JV TASK 45 – MERCURY CONTROL TECHNOLOGIES FOR ELECTRIC UTILITIES BURNING LIGNITE COAL, PHASE I BENCH- AND PILOT-SCALE TESTING

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MERCURY CONTROL TECHNOLOGIES FOR UTILITIES BURNING LIGNITE COAL, PHASE I BENCH- AND PILOT-SCALE TESTING

ABSTRACT

The Energy & Environmental Research Center has completed the first phase of a 3-year, two-phase consortium project to develop and demonstrate mercury control technologies for utilities that burn lignite coal. The overall project goal is to maintain the viability of lignite-based energy production by providing utilities with low-cost options for meeting future mercury regulations. Phase I objectives are to develop a better understanding of mercury interactions with flue gas constituents, test a range of sorbent-based technologies targeted at removing elemental mercury (Hg^0) from flue gases, and demonstrate the effectiveness of the most promising technologies at the pilot scale. The Phase II objectives are to demonstrate and quantify sorbent technology effectiveness, performance, and cost at a sponsor-owned and operated power plant. Phase I results are presented in this report along with a brief overview of the Phase II plans.

Bench-scale testing provided information on mercury interactions with flue gas constituents and relative performances of the various sorbents. Activated carbons were prepared from relatively high-sodium lignites by carbonization at 400°C (752°F), followed by steam activation at 750°C (1382°F) and 800°C (1472°F). Luscar char was also steam-activated at these conditions. These lignite-based activated carbons, along with commercially available DARCO FGD and an oxidized calcium silicate, were tested in a thin-film, fixed-bed, bench-scale reactor using a simulated lignitic flue gas consisting of 10 $\mu g/Nm^3$ Hg^0, 6% O_2, 12% CO_2, 15% H_2O, 580 ppm SO_2, 120 ppm NO, 6 ppm NO_2, and 1 ppm HCl in N_2. All of the lignite-based activated (750°C, 1382°F) carbons required a 30–45-minute conditioning period in the simulated lignite flue gas before they exhibited good mercury sorption capacities. The unactivated Luscar char and oxidized calcium silicate were ineffective in capturing mercury. Lignite-based activated (800°C, 1472°F) carbons required a shorter (15-minute) conditioning period in the simulated lignite flue gas and captured gaseous mercury more effectively than those activated at 750°C (1382°F). Subsequent tests with higher acid gas concentrations including 50 ppm HCl showed no early mercury breakthrough for either the activated (750°C, 1382°F) Bienfait carbon or the DARCO FGD. Although these high acid gas tests yielded better mercury capture initially, significant breakthrough of mercury ultimately occurred sooner than during the simulated lignite flue gas tests.

The steam-activated char, provided by Luscar Ltd., and DARCO FGD, provided by NORIT Americas, were evaluated for mercury removal potential in a 580 MJ/hr (550,000-Btu/hr) pilot-scale coal combustion system equipped with four particulate control devices: 1) an electrostatic precipitator (ESP), 2) a fabric filter (FF), 3) the *Advanced Hybrid*™ filter, and 4) an ESP and FF in series, an EPRI-patented TOXECON™ technology. The Ontario Hydro method and continuous mercury monitors were used to measure mercury species concentrations at the inlet and outlet of the control technology devices with and without sorbent injection. Primarily Hg^0 was measured when lignite coals from the Poplar River Plant and Freedom Mine were combusted. The effects of activated Luscar char, DARCO FGD, injection rates, particle size, and gas temperature on mercury removal were evaluated for each of the four particulate control device options. Increasing injection rates and decreasing gas temperatures generally promoted mercury capture in all four control

devices. Relative to data reported for bituminous and subbituminous coal combustion flue gases, higher sorbent injection rates were generally required for the lignite coal to effectively remove mercury. Documented results in this report provide the impacts of these and other parameters and provide the inputs needed to direct Phase II of the project.

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NOMENCLATURE

A/C	air-to-cloth ratio
AAS	atomic absorption spectroscopy
ALC	activated Luscar char
AR	as-received
ASTM	American Society for Testing and Materials
CEM	continuous emission monitor
COHPAC	compact hybrid particulate collector
CMM	continuous mercury monitor
CVAFS	cold-vapor atomic fluorescence spectroscopy
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
FF	fabric filter
GFAAS	graphite furnace atomic absorption spectroscopy
Hg^0	elemental mercury
IBG	integrated bench-scale gasifier
ICP–AES	inductively coupled plasma–atomic emission spectroscopy
ICR	information collection request
LOI	loss on ignition
MACT	maximum achievable control technology
MF	moisture-free
MVD	median volume diameter
Nm^3	normal cubic meters
OH	Ontario Hydro
PRB	Powder River Basin
SGLP	synthetic groundwater leaching procedure
TCLP	toxicity characteristic leaching procedure
XPS	x-ray photoelectron spectroscopy
XRF	x-ray fluorescence

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MERCURY CONTROL TECHNOLOGIES FOR UTILITIES BURNING LIGNITE COAL, PHASE I BENCH- AND PILOT-SCALE TESTING

EXECUTIVE SUMMARY

The Energy & Environmental Research Center recently completed the first phase of a 3-year, two-phase consortium project to develop and demonstrate mercury control technologies for utilities burning lignite coal. The overall project goal is to maintain the viability of lignite-based energy production by providing local utilities with low-cost options for meeting future mercury regulations. Phase I objectives were to develop a better understanding of mercury interactions with flue gas constituents, test a range of sorbent-based technologies targeted at removing elemental mercury (Hg^0) from flue gases, and demonstrate the effectiveness of the most promising technologies at the pilot scale. The Phase II objective is to demonstrate and quantify sorbent technology effectiveness, performance, and cost at a sponsor-owned and/or operated power plant. This report documents the Phase I results and provides an overview of the Phase II plans.

Four lignites from the Poplar River, Bienfait, Freedom, and Center coal mines were utilized in this investigation. Lignites from the Bienfait, Freedom, and Center Mines were used to produce potential mercury sorbents, and lignites from the Poplar River and Freedom coal mines were burned in a 580-MJ/hr (550,000-Btu/hr) pulverized coal-fired unit to evaluate the mercury removal effectiveness of injecting a couple of the most promising sorbents upstream of an electrostatic precipitator (ESP), Gore and Ryton fabric filters (FFs), and an *Advanced Hybrid*™ filter and injection between an ESP–FF combination. Injecting a sorbent downstream of an ESP and upstream of an FF is a technology configuration that has been used by Alstom under the designation Filsorption in Europe to control mercury in waste-to-energy plants and is patented by EPRI in the United States as TOXECON™ for controlling mercury in power plants.

Average mercury content in the Poplar River and Freedom coals was 0.153 and 0.077 ppm, respectively, and both contained approximately 20 ppm chlorine on a dry basis. General information on the four coals involved in this investigation is presented in Table ES-1.

Table ES-1. Lignite Coal Information

Organizaton	Mine	Coal	Location	Mine Production,[a] tons
Luscar Ltd.	Poplar River	Ravenscrag	Wood Mountain–Willow Bunch Area, Saskatchewan, Canada	3,837,900
Luscar Ltd.	Bienfait	Ravenscrag	Estevan Area, Saskatchewan, Canada	1,955,800
The Coteau Properties Co.	Freedom	Beulah-Zap	Western, Northern Lignite Basin, North Dakota, United States	16,125,847
BNI Coal Ltd.	Center	Hagel and Kinneman Creek	Western, Northern Lignite Basin, North Dakota, United States	4,415,033

[a] 2000 mine production statistic from *Keystone Coal Industry Manual*; Coal Age, PRIMEDIA Business Magazines & Media, Chicago, IL, 2002; 736 p.

Phase I testing began with carbon preparation and bench-scale testing to aid in sorbent evaluation and selection. Activated carbons were prepared from relatively high-sodium (4–9 wt% Na_2O on an ash basis) Bienfait, Freedom, and Center lignites by carbonization at 400°C (752°F) in nitrogen followed by steam activation at 750°C (1382°F) and 800°C (1472°F) in nitrogen. Luscar char was also steam-activated at 750°C (1382°F) and 800°C (1472°F) in nitrogen. Iodine numbers for the lignite-based activated carbons, including a commercial mercury sorbent DARCO FGD, are compared in Table ES-2. Based on the iodine values, DARCO FGD sorbent has the highest surface area. Carbons activated at 800°C (1472°F) resulted in less surface area than similar carbons activated at 750°C (1382°F), but as is described below, the sorbents activated at higher temperatures were more reactive and effective at capturing mercury. The higher activation temperature could be bringing the carbon closer to gasification, resulting in a change in the carbon pore structure, and could also be causing a positive change in the carbon chemistry.

Table ES-2. Activated Carbon Iodine Numbers

Precursor Material	Activation Temperature, °C (°F)	Iodine No., mg I_2/g Sorbent
Bienfait Coal	750 (1382)	424.3
Bienfait Coal	800 (1472)	398.1
Luscar Char	750 (1382)	439.6
Luscar Char	800 (1472)	427.4
Freedom Coal	750 (1382)	331.5
Center Coal	750 (1382)	352.8
Center Coal	800 (1472)	321.5
DARCO FGD	Unknown	524.8

The lignite-based activated carbons, activated and unactivated Luscar char, and an oxidized calcium silicate sorbent were tested in a thin-film, fixed-bed, bench-scale reactor using a simulated lignitic flue gas consisting of nominally 10 µg/Nm^3 Hg^0, 6% O_2, 12% CO_2, 15% H_2O, 580 ppm SO_2, 120 ppm NO, 6 ppm NO_2, and 1 ppm HCl in N_2. Activated (750°C) Bienfait carbon and DARCO FGD were also tested in an established baseline flue gas consisting of 10 µg/Nm^3 Hg^0, 6% O_2, 12% CO_2, 8% H_2O, 1600 ppm SO_2, 400 ppm NO, 20 ppm NO_2, and 50 ppm HCl in N_2. As exemplified in Figure ES-1, all of the lignite-based activated (750°C, 1382°F) carbons required a 30- to 45-minute conditioning period in the simulated lignite flue gas before they exhibited good mercury sorption capacities and Hg^0 oxidation potentials (>90% Hg^{2+}). The unactivated Luscar char and oxidized calcium silicate were ineffective in capturing or heterogeneously oxidizing mercury.

As shown in Figure ES-2, lignite-based carbons activated at 800°C (1472°F) required a shorter 15-minute conditioning period in the simulated lignite flue gas and captured gaseous mercury more effectively with greater Hg^0 oxidation (>95% Hg^{2+}) than those activated at 750°C (1382°F). Mercury capacities of the activated Luscar char (ALC) (800°C, 1472°F) ranged from 164 to 202 µg/g in the presence of the simulated lignite combustion flue gas.

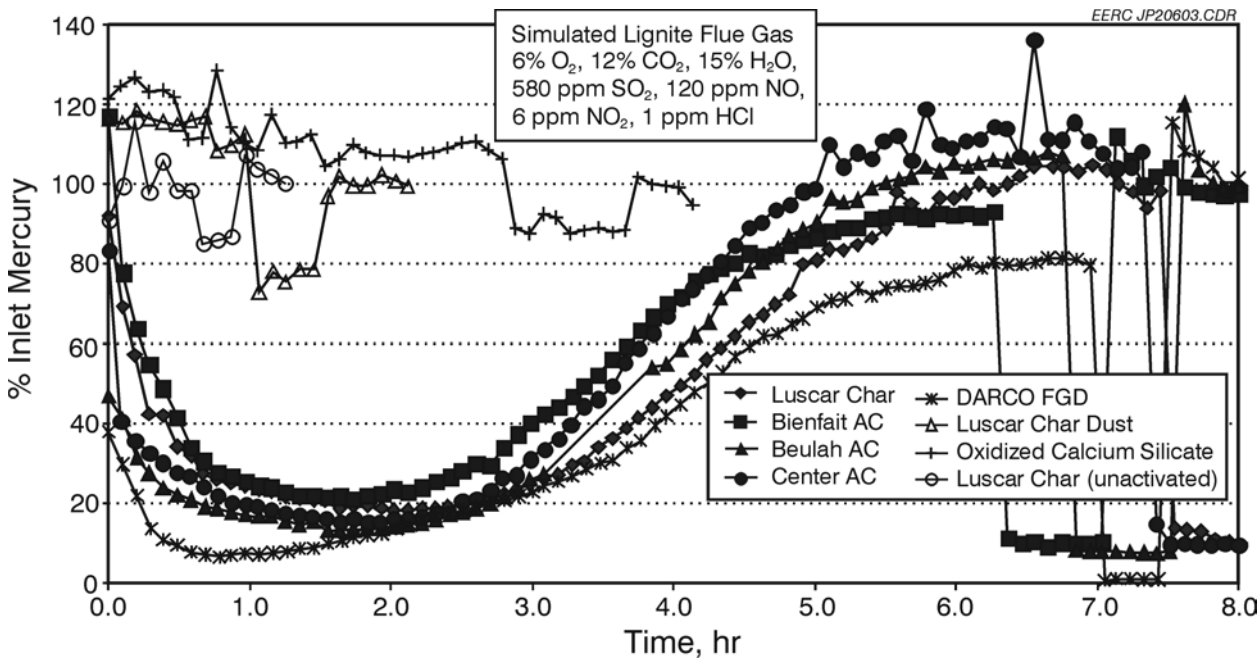

Figure ES-1. Bench-scale fixed-bed testing results for potential mercury sorbents, including lignite-based activated (750°C, 1382°F) carbons.

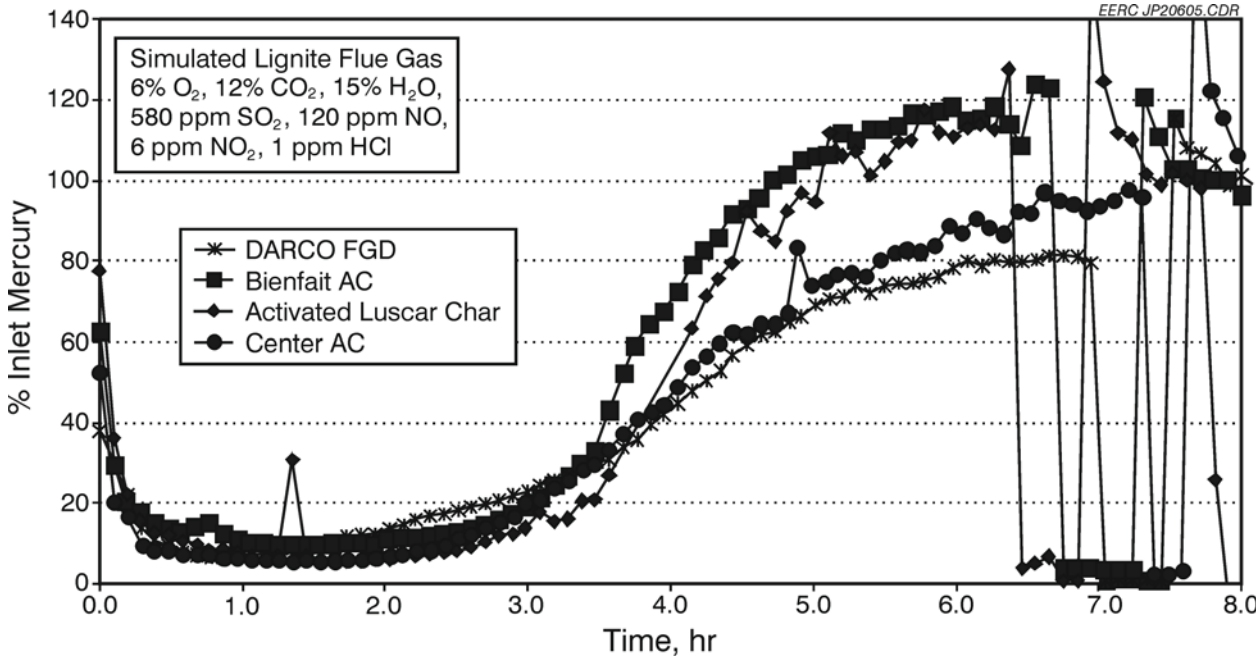

Figure ES-2. Bench-scale fixed-bed testing results for lignite-based activated (800°C, 1472°F) carbons including DARCO FGD.

Activated (750°C, 1382°F) Bienfait carbon and DARCO FGD did not experience significant early mercury breakthrough when tested using the baseline flue gas composition possibly because of the higher acid gas concentrations relative to those in the simulated lignite flue gas. Although the baseline flue gas tests yielded better mercury capture initially, significant breakthrough of mercury ultimately occurred sooner than during the simulated lignite flue gas tests.

The ALC (800°C, 1472°F) and DARCO FGD were selected for additional testing in a 580-MJ/hr (550,000-Btu/hr) pulverized coal-fired unit based on the sorbent screening results (reactivity and capacity), physical properties (particle size and surface area), cost, and consensus among project sponsors. The following variables that could potentially affect mercury emission control were tested: lignite coal source (Poplar River or Freedom Mine), control device type (ESP, FF, ESP–FF, and *Advanced Hybrid*™ filter), FF type (Gore and Ryton), sorbent type (steam-activated [800°C, 1472°F] Luscar char and DARCO FGD), and particle size (approximate median volume diameters [MVDs] of 20 and 5 µm), sorbent injection rate, and flue gas temperature in the pollution control device. Summarized in Table ES-3 is the test matrix that was performed using the pilot-scale combustion system. Unless otherwise noted, the use of ALC throughout the remainder of this summary refers to Luscar char activated at 800°C (1472°F) with an MVD of about 20 µm. The standard DARCO FGD is also roughly 20 µm in MVD.

Figure ES-3 compares the average mercury species distributions, as determined by the American Society for Testing and Materials Method D6784-02 (Ontario Hydro [OH]), for the Poplar River and Freedom coal combustion flue gases. The Poplar River coal combustion flue gas contains a higher total mercury concentration; however, the relative proportions of Hg^0, Hg^{2+}, and Hg(p) in both flue gases were very similar at approximately 85%, 15%, and <1%, respectively.

Pilot-scale test results, as exemplified in Figures ES-4 and ES-5, indicate the following:

- During periods of incomplete combustion (while the firing conditions were being set) of Poplar River and Freedom coals, the resulting production of unburned carbon in the fly ashes promoted the formation of Hg^{2+} and/or Hg(p).

- ALC activated at 800°C (1472°F) and DARCO FGD were much more effective in capturing Hg relative to carbons activated at 750°C (1282°F).

- In all four control devices tested, increasing ALC and DARCO FGD injection rates and decreasing gas temperatures in the control devices significantly improved mercury removal from the Poplar River and Freedom coal combustion flue gases.

- In general, the ALC and DARCO FGD was slightly more effective at capture of mercury when injected into the Freedom flue gas relative to the Poplar River flue gas.

- The two sorbents provided similar results in most cases, with slightly better results seen for the DARCO FGD in a few of the comparisons.

Table ES-3. Sorbent Test Matrix for Pilot-Scale Combustion System

Coal	Control Device	Sorbent	Test No.	Injection Rate, g/hr	Temperature, °F
Poplar River	ESP	NA[a]	1, 4, 10, 28	NA	300
	ESP–FF		13, 17, 19, 24, 26, 49		
	Advanced Hybrid™ filter		31		
	ESP	S1[b]	5, 6, 9, 12, 29	40–150	300
		S1 fine	8, 11, 30	25–75	
	ESP–FF	S1	14, 25, 27	10–50	300
			21	10–60	400
		S1 fine	16	25	300
			20	10–40	400
	FF	S1	35	10–60	300
	Advanced Hybrid™ filter	S1	32	20–120	
	ESP	S2[c]	2, 3	75–150	300
	ESP–FF	S2	18, 50–53	20–60	300
			23	10–60	400
		S2 fine	22	10–60	400
Freedom	ESP	NA	40	NA	300
	ESP–FF		36, 38		
	Advanced Hybrid™ filter		43		
	ESP	S1	42	50–150	300
		S1 fine	41	25–115	
	ESP–FF	S1	37	10–40	300
	Advanced Hybrid™ filter	S1	44	10–40	300
	ESP–FF	S2	39	10–40	300

[a] Not applicable.
[b] Lignite-based steam-activated (800 C, 1472 F) Luscar char.
[c] DARCO FGD.

- A reduction in ALC and DARCO FGD particle size from a MVD of approximately 20 to 5 µm did not consistently provide an improvement in mercury capture, although some improvement was noted for the Poplar River coal with the ESP-only configuration.

- Differences in the FF material, Ryton versus Gore, did not significantly affect mercury capture efficiencies.

- All of the systems that utilize filters (i.e., TOXECON™, FF, and *Advanced Hybrid*™ filter) were much more effective than the ESP in capturing mercury with sorbent injection.

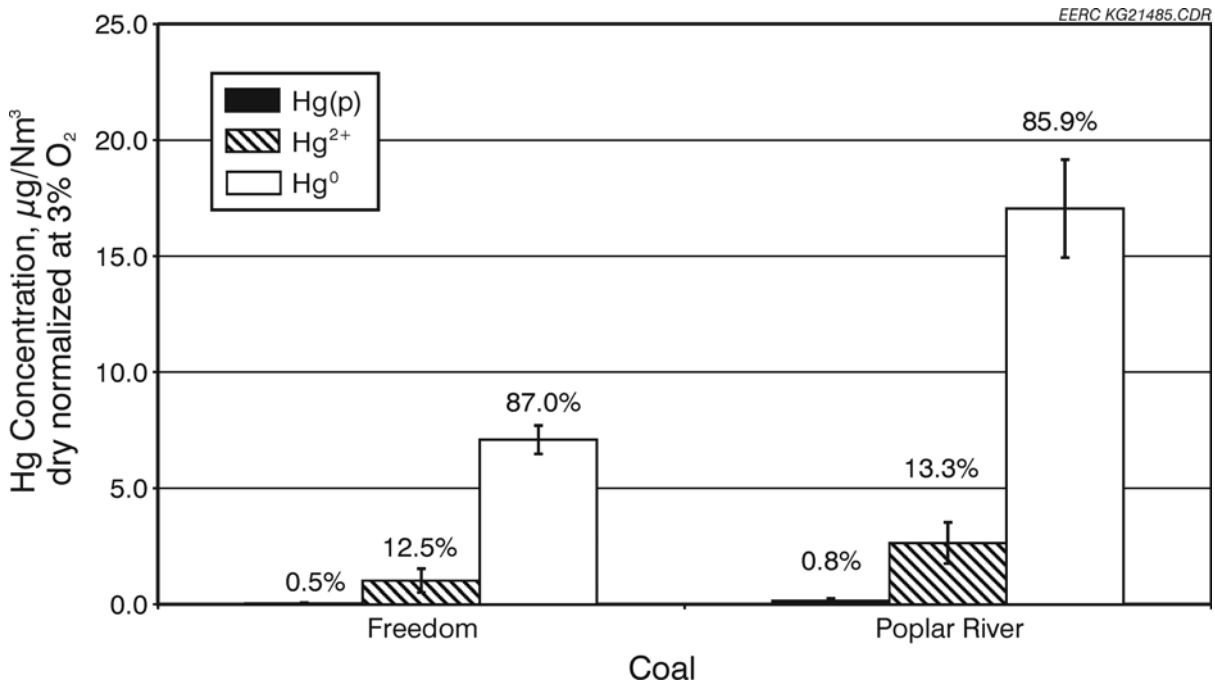

Figure ES-3. Comparison of average Poplar River and Freedom coal combustion flue gas (149°C, 300°F) mercury speciation results obtained using the OH method.

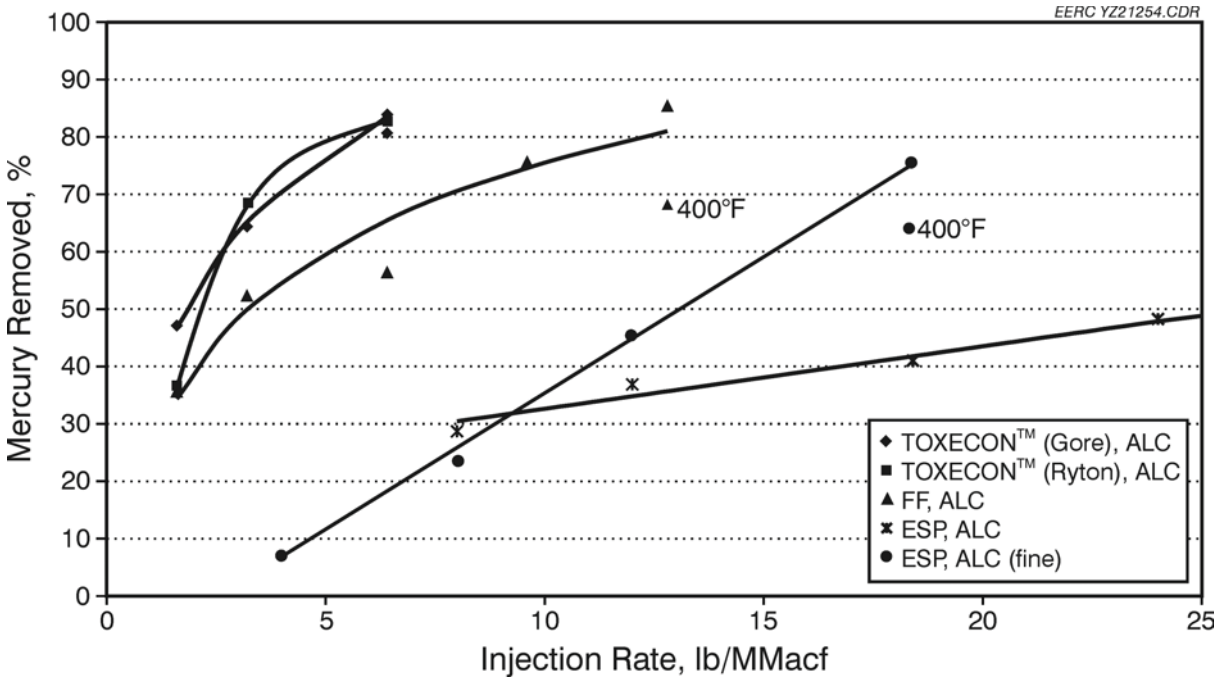

Figure ES-4. Mercury removal from Poplar River coal combustion flue gas at 149°C (300°F) as a function of ALC injection rate.

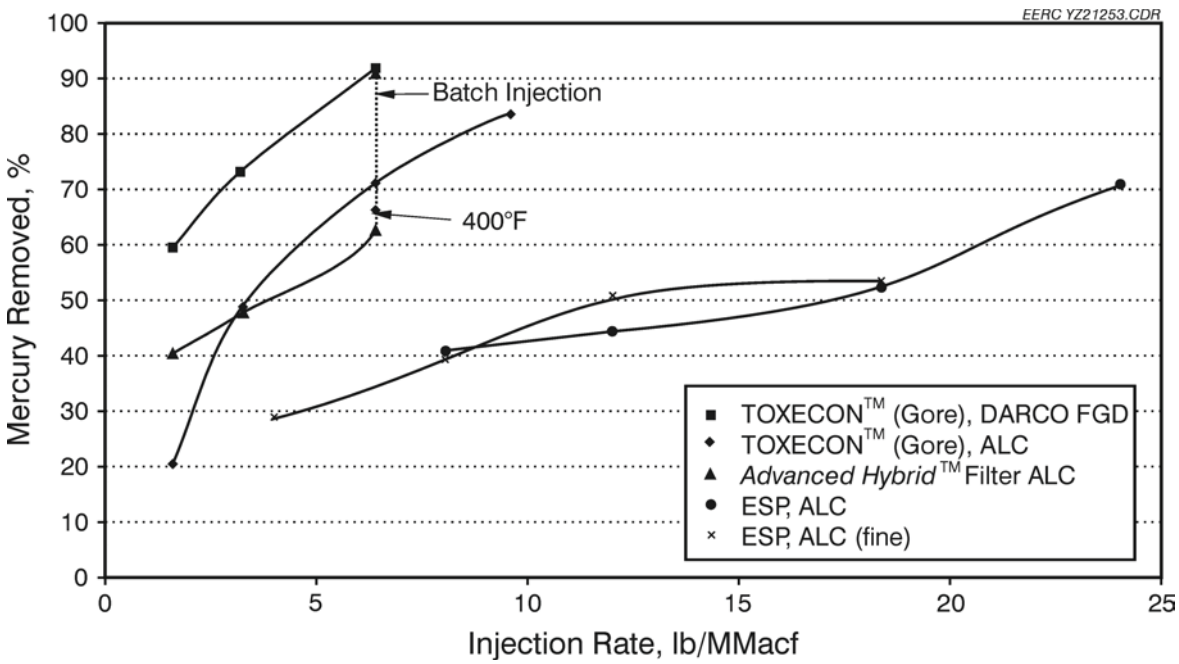

Figure ES-5. Mercury removal from Freedom coal combustion flue gas at 149°C (300°F) as functions of ALC and DARCO FGD injection rates.

- The four control device technologies tested are ranked for their mercury removal effectiveness as follows: 1) TOXECON™ and *Advanced Hybrid*™ filter, 2) FF, and 3) ESP, with the performance varying depending on coal and sorbent injection method.

- Chlorine additives were useful for enhancing the mercury removal effectiveness of activated carbon, thereby reducing the amount of sorbent needed to achieve a given level of mercury emission control.

Figure ES-6 compares the mercury removal effectiveness of ALC injection with pilot-scale ESP and TOXECON™ devices to that obtained by Bustard et al. (2002) using activated carbon injection with ESP and TOXECON™ installed on full-scale utility boilers. Coal type (i.e., composition) is an important parameter that affects the mercury removal efficiency of a control device. During the pilot-scale lignite and utility-scale eastern bituminous coal tests, mercury removal efficiency increased with increasing activated carbon injection rates. Conversely, mercury removal efficiency was never greater than 70%, regardless of the activated carbon injection rate into the Powder River Basin (PRB) subbituminous coal combustion flue gas. This limitation is probably caused by the low amount of flue gas chloride components that promote mercury-activated carbon adsorption. In addition, the generally abundant lime (CaO) component of PRB subbituminous coal fly ashes reactively scavenges chlorine species (Cl, HCl, and Cl_2) from the flue gas to form $CaCl_2$. Figure ES-6 indicates that activated carbon injection combined with the particulate control devices installed on the full-scale boilers generally provided better mercury removal efficiency at a given injection rate relative to results from the pilot-scale ESP. The pilot-scale TOXECON™ mercury

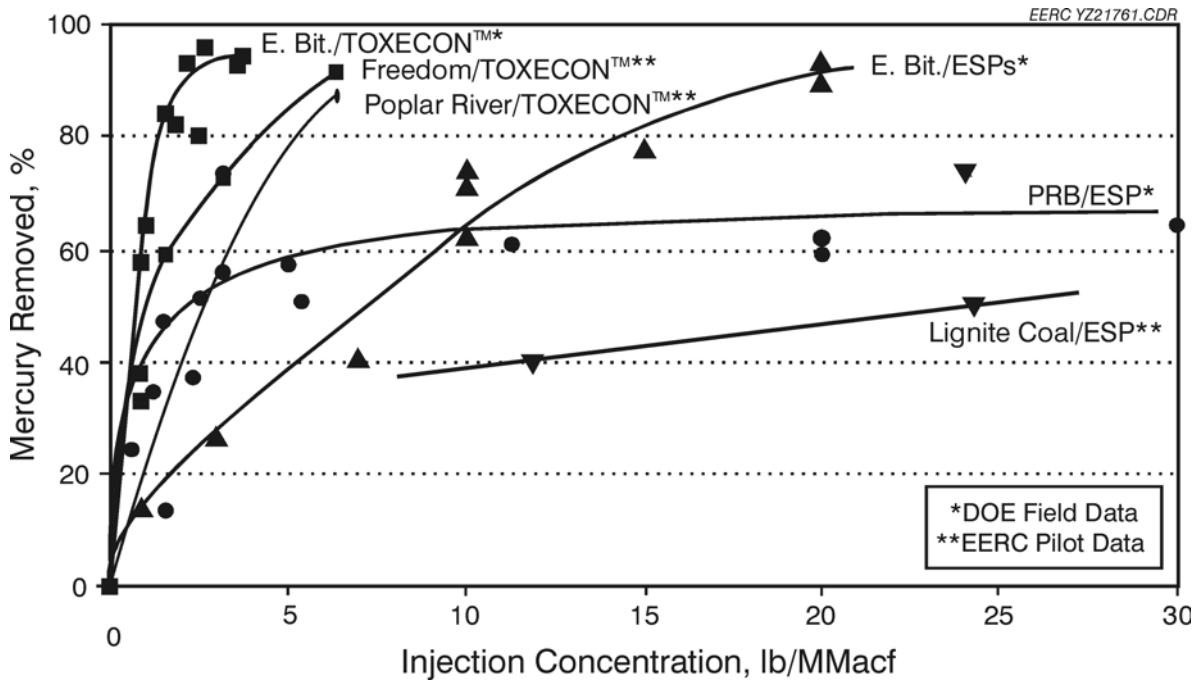

Figure ES-6. Mercury removal trends with activated carbon injection.

removal efficiencies with lignite coal in Figure ES-6 are intermediate relative to those obtained with TOXECON™ and ESPs on eastern bituminous flue gases.

Selected samples of fly ash were collected in the pilot-scale control devices with and without activated carbon present and were subjected to a synthetic groundwater leaching procedure with equilibration periods of 18 hours, 30 days, and 60 days. Mercury in Poplar River and Freedom coal fly ashes remained insoluble after 18-hour, 30-day, and 60-day exposures to deionized water, suggesting that mercury is chemically adsorbed to the fly ash and activated carbon particles and is relatively immobile.

As part of the second phase of this ongoing project, the applicability of the conclusions from the Phase I bench- and pilot-scale investigations will be evaluated by performing similar sorbent injection and flue gas and fly ash measurements at a utility host site equipped with TOXECON™ technology. Sorbent injection upstream of a pulse-jet type FF is the mercury control technology that will be field-tested at the Poplar River Power Station, which is owned and operated by SaskPower. Activities planned for the field demonstration at the Poplar River Power Station include field-testing the selected sorbent-based technology, preparing the site and installing the appropriate technology hardware, evaluating sorbent impacts and performance, assessing technology impact on unit operations, assessing ash reuse and disposal impacts, and estimating cost to control mercury. The results from Phase II of the project should provide the lignite industry with a technology option that can be considered by other utilities as they develop their own mercury control strategies.

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Bustard, J.; Durham, M.; Starns, T.; Lindsey, C.; Martin, C.; Schlager, R.; Baldrey, K. Full-Scale Evaluation of Sorbent Injection for Mercury Control on Coal-Fired Power Plants. In *Proceedings of the International Conference on Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 9–12, 2002.

MERCURY CONTROL TECHNOLOGIES FOR UTILITIES BURNING LIGNITE COAL, PHASE I BENCH- AND PILOT-SCALE TESTING

1.0 PROJECT DESCRIPTION

1.1 Project Overview

Based on health, emissions, and scientific data, the U.S. Environmental Protection Agency (EPA) and the Canadian Council of the Ministries of Environment have determined that the amount of mercury emitted from utility power plants should be reduced. U.S. and Canadian power plants burning lignite generally release greater proportions of elemental mercury (Hg^0) than plants burning bituminous coals. This form of mercury is much more difficult to remove from flue gas and, therefore, requires an innovative approach.

Bench- and pilot-scale tests associated with Phase I of a 3-year, two-phase consortium project to develop and demonstrate mercury control technologies for utilities that burn lignite coal were completed. The overall intent of this project is to help maintain the viability of lignite-fired energy production by providing local utilities with low-cost options for meeting future mercury regulations. Phase I objectives were to develop a better understanding of mercury interactions with flue gas constituents by bench-scale testing a range of sorbent-based technologies targeted at removal of Hg^0 from lignitic flue gases and evaluating the effectiveness of the most promising technologies at the pilot scale. The most promising sorbents were injected upstream of an electrostatic precipitator (ESP), a fabric filter (FF), an *Advanced Hybrid*™ filter, and in between an ESP–FF. Note: injecting a sorbent downstream of an ESP and upstream of an FF is a technology configuration that has been used by Alstom under the designation Filsorption in Europe to control mercury in waste-to-energy plants and is patented by EPRI in the United States as TOXECON™ for controlling mercury in power plants. The pilot-scale tests performed were short-term, focused on assessing performance and effectiveness. Longer-term tests will be performed under Phase II to assess operability issues associated with the most promising mercury control technologies. The Phase II objective is to demonstrate and quantify sorbent technology effectiveness, performance, and cost at a large power plant burning Fort Union lignite.

The overall project goal is to develop and demonstrate mercury control technologies for utilities that burn lignite coal. Specific objectives designed to meet the goal of the project include:

- Develop and demonstrate effective mercury control technologies for lignite-fired systems.
- Test sorbent-based technology options that target Hg^0 adsorption and removal from power plant flue gases.
- Evaluate the effectiveness of sorbent-based technologies to capture mercury in pilot-scale facilities.

- Select the most promising technology for Phase II demonstration and quantify the sorbent technology effectiveness, performance, and cost at the SaskPower Poplar River Power Plant.

1.1.1 Phase I Goals, Objectives, Approach

Phase I efforts included bench- and pilot-scale testing to identify sorbents, operating and process conditions, and combinations of particulate control devices that are most effective for removing mercury from lignite combustion flue gases.

1.1.2 Phase II Goals, Objectives, Approach

Phase I pilot-scale tests suggest that injecting a sorbent upstream of an FF or the Energy & Environmental Research Center's (EERC's) *Advanced Hybrid*™ filter are the two technologies that appear to be the most effective at reducing mercury emissions. Based on these results, SaskPower has selected the sorbent upstream of an FF option as the technology to field-test at the Poplar River Plant. Consequently, Phase II activities will focus on demonstration of this technology with specific objectives as follows:

- Continue to develop an improved scientific understanding of mercury interactions with flue gas constituents and sorbent-based technologies specifically for lignite-fired systems.

- Design slipstream technology and field test plan based on Phase I results.

- Design, construct, and install the selected technology at appropriate scale at the Poplar River Power Station located near Coronach, Saskatchewan.

