}/\text{Nm}^3$ )	0.8	9.0	9.8
	ESP Outlet ( $\mu\text{g}/\text{Nm}^3$ )	0.4	7.7	8.1

Coal samples were collected at the mine and sent to ADA-ES. A composite sample was sent to the lab for analysis to help calculate an expected coal quality for the blended coal. Results from the coal analysis are presented in Table 12. The mercury concentration estimated from the PRB and western bituminous samples blended at 84/16 indicated the expected concentration at the inlet to the SDA of 9.7  $\mu\text{g}/\text{Nm}^3$ , which is very close to the measured range of 9.8 to 10.4  $\mu\text{g}/\text{Nm}^3$  at 3%  $\text{O}_2$ .

**Table 12. Results from Western Bituminous #2 Coal Analysis.**

Sample Description	Date Collected	Btu/lb	% Sulfur	Hg (ng/g)	Cl ( $\mu\text{g}/\text{g}$ )
100% PRB	03/05/05	11,573	0.5	95.0	66
100% WBIT (Coal #2)	03/01/05– 03/04/05	12,434	0.54	46.5	15
Blended Coal – ~84/16	003/07/05	11,932	0.44	69.8	30
Expected Coal Quality for Blended Coal (84/16)		11,711	0.51	87.3	87.3
% Difference (Blended/Calculated)		<b>-1.9</b>	<b>13.1</b>	<b>20.0</b>	<b>44.6</b>

## Activated Carbon Injection

Two sorbents were evaluated at Laramie River Station: non-treated DARCO<sup>®</sup> Hg, and bromine-treated DARCO<sup>®</sup> Hg-LH. Sorbent injection tests began on February 28, 2005. All tests were conducted at standard full-load conditions.

Vapor-phase mercury removal efficiencies were limited to approximately 50% while injecting the benchmark DARCO<sup>®</sup> Hg sorbent at injection concentrations up to 6.2 lb/MMacf. Results with DARCO<sup>®</sup> Hg from other cold-side ESP sites burning low-rank coals (PRB or North Dakota lignite), presented in Figure 11, show similar limitations in mercury capture with this sorbent. Halogen species, such as HCl, are critical for the effective adsorption of elemental mercury by activated carbon. Chlorine concentrations are typically low in low-rank coals. Activated carbon injection concentrations of 3 to 10 lb/MMacf are sufficient to absorb the available halogens, so subsequent increases in sorbent injection concentrations are ineffective. The spray dryer at Laramie River removes HCl from the flue gas, which may contribute to the lower mercury removal efficiency as compared to the PRB plants (Meramec, Pleasant Prairie) with ESPs but no  $\text{SO}_2$  control.

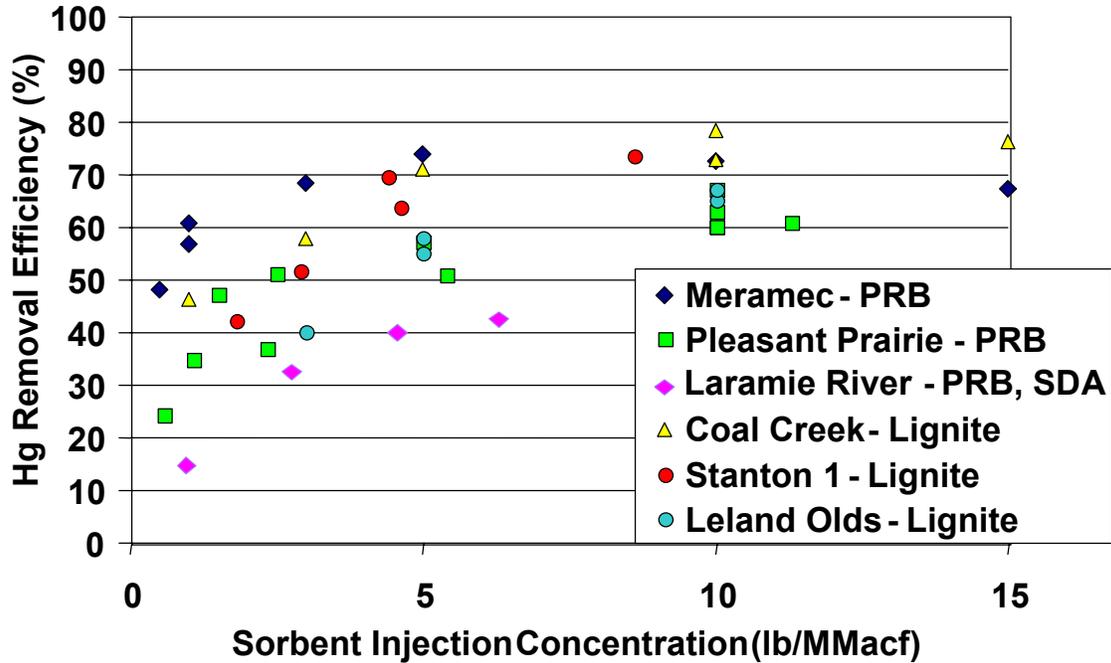


Figure 11. Summary of DARCO<sup>®</sup> Hg Results on Cold-Side ESPs.

Activated carbon can be treated with halogens prior to injection to enhance performance in halogen-deficient flue gas. DARCO<sup>®</sup> Hg-LH, an activated carbon treated with bromine, was chosen for testing at Laramie River because it was specifically designed for use in halogen-deficient gas streams and has demonstrated effective high mercury removal at other sites firing low-rank coals. DARCO<sup>®</sup> Hg-LH was injected upstream of the SDA at Laramie River. No mercury removal was measured across the SDA/ESP prior to carbon injection. More than 50% mercury removal was achieved at injection concentrations above 2 lb/MMacf, and 90% mercury removal was achieved at injection concentrations above 4.5 lb/MMacf. The emissions rate at 50% and 90% removal during these tests was 3.5 lb/TBtu and 0.6 lb/TBtu, respectively. This corresponds to mass emissions of 3,600 and 650 oz/yr. The results of DARCO<sup>®</sup> Hg and DARCO<sup>®</sup> Hg-LH injection are presented in Figure 12 and summarized in Table 13. These results confirm that a bromine-treated carbon outperformed a non-treated carbon on a configuration such as Laramie River Unit 3.

