MERCURY INFORMATION CLEARINGHOUSE

Final Report

(For the period October 1, 2003 through March 31, 2006)

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This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650 and the CEA Mercury Program Web site (www.ceamercuryprogram.ca).

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ABSTRACT

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC developed comprehensive quarterly information updates that provide a detailed assessment of developments in the various areas of mercury monitoring, control, policy, and research. A total of eight topical reports were completed and are summarized and updated in this final CEA quarterly report. The original quarterly reports can be viewed at the CEA Web site (www.ceamercuryprogram.ca).

In addition to a comprehensive update of previous mercury-related topics, a review of results from the CEA Mercury Program is provided. Members of Canada's coal-fired electricity generation sector (ATCO Power, EPCOR, Manitoba Hydro, New Brunswick Power, Nova Scotia Power Inc., Ontario Power Generation, SaskPower, and TransAlta) and CEA, have compiled an extensive database of information from stack-, coal-, and ash-sampling activities. Data from this effort are also available at the CEA Web site and have provided critical information for establishing and reviewing a mercury standard for Canada that is protective of environment and public health and is cost-effective. Specific goals outlined for the CEA mercury program included the following:

1. Improve emission inventories and develop management options through an intensive 2-year coal-, ash-, and stack-sampling program

2. Promote effective stack testing through the development of guidance material and the support of on-site training on the Ontario Hydro method for employees, government representatives, and contractors on an as-needed basis

3. Strengthen laboratory analytical capabilities through analysis and quality assurance programs

Create and maintain an information clearinghouse to ensure that all parties can keep informed on global mercury research and development activities.

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EXECUTIVE SUMMARY

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC developed comprehensive quarterly information updates that provide a detailed assessment of developments in the various areas of mercury monitoring, control, policy, and research. A total of eight topical reports were completed and are summarized and updated in this final CEA quarterly report. The original quarterly reports can be viewed at the CEA Web site (www.ceamercuryprogram.ca).

In addition to a comprehensive update of previous mercury-related topics, a review of results from the CEA Mercury Program is provided. Members of Canada's coal-fired electricity generation sector (ATCO Power, EPCOR, Manitoba Hydro, New Brunswick Power, Nova Scotia Power Inc., Ontario Power Generation, SaskPower, and TransAlta) and CEA, have compiled an extensive database of information from stack-, coal-, and ash-sampling activities. Data from this effort are also available at the CEA Web site and have provided critical information for establishing and reviewing a mercury standard for Canada that is protective of environment and public health and is cost-effective. Specific goals outlined for the CEA mercury program included the following:

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3. Strengthen laboratory analytical capabilities through analysis and quality assurance programs

4. Create and maintain an information clearinghouse to ensure that all parties can keep informed on global mercury research and development activities

CEA members committed to a program of quarterly sampling and reporting of mercury in coal, residue, and stack emissions. Over the past 2 years, a large data set of approximately 35,000 data points has been generated that characterizes the range and variability of mercury present in the coal and the resulting variability of mercury present in by-products and stack emissions. Quarterly reports from each of the member companies provide detailed data on coal characteristics, ash, and stack gas measurements and can be viewed at www.ceamercuryprogram.ca. Through this sample and analysis effort, CEA met the goal to improve emission inventories to support mercury

management strategies (Goal 1) and provide member utilities experience with mercury measurement methods (Goal 2). The findings of this effort have helped to reduce the uncertainty around mercury emissions and concentrations in coal and combustion by-products and provided critical information for establishing and reviewing a mercury standard for Canada.

In conjunction with quarterly sampling, a laboratory quality assurance and quality control program was conducted. In general the goal of improving and validating laboratory proficiency in mercury analysis (Goal 3) was achieved through the laboratory round-robin. Through this effort, quality assurance of lab procedures and methods was achieved, and a database of coal characteristics from across Canada was enhanced.

Finally, through the compilation of this report and the previous eight quarterly Information Clearinghouse Reports, the goal of creating and maintaining a database of global mercury research has been achieved (Goal 4).

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QUARTER 9 – MERCURY INFORMATION CLEARINGHOUSE FINAL REPORT

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC developed comprehensive quarterly information updates that provide a detailed assessment of developments in the various areas of mercury monitoring, control, policy, and research.

In order to adequately address the many topics and provide the detail necessary for the various stakeholders to make informed decisions, selected topics were discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that have been addressed in previous quarterly reports include the following and can be found in Appendix A:

- Quarterly 1 – Sorbent Control Technologies for Mercury Control
- Quarterly 2 – Mercury Measurement
- Quarterly 3 – Advanced and Developmental Mercury Control Technologies
- Quarterly 4 – Rerelease of Mercury from Coal Combustion By-Products
- Quarterly 5 – Mercury Fundamentals
- Quarterly 6 – Mercury Control Field Demonstrations
- Quarterly 7 – Mercury Regulations in the United States: Federal and State
- Quarterly 8 – Commercialization Aspects of Sorbent Injection Technologies in Canada

In this last of nine quarterly reports, an update of these mercury issues is presented that includes a summary of each topic, with recent information pertinent to advances made since the quarterly reports were originally presented. As a result of significant advances made in some areas of mercury research and development, several of the updated reports contain a comprehensive and detailed discussion, as is the case for Quarterly 4 – Rerelease of Mercury from Coal Combustion By-Products, and Quarterly 3 – Advanced and Developmental Mercury Control Technologies. For other topics; Quarter 8– Commercialization Aspects of Sorbent Injection Technologies in Canada; for example, only limited new information is available and a brief summary of the original topical reports is provided. Each of the updated summary reports is provided in a section of this final Quarter 9 report.

In addition to a comprehensive update of previous mercury-related topics, a review of results from the CEA Mercury Program is provided. Members of Canada's coal-fired electricity generation sector are committed to reducing mercury releases and, with CEA, have compiled an extensive database of information from stack-, coal-, and ash-sampling activities. Data from this effort are available at the CEA Web site (www.ceamercuryprogram.ca) and has provided critical information for establishing and reviewing a mercury standard for Canada that is protective of environment and public health and is cost-effective.

EXPERIMENTAL

CEA MERCURY PROGRAM OVERVIEW

CEA with the cooperation of eight coal-fired power generation companies in Canada joined forces to develop and implement the CEA Mercury Program designed to improve the information base around the measurement and control of mercury emissions. These utilities included ATCO Power, EPCOR, Manitoba Hydro, New Brunswick Power, Nova Scotia Power Inc. (NSPI), Ontario Power Generation (OPG), SaskPower, and TransAlta. The focus of the program is to improve the understanding of both human and natural sources of mercury releases, mercury movement through the environment, effects on human health, and the best ways to minimize these impacts. The coal-fired electricity generation industry is one of the largest point sources of mercury emissions currently and is working with governments, researchers, and other stakeholders to help develop effective and efficient ways of reducing these emissions.

The first priority of the CEA Mercury Program is to reduce the uncertainty of mercury measurement and emission control. The key components of the program, which have been ongoing for almost 3 years, include a laboratory quality assurance round-robin, research and development, and a mercury-sampling and analysis program. Activities continue in all of these areas; however, significant progress has been made, and the findings have provided critical information in support of the Canada-Wide Standard (CWS) for mercury from the coal-fired-electricity generating sector.

When the program was initiated, several goals were outlined. Through the laboratory round-robin, research and development, and sampling and analysis activities these goals have largely been met. Goals originally outlined included the following:

1. Improve emission inventories and the development of management options through an intensive 2-year coal-, ash-, and stack-sampling program

2. Promote effective stack testing through the development of guidance material and the support of on-site training on the Ontario Hydro method for employees, government representatives, and contractors on an as-needed basis

3. Strengthen laboratory analytical capabilities through analysis and quality assurance programs

4. Create and maintain an information clearinghouse to ensure that all parties can keep informed on global mercury research and development activities

Laboratory Quality Assurance Assessment

The laboratory quality assurance assessment was conducted to verify and ensure the accuracy and precision of mercury analysis in coal, ash, and scrubber effluent samples from coal-fired utilities. Proper analysis, by Canadian laboratories, of mercury in coal and ash samples is critical to accurately evaluate the fate of mercury across a coal-fired unit. Concentrations of mercury in coal, ash, scrubber effluents, and stack gas samples tend to be very low, near the detection limits in some cases, making consistent, reliable results difficult to achieve. To address these challenges, CEA member companies conducted a two-phase program. In the first phase, performance of 13 laboratories was assessed over a 6-month period by analyzing standard samples and comparing results with known values. Analysis included mercury, total chlorine, moisture, sulfur, total carbon (ash), and heating value (coal). Results were reviewed statistically to determine the laboratory's competency to accurately analyze the parameters in specific coals and ashes as well as limits of quantification. According to the Mercury Laboratory Round-Robin Project Canadian Council of Ministers of the Environment (CCME)–CEA Project 257-2003 Phase 1 CRM/RM Sample Report, nine of the 13 laboratories produced mercury values at least as good as the reference confidence limit, and "Canadian utilities produce mercury results of exceptional quality for coal…" (1).

Phase II consisted of a longer-term quality control and quality assurance effort. During Phase II, quarterly analysis was conducted that included reference coals and coal samples representative of fuel burned by Canadian utilities. Reference coal analysis provided ongoing measurement of laboratory performance relative to known standards. Analysis of utility coal samples provided valuable results from which to build a database of Canadian coal characteristics, which, in turn, supported the mercury emission standards development. Phase II of the laboratory quality assurance assessment builds upon the Coal and Ash Sampling Proficiency Exchange (CANSPEX) program, which was developed in 1990 to provide quality assurance management of coal analysis.

In general the goal of improving and validating laboratory proficiency in mercury analysis (Goal 3) was achieved through the laboratory quality assurance assessment. Through this effort, quality assurance of lab procedures and methods was achieved, and a database of coal characteristics from across Canada was enhanced.

Mercury Research and Development

Significant research and technology development has been ongoing in Canada, the United States, and internationally. Through a variety of governmental and commercial collaborations, CEA member companies have been conducting research on mercury as well as other emissions and greenhouse gases from coal-fired boilers.

Through the compilation of this report and the previous eight quarterly Information Clearinghouse Reports, the goal of creating and maintaining a database of global mercury research has been achieved (Goal 4).

Mercury-Sampling and Analysis Program

One of the most important factors influencing mercury regulation is an accurate understanding of mercury fate across the process, both at specific facilities and in general for the coal-fired electric generating sector. In the United States, this understanding came from the Information Collection Request (ICR) conducted between November 1998 and July 2000. To support U.S. Environmental Protection Agency (EPA) regulation development, an intensive sampling and analysis program was undertaken to determine mercury values in coal, by-product effluents (bottom ash, fly ash, scrubber effluent), and stack emissions. Sampling activities were conducted at facilities across the United States of various emission control configurations and fuel types. Results from these data were compiled and helped develop a better understanding of how mercury behaves in these systems and to set priorities for control.

In Canada, the CEA Mercury Program has stated that “the first priority in managing mercury is to improve the inventory of mercury emissions from coal-fired power plants across the country” (2). In support of ongoing and historical efforts to quantify mercury emissions from coal-fired utilities, CEA members committed to a program of quarterly sampling and reporting of mercury in coal, residue, and stack emissions. Over the past 2 years, a large data set has been generated that characterizes the range and variability of mercury present in the coal and resulting variability of mercury present in by-products and stack emissions. Quarterly reports from each of the member companies provide detailed data on coal characteristics, ash, and stack gas measurements and can be viewed at www.ceamercuryprogram.ca.

The mercury-sampling and analysis program was designed to function in cooperation with the laboratory quality assurance assessment to provide accurate and precise information. The findings of this effort have helped to reduce the uncertainty around mercury emissions and concentrations in coal and combustion by-products and provided critical information for establishing and reviewing a mercury standard for Canada and finding cost-effective and efficient management options. Data generated from this sampling and analysis program have helped to meet CEA’s goal (Goal 1) to improve emission inventories to support mercury management strategies and provided member utilities experience with mercury measurement methods (Goal 2). A brief summary of the data compiled through this effort is provided in the following section.

CEA Mercury Program Coal Data

The mercury emitted from coal-fired power plants, evolves directly from the mercury present in the coal at the time of firing. Typically, mercury is present in the coal in the tens of parts-per-billion range; however, it can vary significantly depending upon the type of coal and its source. A summary of results from sampling conducted by Canadian utilities is provided in Table 1 and shows that across Canada, mercury in the coal ranges from 0.007–0.640 mg/kg (ppm), with typical concentrations around 0.05–0.09 mg/kg. The data presented in Table 1 comprise average coal characteristics from sampling activities conducted at several collaborating CEA member companies. In general, the data are a compilation of many coal analyses conducted since the effort began

Table 1. CEA Mercury Program Coal Data

Power Plant	MW	Coal Type	Blend Ratio	Moisture, %	Ash, % (dry)	Mercury, mg/kg (dry)	Mercury, Min/Max, mg/kg[1]	Chloride, mg/kg (dry)	Chlodine**,** Min/Max, mg/kg*
ATCO Power									
Battle River – 5	375	sub-b.	NA	24.56	16.81	0.040	0.023/0.063	28	14/62
Sheerness – 1 and 2	767	sub-b.	NA	24.59	18.53	0.060	0.034/0.089	29	22/49
EPCOR Power									
Genesee – 1 and 2	820	sub-b.	NA	18.57	21.62	0.043	0.029/0.066	105	33/1188
Manitoba Hydro									
Brandon GS – 5	105	sub-b.	NA	10.83	6.28	0.077	0.032/0.172	18	6/46
New Brunswick Power									
Belledune	490	bit.	NA	11.08	10.11	0.044	0.018/0.095	245	122/468
NSPI									
Lingan – 1 and 2	300	petc./bit.	21/79	10.94	7.36	0.053	0.023/0.160	378	23/1558
Lingan – 3 and 4	300	petc./bit.	21/79	10.94	7.36	0.053	0.023/0.160	378	23/1558
Point Aconi – 1	165	petc./bit.	75/25	7.83	2.75	0.023	0.007/0.071	294	<15/4600
Point Tupper	150	petc./bit.	18/82	10.65	6.20	0.047	0.012/0.114	297	29/1600
Trenton – 5	150	petc./bit.	4/96	8.13	8.39	0.100	0.035/0.195	816	<14/1500
Trenton – 6	160	petc./bit.	26/74	6.57	17.93	0.039	0.012/0.087	756	160/2000
OPG									
Atikokan	215	lig	NA	34.19	15.26	0.089	0.060/0.136	25	10/622
Lambton – 1 and 2	1000	bit.	NA	8.72	9.24	0.063	0.018/0.640	641	207/1564
Lambton – 3 and 4	505 each	bit.	NA	6.75	8.44	0.096	0.063/0.322	861	427/1060
Nanticoke – 5, 6, and 7	500 each	sub-b./bit.	70/30	21.83	7.93	0.066	0.039/0.102	471	22/2001
Thunder Bay – 2 and 3	310	lig./sub-b.	80/20	31.02	12.39	0.084	0.010/0.310	17	10/82
TAU									
Sundance – 5 and 6	760	sub-b.	NA	19.14	20.92	0.069	0.040/0.100	70	17/281
SaskPower[2]									
Boundary Dam – 1	66	lig.	NA	32.72	13.54	0.073	0.055/0.098	10	8.32/11.85
Boundary Dam – 2	66	lig.	NA	32.91	13.45	0.072	0.055/0.097	10	8.45/11.46
Boundary Dam – 3	150	lig.	NA	32.82	13.53	0.073	0.053/0.098	10	8.45/11.44
Boundary Dam – 4	150	lig.	NA	32.39	13.62	0.075	0.055/0.098	10	8.54/10.77
Boundary Dam – 5	150	lig.	NA	32.37	13.70	0.076	0.052/0.109	10	8.69/10.53
Boundary Dam – 6	300	lig.	NA	32.44	13.72	0.073	0.052/0.093	10	8.76/10.53
Poplar River – 1	300	lig	NA	36.84	13.69	0.090	0.068/0.114	12	10.36/13.2
Poplar River – 2	300	lig.	NA	36.83	13.72	0.089	0.068/0.114	12	10.44/13.2
Shand	305	lig.	NA	31.97	13.88	0.078	0.044/0.119	9	6.88/10.6

Note: bit.=bituminous, sub-b.=sub-bituminous, lig.=lignite, petc.=petcoke

[1] Quarterly Data Reports

[2] SaskPower coal and ash results are as-received, not dry basis.

in the fall of 2002, with the maximum and minimum mercury and chlorine values presented to illustrate the range across Canadian fuels.