- Examine effect of critical design and process parameters on mercury capture by performing parametric tests.

- Test the selected technology's ability to capture mercury using various sorbents, injection rates, and short-to-long test periods.

- Monitor mercury emissions over long periods of time to determine technology effectiveness and identify operational problems.

- Quantify the effectiveness, performance, and cost of the selected technology.

1.2 Project Plan/Approach

The project focus is testing and demonstrating effective sorbents and sorbent-based technologies for mercury control from electrical power plants firing lignite coal. Preliminary data from both laboratory and field tests indicate that both oxidation and removal can be achieved by injecting finely dispersed solid catalytic sorbents that can be removed in an ESP or FF (Pavlish et al., 2002). Sorbent preparation (i.e., grinding) and production to a small and narrow size range and

good dispersion into the flue gas promote a high level of diffusional mass transfer from the bulk flue gas to the particle surfaces. Competing reactions with the gas species commonly found in flue gas, including SO_2, NO_x, HCl, and water vapor, have been found to be immensely important and must be considered during sorbent performance tests (Pavlish et al., 2002). A combination of SO_2 and NO_2 (even small amounts) has been found to reduce the effective capacity of sorbents tested in a laboratory thin-bed reactor, apparently because of the possible formation and desorption of oxidized mercury species such as mercury nitrate hydrate and the adsorption of sulfur species contaminating available sorption sites. Several different avenues of research can be pursued to improve mercury conversion and collection via sorbent technology by addressing improvements in dispersion and diffusion, surface chemistry of sorbent materials, sorbent utilization, optimization of operating conditions, and addition of sorbent contactor collectors.

Based on interest expressed by project sponsors, the work plan focused primarily on the development, testing, and demonstration of sorbent injection technologies in combination with particulate removal devices for effective mercury removal.

2.0 BACKGROUND

2.1 Regulatory Status for Mercury

Mercury is an immediate concern for the U.S. electric power industry because of EPA's December 2000 decision that regulation of mercury from coal-fired electric utility steam-generating units is appropriate and necessary under Section 112 of the Clean Air Act. After extensive study, EPA determined that mercury emissions from power plants pose significant hazards to public health and must be reduced. The EPA *Mercury Study Report to Congress* (U.S. EPA, 1997) and *A Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units: Final Report to Congress* (U.S. EPA, 1998) both identified coal-fired boilers as the largest single category of atmospheric mercury emissions in the United States, accounting for about one-third of the total anthropogenic emissions. EPA is scheduled to propose regulations by December 2003 and promulgate them by December 2004, with full compliance expected by 2007. The exact form of regulation is uncertain at this time. While EPA is developing a regulation based on a maximum achievable control technology (MACT) approach, Congress is discussing various multipollutant (SO_x, NO_x, and Hg) bills. Under the different approaches, mercury is expected to be reduced by 45% to 90% by time frames ranging from 2007 to 2010, with reductions of 70% to 90% by 2018. Currently, the MACT approach is being followed, and a bill from Congress would be required to change direction.

Similarly, Canada has established a consultative process to develop "Canadawide standards" for mercury emissions from coal-fired electricity generation. The process is to evaluate and discuss, in conjunction with a multistakeholder advisory group, options for achieving cost-effective reductions in mercury emissions. The most common discussion points for this standard are to achieve significant (>50%) emission reductions by 2010, with a review in 2005 to address the emerging science in the United States and elsewhere on mercury control. The emission reductions are likely to be achieved by controlling emissions based on coal mercury concentrations rather than

directly from some baseline emission rate. The question of controlling mercury emissions from lignite is particularly important in Canada, as up to 30% of the mercury emitted from this sector in Canada is derived from Saskatchewan lignite.

2.2 Mercury-Specific Issues Facing Utilities Firing Fort Union Lignites

In general, lignite coals contain comparable levels of mercury but significantly lower levels of chlorine compared to bituminous coals. Lignite coals are also distinguished by their much higher calcium contents. These compositional differences have important effects on the quantity and form of mercury emitted from a boiler and on the capabilities of different control technologies to remove mercury from flue gas. The high chlorine content (>200 ppm) that is characteristic of many bituminous coals increases the fraction of the more easily removable mercuric compounds (Hg^{2+}), most likely mercuric chloride ($HgCl_2$), in the total mercury emission. Conversely, experimental results and information collection request (ICR) data indicate that low-chlorine (<200 ppm) coal combustion flue gases contain predominantly Hg^0 which is substantially more difficult to remove than Hg^{2+} (CATM Newsletter, August 2001). Additionally, the generally high calcium contents of lignite coals may reduce the oxidizing effect of the already low chlorine content by reactively scavenging chlorine species (Cl, HCl, and Cl_2) from the combustion flue gas (Galbreath and Zygarlicke, 2000).

2.3 Possible Technology Options

The most commonly considered strategy for removing mercury from coal combustion flue gas streams is the adsorption of mercury species by a solid sorbent injected upstream of a particulate control device such as an FF (baghouse) or ESP. Many potential mercury sorbents have been evaluated (Table 9 in Pavlish et al., 2002). These evaluations have demonstrated that the chemical speciation of mercury affects its capture mechanism and ultimate environmental fate.

Activated carbon injection is the most mature, thus promising, technology available for mercury control. Activated carbons can effectively sorb both Hg^0 and Hg^{2+}. Most activated carbon mercury control research has been performed in fixed-bed reactors that simulate relatively long residence time (minutes or hours) and intimate gas solids contact mercury capture by an FF cake (Carey et al., 1997; 1998; Dunham et al., 1998, 2000; Miller et al., 1999; Olson et al., 1999). However, it is important to investigate short residence time (seconds) in-flight capture of Hg^0 because most of the coal-burning boilers in the United States employ cold-side ESPs for controlling particulate matter emissions. The projected annual cost for activated carbon adsorption of mercury in a duct injection system is significant. Carbon-to-mercury weight ratios of 3000 18,000 (gram of carbon injected per gram of mercury in flue gas) have been estimated to achieve 90% mercury removal from a coal combustion flue gas containing 10 $\mu g/Nm^3$ of mercury (Pavlish et al., 2002). More efficient carbon-based sorbents and contacting systems are required to enable lower carbon-to-mercury weight ratios to be used, thus reducing the operating costs of carbon injection.

Researchers at the EERC and elsewhere are striving to attain a more thorough understanding of mercury species reactions on activated carbon surfaces in order to produce more efficient sorbents. The removal of mercury from flue gas by activated carbon is believed to occur through reactions

with surface functional groups. Mercury-reactive surface functional groups may include acidic carboxyl, lactone, hydroxyl, and carbonyl functionalities or alkaline pyrone and chromene functionalities (Coughlin and Ezra, 1968; Tessmer et al., 1997; Liu et al., 2000; Ghorishi et al., 2002a). The potential role of acidic and alkaline surface functional groups on mercury capture is unknown and needs to be investigated. Functional groups containing inorganic elements such as chlorine or sulfur are also possibilities (Otanik et al., 1988; Krishnan et al., 1994; Vidic and McLaughlin, 1996; Liu et al.; 1998; Laumb et al., 2002). Although chlorine- and sulfur-bearing surface functional groups are not well characterized, the beneficial role of chlorine and sulfur in capturing mercury species on activated carbons is well established (Dunham et al., 2000; Ghorishi et al., 2002a).

A few years ago, the EERC evaluated mercury emissions and potential controls for several North Dakota lignites and found that most of the mercury is emitted as Hg^0. Additionally, two Canadian utilities (Ontario Power Generation and SaskPower) that use lignite have performed tests that consistently showed that mercury is emitted primarily as Hg^0. Changes in mercury speciation and removal measured across different pollution control devices have been correlated with fuel properties (Chu et al., 2000; Senior et al., 2000). Mercury removals were consistently lower for low-chlorine coals. Based on limited data, test results show that certain sorbents have promise in controlling Hg^0 emissions. EPRI has also tested some sorbent-based technologies on a small slipstream that may have merit to demonstrate at a larger scale, such as a pilot-scale combustion, system. In short, recent findings have indicated that several factors impact mercury control, which may provide new opportunities and options for control. This project explores these options by first performing bench- and pilot-scale testing to gather data needed to determine technology viability and effectiveness before performing large-scale technology demonstration, as proposed under Phase II.

3.0 EXPERIMENTAL: DESCRIPTIONS OF TEST EQUIPMENT AND METHODS

3.1 Sorbent Development and Preparation Systems

Activated carbons were prepared by carbonizing relatively high-sodium lignites in a quartz tube reactor followed by steam activation in a vertical stainless steel tube reactor. In addition, larger quantities of steam-activated carbon were prepared in a 10-lb integrated bench-scale gasifier (IBG) shown schematically in Figure 3-1.

3.2 Bench-Scale Sorbent Screening Systems

A schematic of the bench-scale apparatus used to identify potentially effective mercury sorbents is presented in Figure 3-2. Test protocol consisted of continuous emission monitor (CEM) measurements of total mercury at the outlet of the fixed sorbent bed until mercury breakthrough reached a steady state, usually between 6 and 7 hours into the test (in this report, CMM [continuous mercury monitor] is interchangeable with CEM). At that point, the CEM was switched to analyze Hg^0 at the outlet followed by Hg^0 at the inlet to the sorbent bed before the test was terminated. Test results are presented in the subsequent section of this report as the total gaseous outlet mercury

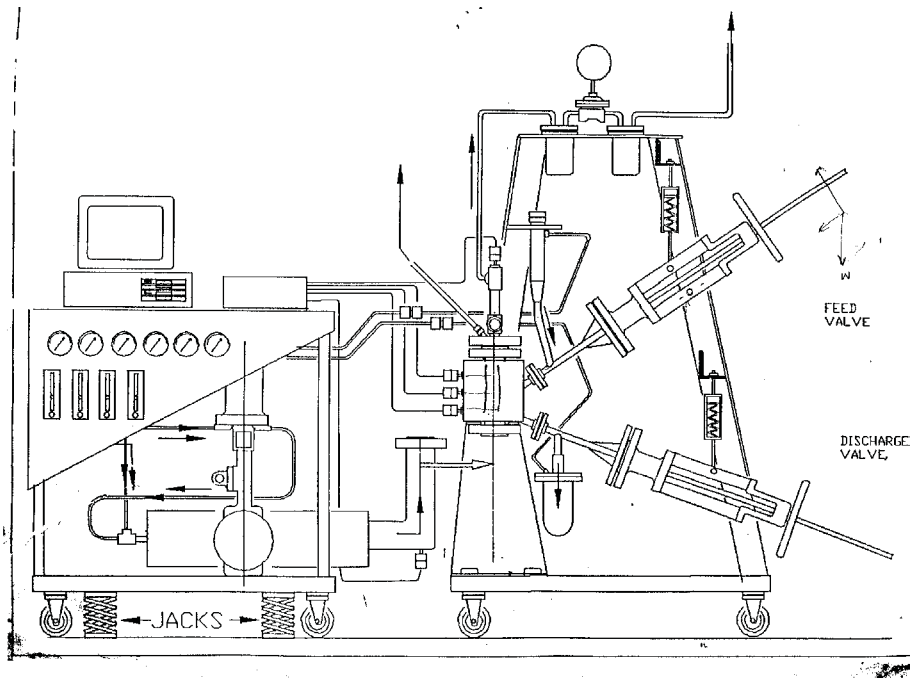

Figure 3-1. Schematic of the IBG.

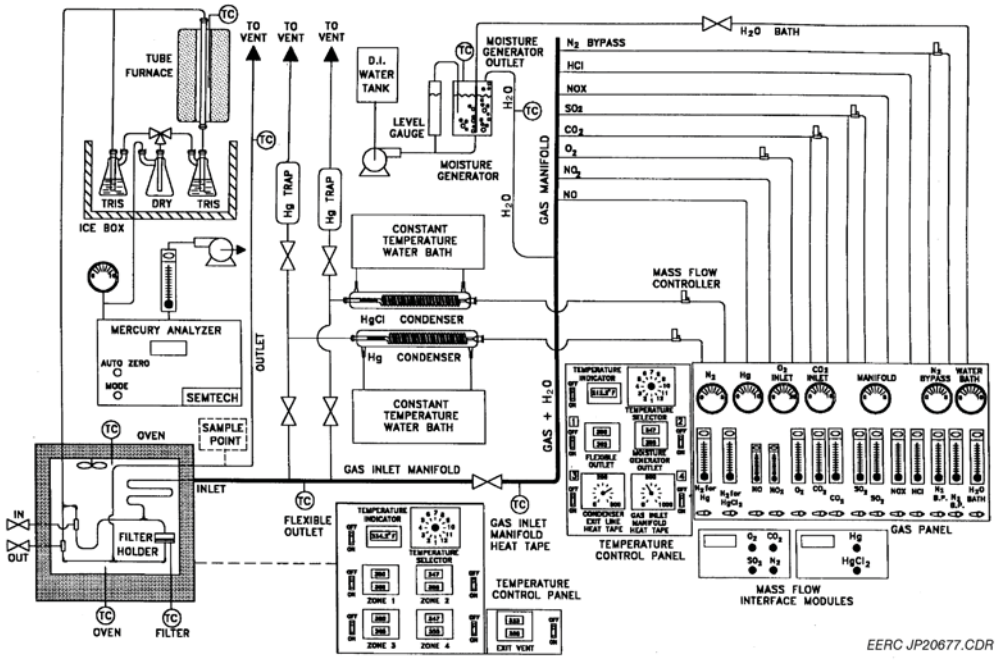

Figure 3-2. Schematic of the bench-scale mercury sorbent testing system.

concentration expressed as a percentage of Hg^0 input into the system as a function of time. These results provide information relating to mercury sorbent capacity and oxidation potential.

3.3 Pilot-Scale Combustor

A 580-MJ/hr (550,000-Btu/hr) pulverized coal-fired unit was used to evaluate mercury sorbent effectiveness in coal combustion flue gases. The unit, shown schematically in Figure 3-3, is designed to generate fly ash and flue gas representative of that produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature.

The following particulate control devices in conjunction with sorbents were evaluated on the pilot-scale combustor as potential mercury control options: ESP, FF, combined ESP–FF, and *Advanced Hybrid*™ filter technology. Instrumentation enables system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device operating data to be monitored continuously and recorded on a data logger.

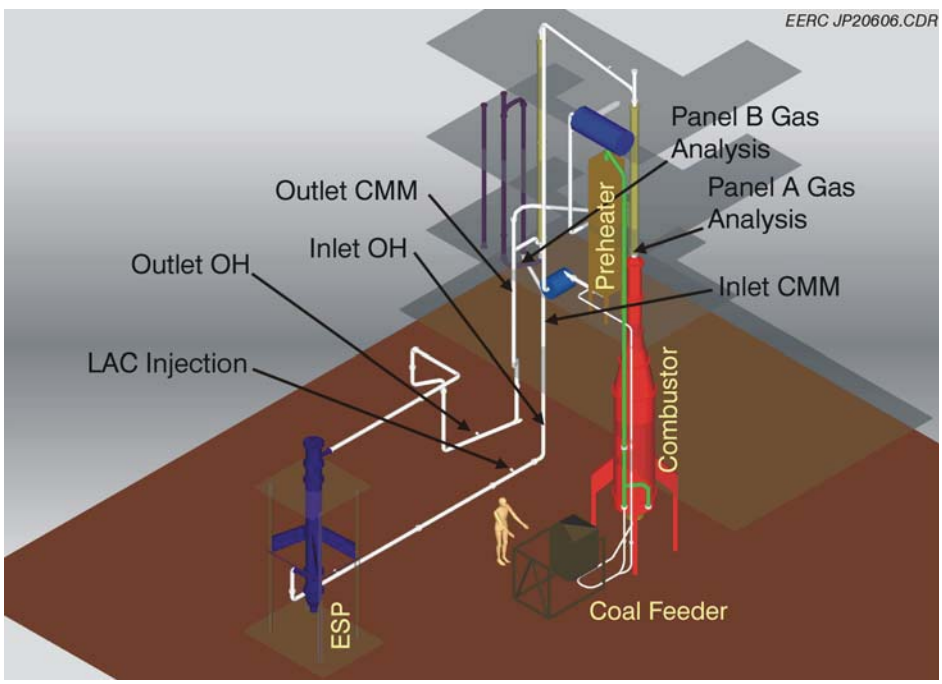

Figure 3-3. Schematic of the 580-MJ/hr (550,000-Btu/hr) combustion system.

3.4 Pilot-Scale Electrostatic Precipitator

A single-wire, tubular ESP, shown schematically in Figure 3-4, is designed to provide a specific collection area of 125 at 149°C (300°F). Gas velocity through the ESP is 1.5 m/min (5 ft/min). Plate spacing for the unit is 28 cm (11 in.). The ESP has an electrically isolated plate that is grounded through an ammeter, allowing continual monitoring of the actual plate current to ensure consistent operation of the ESP. The tubular plate is suspended by a load cell which helps to monitor rapping efficiency. In addition, sight ports are located at the top of the ESP to allow for on-line inspection of electrode alignment, sparking, rapping, and dust buildup on the plate. The ESP was

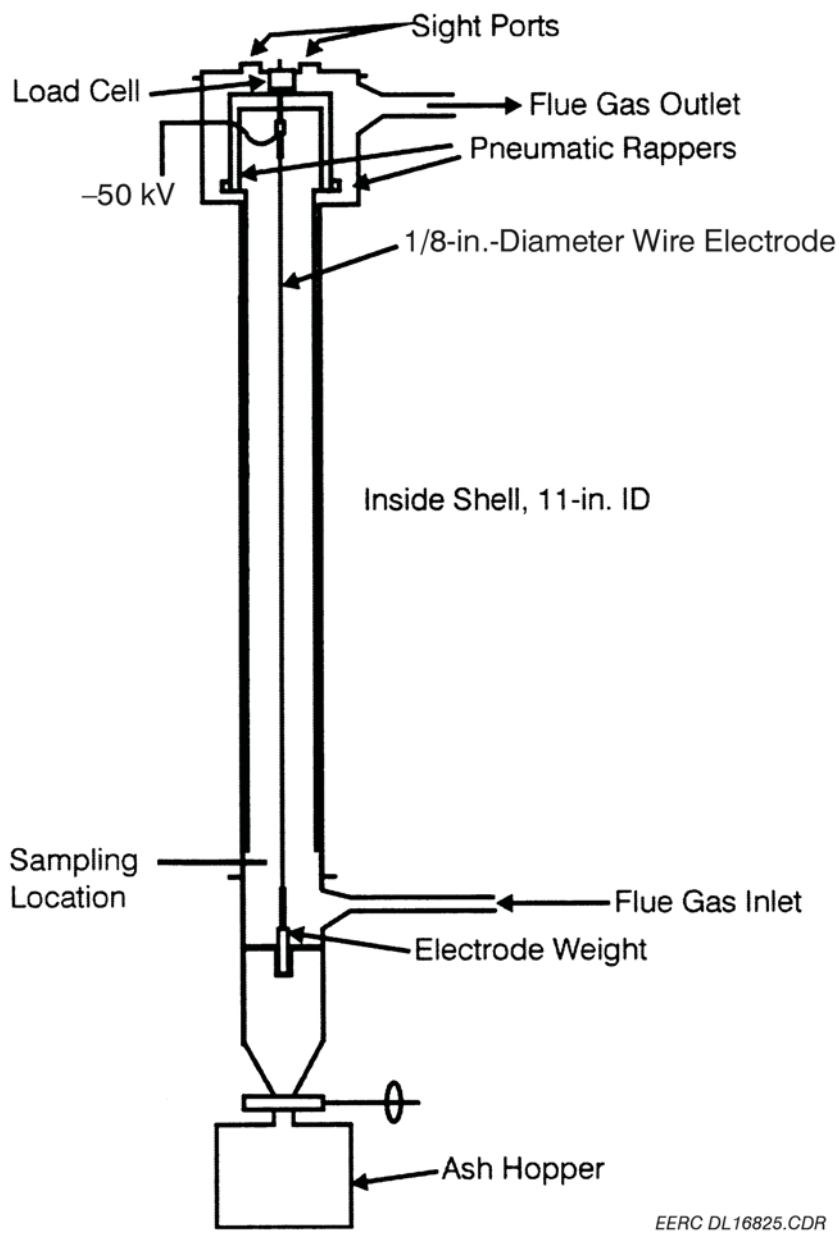

Figure 3-4. Schematic of the pilot-scale ESP.

designed to facilitate thorough cleaning between tests so that all tests begin on the same basis. The ESP and FF (discussed below) were used in series to evaluate this combination as a potential mercury control strategy.

3.5 Pilot-Scale Fabric Filter

The FF vessel (baghouse) is a heat-traced and insulated 20-in.-ID chamber. Flue gas enters the bottom of this chamber. The pilot-scale combustor produces about 5.7 m^3/min (200 acfm) of flue gas at 149° 204°C (300° 400°F); thus three 4-m by 13-cm (13-ft by 5-in.) bags provide an air-to-cloth (A/C) ratio of 1 m/min (3.3 ft/min). For tests performed under this project, the A/C was varied between 1.8 3.7 m/min (6 12 ft/min), with most of the tests run as an A/C of 1.8 m/min (6 ft/min). Each bag is cleaned separately with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags can be cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning is initiated, all three bags are pulsed in rapid succession on-line.

3.6 Pilot-Scale ADVANCED HYBRID™ Filter System

The *Advanced Hybrid*™ filter system combines electrostatic and fabric filtration into the same vessel. As shown schematically in Figure 3-5, the *Advanced Hybrid*™ filter is composed of alternating rows of FFs, discharge electrodes, and perforated collection plates in close proximity. Extensive pilot-scale testing indicates that the *Advanced Hybrid*™ filter provides very high, >99.99%, particulate matter collection efficiency, high A/C ratio, reasonable pressure drop, and long bag-cleaning intervals leading to long bag life. The *Advanced Hybrid*™ filter may have unique advantages

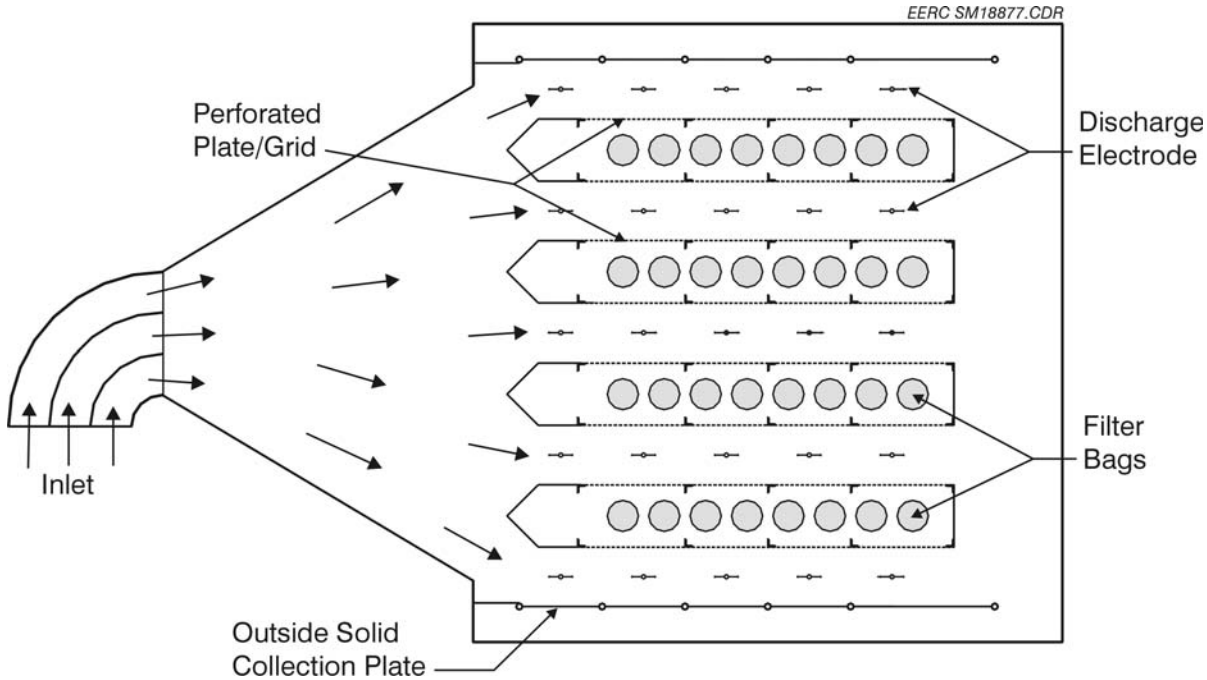

Figure 3-5. Schematic of the *Advanced Hybrid*™ filter system.

for mercury control in that it should provide excellent gas–solid contact in sorbent injection applications.

3.7 Measurement Methods

Measurement methods used specific to this project are discussed as follows.

3.7.1 ASTM Method D6784-02, Ontario Hydro Method

Mercury speciation analyses were performed using the Ontario Hydro (OH) method, which was used by the EPA for its ICR. The OH method has been demonstrated by the EERC and others to provide accurate and precise mercury speciation results for coal-fired boilers (Laudal et al., 1997). The method has been approved by American Society for Testing and Materials (ASTM) Subcommittee D22.03.01 and designated as Method D6784-02. A summary of the method is available on the ASTM Web site at http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/PAGES/D6784.htm?E+mystore. In addition, a detailed description of the original draft OH method is available on the EPA Web site at http://www.epa.gov/ttn/emc/prelim.html. The OH method was also used to evaluate the particulate matter removal efficiencies of the control devices described in Sections 3.4, 3.5, and 3.6 because EPA Method 17 or EPA Method 5 particulate matter measurements are part of the OH method.

3.7.2 Mercury Continuous Emission Monitors

To measure gaseous mercury concentrations on a nearly continuous basis, three different mercury CEMs were employed: 1) PS Analytical Sir Galahad, 2) Tekran, and 3) Semtech Hg 2000. These instruments were equipped with a proprietary EERC conversion system to enable the measurement of both Hg^0 and total gaseous mercury (Hg[tot]) and thus gaseous mercuric compounds (Hg^{2+}) by difference (i.e., $Hg^{2+} = Hg[tot] - Hg^0$). Since the Semtech was only used for a brief time, it will not be discussed further. More detail on the other two instruments are briefly described below.

3.7.2.1 PS Analytical Sir Galahad

The Sir Galahad analyzer is based on the principle of cold-vapor atomic fluorescence spectroscopy (CVAFS) which provides an inherently more sensitive signal than atomic absorption. The system uses a gold-impregnated silica support for preconcentrating gaseous mercury and separating it from potential interferences that degrade sensitivity.

The Sir Galahad requires a four-step process to obtain a flue gas mercury measurement. In the first step, 2 L of flue gas is pumped through a gold trap which is maintained at a constant temperature. Before the mercury is desorbed from the gold trap, a flushing step is initiated to remove any flue gas that may be present, because it has a damping effect on the mercury fluorescence. When this is completed, the analysis step begins. The heating coil is activated, and the gold-impregnated silica support is heated to approximately 500°C. This desorbs mercury from the trap as Hg^0, and Hg^0 is then carried into the fluorescence detector. The gold trap is cooled rapidly by pumping argon over it, in preparation for the next sample. The total time for the entire process is about 5 minutes.

The system is calibrated using Hg^0 as the primary standard. The Hg^0 is contained in a closed vial which is held in a thermostatic bath. The temperature of the mercury is monitored, and the amount of mercury is measured using vapor pressure calculations. Typically, the calibration of the unit has proven stable over a 24-hour period.

3.7.2.2 Tekran

Similar to the Sir Galahad analyzer, the Tekran is based on CVAFS. The Tekran's sampling system is constructed of Teflon® and quartz glass. The analyzer employs a system of parallel gold amalgamation cartridges that automatically alternate between adsorb and desorb cycles. CVAFS is used for detecting and quantifying Hg^0 concentrations ranging from 0.002 to 2.0 $\mu g/Nm^3$. An internal permeation source provides automatic recalibration.

3.7.3 Gaseous Monitors

An ECOM-America portable O_2 analyzer was used during most of the pilot-scale combustion tests. This portable O_2 analyzer's linearity was verified using EPA Protocol 1 certified gas standards. Flue gas velocity, moisture, and flow rate determinations were performed according to EPA Methods 2 and 4 in conjunction with the OH method.

Flue gases were sampled at any combination of two of three available sample points on the pilot-scale combustor: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O_2, CO, CO_2, SO_2, and NO_x. Except for CO and CO_2, each constituent is normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments are recorded continuously, using circular charts. In addition, data are manually recorded at set time intervals. NO_x is determined using two Thermoelectron chemiluminescent NO_x analyzers. The O_2 and CO_2 analyzers are made by Beckman, and the SO_2 analyzers are manufactured by DuPont. Each of these analyzers is regularly calibrated and maintained to provide accurate flue gas concentration measurements.

3.7.4 Coal, Fly Ash, and Carbon-Based Sorbent Sampling and Analytical Methods

The methods identified in Table 3-1 were used to sample and analyze selected samples of coal, fly ash, and carbon-based sorbent.

In addition, the surface chemistries of activated carbon sorbents exposed to Hg^0 in the bench-scale flue gas simulator were characterized using x-ray photoelectron spectroscopy (XPS). XPS, also known as electron spectroscopy for chemical analysis, involves irradiating a sample with a monoenergetic x-ray beam that causes photoelectrons to be emitted from the samples. The photoelectrons are emitted from the first 30–50 angstroms of the sample surface. An energy analyzer is used to determine the binding energy of the emitted electrons. From the binding energy and intensity of the photoelectron peak, the elemental identity, chemical state, and quantity of an element is determined.

Table 3-1. Coal, Fly Ash, and Carbon-Based Sorbent Sampling and Analytical Methods

Sample Type	Sampling Method	Analyte(s)	Analytical Method(s)
Coal and Carbon-Based Sorbents	Grab composite sampling (ASTM D2234)	Hg	CVAAS (EPA 245.1 and SW-846 Method 7470)
		Na, Mg, Al, Si, P, S, K, Ca, Mn, Ti, Ba, and Fe	XRF[a] (ASTM D4326)
		As, Ba, Be, Cd, Cr, Co, Pb, Mn, Ni, and Se	Microwave-assisted digestion (EPA Method 3050 and ASTM Method D3683); AAS[b], GFAAS[c], and ICP–AES[d] (EPA Methods D3682, 249.2, and 6010)
		Chlorine	ASTM D4208 or oxidative hydrolysis microcoulometry (EPA SWA-846)
		S, C, H, N, O, moisture, ash, heating value, fixed C, and volatile matter	Ultimate (ASTM D3176) and proximate (ASTM D3172 and D5142)
Fly Ash	Grab composite sampling (EPA Method S007)	Hg	CVAAS (EPA SW-846 and Method 7470 or EPA Method 7473)
		Na, Mg, Al, Si, P, S, K, Ca, Mn, Ti, Ba, and Fe	XRF (ASTM D4326)
		LOI[e]	ASTM C114
		C	Leeman Labs Model CE440 elemental analyzer

[a] X-ray fluorescence spectrometry.
[b] Atomic absorption spectroscopy.
[c] Graphite furnace atomic absorption spectroscopy.
[d] Inductively coupled plasma–atomic emission spectroscopy.
[e] Loss on ignition.

3.7.5 Fly Ash Mercury Leaching Procedure

Leaching of selected coal fly ash samples was performed using the synthetic groundwater leaching procedure (SGLP) with 18-hour and 30- and 60-day equilibration times. This test of leachability, developed at the EERC, has been used for nearly 20 years to predict the metal leaching of coal combustion residues and other similar solid waste materials. The SGLP is appropriate for the screening of ash for potential environmental impact. The liquid-to-solid ratio at 20:1 is the same as specified in the EPA toxicity characteristic leaching procedure (TCLP) and has a scientific basis for determining hazardousness. As with the TCLP, end-over-end agitation is used; however, the leaching solution in the SGLP is dependent on local conditions at the disposal location and also determined by the solution most likely to contact the waste material. Solutions that have been used include synthetic acid precipitation, distilled deionized water, and groundwater either from the site or prepared in the laboratory based on groundwater analyses from the disposal site. Distilled deionized water was used in this project. At the present time, the SGLP test has been used in many states, including Minnesota, North Dakota, Mississippi, and Indiana, for evaluating the

environmental effects of coal conversion solids. The test has been submitted in draft form for consideration by ASTM as a standard for coal ash leaching.

4.0 TEST COALS

Four lignites from the Poplar River, Bienfait, Freedom, and Center coal mines were utilized in this investigation. Lignites from the Bienfait, Freedom, and Center Mines were used to produce potential mercury sorbents, and lignites from the Poplar River and Freedom coal mines were burned in the 580-MJ/hr (550,000-Btu/hr) combustion system to evaluate the mercury-removal effectiveness of injecting these sorbents upstream of the particulate control device configurations described in Sections 3.4, 3.5, and 3.6. Information on the four coals involved in this investigation is presented in Table 4-1. All four lignites are part of the same extensive basin, Great Plains coal area, which is centered in North Dakota and Montana and extends northward into Saskatchewan and southward into Wyoming and South Dakota.

Table 4-1. Lignite Coal Information

Organizaton	Mine	Coal	Location	Mine Production,[a] tons
Luscar Ltd.	Poplar River	Ravenscrag	Wood Mountain-Willow Bunch Area, Saskatchewan, Canada	3,837,900
Luscar Ltd.	Bienfait	Ravenscrag	Estevan Area, Saskatchewan, Canada	1,955,800
The Coteau Properties Co.	Freedom	Beulah-Zap	Western, Northern Lignite Basin, North Dakota, United States	16,125,847
BNI Coal Ltd.	Center	Hagel and Kinneman Creek	Western, Northern Lignite Basin, North Dakota, United States	4,415,033

[a] 2000 mine production statistic from Keystone, (2002).

Coal proximate and ultimate analysis results for the four lignites are presented in Tables 4-2 and 4-3. The Saskatchewan lignites are distinguished from the North Dakota lignites by possessing slightly higher ash concentrations. Major and minor element compositions of these ashes are presented in Table 4-4. The Poplar River coal ash contains much lower Na_2O and higher Al_2O_3 contents relative to the other three lignite ashes. The Freedom coal ash is distinguished by much lower SiO_2 and higher CaO contents relative to the other lignites. The Bienfait and Center coal ash compositions are similar except that the Center ash has approximately half the concentration of Na_2O.

Trace element concentrations for the Poplar River and Freedom coals are presented in Table 4-5. Chlorine concentrations for the Bienfait and Center coals are also included in Table 4-5. The Poplar River coal contains significantly higher concentrations of Be, Cr, Pb, Mn, and Hg but less Ba, Cd, Ni, and Se relative to the Freedom coal. As, Co, and Cl contents of the two coals are very similar. Chlorine concentrations for all four lignites are similar and low compared to most bituminous coals which generally contain 200 to 1400 ppm Cl (Pavlish et al., 2002).

Table 4-2. Coal Proximate Analysis Results, moisture-free wt%

Analysis Parameters	Poplar River[a]	Bienfait	Freedom[b]	Center
Volatile Matter	46.0	41.2	45.5	43.0
Fixed Carbon	33.7	39.3	42.3	45.2
Ash	20.4	19.7	12.2	11.6
Higher Heating Value, Btu/lb	8610	NA[c]	9990	NA

[a] Average based on six analyses. Individual analysis results are presented in Appendix A.
[b] Average of two analyses. Individual analysis results are presented in Appendix A.
[c] Not analyzed.

Table 4-3. Coal Ultimate Analysis Results, moisture-free wt%

Analysis Parameters	Poplar River[a]	Bienfait	Freedom[b]	Center
Carbon	52.8 ± 0.5	64.9	60.4	59.9
Hydrogen	3.48 ± 0.11	4.21	3.92	3.94
Nitrogen	0.81 ± 0.02	1.22	1.02	1.09
Sulfur	0.90 ± 0.09	0.90	0.86	1.29
Ash	20.3 ± 0.7	19.6	12.2	11.6
Oxygen	21.9 ± 0.6	9.21	21.6	22.1

[a] Average ±95% confidence limit based on six analyses. Individual analysis results are presented in Appendix A.
[b] Average of two analyses. Individual analysis results are presented in Appendix A.

Table 4-4. Comparison of Coal Major and Minor Elemental Oxide Compositions, ash wt%

Elemental Oxide	Poplar River[a]	Bienfait	Freedom	Center
SiO_2	40.4	38.3	25.3	43.8
Al_2O_3	26.6	15.2	14.3	14.3
Fe_2O_3	6.93	6.0	8.35	7.6
TiO_2	0.64	0.6	0.45	0.5
P_2O_5	0.04	0.2	0.27	0.1
CaO	16.0	15.5	23.0	11.6
MgO	5.08	3.5	7.10	4.5
Na_2O	0.06	8.7	6.44	4.3
K_2O	0.69	1.4	0.65	2.0
SO_3	8.45	10.6	17.0	11.2
Total	104.9	100	102.9	99.9

[a] Average of two XRF analyses. Individual analysis results are presented in Appendix A.

Table 4-5. Coal Trace Element Compositions, ppm dry

Trace Element	Poplar River	Bienfait	Freedom	Center
As	4.99 ± 0.13[a]	NA[b]	4.63	NA
Ba	367 ± 57[a]	NA	639	NA
Be	0.89 ± 0.04[a]	NA	0.40	NA
Cd	0.071 ± 0.021[a]	NA	0.18	NA
Cr	10.6 ± 1.4[a]	NA	8.5	NA
Co	14.8 ± 2.3[a]	NA	13.5	NA
Pb	10.3 ± 0.9[a]	NA	4.69	NA
Mn	118 ± 20[a]	NA	59.8	NA
Ni	2.96 ± 0.17[a]	NA	4.45	NA
Se	0.713 ± 0.017[a]	NA	0.963	NA
Hg	0.153 ± 0.024[c]	NA	0.077[d]	NA
Cl	21.8 ± 2.05[c]	18.0	19.6[d]	14.3

[a] Average ±95% confidence limit based on three analyses. Individual analysis results are presented in Appendix A.
[b] Not analyzed.
[c] Average ±95% confidence limit based on four analyses. Individual analysis results are presented in Appendix A.
[d] Average of two analyses. Individual analysis results are presented in Appendix A.