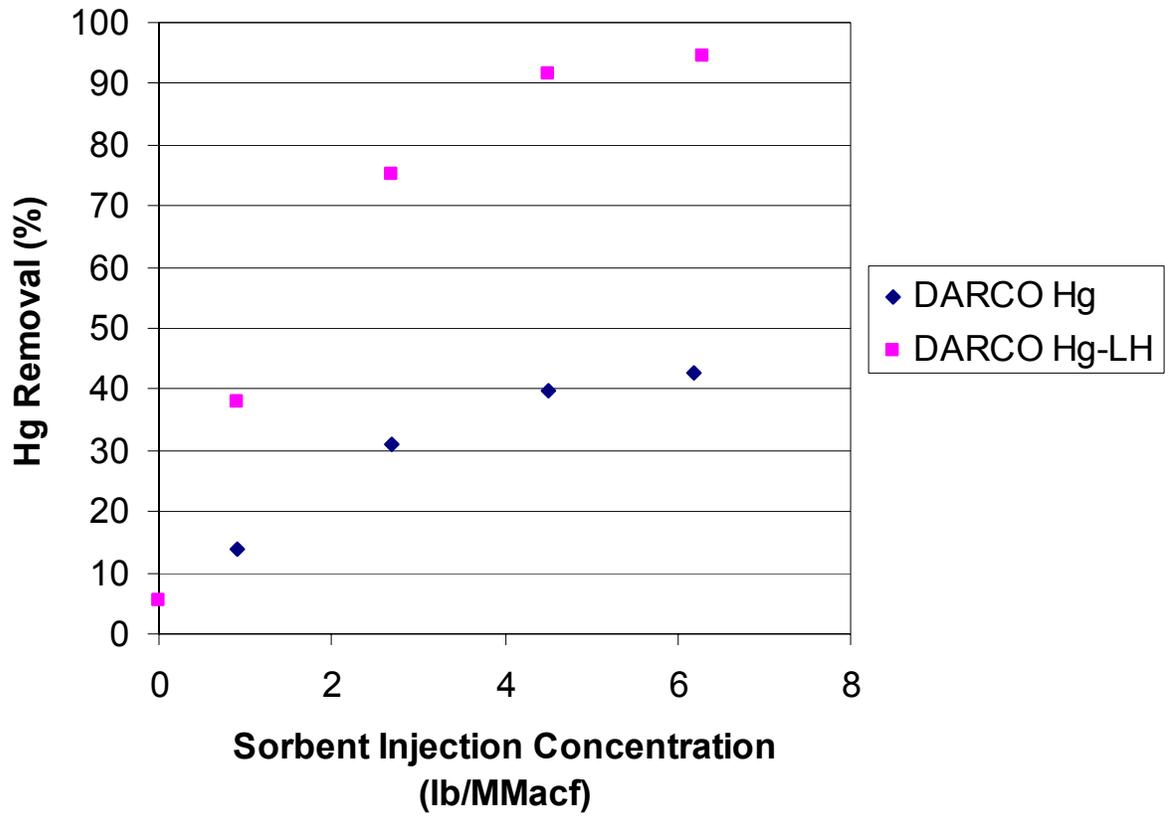


Figure 12. Results from Sorbent Injection Tests at Laramie River.

**Table 13. Mercury Concentrations during Sorbent Injection Testing at Laramie River (corrected to 3% O<sub>2</sub>).**

Date/Time	Sorbent Type	Sorbent Injection Concentration (lb/MIMacf)	Inlet Hg Total (µg/Nm <sup>3</sup> )	Inlet Hg Elemental (µg/Nm <sup>3</sup> )	Outlet Hg Total (µg/Nm <sup>3</sup> )	Outlet Hg Elemental (µg/Nm <sup>3</sup> )	Hg Removal Efficiency (%)
02/28/05 08:30–10:41	None	0	12.9	12.4	13.6	12.2	-6
02/28/05 11:42–13:02	DARCO <sup>®</sup> Hg	0.9	13.2	12.8	11.4	NA	14
02/28/05 14:02–16:52	DARCO <sup>®</sup> Hg	2.7	13.2	12.8	9.1	8.5	31
03/01/05 10:20–12:20	None	0	11.6	N/A	12.0	10.0	-3
03/01/05 13:20–14:20	DARCO <sup>®</sup> Hg	4.5	11.4	N/A	6.9	6.4	40
03/01/05 15:20–18:24	DARCO <sup>®</sup> Hg	6.2	13.2	10.9	7.6	2.8	43
03/02/05 10:02–11:02	None	0	13.1	12.6	13.7	N/A	-5
03/02/05 12:51–13:51	DARCO <sup>®</sup> Hg-LH	0.9	12.7	12.1	7.9	N/A	38
03/02/05 15:43–16:43	DARCO <sup>®</sup> Hg-LH	2.7	12.5	N/A	3.1	2.8	75
03/03/05 09:43–10:43	None	0	10.2	9.4	9.6	N/A	6
03/03/05 12:43–13:43	DARCO <sup>®</sup> Hg-LH	4.5	10.2	9.4	0.9	N/A	91
03/03/05 16:10–17:10	DARCO <sup>®</sup> Hg-LH	6.3	9.3	8.8	0.5	N/A	94

Mercury concentration measurements were also made with the STM during the high injection concentration tests with both the DARCO<sup>®</sup> Hg and the DARCO<sup>®</sup> Hg-LH. The results of the duplicate simultaneous STM tests are presented in Table 14, along with SCSEM concentrations at the ESP outlet. STM results from the other test periods are also included for comparison.

**Table 14. Comparison of SCEM and STM Measurements.**

<b>Condition</b>	<b>Date</b>	<b>STM 1 (<math>\mu\text{g}/\text{Nm}^3</math>)</b>	<b>STM 2 (<math>\mu\text{g}/\text{Nm}^3</math>)</b>	<b>SCEM (<math>\mu\text{g}/\text{Nm}^3</math>)</b>	<b>Difference (%)</b>
Baseline	02/24/05 16:20–16:41	10.4	10.0	8.8	-15.6
Coal Blend #1	02/26/05 15:56–16:21	7.7	7.6	8.9	14.2
Coal Blend #2	03/07/05 16:50–17:27	5.4	5.3	6.3	14.8
DARCO <sup>®</sup> Hg	03/01/05 16:00–16:33	4.6	5.0	5.7	16.6
DARCO <sup>®</sup> Hg-LH	03/03/05 13:33–17:04	0.35	0.36	0.5	22.8

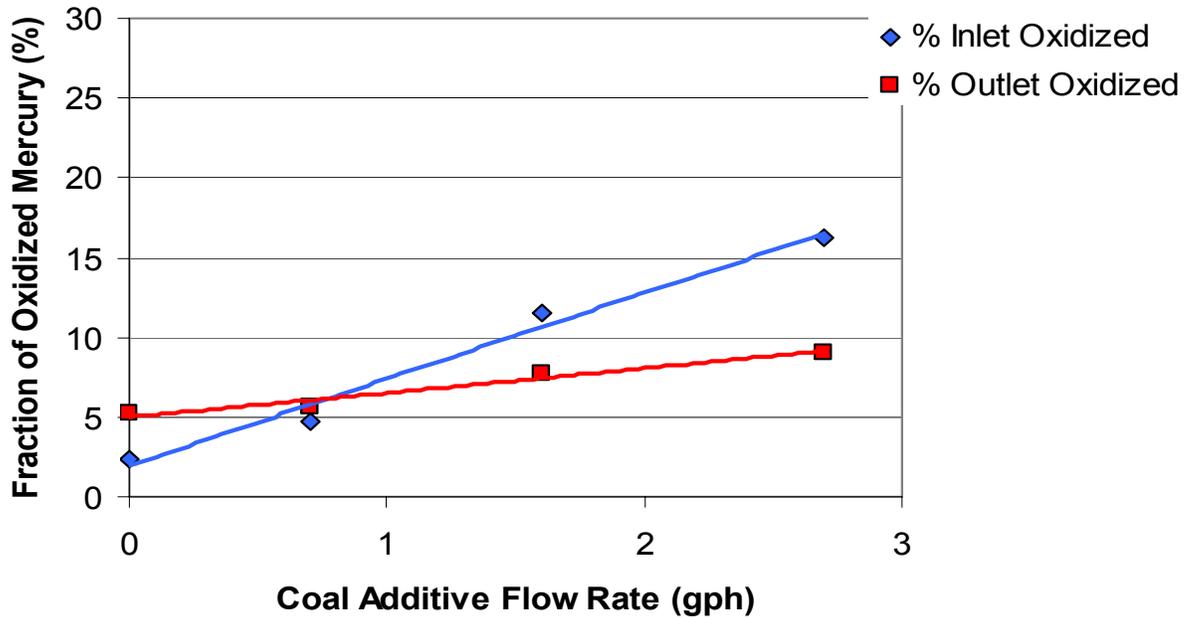
The discrepancies between the STM and SCEM are within or very close to the 20% range usually specified by the DOE for comparisons between OH measurements and SCEM and used here to compare STM and SCEM measurements.