Based on the mercury data presented in Table 1, it is clear that variability exists both among the various power plants and within coal samples from a single facility. It is reasonable to expect similar relative variability in stack emissions, with additional variability due to the range of effectiveness of electrostatic precipitators (ESPs), fabric filters (FFs), and flue gas desulfurization (FGD) units at capturing mercury.

CEA Mercury Program Ash Data

Mercury present in the coal is volatilized during combustion and exits the boiler with the flue gas. As the gas cools in the preheater and ductwork, opportunities for the mercury to react or adsorb to other constituents in the flue gas exist. One pathway by which mercury finds its way out of the flue gas is by adsorbing to fly ash. Typically, ash with relatively high levels of unburned carbon exhibit the highest mercury concentration. Particulate control devices, therefore, become mechanisms for mercury capture depending upon the flue gas characteristics, ash composition, and operating conditions. Typically, mercury is not found in large quantities in bottom ash because of the high temperature in the boiler. This is consistent with data collected from Canadian utilities and presented in Table 2. The concentration of mercury in bottom ash ranged from less than 0.003 to 0.228 mg/kg; however, the average value was 0.02 mg/kg.

Mercury present in fly ash was typically one or two orders of magnitude higher than measured in the bottom ash. The concentration of mercury in the fly ash ranged from less than 0.003–0.847 mg/kg. Several plants, including OPG’s Nanticoke Units 5–7 and Lambton Units 1–4, had the highest mercury concentration in the ash. At Nanticoke Units 5–7, high levels of mercury in the fly ash, 0.637, could be related to the higher chloride concentration of the fuel. Table 1 shows an average chloride concentration for these fuels of 471 mg/kg for Units 5, 6, and 7. At chloride levels in the mid-100s, higher mercury concentrations are sometimes observed in the ash. Based on the present understanding of mercury fundamentals, it is believed that the presence of halogens in the flue gas improves the adsorption of mercury to carbon and/or ash, resulting in greater mercury capture and higher concentrations in hopper ash. This is consistent with the high carbon content measured in the ash at all of the Nanticoke and Lambton Units.

At Lambton Units 1 and 2 and Units 3 and 4 the percentage of carbon exceeded 10%, similar to fly ash at Nanticoke. This high carbon content coupled with coal chloride greater than 500 ppm (Table 1) likely contributed to the higher-than-average mercury concentration measured in the fly ash. At Lambton 1 and 2, the average fly ash concentration was 0.326 mg/kg and at Lambton 3 and 4 0.274 mg/kg, nearly twice the level measured from the next highest unit.

CEA Mercury Program Flue Gas Data

Stack sampling was generally conducted by either Ontario Hydro method or EPA Method 29 (multimetal sampling method) to quantify mercury emissions from the stacks of several Canadian utilities. Results from these tests in terms of emission rate in grams/hour and, in some cases, speciated mercury concentration are summarized in Table 3. In general, the values presented are an average of triplicate sampling (not necessarily representative of overall annual emissions), and the emission rate represents the estimated mercury emission from each unit. For those facilities that list two units, flue gas is exhausted through a common stack and the emission rate represents the mercury emission from the two units combined.

The stack gas mercury measurements conducted for the CEA Mercury Program typically represent snapshots of emission rates and have not been conducted over long enough periods to fully characterize emissions. However, they do provide useful information when reviewed relative to coal and ash results. The coal and ash data presented in Table 3 differ from the values presented in Tables 1 and 2 in that Table 3 data correspond only with coal and ash data collected during stack test activities. The two factors influencing stack mercury concentrations and emissions are the mercury content in the fuel and subsequent removal via pollution control devices. The mercury concentrations measured from CEA utilities range from 0.32 to 22.05 $\mu g/Rm^3$. NSPI's Point Aconi (only continuous fluidized-bed combustor tested) measured a stack gas mercury concentration of 0.32 $\mu g/Rm^3$ (one of the lowest measured) and, showed a relatively high mercury content in the ash, indicating that significant mercury capture is occurring across the FF. A similarly low stack mercury concentration was measured at OPG's Lambton Unit 4, indicating mercury capture is occurring across the ESP and/or FGD.

The highest mercury concentrations measured at the stack were at SaskPower's Poplar River, Boundary Dam, and Shand facilities, where the concentration was greater than 10 $\mu g/Rm^3$ from each of the five stacks tested. Speciation data from each of these three stacks show an elemental mercury fraction greater than 70%, consistent with lignite fuels. Coal data from these plants during stack sampling show mercury concentrations typically between 0.05 and 0.10 mg/kg and typically low chloride concentrations, 15 mg/kg. Based on these characteristics, it is not surprising that very little mercury was measured in the ESP ash and emission rates are higher than at other units.

The predominant emission control for Canadian utilities is a cold-side ESP, with the exception of Point Aconi, which has a FF. The other units that are unique among those tested include New Brunswick Power's Belledune, which operates an ESP and FGD and OPG's Lambton Unit 4 which has SCR, a C-ESP and FGD. Ash data from Belledune suggest that a significant amount of mercury is not captured by the ESP. However, the stack mercury concentration (1.08–1.2 $\mu g/Rm^3$) is lower than most of the units tested and suggests that some mercury capture is occurring across the FGD similar to Lambton Unit 4.

Mercury Policy

The Government of Canada, working closely with provincial and territorial partners, has accepted in principle a draft of the CWS for mercury emissions from coal-fired power plants (www.ccme.ca/initiatives/standards.html). Later this year, the draft will be reviewed by the Air Management Committee, Environmental Planning and Protection Committee, and Deputy Ministers Committee, and a finalized version will be developed. The final CWS is expected to be endorsed by the CCME in the first half of 2006. According to John Mayes, Assistant Director of the Standards Development Branch at the Ontario Ministry of the Environment at Air Quality V, the primary goals for the standard were (3):

- Develop a CWS by 2005
- Explore national capture of 60% to 90% of mercury
- Provide for mercury emission reductions by 2010
- Align with U.S. standards for mercury

The first three of these goals are being met. In accordance with provincial caps provided for under the draft CWS, mercury emissions would be reduced from the current 2695 kg/yr to 1130 kg/yr (58% reduction) by 2010 based on best achievable control technology economically available (BATEA). Therefore, the coal-fired utilities will need to install mercury technologies that can provide 50%–60% control. In addition, as part of the CWS, a review process will be implemented to evaluate requiring much higher levels of control, up to 80% by 2018. For new facilities, the use of best available control technologies (BACT) for mercury will be required upon start-up. Based on current estimates, BACT levels would be 85% control for bituminous coals and blends (emission rates of 3 kg/TWh) and 75% control for lignites (15 kg/TWh) and subbituminous fuel (8 kg/TWh).

The reporting and measurement protocols for the CWS have not yet been issued. Based on a recent conversation with Don Rose of Environment Canada, it is expected that these will be issued in early spring of 2006.

Based on the draft, the CWS will require a higher level of mercury control from power plants and in a shorter time frame than the EPA Clean Air Mercury Rule (CAMR). However, by 2018, the CAMR and CWS will be similar. Although trading will be allowed under CAMR, it is not part of the draft CWS.

In March 2005, `EPA issued the first-ever mercury regulation titled the CAMR. At Air Quality V, Robert Weyland of EPA said the rationale for the rule was EPA's desire to allow electric generating utilities as much flexibility as possible and still protect public health (4). As a result, EPA issued the rule under Section 111 rather than Section 112 of the Clean Air Act Amendment (CAAA), thereby providing a cap-and-trade mechanism. The rule is designed to be implemented in two phases. The first phase would cap mercury emissions from coal-fired power plants at 38 tons/year by 2010 (about 48 tons/year is currently being emitted) and the second phase would permanently cap emissions at 15 tons/year by 2018. It is EPA's position that the first phase will be accomplished as a

Table 2. CEA Mercury Program Ash Data

					BOTTOM ASH ANALYSIS				FLY ASH ANALYSIS			
Power Plant	MW	Coal Type	Blend Ratio	Bottom Ash: Fly Ash Ratio	Moisture, %	Carbon, % (dry)	Mercury[1], mg/kg (dry)	Mercury, Min/Max.	Moisture, %	Carbon, % (dry)	Mercury, mg/kg (dry)	Mercury, Min/Max.
ATCO Power												
Battle River – 5	375	sub-b.	NA	40:60	0.42	0.27	0.006	<0.003/0.011	0.01	0.14	0.072	0.039/0.126
Sheerness – 1 and 2	767	sub-b.	NA	40:60	0.46	1.77	0.006	<0.003/0.031	0.04	0.25	0.124	0.03/0.243
EPCOR Power												
Genesee – 1 and 2	820	sub-b.	NA	40:60	0.12	2.21	0.003	<0.003/0.005	0.22	0.37	0.088	0.069/0.193
Manitoba Hydro												
Brandon GS – 5	105	sub-b.	NA	25:75	0.410	0.524	0.029	<0.003/0.102	0.219	0.32	0.166	0.042/0.369
New Brunswick Power												
Belledune	490	bit.	NA	20:80	-	-	0.021	0.0010/0.076	0.12	13.49	0.043	0.004/0.156
NSPI												
Lingan – 1 and 2	300	petc./bit.	21/79	15:85	0.29	-	0.002	<0.003	0.42	-	0.008	0.003/0.107
Lingan – 3 and 4	300	petc./bit.	21/79	15:85	0.29	-	0.002	<0.003	0.42	-	0.008	0.003/0.107
Point Aconi – 1	165	petc./bit.	75/25	47:53	0.25	-	0.080	0.074/0.086	0.31	-	0.150	0.069/0.493
Point Tupper	150	petc./bit.	18/82	18:82	0.58	-	0.012	0.009/0.015	0.36	-	0.008	<0.003/0.023
Trenton – 5	150	petc./bit.	4/96	10:90	0.25	-	0.002	<0.003	0.36	-	0.099	0.004/0.343
Trenton – 6	160	petc./bit.	26/74	10:90	0.28	-	0.003	<0.003/0.007	0.31	-	0.029	0.004/0.139
OPG												
Atikokan	215	lig.	NA	20:80	0.07	0.17	0.0034	<0.003/0.053	0.04	0.07	0.016	0.003/0.037
Lambton – 1 and 2	1000	bit.	NA	15:85	-	-	0.053	0.020/0.116	10.24	11.19	0.326	0.026/0.530
Lambton – 3 and 4	505 each	bit.	NA	15:85	0.20	10.69	0.119	0.031/0.228	10.43	10.09	0.274	0.001/0.456
Nanticoke – 5, 6, and 7	500 each	sub-b./bit.	70/30	15:85	0.30	8.89	0.019	0.014/0.022	0.16	10.08	0.637	0.322/0.847
Thunder Bay – 2 and 3	310	lig./sub-b.	80/20	25:75	0.055	0.60	0.063	<0.003/0.342	0.16	0.08	0.002	<0.002/0.003
TAU												
Sundance – 5 and 6	760	sub-b.	NA	40:60	0.73	5.24	0.014	0.008/0.020	0.22	1.43	0.141	0.094/0.483
SaskPower												
Boundary Dam – 1	66	lig.	NA	20:80	0.15	2.24	0.013	ND/0.081	0.04	0.47	0.047	0.014/0.079
Boundary Dam – 2	66	lig.	NA	20:80	0.73	14.46	0.009	ND/0.037	0.07	0.52	0.054	0.017/0.087
Boundary Dam – 3	150	lig.	NA	20:80	0.19	1.72	0.011	ND/0.060	0.08	0.42	0.044	0.019/0.082
Boundary Dam – 4	150	lig.	NA	20:80	0.37	13.44	0.072	0.012/0.195	0.05	0.25	0.068	0.041/0.101
Boundary Dam – 5	150	lig.	NA	20:80	0.13	3.01	0.061	<0.001/0.214	0.12	0.70	0.018	0.002/0.035
Boundary Dam – 6	300	lig.	NA	20:80	0.32	3.50	0.003	<0.001/0.006	0.03	0.44	0.081	0.042/0.120
Poplar River – 1	300	lig	NA	20:80	0.17	1.08	0.003	0.001/0.010	0.09	0.14	0.036	<0.002/0.104
Poplar River – 2	300	lig.	NA	20:80	0.13	1.06	0.003	ND/0.005	0.07	0.19	0.094	0.021/0.221
Shand – A Side	305	lig.	NA	20:80	0.13	0.93	0.004	ND/0.034	0.09	1.79	0.031	0.004/0.133
Shand – B Side									0.06	1.13	0.052	0.012/0.159

Note: bit.=bituminous, sub-b.=sub-bituminous, lig.=lignite, petc.=petcoke

*Quarterly Data Reports

[1] Where average Hg concentration is below the lower limit of quantification (LoQ), ½ of the LoQ was reported.

Table 3. CEA Mercury Program Flue Gas Data

						Total Hg Emissions		Speciation of Mercury Emissions		
Power Plant	MW/Coal Type	Method Used	Coal Mercury, mg/kg (dry)	Bottom Ash Mercury, mg/kg (dry)	Fly Ash Mercury, mg/kg (dry)	Concentration, µg/Rm^3	Emission Rate, g/h	Particulate, %	Oxidized, %	Elemental, %
ATCO Power										
Battle River – 5	375 Sub-b	M-29[1]	0.039	0.004	0.060	4.66 dry	8.05	<1	12	88
Sheerness – 1 and 2	767 Sub-b	M-29[1]	0.060	0.002	0.042	3.35 dry	10.33	<1	19	81
EPCOR Power										
Genesee – 1 and 2	820 Sub-b	M-29 (2), OH (1)[2]	0.043	0.003	0.133	3.25-6.43	7.88-20.66	<1	4	96
Manitoba Hydro										
Brandon GS – 5	105 Sub-b	OH	0.050	<0.003	0.150	3.76-6.38	2.05-2.56	<1	11	89
New Brunswick Power										
Belledune	490 Bit.	OH	0.033	0.010	0.059	1.08-1.20	2.03-2.16	2–5	12–22	74–85
NSPI										
Lingan – 1 and 2	300 Petc/Bit	OH	0.058	<0.003	0.014	4.82	5.82	1	60	40
Lingan – 3 and 4	300 Petc/Bit	OH	0.1275	0.002	0.018	-	12.52	-	-	-
Point Aconi – 1	165 Petc/Bit	OH	0.032	0.003	0.149	0.32	0.23	4	66	30
Point Tupper	150 Petc/Bit	OH	0.062	0.094	0.016	5.24	3.60	<1	56	44
Trenton – 5	150 Petc/Bit	OH	0.093	<0.003	0.069	7.02	4.33	1	61	38
Trenton – 6	160 Petc/Bit	OH	0.046	0.004	0.050	3.71	2.28	1	54	46
OPG										
Lambton – 4[3]	505 Bit.	OH	0.095	0.051	0.226	0.36	0.76	1	32	67
Nanticoke – 5	500 Sub-b/Bit	OH	0.0643	0.009	0.562	2.73	10.58	1	77	21
Nanticoke – 6	500 Sub-b/Bit	OH	0.0703	0.010	0.899	2.50	14.70	<1	48	52
Nanticoke – 7	500 Sub-b/Bit	OH	0.0607	0.016	0.721	3.32	13.86	4	86	10
TAU										
Sundance – 5 and 6	760 Sub-b	OH	0.056	0.010	0.146	3.27	10.09	0	5	95
SaskPower										
Boundary Dam – 1 and 2[4]	132 Lig.	OH	0.073	0.008	0.080	17.68 (3% O_2 dry)	11.45	<1	16	84
Boundary Dam – 5[4]	150 Lig.	OH	0.090	-	0.037	19.39 (3% O_2 dry)	12.13	<1	17	83
Boundary Dam – 6	150 Lig.	OH	0.052	0.002	0.098	14.00 (6% O_2 dry)	14.30	2	30	73
Poplar River – 1	300 Lig.	OH	0.099	0.006	0.072	22.05 (7.7% O_2 dry)	20.70	0	23	77
Shand – 1	300 Lig.	OH	0.052	0.002	0.056	11.8 (6% O_2 dry)	14.08	<1	6	93

N/A = not applicable

1 Results from 1999 OH tests.

2 Average of two Method 29 and one OH test, speciation data from EERC.

3 Data from September 10–12, 2003, test.

4 Average of two tests (1-EERC, 1-SaskPower); speciation data from EERC.

cobenefit of the February 2005 Clean Air Interstate Rule (CAIR), which requires that a number of utilities in the eastern states install wet FGD systems for SO_2 control and selective catalytic reduction (SCR) for NO_x control. Mitchell Baer of DOE added that, although the second phase of the rule will require addition mercury controls, it is expected that a number of mature economical technologies will be available to meet CAMR requirements (5).