5.0 DESCRIPTIONS OF SORBENT, CHAR, AND ACTIVATED CARBONS

A commercially available sorbent, DARCO® FGD, supplied by NORIT Americas, Inc.; a calcium silicate sorbent; and a char produced by Luscar Ltd. were evaluated as potential mercury sorbents. In addition, the relatively high-sodium Bienfait, Freedom, and Center lignites (Table 4-4) and Luscar char were used to prepare activated carbons. Descriptions, preparation procedures, and physical and chemical information on these potential mercury sorbents are presented below.

5.1 Preprepared Sorbents

5.1.1 NORIT Americas Inc. DARCO® FGD

DARCO FGD is a lignite-based activated carbon manufactured specifically for the removal of heavy metals and other pollutants typically found in incinerator flue gas streams. It has been proven in numerous incinerator facilities to be highly effective for removing gaseous mercury, dioxins, and furans. Bench-scale tests indicate a Hg^0 sorption capacity of about 100 µg/g (Ghorishi et al., 2002a). Testing in pilot-scale combustion systems indicates that the effectiveness of DARCO FGD to remove mercury from coal combustion flue gases is variable depending on the flue gas composition, residence time, pollution control device, and temperature (Dunham et al., 1998; Butz et al., 2000; Hargis et al., 2001). General properties and characteristics of DARCO FGD, as advertised by NORIT Americas Inc., are presented in Table 5-1. Duplicate Malvern particle-size analyses of the DARCO FGD indicated median volume diameters (MVDs) of 16.2 and 18.1 µm. The chemical composition of inorganic constituents making up DARCO FGD is presented in Table 5-2.

Table 5-1. Physical and Chemical Characteristics of DARCO FGD

Property or Characteristic, unit	Value
Moisture, wt% as-received	≤8
Particle Size <325 mesh (45 µm), wt%	≥95
Iodine Number, mg/g	600
Bulk Density, tamped, g/mL	0.53
Surface Area, m^2/g	600
Heat Capacity	0.22
Total Sulfur, wt%	1.8
Ignition Temperature, °C (°F)	450 (842)

Table 5-2. Elemental Oxide Composition of DARCO FGD, ash wt%

Elemental Oxide	DARCO FGD
SiO_2	38.5
Al_2O_3	15.6
Fe_2O_3	10.6
TiO_2	1.3
P_2O_5	<0.1
CaO	18.1
MgO	4.7
Na_2O	0.7
K_2O	0.6
SO_3	10.0
Total	100.1

The inorganic fraction of DARCO FGD is primarily an Fe_2O_3-, CaO-, and SO_3-rich aluminosilicate material. It lacks alkali metals, Na_2O and K_2O, but contains relatively high alkaline-earth metal, CaO and MgO, contents.

5.1.2 Luscar Ltd. Char

Luscar Ltd. produces char from Ravenscrag lignite (Bienfait Mine) using the Salem carbonizer processing method. A rotary-hearth calciner is used to heat the coal to ≥1100°C (2012°F) in an oxygen-deficient atmosphere to reduce moisture and volatile matter. Proximate and ultimate analysis results for the precursor Bienfait Mine coal and char product in Tables 5-3 and 5-4 indicate the large increase in carbon concentration associated with the reduction in moisture and volatile matter. This creates a porous, lightweight char that has nearly double the heating value of the original lignite coal. The char is used primarily for the manufacture of barbeque briquettes.

Table 5-3. Bienfait Coal and Char Proximate Analyses, wt%

	Bienfait Coal		Luscar Char	
	AR[a]	MF[b]	AR	MF
Moisture	32.5	NA[c]	7.8	NA
Volatile Matter	27.8	41.1	22.4	24.2
Fixed Carbon	26.5	48.8	54.8	71.0
Ash	13.3	19.6	15.0	16.3

[a] As-received.
[b] Moisture-free.
[c] Not applicable.

Table 5-4. Bienfait Coal and Luscar Char Ultimate Analyses, wt%

	Bienfait Coal		Luscar Char	
Sample	AR[a]	MF[b]	AR	MF
Hydrogen	6.45	4.21	3.35	2.69
Carbon	43.8	64.9	60.9	66.1
Nitrogen	0.82	1.22	1.12	1.21
Sulfur	0.61	0.90	0.80	0.87
Oxygen	35.0	9.21	18.8	12.9
Ash	13.3	19.6	15.0	16.3

[a] As-received.
[b] Moisture-free.

Table 5-5 compares the chemical compositions of the Bienfait coal and char inorganic ash fractions. The two ash compositions are very similar except for the lower K_2O content of the char. Apparently, the char preparation process does not significantly affect the chemical composition of the Bienfait coal ash fraction.

5.1.3 Calcium Silicate

A calcium silicate sorbent has been developed for simultaneously removing acid gases and mercury from coal combustion flue gases. The sorbent is produced by reacting portlandite ($Ca[OH]_2$), silica (SiO_2), and a proprietary oxidant to produce calcium silicate gel that has a Brunauer–Emmett–Teller surface area of approximately 100 m^2/g and thin layers of $Ca[OH]_2$ (Ghorishi et al., 2002b). Bench-scale tests involving a simulated coal combustion flue gas indicate a Hg^0 sorption capacity of about 100 µg/g, comparable to commercially available activated carbons, and SO_2 and NO_2 sorption capacities of approximately 180 and 15 mg/g, respectively (Ghorishi et al., 2002b). Advantages of a calcium silicate mercury sorbent versus carbon are projected lower cost, simultaneous removal of SO_2 and NO_x, and enhancement of the cementitious properties of the resulting fly ash so that it could potentially be used as a cement additive.

Table 5-5. Major and Minor Elemental Oxide Compositions of Bienfait Coal and Char, wt%

Elemental Oxide	Bienfait Coal	Char
SiO_2	38.3	32.9
Al_2O_3	15.2	17.3
Fe_2O_3	6.0	6.4
TiO_2	0.6	0.6
P_2O_5	0.2	0.2
CaO	15.5	16.4
MgO	3.5	3.8
Na_2O	8.7	9.9
K_2O	1.4	0.6
SO_3	10.6	12.0
Total	100.0	100.1

5.2 Lignite-Based Activated Carbons Prepared by the EERC

5.2.1 Lignite-Based Activated Carbons for Bench-Scale Testing

The relatively high-sodium Bienfait, Freedom, and Center lignites (Table 4-4) and Luscar char were used to prepare activated carbons. The lignites were air-dried, ground, and sieved. Approximately 1-mm-diameter lignite particles were used to prepare chars. Representative samples, 150 g, of the lignites were carbonized in a quartz tube reactor at 400°C (752°F) in a gentle flow of nitrogen. The reactor was held at 400°C (752°F) until tarry material ceased to evolve. The resulting char was stored in a nitrogen atmosphere before being steam-activated.

Each char was steam-activated in a vertical steel tube reactor. The tube reactor was heated to 750° (1382°F) or 800°C (1472°F) in a gentle flow of nitrogen. Steam at 450°C (842°F) was then introduced into the bottom of the reactor at 65 cm^3/min for 30 minutes. After the activation process, the reactor was cooled to room temperature in flowing nitrogen. The activated carbon was removed from the reactor, weighed, and stored in a nitrogen atmosphere. Yields of char and carbon produced in this manner are listed in Table 5-6.

Iodine numbers of the activated carbons, ground to pass through a 200-mesh sieve, were determined according to ASTM Procedure D4607. Iodine numbers indicate approximate surface area. The results, presented in Table 5-7, indicate that the commercial DARCO FGD sorbent has the highest surface area. The iodine number in Table 5-7 is slightly less than the nominal 600 mg I_2/g sorbent value reported by NORIT Americas Inc. in Table 5-1. Carbons from the Bienfait coal and Luscar char had roughly 20% less surface area, and carbons from the other coals averaged 36% less surface area. In all cases, the carbon activated at 800°C (1472°F) had less surface area than the same carbon activated at 750°C (1382°F), but as is described in subsequent sections, the carbons activated at higher temperature were more reactive and effective at capturing mercury. The higher activation

Table 5-6. Char and Carbon Yields from Lignite-Based Activated Carbon Production

Precursor Material	Activation Temp., °C	Char:Coal	Carbon:Coal	Carbon:Char
Bienfait Coal	750	0.481	0.367	0.764
Bienfait Coal	800	0.493	0.356	0.722
Luscar Char	750	NA[a]	NA	0.647
Luscar Char	800	NA	NA	0.576
Freedom Coal	750	0.510	0.370	0.726
Center Coal	750	0.496	0.360	0.725
Center Coal	800	0.521	0.346	0.665

[a] Not applicable.

Table 5-7. Activated Carbon Iodine Numbers

Precursor Material	Activation Temperature, °C (°F)	Iodine No., mg I_2/g Sorbent
Bienfait Coal	750 (1382)	424.3
Bienfait Coal	800 (1472)	398.1
Luscar Char	750 (1382)	439.6
Luscar Char	800 (1472)	427.4
Freedom Coal	750 (1382)	331.5
Center Coal	750 (1382)	352.8
Center Coal	800 (1472)	321.5
DARCO FGD	Unknown	524.8

temperature could be bringing the carbon closer to gasification resulting in a change in the carbon pore structure and could also be causing a positive change in the carbon chemistry.

5.2.2 Preparation of Lignite-Based Activated (800°C, 1472°F) Luscar Char for Pilot-Scale Testing

Additional quantities of steam-activated (800°C, 1472°F) Luscar char were prepared in a 10-lb IBG and in a 1-in. tube reactor. The as-received char was sieved, and approximately 1-mm-diameter particles were collected for activation. Luscar char (4.5 kg) was placed in the IBG and heated to 800°C (1472°F) in a N_2 flow. When the internal temperature of the char reached 800°C (1472°F), a 50/50 mixture of N_2 and steam was introduced. Steam flow was discontinued when the internal char temperature was reduced to 750°C (1382°F) to enable the temperature to return to 800°C (1472°F). This steam activation process was continued for 30 minutes. Luscar char (95 g) was also placed in a vertical stainless steel tube reactor. The tube reactor was heated to 800°C (1472°F) in a gentle flow of N_2. Steam was then introduced from the bottom of the reactor. The char was maintained at 800°C (1472°F) in a gentle flow of steam and nitrogen for 30 minutes. After cooling, the activated Luscar char (ALC) was removed from both of the reactors, weighed, and stored in a nitrogen atmosphere. These two processes produced an average 70% yield by mass resulting in 5.3 kg of ALC with an MVD of 19.5 µm for pilot-scale testing. A portion of the ALC was reduced

further in size to an MVD of about 5 µm (duplicate laser diffraction particle-size measurements indicated MVDs of 5.52 and 4.86 µm) to test the effects of particle size on mercury capture. Similarly, the DARCO FGD was tested at its as-received MVD of 17 µm and a finer MVD of 7.6 µm.

6.0 RESULTS AND DISCUSSIONS: BENCH-SCALE SORBENT SCREENING TESTS

The lignite-based activated carbons, calcium silicate, and Luscar char were screened in a thin-film fixed-bed reactor, described in Section 3.2, to identify the most promising mercury sorbents for additional pilot-scale evaluations. The screening test matrix is presented in Table 6-1. The potential mercury sorbents were ground to pass through a 400-mesh sieve before testing. In addition, the Luscar char was pulverized to a dustlike consistency for testing the effects of particle size on mercury sorption. The fixed-bed tests were performed using a simulated lignitic flue gas consisting of nominally 10 µg/Nm^3 Hg^0, 6% O_2, 12% CO_2, 15% H_2O, 580 ppm SO_2, 120 ppm NO, 6 ppm NO_2, and 1 ppm HCl in N_2.

Table 6-1. Bench-Scale Mercury Sorbent Screening Matrix

		Flue Gas Composition	
Material	Activation Temp., °C (°F)	Lignite	Baseline
Freedom Coal	750 (1382)	X	
Center Coal	750 (1382)	X	
Center Coal	800 (1472)	X	
Bienfait Coal	750 (1382)	X	X
Bienfait Coal	800 (1472)	X	
Luscar Char	750 (1382)	X	
Luscar Char	800 (1472)	X	
Luscar Char	NA[a]	X	
Luscar Char Dust	NA	X	
DARCO FGD	unknown	X	X
Calcium Silicate	NA	X	

[a] Not applicable.

6.1 Sorbent Screening Results

Figure 6-1 shows screening results for lignite-based activated (750°C, 1382°F) carbons, including DARCO FGD, unactivated Luscar char and char dust, and oxidized calcium silicate when the simulated lignite flue gas was used. The activated carbons showed some initial mercury breakthrough followed by gradually increasing mercury capture. Effective capture was then measured for about the next 3 hours. Apparently, the activated carbons require a conditioning period

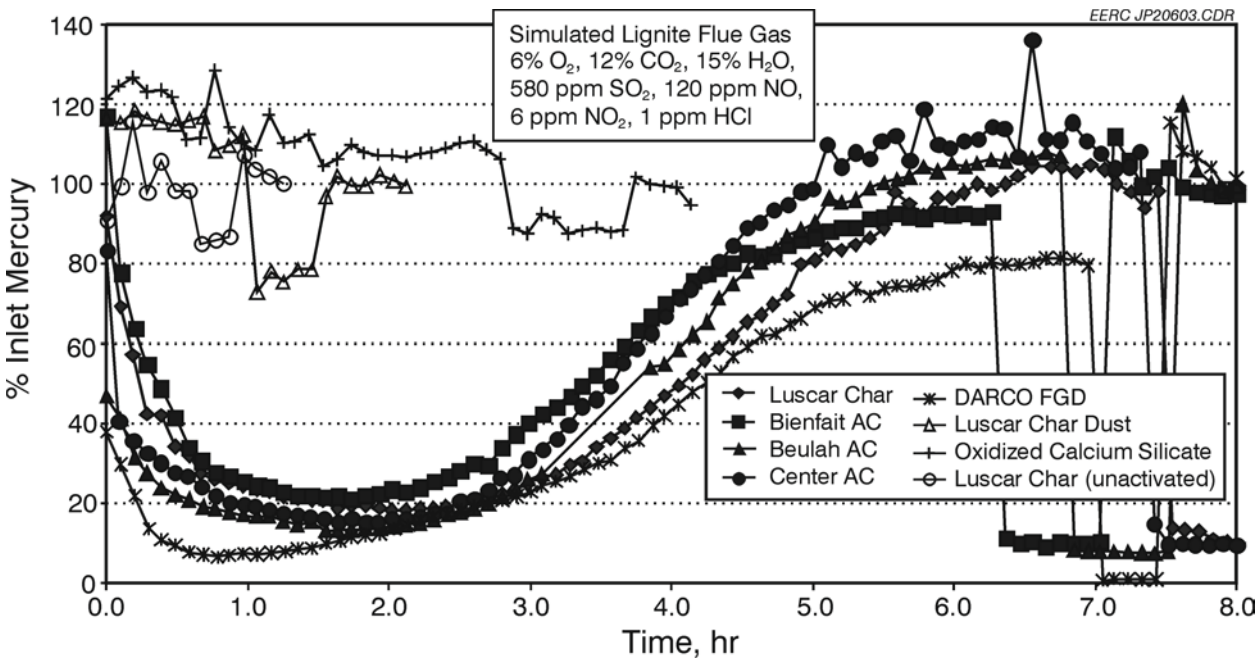

Figure 6-1. Bench-scale fixed-bed testing results for potential mercury sorbents including lignite-based activated (750°C, 1382°F) carbons.

(30–45 minutes) in the simulated lignitic flue gas before they efficiently capture mercury. After 3 hours of mercury capture, breakthrough occurred. The mercury released from the activated carbons was primarily in an oxidized form (>90% Hg^{2+}). The unactivated Luscar char and char dust and calcium silicate were ineffective at capturing mercury and, therefore, were only tested for 2 to 4 hours. Similar to results found in this study, Southern Research Institute recently tested the effectiveness of calcium silicate injection to remove mercury in a 1-MW (3.4-MMBtu/hr) coal Combustion Research Facility and found that it was ineffective in capturing Hg^0 or Hg^{2+} (June 2002).

Screening results for the lignite-based activated (800°C, 1472°F) carbons, including DARCO FGD, are presented in Figure 6-2. The initial mercury breakthrough for these 800°C (1472°F) activated carbons was less than those for the 750°C (1382°F) activated carbons (Figure 6-1). The results in Figure 6-2 indicate better mercury capture than the carbons activated at 750°C (1382°F) and greater Hg^0 oxidation with Hg^{2+} composing >95% of the gaseous mercury released from the carbons. The results in Figure 6-2 also indicate that mercury broke through the activated Bienfait carbon and ALC sooner than the activated Center carbon and DARCO FGD.

The activated (750°C, 1382°F) Bienfait carbon and DARCO FGD were tested using an established baseline flue gas composition consisting of nominally 10 µg/Nm^3 Hg^0, 6% O_2, 12% CO_2, 8% H_2O, 1600 ppm SO_2, 400 ppm NO, 20 ppm NO_2, and 50 ppm HCl in N_2. Note that these concentrations are representative of typical bituminous coals. Contrary to the tests conducted with the simulated lignite flue gas (Figures 6-1 and 6-2), the activated Bienfait carbon and DARCO FGD did not experience significant early mercury breakthrough in the baseline flue gas as shown in Figure 6-3. Perhaps, the higher acid gas concentrations in the baseline flue gas relative to the

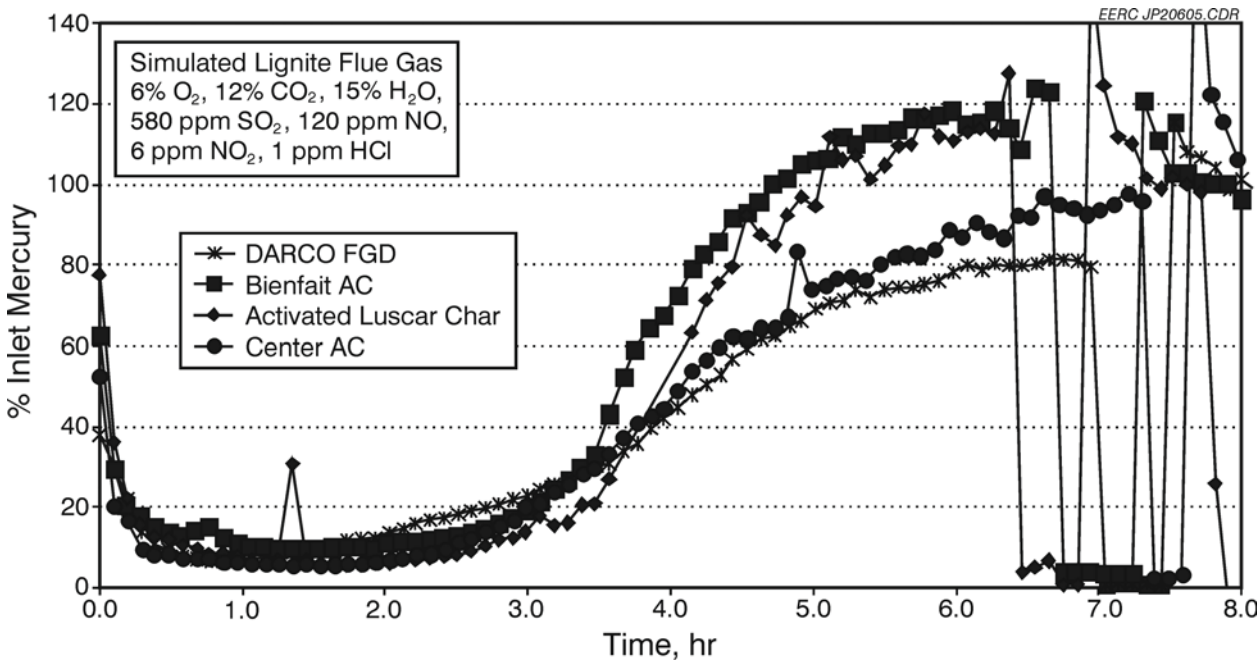

Figure 6-2. Bench-scale fixed-bed testing results for lignite-based activated (800°C, 1472°F) carbons including DARCO FGD.

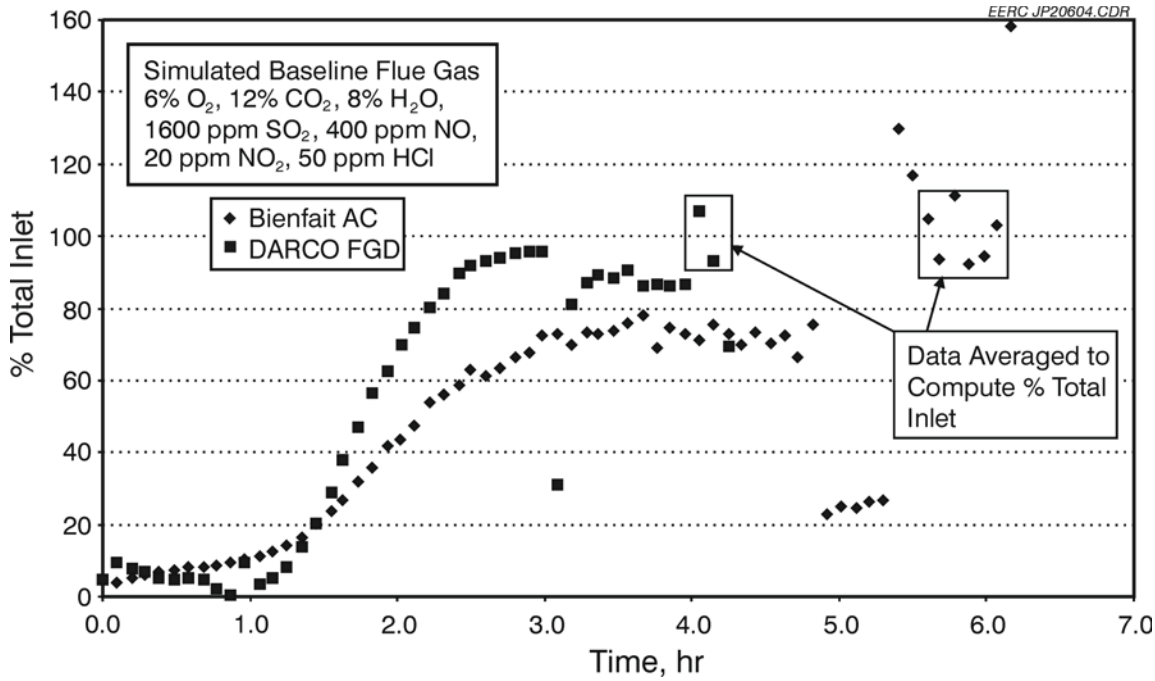

Figure 6-3. Bench-scale fixed-bed testing results for activated (750°C, 1382°F) Bienfait carbon including DARCO FGD.

simulated lignite flue gas promoted mercury capture. Although these baseline flue gas tests yielded better mercury capture initially, significant breakthrough of mercury ultimately occurred sooner than during the lignite flue gas tests. After approximately 1.5 hours, mercury broke through the DARCO FGD much more quickly than the activated Bienfait carbon.

In summary, all of the lignite-based activated carbons exhibited good mercury sorption capacity and oxidation potential during the bench-scale tests. Conversely, the unactivated Luscar char and oxidized calcium silicate were ineffective in capturing or oxidizing mercury. The ALC (800°C, 1472°F) and DARCO FGD were selected for additional testing in the pilot-scale combustor based on the sorbent screening results and consensus among the project sponsors. These two sorbents have relatively high surface areas (Table 5-7) and are readily available.

6.2 Mercury Sorbent Capacity of Activated (800°C, 1472°F) Luscar Char

The bench-scale test results in Figure 6-2 were used to calculate temporal variations in the mercury capacity of the thin-film, 0.15-g, fixed-bed of ALC. As indicated in Table 6-2, calculated mercury capacities range from 164 to 202 µg Hg/g ALC. These capacities are probably maximum values because in an actual lignitic combustion flue gas environment, mass-transfer limitations and interactions with fly ash and other flue gas components are anticipated to reduce capacity.

Table 6-2. Mercury Capacities of Activated Luscar Char in the Bench-Scale System

Time, hr	3.1	3.7	4.7	8
% Inlet Hg	<20	50	100	120
Adsorbed Hg, µg	24.6	28.3	30.3	26.4
Total Hg Feed, µg	28.7	34.1	43.9	74.5
Capacity, µg Hg/g sorbent	164	188	202	176

6.3 Surface Chemical Composition and Speciation of Activated Luscar Char

Four 500-mg aliquots of ALC were loaded with Hg^0 (nominally 10 µg/m^3) using the fixed-bed bench-scale apparatus and the simulated lignite flue gas (6% O_2, 12% CO_2, 15% H_2O, 580 ppm SO_2, 120 ppm NO, 6 ppm NO_2, and 1 ppm HCl in N_2) according to the conditions listed in Table 6-3. The loading times listed in the table are based on the usual fixed-bed thin-layer and, therefore, do not reflect the actual time needed to reach the conditions. Figure 6-4 shows the approximate state of mercury loading level for each sample with respect to time. The curve does not correspond to other bench-scale test curves reported in this document because the fixed bed contained larger masses of activated carbon than the 150 mg used in a typical bench-scale test. Once each sample was exposed for the appropriate time, the sample was recovered by tapping the inverted filter onto weigh paper and storing the powder under nitrogen in a vial.

The five samples listed in Table 6-3 were analyzed using XPS at Physical Electronics in Eden Prairie, Minnesota. The chemistry of carbon, nitrogen, oxygen, sodium, magnesium, calcium, iron,

Table 6-3. Conditions for Loading Activated Carbons with Mercury

Sample	Description	Sampling Time	Simulated Flue Gas Conditions
Baseline Material (1388S-47-1)	Baseline activated carbon	Not exposed	None
BS-1332	Initial breakthrough	Onset of testing (20 minutes)	6% O_2, 12% CO_2, 15% H_2O, 580 ppm SO_2, 120 ppm NO, 6 ppm NO_2, 1 ppm HCl
BS-1331	Complete capture begins	Efficient mercury capture begins (1.5 hours)	
BS-1330	Breakthrough begins	Mercury evolution begins (5 hours)	
BS-1329	Breakthrough condition	Mercury begins to evolve at the same rate as applied (11 hours)	

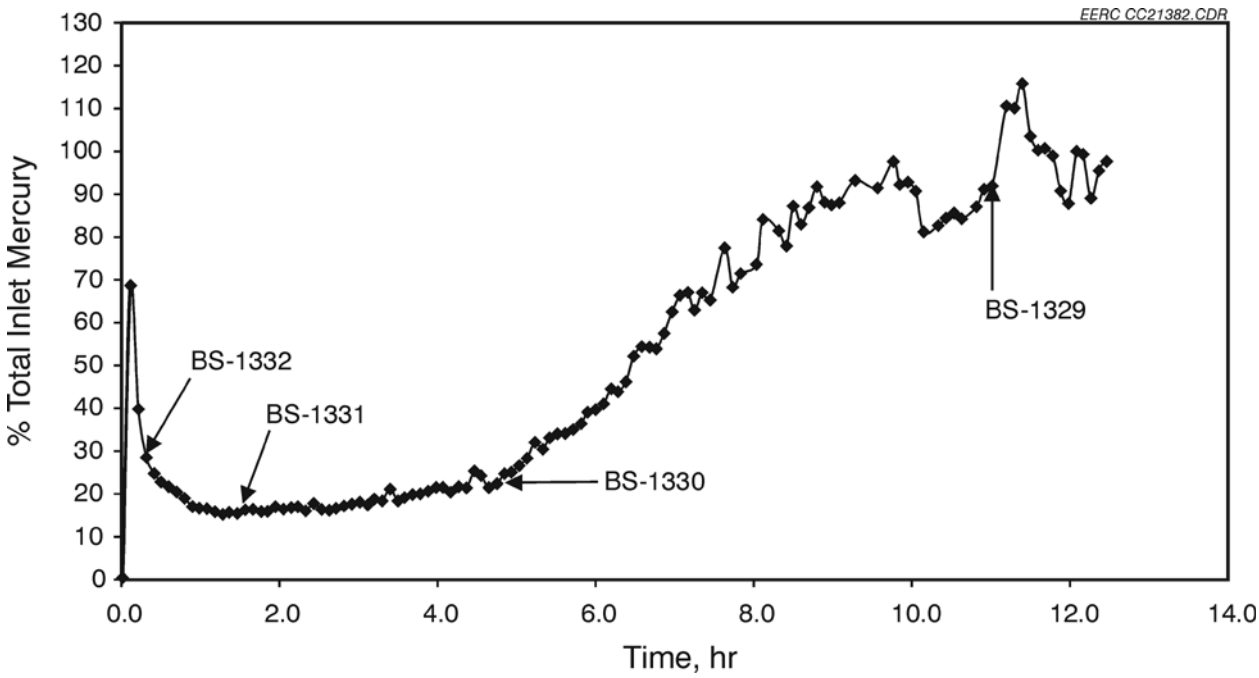

Figure 6-4. Mercury loading rates for ALC (loaded for subsequent XPS analyses).

aluminum, silicon, phosphorus, sulfur, and chlorine was determined. Table 6-4 shows the results of the survey scan as atomic percent (>0.1%) for the most concentrated elements. Mercury was not present in quantities great enough to be detected by XPS.

The greatest measurable change in surface elemental concentration over time occurred for carbon, sulfur, oxygen, and chlorine. The carbon concentration decreased by 20%, while the sulfur, and oxygen concentrations increased by factors of greater than 40 and 2, respectively. While chlorine

Table 6-4. Concentration of Elements from the XPS Survey Scan, atomic percent

	C	N	O	Na	Mg	Al	Si	P	S	Cl	Ca	Fe
Baseline Material (1388S-47-1)	86.4	0.3	9.3	1.4	0.1	0.5	0.3	<0.1	0.1	<0.1	0.9	0.1
BS-1332	85.0	0.2	11.3	1.4	<0.1	<0.1	0.4	<0.1	1.1	<0.1	0.8	<0.1
BS-1331	80.3	0.2	14.5	1.4	<0.1	<0.1	0.3	<0.1	2.5	0.1	0.8	0.1
BS-1330	75.5	0.2	17.9	1.3	<0.1	<0.1	0.2	0.1	3.6	<0.1	0.9	0.2
BS-1329	70.2	0.4	22.5	1.0	<0.1	<0.1	0.4	<0.1	4.1	<0.1	1.0	0.1

was not present initially at a detectable concentration, its presence became detectable for the midtest sample. The chlorine concentration decreased once the mercury breakthrough level reached the inlet concentration.

High-resolution XPS scans were performed on the samples to examine specific species for selected elements. The high-resolution scans show the specific chemistry of each desired element. The largest differences were with the nitrogen, chlorine, and sulfur species. The XPS nitrogen 1s species analysis indicated that little, if any, ammonium ion was present initially. No nitrate or nitrite nitrogen was identified at the sample surface. Its binding energy region is shown in Figure 6-5; ammonium appears in increasing increments with time. This increase may result from the reaction of acids from the gas stream with amine groups attached to the carbon edges.

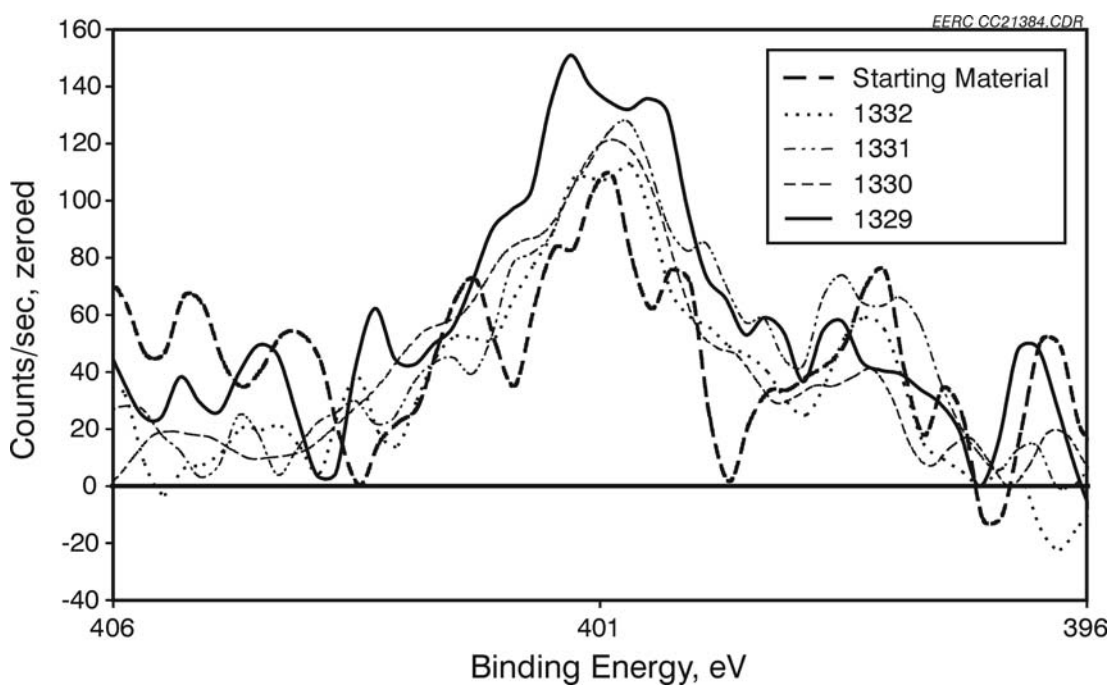

Figure 6-5. Ammonium XPS peak region.

The peaks in the chlorine 2p species region are illustrated in Figure 6-6. The XPS chlorine analysis indicated absence of chlorine species in the starting material. After 20 minutes of exposure to simulated lignitic flue gas, the sample surface begins to accumulate organically associated chlorine. The chlorine continues to attach to the surface during the period of optimal mercury capture. Coincident with the evolution of mercury from the sample, chlorine is once again absent from the sample surface. These data suggest that HCl interacts with the sample, with chlorine attaching temporarily to the surface. Eventually, the surface can no longer bind chlorine, and it detaches. Because of the relative abundance of chlorine versus mercury present, most of the chlorine desorbing from the surface would leave as HCl, but some could form $HgCl_2$ from the available Hg(II) species.

Figure 6-7 shows the peaks in the sulfur 2p region. Sulfur in the starting material occurred as S(VI) (sulfates/sulfones), thiophenes, and S(II) (sulfides). Mathematical integration of the peaks suggests a nearly even split between the three species 34%, 34%, and 32%, respectively. That is approximately 0.02 at% of the sample. Within the first 20 minutes, the total sulfur concentration increased tenfold. Most (>89%) occurred as S(VI), mostly sulfate, with a nominal concentration of the two other species, as indicated in Table 6-5. As the S(VI) concentration increased to 4 at%, the thiophene concentrations level off at ca. 0.12 at%, and the sulfide disappears, probably through oxidation. When normalized to carbon, the S(VI) ratio is 0.057, and the thiophene ratio is 0.002. Oxygen concentrations in the starting material were more than adequate to support the presence of S(VI) and S(IV) species. The increase in oxygen concentration at the surface over time was sufficient to offset the rapid increase in sulfur concentration as S(VI). This increase in S(VI) is illustrated in Figure 6-8. The buildup of sulfur species on the surface of the sample suggests sorption and oxidation of SO_2 from the flue gas stream. As the activated carbon began to evolve mercury at an

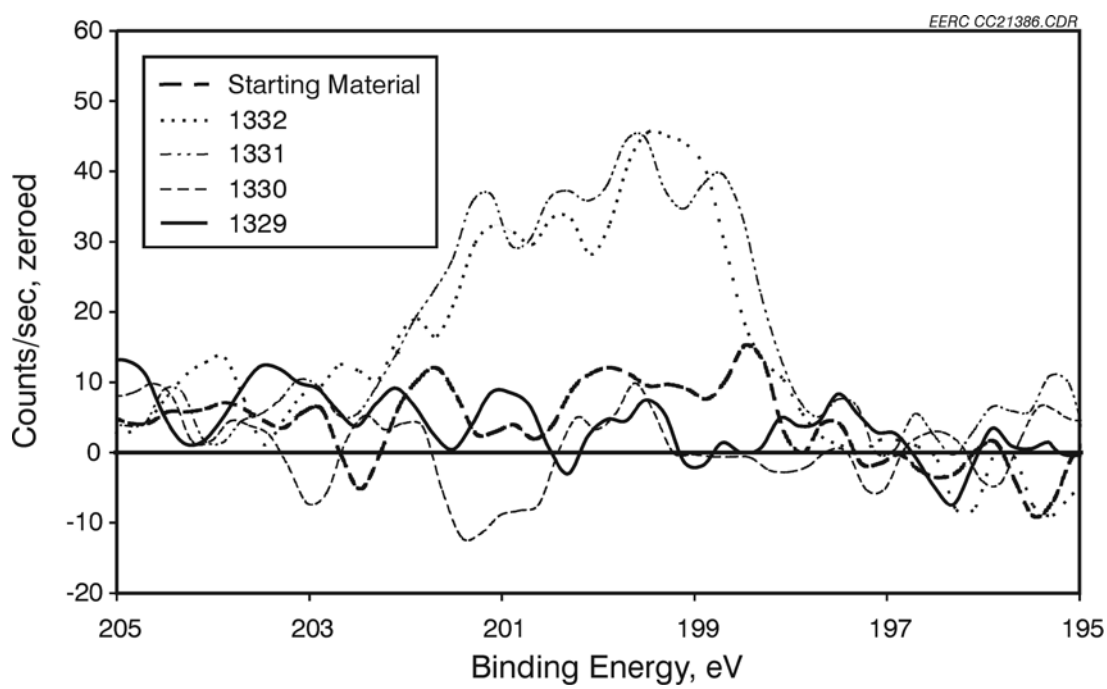

Figure 6-6. Organic chlorine XPS peak region.