### **Coal Additive With and Without Activated Carbon Injection**

Another option for introducing halogens into the flue gas stream is to treat the coal prior to the boiler. Tests were conducted at Laramie River to determine the effectiveness of KNX, a proprietary ALSTOM Power coal additive, on native mercury removal and whether the KNX additive could enhance the mercury removal of untreated activated carbon.

Unit 3 is a wall-fired unit fed from seven coal feeders. KNX was applied at two feeders, 3B and 3C, which supply the lower burner elevations on each side of the boiler. At this location, the treated coal is fired in the boiler within a few seconds after KNX was applied. The KNX additive was applied at injection rates up to 2.7 gph (0.008 gal/ton coal).

Prior to the start of KNX testing, the fraction of oxidized mercury at the SDA inlet was 2.4%. While injecting KNX onto the coal at a rate of 0.7 gph, the fraction of oxidized mercury at the SDA inlet increased to 4%. It should be noted that due to low turndown ratio of the chemical injection pump, flow rates less than 1 gph were unsteady and may have deviated from the target halogen concentration. At a KNX injection rate of 2.7 gph, the fraction of oxidized mercury at the SDA inlet increased to 16%. Mercury speciation data from KNX testing are presented in Figure 13.



**Figure 13. 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%. No mercury removal was noted prior to introducing KNX. The fraction of oxidized mercury at the outlet of the ESP was also lower than compared to the SDA inlet. This suggests that either KNX addition produced 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 addition of the DARCO<sup>®</sup> Hg sorbent at the SDA inlet location. The sorbent injection concentration at the SDA inlet was 4.5 lb/MMacf, while the chemical additive flow rate was held steady at 1.6 gph (0.005 gal/ton coal). This combination resulted in a total mercury capture across the system of 94% compared to 50% with DARCO<sup>®</sup> Hg alone (no KNX). Figure 14 shows that there was no difference in performance between pretreating the coal with bromine and pretreating the activated carbon with bromine.

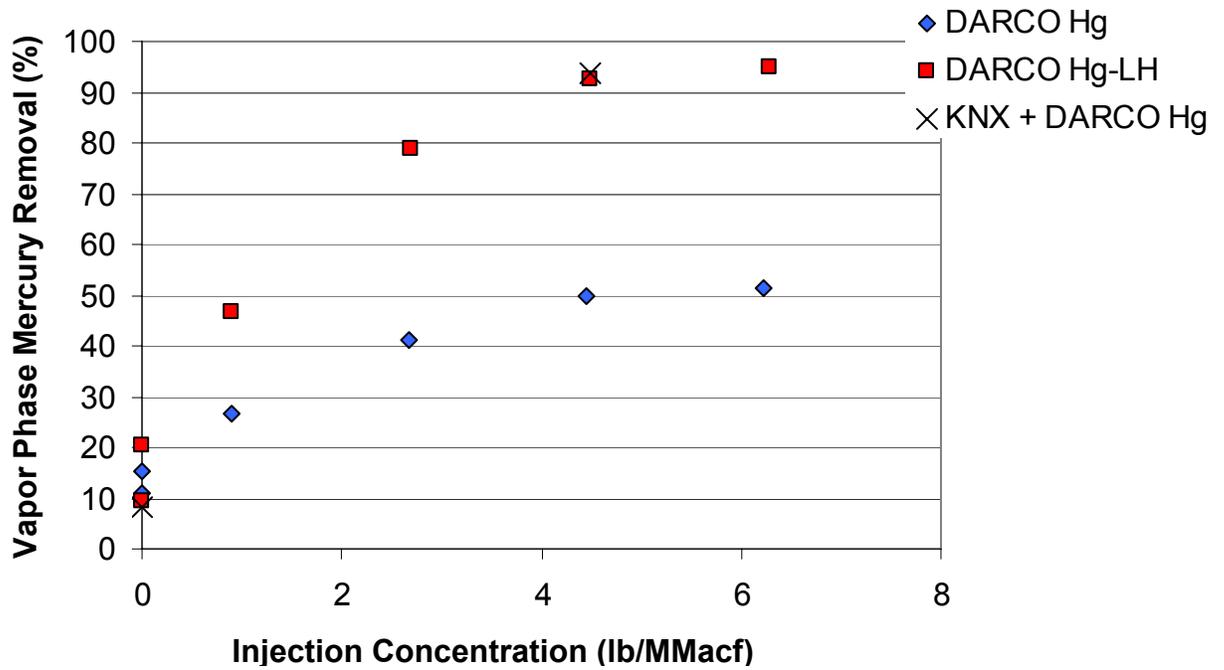


Figure 14. Impact of KNX Coal Additive on DARCO<sup>®</sup> Hg Performance

## BALANCE-OF-PLANT IMPACTS

An important part of evaluating different mercury control technologies is determining their impact on plant operation. This is the single most important step in gaining acceptance of these technologies across the industry. During parametric testing at Laramie River, no balance-of-plant impacts were noted as a result of sorbent injection or coal additive injection. It should be noted that the tests conducted at Laramie River Station were short, proof-of-concept tests and additional, long-term testing is needed to accurately quantify balance-of-plant impacts.

A trend graph of Unit 3 opacity, NO<sub>x</sub>, and SO<sub>x</sub> emissions is presented in Figure 15. No measurable changes in these stack parameters were noted. Recall that only one quarter of the unit was tested and overall stack emissions are not an ideal measure of the impact on the test portion. Therefore, some of the key parameters monitored during testing were the ESP electrical conditions in the gas path affected by sorbent injection. Figure 16 shows the inlet field power and spark rate presented along with the sorbent injection concentration during parametric testing. No detrimental impacts to ESP performance were observed during any of the sorbent injection tests. This was to be expected considering the size of the ESP and that approximately 7,500 lb of fly ash enters the test ESP each hour compared to a maximum carbon injection rate of 250 lb/hr. The incremental increase in particulate matter entering the ESP as a result of sorbent injection was approximately 3.3%.