As presented in Quarter 7 – Mercury Regulations in the United States: Federal and State, CAMR has been controversial, and 11 states and four environmental groups have filed suit. Of particular concern to the states and organizations is the delisting of mercury from Section 112 of the CAAA which provides for maximum achievable control technology and the decision to regulate mercury under Section 111, providing for a cap-and-trade structure. At the same time, these lawsuits were filed, petitions for reconsideration were sent to the EPA administrator. The petitions requested EPA reconsider both CAMR and the legality of delisting utilities from Section 112 of the CAAA to Section 111. There were four petitions asking reconsideration of the delisting. One petition was submitted by 14 states: New Jersey, California, Connecticut, Delaware, Illinois, Maine, Massachusetts, New Hampshire, New Mexico, New York, Pennsylvania, Rhode Island, Vermont, and Wisconsin. The second petition was submitted by five environmental groups: The Natural Resources Defense Council, the Clean Air Task Force, the Ohio Environmental Council, the U.S. Public Interest Research Group, and the Natural Resources Council of Maine. The two other petitions received by the EPA were from the Jamestown Board of Public Utilities and the Integrated Waste Service Association. Two petitions were received to reconsider the methodology of CAMR in determining caps and NSPS. One petition was received from the same 14 states and the other from five environmental groups and four Indian tribes. As a result, the EPA elected to reconsider on June 24, 2005, by asking for public comment. However, the reconsideration process will not stay the rule.

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RESULTS AND DISCUSSION

SORBENT CONTROL TECHNOLOGIES FOR MERCURY CONTROL AND MERCURY CONTROL FIELD DEMONSTRATIONS (QUARTER 1 AND QUARTER 6 REPORTS)

Field Demonstrations of Carbon Injection

In 1999, the DOE National Energy Technology Laboratory (NETL) issued a request for proposal (RFP) to test mercury control technologies at full scale. The near-term goal of the RFP was to evaluate technologies that could achieve 50%–70% mercury removal at a cost of less than three-quarters of the estimated cost of $50,000–$70,000/lb (CAN$136,000–CAN$191,000/kg) mercury removed. The longer-term goal was to develop technologies that could provide up to 90% control at a cost of half to three-quarters of activated carbon injection technology by the year 2010. During 2003 and 2004, NETL issued three more RFPs to evaluate mercury control technologies through its Office of Fossil Energy's Innovation Program and through the Clean Coal Initiative. In 2005, they issued the Phase III RFP to demonstrate control technologies on a longer-term basis that can obtain 90% mercury control. In addition, pilot-scale tests for more novel technologies were encouraged, as well as new techniques for cleaning coal that can remove mercury. It is expected that awards will be made in early spring of 2006.

In September 2005, at Air Quality V: International Conference on Mercury, Trace Elements, SO_3, and Particulate Matter, Tom Feeley of DOE–NETL presented an update regarding the status of mercury control programs (1). It is clear that significant strides have been made in developing effective mercury control technology over the past several years, particularly for low-rank coals. Based on the status of the Phase II program, Tom Feeley concluded the following:

- Activated carbon/sorbent injection and oxidation systems (i.e., catalysts, chemical additives) are the most promising Hg control technologies.

- The estimated cost of mercury control on a $/lb-removed basis has been significantly reduced.

- DOE's current field testing activity is a research and development (R&D) program and, therefore, further long-term field testing is needed to bring technology to commercial demonstration readiness.

- DOE's research, development, and demonstration (RD&D) model projects broad commercial availability of mercury control technologies in the 2012–2015 time frame.

- The fate of mercury in combustion and gasification by-products remains an issue.

Table 4 summarizes 42 large-scale mercury control projects. This information identifies the lead contractor for each project, the demonstration site, boiler type and size, fuel type, air pollution control device (APCD) employed, mercury control technology being evaluated, and project status. The demonstration sites represent utility boilers across the United States and one in Canada. Boiler types representing the major North American boiler manufacturers are included. Fuel types represented include U.S. northern plains and Gulf Coast lignite, PRB subbituminous coal, high- and low-sulfur bituminous coal, and Canadian lignite. Air pollution control technologies represented include c-ESPs and h-ESPs, various types of wet FGD systems, and SDA–FFs. All of these projects involve the evaluation of some type of additive, reagent, or sorbent for its potential to control Hg emissions in conjunction with existing air pollution control technology or modify Hg speciation in the flue gas to facilitate Hg control.

Most of these tests were previously reported in "CEA Quarter 6 – Mercury Control Field Demonstrations"; therefore, this report will only summarize the key findings and provide reported results for those tests completed recently. Although several projects have been completed, most projects are ongoing, with a significant number scheduled to begin in 2006.

The use of sorbent injection and/or ACI as a means of removing mercury from coal combustion flue gas is widely accepted as the most developed and commercially viable alternative. Many other technologies are being investigated, but the demonstrated performance of activated carbon in pilot- and full-scale tests make it the leading candidate for achieving the goals of the draft CWS for mercury emissions from coal-fired power plants. Although, ACI is considered the most promising and, therefore, the most tested technology option, it should be recognized that not all plant configurations or fuels have been tested to the same degree and additional data are needed to minimize uncertainty and ensure commercial readiness. Clearly, whether ACI is considered a commercially available technology by all groups depends on the level of testing that has been performed thus far and the confidence that the providers (vendors) and buyers (utilities) have in these data. Recent comments by the Institute of Clean Air Companies (ICAC) state that "companies are providing firm price proposals with performance guarantees for every coal and boiler type (2)." However, at the time of this review, there were no guarantees in place at plants in Canada. The President of ADA-ES was recently quoted as saying, "We can take an order for design and install, and a utility could be reducing mercury within six months." Based on comments that were submitted to EPA prior to the CAMR being announced, utilities and coal suppliers dispute vendors' ability to make performance guarantees and emphasize that additional testing is needed (3).

There are a number of major producers of powdered activated carbon (PAC) in the United States, Canada, Europe, and China, including the following:

- Norit Americas
- Calgon
- Nucon International
- Luscar, Ltd.
- Barnebey and Sutcliffe Corporation
- RWE Rheinbraun
- Ningxia Huahui

Table 4 .Mercury Control Demonstration Projects Funded by the U.S. Department of Energy

Lead Contractor	Demonstration Site	Boiler Type/Size	Fuel Type	APCD	Hg Control Technology	Status
UND EERC	Leland Olds Station Unit 1 Basin Electric Power Cooperative	B&W wall-fired 220 MW	ND lignite	c-ESP	ACI with SEA	Complete
ADA-ES Inc.	Coal Creek Station Unit 1 Great River Energy	CE t-fired 546 MW	ND lignite	c-ESP Wet FGD	TOXECON II™	Complete
B&W	Endicott Station Michigan South Central Power Agency	B&W Stirling boiler 55 MW	Bituminous	c-ESP Wet FGD	FGD reagent additive	Complete
B&W	Zimmer Station Cinergy	B&W Carolina boiler 1300 MW	Bituminous	c-ESP Wet FGD	FGD reagent additive	Complete
Mobotec USA	Cape Fear Station Unit 5 Progress Energy	CE t-fired 154 MW	Low-sulfur bituminous	c-ESP	Sorbent injection ROFA™/ROTAMIX™	Complete
Southern Company	E.C. Gaston Station Unit 3 Alabama Power	CE t-fired 270 MW	Low-sulfur bituminous	h-ESP COHPAC™	ACI	Complete
URS	Plant Yates Unit 1 Georgia Power	CE t-fired 100 MW	Low-sulfur bituminous	c-ESP	ACI	Complete
URS	Plant Yates Unit 2 Georgia Power	CE t-fired 100 MW	Low-sulfur bituminous	c-ESP Wet FGD	ACI	Complete
Sorbent Technologies Corporation	St. Clair Station Unit 1 DTE Energy	B&W wall-fired 160 MW	PRB PRB–bit. blend	c-ESP	Brominated ACI	Complete
Sorbent Technologies Corporation	Buck Station Duke Energy	NA	Low-sulfur bituminous	h-ESP	Brominated ACI	Complete
ADA-ES Inc.	Holcomb Station Sunflower Electric Power Corporation	B&W Carolina Boiler 360 MW	PRB PRB–W-bit.	SDA–FF	ACI Coal blending	Complete
URS	Stanton Station Unit 1 Great River Energy	FW wall-fired 150 MW	PRB	c-ESP	ACI	Ongoing
URS	Stanton Station Unit 10 Great River Energy	CE t-fired 60 MW	ND lignite	SDA–FF	ACI	Complete
SaskPower and UND EERC	Poplar River Power Station Units 1 and 2 SaskPower	NA 300 MW	Poplar River lignite	c-ESP	ACI Pilot-scale slipstream	Ongoing
ADA-ES Inc.	Meramec Station AmerenEU	NA 140 MW	PRB	c-ESP	ACI	Complete
UND EERC	Stanton Station Unit 1 Great River Energy	FW wall-fired 150 MW	PRB	c-ESP	ACI	Ongoing
UND EERC	Antelope Valley Station Unit 1 Basin Electric Power Cooperative	CE t-fired 440 MW	ND lignite	SDA–FF	ACI ACI with SEA	Complete

Continued . . .

Table 4. Mercury Control Demonstration Projects Funded by the U.S. Department of Energy (continued)

Lead Contractor	Demonstration Site	Boiler Type/Size	Fuel Type	APCD	Hg Control Technology	Status
UND EERC	Milton R. Young Station Unit 2 Minnkota Power Cooperative	B&W cyclone-fired 450 MW	ND lignite	c-ESP Wet FGD	Mercury oxidation fuel/FG additives	Complete
UND EERC	Monticello Station Unit 3 Texas Utilities Company	B&W wall-fired 750 MW	Texas lignite	c-ESP Wet FGD	Mercury oxidation fuel/FG additives	Ongoing
UND EERC	Big Brown Station Texas Utilities Company	CE t-fired 600 MW	Texas lignite Lignite–PRB	c-ESP	ACI	Ongoing
URS	Monticello Station Unit 3 Texas Utilities Company	B&W wall-fired 750 MW	Texas lignite	c-ESP Wet FGD	Wet FGD additives	Ongoing
URS	Plant Yates Unit 2 Georgia Power	CE t-fired 100 MW	Low-sulfur bituminous	c-ESP Wet FGD	Wet FGD additive	Ongoing
URS	Conesville Station American Electric Power	NA 400 MW	Bituminous	c-ESP Wet FGD	Wet FGD additive	2005
ADA-ES Inc.	Conesville Station American Electric Power	NA 400 MW	Bituminous	c-ESP Wet FGD	ACI	2005
ADA-ES Inc.	Laramie River Station Unit 3 Missouri Basin Power Project	B&W 550 MW	PRB	SDA–ESP	ACI	Ongoing
ADA-ES Inc.	Monroe Station Unit 4 Detroit Edison	B&W 785 MW	PRB–bit. blend	c-ESP	ACI	Ongoing
ADA-ES Inc.	Louisa Station Unit 1 MidAmerican	B&W 650 MW	PRB	h-ESP	Sorbent injection	2006
ADA-ES Inc.	Independence Station Unit 1 Entergy	CE 840 MW	PRB	c-ESP	TOXECON II™	TBD
ADA-ES Inc.	Gavin Station American Electric Power	B&W 1300 MW	Bituminous	c-ESP	TOXECON II™	TBD
ADA-ES Inc.	Council Bluff Unit 2 MidAmerican	NA	PRB	h-ESP	Sorbent injection	TBD
ALSTOM Power, Inc.	Dave Johnston Station PacificCorp	NA	PRB	c-ESP	ACI with additives	Complete
ALSTOM Power, Inc.	Leland Olds Station Unit 1 Basin Electric Power Cooperative	B&W 440 MW	ND lignite	c-ESP	ACI with additives	2006
ALSTOM Power, Inc.	Portland Station Reliant Energy	NA	Bituminous	c-ESP	ACI with additives	2006
GE EER	John Sevier Station Tennessee Valley Authority	NA	Bituminous	NA	Combined Hg and NO_x Control	2006

Continued . . .

Table 4. Mercury Control Demonstration Projects Funded by the U.S. Department of Energy (continued)

Lead Contractor	Demonstration Site	Boiler Type/Size	Fuel Type	APCD	Hg Control Technology	Status
Southern Company	Daniel Station Unit 1	CE t-fired 540 MW	60–40 Blend PRB–Bit.	c-ESP	ACI and brominated ACI	Ongoing
GE EER	Lee Station Unit 3 Progress Energy	NA	Bituminous	c-ESP	Combined Hg and NO_x control	Ongoing
Sorbent Technologies Corporation	Lee Station Unit 1 Progress Energy	NA	Bituminous	c-ESP	Brominated ACI	2006
Sorbent Technologies Corporation	Crawford Station Unit 7 Midwest Generation	NA	PRB	c-ESP	Brominated ACI	2006
Sorbent Technologies Corporation	Will County Station Midwest Generation	NA	PRB	h-ESP	Brominated ACI	TBD
Mobotec USA	Whitewater Station Richmond Power and Light	NA	NA	NA	Sorbent injection ROFA™/ROTAMIX™	Ongoing
ADA-ES Inc.	Presque Isle Station WE Energy	NA	NA	NA	TOXECON II™	Ongoing
Amended Silicates, LLC	Miami Fort Station Unit 6 Cinergy	NA 175 MW	Bituminous	c-ESP	Amended Silicates™	2006

ACI – activated carbon injection
CE – Combustion Engineering
FGD – flue gas desulfurization
h-ESP – hot-side electrostatic precipitator
ROFA™ – Rotating Opposed-Fire Air
SEA – sorbent enhancement additive
UND EERC – University of North Dakota Energy & Environmental Research Center
ADA-ES Inc. – ADA Environmental Solutions Inc.
COHPAC – compact hybrid particulate collector
FW – Foster Wheeler
NA – not available
ROTAMIX™ – Rotating Mixing
TBD – to be determined
URS – URS
B&W – Babcock & Wilcox Company
c-ESP – cold-side electrostatic precipitator
GE EER – GE Energy and Environmental Research
PRB – Powder River Basin subbituminous coal
SDA–FF – spray dryer absorber–fabric filter
t-fired – tangentially fired
W-bit. – western bituminous coal

With a few exceptions, most of the testing has been done with Norit Americas DARCO™ HG (formerly called DARCO™ FGD). However, in practice the carbons have provided similar results and have an average cost of about $0.50/lb.