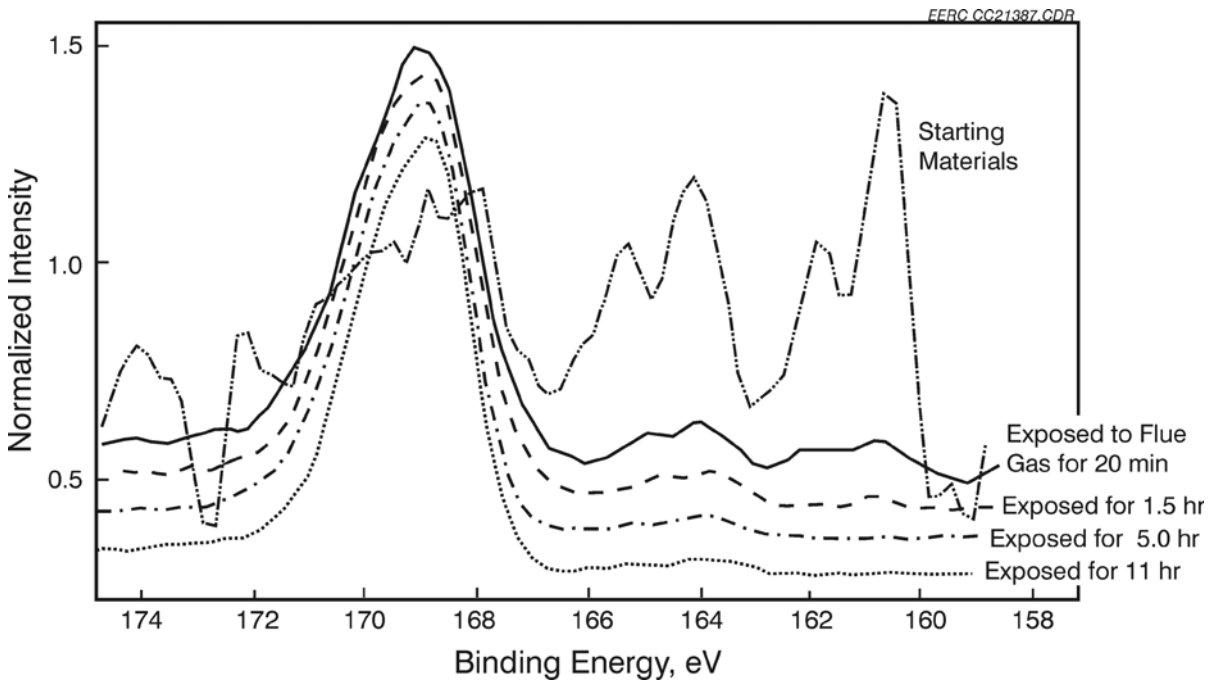

Figure 6-7. Sulfur XPS peak region.

Table 6-5. XPS Analysis of Sulfur Species Apportionment, normalized to carbon

	Total S	S(VI)	Thiophene	Sulfide	S(VI)	Thiophene	Sulfide
Baseline Material (1388S-47-1)	0.07	34%	34%	32%	0.000	0.000	0.000
BS-1332	1.1	89%	6%	5%	0.011	0.001	0.001
BS-1331	2.5	94%	5%	1%	0.030	0.002	0.000
BS-1330	3.6	97%	3%	0%	0.046	0.001	0.000
BS-1329	4.1	97%	3%	0%	0.057	0.002	0.000

increasing rate (Sample BS-1330), the sulfur-to-oxygen ratio (1:5) approached the stoichiometric ratio in sulfate. It also suggests that sulfate bonding on the surface increased coincident with the mercury breakthrough level reaching the inlet concentration. It is likely, therefore, that the evolved mercury species are not associated with sulfates, and it is possible that sulfate formation interferes with mercury bonding at the surface.

XPS analysis of these samples led to the following conclusions:

- XPS analysis showed increased ammonium concentrations over time as the sample is exposed to simulated flue gas. Oxidized nitrogen was not observed in the analysis.

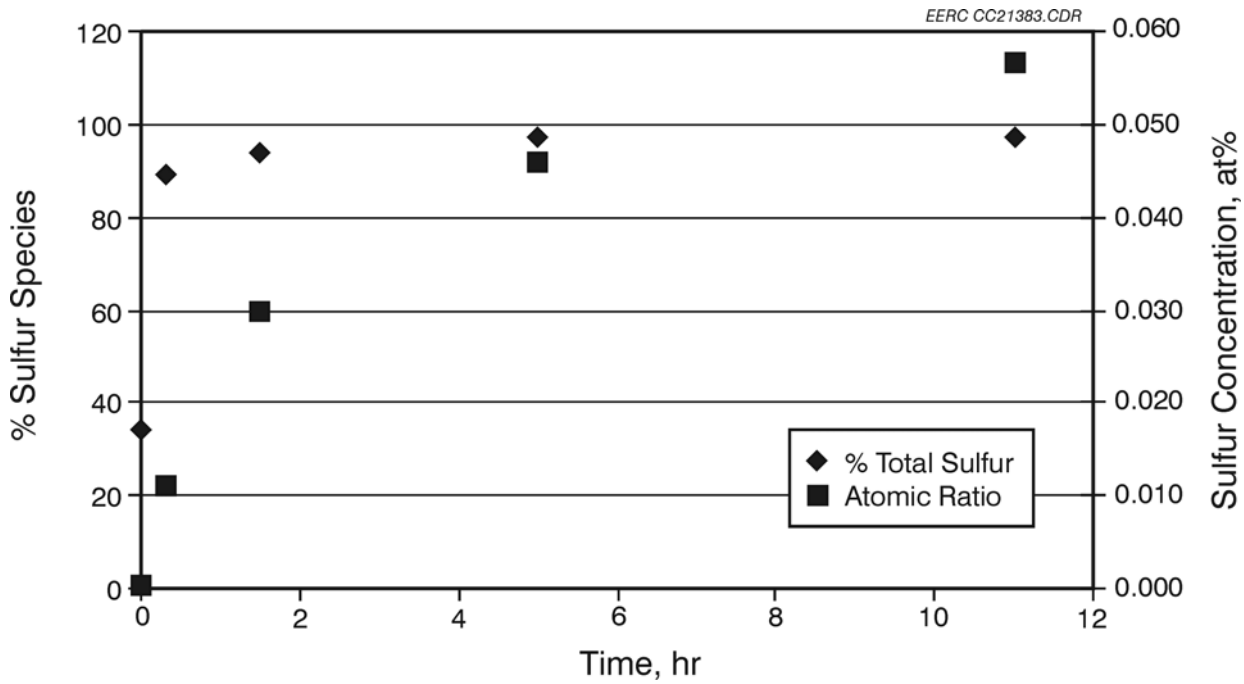

Figure 6-8. Sulfur(VI) composition over time.

- Chlorine content increased during the period of optimal mercury capture and decreased as mercury was released from the surface, which supports the hypothesis that Hg^0 is oxidized to mercury chloride.

- XPS analysis showed most sulfur occurred initially as sulfate, thiophene, and sulfide. Sulfate concentration increased significantly as the sample was exposed to simulated flue gas. Sulfur remains on the surface while the mercury desorbs.

- Oxygen concentration on the sample increased over time, indicating oxidation of constituents such as sulfur at the sample surface.

- There is competition for active sites by chlorine and sulfur species, which the sulfur species ultimately wins.

- Mercury sorption on surface depends upon sulfide-to-sulfate conversion, buildup of chlorine, and the desorption.

- Mercury on the sorbent is not sulfate.

Based on these conclusions, the hypothesized bonding site for mercury is a base site that may be a carbon-edge structure having Lewis-base characteristics. The base can donate electrons to Hg^{2+}, HCl, H_2SO_4, and SO_2. These acid gases will poison the mercury bonding sites after prolonged exposure.

7.0 RESULTS AND DISCUSSIONS: PILOT-SCALE TESTS

7.1 Test Parameters

The sorbent tests performed with the pilot-scale combustion system are described in Table 7-1. Additional details for each test are provided in Appendix B. The following variables that could potentially affect mercury emission control were tested: lignite coal source (Poplar River or Freedom mine), control device type (ESP, FF, ESP FF, and *Advanced Hybrid*™ filter), FF type (Ryton versus Gore), sorbent type (steam-activated [800°C, 1472°F] Luscar char or DARCO FGD), particle size (approximate MVDs of 20 and 5 µm), sorbent injection rate, flue gas temperature in the pollution control device, and flue gas chlorine contents. Unless otherwise noted, the use of ALC throughout the remainder of this report refers to Luscar char activated at 800°C (1472°F) with an MVD of about 20 µm. The standard DARCO FGD is also roughly 20 µm in MVD.

7.2 Inlet Mercury Concentrations

The OH method was used during most of the Poplar River and Freedom coal combustion tests to measure the concentrations of mercury species entering the pollution control devices as well as to validate the quality of CEM measurements of gaseous mercury. The OH method is advantageous for distinguishing among the effects of sorbent injection on Hg^0, Hg^{2+}, and Hg(p) capture. In order to distinguish these effects, however, it was necessary to establish the average and variability of mercury species distributions for the Poplar River and Freedom coal combustion flue gases.

7.2.1 Poplar River Coal

OH method and CEM measurements of mercury species distributions for representative Poplar River coal combustion flue gases (approximately 149°C [300°F]) measured upstream of pollution control devices are compared in Figure 7-1. Total mercury measurement results compare favorably; however, CEM measurements of Hg^0 and estimates of Hg^{2+} are generally slightly lower and greater, respectively, than those measured by the OH method. Apparently, the CEM (or conditioning system) has a slight positive bias toward overestimating oxidized mercury. Bias of the OH results is not as likely because in this case, with three unreactive fly ashes, a filtering effect is not expected.

The mercury species distribution for a representative Poplar River coal combustion flue gas (Figure 7-1) is characterized by a lack of Hg(p), low ($\leq$4 µg/Nm^3) Hg^{2+} concentrations, and dominance of Hg^0 (13 20 µg/m^3). Acceptable mercury mass balance closures of 80% to 120% were generally attained during the Poplar River coal tests. Mercury mass balances for individual tests are presented in Appendix C.

Note: speciation results for the Poplar River Tests 1 14 are not presented in Figure 7 1 because they were not representative of steady-state combustion conditions. Inconsistencies in the coal feed during Poplar River Tests 1 14 resulted in unsteady combustion conditions, which produce higher than normal amounts of unburned carbon. Later, it was found that the presence of unburned carbon particles promoted the formation of Hg^{2+} and/or Hg(p).

Table 7-1. Sorbent Test Matrix for Pilot-Scale Combustion System

Coal	Control Device	Sorbent	Test No.	Injection Rate, g/hr	Temperature, °F
Poplar River	ESP	NA[a]	1, 4, 10, 28	NA	300
	ESP FF		13, 17, 19, 24, 26, 49		
	Advanced Hybrid™ Filter		31		
	ESP	S1[b]	5, 6, 9, 12, 29	40 150	300
		S1 fine	8, 11, 30	25 75	
	ESP FF	S1	14, 25, 27	10 50	300
			21	10 60	400
		S1 fine	16	25	300
			20	10 40	400
	FF	S1	35	10 60	300
	Advanced Hybrid™ Filter	S1	32	20 120	
	ESP	S2[c]	2, 3	75 150	300
	ESP FF	S2	18, 50 53	20 60	300
			23	10 60	400
		S2 fine	22	10 60	400
Freedom	ESP	NA	40	NA	300
	ESP FF		36, 38		
	Advanced Hybrid™ Filter		43		
	ESP	S1	42	50 150	300
		S1 fine	41	25 115	
	ESP FF	S1	37	10 40	300
	Advanced Hybrid™ Filter	S1	44	10 40	300
	ESP FF	S2	39	10 40	300

[a] Not applicable.
[b] Lignite based steam activated (800°C, 1472°F) Luscar char.
[c] DARCO FGD.

7.2.2 Freedom Coal

The mercury speciation characteristics of Freedom coal combustion flue gases were determined with the OH and CEM methods at the pollution control device inlets (approximately 149°C, 300°F) during Tests 36, 38, 40, and 43. Mercury species distributions during these tests were very similar, as shown in Figure 7-2. Similar to the Poplar River flue gas, the mercury CEM generally underestimates Hg^0 and overestimates Hg^{2+} to a small degree relative to the OH method. The Freedom flue gas lacks Hg(p), and Hg^{2+} concentrations are very low (<1.5 µm/Nm^3). Acceptable mercury mass balance closures of 80% to 120% were generally reached during the Freedom coal tests. Mercury mass balances for each test involving the Freedom coal combustion flue gas are presented in Appendix D.

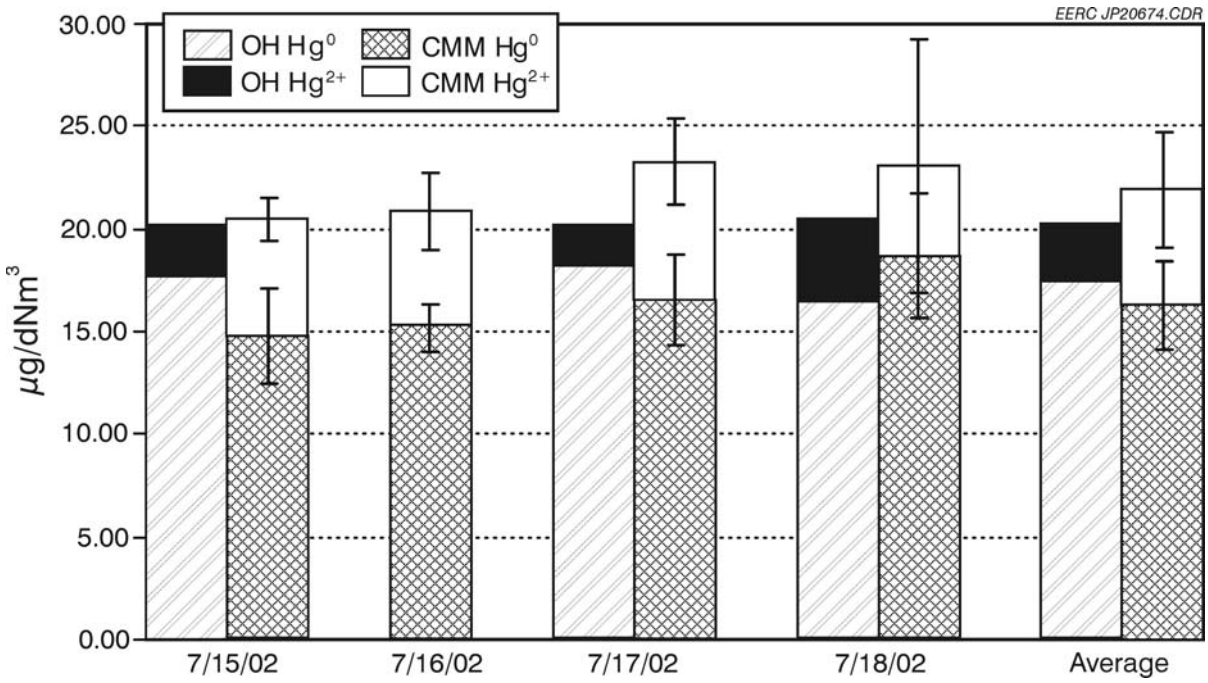

Figure 7-1. Comparison of OH and CMM measurement results for Poplar River coal combustion flue gases (149°C, 300°F).

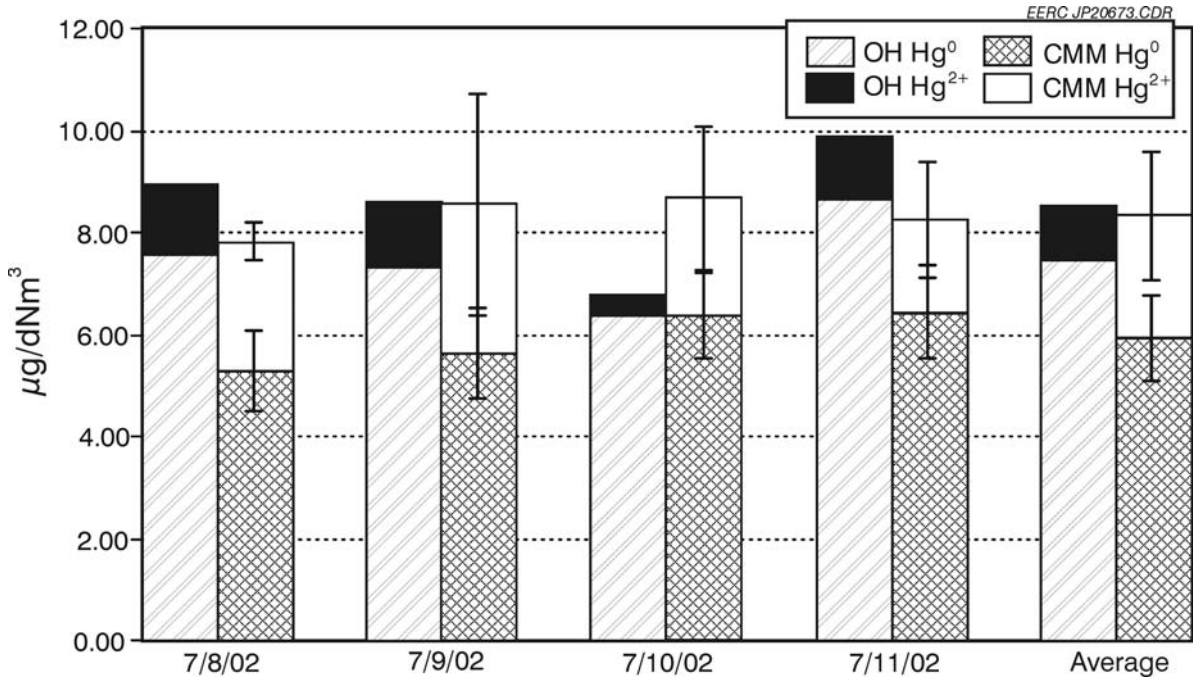

Figure 7-2. Comparison of OH and CMM measurement results for Freedom coal combustion flue gases (149°C, 300°F).

7.2.3 Comparison Between Poplar River and Freedom Coals

Compared in Figure 7-3 are the average mercury species distributions, as determined by the OH method, for the Poplar River and Freedom coal combustion flue gases. As expected from their coal mercury contents (Table 4-5), the Poplar River coal combustion flue gas contains a higher Hg(tot) concentration. Hg^0 is the dominant mercury species in both flue gases, which is typical of North American lignite coals. The relative proportions of Hg^0, Hg^{2+}, and Hg(p) in both flue gases are very similar.

7.3 Comparison of Poplar River and Freedom Coal Combustion Flue Gas Compositions

Compared in Table 7-2 are the average compositions for the Poplar River and Freedom coal combustion flue gases produced in the pilot-scale combustor and the simulated lignite flue gas used in the bench-scale sorbent screening tests. The average gas compositions in Table 7-2 were measured at the inlet to the pollution control devices. The CO_2 and O_2 concentrations used in the simulated lignite flue gas compare favorably to those for the Poplar River and Freedom coal combustion flue gases. SO_2 and NO_x concentrations, however, are lower in the simulated flue gas. Even though the Poplar River and Freedom coals have very similar sulfur contents (Table 4-3), the average sulfur concentration for the Poplar River flue gas was much higher relative to the Freedom flue gas. As indicated in Table 4-4, the Freedom coal fly ash is more effective in scavenging SO_2 from the flue gas because of its much greater alkali and alkaline-earth metal (sodium, potassium, calcium, and magnesium) concentrations.

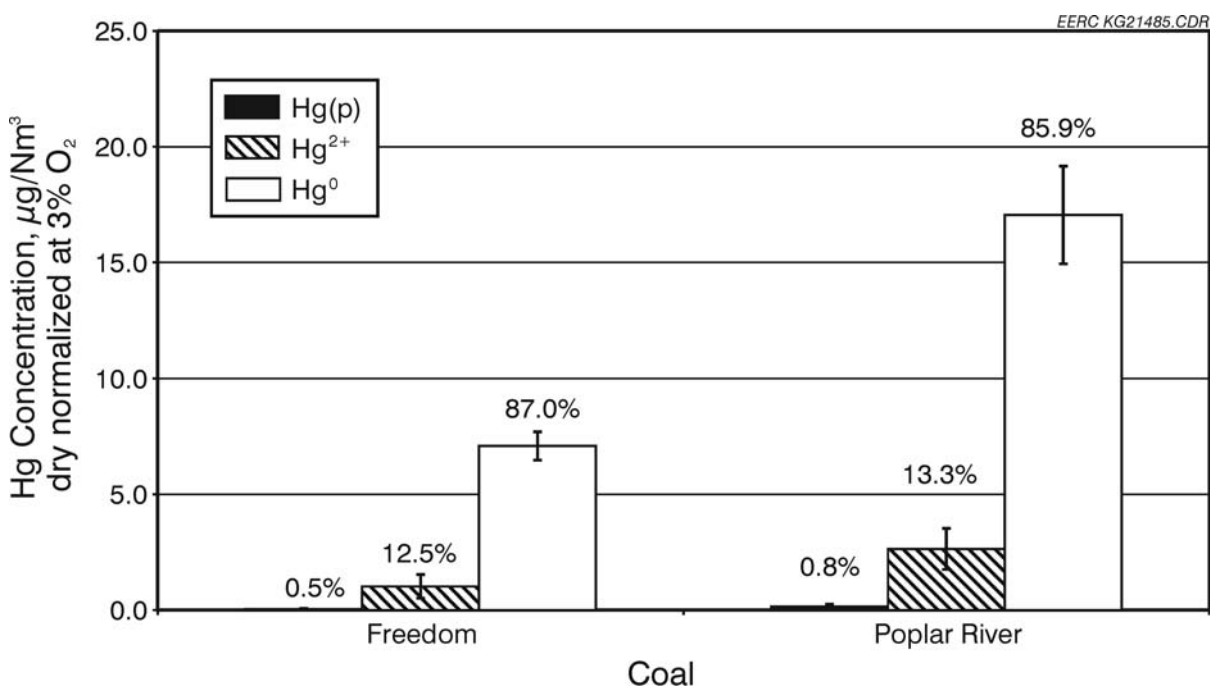

Figure 7-3. Comparison of average Poplar River and Freedom coal combustion flue gas (149°C, 300°F) mercury speciation results obtained using the OH method.

Table 7-2. Average Poplar River and Freedom Coal Combustion Flue Gas Compositions

Species	Poplar River Average	Poplar River Std. Dev.[a]	Freedom Average	Freedom Std. Dev.	Bench-Scale Simulated Lignite
SO_2, ppmv	1073	120	706	147	580
CO, ppmv	0.48	1.97	2.57	1.40	0.00
CO_2, mol%	14.3	1.5	13.8	1.5	12.0
O_2, mol%	5.68	0.95	5.90	1.16	6.00
NO_x, ppmv[b]	612	71	614	92	126

[a] Sample standard deviation.
[b] NO_x levels are slightly higher in these pilot results compared to typical plant values.

7.4 Mercury Control Technology Results

The results discussed within this section are from short-term pilot-scale tests. Longer-term operability issues such as bag blinding, cleaning frequency, pressure drop, etc., were not considered, but will be addressed under Phase II of the project.

7.4.1 ESP with Powdered Activated Carbon Injection

Figure 7-4 shows the temporal variations in total gaseous mercury concentrations downstream from the ESP as relatively coarse lignite-based ALC was injected into the Poplar River coal

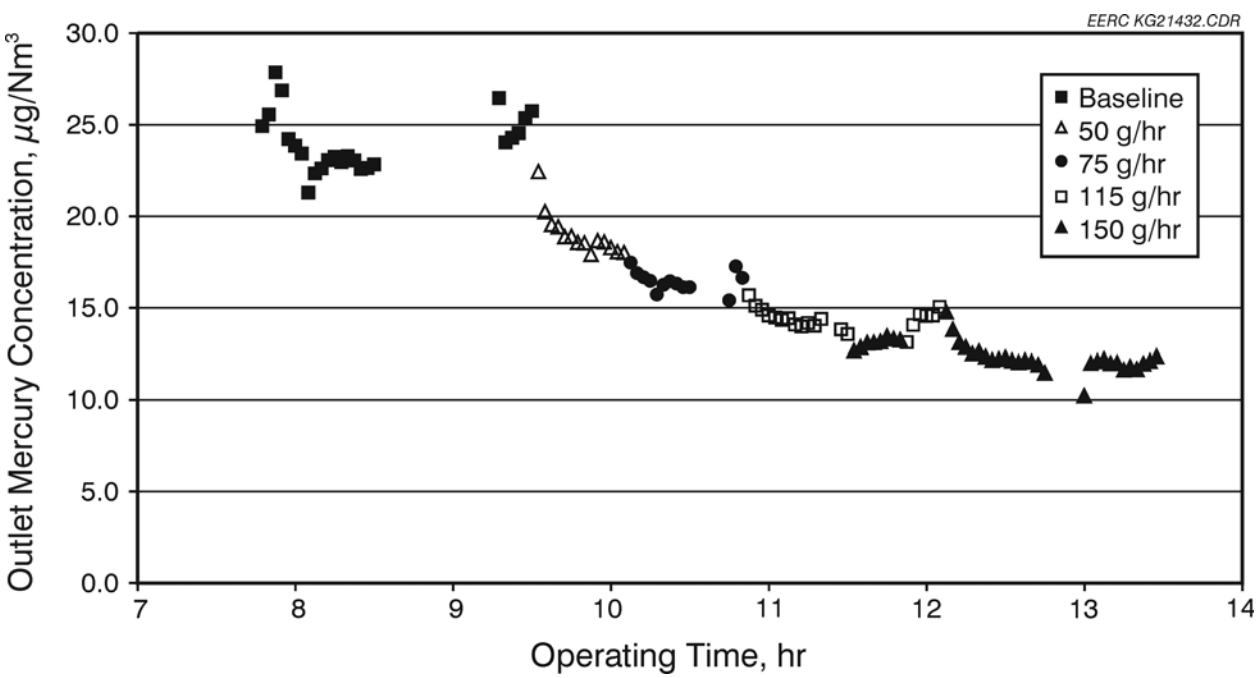

Figure 7-4. Temporal variations in total gaseous mercury concentrations at the 149°C (300°F) ESP outlet during injections of ALC into the Poplar River coal combustion flue gas.

combustion flue gas at different rates upstream of the ESP. The CEM data plotted in Figure 7-4 and those presented in Appendices E1 E5 for other tests were used to calculate the effects of gas temperature, injection rates, ALC particle size, and flue gas composition (Poplar River and Freedom coal combustion flue gases) on ESP mercury removal efficiency. The results in Figure 7-5 indicate that at injection rates of >8 lb/MMacf the fine (MVD 5 µm) ALC provides much better ESP mercury removal efficiencies relative to those attained with the coarser (MVD 20 µm) ALC. In addition, the injection of fine ALC when the ESP gas temperature was maintained at 204°C (400°F) provided significantly better ESP mercury removal efficiencies relative to those obtained with the coarser ALC at an ESP gas temperature of 149°C (300°F). The OH mercury speciation results in Figure 7-6 are similar to the CEM measurement results presented in Figure 7-5 and indicate that coarse and fine ALC provide reactive surface sites for mercury removal from the Poplar River flue gas.

The effects of varying ALC injection rates and particle size on ESP mercury removal were also investigated using a Freedom coal combustion flue gas and a 149°C (300°F) ESP. The ESP mercury removal results presented in Figure 7-7 indicate that an increase in the rate of ALC injection improves ESP mercury capture and, contrary to the results for the Poplar River flue gas (Figures 7-5 and 7-6), a reduction in ALC particle size did not greatly improve ESP mercury capture. The OH mercury speciation results in Figure 7-8 indicate that similar to the Poplar River flue gas, Luscar char injection is effective in providing active surface sites for Hg^0 oxidation and capture.

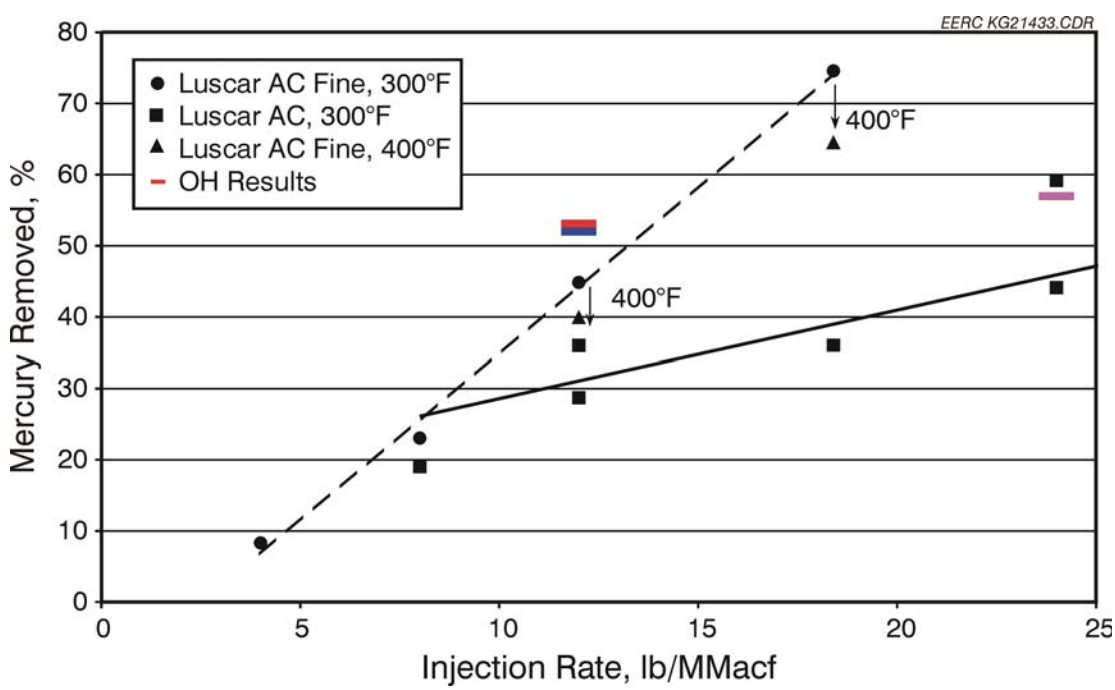

Figure 7-5. ESP mercury removal efficiencies for 149° and 204° C (300° and 400°F) Poplar River coal combustion flue gases as functions of coarse and fine (MVDs of 20 and 5 µm, respectively) ALC injection rates.

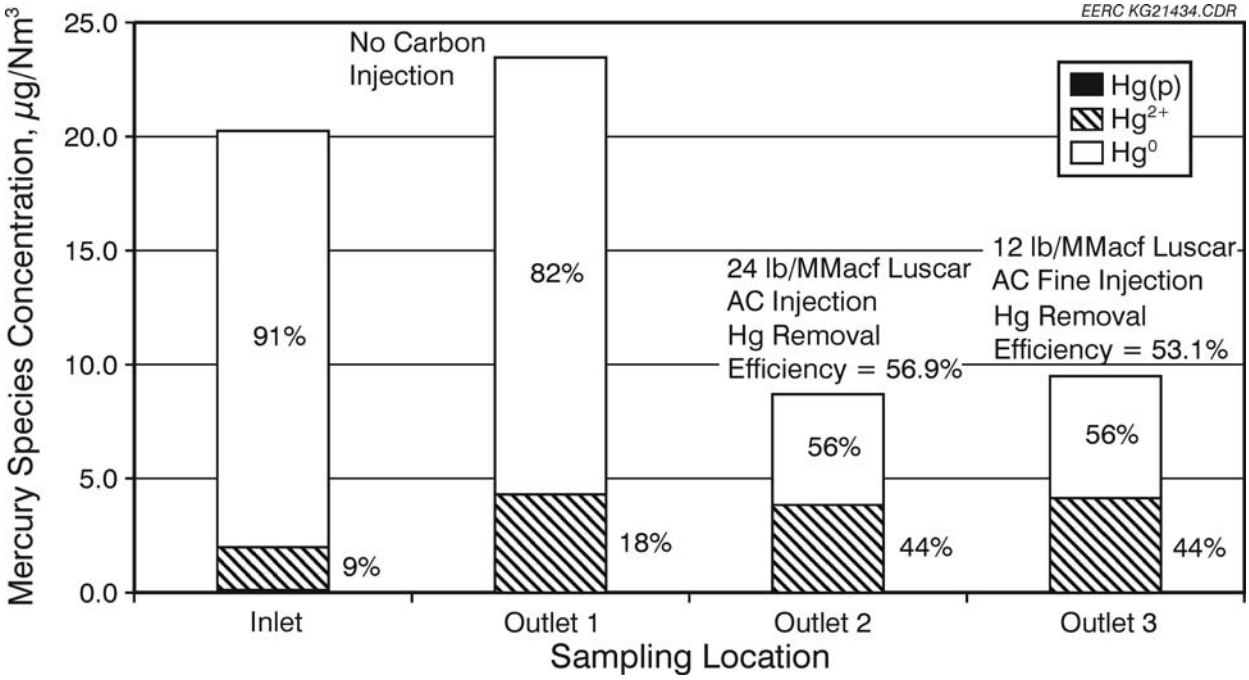

Figure 7-6. ESP inlet and outlet OH mercury speciation results measured in the presence and absence of coarse and fine (MVDs of 20 and 5 μm, respectively) ALC injection (24 and 12 lb/MMacf, respectively) into the Poplar River coal combustion flue gas.

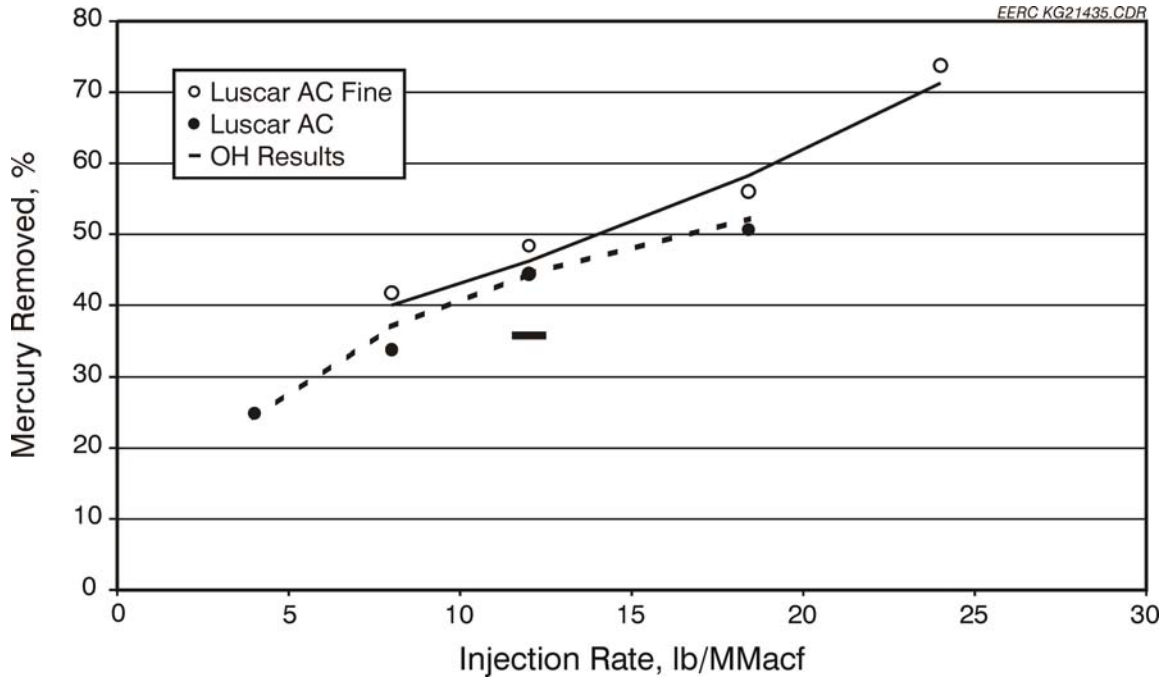

Figure 7-7. ESP mercury removal efficiency for 149°C (300°F) Freedom coal combustion flue gas as a function of coarse and fine (MVDs of 20 and 5 μm, respectively) ALC injection rates.

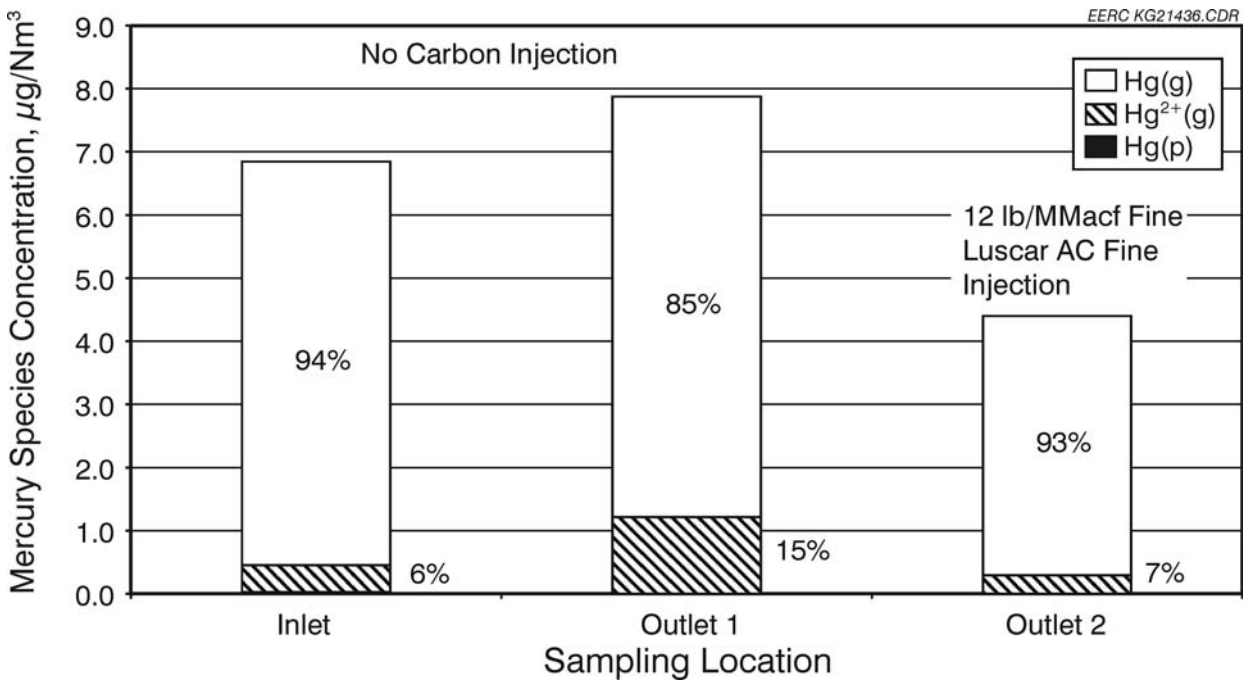

Figure 7-8. ESP inlet and outlet OH mercury speciation results measured in the presence and absence of fine (MVD 5 µm) ALC injection (12 lb/MMacf) into the Freedom coal combustion flue gas.