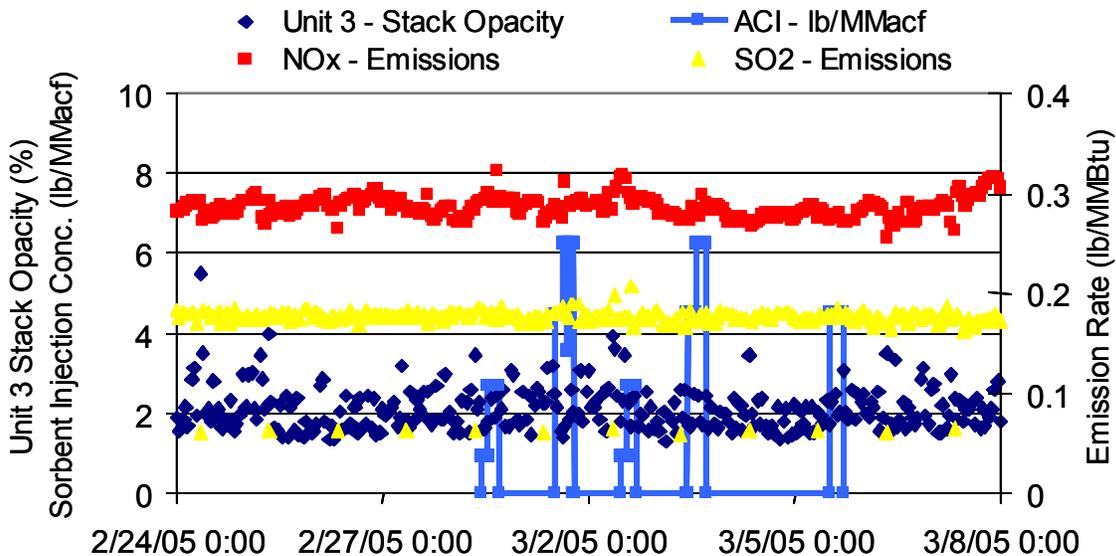
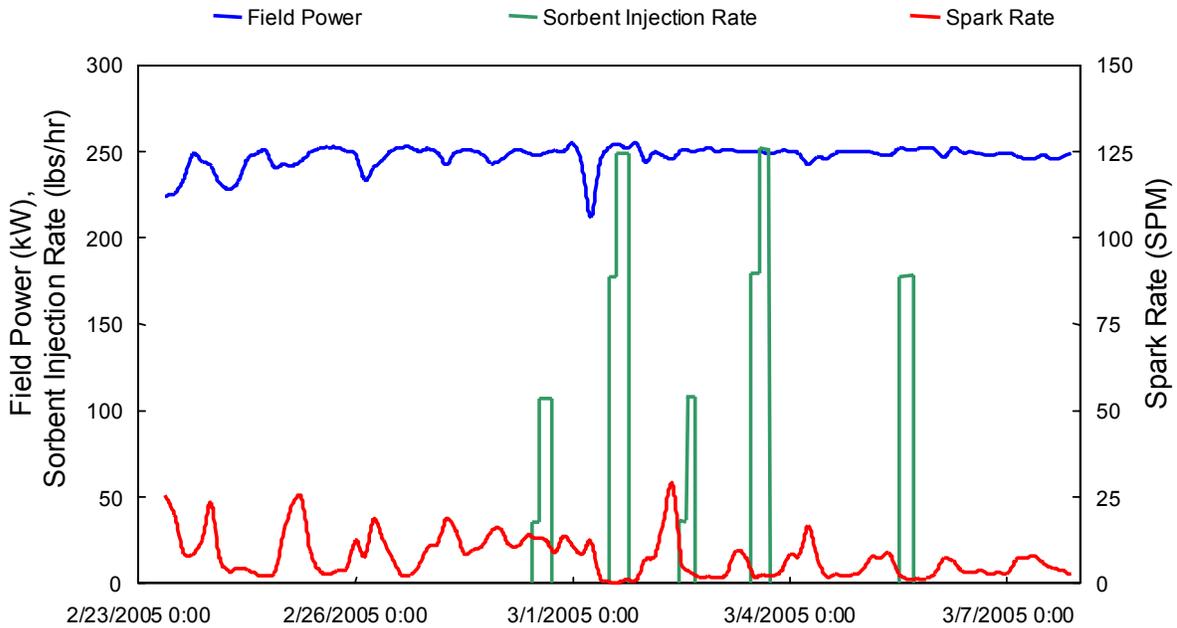


Figure 15. Stack Emissions during Mercury Control Testing at Laramie River.



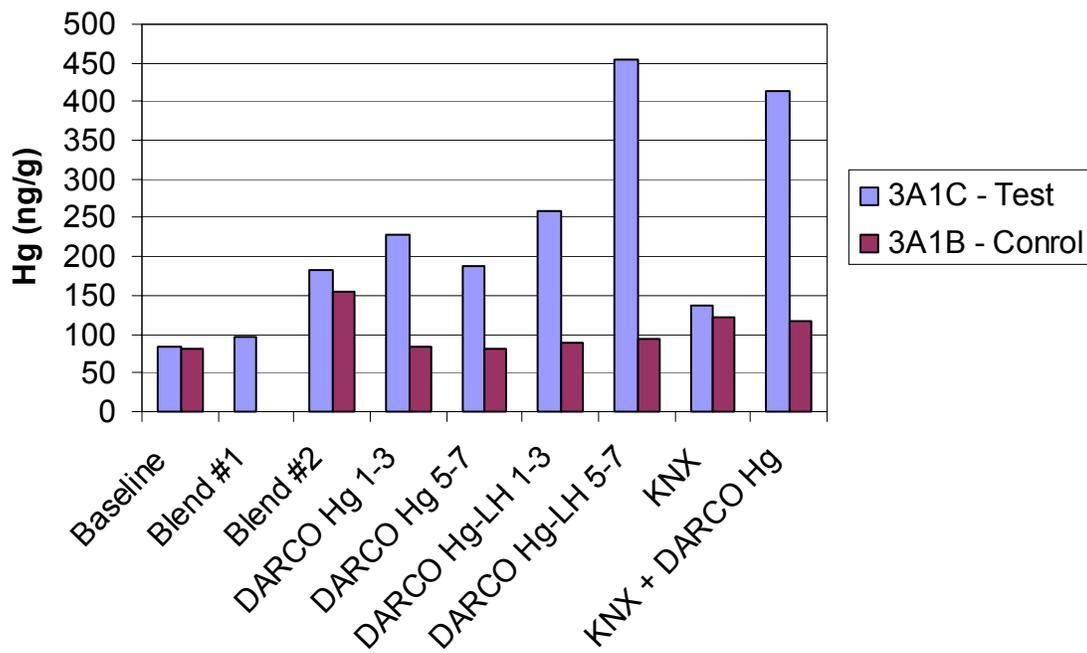
**Figure 16. ESP Electrical Conditions (Test-Side) during Mercury Control Tests.**

During coal additive testing, the maximum chemical flow rate was limited due to the potential of increased corrosion throughout the system. To the best of ADA-ES' knowledge, nothing is known in the literature of adverse effects of KNX on coal-fired boilers. Halogens, in certain flue gas environments, can accelerate corrosion on various steel structures located throughout the plant (e.g., boiler tubes, structural steel). However, the amounts of bromine added to the flue gas stream during coal additive testing were at or below bromine concentrations measured in flue gas streams typical of plants burning eastern bituminous coals.