Results from full-scale tests using ACI at three sites are shown in Figure 1. As was expected, the use of a FF (high air-to-cloth ratio, COHPAC™) with ACI at the E.C. Gaston Station provided the best mercury removal at the lowest ACI rate, 87%–90% removal at an ACI rate of 1.5 lb/Macf. However, as a result of increased particulate loading to the COHPAC™, the cleaning frequency increased significantly. At Brayton Point Station (ESP alone), burning a similar coal (low-sulfur bituminous), an ACI rate of 20 lb/Macf was needed to obtain 90% mercury removal. At an ACI rate of 1.5 lb/Macf, only about 15% mercury removal was achieved at the Brayton Point Station.

Testing at Pleasant Prairie Station using PRB coal and a c-ESP, resulted in a maximum mercury removal of 66% regardless of the ACI rate. However, at an ACI rate of 1.5 lb/Macf, mercury removal was ~40%. EERC pilot-scale tests showed relatively low mercury capture when Fort Union lignite was fired with an ESP only. Mercury removal of only 45% was achieved even at a high ACI rate of 20 lb/Macf (4).

In general, the results shown in Figure 1 are representative of results achieved at many sites. For example a full-scale evaluation of ACI at the Yates plant, was conducted by URS Corporation working with Southern Company (5). The test unit fires an eastern bituminous coal and has a small ESP (SCA of 173 ft^2/kacfm). Results showed that 60%–70% removal is achievable at 4.5 lb/MMacf, improving to 70%–80% at 6.5 lb/MMacf, with no further improvement at the higher injection rate. In addition to demonstrating mercury removal, another purpose for the test was to determine the effects of ACI on ESP performance. At low loads there did appear to be increased arcing across the ESP. However, longer-term tests need to be completed before final conclusions can be made.

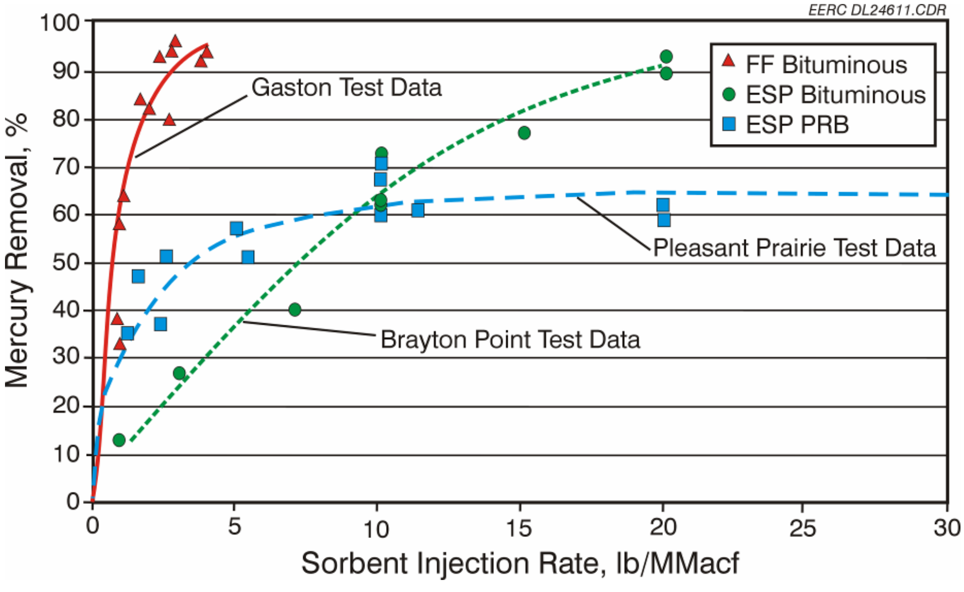

Figure 1. Mercury removal as a function of ACI rate at three sites.

Another test recently completed evaluating ACI for a PRB coal was conducted by a team led by ADA-ES (6). Sites tested included Holcomb, Laramie River, Meramec, and Monroe Power Plants. The first three sites fired 100% PRB coal, and the fourth, Monroe, uses a 60–40 blend of PRB–eastern bituminous coal. The emission control configuration was unique for each of the units tested. Holcomb has a SDA–FF, Laramie River a SDA–ESP combination, Meramec only an ESP, and the Monroe plant an SCR followed by an ESP. Mercury removal at Meramec and Laramie River gave results similar to those presented in Figure 1 for Pleasant Prairie. At these plants, the percent mercury removal reaches a maximum and then flattens out, and there is little or no improvement regardless of the amount of carbon added. For Meramec the maximum mercury removal was about 75% at an ACI rate of 5 lb/MMacf; at Laramie River, the maximum was only 45% at the same ACI rate. It is likely that the lower removal at Laramie River was a result of the SDA removing the chloride. However, very different results were obtained at Monroe and Holcomb. At Monroe, which blends eastern bituminous coal with PRB, over 90% mercury removal was achieved at an ACI rate of 5 lb/MMacf, with similar results at Holcomb, 90% removal of mercury at an ACI rate of 6 lb/MMacf.

Field Demonstrations Using Chemically Treated Carbons

It has been determined, based on bench- and pilot-scale tests, that a limiting factor for western fuels is the relatively low level of chlorides in the coal compared to eastern bituminous coals. Therefore, one method to improve ACI performance is to treat the carbon with a halogen, chlorine, bromine, or iodine. The primary focus for many of the Phase II field demonstration projects was to use these halogenated carbons to achieve higher levels of mercury control. For example, Sorbent Technologies has developed brominated powered activated carbons (B-PACs) that have proven very effective at removing mercury at a variety of power plants (7). Some plants have achieved >90% mercury removal at a cost that is <50% of DOE's baseline estimate. Based on this and other work, it appears that halogenated carbons can improve mercury capture for low-chloride coals but provide less benefit for eastern fuels.

In similar testing led by URS Corporation, a Darco-Hg LH™ carbon (a brominated carbon) was tested at Great River Energy's Stanton Station Units 1 and 10 (8). Unit 10 is small (60 MW) boiler burning a North Dakota lignite with a SDA–FF combination, and Unit 1 is a larger boiler (150 MW) burning a PRB coal and operating an ESP. For Unit 1, the target of 60% mercury removal was achieved (ranged from 45% to 80%) at an average injection rate of only 0.7 lb/MMacf. Tests are just getting under way on Unit 1.

In addition to using halogenated carbon, additives can be used with ACI to improve mercury removal for low-rank fuels. The EERC recently completed longer-term testing at Antelope Valley Station (AVS) using a combination of SEA with ACI (9). AVS fires North Dakota lignite and has a SDA–FF. Month long test results have shown that with only 0.81 lb/MMacf ACI and 0.033 lb/MMacf of SEA, >90% mercury removal was achieved. This is compared to a near-zero baseline capture and 43% capture with ACI only.

There has also been research ongoing to utilize other sorbent materials or substrates that are not carbon-based such as amended silicates. However, these materials have yet to be demonstrated at the full-scale level.

Economics of ACI

Based on an economic study done by Hoffman and Ratafia-Brown for DOE (10), it was estimated that the capital cost for ACI equipment for a 500-MW plant would be US$3–US$4/KW. For smaller systems, the cost can be as high as US$8/KW. Typically capital costs for an ACI system include the following:

- Equipment transportation costs
- Equipment installation costs including concrete pads and injection ports
- Activated carbon storage silo
- A feeder skid that includes blowers, variable screw feeders, and control system
- Injection lances including piping and distribution manifolds

The following are variable operating and maintenance (O&M) costs associated with ACI:

- Sorbent
- Activated carbon disposal
- Power
- Operating labor
- ACI equipment maintenance
- Water (for spraying additives if used)
- Cost of money (inflation and interest)

In addition to these items another potential cost would be the loss of revenue from selling fly ash and the resultant increased disposal costs. An alternative to lost ash revenue is installation of a FF. Costs for this option include capital improvements, pressure drop (increased power requirements), general maintenance of the baghouse, and bag replacement. Table 5 presents the total O&M cost for each plant in Canada based on the carbon usage for each plant (CCME). The cost of the sorbent is 90%–95% of the total O&M cost.

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Table 5. Additional O&M Costs for Canadian Power Plants as a Result of Adding ACI (11)

Power Station	Net Capacity, MW	Units	Total O&M[1] For All Units, million $/yr (US)
Alberta			
Battle River	675	3	8.95–12.41
Sheerness	766	2	6.44–8.00
Genesee	1182	3	6.46–12.61
Keephills	766	2	4.44–8.66
Sundance	2020	6	11.50–22.40
Manitoba			
Brandon	95	1	0.30–0.59
New Brunswick			
Belldune	450	1	0[2]
Nova Scotia			
Lingan	600	4	1.32–4.92
Point Aconi	165	1	0[3]
Point Tupper	150	1	0.60–1.16
Trenton	310	2	1.23–2.37
Saskatchewan			
Boundary Dam	814	6	5.11–19.86
Poplar River	562	2	3.38–13.08
Shand	279	1	1.71–6.60

[1] O&M costs are based on a report to DOE (11).

[2] Belldune is already achieving 70% mercury control (w-FGD).

[3] Point Aconi is already achieving 60%–90% mercury control (CFB).

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MERCURY MEASUREMENT (QUARTER 2 REPORT)

With mercury regulations in place and full-scale, long-term demonstration of control technologies being conducted, measurement of mercury in combustion flue gas is of critical importance to demonstrate compliance and to allow evaluation of mercury control technologies. However, collecting a representative flue gas sample for mercury analysis presents many challenges owing to complex flue gas chemistry, high temperatures, mercury reactivity, and particulate loading. Given these challenges, many methods and instruments are available under varying degrees of development.

The most common approach for measuring mercury emissions from anthropogenic point sources consists of sampling train methods. Several common impinger-based methods include EPA Method 29, and the Ontario Hydro method (ASTM D6784-02). Each of these methods relies upon an isokinetic nozzle and filter to collect a flue gas sample, which is transported through a variety of liquid and solid sorbents to separate and preconcentrate gaseous mercury species. Quantification of the collected mercury species is then conducted using cold-vapor atomic absorption spectroscopy (CVAAS), cold-vapor atomic fluorescence spectroscopy (CVAFS), or energy-dispersive x-ray fluorescence (EDXRF).

A similar sample collection approach can also be applied to capture mercury species on a solid sampling medium through adsorption, amalgamation, diffusion, or ion exchange. These methods offer advantages in easier handling and greater stability; however, they are limited to time-averaging applications. Examples of these methods are the FAMS, QuickCEMs, and EON methods.

Real- or near-real-time data collection can only be obtained using continuous mercury monitors (CMMs). A large variety of CMMs are available utilizing a variety of flue gas-conditioning approaches; however, all commercially available instruments measure elemental mercury and use either chemical or thermal treatment to convert mercury. As they are currently configured, CMMs possess several challenges to long-term, low-maintenance operation, the most significant of which include sample collection and flue gas conditioning. Mercury species reactivity and particulate loading make transporting a representative gas sample to the instrument a challenge and require heated sample lines and particulate removal techniques which prevent the buildup of a filter cake. Flue gas conditioning is an area where the greatest development is occurring. Wet-chemistry methods have typically been used to convert mercury to the elemental form that the analyzer can detect. These solutions are corrosive or caustic chemicals, and challenges associated with their use are considered the limiting factor in CMM reliability. Dry conversion units are now being marketed and are being used in field demonstrations. These systems focus on high-temperature catalysts and thermal reduction to convert oxidized mercury to the elemental form for analysis. It is anticipated that developments in this area will be the critical factor in ensuring real-time mercury measurements can be conducted reliably under steady-state operation.

The new regulations for mercury emissions from U.S. coal-fired boilers will require some form of continuous monitoring. EPA has announced that two measurement methods will be accepted: the sorbent trap methods as prescribed by 40 CFR, Part 75, Appendix K (Appendix K), and CMMs. Initially a number of utilities will opt for the sorbent trap methods; however, this could change as more robust CMMs become available. For both of these methods, EPA has established performance specifications (PS 12A), which relate to the setup, certification, and quality assurance/quality control (QA/QC) for each method. A summary of these specifications is provided; details can be found at www.epa.gov/mercuryrule.

Since May 2005, when the Mercury Information Clearinghouse second quarterly report was last updated, there have been a number of developments in mercury measurement, including the following:

- Additional experience gained with 40 CFR, Part 75, Appendix K Specifications
- Establishment of performance specifications and clarification of QA/QC requirements including relative accuracy test
- Additional experience gained with next-generation CMMs
- Possibility of an instrument-based reference method for mercury measurement

Additional Experience with 40 CFR, Part 75, Appendix K Specifications

To date, mercury emissions at over 85 stacks have been characterized using the two-section traps or the QuickCEM method (Dene). However, the QuickCEM as initially configured used only two sections, and Appendix K now requires the use of a third trap section designated for QA/QC purposes. The first two sections are still used to trap the gas-phase mercury and ensure there is no breakthrough. The third section is spiked with a known quantity of elemental mercury, and a correction factor based on the recovery is applied to the concentrations measured in the first two sections. Results presented at a recent Electric Power Research Institute (EPRI)-sponsored mercury measurement workshop indicated there are problems with the consistency of the spiking and recovery of the third section. Spike recoveries as low as 30% have been observed. The existing spiking method needs to be refined or a new method developed in order to ensure reliable and consistent third sections that can be used for QA/QC. The addition of the third section has also increased the cost of the dry sorbent method. Traps with a spiked third section can cost from $590 to $710 per trap to purchase and analyze. This cost does not include the cost of equipment or labor. It is expected that during the next 1–2 years, costs will be reduced considerably as more cost-effective spiking and analytical methods are developed.

QA/QC Requirements for Mercury Measurement RATAs

In the draft of PS 12A the paired reference method samples were required to be within 10% of the relative standard deviation of the results. That requirement was changed in the final version. The paired samples are now required to meet the following relative difference (RD) criteria:

$$\mathrm{RD} = \frac{\left|C_a - C_b\right|}{(C_a + C_b)} \times 100\%$$

$\mathrm{RD} \leq 10\%$ for Hg concentration $> 1\ \mu g / m^3$

or

$\mathrm{RD} \leq 20\%$ for Hg concentration $\leq 1\ \mu g / m^3$

Additional Experience Gained with Next-Generation Continuous Mercury Monitors

In addition to the use of CMMs during large-scale mercury control demonstration projects, EPA (Segall) has been evaluating several commercially available CMMs at two tests sites (Sites 1 and 2), which both burn eastern bituminous coals. Instruments that have been evaluated to date include the Tekran Model 3300, Thermo Electron Mercury Freedom System, Horiba/NIC DM-6B, Forney/Genesis Model 6500, Durag HM-1400, and the Opsis HG200. In addition to these instruments, Appendix K sorbent traps were also tested. All of the instruments at some point have passed the initial certification requirements of PS-12A, but to date, only two instruments have passed at least one of the RATAs: the Thermo Electron (passed at the first site) and Tekran systems (passed at both sites). EPA is planning additional RATAs in 2006. The Thermo Electron instrument will be commercially available in late 2005 or early 2006.

Now that EPA has issued performance specification for mercury monitors, vendors have a much better idea of what will be required As a result, mercury measurement technology is moving forward rapidly, and reliable, rugged systems should be available well before the January 1, 2009, deadline. Mercury control demonstration projects are now using CMMs for long-term monitoring of mercury concentrations at stacks and other locations within the power plant with good success. These tests (3 to 6 months in duration) should provide additional data as to the overall reliability of CMMs.