Compared in Figure 7-9 are 149°C (300°F) ESP mercury removal efficiencies as a function of ALC injection rates for the Poplar River and Freedom coal combustion flue gases. ALC injection into the Freedom flue gas provided 10% to 15% greater ESP mercury capture efficiencies relative to its injection into the Poplar River flue gas.

7.4.2 Fabric Filter with Powdered Activated Carbon Injection

The effects of varying ALC injection rates on the mercury removal effectiveness of a 149°C (300°F) FF (equipped with Gore bags) were investigated using the Poplar River coal combustion flue gas. In addition, the effect of increasing the gas temperature in the FF to 204°C (400°F) on mercury removal was investigated. CEM data presented in Figure 7-10 indicate that increases of 10 or 20 g/hr in the rate of ALC injection gradually improved FF mercury capture. Also shown in Figure 7-10 is the adverse effect of FF pulsing on FF mercury removal. Pulsing removes most of the ALC from the FFs, thus decreasing the sorbent mercury contact time. In a commercial baghouse, this effect will likely be less noticeable since only a portion of the bags are pulsed at a time. Between pulsing episodes, as the amount of sorbent increases on the FF, the mercury removal efficiency of the FF increases. Increasing the gas temperature in the FF from 149°C (300°F) to 204°C (400°F) significantly reduced the effectiveness of injecting 80-g/hr ALC for enhancing FF mercury removal.

The effects of Luscar char injection rates and gas temperature on the FF mercury removal efficiency for the Poplar River flue gas are shown in Figure 7-11. The greatest mercury removal efficiency of 85% was attained during 80-g/hr Luscar char injection, corresponding to a C Hg weight

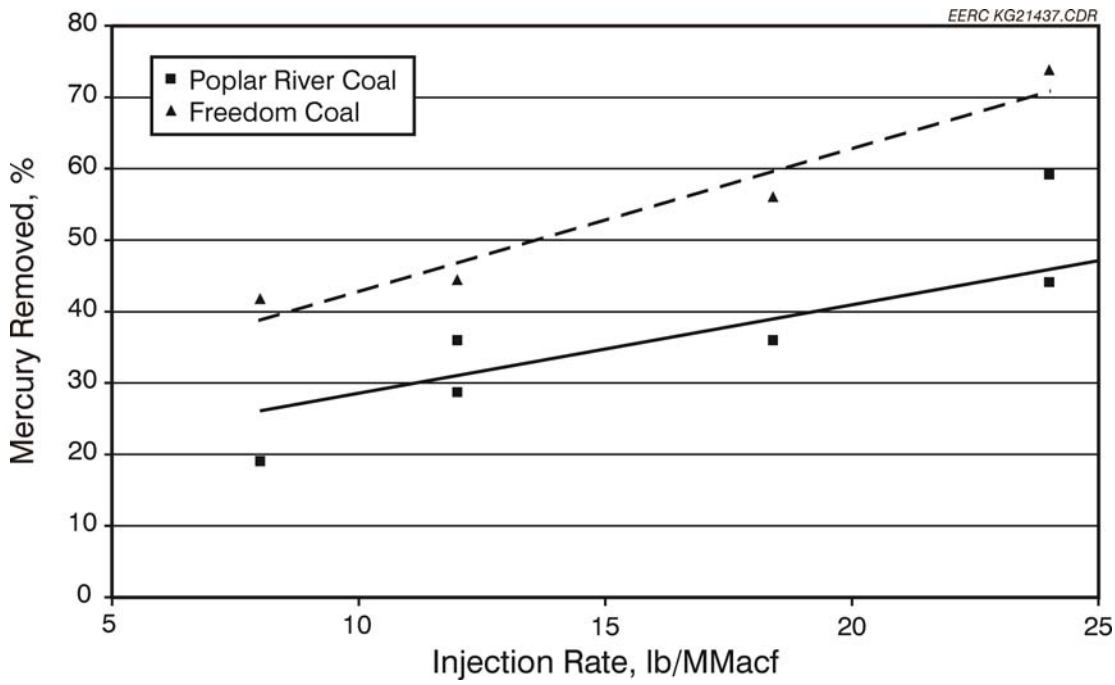

Figure 7-9. ESP mercury removal efficiencies as functions of ALC injection rates for 149°C (300°F) Poplar River and Freedom coal combustion flue gases.

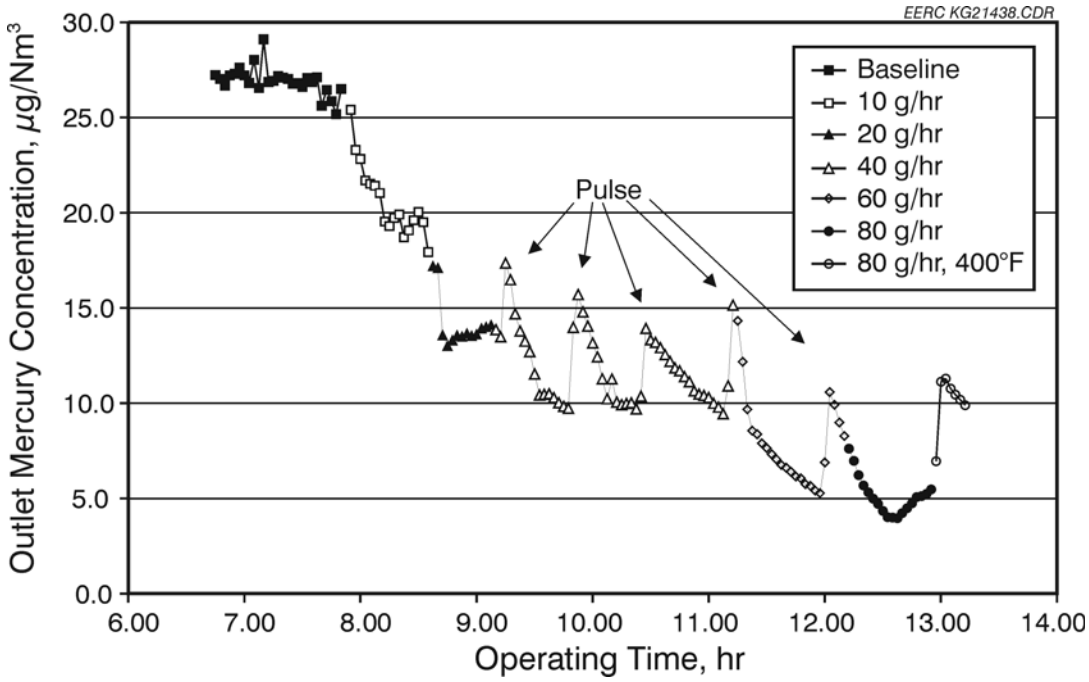

Figure 7-10. Temporal variations in total gaseous mercury concentrations at the 149°C (300°F) Gore FF outlet during injections (10 80 g/hr) of lignite-based ALC into the Poplar River coal combustion flue gas.

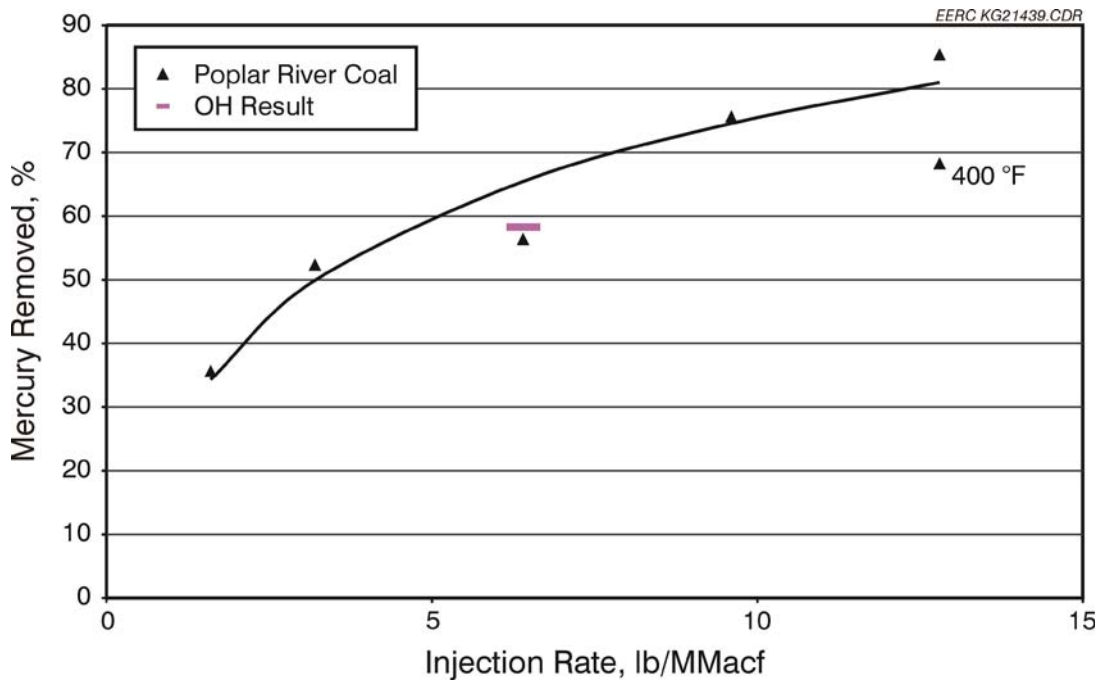

Figure 7-11. Gore FF mercury removal efficiencies as functions of ALC injection rates for 149°C (300°F) and 204°C (400°F) Poplar River coal combustion flue gases.

ratio of 15,000:1, while the FF gas temperature was maintained at 149°C (300°F). While 80-g/hr ALC was injected, a 56°C (100°F) increase in the FF gas temperature reduced FF mercury collection efficiency by about 15%.

7.4.3 ESP–FF Combination with Powdered Activated Carbon Injection, TOXECON™

The mercury removal effectiveness of injecting a sorbent between an ESP and FF were investigated by injecting ALC and DARCO FGD sorbents into Poplar River and Freedom coal combustion flue gases. Figures 7-12 and 7-13 show the temporal variations in total gaseous mercury concentrations as ALC and DARCO FGD were injected into the Poplar River coal combustion flue gas at different rates between the ESP and FF. The CEM data plotted in Figures 7-12 and 7-13 and those in similar figures presented in Appendices B1 B6 for other tests were used to evaluate the effects of sorbent type (DARCO FGD and ALC), gas temperature, injection rates, FF type (Gore or Ryton), sorbent particle size, and flue gas composition (Poplar River and Freedom coal combustion flue gases) on TOXECON™ mercury removal efficiency.

Compared in Figure 7-14 are the effects of FF material (Ryton versus Gore), gas temperature, sorbent injection rate, and ALC particle size on the efficiency of the TOXECON™ mercury removal from the Poplar River flue gas. The results in Figure 7-14 indicate that a 56°C (100°F) reduction in flue gas temperature improves the mercury capture efficiency of the TOXECON™ system. Differences in the FF material did not significantly affect mercury capture efficiencies. Results for

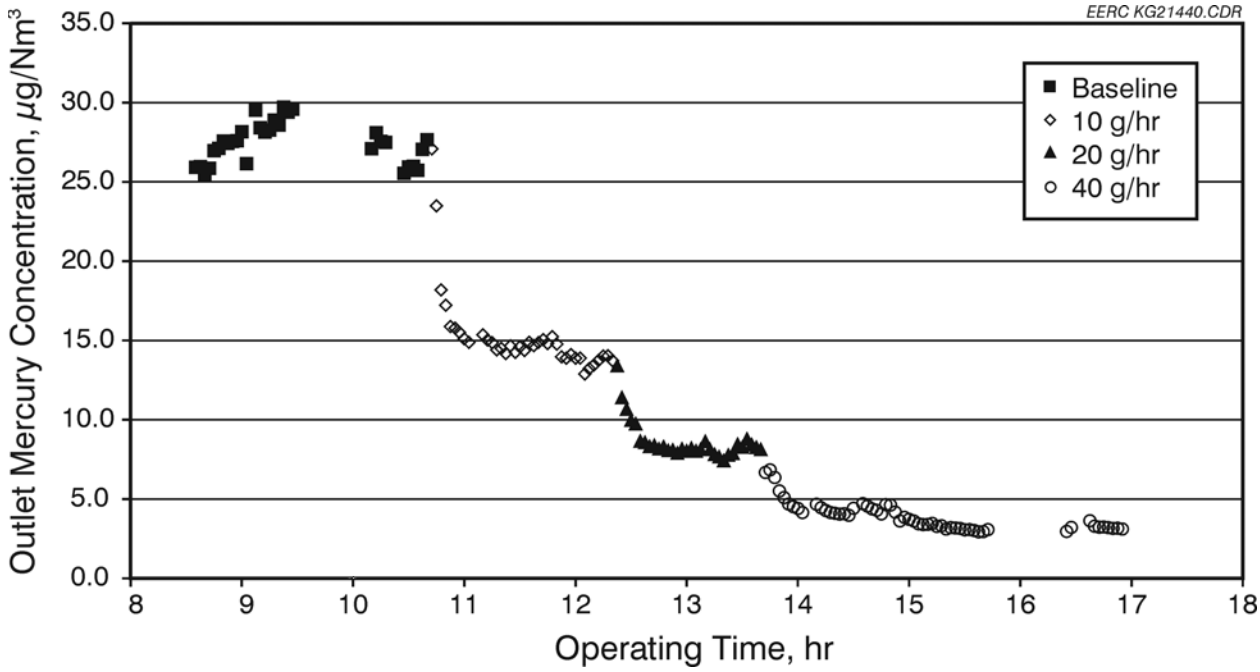

Figure 7-12. Temporal variations in total gaseous mercury concentrations at the 149°C (300°F) TOXECON™ system outlet during injections (10 40 g/hr) of ALC into the Poplar River coal combustion flue gas.

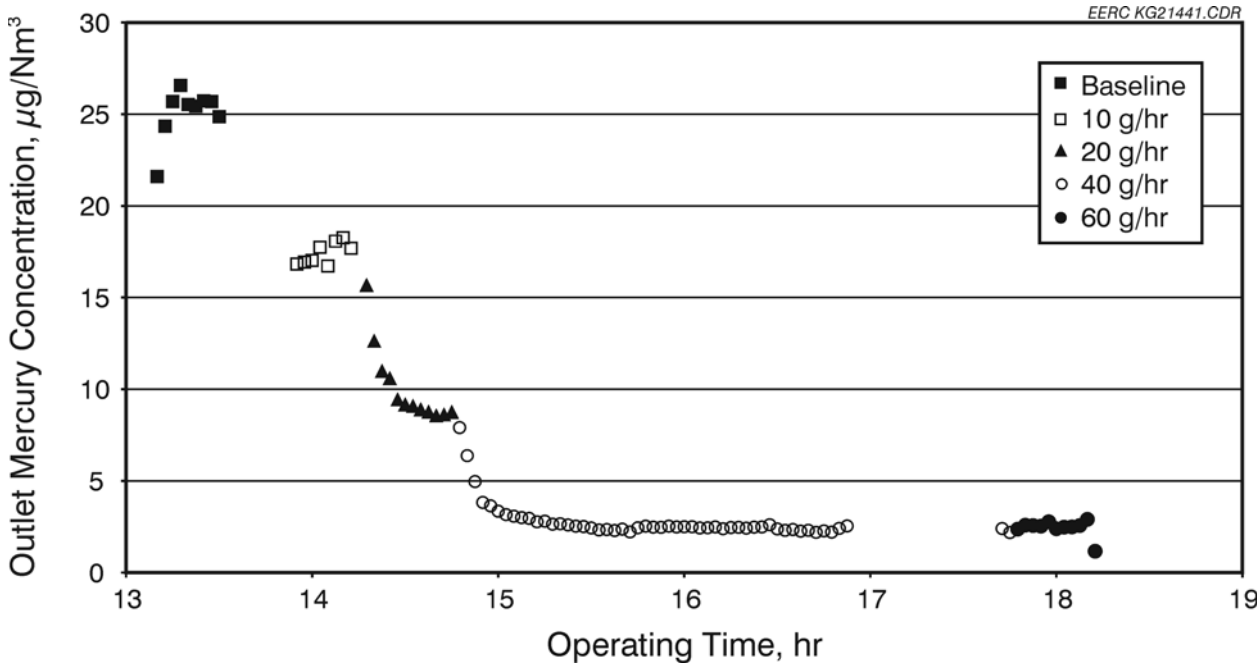

Figure 7-13. Temporal variations in total gaseous mercury concentrations at the 149°C (300°F) TOXECON™ system outlet during injections (10 60 g/hr) of DARCO FGD into the Poplar River coal combustion flue gas.

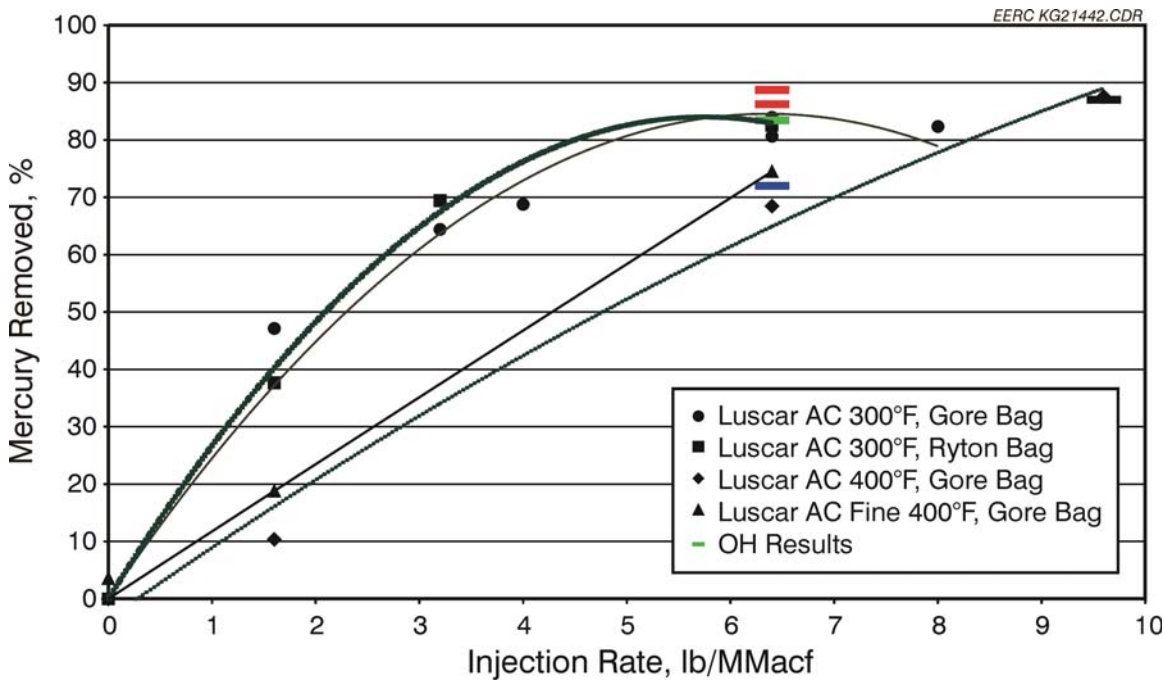

Figure 7-14. TOXECON™ (Gore and Ryton) mercury removal efficiencies as functions of coarse and fine ALC and injection rate for 149°C (300°F) and 204°C (400°F) Poplar River coal combustion flue gases.

the 149°C (300°F) Poplar River flue gas best approximate an exponential decay or polynomial fit, whereas results for the 204°C (400°F) Poplar River flue gas are more linear.

Plotted in Figure 7-15 are TOXECON™ efficiencies for removing mercury from 149°C (300°F) and 204°C (400°F) Poplar River flue gases at varying injection rates of relatively coarse- and fine-grained (MVDs of 17 µm and 7.6 µm, respectively) DARCO FGD. Similar to Figure 7-14, the results in Figure 7-15 indicate that the TOXECON™ is more effective at removing mercury from 149°C (300°F) rather than 204°C (400°F) Poplar River flue gases. In addition, a reduction in the DARCO FGD particle size did not significantly improve the TOXECON™ mercury capture efficiency.

Figure 7-16 compares the effects of varying ALC and DARCO FGD injection rates on TOXECON™ mercury capture from 149°C (300°F) Freedom flue gas. Results in Figure 7-16 indicate that DARCO FGD injection significantly improves the mercury capture efficiency of the TOXECON™ system unlike many of the sorbent comparisons, in this case the ALC for a similar injection rate.

The effects of gas temperature and sorbent type (ALC versus DARCO FGD) on the efficiency of the TOXECON™ system to remove mercury from the 149°C (300°F) Poplar River flue gas are compared in Figure 7-17. The ALC and DARCO FGD produce similar TOXECON™ removal

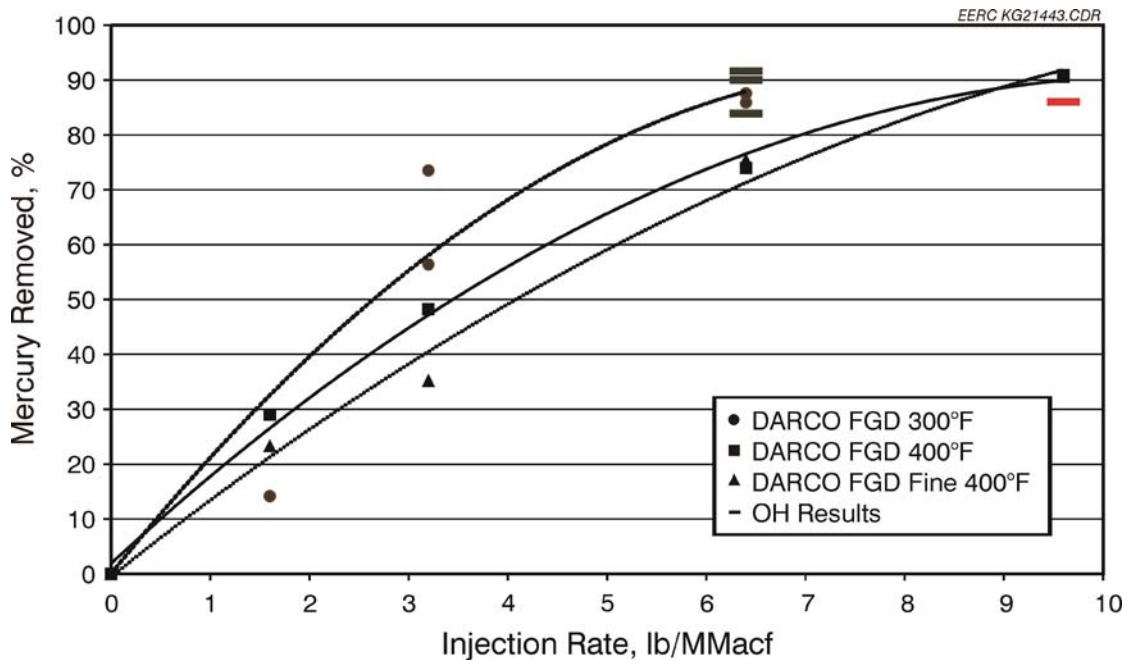

Figure 7-15. TOXECON™ mercury removal efficiencies as functions of DARCO FGD particle-size injection rate for 149°C (300°F) and 204°C (400°F) Poplar River coal combustion flue gases.

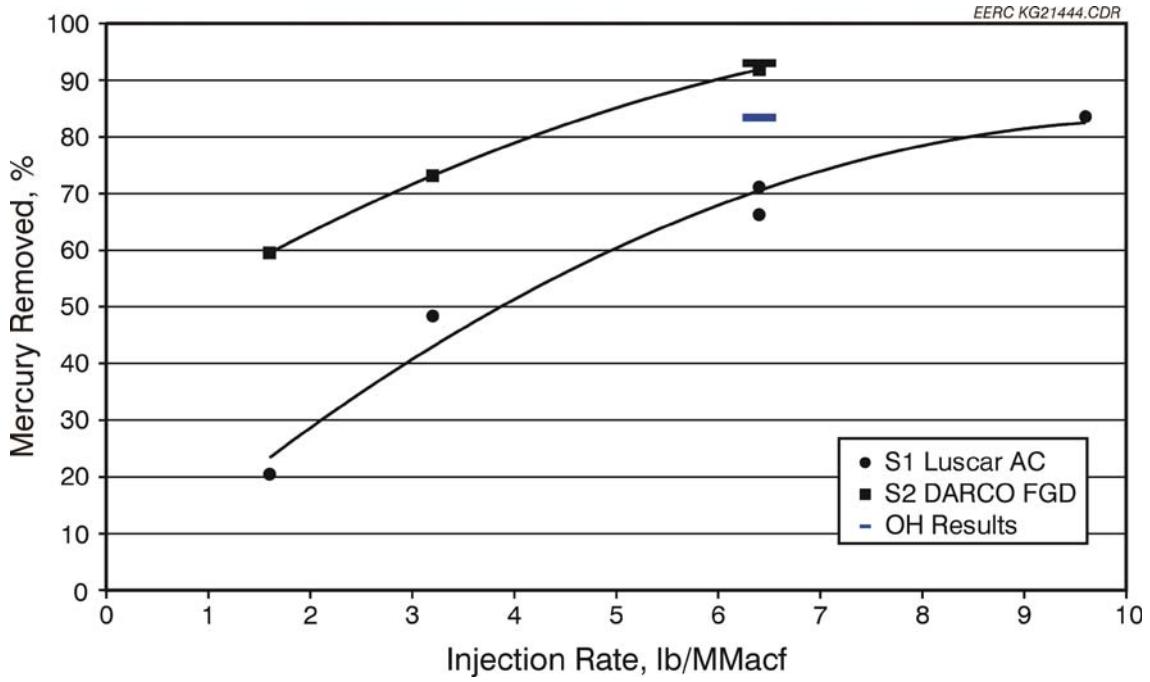

Figure 7-16. Comparison of the effects of varying ALC and DARCO FGD injection rates on TOXECON™ mercury removal from a 149°C (300°F) Freedom coal combustion flue gas.

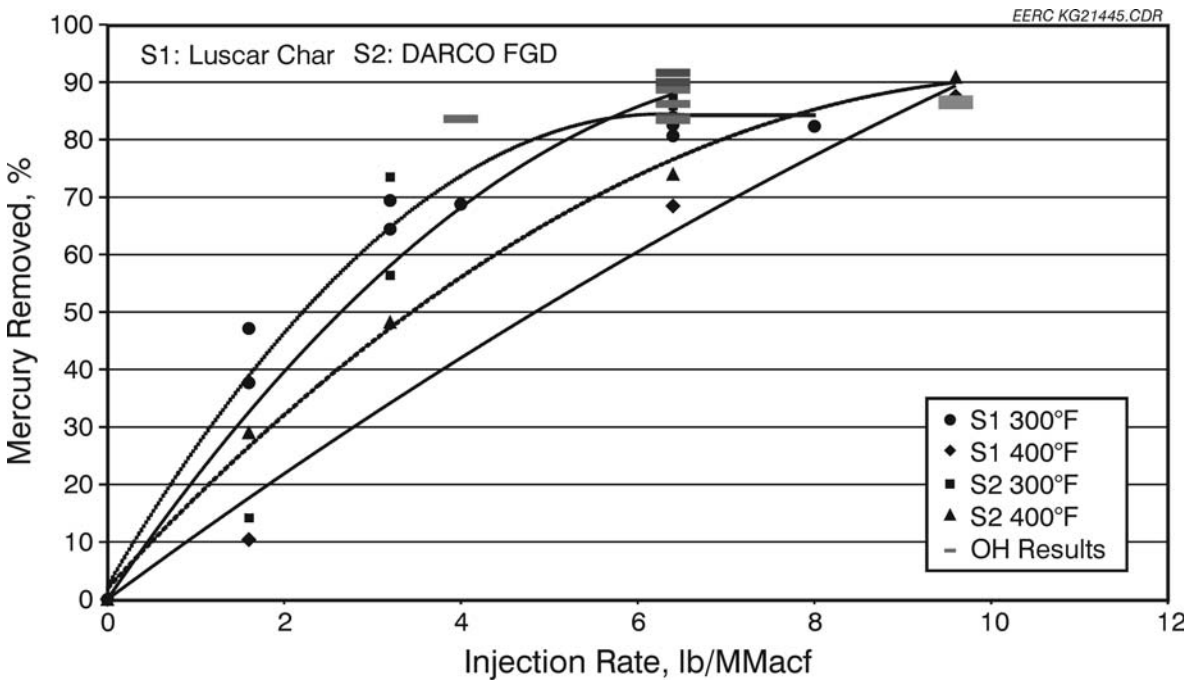

Figure 7-17. Comparison of the effects of varying ALC and DARCO FGD injection rates on TOXECON™ mercury removal from 149°C (300°F) and 204°C (400°F) Poplar River coal combustion flue gases.

efficiencies at a given gas temperature and injection rate, and both provide better mercury removal efficiencies at the lower gas temperature.

The effects of different 149°C (300°F) flue gases produced from the combustion of Poplar River and Freedom coals on TOXECON™ mercury removal efficiency during ALC and DARCO FGD injections are compared in Figures 7-18 and 7-19, respectively. Contrary to the ESP results in Figure 7-9, results in Figure 7-18 indicate that TOXECON™ was more effective in removing mercury from the 149°C (300°F) Poplar River flue gas during ALC injection rather than from the 149°C (300°F) Freedom flue gas. Conversely, TOXECON™ with DARCO FGD injection was generally more effective in removing mercury from the Freedom flue gas than from the Poplar River flue gas.

7.4.4 ADVANCED HYBRID™ *Filter System with Powdered Activated Carbon Injection*

The effect of ALC injection on *Advanced Hybrid*™ filter mercury removal effectiveness was investigated using the combustion flue gases produced from the Poplar River and Freedom coals. Presented in Figure 7-20 are CEM results which were recorded when relatively coarse Luscar char (MDV 20 µm) was injected at 20, 40, 60, or 120 g/hr into the Poplar River coal combustion flue gas and the *Advanced Hybrid*™ filter gas temperature was maintained at 149°C (300°F). OH measurements indicated that during the first and second part of testing the *Advanced Hybrid*™ filter, particulate matter (fly ash/ALC) removal efficiencies were 99.88% and 99.82%, respectively.

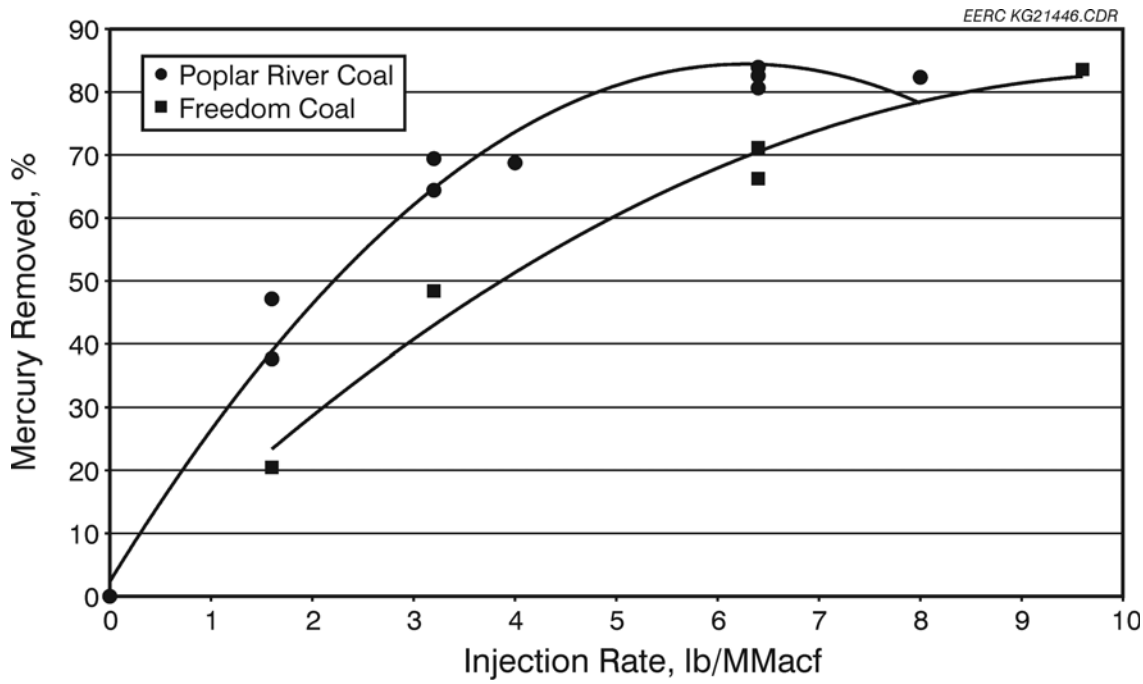

Figure 7-18. TOXECON™ mercury removal efficiencies as functions of ALC injection rates for 149°C (300°F) Poplar River and Freedom coal combustion flue gases.

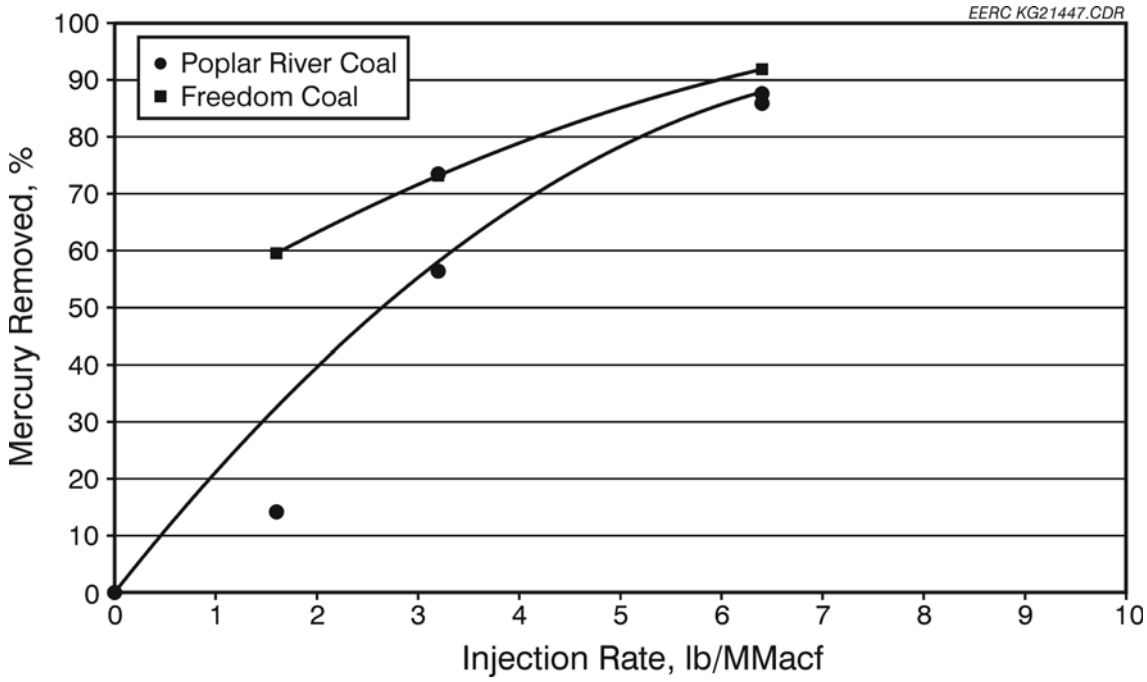

Figure 7-19. TOXECON™ mercury removal efficiencies as functions of DARCO FGD injection rates for 149°C (300°F) Poplar River and Freedom coal combustion flue gases.

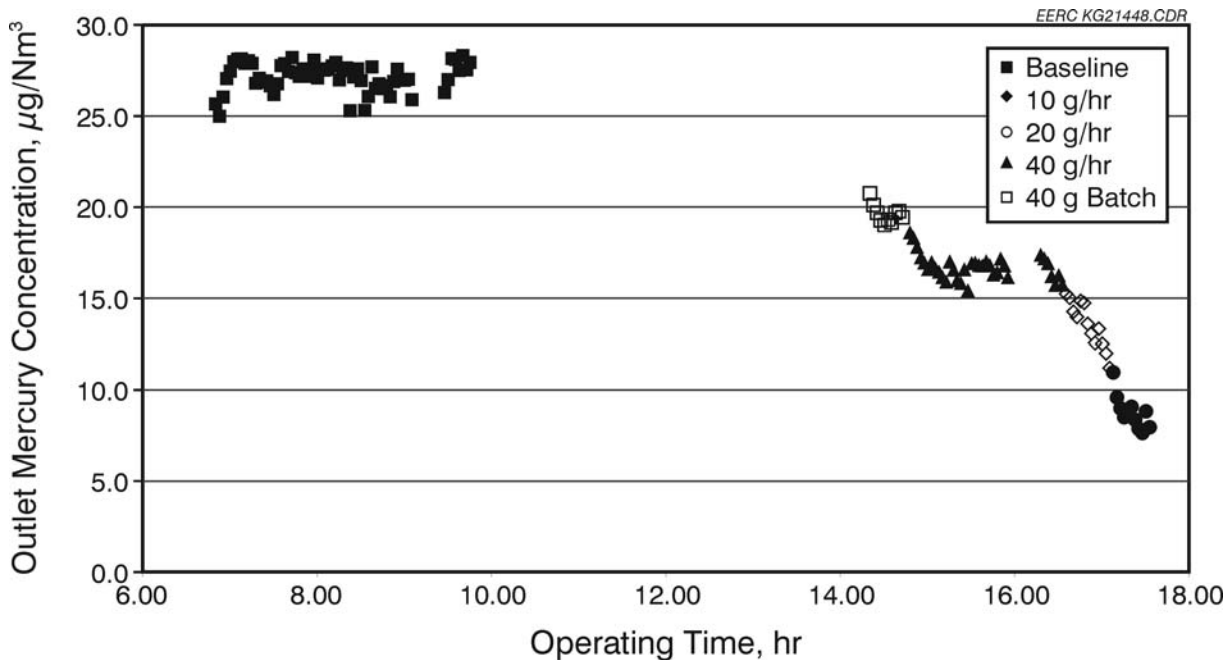

Figure 7-20. Temporal variations in total gaseous mercury concentrations at the 149°C (300°F) *Advanced Hybrid*™ filter outlet during injections (20 120 g/hr) of ALC into the Poplar River coal combustion flue gas.