## COAL AND BYPRODUCT EVALUATION

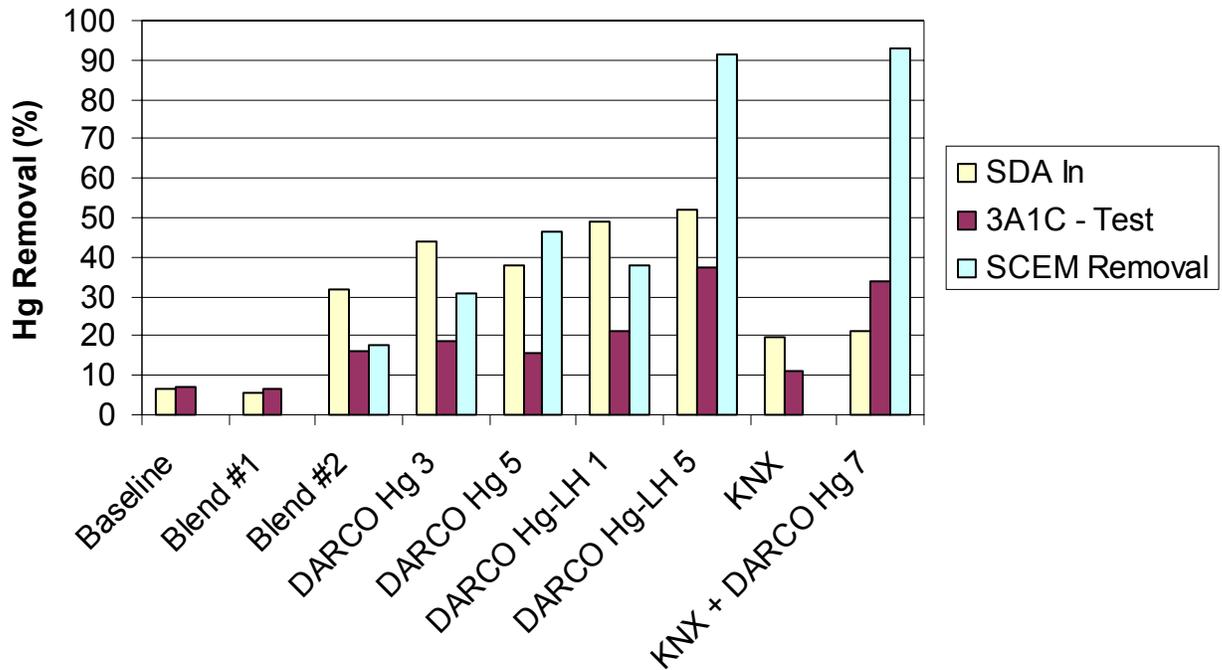
Several coal and ash samples were collected during mercury control testing at Laramie River. Coal samples were characterized and analyzed for mercury and chlorine content. All ash samples collected were also analyzed for mercury. Additional testing included thermal stability of mercury in baseline samples and an ash sample collected during one of the parametric tests with carbon injection.

The mercury content of ash samples collected in the inlet field hoppers on the test- and control-sides of the ESP (hoppers 3A1C and 3A1B) throughout testing are presented in Figure 17. The control-side mercury concentration from the inlet ESP hopper for all tests except KNX and coal blending was fairly consistent and ranged from 80 to 95 ng/g. Based upon coal analyses, this represents 6.6 to 7.8% of the available mercury, which corresponds well with SCEM measurements. The mercury concentration in the test-side ESP hopper during baseline testing is within the range measured in the control-side ash at 85 ng/g.



**Figure 17. Mercury Concentrations in Test-Side (Hopper 3A1C) and Control-Side (Hopper 3A1B) Inlet Hoppers.**

The activated carbon injection tests were fairly short, from 2.3 to 3.9 hours for each injection concentration. It is difficult to get a representative ash sample for such a short test, particularly on a unit that recycles the ash and SDA product into the inlet of the SDA. The fraction of mercury collected on the ash samples compared to the fraction expected based upon SCEM measurements is presented in Figure 18. As shown, the hopper ash samples are biased low for all of the cases with carbon injection.



**Figure 18. Comparison of Mercury Removal based on Ash Samples and SCEM Measurements**

In-situ ash samples were also collected for most of the test conditions. During carbon injection, the mercury concentration of the in-situ ash samples collected at the inlet to the SDA was higher than the ash samples collected from the ESP hoppers. This is expected because the in-situ samples are more representative of the current test condition. In general, the mercury removal calculated from the SDA inlet ash samples was similar to the removal measured with the SCEM across the SDA + ESP except for the two conditions with >90% removal measured by the SCEMs. This suggests that for the low injection concentrations, most of the mercury removal is achieved before the carbon enters the SDA. Based upon this very limited data set, it appears that the in-flight mercury removal upstream of the SDA may be limited to nominally 50%. The in-situ sample collected during KNX + DARCO<sup>®</sup> Hg injection does not follow the trend established during the other carbon injection tests and may be an anomaly.

In-situ samples were also collected downstream of the SDA. These samples were difficult to collect because of the moisture present in the flue gas at this location. The mercury concentration of these samples was typically lower than that of SDA inlet samples, as shown in Table 15. This is likely due to the presence of fresh lime and recycle product that had not reached equilibrium.

During coal blending and KNX testing, both the control- and test-side ESP were affected. The mercury concentration in the test-side ash sample was slightly elevated during coal blend #1 testing (97 ng/g). No control-side ash sample was available from coal blend #1. During coal blend #2 testing, the ESP inlet hopper ash concentration was higher for both

the control- and test-side samples (156 and 182 ng/g, respectively). The mercury removal calculated using the ash samples from coal blend #2 was similar to the removal measured with the SCEMs. A slight increase in the Loss on Ignition (LOI) was measured during the coal blend #2 test, as shown in Table 16, which may have contributed to the increased mercury removal.

A slight increase in both the control- and test-side ESP inlet hopper mercury concentration was also noted during the KNX injection test, but no corresponding increase in removal was noted with the SCEMs.

**Table 15. Mercury Results for In-Situ and Inlet Hopper Ash Samples Collected during Mercury Control Evaluation Upstream of the SDA**

Date	Test Description	Test-Side SDA Inlet Hg (ng/g)	Test-Side SDA Outlet Hg (ng/g)	Test-Side ESP Inlet Hopper Hg (ng/g)	Control-Side ESP Inlet Hopper Hg (ng/g)
02/24/05	Baseline	45		65	
02/25/05	Baseline	78	106	85	81
02/26/05	Coal Blend #1	81		97	
02/28/05	DARCO <sup>®</sup> Hg	535		229	83
03/01/05	DARCO <sup>®</sup> Hg	461	73	188	80
03/02/05	DARCO <sup>®</sup> Hg-LH	600		260	88
03/03/05	DARCO <sup>®</sup> Hg-LH	633	266	454	95
03/04/05	KNX (No ACI)	240	107	136	123
03/05/05	KNX + DARCO <sup>®</sup> Hg	258	207	414	117
03/07/05	Coal Blend #2	353	144	182	156