An Instrument-Based Reference Method for Mercury Measurement

A major concern for both certifying a CMM based on PS 12A and ongoing QA/QC requirement under 40 CFR, Part 75 is the requirement that all RATAs are to be conducted using the Ontario Hydro method. Obtaining nine valid paired sample trains is a challenge and will be very expensive for utilities. Therefore, EPA is trying to develop criteria for an instrument-based reference method. While a draft procedure may be available soon, there will be some major obstacles to overcome before an instrument-based reference method can be used. One of the main obstacles is the ability to dynamically spike both elemental (Hg^0) and oxidized mercury (Hg^{2+}) to the tip of the sampling probe. Dynamic spiking requires the addition of a small amount of spike gas into the sample gas matrix. This is not required in the new regulations for the CMMs. All of the major CMM manufacturers are working on developing some type of mercury generation and delivery system. In order for the results from these systems to be accepted, they will need to be National Institute of Standards and Technology (NIST)-traceable. EPA has asked NIST to help provide traceability for gas standards. NIST is currently working on certification of Hg^0 gas cylinders and mercury gas generators, such as those provided by the PS Analytical and Tekran systems, for delivering Hg^0. They have determined that the expanded uncertainty for the gas cylinders is approximately 6%, which is an order of magnitude higher than they usually get with other types of gas cylinders and not acceptable as a standard. A new equation for the mercury vapor pressure curves is also being proposed by NIST. Currently NIST, PS Analytical, and Tekran all use slightly different equations for Hg vapor pressure. NIST also plans to look at the long-term stability of the gas cylinders and mercury generators.

ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES (QUARTER 3 REPORT)

A variety of approaches for mercury control are under development, ranging from combustion modification to multipollutant technologies. Many of these unique technologies have passed the bench- and pilot-scale developmental phases and are now being tested at full scale. Many of these technologies were discussed in Quarter 3 and updated in Quarter 6 and include:

- Pretreatment of coal to remove mercury.
- Combustion modification and in situ generation of sorbents.
- Non-carbon-based sorbent and amended silicates.
- Stationary mercury traps positioned in the flue gas stream.
- EnviroScrub Pahlman Process.
- Combined oxidation of NO_x and mercury.
- Mercury control with the Advanced Hybrid™ Filter.

Since the amount of mercury in coal is very small (typically about 0.1 µg/g), the total amount of mercury input (and potential emissions) for a 500-MW plant in a year is only about 300 lb. This suggests that there is potential for generating a minimum amount of waste material if the mercury can be effectively captured and concentrated. On the other hand, if the captured mercury is highly dispersed in waste material or by-product, the mercury must be proven to be in a stable form so that there is little possibility of reemission into the atmosphere. This will be a significant factor in the development of new technologies for long-term mercury control.

Pretreatment of the Coal to Remove Mercury

Removal of mercury from the fuel prior to combustion is a mercury control approach that has been considered for many years. Standard coal-washing methods for bituminous fuels to remove pyrites and other mineral matter result in the removal of some of the mercury; however, not to the extent that would be needed to meet future control requirements. Coal washing for ash reduction has proven to be effective primarily for bituminous fuels with large mineral grains. With subbituminous and lignite fuels, conventional coal washing is not effective because of the way the inorganic material is distributed within the coal. However, for subbituminous coals, deep cleaning or pretreatment of the coal, such as with the KFx K-Fuel process, has the potential to remove a significant fraction of the mercury.

A large-scale plant that can produce 750,000 tons per year of K-Fuel is nearing completion. The actual level of Hg reduction in the final fuel product as well as the fate of the removed mercury within the process will be demonstrated when the process becomes fully operational. PRB coals already account for about one-third of U.S. production and represent most of the growth in U.S. production in the last 10 years. Whether a significant portion of that production could eventually be upgraded as K-Fuel or similar products is primarily an economic one and highly dependent on tighter regulations. The current upward trend in world oil prices and focus on CO_2 emission reduction would both appear to make K-Fuel more attractive in the marketplace. The success of the first full-scale plant as well as the strength of the market will determine how fast new capacity is developed to meet demand.

Another example of fuel-upgrading is the Great River Energy project, funded by DOE, which focuses on drying of high-moisture North Dakota lignite. The process does not claim to remove mercury from the lignite but upgrades the fuel with waste heat, resulting in overall plant efficiency improvement, with some subsequent reduction in mercury emissions. However, even with mild thermal processing of a raw fuel, there is potential for removing some of the mercury along with the moisture by increasing the drying temperature.

In the recent Phase III RFP issues by DOE, one of the topics was new coal-cleaning technologies that would enhance mercury removal for lower-rank fuels.

Combustion Modification and in Situ Generation of Sorbents

An attractive approach to mercury control is to enhance the capture of mercury by modification of the combustion process to produce fly ash or unburned carbon that results in better mercury retention. The thought is that either increased carbon in the ash or generation of carbon in the ash with the appropriate characteristics will enhance mercury capture. Since low-NO_x burner (LNB) technology is already known to produce more carbon in the ash, a logical extension of LNB approaches is to specifically modify the process for enhanced mercury control, such as is being investigated in a DOE-funded project by General Electric Energy and Environmental Research Corporation (GE EER) and Lehigh University. Another interesting approach is extracting a portion of the coal from the combustion zone and then quenching it prior to complete combustion to produce a material with good mercury sorption characteristics. This approach is know as the Thief process and is being developed at DOE NETL. Another somewhat similar approach is detailed in two EPRI patents that describe a method for in situ activation of carbon-based sorbents by injecting carbonaceous material at the appropriate location in a boiler.

The largest single advantage for all three control technologies is that mercury capture could potentially be achieved with the coal. The GE EER process is the furthest along and is being tested at full scale. Of the three processes, this is also the simplest and would appear to be most likely implemented in the near future. One of the main concerns is that the process depends on incomplete combustion and the presence of significant unburned carbon in the ash. This makes fly ash utilization and disposal more challenging.

The Thief process appears to offer more flexibility in achieving a much higher-capacity carbon but with additional complexity. Since the Thief process can include injection downstream of a primary particulate control device, it also offers an opportunity for separating the fly ash from the spent carbon. However, similar techniques can be implemented with many sorbent injection technologies.

The EPRI process offers flexibility with the raw feed materials which may offer an opportunity to generate a very highly reactive, high-capacity sorbent. Since the generated sorbent material does not have to be collected and reinjected, the process may offer an opportunity to generate a very fine particle-size material. If so, in-flight capture would be enhanced, making it an attractive application for ESP-controlled units. This process, however, has not been substantially tested, so near-term development is unlikely.

Non-Carbon-Based Sorbent, Amended Silicates™

ADA Technologies, Inc., has been developing a non-carbon-based mercury sorbent for several years. The Amended Silicates material will be tested in 2006 under the DOE-funded large-scale mercury demonstration program. Amended Silicates, LLC (a joint venture of ADA Technologies, Inc., and CH2M Hill), Littleton, Colorado, will test the material at Cinergy’s 175-MW Miami Fort Unit 6 that burns bituminous coal. The research team also includes the EERC, Western Kentucky University, and Boral Materials Technologies. Current plans are for this testing to begin in February–March 2006.

A sorbent that is non-carbon-based is highly attractive because of the potential for ash utilization without concern over additional carbon in the ash. Based on material properties and test results to date, no impact of the material on fly ash utilization is expected.

Critical developmental questions concern the level of control that can be demonstrated compared to existing and new activated carbons and the stability of the mercury in the ash. The ability to manufacture large amounts of the material at a reasonable cost also needs to be demonstrated.

The concept has moved beyond the bench-scale level and has been tested at the pilot level at a coal-fired power station. The current DOE-funded project will take the evaluation to the full-scale demonstration level.

Stationary Mercury Traps Positioned in the Flue Gas Stream

MerCAP™

The general MerCAP (Mercury Control via Adsorption Process) concept is to place fixed structures into a flue gas stream to adsorb mercury and then periodically regenerate them and recover the captured mercury. While a variety of regenerable sorbent materials could be used, most of the development work has focused on the use of gold-coated substrates in the form of parallel plates spaced about 0.5 to 1 in. apart. Previous work has shown that the level of control is impaired in an unscrubbed flue gas environment. Subsequently, current development efforts seek to achieve high levels of mercury removal in scrubbed flue gases, either downstream from a spray dryer scrubber or a wet scrubber.

DOE NETL is currently funding a demonstration of MerCAP, conducted by URS Group. Testing has already been completed at Great River Energy’s Stanton Station, which burns North Dakota lignite, where MerCAP sorbent structures treated 6 MW_e equivalence of flue gas when retrofitted into a single compartment in the outlet plenum of the Unit 10 baghouse. Additional testing is planned this year at Southern Company Services’ Plant Yates, which burns eastern bituminous coal.

The MerCAP process by itself has the potential to achieve >90% mercury removal when installed downstream of a scrubber. However, any upstream removal of oxidized mercury by the scrubber makes the total mercury removal of >90% even more likely. With regeneration, the mercury can be isolated for disposal, and since the mercury can be concentrated, permanent sequestering of the captured mercury is possible with a minimum volume of material.

Since the concept depends on the amalgamation of mercury with gold, a key concern is the absorption ability of the gold as well as the regeneration ability and lifespan of the material. A very critical developmental question is how sensitive the material is to small concentrations of HCl or other gases that affect the absorption of mercury. In longer-term testing up to 5000 hr, actual mercury removal levels have only been in the range of 30%–40%. However, at the recent AQV Conference, URS reported that new regeneration technologies are being employed that enhance overall removal.

W.L. Gore & Associates, Inc.,-Promoted Felt Filter Bag Inserts

W.L. Gore & Associates, Inc., has developed an innovative technology for control of mercury emissions in flue gas streams. The configuration involves a mercury control filter placed inside the existing particulate control filter bag. This concept is similar to the MerCAP technology in that both attempt to achieve mercury capture by placing an adsorbent material in a convenient location within the system and then periodically (e.g., every 6 months) removing the components for regeneration and/or mercury concentration.

The Gore mercury filter system has been tested at the small pilot-scale level both at EPA facilities and at the EERC. Operationally, the mercury filter elements did not appear to impair the pulse cleaning of the bags. Results showed that, initially, nearly 100% mercury removal could be achieved. However, for the materials tested, early breakthrough occurred under some conditions. The process appears to have potential, but currently there are no known testing programs outside of Gore to further develop this technology.

EnviroScrub Pahlman Process

A multipollutant control technology that is truly unique is being developed by EnviroScrub Technologies Corporation. In 2000, EnviroScrub acquired the dry Pahlman™ scrubbing technology, which can simultaneously remove SO_x, NO_x, and Hg. The Pahlman process uses a sorbent composed of oxides of manganese. These specialized sorbents have been generically named Pahlmanite™ sorbent in honor of the late Dr. John E. (Jack) Pahlman who led the early research and development work on the process.

As presented, the technology is placed downstream of a particulate control device so that the captured mercury will not be mixed with the fly ash. This facilitates fly ash disposal as well as fly ash utilization as a by-product.

The concept has moved beyond the bench-scale level and has been tested with a 1000-acfm trailer-mounted slipstream device at a number of coal-fired power stations. However, only the collection step has been demonstrated. The fairly complex regeneration and recycling steps have not been tested. Much longer-term and larger-scale testing needs to be completed to address all aspects of the process, but little additional development work has been done within the last year.

Combined Oxidation of NO_x and Mercury

Two processes that oxidize mercury along with NO_x for capture in an ammonia-based wet scrubber are unique. Both the BOC LoTOx™ and ECO™/Powerspan are NO_x control approaches whereby the NO_x is oxidized to a soluble form to allow capture in a wet scrubber. Even though the oxidation approaches for the two processes are different, both of these processes claim that elemental mercury is also oxidized to HgO and subsequently captured in the wet scrubber along with SO_2 and NO_x. Both of the processes are coupled with an ammonia-based wet scrubber.

LoTOx™

The BOC LoTOx system is based on the patented Low-Temperature Oxidation (LTO) Process for Removal of NO_x Emissions, exclusively licensed to BOC Gases by Cannon Technology. Marsulex Inc. and the BOC Group have signed a joint marketing agreement that will enable each company to offer electric utilities an integrated multipollutant control solution that provides maximum compliance for emissions of sulfur dioxide, sulfur trioxide, nitrous oxides, mercury, and other heavy metals in conjunction with ammonia-based wet scrubbing. The LoTOx system is a NO_x removal system that injects ozone into the flue gas stream to oxidize insoluble NO_x to soluble oxidized compounds. The mercury removal is achieved by oxidizing elemental mercury with ozone to produce soluble HgO, which is captured in a downstream wet scrubber. The current status of the LoTOx process for mercury control is unknown.

ECO/Powerspan

Powerspan Corporation is the primary researcher and proprietary owner of the ECO process. However, Powerspan has entered into an alliance with Wheelabrator Air Pollution Control, Inc., to commercialize the system. Powerspan and First Energy jointly funded the latest pilot plant. In addition, DOE awarded a grant to Powerspan to optimize the mercury removal capability of the technology on a 50-MW demonstration facility at the R.E. Burger Plant.

In the ECO process, flue gas exiting the ESP or FF is routed to the ECO reactor where it is exposed to a high-voltage discharge, which generates high-energy electrons. These high-energy electrons initiate chemical reactions that lead to the formation of oxygen and hydroxyl radicals. These radicals then oxidize the pollutants in the flue gas, leading to the formation of particulate matter and aerosol mist. These components are removed downstream in an ammonium salt wet scrubber and wet ESP forming the ammonium sulfate and ammonium nitrate by-products. Approximately 90% of the NO in the flue gas is oxidized to NO_2 and is removed in the scrubber (the other 10% remains unoxidized). Less than 10% of the SO_2 in the gas is oxidized to form SO_3, which eventually forms sulfuric acid (H_2SO_4). Elemental mercury vapor is oxidized to form mercuric oxide (HgO), which is removed by the wet scrubber/wet ESP.

Extensive mercury removal results have been reported in the last year from the pilot unit tests at the Burger Plant. Results showed that over 90% mercury removal was achieved, but most of the inlet mercury was already oxidized. Additional testing in which supplemental elemental mercury was injected upstream showed that up to 75% of the elemental mercury was converted to oxidized mercury across the reactor, and the total mercury removal for the system was still over 80%. Testing to evaluate removal of the collected mercury from the scrubber liquor showed that well over 90% of the mercury was removed so that in many cased the mercury level in the scrubber liquid was below detection limits.

FirstEnergy recently announced plans to install an ECO system on the 215-MW Unit 4 boiler at its Bay Shore Plant in Ohio.

Mercury Control with the *Advanced Hybrid*™ Filter

Since 1995, DOE has supported development of a new concept in particulate control, called the advanced hybrid particulate collector marketed as the *Advanced Hybrid* filter. The *Advanced Hybrid* filter combines the best features of ESPs and baghouses to provide ultrahigh collection efficiency, overcoming the problem of excessive fine-particle emissions with conventional ESPs. Additionally, it solves the problem of reentrainment and re-collection of dust in conventional baghouses. The *Advanced Hybrid* filter also appears to have unique advantages for mercury control over baghouses or ESPs as an excellent gas–solid contactor. Since most of the sorbent material will collect on the perforated plates, there will be minimal effect on the pressure drop across the filter bags. In addition, better gas–solid contact is achieved than in conventional ESPs because the distance that gas must cross streamlines to reach sorbent particles is much smaller than in ESPs. Mercury control with commercially available sorbents was demonstrated with a 2.5-MW *Advanced Hybrid* filter at the Big Stone Power Plant, which burns subbituminous coal from several different PRB mines.