Injections of ALC into the Poplar River flue gas significantly improved the mercury removal effectiveness of the *Advanced Hybrid*™ filter.

The effects of Luscar char injections on *Advanced Hybrid*™ filter mercury removal from the Freedom coal combustion flue gas are shown in Figure 7-21. OH measurements indicated that the *Advanced Hybrid*™ filter removed >99.99% of the Freedom coal fly ash ALC mixture. Similar to the Poplar River test results, increases in the ALC injection rate improved the mercury removal effectiveness of the *Advanced Hybrid*™ filter. Also shown in Figure 7-21 is the effect of batch-injecting 40 g of ALC into the Freedom flue gas with the electrostatics temporarily turned off. Batch injection in this way creates a much greater loading of ALC onto the bags, thus greatly improving mercury capture.

Efficiencies of the *Advanced Hybrid*™ filter for removing mercury from 149°C (300°F) Poplar River and Freedom flue gases at different ALC injection rates are compared in Figure 7-22. The results in Figure 7-22 indicate that the *Advanced Hybrid*™ filter ALC injection combination was much more effective in removing mercury from the 149°C (300°F) Freedom flue gas relative to the 149°C (300°F) Poplar River flue gas. In addition, the batch injection of 40 g ALC greatly enhanced *Advanced Hybrid*™ filter mercury removal efficiency. Note that for the Poplar River flue gases, bag-pulsing was much more frequent because of high ash resistivity. Slight design changes could be expected to bring the mercury removal performances in line with that seen with the Freedom coal. Thus the *Advanced Hybrid*™ filter results for the Poplar River coal should be disregarded.

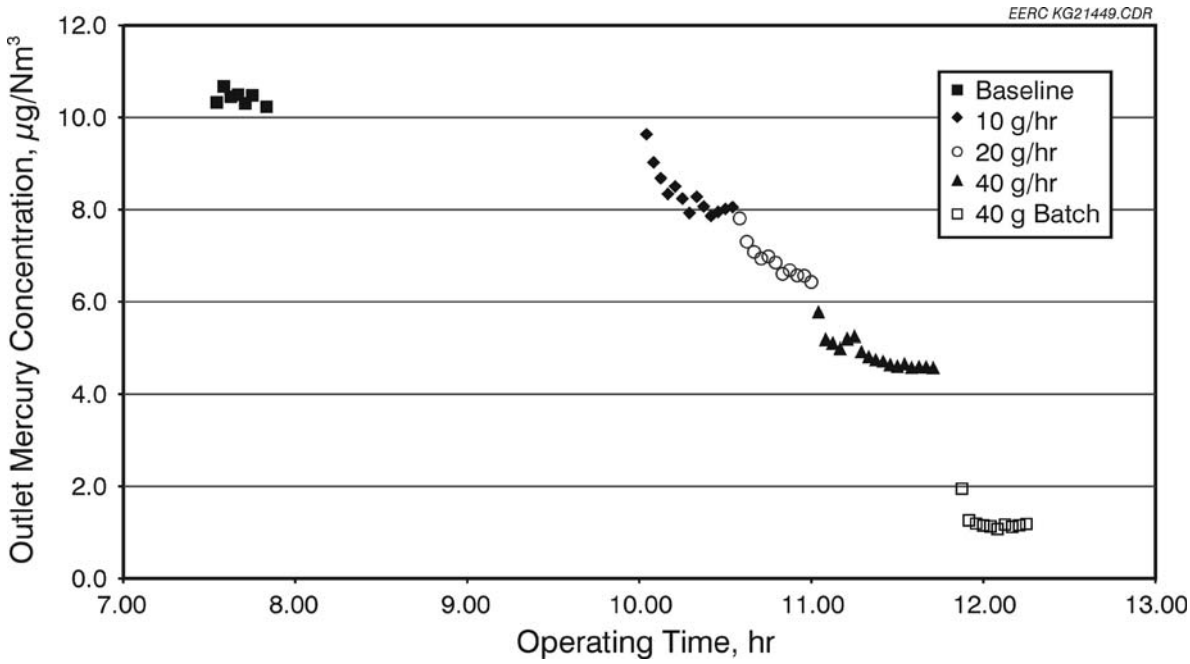

Figure 7-21. Temporal variation in total gaseous mercury concentrations at the 149°C (300°F) *Advanced Hybrid*™ filter outlet during dynamic (10 40 g/hr) and batch (40 g/hr) injections of ALC into the Freedom coal combustion flue gas.

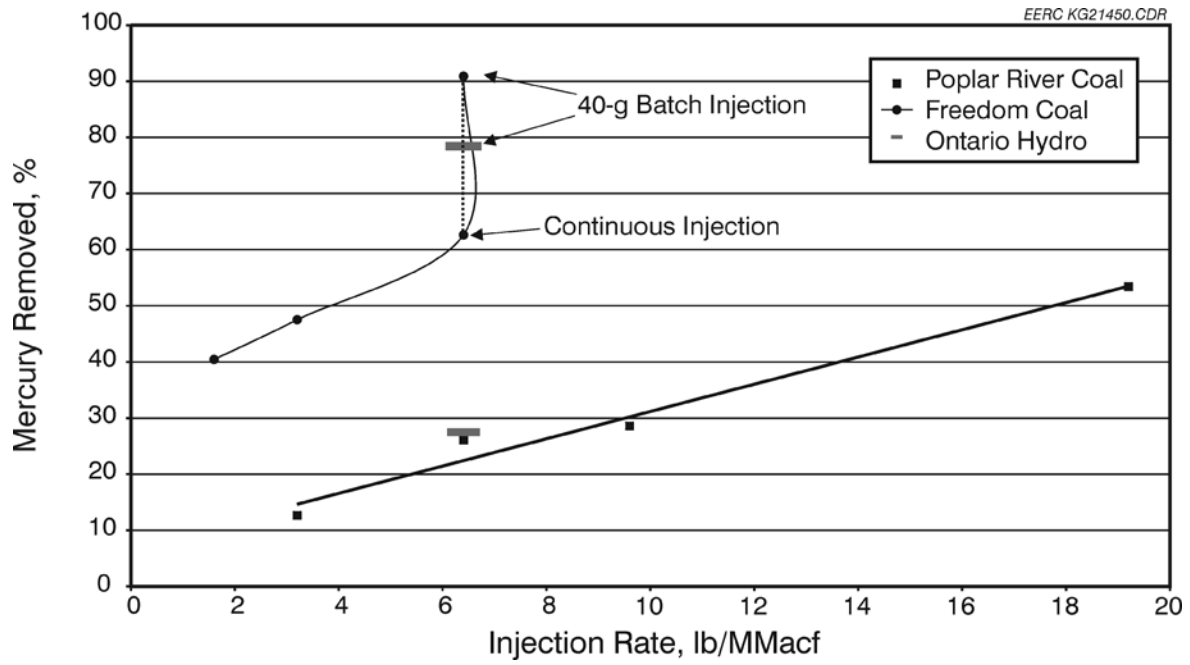

Figure 7-22. *Advanced Hybrid*™ filter mercury removal efficiencies as functions of ALC dynamic injection rates and 40-g batch injection for 149°C (300°F) Poplar River and Freedom coal combustion flue gases.

7.5 Effects of Lignite-Based Activated Carbon Injection on Fly Ash Carbon Contents

The carbon contents of selected fly ashes were determined as indicated in Table 7-3. Carbon contents of the fly ashes produced during the baseline Poplar River coal combustion tests are much lower relative to those produced when ALC was injected. The FF enabled a filter cake of injected activated carbon to form, thus increasing flue gas carbon contact time and providing for more effective mercury capture.

Table 7-3. Coal Fly Ash Carbon Contents, wt%

			Fly Ash Carbon, wt%		
			ESP/FF Combined		
Coal	Activated Carbon	Injection Rate, g/hr	ESP	FF	*Advanced Hybrid*™ Filter
Poplar River	NA[a]	NA	0.18	1.72	NA
Poplar River	NA	NA	0.11	0.61	NA
Poplar River	Luscar char	10 60	0.16	6.56	NA
Poplar River	Luscar char	10 50	0.12	5.64	NA
Poplar River	Luscar char	40 150	0.70	NA	NA
Freedom	Luscar char	10 40	0.21	5.04	NA
Freedom	NA	NA	NA	NA	0.16
Freedom	Luscar char	10 40	NA	NA	2.05

[a] Not applicable.

7.6 Comparative Technology Results

Theoretically, the emission control system that maximizes mercury sorbent contact time, thus enabling the capacity (Table 6-4) to be more fully utilized, should be the most effective at removing mercury. Total gaseous mercury concentrations in the Poplar River coal combustion flue gas varied from 20 to 30 µg/Nm^3, and the pilot-scale combustor flue gas flow rate averaged 132 scfm; thus mercury feed rates ranged from 4485 to 6728 µg/hr. Calculated mercury ALC weight ratio ranges for a given sorbent injection rate are presented in Table 7-4. The mercury sorbent capacity range of 112 to 168 µg Hg/g for the ALC, corresponding to a sorbent injection rate of 40 g/hr (6.4 lb/MMacf), most closely approximates the mercury capacity limits calculated from the bench-scale system results (Table 6-4). The reader should be aware, however, that sorbent capacities are determined based on many factors (mercury concentration, flue gas constituents, fly ash loading, temperature, etc.) and are expected to be different when comparing values from bench and pilot tests.

Compared in Figure 7-23 are the mercury removal efficiencies of injecting ALC into Poplar River flue gases at different rates with the ESP, FF, and TOXECON™, with Gore and Ryton filters. In the ESP, carbon was collected on plates, and although the residence time in the ESP can be several seconds, the actual contact time between the injected ALC and flue gas is very limited. Consequently, the available mercury capacity of the ALC was not fully utilized because of mass-

Table 7-4. Calculated Mercury–Sorbent Capacities

Injection Rate, g/hr	Mercury:Sorbent, µg Hg/g activated Luscar char
10	448 673
20	224 336
40	112 168
80	56 84

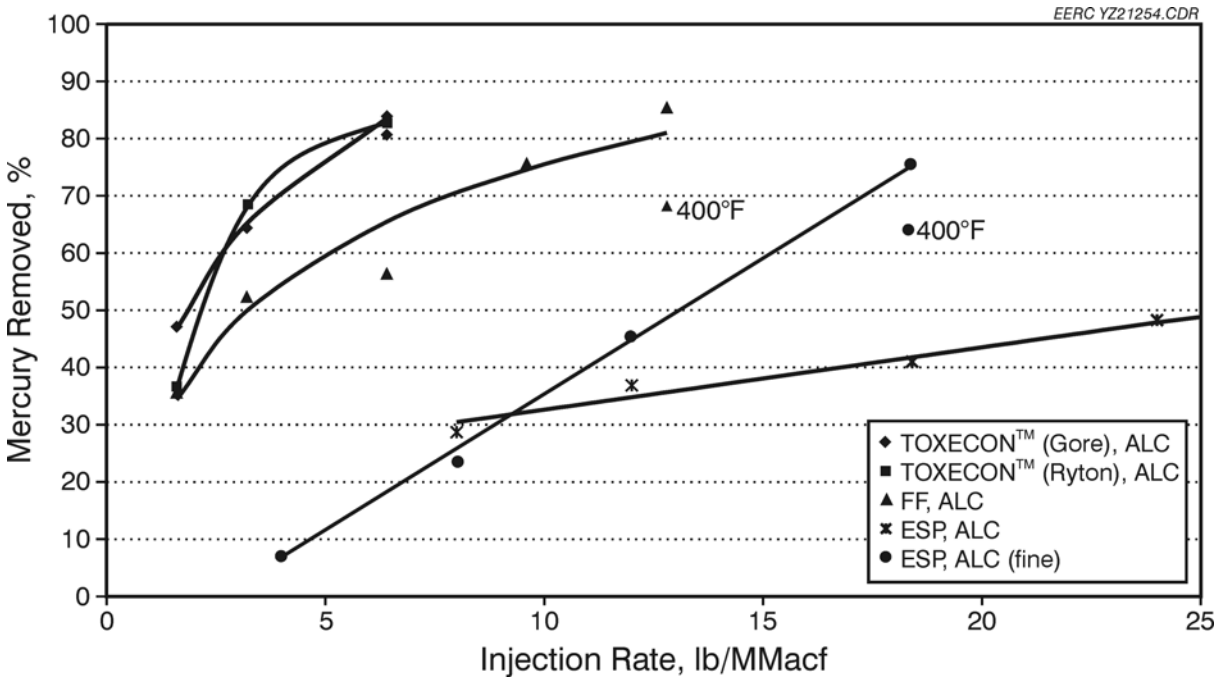

Figure 7-23. Particulate matter control device efficiencies for removing mercury from 149°C (300°F) Poplar River coal combustion flue gas as a function of ALC injection rate.

transfer limitations. As indicated in Figure 7-23, ESP mercury removal efficiencies were <30% at the 40-g/hr (6.4 lb/MMacf) injection rate. Because of high pulse rates with the Poplar River coal, the *Advanced Hybrid*™ mercury removal effectiveness was similar to the ESP. During the FF and TOXECON™ testing, however, most of the injected ALC became part of the filter cake on the FF (Table 7-3), providing longer solids residence time and more intimate contact between the ALC and flue gas. Thus mercury capture was not mass transfer-limited, but rather capacity-limited. FF and TOXECON™ mercury removal efficiencies ranged from about 65% to 90% at the injection rate of 40 g/hr (6.4 lb/MMacf) (Figures 7-14, 7-16, 7-17, and 7-23), indicating that the ALC mercury capacity was probably maximized.

Compared in Figure 7-24 are the mercury removal efficiencies of injecting ALC and DARCO FGD into Freedom flue gases at different rates with the ESP, TOXECON™, and *Advanced Hybrid*™ filter. In addition, the effect of batch-injecting 40 g of ALC on *Advanced Hybrid*™ filter mercury

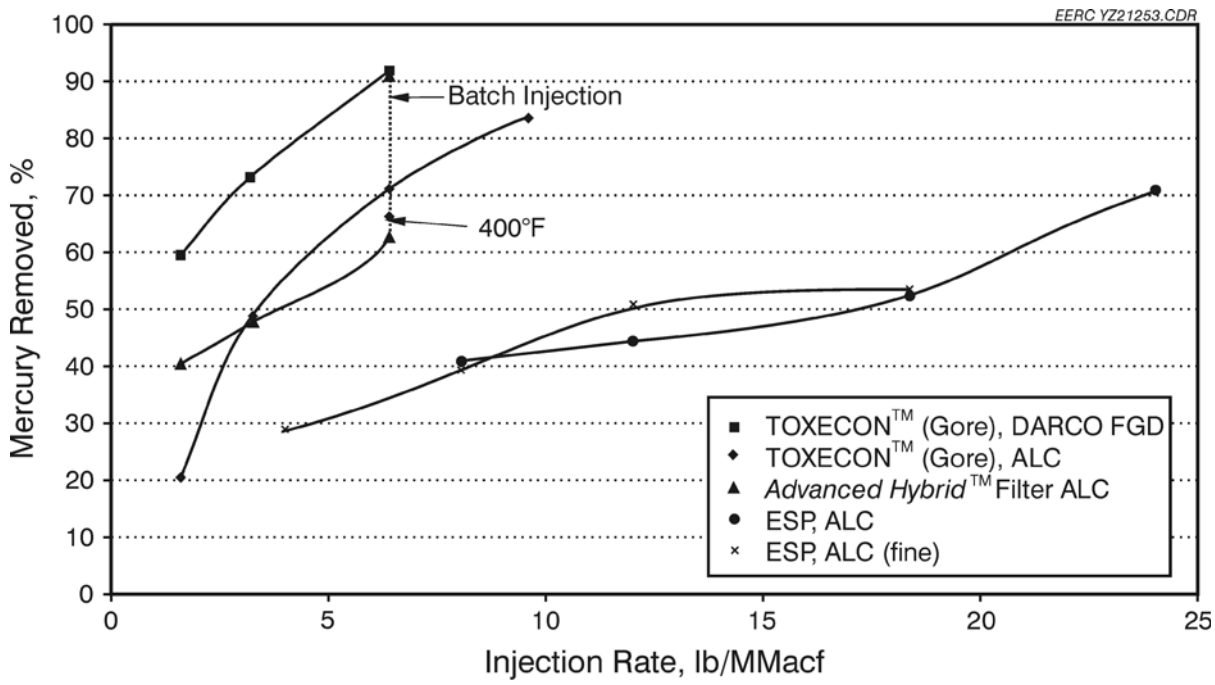

Figure 7-24. Particulate matter control device efficiencies for removing mercury from 149°C (300°F) Freedom coal combustion flue gas as functions of ALC and DARCO FGD injection rates.

removal performance is shown in Figure 7-24. Similar to the Poplar River coal test results in Figure 7-23, the combination of lignite-based activated carbon injection and TOXECON™ was generally the most effective mercury removal strategy. The *Advanced Hybrid*™ filter was also effective in removing mercury from the Freedom coal combustion flue gas, especially when ALC was batch-injected.

EERC pilot-scale ESP and TOXECON™ mercury removal efficiencies for the Poplar River and Freedom flue gases are compared in Figure 7-25 to those obtained by Bustard et al. (2002) at full-scale utility boilers, described in Table 7-5, while injecting activated carbons into a bituminous coal combustion flue gas upstream of a compact hybrid particulate collector (COHPAC) (pulse-jet FF) and into bituminous and Powder River Basin (PRB) subbituminous coal combustion flue gases upstream of an ESP. Coal type (i.e., composition) is an important parameter that affects the mercury removal efficiency of a control device. During the pilot-scale lignite and utility-scale eastern bituminous coal tests, mercury removal efficiency increased with increasing activated carbon injection rates. Conversely, mercury removal efficiency was never >70%, regardless of the activated carbon injection rate into the PRB subbituminous coal combustion flue gas with an ESP. This limitation is probably caused by the sparsity of acidic flue gas constituents, such as HCl and sulfur oxides (SO_x), that promote mercury activated carbon adsorption respectively. In addition, the generally abundant lime (CaO) component of PRB subbituminous coal fly ashes reactively scavenges chlorine species (Cl, HCl, and Cl_2) in a small amount from the flue gas to form $CaCl_2$.

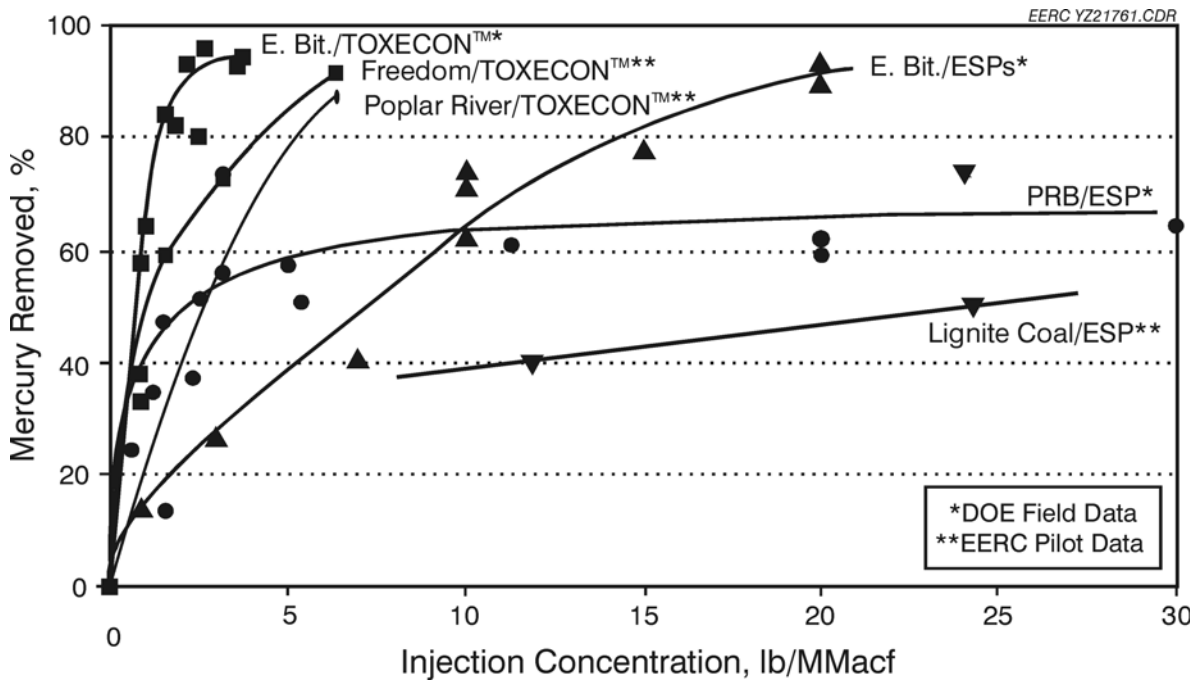

Figure 7-25. Mercury removal trends with activated carbon injection.

Table 7-5. Descriptions of Coal-Burning Power Plants That Employed Activated Carbon Injection

Host Site	Coal	Control Device
Alabama Power Plant Gaston	Washed eastern bituminous	Hot-side ESP and COHPAC[a]
We Energies Pleasant Prairie	PRB subbitiminous	ESP[b]
PG&E NEG Brayton Point	Eastern bituminous	ESPs in series[c]

[a] COHPAC is a pulse jet FF installed downstream of an existing particulate control device. Activated carbon was injected directly into COHPAC FF.
[b] Sulfur trioxide (SO_3) flue gas conditioning.
[c] Activated carbon was injected between ESPs, SO_3 flue gas conditioning.

Figure 7-25 indicates that activated carbon injection combined with the particulate control devices installed on the full-scale boilers generally provided better mercury removal efficiency at a given injection rate relative to ALC injection followed by the pilot-scale ESP. The TOXECON™ mercury removal efficiencies in Figure 7-25 are intermediate relative to those obtained with the COHPAC and ESP on eastern bituminous flue gases.

7.7 Chlorine Additives

NaCl and gaseous HCl were added to the Poplar River and Freedom coal and combustion flue gases, respectively, to determine if the DARCO FGD sorbent reactivity/capacity could be improved. The addition of chlorine and its impact on carbon-based sorbents is suspected because of how

effective high concentrations of chlorine are in municipal, hazardous, and hospital waste incineration flue gases. HCl was injected upstream of the ESP and carbon injection at the furnace outlet where the flue gas is approximately 930°C (1700°F). NaCl was either blended with the coals or DARCO FGD to evaluate whether the time-temperature history that the chlorine additive experienced in the combustor affected mercury capture. For example, the NaCl coal mixture experienced the entire time-temperature regime of the pilot-scale combustor, whereas the NaCl DARCO FGD mixture was injected in the postcombustion environment where the average gas temperature was about 149°C (300°F).

The effects of varying DARCO FGD and Cl injection rates on mercury removal in a TOXECON™ arrangement from the Poplar River coal combustion flue gas are shown in Figure 7-26. At a DARCO FGD injection rate of 10 g/hr, injection of HCl resulted in an additional reduction of 3 to 5 µg/Nm^3 of gaseous mercury relative to that achieved through DARCO FGD injection alone. The injection of 20 ppmv HCl together with 20-g/hr DARCO FGD injection did not significantly improve the mercury removal effectiveness, probably because gaseous mercury concentrations were already low. When NaCl was blended with the Poplar River coal, significant reductions were observed, as shown in Figure 7-26. Note: the addition of NaCl directly with the DARCO FGD was ineffective in enhancing the mercury removal effectiveness. Thus the results are not shown.

The CEM results in Figure 7-27 show the effects of NaCl additions on the effectiveness of DARCO FGD injection to remove mercury from the Freedom coal combustion flue gas using the TOXECON™, *Advanced Hybrid*™ filter, or ESP systems. The injection of 25 g/hr NaCl with 20 g/hr

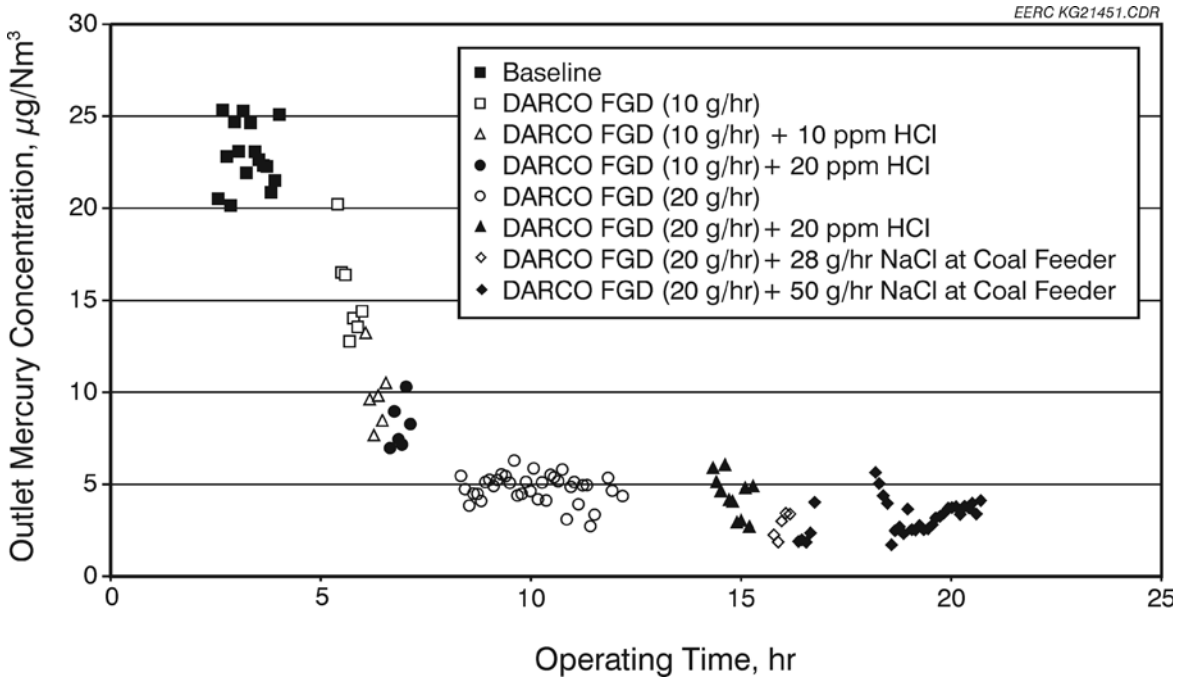

Figure 7-26. Temporal variations in total gaseous mercury concentrations at the 149°C (300°F) TOXECON™ outlet during injections of DARCO FGD and HCl into flue gas and addition of NaCl to the Poplar River coal.

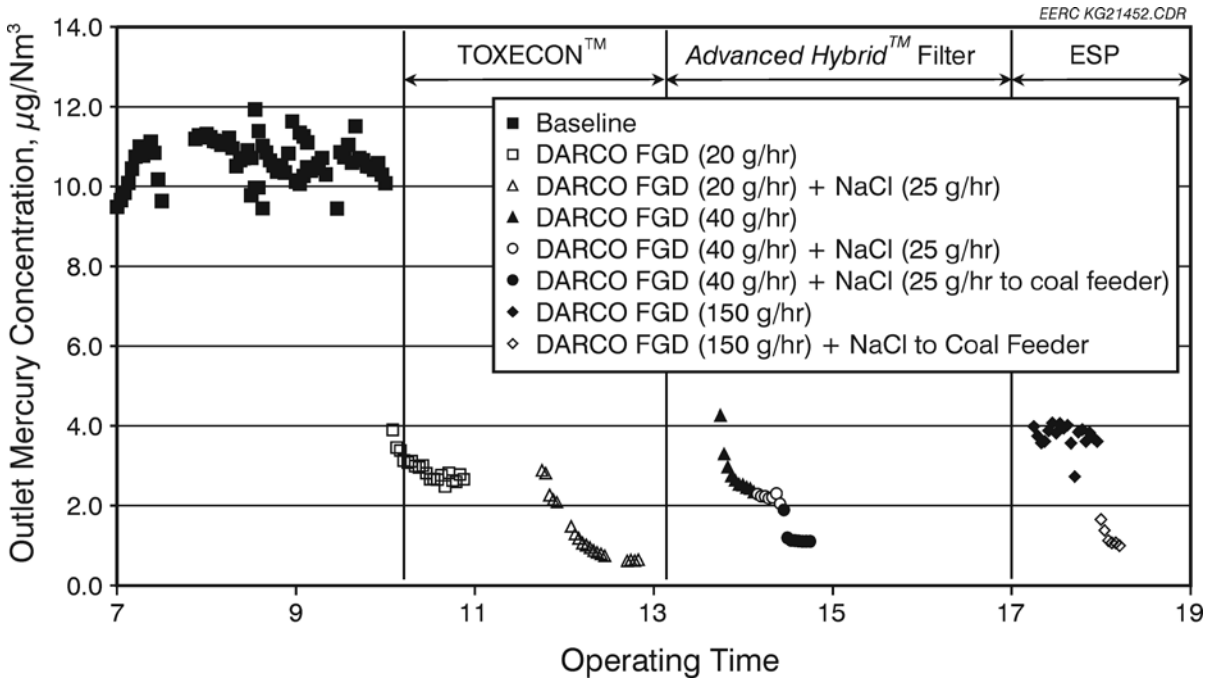

Figure 7-27. Temporal variations in total gaseous mercury concentrations at the particulate matter control device inlet (baseline) and at the 149°C (300°F) TOXECON™, *Advanced Hybrid*™ filter, or ESP outlet during injections of DARCO FGD and NaCl into the Freedom coal combustion flue gas.

DARCO FGD resulted in the TOXECON™ removing an additional 2 μg/Nm^3 of gaseous mercury relative to 20-g/hr DARCO FGD injection alone. *Advanced Hybrid*™ filter test results in Figure 7-27 indicate that the injection of 25 g/hr NaCl to the Freedom coal significantly improved the capture efficiency of DARCO FGD. Similar results are shown in Figure 7-27 for the ESP test when much greater DARCO FGD and NaCl injection rates of 150 g/hr were applied. Note, for comparison, the addition of 25 g/hr of NaCl is equivalent to approximately 370 ppm of chlorine in coal.

The preliminary results in Figures 7-26 and 7-27 suggest that chlorine additives could be used to enhance the mercury removal effectiveness of DARCO FGD, thereby reducing the amount of DARCO FGD needed to achieve a given level of mercury emission control. Very limited results in Figure 7-26 also suggest that adding NaCl to a coal is more effective in enhancing mercury capture than adding it to DARCO FGD. Note, the addition of Cl also appeared to oxidize a portion of the mercury. Theoretically, this makes sense because chemical kinetic modeling of bench-scale testing results indicates that the introduction of HCl or NaCl into the high-temperature furnace region is more likely to result in the production of atomic chlorine (Cl) and/or molecular chlorine (Cl_2) which are generally thought to be the dominant Hg^0 reactants in coal combustion flue gases (Widmer et al., 1998, 2000; Mamani-Paco and Helble, 2000; Sliger et al., 2000; Niksa et al., 2001; Edwards et al., 2001; Wang et al., 2001).

8.0 RESULTS AND DISCUSSIONS: MERCURY STABILITY IN ASH

Selected coal fly ashes were analyzed for their mercury contents and subjected to 18-hour, 30-day, and 60-day leaching conditions in distilled deionized water to evaluate mercury solubility and mobility. Mercury was below the limit of quantification (i.e., <0.01 µg/L) in the leachates after 18-hour and 30-day leaching conditions indicating that mercury was essentially insoluble during these relatively short-term leaching durations. However, as indicated in Table 8-1, the 60-day leaching mobilized a very small fraction of the mercury in two of the fly ashes. In similar experiments, Heebink and Hassett (2002) also found that the mercury release rate from coal fly ashes was very low. The results in Table 8-1 also indicate that the FF and *Advanced Hybrid*™ filter were more effective in capturing Hg(p) relative to the ESP.

Table 8-1. Coal Fly Ash and Leachate (60-day) Mercury Contents, ppm

			Fly Ash (leachate) Mercury, ppm		
Coal	Activated Carbon	Injection Rate, g/hr	ESP	FF	*Advanced Hybrid*™ Filter
Poplar River	NA[a]	NA	0.030 (<0.01)	NA	NA
Poplar River	Luscar char	40 150	0.218 (0.032)	NA	NA
Poplar River	Luscar char	10 50	0.011 (<0.01)	8.66 (<0.01)	NA
Poplar River	Luscar char	20 120	NA	NA	1.15 (<0.01)
Freedom	Fine Luscar char	25 115	0.198 (<0.01)	NA	NA
Freedom	DARCO FGD	10 40	Not analyzed	17.8 (0.057)	NA
Freedom	Luscar char	10 40	0.040 (<0.01)	5.73 (<0.01)	NA
Freedom	Luscar char	10 40	NA	NA	0.865 (<0.01)

[a] Not applicable.

9.0 SUMMARY AND CONCLUSIONS

9.1 Bench-Scale Preparation and Testing of Potential Mercury Sorbents

Activated carbons were prepared from relatively high-sodium Bienfait, Freedom, and Center lignites by carbonization at 400°C (752°F) in nitrogen followed by steam activation at 750°C (1382°F) and 800°C (1472°F) in nitrogen. Luscar char was also steam-activated at 750°C (1382°F) and 800°C (1472°F) in nitrogen. The lignite-based activated carbons, including a commercial mercury sorbent DARCO FGD, activated and unactivated Luscar char, and an oxidized calcium silicate, were tested in a thin-film, fixed-bed, bench-scale reactor using a simulated lignitic flue gas consisting of nominally 10 µg/Nm^3 Hg^0, 6% O_2, 12% CO_2, 15% H_2O, 580 ppm SO_2, 120 ppm NO, 6 ppm NO_2, and 1 ppm HCl in N_2. Activated (750°C) Bienfait carbon and DARCO FGD were also tested in an established baseline flue gas consisting of nominally 10 µg/Nm^3 Hg^0, 6% O_2, 12% CO_2, 8% H_2O, 1600 ppm SO_2, 400 ppm NO, 20 ppm NO_2, and 50 ppm HCl in N_2. All of the lignite-based activated (750°C, 1382°F) carbons required a 30- to 45-minute conditioning period in the simulated lignite flue gas before they exhibited good mercury sorption capacities and Hg^0 oxidation potentials (>90% Hg^{2+}). The unactivated Luscar char and oxidized calcium silicate were ineffective in capturing or heterogeneously oxidizing mercury. Lignite-based activated (800°C, 1472°F) carbons

required a shorter (15-minute) conditioning period in the simulated lignite flue gas and captured gaseous mercury more effectively with greater Hg^0 oxidation (>95% Hg^{2+}) than those activated at 750°C (1382°F). Mercury capacities of the ALC ranged from 164 to 202 µg/g in the presence of the simulated lignite combustion flue gas. Activated (750°C, 1382°F) Bienfait carbon and DARCO FGD did not experience significant early mercury breakthrough in the baseline flue gas likely because the higher acid gas concentrations in the baseline flue gas relative to the simulated lignite flue gas promoted the initial mercury capture. Although these baseline flue gas tests yielded better mercury capture initially, significant breakthrough of mercury ultimately occurred sooner than during the simulated lignite flue gas tests.

9.2 Pilot-Scale Tests

The ALC and DARCO FGD were selected for additional testing in a 580-MJ/hr (550,000-Btu/hr) pulverized coal-fired unit, based on the sorbent screening results, costs, and consensus among project sponsors. The following variables that could potentially affect mercury emission control were tested: lignite coal source (Poplar River or Freedom Mine), control device type (ESP, FF, TOXECON™, and *Advanced Hybrid*™ filter), FF type (Gore and Ryton), sorbent type (steam-activated Luscar char and DARCO FGD) and particle size (approximate MVDs of 20 and 5 µm), sorbent injection rate, mercury speciation, and flue gas temperature in the pollution control device. Pilot-scale test results indicated the following:

- The relative proportions of Hg^0, Hg^{2+}, and Hg(p) in the Poplar River and Freedom coal combustion flue gases were very similar at approximately 85%, 15%, and <1%, respectively.

- During periods of incomplete combustion of Poplar River and Freedom coals and subsequent production of unburned carbon in the resulting fly ashes promoted the formation of Hg^{2+} and/or Hg(p).

- ALC and DARCO FGD were much more effective in capturing mercury compared to other sorbents tested.

- In all four control devices tested, increasing ALC and DARCO FGD injection rates and decreasing gas temperatures in the control devices significantly improved mercury removal from the Poplar River and Freedom coal combustion flue gases.

- In general, the ALC and DARCO FGD sorbents were slightly more effective when injected into the Freedom flue gas relative to the Poplar River flue gas.

- In a few cases, the DARCO FGD provided better mercury capture at a given injection rate relative to ALC. However, the conditions under which the Luscar char was activated have not been optimized.

- A reduction in ALC and DARCO FGD particle size did not consistently improve mercury capture, although significant improvement was noted for the ESP only with the Poplar River coal.

- Differences in the FF material (Ryton versus Gore) did not significantly affect mercury capture.

- The FF and *Advanced Hybrid*™ filter were much more effective in capturing injected ALC and DARCO FGD and thus mercury relative to the ESP.