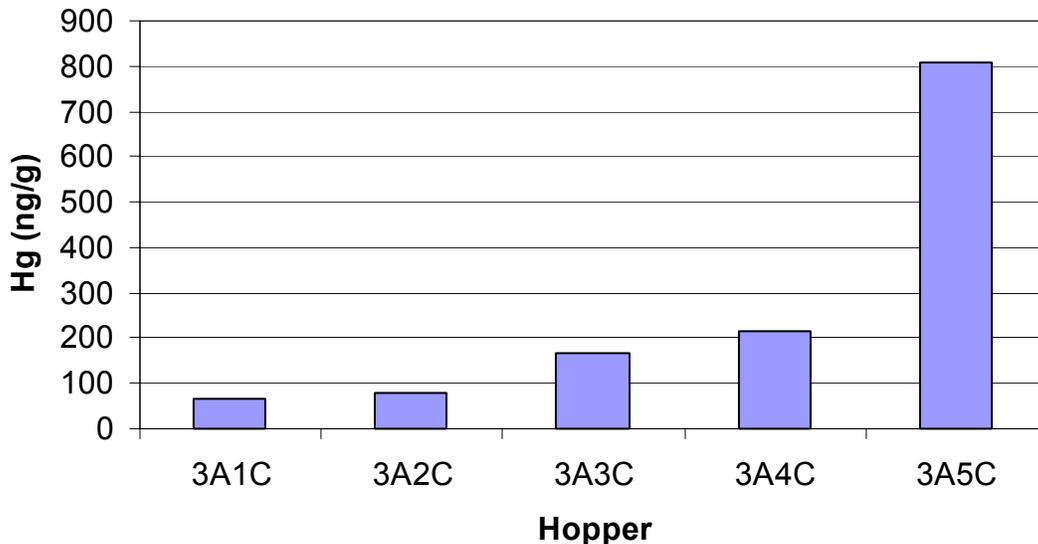
Ash samples collected with the sampling cyclone downstream of carbon injection may also be biased high or low because the carbon has not had an opportunity to become homogenized in the flue gas. All SDA inlet samples were collected from the same port and any maldistribution of carbon should be similar for all test runs. Therefore, although the in-flight capture reported may be high or low in general, it should have the same bias for all tests.

In-situ ash samples represent a small volume of ash. Sufficient ash was present for some samples to conduct an LOI analysis in addition to the mercury analysis. One of these was the ash sample collected during the second coal blend test. The LOI during coal blending, presented in Table 16, was significantly higher than the baseline ash sample. The elevated LOI in the blend suggests an increase in unburned carbon from the blend, although LOI does not give a quantitative measure of the unburned carbon for PRB fly ash collected in the hoppers at this plant. LOI is not a good technique to determine the fraction of unburned carbon in samples with spray dryer solids because the samples can lose weight as the lime decomposes at high temperatures. Samples of hopper ash have been submitted for precise carbon analysis, but results are not yet available.

**Table 16. LOI Measured in In-Situ Ash Samples.**

Date	Test Description	LOI %
02/24/05	Baseline	0.168
02/25/05	Baseline	0.112
03/04/05	KNX (No ACI)	0.341
03/07/05	Coal Blend #2	0.632

There are five collection fields in the Unit 3 ESP. Fly ash samples were collected from one hopper in each field during baseline testing to determine if mercury concentration differences develop as the ash migrates through the ESP. The results, presented in Figure 19, indicate that mercury becomes concentrated in the ash as it moves through the ESP from the inlet (hopper 3A1C) to the outlet (hopper 3A5C) fields. Ash in the latter fields is often exposed to the flue gas longer as it is rapped from the inlet fields and is re-entrained in the gas. In this case, it is exposed to flue gas much longer than fly ash collected in the front of the ESP. Less ash is collected in the back fields of the ESP as compared to the front fields. While the mercury concentrations are high in the back fields of the ESP, the ash in these hoppers represents a small fraction of the total ash.



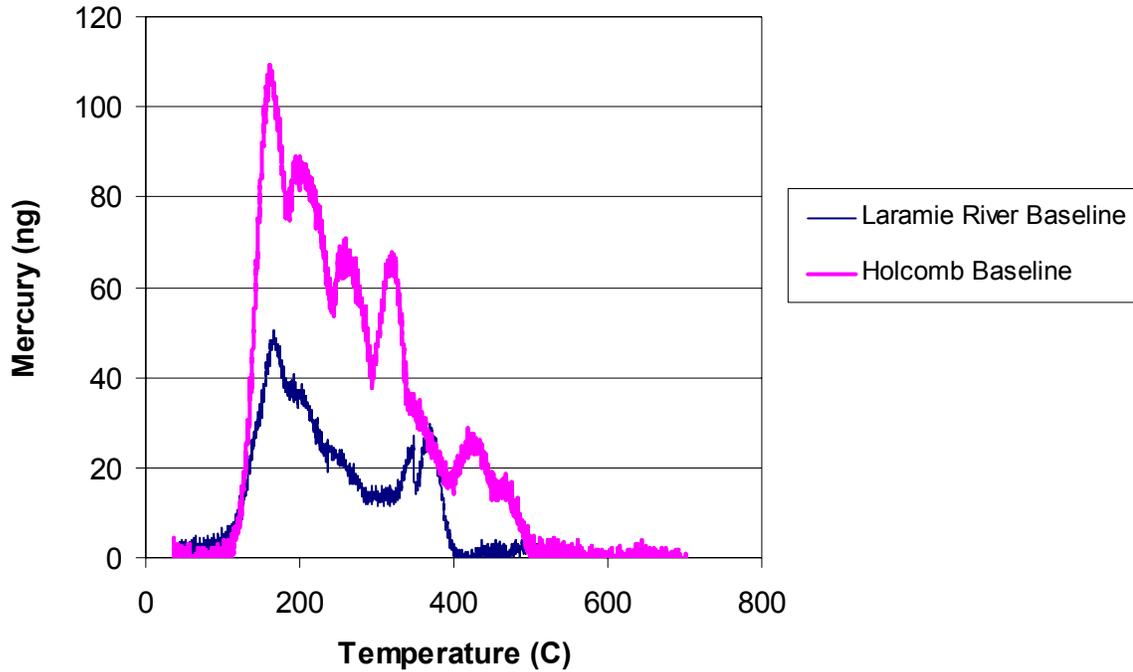
**Figure 19. Mercury Concentration in Ash across Unit 3 ESP (Test Lane).**

### Stability of Mercury on Ash

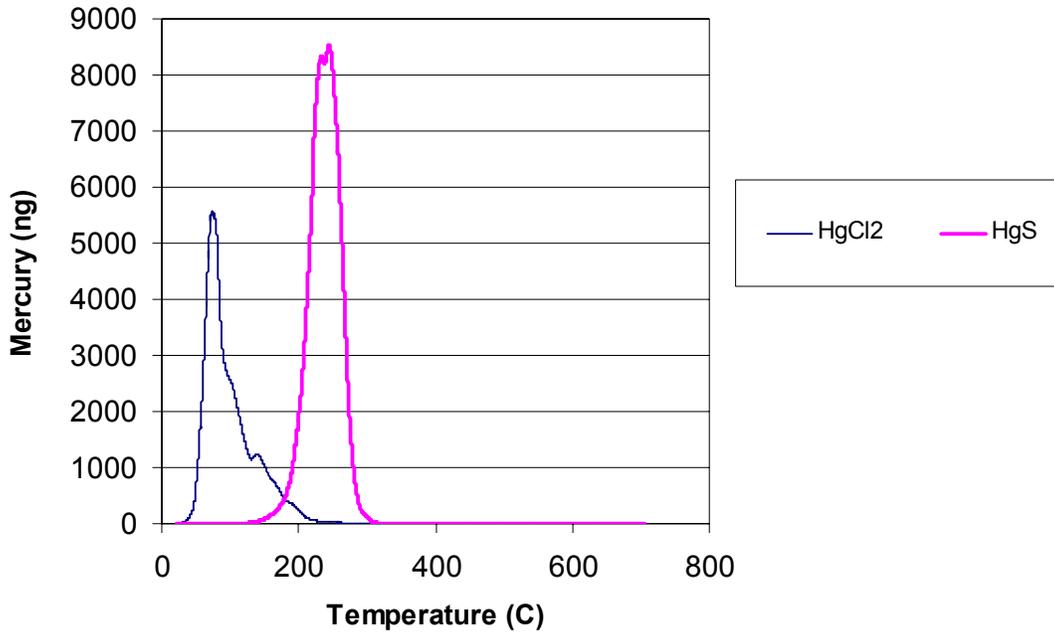
An ash sample collected during baseline testing was analyzed to determine the thermal stability of the mercury and the potential of the mercury to leach in various solutions. The thermal desorption profile of the ash is presented in Figure 20. As shown, the profile is fairly complex and suggests that the mercury is bound to the ash as more than one compound. For reference, the thermal desorption profile of ash collected during baseline testing at Holcomb Station is also included in Figure 20. Although there is more structure in the Holcomb profile, the two profiles are similar and indicate more than one mercury