Over 90% mercury control was demonstrated at low carbon addition rates upstream of the *Advanced Hybrid* filter with commercially available NORIT FGD activated carbon. However, the level of control was dependent on other flue gas components. One of the very interesting findings was the discovery that when the plant cofired a small amount of tire-derived fuel, the level of mercury captured in the fly ash, the fraction of oxidized mercury in the inlet flue gas, and the level of total mercury removal with activated carbon all were significantly increased, likely due to the increased chlorine content from tire-derived fuel. Another significant result was that the injection of activated carbon for mercury control had no effect on bag-cleaning interval or pressure drop. The perforated plate geometry of the *Advanced Hybrid* filter allows sufficient gas–solid contact to achieve over 90% mercury removal at low carbon addition rates, even though most of the carbon is collected on the perforated plates.

The concept for mercury control has moved beyond the bench scale and has been tested at the 2.5-MW pilot level at a coal-fired power station. However, there are currently no plans for a full-scale demonstration to evaluate mercury control effectiveness *with the Advanced Hybrid* filter.

RERELEASE OF MERCURY FROM COAL COMBUSTION BY-PRODUCTS (QUARTER 4 REPORT)

At the time the CEA Quarter 4 report was written, only a limited amount of empirical data were available on mercury stability in coal combustion by-products (CCBs). Early work on rerelease of mercury from CCBs focused on developing and adapting methods to determine the potential for mercury to be rereleased from CCBs. Since that time, additional data have become available including results of field testing from mercury in ground and surface water at CCB disposal sites and vapor-phase mercury measurements at disposal and utilization sites.

In August 2005, DOE NETL selected Frontier Geosciences (Seattle, Washington) to conduct research on by-products generated from DOE's mercury control program. As the majority of mercury control technologies result in additional concentrations of mercury being deposited in the fly ash or FGD material, Frontier will analyze multiple by-product samples for mercury and other elements from 31 different field sites. The tests will include volatilization, leaching (both abiotic and biotic), total element concentrations, and limited halide analyses (1). It is anticipated that some of the materials to be evaluated under the new DOE NETL program will include those with combinations of activated carbon and mercury capture-enhancing agents. Additional work is also expected on FGD materials under this program.

The most significant concern associated with CCB management and mercury emission controls continues to be the use of ACI to achieve mercury capture in the particulate control device. The result of ACI is an elevated carbon and mercury content in fly ash which has implications on ash reuse and raises concerns related to the stability of mercury in subsequent uses of the fly ash. The major utilization application for coal combustion fly ash is concrete and concrete products. The impact of ACI on ash suitability for the concrete industry has been apparent and reported by Starns (2) for an ACI demonstration at We Energies' Pleasant Prairie Power Plant. Additional questions have been raised more recently about how additives, added to ACI systems to improve mercury capture, will impact not only fly ash, but other CCBs as well. While these additives are designed to enhance the removal of mercury from emissions, the fate of these chemical additives remains unclear and will also be investigated as mercury emission control testing continues.

The other CCB being evaluated relative to mercury capture and rerelease is FGD materials. FGD effluents had only been evaluated for mercury rerelease on a very cursory level at the time of the original report submission. Since that time, additional work has been done to determine total concentrations of mercury in various FGD materials as well as on the rerelease of mercury from FGD materials under different environmental conditions.

Stability of Mercury on CCBs

Total mercury concentrations for CCBs are of interest because these data are valuable in developing mercury balances across emission control systems. Additional data have been reported by several groups primarily on those CCBs most directly impacted by potential mercury emission controls. Table 6 provides a summary of data on fly ash and FGD materials collected without and

Table 6. Total Mercury in CCBs and Mercury-Leaching Results Reported by Various Groups

Information Source	CCB Type	Number of Samples in Sample Set	Range of Total Hg (µg/g) Reported	Leaching Method	Number of Samples in Sample Set	Range of Mercury Leachate Concentrations Hg, µg/L
EERC (3)	Fly ash without Hg control	40	<0.01–2.03	Batch DI H_2O	72	<0.01–0.32
EERC (3)	Fly ash with Hg control	28	0.15–120	Batch DI H_2O	43	<0.01–0.07
EERC (3)	FGD material without Hg control	10	<0.01–0.22	Batch DI H_2O	18	<0.01–0.40
EERC (3)	FGD with Hg control	1	0.33			
Schroeder and Kairies (4)	FGD gypsum	2	0.140–0.142			
Schroeder and Kairies (4)	FGD sludge – top layer (from nonoxidized wet scrubber)	2	2.90–13.0			
Schroeder and Kairies (4)	FGD sludge – bottom layer (from nonoxidized wet scrubber)	2	0.072–0.70			
Kim and Schroeder (5)	Fly ash without Hg control	3	0.074–1.67	Column with H_2O/ HAc/ Na_2CO_3/ SP/ H_2SO_4	3	12.2–47.8 ng/g 44.7–1614.8 6.69–517.0 0.39–9.34 12.2–68.3
Kim and Schroeder (5)	Fly ash with Hg control	6	0.348–92.1	Column with H_2O/ HAc/ Na_2CO_3/ SP/ H_2SO_4	6	2.74–845.8 ng/g 35.5–410.1 8.04–1263.1 2.71–464.8 4.15–147.7
Withum (6)	Fly ash	17	0.06–1.49	Batch leaching at pH 2.8/ pH 4.9/ DI H_2O	17	All <1 All < 1 All <1
Withum (6)	FGD sludge (not fixated)	5	0.21–0.65	Batch leaching at pH 2.8/ pH 4.9/ DI H_2O	5	<1–10.9 <1–5.2 All <1
Withum (6)	FGD sludge (fixated)	9	0.26–0.90	Batch leaching at pH 2.8/ pH 4.9/ DI H_2O	9	<1–6.6 <1–2.5 All <1
Withum (6)	FGD gypsum	3	0.33–0.52	Batch leaching at pH 2.8/ pH 4.9/ DI H_2O	3	All <1 All <1 All <1
Withum (6)	Bottom ash	2	0.01–0.04	Batch leaching at pH 2.8/ pH 4.9/ DI H_2O	2	All <1 All <1 All <1
Hower et al. (7)	Fly ash	85	0.000–0.894			
Hower et al. (7)	Bottom ash and boiler slag	27	0.000–0.086			
Hower et al. (7)	FGD (predominantly sulfate)	7	(Av value) 0.176			
Hower et al. (7)	FGD (predominantly sulfite)	3	(Av value) 0.463			
Gustin (8)	Fly ash without mercury control			Batch leaching SPLP	23	0–8 ng/L
Gustin (8)	Fly ash with activated carbon			Batch leaching SPLP	9	0–2 ng/L
Gustin (8)	FGD			Batch leaching SPLP	8	0–4 ng/L
Starns (9)	Fly ash without mercury control (baseline)	2	291–734 ng/g	Batch leaching	2	<0.0002 mg/L
Starns (9)	Fly ash with activated carbon	2	1250–1520 ng/g	Batch leaching	2	<0.0002 mg/L

with mercury emission controls present. These data are presented as ranges reported by the referenced researchers and may include data reported previously.

Hower et al. (10) also investigated the mercury concentrations of fly ash collected in various hoppers of an ESP at one power plant. He concluded that mercury capture is fairly uniform through an ESP system.

Leaching[1]

Table 6 also summarizes recent leaching data reported in several forums since October 2005. EPA has performed leaching tests on a variety of CCB samples including fly ash samples with activated carbon, fly ash from systems with SCR on and off, and FGD materials (11), but no data were reported for inclusion in this update. The available leaching data indicate strong agreement among researchers (3–6, 8–9) that the mobility of mercury from direct leaching is very limited. In fact, the researchers (3, 5) have concluded that:

- The leachate concentrations of mercury do not correlate to total mercury concentrations for fly ash samples.

- Mercury in CCBs has extremely low mobility based on direct leaching.

Researchers (3, 5, 9, 12, 13) also all have reported that a range of leaching methods and leachate solutions provide similar results indicating extremely low concentrations of mercury in leachates. They and Schroeder (3, 5, 11) all have indicated that leachates from CCBs have mercury concentrations below the Drinking Water maximum contaminant level (MCL) of 0.002 µg/mL. Thornloe (11) also stated that test values for mercury leachates indicate that engineering controls for CCB disposal are protective when compared both with MCL and the recommended ambient water quality criteria. Other data reported (3, 8) on leaching of fly ash samples without and with mercury control (activated carbon) indicated that the leachate concentrations of mercury are lower from fly ash with activated carbon present than fly ash that was generated without mercury controls, even though the total mercury content can be significantly higher for samples with activated carbon.

Vapor Release[2]

Evaluations of potential for vapor-phase rereleases both at elevated and ambient temperatures have been ongoing by several groups.

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[1] The authors of the various documents have reported data in several different formats. The following concentrations are equivalent: ppm (parts per million) = µg/g; ppb (parts per billion) = µg/kg, ng/g, µg/L; and ppt (parts per trillion) = pg/g, ng/L. The EERC has used ppm, ppb, and ppt to express concentrations associated with solid materials and vapor-phase releases. µg/L and ng/L have been used for concentrations in liquids such as leachate concentrations.

[2] The authors of the various documents have reported data in several formats. The following concentrations are equivalent: ppm (parts per million) = µg/g; ppb (parts per billion) = µg/kg, ng/g, µg/L; and ppt (parts per trillion) = pg/g, ng/L.

Elevated Temperature Vapor-Phase Rerelease

Withum (6) performed volatilization tests on fly ash, FGD materials, spray dryer solids, and products that incorporated CCBs (aggregate, cement, and wallboard) at 38°C and 60°C (100° and 140°F) with a continuous Hg-free nitrogen purge. The experiment duration was 6 months and indicated no detectable mercury loss from most samples; however, Withum did indicate that there were sampling and storage difficulties with the samples used in the effort. Hower et al. (10) used thermal gravimetric analysis (TGA) to evaluate the potential for mercury releases at elevated temperatures and concluded that mercury was not released until 300°C. Starns evaluated baseline fly ash samples (without mercury control) and comparable fly ash samples with PAC from two different demonstrations of mercury emission controls for thermal stability and reported that for both demonstrations, the thermal stability of mercury increased when PAC was present in the sample, as evidenced by increased first mercury desorption peaks (240°C for baseline compared to 315°C for fly ash–PAC for one site and 358°C for baseline compared to 419°C for the fly ash–PAC from a second site). Pflughoeft-Hassett (3) generated mercury thermal desorption curves for 61 CCBs, including 36 samples without mercury control and 25 samples with mercury control. The samples were primarily fly ash but also included various types of FGD materials. Most samples generated either one or two mercury peaks with a range of 0–4 peaks. The temperature of the mercury peaks ranged from 256° to 750°C, with an average of 429°C. Some samples continued to show increasing mercury release at 750°C, so the peak temperature at which the mercury was released could not be determined. FGD materials tended to release mercury at a lower temperature than fly ash. Fly ash samples with activated carbon were more likely to indicate continued mercury release at 750°C than fly ash generated without any mercury controls present.

Ambient-Temperature Vapor-Phase Rerelease

Gustin et al. (8) reported on ambient-temperature releases for air–CCB mercury exchange experiments performed under varied laboratory conditions (temperature, time, light, and dark). Gustin also investigated the impact of loss on ignition (LOI) and moisture on mercury release in laboratory experiments. She concluded that deposition (or sorption) was the predominant atmospheric flux (air–CCB mercury exchange) for fly ash from bituminous and subbituminous coal. Fly ash from lignite was found to emit mercury. Fly ash with activated carbon present sorbed mercury from the atmosphere at a higher rate than fly ash without activated carbon. Wet FGD material had a higher potential to release mercury to the atmosphere than dry FGD material or fly ash, and water content greatly influenced emission or release rate.

The ambient-temperature release of mercury was also investigated by Pflughoeft-Hassett (3) on 19 CCB samples. In long-term release measurements, six of the samples showed overall mercury release and 13 samples showed overall mercury sorption. Pflughoeft-Hassett also indicated that a wet FGD material included in these experiments released considerably more mercury than fly ash or dry FGD as long as the sample remained wet, but after the water evaporated from the sample the mercury release rate slowed.

Microbiologically Mediated Release

The EERC (3) continued its efforts to quantitate mercury rerelease from fly ash and FGD materials on exposure to microbiological activity. Improved methods were described and included measurement of the rerelease in the liquid phase as well as the vapor-phase for elemental and organomercury. Aerobic and anaerobic glucose-fed conditions were used in the experiments on fly ash and wet limestone FGD filter cake material. The fly ash samples evaluated were both from lignite-fired power plants with total mercury contents of 0.689 µg/g and 0.785 µg/g. The FGD material had a mercury content of 0.218 µg/g and a significant natural population of sulfate-reducing bacteria. The FGD material had an average vapor-phase release of 0.13 pg/g/day under anaerobic conditions and 9.44 pg/g/day under aerobic conditions during a 3-week time period when the samples were being pH-stabilized with buffer addition. This release was attributed to the naturally occurring sulfate-reducing bacteria in the FGD material. Following the preliminary pH adjustment phase, the highest vapor-phase release of both elemental and organomercury was from the FGD material under aerobic conditions, even though it had the lowest level of total mercury. Analytical difficulties were noted and interfered with the final analysis of vapor-phase mercury release from the FGD material. The fly ash samples released similar levels of vapor-phase mercury in these experiments ranging from 0.036 to 0.147 pg/g/day elemental mercury and from 0.108 to 1.25 pg/g/day for organomercury. Organomercury was also measured in the liquid separated from these experiments. Again the FGD material had significantly greater concentrations of organomercury in solution compared to the fly ash samples with a release of ~1800 pg/g for anaerobic conditions and a release of ~400 pg/g for aerobic conditions. Fly ash releases were 70 pg/g and 170 pg/g for anaerobic conditions and 128 pg/g and 195 pg/g for aerobic conditions. The EERC indicated that the data were variable and that work would continue on the experimental release method and the analytical methods to address interference from sulfur in the samples and the development of mold in the samples during the experiments.

Field Studies of Mercury Releases

Disposal Site Water Evaluations

Withum (6) evaluated groundwater collected at active fly ash and FGD disposal sites using existing monitoring wells. No mercury was detected in any monitoring well samples. Ladwig (14) also collected and evaluated a variety of water samples from a large number of CCB disposal sites (including ash ponds, ash landfills, and FGD disposal sites) across the United States. Samples collected and analyzed were from the following locations depending on the site:

- Leachate wells
- Lysimeters
- Leachate collection systems
- Drive point
- Direct push
- Pond/seep grab
- Sluice lines

Data were summarized by site type (see Figure 2), and Ladwig indicated that the mercury concentration range was low at 0.25 to 60 ng/L, with a median concentration of 3 ng/L. Methyl mercury was generally less that 1 ng/L, and dimethyl mercury was usually not detected.

Field Vapor-Phase Releases

Xin et al. (16) presented results of field studies designed to determine mercury flux. A variety of disposal sites at facilities utilizing bituminous, subbituminous, and lignite were included in Xin's work. Table 7 summarizes Xin's findings.

A summary of similar work also performed by University of Nevada Reno (UNR) indicated that field data were consistent with laboratory data, with bituminous and subbituminous fly ash disposal sites sorbing mercury from the atmosphere, while lignite-derived fly ash exhibited emissions even though in the field that emission rate was low and comparable to surrounding soil (8).