- The relative mercury removal efficiencies for the control device technologies were TOXECON™ > *Advanced Hybrid*™ filter > FF > ESP.

- Additives can significantly enhance the mercury removal effectiveness of DARCO FGD, thereby reducing the amount of DARCO FGD needed to achieve a given level of mercury emission control.

The mercury removal effectiveness of ALC injection combined with pilot-scale ESP and TOXECON™ systems was compared to that obtained with activated carbon injection and COHPAC or ESP equipment installed on full-scale utility boilers (Bustard et al., 2002). Activated carbon injection combined with COHPAC and ESP devices installed on full-scale boilers generally provided better mercury removal efficiency at a given injection rate relative to ALC injection followed by the pilot-scale ESP. The TOXECON™ mercury removal efficiencies were intermediate relative to those for full-scale units burning eastern bituminous coals and equipped with COHPAC and ESP control devices, but much better relative to a PRB subbituminous coal-fired unit equipped with an ESP.

Selected fly ashes collected in the control devices with and without activated carbon present were subjected to an SGLP with equilibration periods of 18 hours, 30 days, and 60 days. Mercury in Poplar River and Freedom coal fly ashes generally remained insoluble after 18-hour, 30-day, and 60-day exposures to deionized water, suggesting that mercury is chemically adsorbed and relatively immobile.

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APPENDIX A

INDIVIDUAL COAL COMPOSITION ANALYSIS RESULTS

Coal Supply Information

Coal Mine	Coal Company	Provider	Quantity Used
Poplar River	Luscar Ltd.	Luscar Ltd.	18,000 lb
Freedom	Coteau Properties	Basin Electric Power Cooperative	4500 lb

Coal Proximate, Ultimate, Mercury, and Chloride Analysis Results, (all as-received except heating value)

	Proximate Analysis Poplar River Coal							Proximate Analysis Freedom Coal		
	6/7/2002	T1*	T4	T12	T20	7/8/2002	Average	6/7/2002	7/15/2002	Average
Moisture**	40.20	27.50	27.60	27.90	22.70	20.70	27.77	36.60	30.20	33.40
Volatile Matter	26.96	33.22	33.63	32.97	36.29	36.41	33.25	28.21	32.43	30.32
Fixed Carbon	20.62	24.13	23.56	24.04	26.09	27.72	24.36	26.42	29.96	28.19
Ash	12.22	15.15	15.21	15.09	14.92	15.72	14.72	8.77	7.40	8.09
	Heating Value (Btu/lb)									
	5041	6158	6161	6251	6835	6923	6228	6153	7172	6663

	Ultimate Analysis Poplar River Coal							Ultimate Analysis Freedom Coal		
	6/7/2002	T1	T4	T12	T20	7/8/2002	Average	6/7/2002	7/15/2002	Average
Hydrogen	6.62	5.50	5.49	0.00	5.20	5.16	5.66	6.49	6.16	6.33
Cabon	31.83	37.75	38.00	0.00	40.67	42.52	38.34	37.89	42.63	40.26
Nitrogen	0.51	0.59	0.58	0.00	0.62	0.63	0.59	0.64	0.71	0.68
Sulfur	0.42	0.69	0.72	0.61	0.74	0.71	0.62	0.50	0.64	0.57
Oxygen (ind.)	48.40	40.33	40.00	0.00	37.85	35.82	40.69	45.71	42.46	44.09
Ash	12.22	15.15	15.21	15.09	14.92	15.17	14.10	8.77	7.40	8.09

	Poplar River Mercury and Chlorine Results							Freedom Mercury and Chlorine Results		
	6/7/2002	T1	T4	T12	T20	7/8/2002	Average	6/7/2002	7/15/2002	Average
Mercury dppm	0.083	0.134	0.129	0.125	NA	NA	0.118	0.045	0.071	0.058
Chlorine dppm	7.846	NA	18.809	NA	18.745	14.664	15.016	13.104	16.359	14.732

* T = Test number.

** Note: coal was partially dried to facilitate handling in pilot combustor.

Coal Characteristics, (all moisture-free except for heating value)

	Proximate Analysis Poplar River Coal							Proximate Analysis Freedom Coal		
	6/7/2002	T1	T4	T12	T20	7/8/2002	Average	6/7/2002	7/19/2002	Average
Moisture	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Volatile Matter	45.08	45.81	46.43	45.74	46.95	45.93	45.99	44.48	46.47	45.475
Fixed Carbon	34.49	33.30	32.57	33.32	33.74	34.94	33.73	41.69	42.92	42.305
Ash	20.43	20.89	21.00	20.94	19.31	19.13	20.28	13.83	10.61	12.22
	Heating Value, Btu/lb									
	8428	8493	8507	8673	8843	8732	8613	9702	10276	9989

	Ultimate Analysis Poplar River Coal							Ultimate Analysis Freedom Coal		
	6/7/2002	T1	T4	T12	T20	7/8/2002	Average	6/7/2002	7/19/2002	Average
Hydrogen	3.61	3.37	3.35	0.00	3.46	3.60	3.48	3.83	4.01	3.92
Carbon	53.22	52.06	52.47	0.00	52.62	53.63	52.80	59.74	61.08	60.41
Nitrogen	0.85	0.81	0.80	0.00	0.80	0.80	0.81	1.01	1.02	1.015
Sulfur	0.70	0.95	1.00	0.85	0.96	0.90	0.90	0.79	0.92	0.855
Oxygen (ind.)	21.19	21.92	21.38	0.00	22.85	21.94	21.86	20.8	22.36	21.58
Ash	20.43	20.89	21.00	20.94	19.31	19.13	20.15	13.83	10.61	12.22

	Poplar River Mercury and Chlorine Results							Freedom Mercury and Chlorine Results		
	6/7/2002	T1	T4	T12	T20	7/8/2002	Average	6/7/2002	7/19/2002	Average
Mercury dppm	0.117	0.171	0.165	0.160	NA	NA	0.153	0.0621	0.0926	0.07735
Chlorine dppm	11	NA	24	NA	23	17.7	18.925	17.9	21.3	19.6

Trace Element Analyses, moisture-free basis, µg/g of coal

µg/g	PR-T4	PR-T20	PR-7/11/2002	Average PR	Freedom
As	4.87	5.1	5.01	4.99	4.63
Ba	364	318	419	367	639
Be	0.91	0.92	0.85	0.89	0.4
Cd	0.092	0.058	0.062	0.07	0.18
Co	17	14.5	13	14.83	13.5
Cr	12	10	9.7	10.57	8.5
Mn	138	106	109	117.67	59.8
Ni	3.09	2.79	2.99	2.96	4.45
Pb	10.6	9.39	10.8	10.26	4.69
Se	0.704	0.73	0.704	0.71	0.963
Totals	551.27	467.49	571.12	529.96	736.11

Elemental Ash Analysis, wt% (total oxide basis)

	Freedom	Poplar River (T4)	Poplar River (T20)
SiO_2	24.6	39.4	37.6
Al_2O_3	13.9	25.7	25
Fe_2O_3	8.12	6.36	6.86
TiO_2	0.44	0.61	0.61
P_2O_5	0.26	0.03	0.03
CaO	22.4	14.9	15.7
MgO	6.9	4.7	4.98
Na_2O	6.26	0.06	0.03
K_2O	0.63	0.69	0.63
SO_3	16.5	7.55	8.57

Elemental Ash Analysis, wt% (SO_3 free basis)

	Freedom	Poplar River (T4)	Poplar River (T20)
SiO_2	29.5	42.6	41.1
Al_2O_3	16.7	27.8	27.3
Fe_2O_3	9.73	6.88	7.5
TiO_2	0.52	0.66	0.67
P_2O_5	0.31	0.03	0.04
CaO	26.8	16.1	17.2
MgO	8.27	5.08	5.45
Na_2O	7.5	0.07	0.04
K_2O	0.75	0.74	0.69
SO_3	—	—	—

Elemental Ash Analysis, wt%

	Freedom	Poplar River (T4)	Poplar River (T20)
Si	20.2	34.2	32.4
Al	12.9	25.2	24.4
Fe	9.99	8.24	8.85
Ti	0.46	0.68	0.67
P	0.2	0.02	0.03
Ca	28.1	19.7	20.7
Mg	7.33	5.25	5.55
Na	8.2	0.1	0
K	0.92	1.06	0.96
S	11.65	5.6	6.33

APPENDIX B

PILOT-SCALE TEST AND OPERATIONS SCHEDULE

Mercury Control Technologies for Electric Utilities Burning Lignite Coals
Particulate Test Combustor
Run **PTC-633**
Fund Number – 4680
Test Dates: June 17–June 28, July 8–July 19, and August 12–August 16

Project Manager: John Pavlish – Office Telephone No. 777-5268
Principal Investigators: Mike Holmes – Office Telephone No. 777-5276
Home No. 599-2164
Jay Almlie – Office Telephone No. 777-5260

SAFETY NOTE

We will be using a high-voltage source to operate the ESP similar to recent Syncrude tests and *Advanced Hybrid*™ filter tests. **Do not ever open the ESP sight ports or vessel with the high voltage on unless instructed to do so by project engineers for shakedown or troubleshooting.** When making changes inside the ESP, turn off the main power supply and shut off the circuit breaker. Make sure all operators know the procedure for turning off ESP power.

INTRODUCTION

The project will focus on the testing of effective sorbents, hardware configurations, and operation for mercury control from electric power plants firing lignite coals. Extensive sampling activities are planned during the day shift, which may carry over into some evenings. Overnight, the PTC system will be kept hot firing coal unless natural gas firing is specified for that given night. The schedule calls for 4 weeks of PTC testing with a fifth week earmarked on the schedule for contingency if necessary.

Four hardware configurations will be evaluated. These include ESP-only tests, baghouse-only tests, tests with the ESP followed by the baghouse (sorbent injection following the ESP), and some *Advanced Hybrid*™ filter tests.

Sorbent injection will occur in the flue gas pipe prior to the selected control devices. The sorbent injection will be performed using a feeder and transport air. When sorbent is not injected, the airflow to the feeder should be kept on. For the ESP/baghouse combination, sorbent injection will be at the ESP exit upstream of the baghouse (same as for the baghouse-only tests).

PRERUN CONSIDERATIONS

1. **Set up for the hardware configurations listed above.** Clean inlet and outlet piping, and then reinstall.

2. **Clean ESP and baghouse.**

3. Check the orifice plate and annubars to be sure they are clean and installed correctly. Blow-back pressure lines.

4. Check to be sure swirl burner is working properly.

5. Check ESP to be sure it is working properly, including rappers, heaters, measurements, and electrical controls. Check baghouse to be sure it is working properly, including measurements, cleaning system, and controls. Install new set of GORE-TEX bags. For second hardware configuration (ESP/baghouse combination), set up the baghouse so that only two bags are in service.

6. Check electrical heaters to be sure that they are all working. The pipe heaters on the ESP inlet and outlet are to be set at least 10°F above the ESP operating temperature. Check operation of the baghouse heaters and all pipe heaters.

7. Check all instrumentation and recorders to be sure they are in working order.

8. Check all gas cylinders to be sure the needed calibration gases and regulators are available.

9. Check all sample conditioners to be sure they are hooked up and working properly.

10. The ESP and baghouse temperatures will include operation at **300° to 400°F** during this test series. Use your judgment concerning the heat exchange surface that may be needed.

11. Be sure to keep an accurate and comprehensive logbook. Note <u>everything</u> that occurs during each test period.

12. During this test series the PTC flue gas analyzers will monitor the exit of the PTC combustor and the CTF analyzers will monitor the exit of the ESP, baghouse, or *Advanced Hybrid*™ filter. Make sure we are logging data from the CTF analyzers.

RUN PARAMETERS

- Coal
- Sorbent type—activated carbon, lignite-derived carbons, etc.
- Sorbent concentration—2000 to 20,000 sorbent-to-Hg ratio
- Particulate control device temperature—300° to 400°F
- Hardware configuration—ESP, baghouse, baghouse following the ESP, or *Advanced Hybrid*™ filter.
- Sorbent preparation method
- Particle size—As received and grinded, size TBD
- Residence time or mixing—entrained flow-reaction tests

Combustor:
First Transition Temperature: 1700°–1800°F (not critical parameter)
O_2 (Sample Point 1): 4.5 ± 0.5%
Furnace Static: −1.0 in. W.C.
Primary Air: 10–15 W.C.
Secondary Air: 15–20 in. W.C.

Total Air: 12 in. W.C.
Flue Gas Flow Rate: **132 scfm, acfm flow rate will vary depending on the particulate control device temperature.**

ESP:
Inlet Temperature: Chamber temperature plus 10°F
Chamber Temperature: Planned tests will be conducted at either 300° or 400°F ± 10°F
Rapping Cycle: ESP rapping will occur off-line between sampling periods.
Rapping Duration: To be determined (1 to 30 sec)
Electrode: Single rigid mast (square tubing) with discharge spikes
Electrode Tip to Plate Distance: Nominally 4.5 in.
Current: 4.0 mA at start and 40 to 50 kV

Baghouse:
Inlet Temperature: Chamber temperature plus 10°F
Chamber Temperature: Planned tests will be conducted at either 300° or 400°F ± 10°F
Cleaning Cycle: Bag pulsing will occur every 1 to 2 hours
Baghouse Delta P: 4 to 8
Bags in Service: 3-Baghouse only, 2-ESP/Baghouse
Sampling: 1 solids sample/test

REQUIRED READINGS

Data Sheet 1: Bag weights before and after testing

ESP Data Sheet: Every ½ hour as well as before and after every rapping cycle.

Baghouse Data: Every hour as well as before and after every cleaning cycle.

Data Sheet 3: System pressures: once an hour

Coal Record: Enter data when coal is added to the hopper. Also enter the time coal feed begins and when it ends. If at any time during the run the coal feed is shut off, this should also be noted on the data sheet, as well as in the logbook. At the end of each test, the remaining coal should be weighed and recorded.

Sorbent Data: Feeder RPM and Air Pressure Regulator Settings: At start and upon changes. Enter data when sorbent is added to the hopper. Also, enter the time sorbent feed begins and when it ends. If at any time during a test, the feed is shut off, this should also be noted on the data sheet, as well as in the logbook. At the end of each day of testing or before changing sorbent flow rate, the feeder should be weighed, refilled, and weighed again (record all weights).

Data Sheet 5: Flue Gas Analysis: once an hour

Data Sheet 6: Cooling Water: twice a shift (every 4 hours)

Data Sheet 7:	Inst. Calibration:	Calibration should be done before and after each test (or more often if necessary) and recorded.
Data Sheet 9:	Gas Flow Rate: (Orifice)	once every 2 hours
Data Sheet 13:	Gas Flow Rate: (Annubar)	once an hour
Data Sheet 16:	When coal and sorbent weights are determined, fill out data sheet.	

POSTRUN CONSIDERATIONS

1. Take all appropriate samples, as shown in sampling schedule, and be sure all samples are labeled properly.
2. Note total times of coal feed and weigh-back, and of natural gas firing in the log.
3. Carefully recover and weigh the ash collected from the particulate control devices and note in the log.
4. Begin cleanup activities. The ESP and hopper are to be thoroughly cleaned, washed clean with water if necessary. Both the inlet and outlet pipes will be inspected and may be cleaned.
5. After pipes and ESP have been cleaned and put back together, verify that all electrical heating elements are working properly.
6. Carefully remove the bags from the baghouse, and record the weights on Data Sheet 1.
7. Perform baghouse cleanup activities.
8. After pipes and baghouse have been cleaned and put back together install the preweighed bags.

Notes concerning probable schedule:

Graveyard Shift: Complete PTC heatup firing natural gas.
Day Shift: Complete tests for that day.
Swing Shift: Maintain PTC temperatures firing coal unless advised to switch to natural gas. Add ice to CMM systems as required. Fill sorbent hopper if required for that evening.

General Sampling Plan:
Note: All samples will be submitted for analysis on the day they are collected or as otherwise instructed by the project engineer. Samples not submitted for immediate analysis will be stored appropriately in the PTC Lab. When samples are taken they will be dated and initialed on attached Sample Analysis Tracking Sheet (under sampled column). These sheets will follow the samples for each test. The analyses requested for the different samples may be different for each test and in some cases will depend on the results of previous tests.

Coal Samples
Take a 1-gallon composite sample per day during the run and place it in the sample area in the PTC lab designated for samples. Also, take at least one Method 26a measurement a week, and a Hg and chlorine reading from the coal at least once a day.

ESP and Baghouse Ash
Weigh all ash recovered from the ESP and baghouse hoppers. One hopper ash sample will be taken after each test following cleaning and/or off-line rapping cycles for each device in service for that run. These ash samples are to be placed in area designated in the PTC lab.

Bottom Ash
One-quart sample a week

Heat Exchanger Ash
One-quart sample a week

Two mercury CMMs will be used
Particulate control system inlet (before sorbent injection)
Particulate control system outlet

Ontario Hydro
One pair of simultaneous inlet (upstream of sorbent injection) and outlet samples for the first test each day. One additional Ontario Hydro measurement at the outlet for each test beyond the first of that day.
Analyze OH samples and filter catches for mass balance information.

Analytical Plan:

Coal, sorbent, and ash sample analyses to be determined

TEST AND OPERATIONS SCHEDULE

Test Period Week 1, June 17–21												
Test No.	T1Base	T2	T3	T4**	T5	T6	T8	T9	T10	T11	T12	T5b
Date	6/17/02	6/18/02		6/19/02				6/20/02			6/21/02	
Coal	C1	C1	C1	C1	C1	C1	C1	C1	C1	C1	C1	C1
Hardware	ESP	ESP	ESP	ESP	ESP	ESP	ESP	ESP	ESP	ESP	ESP	ESP
Temp., °F	300	300	300	300	300	300	300	400	400	400	300	300
Sorbent	None	S2	S2	None	S1	S1	S1	S1	None	S1	Pre-Chlor	S1
Sorbent Size	N.A.	A.R.	A.R.	N.A.	A.R.	A.R.	Fine	A.R.	N.A.	Fine	A.R.	A.R.
Sorbent: Hg Ratio	0	5000*	10000*	0	T2 Ratio	T3 Ratio	T2 Ratio	T3 Ratio	0	T2 Ratio	T2 Ratio	T2 Ratio
Sorbent Inject. grams/hr	0	75	150	0	T2 Rate	T3 Rate	T2 Rate	T3 Rate	0	T2 Rate	T2 Rate	T2 Rate
Flue Gas Flow Rate	132 scfm											
FG O_2 Conc. (vol%, dry)	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
Sampling												
Ontario Hydro	Minimum of one a day at the inlet and minimum of one a test at the outlet except for those that are **.											
CMM	Continuous inlet and outlet during day, outlet only at night.											
Solids	One set of coal, sorbent, and ash samples for each test.											

C1 = Luscar Coal, from Poplar.
C2 = North Dakota Lignite, Freedom Mine.
S1 = Luscar char, steam-activated.
S2 = NORIT FGD, lignite-based activated carbon.
A.R. = As Received.

* *Actual sorbent flow rates to be determined based on percent removals from CMM data for Tests T2, T3, and T7. T2 flow = 50%, T3 flow = 70%, and T7 = 90% removal or 30,000:1 ratio whichever comes first (same applies to Tests T14 and T15 at removal targets of 70% and 90%, respectively).*

** *Between runs, conditions will be returned to baseline based on CMM mercury measurements only.*

Test Period Week 2, June 24–28										
Test No.	T13	T14	T16	T17	T18	T19	T20	T21	T22	T23
Coal	C1	C1	C1	C1	C1	C1	C1	C1	C1	C1
Hardware	ESP/FF	ESP/FF	ESP/FF	ESP/FF	ESP/FF	ESP/FF	ESP/FF	ESP/FF	ESP/FF	ESP/FF
Temp., °F	300	300	300	300	300	400	400	400	400	400
Sorbent	None	S1	S1	None	S2	None	S1	S1	S2	S2
Sorbent Size	N.A.	A.R.	Fine	N.A.	A.R.	N.A.	Fine	A.R.	Fine	A.R.
Sorbent: Hg Ratio	0	2000*	40	0	60 Ratio	0	T16 Ratio	T18 Ratio	T14 Ratio	T15 Ratio
Sorbent Inject. grams/hr	0	25	40	0	60	0	T16 Rate	T18 Rate	T14 Rate	T15 Rate
Flue Gas Flow Rate	132 scfm									
FG O_2 Conc. (vol%, dry)	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
Sampling										
Ontario Hydro	In, ESP_{out}, FF_{out}	In, FF_{out}	In, FF_{out}	In, FF_{out}	FF_{out}	In, FF_{out}	In, FF_{out}	In, FF_{out}	Only cmm	In, FF_{out}
CMM	Continuous inlet and outlet during day, outlet only at night.									

C1 = Luscar Coal, from Poplar.
C2 = North Dakota Lignite, Freedom Mine.
S1 = Luscar char, steam-activated.
S2 = NORIT FGD, lignite-based activated carbon.
A.R. = As-received.

* *Actual sorbent flow rates to be determined based on percent removals from CMM data for Tests T2 through T4. T2 flow = 50%, T3 flow = 70%, and T4 = 90% removal or 30,000:1 ratio whichever comes first (same applies to Tests T14 and T15 at removal targets of 70% and 90%, respectively).*

** *Between runs, conditions will be returned to baseline based on CMM mercury measurements only.*

Test Period Week 3, July 8–12										
Test No.	T24	T25	T26	T27	T28	T29	T30	T31	T32	T35
Date	7/8/02		7/9/02		7/10/02			7/11/02		7/12/02
Coal	C1	C1	C1	C1	C1	C1	C1	C1	C1	C1
Hardware	ESP/FF	ESP/FF	ESP/ FF Ryton	ESP/FF Ryton	ESP	ESP	ESP	*Advanced Hybrid*™ Filter	*Advanced Hybrid*™ Filter	FF
Temp., °F	300	300[1]	300	300[1]	300	300	300	300	300	300
Sorbent	None	S1	None	S1	None	S1	S1	None	S1	S1
Sorbent Size	N.A.	A.R.	N.A.	A.R.	N.A.	A.R.	Fine	N.A.	A.R.	A.R.
Sorbent: Hg Ratio	0	Varied	0	T25 Ratios	0	T3 Ratio	T2 Ratio	0	T25 Ratio	T25/ Variable
Sorbent Inject. grams/hr	0	10–40	0	10–40	0	50–150, 300	25–115	0	20–120	10–60
Flue Gas Flow Rate	132 scfm									
FG O_2 Conc. (vol%, dry)	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
Sampling										
Ontario Hydro.	In/Out	Out	None	Out	In/Out	Out	Out	In/Out	Out	Out
CMM	Continuous inlet and outlet during day, outlet only at night.									

C1 = Luscar Coal, from Poplar.
C2 = North Dakota Lignite, Freedom Mine.
S1 = Luscar char, steam-activated.
S2 = NORIT FGD, lignite-based activated carbon.
A.R.= As-received.
[1] At the completion of testing, increase temperature gradually to 400°F (over a period of about 2 hr), and monitor the CMMs.

Test Period Week 4, July 15–19										
Test No.	T36	T37	T38	T39	T40	T41	T42	T43	T44	T45
Date	7/15/02		7/16/02		7/17/02			7/18/02		
Coal	C2	C2	C2	C2	C2	C2	C2	C2	C2	Various *Advanced Hybrid*™ Filter Tests
Hardware	ESP/FF	ESP/FF	ESP/FF	ESP/FF	ESP	ESP	ESP	*Advanced Hybrid*™ Filter	*Advanced Hybrid*™ Filter	
Temp., °F	300	300	300	300	300	300	300	300	300	
Sorbent	None	S_1	None	S_2	S_1	S_1	S_1	None	S1	
Sorbent Size	N.A.	A.R.	N.A.	A.R.	None	Fine	A.R.	N.A.	A.R.	
Sorbent: Hg Ratio	0	TBD	0	T37 Ratio	0	TBD	TBD	0	T37 Ratio	
Sorbent Inject. grams/hr	0	10–40	0	10–40	0	25–115	50–150	0	10–40	
Flue Gas Flow Rate	132 scfm									
FG O_2 Conc. (vol%, dry)	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
Sampling										
Ontario Hydro	In/Out	Out	In/Out	Out	In/Out	Out	Out	In/Out	Out	Out
CMM	Continuous inlet and outlet during day, outlet only at night.									

C1 = Luscar Coal, from Poplar.
C2 = North Dakota Lignite, Freedom Mine.
S1 = Luscar char, steam-activated.
S2 = NORIT FGD, lignite-based activated carbon.
A.R. = As-received.

Test Period Week 5, August 12–15								
Test No.	T49	T50	T51a	T51b	T52	T53	T54	T55
Date	8/13/02		8/14/02		8/15/02			
Coal	C1	C1	C1	C1	C1	C1	C1	C1
Hardware	ESP/FF 1 bags	ESP/FF 1 bags	ESP/FF 2 bags	ESP/FF 2 bags	ESP/FF 2 bags	ESP/FF 2 bags	ESP/FF 2 bags	ESP/FF 2 bags
Temp., °F	300	300	300	300	300	300	300	300
Sorbent	None	S_2	S_2	S_2	S_2	S_2	Recycled BH Ash	IAC
Sorbent Size	N.A.	A.R.	A.R.	A.R.	A.R.	A.R.	A.R.	A.R.
Sorbent: Hg Ratio	0	TBD	T50 Ratio	T50 Ratio	TBD	T52 Ratio		T52 Ratio
Sorbent Inject., grams/hr	0	~40g/hr	20g/hr	20g/hr + salt or HCl	~40g/hr	10–20 + HCl	200–~800	20–40
Flue Gas Flow Rate	132 scfm							
FG O_2 Conc. (vol%, dry)	4%	4%	4%	4%	4%	4%	4%	4%
Sampling								
Ontario Hydro	In/Out	Out	In/Out	In/Out	None	None	None	None
CMM	Continuous inlet and outlet during day, and outlet only at night.							

C1 = Luscar Coal, from Poplar.
S2 = Norit FGD, steam-activated.
A.R. = As-received.

Notes:

- Tests 51 a and b are the same conditions, just over a longer duration.
- Bags should be pulsed at the same ΔP for all tests (8 inches of water).
- During Test 51, an isokinetic sample will be pulled through a heated filter while mercury is measured at the outlet of the filter at temperatures of 200°, 250°, and 300°F.

The research engineer will determine when to begin sorbent injection. The ESP hopper valve should remain normally closed. The ESP hopper valve should be opened only when dumping ash. Always run flue gas analyzers (CO_2, CO, NO_x, SO_2, O_2).

APPENDIX C

MERCURY MASS BALANCES FOR POPLAR RIVER COAL COMBUSTION TESTS

Combustor, ESP, Baghouse, AHPC, and System Mass Balances for PTC

Total Hg µg/dNm³ @3% O_2	Coal + Sorbent	ESP Inlet Impingers	ESP Hopper Ash	ESP Outlet Impingers	BH Inlet Impingers	BH Hopper Ash	BH Outlet Impingers	Combined Out	ESP/BH Balance	System Balance	Combustor Balance (impinger)
Poplar River	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**(C+D)**	**(I/B)**	**(I/A)**	**(B/A)**
ESP Only											
T3	25 0	13 896	9 2	2 820	NA	NA	NA	12 0	86 67%	48 18%	55 59%
T4	25 0	17 215	4 7	13 554	NA	NA	NA	18 3	106 20%	73 13%	68 86%
T5B	25 0	22 201	6 9	10 332	NA	NA	NA	17 2	77 44%	68 77%	88 80%
T6	25 0	22 759	11 1	6 556	NA	NA	NA	17 7	77 60%	70 65%	91 03%
T8	25 0	18 512	9 8	5 084	NA	NA	NA	14 9	80 34%	59 49%	74 05%
T10	25 0	22 328	6 5	21 003	NA	NA	NA	27 5	122 99%	109 84%	89 31%
T29	25 0	20 2	4 5	8 7	NA	NA	NA	13 2	65 44%	52 99%	80 97%
ESP/FF, TOXECON™	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**(C+F+G)**	**(I/B)**	**(I/A)**	**(B/A)**
T17	26 2	20 372	1 59	NA	NA	2 05	16 880	20 5	100 75%	78 22%	77 64%
T18	26 00	20 372	1 58	NA	NA	14 75	1 884	18 2	89 39%	70 04%	78 35%
T19	26 0	21 350	0 2	NA	NA	0 6	23 289	24 2	113 14%	92 90%	82 12%
T21	25 5	22 488	0 3	NA	NA	7 4	2 965	10 6	47 10%	41 54%	88 19%
T24	26 3	20 399	0 4	NA	NA	2 5	19 0	22 0	107 63%	83 49%	77 56%
T25	26 3	20 399	0 2	NA	NA	16 4	2 31	18 9	92 50%	71 75%	77 56%
T27	26 3	20 399	0 4	NA	NA	14 3	2 8	17 6	86 24%	66 89%	77 56%
Baghouse Only	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**(G+H)**	**(I/F)**	**(I/A)**	**(E/A)**
T35	23 0	NA	NA	NA	20 8	13 4	8 7	22 1	106 43%	96 03%	90 23%

APPENDIX D

MERCURY MASS BALANCES FOR FREEDOM COAL COMBUSTION TESTS

Combustor, ESP, Baghouse, AHPC, and System Mass Balances for PTC

Total Hg µg/dNm³ @3% O_2	Coal + Sorbent	ESP Inlet Impingers	ESP Hopper Ash	ESP Outlet Impingers	BH Inlet Impingers	BH Hopper Ash	BH Outlet Impingers	Combined Out	ESP/BH Balance	System Balance	Combustor Balance (impinger)
Freedom											
ESP/FF, TOXECON™	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**(C+F+G)**	**(I/B)**	**(I/A)**	**(B/A)**
T37	9 7	9 0	0 2	NA	NA	5 4	1 5	7 1	79 22%	73 12%	92 31%
T39	10 9	8 6	0 2	NA	NA	7 9	0 6	8 8	101 63%	80 37%	79 08%
ESP Only	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**(C+D)**	**(I/B)**	**(I/A)**	**(B/A)**
T40	10 1	6 8	0 1	7 9	NA	NA	NA	8 0	117 23%	79 45%	67 78%
T41	9 7	6 8	1 2	4 4	NA	NA	NA	5 6	82 09%	57 68%	70 26%
ADVANCED HYBRID™ Filter		**ADVANCED HYBRID™ Filter In**	**ADVANCED HYBRID™ Filter Hopper**	**ADVANCED HYBRID™ Filter Out**				**(C+D)**	**(I/B)**	**(I/A)**	**(B/A)**
T43	9 7	9 9	0 3	10 2	NA	NA	NA	10 5	105 55%	107 47%	101 82%
T44	9 7	9 9	5 4	2 1	NA	NA	NA	7 5	75 81%	77 19%	101 82%

APPENDIX E

CEM MEASURMENT RESULTS FOR PILOT-SCALE COMBUSTION TESTS OF ESP MERCURY CAPTURE

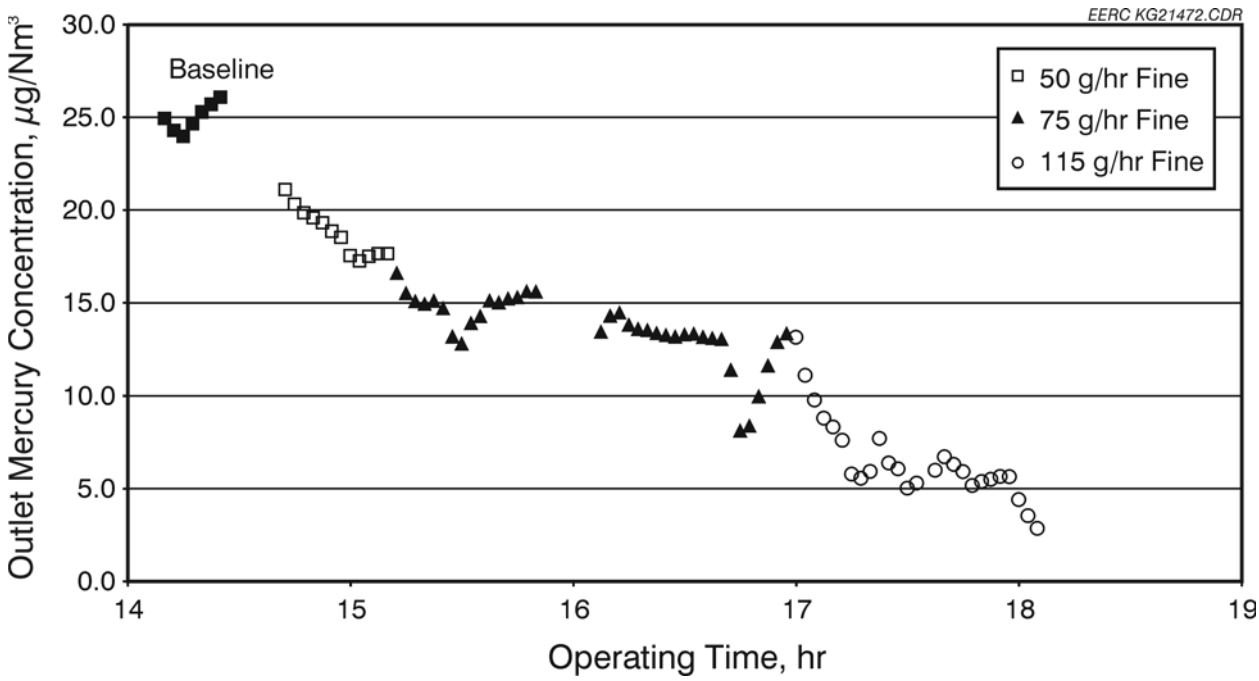

Figure E1. Temporal variations in total gaseous mercury concentrations at the 300°F ESP outlet during injections of fine-grained activated Luscar char into the Poplar River coal combustion flue gas.

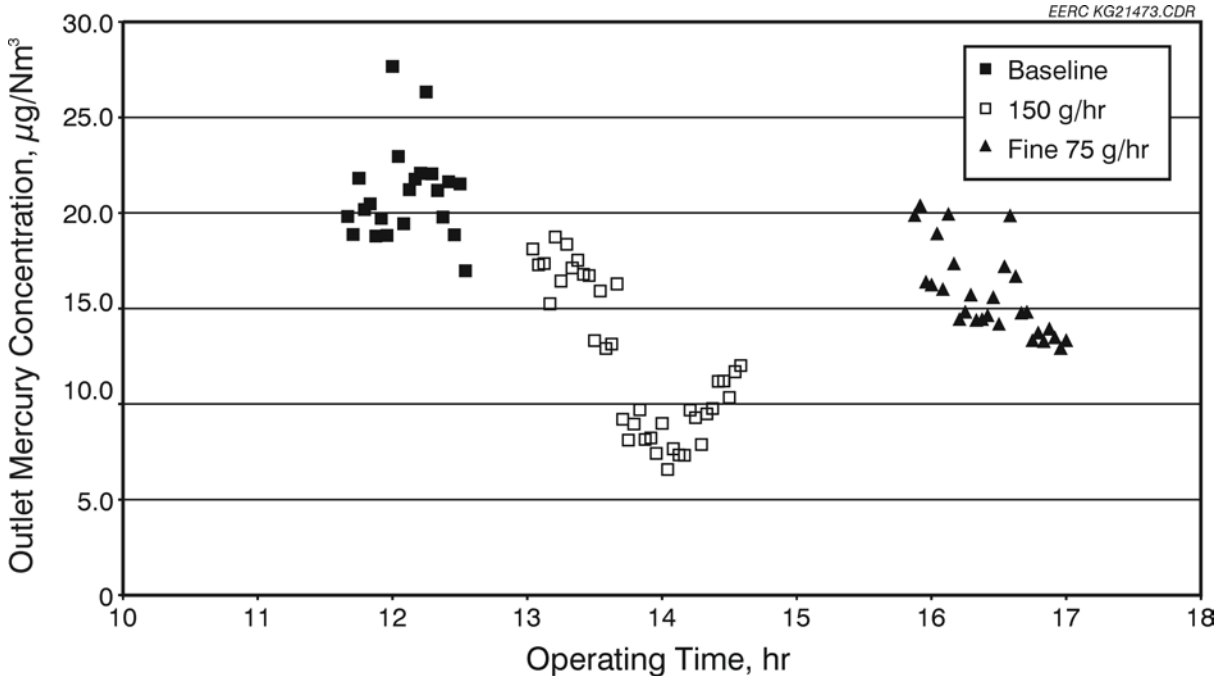

Figure E2. Temporal variations in total gaseous mercury concentrations at the 400°F ESP outlet during injections of activated Luscar char into the Poplar River coal combustion flue gas.

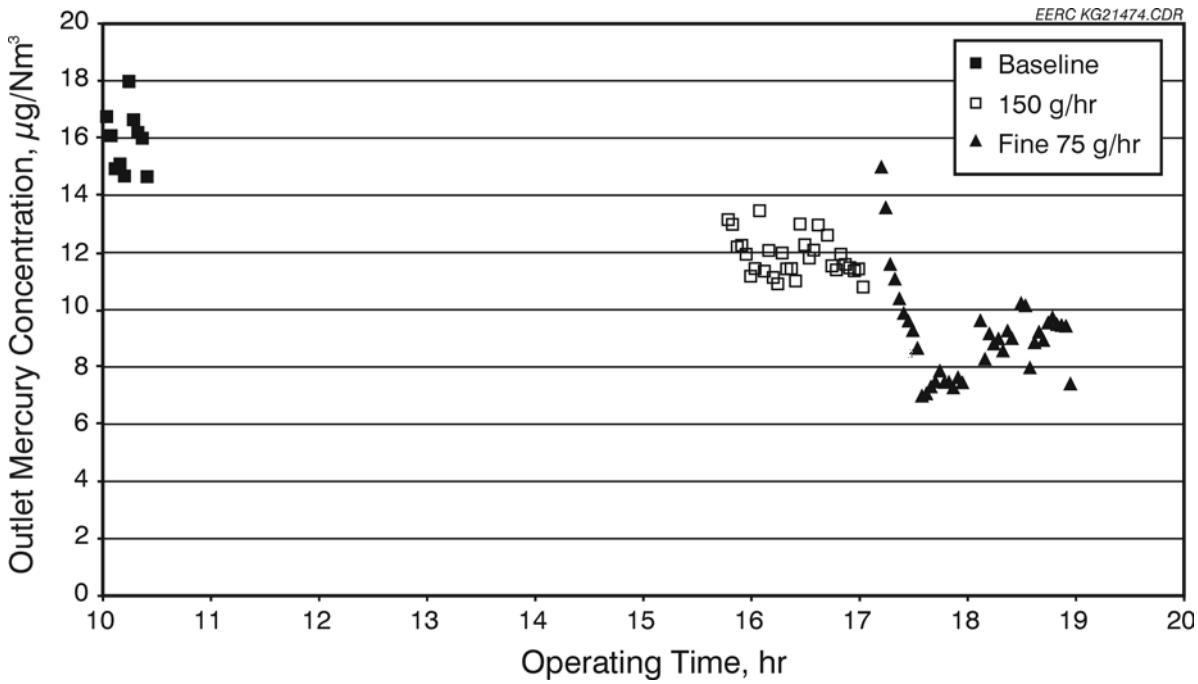

Figure E3. Temporal variations in total gaseous mercury concentrations at the 300°F ESP outlet during injections of DARCO FGD into the Poplar River coal combustion flue gas.