compound is likely associated with the ash. For reference, the desorption profiles of HgCl<sub>2</sub> and HgS are presented in Figure 21.

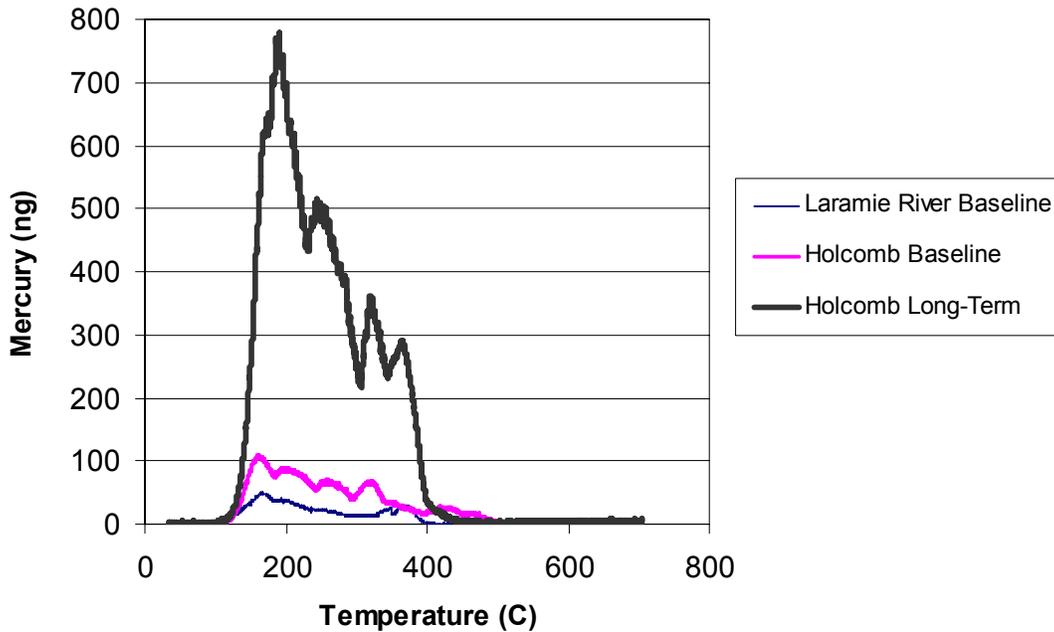
No long-term tests were conducted at Laramie River. However, it is expected that the thermal stability of DARCO<sup>®</sup> Hg-LH mixed with fly ash would be similar for the two plants. The results from Holcomb are presented in Figure 22. As shown, the presence of carbon increases the temperature of the initial desorption peak, but does not reduce the structure of the profile.



**Figure 20. Thermal Desorption Profiles of Laramie River and Holcomb Baseline Ash Samples.**



**Figure 21. Reference Thermal Desorption Profiles for HgCl<sub>2</sub> and HgS.**



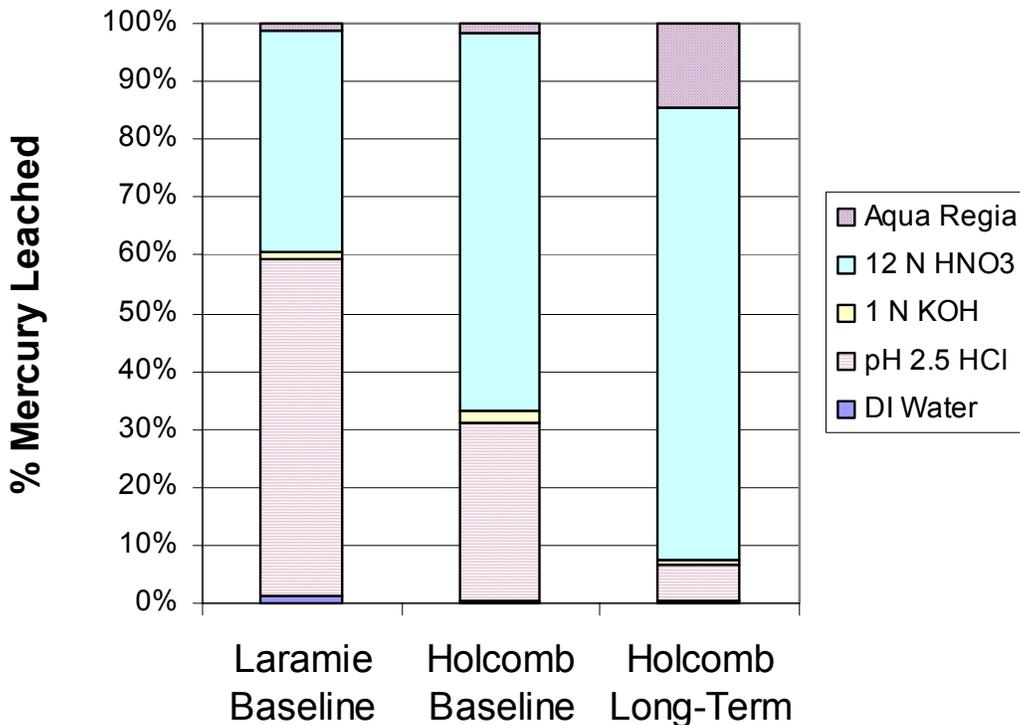
**Figure 22. Thermal Desorption Profiles of Laramie River and Holcomb Ash Samples.**

Selective Sequential Extraction tests were conducted by Frontier Geosciences Inc. to determine the leaching stability of a baseline ash sample from Laramie River. The results are presented in Table 17 with data from a baseline and long-term carbon injection sample from Holcomb. For comparison, the fraction of mercury leached in each step for these three samples is shown in Figure 23. Similar to the thermal desorption test, the data suggest that the mercury is bound in the ash mixture as more than one compound. The data also suggest that a significant fraction of the mercury is leachable from the baseline ash with a fairly mild

digest (HCl to pH of 2.5). Activated carbon appears to stabilize the mercury and a portion is bound so tightly that a very aggressive digestion with aqua regia is required to release the mercury. During a standard fly ash analysis using digestion techniques, most labs will use a digestion solution less aggressive than aqua regia. This could result in under-reporting of the actual mercury present in the ash. All fly ash samples analyzed from Laramie River testing were analyzed using direct combustion. One lab that used a digestion technique analyzed several ash samples from Holcomb and the results were consistently lower than the direct combustion technique. This lab did not use an aggressive digest.