The EERC collected mercury from ambient air at near-surface locations at one field site in conjunction with the UNR work (16) and quantitated the concentrations of elemental and organomercury. Elemental mercury concentration ranged from 0.541 ng/m^3 (the FGD + bottom ash and mill rejects) to 1.456 ng/m^3 (above FGD + mill rejects). Samples collected above natural grassland upwind from the associated power plant had 0.640 ng/m^3 of mercury. For organomercury, the sample collected above the natural grassland gave a reading of 0.017 ng/m^3. Samples collected above various disposal sites ranged from 0.006 ng/m^3 (FGD + pyrite) to 0.354 ng/m^3

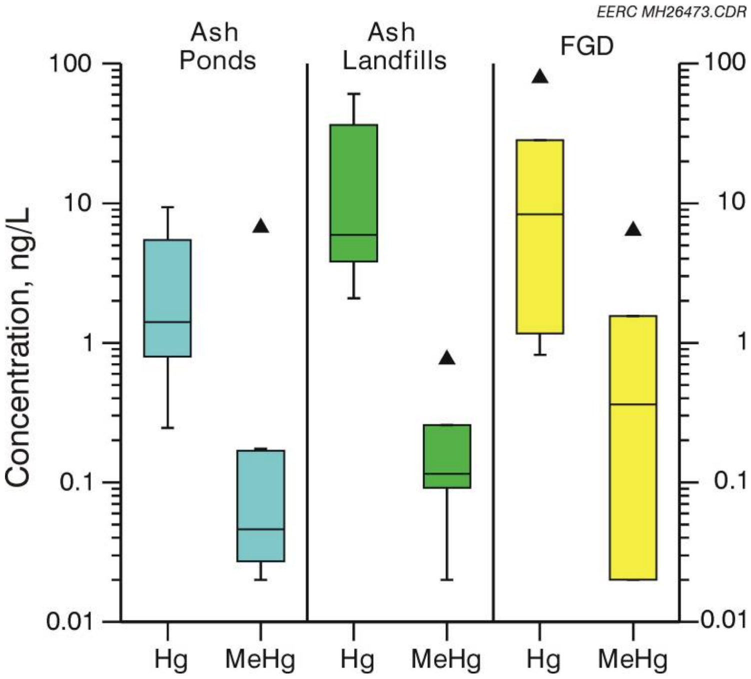

Figure 2. Field leachate – mercury speciation (15).

Table 7. Summary of Field Mercury Flux Data Presented by Xin et al. (16)

Coal Type Used at Associated Power Plant	Material Type Where Flux Measurements Were Taken	Mercury Flux (+ indicates release, - indicates sorption), ng/m^{2}hr
Bituminous–Subbituminous Blend	Vegetated top soil over fly ash	-0.1
Bituminous–Subbituminous Blend	Barren fly ash	+0.9
Bituminous–Subbituminous Blend	Background soil	+0.5
Lignite	Vegetated top soil over fly ash	+1.1
Lignite	Barren fly ash	+1.1
Lignite	Unstabilized wet FGD material	+0.8
Lignite	Wet FGD material + fly ash or pyrite	+11.2 or +10.9

(FGD + fly ash); however, the value measured for the FGD + fly ash was significantly higher than other values (0.006–0.052), and the standard deviation was also high.

Rerelease of Mercury from CCBs in Select Utilization Applications

Gustin et al. (8) used outdoor experiments to evaluate the potential for rerelease of mercury from CCBs. Her experiments were designed to simulate soil stabilization, compacted CCB pads, and agricultural soil amendment, and while work will continue, preliminary data indicated that the mercury flux from CCB-amended substrates was not significantly different from soils used. Golightly et al. (17) captured the volatile mercury species in air directly above curing concrete specimens. The specimens included OPC (ordinary portland cement) concrete, concrete with 33% fly ash added, concrete with 55% fly ash added, and concrete with 33% fly ash and 0.5% mercury-loaded PAC. Sampling was performed at 2 days, 28 days, and 56 days during dry curing at 40°C. Results are shown in Table 8. Golightly et al. (17) concluded that laboratory experiments suggested that curing fly ash concretes contribute little to global anthropogenic mercury emissions but that field work needs to be performed.

Another area of investigation of potential rerelease of mercury from CCBs has focused on FGD gypsum which is used in the production of wallboard. Since gypsum (natural or by-product) needs to be calcined before use in the wallboard-manufacturing process, questions have been raised as to the potential for mercury to be released during the calcining or other phases of the process. Heebink et al. (18) performed laboratory investigations on an FGD gypsum designed to simulate two types of gypsum calcining (kettle and flash). Heebink reported a range of releases from <0.4%–28% of total mercury content present in the FGD gypsum samples evaluated, and Heebink concluded that there was potential for mercury to be released from FGD gypsum in the calcining process used in wallboard-manufacturing plants and that release appeared to be related to total mercury content of the gypsum being used.

Table 8. Mercury Emission from Dry-Curing Concretes

	Mass Release Rate, ng/day/kg			
Curing Interval	OPC Concrete	FA33 Concrete	FA55 Concrete	HgPAC Concrete
n	4	6	3	4
First 2 Days [40 ± 1 °C]	0.07 ± 0.02	0.13 ± 0.07	0.08 ± 0.07	0.26 ± 0.04
First 28 Days [40 ± 1 °C]	0.10 ± 0.03	0.26 ± 0.04	0.34 ± 0.09	0.43 ± 0.12
n	2	0	1	2
Additional 28 Days, [23°C ≤ T ≤ 40°C]	0.08 ± 0.05	–	0.10	0.11 ± 0.01
Initial Mercury Concentration in Concrete, μg/kg	4.1	9.2	12.6	22.4

Marshall et al. (19) reported on an evaluation of mercury releases from FGD gypsum at a variety of full-scale wallboard plants using FGD gypsum from several sources. The effort included an evaluation of mercury releases from gypsum drying, gypsum calcining, and wallboard drying. Using Ontario Hydro and solids analysis, Marshall reported that the mercury releases ranged from 2.3% to 55% of the total mercury content of the FGD gypsum for all wallboard processes evaluated and estimated that a wallboard plant could potentially emit approximately 32 kg (71 lb) of mercury per year. In laboratory experiments, Kairies et al. (20) investigated the distribution of mercury in FGD gypsum and found that FGD gypsum is 99% soluble using a continuous stirred reactor, but that the remaining 1% solid residue contained 100% of the mercury present in the original FGD gypsum sample. Wallboard solubility was similar, with 2% residue remaining containing 100% of the mercury from the original wallboard. Experiments were also designed and performed to determine the partitioning of mercury when FGD gypsum settles. These experiments indicated that after settling, the majority of the mercury was present in the top layer, while the bottom layer had very low mercury content. The top layer was also enriched in iron, and Kairies et al. (20) concluded that an iron-containing phase is responsible for sorption of mercury.

Summary

A large amount of work has been accomplished and reported related to the rerelease of mercury from CCBs since October 2004. The rerelease mechanism that has the most data available is that of direct leaching. Direct leaching evaluations have been performed primarily on fly ash, with limited activities on FGD materials. Several groups have reported similar results from leaching tests of fly ash generated both without and with mercury controls. The reports reviewed generally indicated that direct leaching of mercury from fly ash, even with elevated mercury concentrations, is not expected to require changes to current fly ash management options.

The remaining mechanisms, vapor-phase rerelease and microbiologically mediated leaching and vapor-phase rerelease, have also been investigated during the past year, with additional information reported in the literature. However, the data available are still too limited for conclusions to be drawn. For the vapor-phase rerelease evaluations, results reported from studies performed by different investigators indicated similar ranges of rerelease or sorption from similar materials. To date, the microbiologically mediated rerelease work has been limited to work performed at the EERC under a DOE NETL and industry-funded project. It is also noteworthy that the field-generated data are consistent with the reported laboratory data even though only limited field investigations have been performed.

When the DOE NETL-funded project to conduct research on by-products generated from large-scale mercury emission control demonstrations is initiated, it is anticipated that a large number of CCB samples will be evaluated for mercury volatilization and leaching (both abiotic and biotic). The data from this study will help to fill the existing data gaps and contribute to the information available to aid the CCB industry in making decisions on management of CCBs that have been impacted by mercury emission controls.

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MERCURY FUNDAMENTALS (QUARTER 5 REPORT)

A review of the fundamental chemical principles of sorbent control of mercury in coal combustion flue gas was recently presented in Quarter 5. This update will summarize some of the earlier discussion as well go into more depth in certain areas of sorbent science. Understanding these fundamentals is critically important in the ongoing efforts to improve mercury capture and lower emissions from combustion sources. For low-chlorine coals, much of the mercury in the flue gas is elemental (Hg^0), and only a small amount is oxidized Hg(II), but finely powdered sorbent injection upstream of a particulate collection device has the potential to capture both elemental and oxidized mercury present in the flue gas.

There are several facts and ideas that have been developed in the last few years that are critical to understanding how the capture of mercury takes place on a carbon sorbent in a flue gas stream. Several unequivocal pieces of evidence demonstrated that the sorption at elevated temperatures occurs via an oxidation mechanism (chemisorption) rather than physisorption. The most important evidence is the results of the examination of spent sorbents using x-ray absorption fine structure (XAFS). These studies showed that only Hg (II) was present (1).

Flue Gas Effects

Based on results from an extensive matrix of tests at the EERC using full and partial gas compositions (2), a preliminary chemisorption model was developed (3). The model showed both oxidation of elementary mercury on the carbon surface and binding of the oxidized mercury to a basic site on the carbon surface. The model was supported by x-ray photoelectron spectroscopy (XPS) data for a number of experiments where a sorbent was exposed to various synthetic flue gas compositions for varying lengths of time (4). These data demonstrated the competitive role of the acidic flue gas components and sulfuric acid formed by oxidation of SO_2 at the basic binding sites on the carbon. An updated version of this chemisorption-competitive binding model is shown in Figure 3. NO_2 is shown to effect the oxidation of SO_2 to H_2SO_4 or HSO^{4-} on the carbon surface, a reaction that also requires H_2O. Note, however, that the details of the mercury oxidation reaction as well as the SO_2 oxidation are not included nor are the interactions of SO_3. Thus this illustration is an overview of the reactions on the carbon, with no mechanistic details.

Carbon Structure Effects

Published information of the effect of carbon structure on the capacity or reactivity of sorbents is very scant. The effect of oxygen functional groups on the sorbent surface was investigated by Ghorishi et al. (5), but they found no correlation with mercury capture. Regarding the effect of carbon crystallinity, there is little except the recent report by Rostam Abadi et al. (6). The capture of mercury on the unburned carbon (UBC) of fly ashes was examined, with very careful attention to the particle size and structural organization of the UBC fractions from three different ashes (6). The UBC content decreased with decreasing particle size for all three ashes. There was no correlation between the mercury content and UBC content of different size fractions; however, mercury content of unburned carbons in each size fraction increased with decreasing particle size for the three ashes.

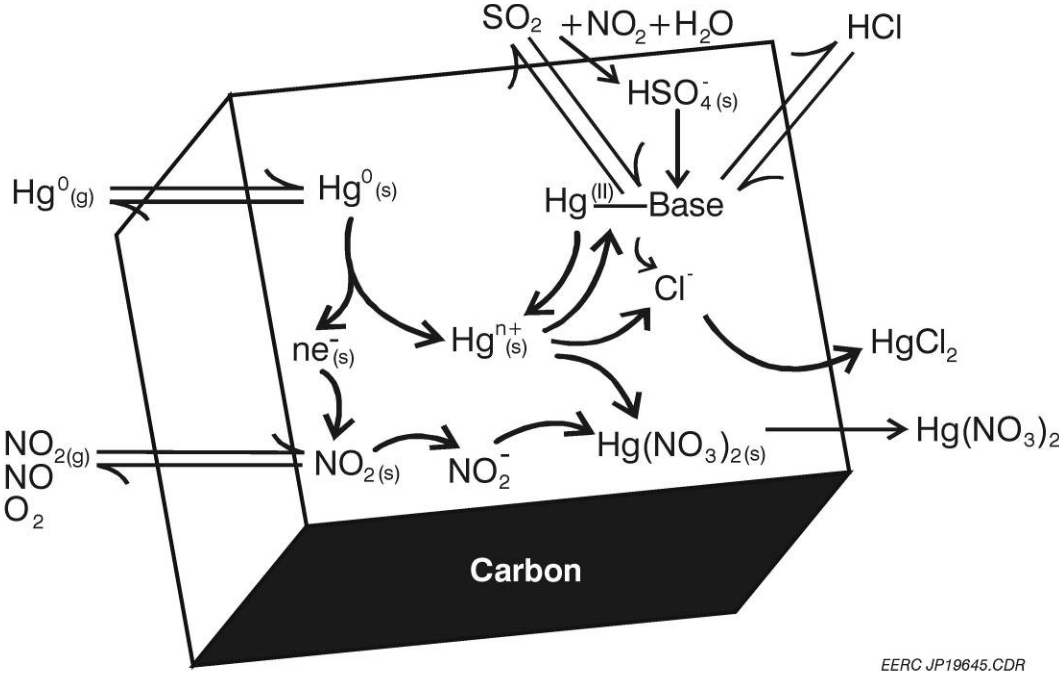

Figure 3. Overview of mercury flue gas interactions on an activated carbon sorbent.

After a normalization with respect to surface area, the data showed a more pronounced dependence on size for the FA1 (baghouse ash). The implications are that the size of the FA1 UBC and the surface area both contributed to the capture, whereas for FA2 (ESP ash) UBC particles size had a larger effect on mercury capture than the surface area, and for FA3 baghouse UBC, the size had a larger effect than surface area.

Comparison of the x-ray diffraction (XRD) spectra of UBCs with activated carbon and with graphite, showed that the UBCs have a less disordered structure than activated carbon. Thus the higher temperature in the combustion system resulted in more extensive ordering and consequently lower surface areas than activated carbons and lower mercury capture potential. The FA3 UBC was the most ordered and exhibited the lowest mercury capture. The implications for mercury capture in coal-fired boilers are that decreasing the UBC size will result in more capture. Also a lower temperature history for the UBC would result in less ordered carbon structures that are favored for mercury capture.

Acid Promotion Effects

In early work, an increase in sorption was observed when HCl was added to flue gas (7), but the reason for the success of this strategy was unknown. It is clear that HCl is not an oxidizing reagent, since it is already in the most reduced state. The possibility of a Deacon reaction of HCl with oxygen on the carbon sorbent could account for generation of an oxidant on the sorbent surface. In the test matrix conducted at the EERC (2), when relatively high HCl concentrations (50 ppm) typical of eastern bituminous coals were used, the capture of mercury at the start was always very high (less than 5% of inlet concentration), but in very low HCl concentrations (1 ppm), such as those obtained when low-Cl coals are burned, an initial breakthrough was observed at only about 50%–60% of inlet (8), followed by an increase in capture efficiency to the 5%–10% level (Figure 4). The higher HCl concentration thus eliminated this induction period where poor capture is obtained (9). Since the increased sorption activity is seen from the very start of exposure to the flue gas, this increased activity is clearly a kinetic effect and therefore results from a promotional effect of the HCl on the carbon sites catalyzing the oxidation of mercury (9).

XPS studies of carbons exposed to synthetic flue gas showed that in either high-HCl or low-HCl conditions, the chlorine concentration on the carbon surface builds up at first, but then diminishes at breakthrough when the sulfuric acid displaces the bound chlorine (4, 10). These studies showed that the chlorine is present mainly in two forms, organochlorine and chloride ion.

An increase in capacity for carbons that were pretreated with dilute aqueous HCl was reported by Ghorishi et al. (5). The effect was observed in both nitrogen and synthetic flue gas. Experimentation at the EERC (9) showed that the main effect was the same as that observed for flue gas containing HCl, as discussed above. A more detailed chemical model of the carbon bonding site was introduced (11) to explain the bonding of the HCl, Hg(II), and the competition with the poisoning agent the sulfuric acid generated by oxidation of SO_2 on the sorbent. The model, shown in Figure 5, uses the concept of zigzag carbene edge structures recently proposed by Radovic and Brockrath (12). The zigzag carbon flanked by the aromatic rings has an electron pair and is the basic binding site for which the HCl, H_2SO_4, and Hg(II) compete, as shown on the left side of the figure, forming a positive carbenium ion intermediate in each case.