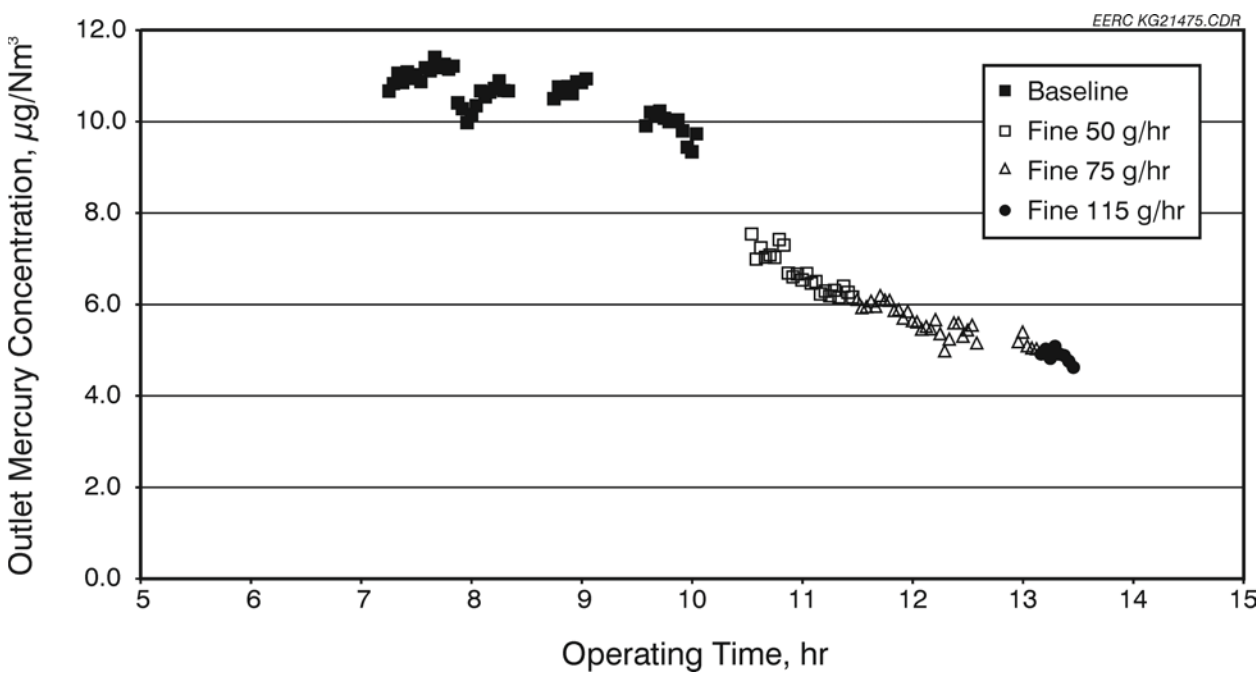

Figure E4. Temporal variations in total gaseous mercury concentrations at the 300°F ESP outlet during injections of fine-grained activated Luscar char into the Freedom coal combustion flue gas.

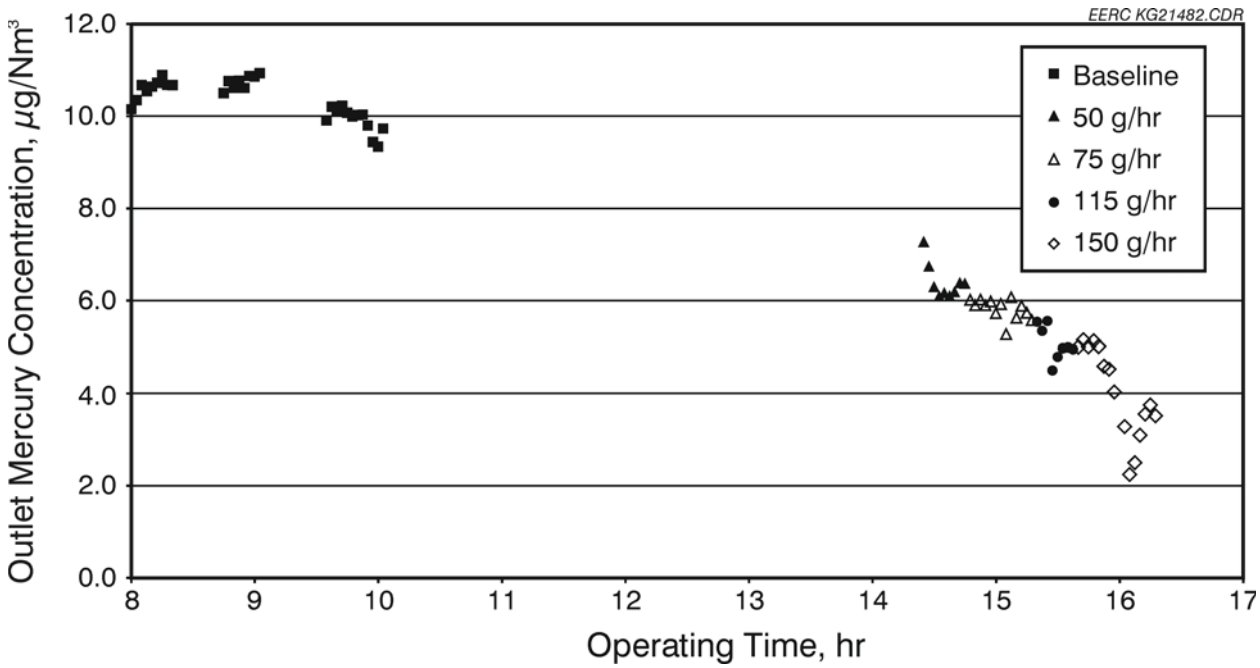

Figure E5. Temporal variations in total gaseous mercury concentrations at the 300°F ESP outlet during injections of activated Luscar char into the Freedom coal combustion flue gas.

APPENDIX F

RESULTS FOR PILOT-SCALE TESTS OF TOXECON™

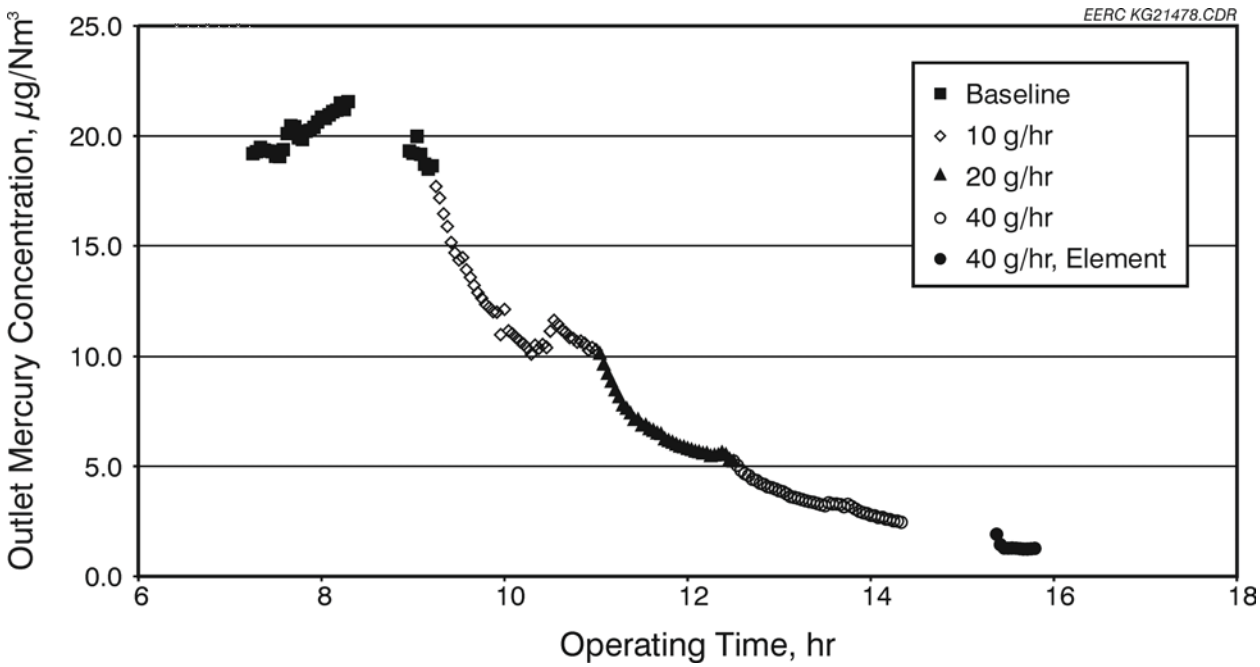

Figure F1. Temporal variations in total gaseous mercury concentrations at the 300°F TOXECON™ system outlet during injections of activated Luscar char into the Poplar River coal combustion flue gas.

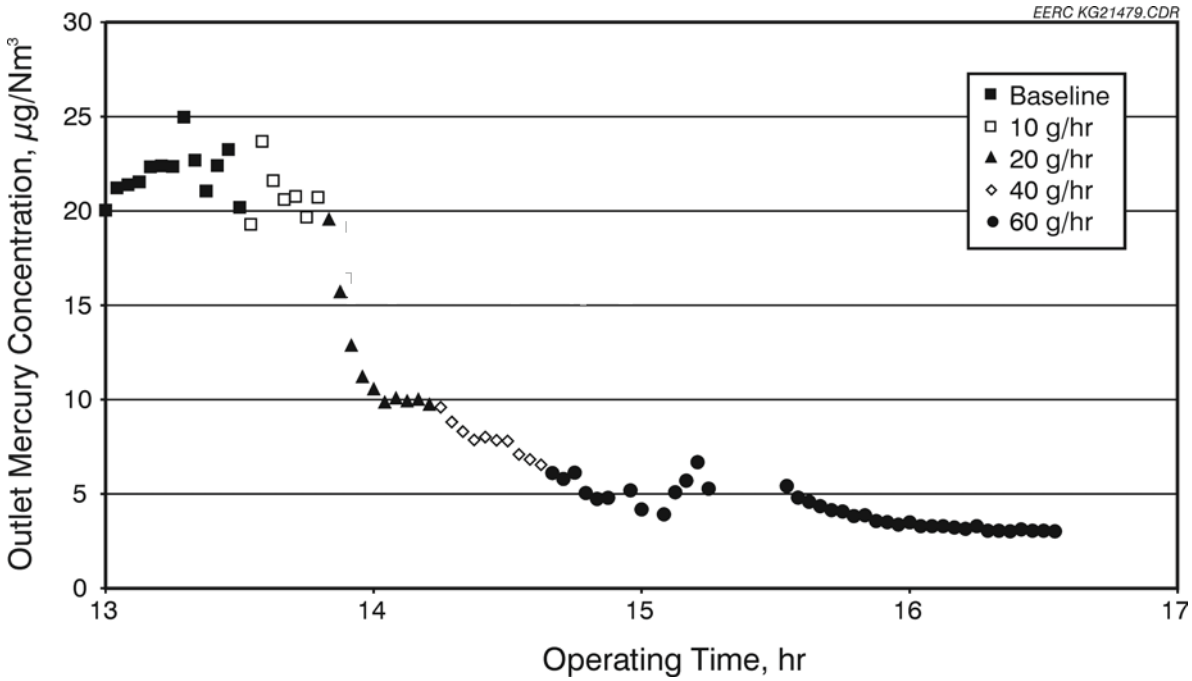

Figure F2. Temporal variations in total gaseous mercury concentrations at the 400°F TOXECON™ system outlet during injections of activated Luscar char into the Poplar River coal combustion flue gas.

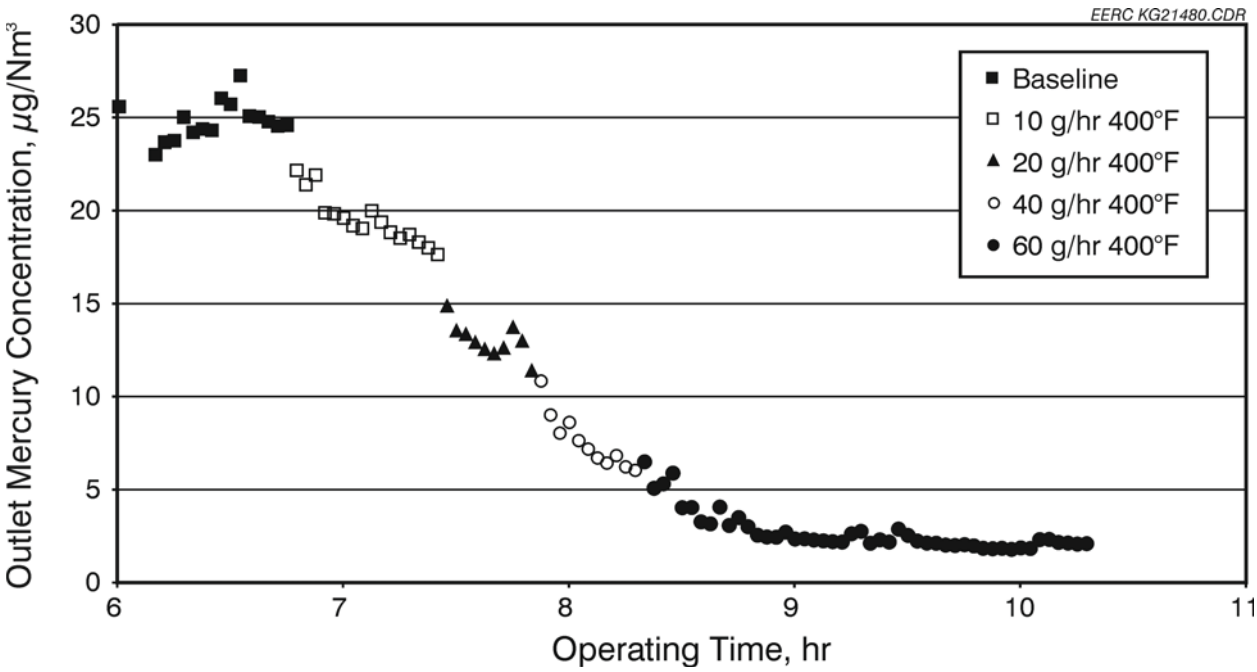

Figure F3. Temporal variations in total gaseous mercury concentrations at the 400°F TOXECON™ system outlet during injections of DARCO FGD into the Poplar River coal combustion flue gas.

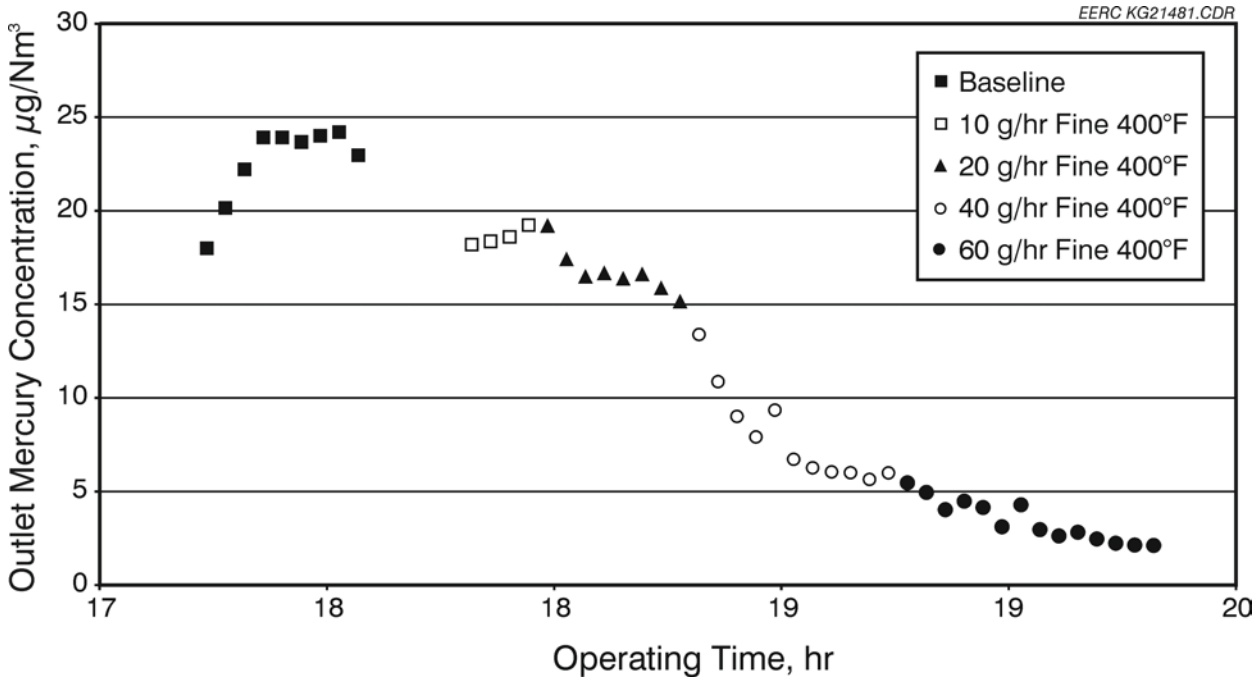

Figure F4. Temporal variations in total gaseous mercury concentrations at the 400°F TOXECON™ system outlet during injections of fine-grained DARCO FGD into the Poplar River coal combustion flue gas.

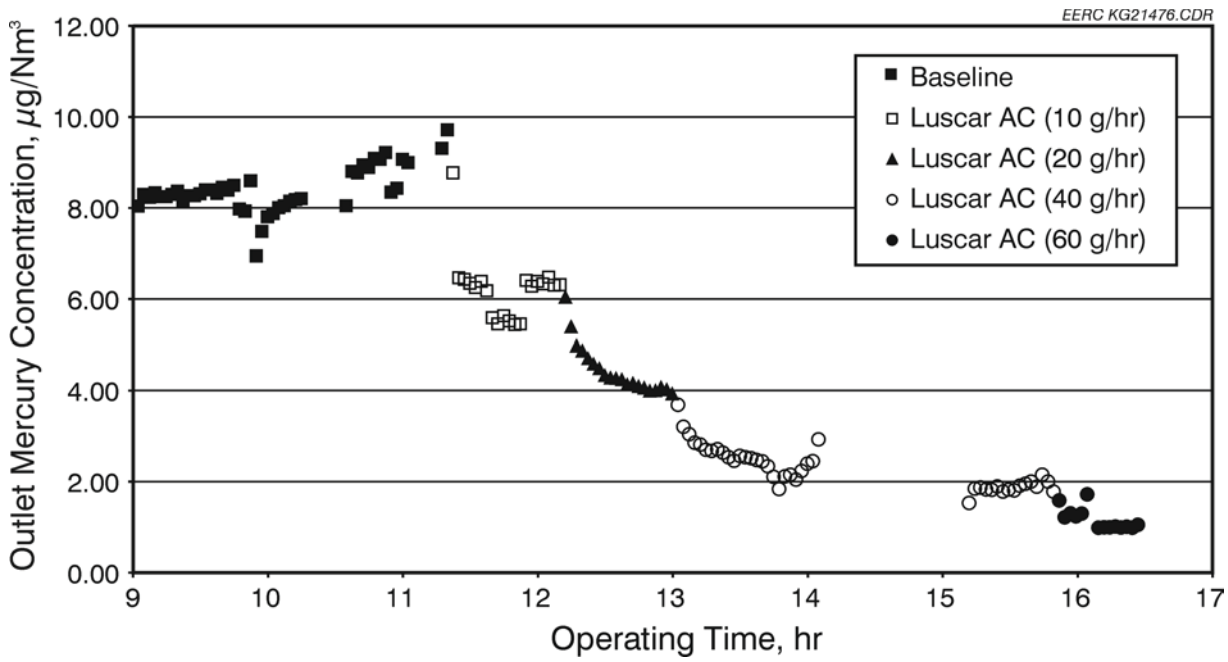

Figure F5. Temporal variations in total gaseous mercury concentrations at the 300°F TOXECON™ system outlet during injections of activated Luscar char into the Freedom coal combustion flue gas.

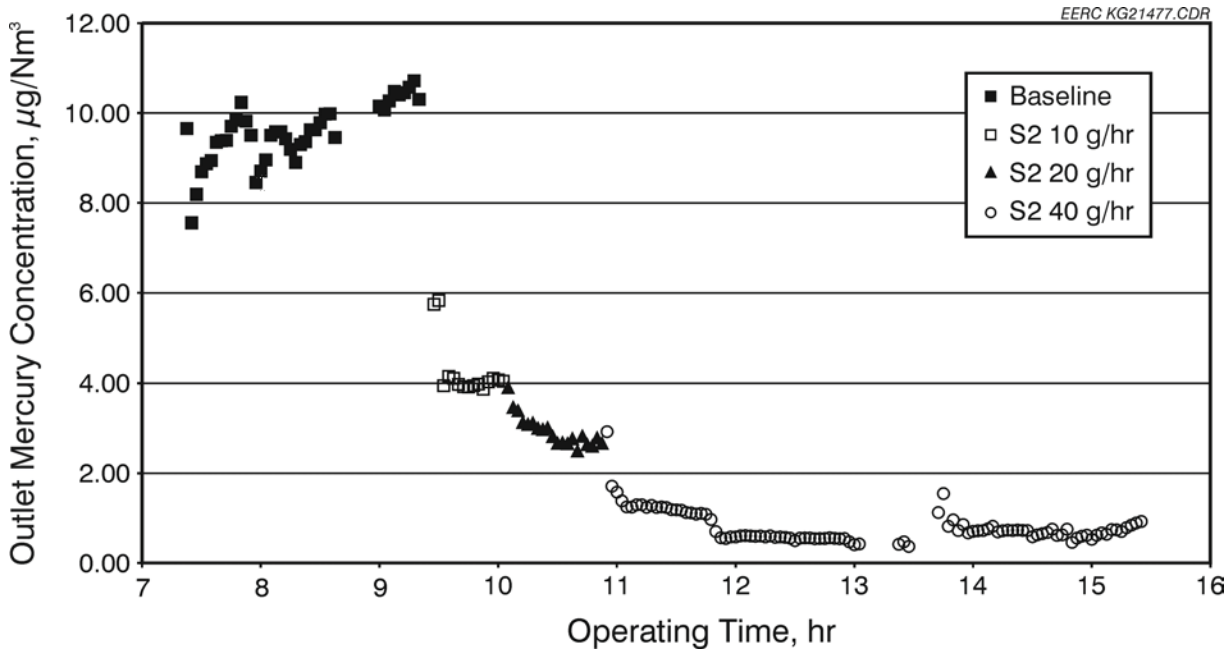

Figure F6. Temporal variations in total gaseous mercury concentrations at the 300°F TOXECON™ system outlet during injections of DARCO FGD into the Freedom coal combustion flue gas.

APPENDIX G

QUALITY ASSURANCE/QUALITY CONTROL FOR PILOT-SCALE TESTS

QUALITY ASSURANCE/QUALITY CONTROL

This appendix provides detailed quality assurance/quality control (QA/QC) procedures that were used for the sampling activities. The most important QA/QC parameter for any sampling activity is the people who perform the work. All who participated in the sampling activities for this project had extensive training and experience in the proper procedures.

Mercury CEM Data

To provide a high level of QA/QC for this project, all personnel associated with the operation of mercury CEMs have been trained and all lead operators have at least one year of experience operating mercury CEMs in the field.

The mercury CEMs used for these tests were Tekran model 2537A instruments. These were used in conjunction with PS Analytical (PSA) conversion systems. The instruments are briefly described below.

The Tekran analyzers are fluorescence-based instruments. The Tekran analyzer was initially used to primarily monitor ambient mercury. As was the case for this project, these instruments can be used in a variety of gaseous media including combustion flue gas. These analyzers are based on the principle of atomic fluorescence (AF), which provides an inherently more sensitive signal than AA. The systems use a gold trap for preconcentrating the mercury and separating it from potential interferences that degrade sensitivity.

These instruments require a four-step process to obtain a flue gas mercury measurement. In the first step, conditioned flue gas is pumped through a gold trap, which is maintained at a constant temperature. Before the mercury is desorbed from the gold trap, a flushing step is initiated to remove any flue gas that may be present, because it has a damping effect on the mercury fluorescence. When this is completed, the analysis step begins. The heating coil is activated, and the gold trap is heated to desorb the mercury from the trap. The mercury is carried into the fluorescence detector in an inert gas stream of argon or nitrogen depending on the mercury concentration. The gold trap is then cooled in preparation for the next sample. The time for the entire process is about 2½ min.

Instrument Set-Up and Calibration

The systems are calibrated using Hg^0 as the primary standard. The Hg^0 is contained in a closed vial, which is held in a thermostatic bath. The temperature of the mercury is monitored, and the amount of mercury is measured using vapor pressure calculations. Typically, the calibration of these units has proven to be stable over a 24-hr period. All acids used for the operation of mercury CEMs were analytical reagent-grade.

As previously stated, some form of gas pretreatment is necessary before accurate measurement of total mercury (or speciated mercury) can be obtained. A pretreatment/conversion system is also needed to remove gaseous contaminants (HCl, SO_3, etc.) from flue gas prior to the gold trap,

thus preventing the trap from becoming poisoned permanently. Additionally, both Hg^{2+} and Hg^0 collect on the trap; if the instrument is to be used to provide mercury speciation data, then the Hg^{2+} must be removed from the gas stream so that the Hg^0 concentration can be measured. To do this, a basic $SnCl_2$ trap (PSA system) is used.

Calculated Efficiencies

For the purposes of this project the mercury CEM data has been corrected to 3% O_2, so that inlet to outlet comparisons, as well as comparisons to Ontario Hydro data, can be accurately made.

The mercury CEM data was averaged for the duration of the test condition, excluding transition periods when the combustor was obviously responding to a change in test conditions. The averaging was done using a time integral average. The inlet mercury CEM data was normalized to match the outlet baseline data for each test run. By doing this, the effect of carbon injection could be calculated by difference for each injection rate. The inherent mercury capture (without carbon injection) was calculated for each coal by averaging the data during the baseline period for all runs using that coal and comparing the inlet and outlet data. For this pilot-scale data, the inherent mercury capture was less than 1% for both coals.

The efficiencies for each test condition (specified coal and sorbent as well as injection rate) were calculated as a percent.

OH Method

To provide a high level of QA/QC for this project, all liquid samples (from the Ontario Hydro [OH] mercury speciation train impingers), including those used as blanks and spikes, were analyzed by the Energy & Environmental Research Center (EERC). The following are specific QC procedures for the OH sampling.

Instrument Set-Up and Calibration

A Cetac M6000A CVAA was used in the field for mercury determination. The instrument was set up for absorption at 253.7 nm with a carrier gas of nitrogen and 10% $SnCl_2$ in 10% HCl as the reductant. Each day, the drying tube and acetate trap were replaced, and the tubing was checked. The rinse container was then cleaned and filled with a fresh solution of 10% HCl. After the pump and lamp were turned on and warmed up for 45 min, the aperture was set to the manufacturer specifications. A four-point calibration curve was then completed using matrix-matched standards. The detector response for a given standard was logged and compared to specifications to ensure the instrument had been properly set up. A QC standard of a known analyte concentration was analyzed immediately after the instrument was standardized in order to verify the calibration. This QC standard was prepared from a different stock than the calibration standards. Requirements stated that the values obtained must read within 5% of the true value before the instrument was used. After the initial QC standardization was completed, standards were run every ten samples to check the slope of the calibration curve. One in every

ten samples was run in triplicate and was spiked to verify analyte recovery. A QC chart was also maintained by the EERC chemist to monitor the long-term precision of the instrument.

Presampling Preparation

All data sheets, volumetric flasks, and petri dishes used for sample recovery were marked with preprinted labels. The liquid samples were recovered into premarked volumetric flasks, logged, and then analyzed on-site. The filter samples were placed in premarked containers and then sent to the lab, where they were analyzed using mixed-acid digestion techniques. The labels contained identifying data, including date, time, run number, and sample port location, which correlate back to the data sheets.

Glassware and Plasticware Cleaning and Storage

All glass volumetric flasks and transfer pipettes used in the preparation of analytical reagents and calibration standards were designated as "Class A" to meet American Society for Testing and Materials specifications. Prior to being used for the sampling, all glassware was washed with hot soapy water, then rinsed with deionized water three times, then soaked in 10% $^{V}/_{V}$ nitric acid for a minimum of 4 hr, then rinsed an additional three times with deionized water, and dried. The glassware was stored in closed containers until it was used at the plant.

Analytical Reagents

All acids used for the analysis of mercury were trace metal-grade. Other chemicals used in the preparation of analytical reagents were analytical reagent-grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification were purchased commercially and certified to be accurate within ±0.5% and traceable to National Institute of Standards and Technology Standard Reference Materials.

Blanks and Spikes

As part of the QA/QC, a field blank was associated with sampling. A field blank is a complete impinger train including all glassware and solutions that is exposed to ambient conditions. These sample trains were then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank showed contamination above instrument background levels, steps were then taken to eliminate or reduce the contamination to below background levels.

As part of the QA/QC, a field spike was also associated with each test condition. A field spike was prepared by the field manager at a level similar to the field samples. These sample trains were then taken apart, and the solution was recovered and analyzed in the same manner as those sample trains used for sampling activities. The target range for recovery of the field spike was ±25%.

The results of the blanks and spikes associated with each of the test sites are shown in Tables 1–2. With very few exceptions, all blanks were less than 5% of the measured values for

the samples and thus within the error of the method. The results of the spiked samples were all within the 25% range required by the method.

Table 1
Results of Mercury Speciation Field Blanks

Day	KCl Solution, µg	H_2O_2 Solution, µg	$KMnO_4$ Solution, µg
37423	0.01	<0.03	0.33
37424	0.4	<0.03	0.49
6/18/02	0.67	<0.03	1.26
6/19/02	0.16	<0.03	0.12
6/20/02	0.25	<0.03	0.14
6/21/02	0.22	<0.03	0.30
6/24/02	0.28	<0.03	0.48
6/26/02	0.12	<0.03	0.18
6/27/02	0.46	<0.03	0.18
6/28/02	0.59	<0.03	0.31
7/08/02	0.29	<0.03	0.41
7/09/02	0.60	0.03	0.14
7/10/02	1.47	0.25	1.11
7/11/02	0.76	<0.03	0.73
7/12/02	0.31	0.20	0.16
7/15/02	0.06	0.08	0.21
7/16/02	0.22	<0.03	0.20
7/17/02	0.15	0.03	0.18
7/18/02	0.53	<0.03	0.18
7/18/02	0.71	<0.03	0.15
8/13/02	0.18	0.06	0.09
37483	0.25	0.03	0.19

Table 2
Results of Mercury Speciation Field Spikes

	KCl			H_2O_2 Solution			$KMnO_4$ Solution		
Date	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %
37423	5.06	5	101	1.98	2	99	5.06	5	101
37432	5.28	5	106	2.04	2	102	5.16	5	103
37445	5.44	5	109	2.1	2	105	6.2	5	124
37453	5.34	5	107	2.02	2	101	4.6	5	92

QA/QC Checks for Data Reduction and Validation

Data Reduction

Data reduction was performed by sampling and analytical personnel and by the team leaders. Calculations include velocity, moisture, stack gas flow, sample gas volume, percent-isokinetic sampling, and flue gas mercury concentrations. Calculations were performed using spreadsheets on a portable computer; some averaging was done with a calculator. Standardized spreadsheets were used. Equations used in the calculations were contained in the method and are included in appendix X, Sample Calculations.

Data Validation

All data, data entry, and calculations were double-checked by the originator and reviewed by a second person. Reviews included recalculation of results, data entry checks, and calculation of known and accepted data sets using the existing spreadsheet.

Sample Identification and Chain of Custody

Samples were identified with unique sample numbers and descriptive notations. Sample custody was maintained by EERC personnel. Data sheets were kept in the custody of the originator, the program manager, or team leaders. The original data sheets were used for report preparation, and any additions were initialed and dated.

SAMPLE CALCULATIONS

Sample calculations are included for each of the calculated parameters.

Volume of Gas Sample

Vm(std) = Volume of gas sample measured by the dry gas meter, connected to standard conditions, dscf

Vm(std) (dscf) = $\frac{K_1 \times Vmc \times Pm}{Tm + 460}$

Vm(std) = $\frac{17.64 \times 45.472 \times 1 \times 29.665}{104 + 460}$ = 42.190 dscf

Where:

K_1 = 17.64°R/in. Hg

Vmc = Vm × Cm = Volume of gas sample as measured by dry gas meter corrected for meter calibration (Cm = meter calibration coefficient) (dcf)

Pm = Meter pressure (in. Hg)

Tm = Meter temperature (°F)

Volume of Water Vapor

Vw(std) = Volume of water vapor in the gas sample, corrected to standard conditions, scf

Vw(std) (scf) = $K_2 \times H_2O(g)$

Vw(std) = 0.04715 × 137.5 = 6.483 scf

Where:

K_2 = 0.04715 ft^3/g

$H_2O(g)$ = Mass of liquid collected in impingers and silica gel (g)

Water Vapor in the Gas Stream

Bws = Water vapor in the gas stream, proportion by volume

$$Bws = \frac{Vw(std)}{Vm(std) + Vw(std)}$$

$$Bws = \frac{6.483}{42.190 + 6.483} = 0.1332$$

Dry Molecular Weight

Md = Dry molecular weight of stack gas, lb/lb-mole

Md (lb/lb-mole) = $0.440 \times (\%CO_2) + 0.320 \times (\%O_2) + 0.280 \times (\%N_2 + \%CO)$

Md = $0.440 \times 15.9 + 0.320 \times 3.1 + 0.280 \times 81.0 = 30.7$ lb/lb-mole

Where:

$\%(CO_2, O_2, N_2, CO)$ = Percent (CO_2, O_2, N_2, CO) by volume, dry basis

Molecular Weight

Ms = Molecular weight of stack gas, wet basis, lb/lb-mole

Ms (lb/lb-mole) = $Md \times (1 - Bws) + 18.0 \times Bws$

Ms = $30.7 \times (1 - 0.1332) + 18.0 \times 0.1332 = 29.0$ lb/lb-mole

Average Stack Gas Velocity

Vs = Average stack gas velocity, ft/sec

$$Vs\ (ft/sec) = K_3 \times Cp \times (\Delta p)^{1/2}(avg) \times \left[\frac{Ts + 460}{Ps \times Ms}\right]^{1/2}$$

$$Vs = 85.49 \times 0.84 \times 0.4472 \times \left[\frac{685 + 460}{30.49 \times 29.0}\right]^{1/2} = 36.6 \text{ ft/sec}$$

Where:

K_3 = $85.49 \text{ ft/sec} \times \left[\dfrac{\dfrac{\text{lb}}{\text{lb} - \text{mole}} \times \text{in. Hg}}{^\circ\text{R} \times \text{in. H}_2\text{O}} \right]^{1/2}$

Cp = Pitot tube coefficient, dimensionless

Δp = Velocity head of stack gas (in. Hg)

$(\Delta p)^{1/2}(\text{avg})$ = Average of the square root of Δp values

Ts = Stack gas temperature (°F)

Ps = Stack pressure (in. Hg)

Isokinetric Sampling Rate

I = Percent of isokinetic sampling, %

$$I\ (\%) = \frac{K_4 \times (Ts + 460) \times Vm(std) \times 144}{Ps \times Vs \times An \times \theta \times (1 - Bws)}$$

$$I = \frac{0.09450 \times (685 + 460) \times 42.190 \times 144}{30.49 \times 36.6 \times 0.0707 \times 90 \times (1 - 0.1332)} = 107\%$$

Where:

K_4 = $\dfrac{0.09450\%(\text{in. Hg})(\text{min})}{^\circ\text{R} \times \text{sec}}$

An = Cross-sectional area of nozzle (in.^{2})

θ = Total sampling time (min)

Volume of Gas Sample Corrected to 3% O_2

Vm*(std) = Volume of gas sample measured by the dry gas meter (Vm(std)), * corrected to 3% oxygen, Nm^3

$$Vm^*(std) = K_5 \times Vm(std) \times \frac{21 - \%O_2}{18}$$

$$Vm^*(std) = 0.02832 \times 42.190 \times \frac{21 - 3.1}{18} = 1.188\ Nm^3$$

Where:

K_5 = $0.02832\ m^3/ft^3$

Mercury

$$Hg\ (\mu g/Nm^3) = \frac{\mu g}{Vm^*(std)}$$

$$Hg = \frac{6.99}{1.188} = 5.88\ \mu g/Nm^3$$

Particulate Hg = Sum of mercury from filter and nozzle rinse (note: all nozzle rinse values were nondetects)

Oxidized Hg = Sum of mercury from KCl impingers

Elemental Hg = Sum of mercury from H_2O_2 and $KMnO_4$ impingers. Since typically less than 5% of the elemental mercury (Hg^0) is trapped in the H_2O_2 impinger, the less-than values were not added to the total Hg^0. Thus the Hg^0 was calculated from the values obtained from the $KMnO_4$ impingers only.