**Table 17. Results of Sequential Extraction tests on Laramie River and Holcomb Fly Ash Samples.**

Sample	Hg Concentration in Digest					
	DI Water	pH 2.5 HCl	1 N KOH	12 N HNO <sub>3</sub>	Aqua Regia	Sum
LRS Baseline (ng/g)	1.301	64.0	1.32	42.0	1.33	110
Holcomb Baseline (ng/g)	0.46	55.2	3.53	117	2.97	179
Holcomb Long-Term (ng/g)	2.33	67.0	6.55	800	150	1,026



**Figure 23. Mercury Leaching Characteristics of Select Ash Samples.**

## ECONOMICS

After completion of testing and analysis of the data, the requirements and costs for full-scale, permanent commercial implementation of the necessary equipment for mercury control using sorbent injection technology at the 550-MW Laramie River Station Unit 3 were determined. The cost of process equipment is sized and designed based on the long-term test results for approximately 50% and 90% mercury control using DARCO<sup>®</sup> Hg-LH sorbent. Other design considerations include sorbent storage capacity, number of operating trains, and number of spare trains.

Sorbent costs were estimated based on activated carbon injection concentrations needed to achieve 50% and 90% mercury removal efficiencies. For Laramie River Unit 3, this would require an injection rate of nominally 600 lb/hr for 90% mercury removal and 200 lb/hr for 50% mercury removal at full load. Assuming a unit capacity factor of 90% and a delivered cost for DARCO<sup>®</sup> Hg-LH sorbent of \$0.95/lb, the annual sorbent cost for injecting sorbent at the SDA inlet would be about \$4,800,000 for 90% mercury removal and \$1,600,000 for 50% removal. The 90% removal case is equivalent to a sorbent cost of nominally \$3,980/lb (\$660/oz) mercury removed, or \$1/MWhr to achieve an outlet mercury emission of 805 oz/yr. These calculations assume the mercury concentration in the coal is 7.9 lb/TBtu. ALSTOM has not finalized costs associated with KNX; however, they have indicated they expect costs to be comparable to treated activated carbon injection.

The sorbent injection system equipment was sized based on a maximum injection concentration of 8 lb/MMacf (1,060 lb/hr at full load) even though injection rates estimated to achieve 50% and 90% removal efficiencies are expected to be much lower. The estimated uninstalled cost for a sorbent injection system for Unit 3 is \$750,000 ±10% with a 9-day storage capacity and includes one 76-foot-tall sorbent storage silo with two operating trains and one spare train. The cost of an injection system with a 15-day storage capacity is \$1.3 million ±10%, which includes two 65-foot-tall sorbent storage silos, each with two operating trains and one spare train. The storage capacity of the systems increases as the injection rate decreases from the design injection rate. The storage capacity of the one-storage-silo system at injection rates of 1.5 and 4.5 lb/MMacf would be 48 days and 16 days respectively, while the storage capacity of the two-storage-silo system would be 80 days and 26 days respectively.

## CONCLUSIONS

Power plants that burn PRB coal and have SDAs and ESPs for air pollution control systems represent a challenging application for controlling mercury emissions. ICR measurements and subsequent full-scale field tests have confirmed that the spray dryer removes a key gas-phase constituent that is critical for the adsorption of vapor-phase mercury onto solid surfaces. This results in very low levels of native mercury removal, typically <20%, at plants with this configuration. In addition, the effectiveness of injecting standard activated carbon is greatly diminished by this same effect.

The test program at Laramie River was designed to provide a full-scale evaluation of three different technologies that can overcome the limited mercury removal achievable at similar sites. Each technology was based on supplementing certain halogens that are not available in sufficient quantities in these coals.

Results from Laramie River testing identified two technologies that have the potential to produce high levels (>80%) of mercury removal in this difficult application. These technologies are:

1. 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 94% was measured at a carbon feed rate of 4.5 lb/MMacf and a KNX injection rate of 1.6 gph (0.005 gal/ton coal) during short-term parametric testing.
2. Chemically Enhanced Sorbent: A bromine-treated activated carbon available through NORIT Americas, DARCO<sup>®</sup> Hg-LH, resulted in mercury removal in excess of 90% at injection concentrations of 4.5 lb/MMacf during short-term parametric tests. For coal with a mercury content of 7.9 lb/TBtu, 90% removal would result in mass emissions of 0.8 lb/TBtu (805 oz/yr).

Because the Laramie River Station has the capability to fire a blended coal, two western bituminous coals were tested to evaluate their effectiveness in altering native mercury behavior. During both tests, adjusting the blend ratio did not appear to alter mercury speciation at any point in the system and mercury removal efficiencies were at or near their respective baseline levels. The goals for the program established by DOE/NETL were to reduce the uncontrolled mercury emissions by 50 to 70% at a cost 25 to 50% below the target of \$60,000/lb mercury removed. The goals of the program were exceeded by achieving 90+% mercury removal at a sorbent cost of \$3,980/lb (\$660/oz) mercury removed for coal with a mercury concentration of 7.9 lb/TBtu.

## REFERENCES

1. Sjostrom, S. et al., "EVALUATION OF SORBENT INJECTION FOR MERCURY CONTROL," Topical Report for Sunflower Electric's Holcomb Station, U.S. DOE Cooperative Agreement No. DE-FC26-03NT41986, Topical Report No. 41986R07," Reporting Period: October 1, 2003 – June 30, 2005.
2. Sjostrom, S. et al., "EVALUATION OF SORBENT INJECTION FOR MERCURY CONTROL," Topical Report for AmerenUE's Meramec Station Unit 2, U.S. DOE Cooperative Agreement No. DE-FC26-03NT41986, Topical Report No. 41986R09," Reporting Period: October 1, 2003 – September 30, 2005.

## ACRONYMS AND ABBREVIATIONS

ACI	Activated carbon injection
APH	Air preheater
CVAAS	Cold-vapor atomic absorption spectrometer
CVAFS	Cold-vapor atomic fluorescence spectroscopy
DARCO <sup>®</sup> Hg	Sorbent manufactured by NORIT Americas Inc. Formerly known as DARCO <sup>®</sup> FGD.
DARCO <sup>®</sup> Hg-LH	Sorbent manufactured by NORIT Americas Inc. Formerly known as DARCO <sup>®</sup> FGD-E3.
DOE	Department of Energy
EC	Equivalent sorbent injection concentration
ESP	Electrostatic precipitator
FF	Fabric filter
FGD	Flue gas desulfurization
GRE	Great River Energy
ICR	Information Collection Request
kacfm	Thousand actual cubic feet per minute
kW	Kilowatt
MW	Megawatt
NETL	National Energy Technology Laboratory
O&M	Operating and Maintenance
PAC	Powdered activated carbon
PLC	Programmable Logic Controller
PRB	Powder River Basin
SCA	Specific collection area
SCEM	Semi-continuous emission monitor
SDA	Spray dryer absorber
SGLP	Synthetic groundwater leaching procedure
SSD	Sorbent screening device
STM	Sorbent Trap Method
TAG	Technical Assessment Guide
TCLP	Toxicity characteristic leaching procedure