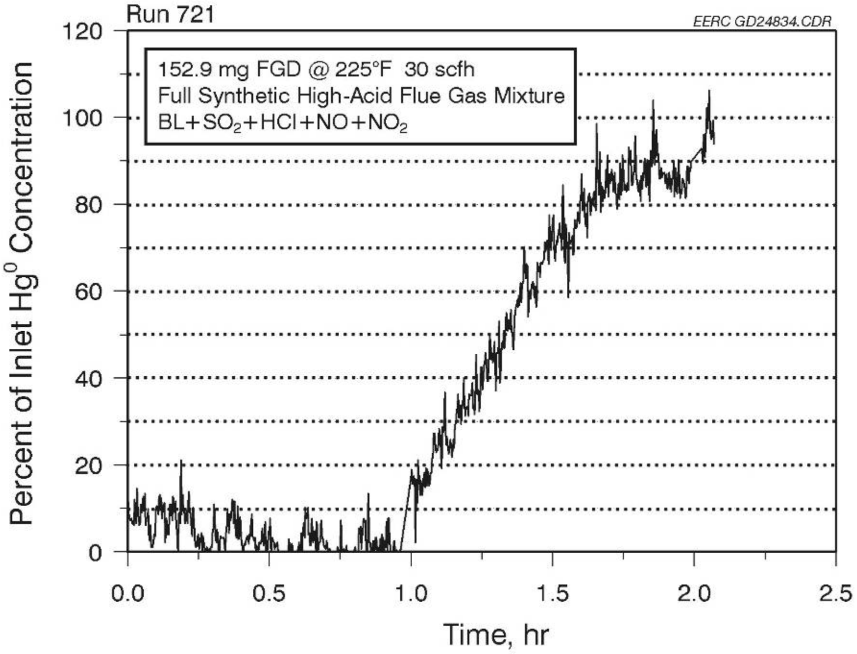

Figure 4. Breakthrough curves for high and low acid gas.

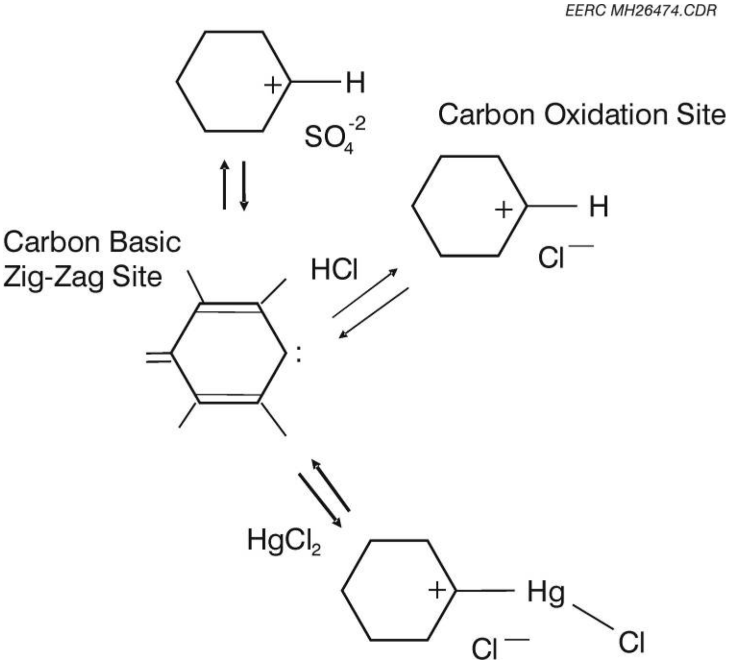

Figure 5. Mercury and acid gas-binding mechanism at carbon edge.

Mercury Oxidation Mechanism

Several features of the oxidation site were inferred from the HCl promotion and bonding effects (9) that led to development of a more comprehensive model (Figure 6) of the chemical mechanism of mercury capture (9, 13, 14). This mechanism uses a single carbon site for oxidation and bonding but in two different forms and thus offers more chemical detail on the nature of the oxidation-bonding site and its interaction with flue gases and mercury. The model thus provides a detailed mechanism for the catalytic role of acids, such as HCl, in the oxidation step. The conversion of carbene to carbenium ion by HCl and other acids generates the oxidation site (Lewis acid). The mechanistic model shows Hg^0 oxidation by the carbenium cation to the organomercury intermediate and subsequent oxidation by NO_2 to the bound Hg(II) species. At the breakthrough point, $HgCl_2$ is continuously released as sulfuric acid drives the formation of the carbenium sulfate. Comparative testing of a large number of acid-promoted AC showed that they exhibit a specific acid catalysis, not a general acid catalysis. That is, those acids with polarizable counterions (HI>HBr>HCl) show faster initial rates compared with strong and weak oxyacids and fluoroacids (13). This finding is consistent with a mechanism where the halide ion proximate to the cation actually can assist in the oxidation mechanism by stabilizing the incipient mercurinium ion forming in the transition state.

Halogenated Carbons

It has been known since 1934, when the first patent for mercury sorption was granted, that adding molecular halogens such as chlorine (Cl_2), bromine (Br_2), or iodine (I_2) to carbons results in effective sorbents for Hg^0 capture in air (15). The first application used iodine as the halogen, but

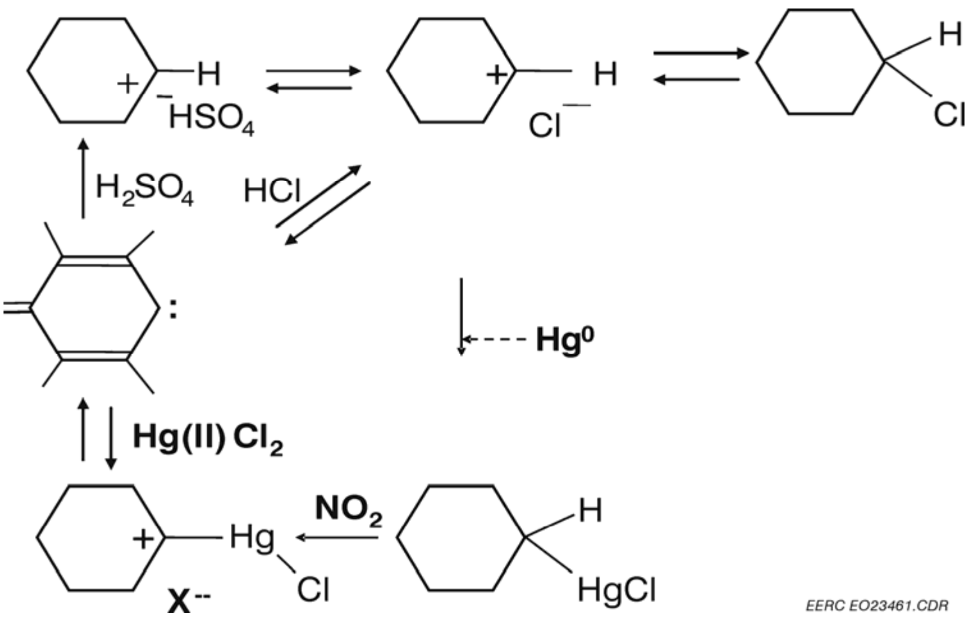

Figure 6. Oxidation mechanism – carbenium ion oxidant.

later applications used chlorine (16) and bromine (17) or a mixed halogen compound (18). Originally, the model for this type of sorbent was that the halogens on the carbon were responsible for reactions with the Hg^0, but a considerable amount of chemical evidence (19) showed that the halogens that are impregnated into carbon react with the carbon and are strongly bound to the carbon. So it is more likely that the halogens promote the reactivity of the carbon, as we have demonstrated for HCl, rather than react as such with the Hg^0.

To provide greater insight into the mechanisms for mercury capture on a chlorine-treated sorbent, a comparison of the structures and mercury sorption activities of several carbon sorbents that had been subjected to various chlorine treatments was recently conducted (20). The NORIT FGD carbon was pretreated with gaseous HCl, aqueous HCl, and gaseous Cl_2. All the pretreated sample showed high initial activity for capture, and thus the induction peak has been eliminated. Exceptionally high capacities were not observed since the ability to oxidize SO_2 to sulfuric acid, the main position of the binding sites, is not impaired by the chlorination.

Several of the pretreated sorbents were exposed to flue gas containing elemental mercury for various lengths of time, and the samples were analyzed with XPS. The Cl spectra of the pretreated samples that had not been exposed to flue gas showed peaks corresponding to both organochlorine and inorganic chloride. No clearly resolved peaks for physisorbed or intercalated molecular chlorine were found, but some may have been present in the wings of the organochlorine peak at high energy. As a result of exposure to the flue gas for a short time (20 min), all the chlorine-treated samples lost chlorine, but mainly the inorganic chloride. This could have been lost as HCl via displacement by sulfuric acid as it began to accumulate, as predicted by the model. Heating the chlorinated sorbents in air or an inert gas did not evolve either HCl or Cl_2, so the chlorine is strongly bound and must be exchanged or reacted off the carbon by a strong acid. Further exposure to flue gas resulted in further loss of both organochlorine and inorganic chloride. Although these chlorine spectra indicate the structures of the chlorine but not the mercury, the results contribute to our understanding of the reactive sites and allow us to extend the model to the chlorinated sorbents with little modification (see Figure 5).

The mechanism depicted in Figure 7 shows chlorination of the carbon edge structure to form the organochlorine species, consisting of the dichloro intermediate in equilibrium with the chlorocarbenium chloride ion pair. The latter represents the active oxidation site for elemental mercury, and the result of the oxidation is the organomercury chloride. The breakthrough mechanism proceeds as with the unchlorinated carbon (Figure 6).

Potential for More Effective Capture

Owing to the high reactivity of the halogenated carbons, full-scale testing of these sorbents is being conducted. Preliminary results show that indeed the halogenated carbon capture mercury more effectively and faster. Since improved capture is found in ESP systems for halogenated carbon injection, the capture is not mass transfer-limited even in these short contact time situations.

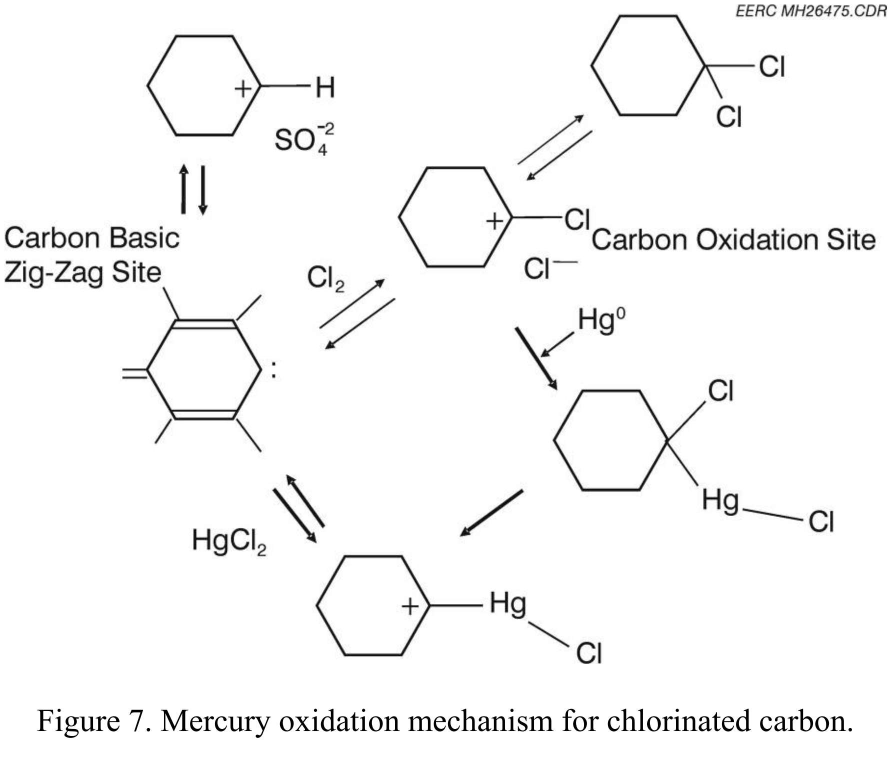

Figure 7. Mercury oxidation mechanism for chlorinated carbon.

A better understanding of the interactions and effects of flue gas constituents and conditions has resulted in an improved mechanistic model and the development of more improved sorbents for mercury capture and control. We can actually derive and compare rate constants for the oxidation reactions. Ultimately, the refined model will have the potential to be used to describe carbon–Hg–flue gas rates and equilibria for various kinds of carbons and to predict capture rates under a variety of conditions. Based on the developed models, capture rates for given sorbent loadings have increased. These embellishments to the sorbent comprise variations of the cation and anion structures in the oxidation site, but exact details cannot be revealed until patent protection has been acquired.

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HEALTH ASPECTS OF MERCURY EMISSIONS (QUARTER 5 REPORT)

Mercury released into the atmosphere from coal-fired power plants is deposited in the environment, becomes methylated, and accumulates in fish as they grow and age. Because of the higher methylmercury (CH_3Hg) concentrations present in larger and older fish, consumption of these fish may be associated with health risks. This is of special concern in the case of prenatally exposed children. Although the dangers of acute exposures to high doses of Hg are well recognized, controversy over fish consumption and the actual risks of CH_3Hg ingestion continue. Threshold levels for toxic effects of chronic exposure to low-dose Hg have not been possible to agree upon since no biochemical marker of risk has been established. However, insights into the physiological effects of Hg poisoning have the potential to reconcile these differences.

Dietary selenium's ability to decrease the toxic action of Hg has been established in all investigated species of mammals, birds, and fish (1, 2). Since 1967, when the first report on the protective effect of Se against Hg toxicity appeared (3), numerous studies have shown that Se counteracts the negative impacts of Hg exposure. The Hg–Se interaction has previously been assumed to occur when supplemental Se complexes with Hg and prevents toxic effects in animals fed otherwise debilitating amounts of Hg (4–6). However, scientific understanding of this effect is rapidly changing.

Selenium is a nutritionally essential element required to support the activity of enzymes that are normally present in all cells of all creatures (7). Researchers are currently aware of 25 selenoproteins, many of which are enzymes whose activities appear to be especially important in the brain, pituitary, and thyroid since these tissues are virtually impossible to deplete of Se (58). The selenide formed during each cycle of selenocysteine synthesis has an exceptionally high affinity constant for Hg: 10^{45}—a millionfold higher than Hg's affinity for sulfide: 10^{39} (8).

The high binding affinities between Se and Hg are clearly important in Se's well-known protective effect against Hg toxicity. It has previously been assumed that Se's protective effect was the result of Se-dependent binding of Hg, limiting its availability for causing harm in tissues. However, it is possible that instead of Se acting to immobilize Hg, Hg-dependent sequestration of Se could inhibit formation of selenium-dependent proteins. These proteins are normally present in all cells of all creatures. Since these enzymes are essential to support normal enzyme metabolic functions, especially in brain tissues, excessive exposure to Hg would be expected to disrupt selenium-dependent processes that occur in the brain. Hg-dependent sequestration of Se that leads to inhibition of selenium-dependent enzyme functions may explain why selenium-deficient rodents are more susceptible to prenatal toxicity of CH_3Hg than those fed Se-adequate diets. This mechanism would also explain why maternal exposure to CH_3Hg reduced Se-dependent enzyme activity in the brains of fetal/neonatal rats (9).

The contrasting observations reported by studies of Hg exposure performed in fish-eating populations of the Seychelles and the Faroe Islands may be related to differences in Hg exposure relative to Se in the foods consumed by of their respective study populations.

In the Faroe Islands (10, 11), adverse associations from prenatal CH_3Hg exposure have been found. Although adult Faroe Islanders consume ~72 g of fish a day, the fish they consume have relatively low total Hg contents: ~0.07 ppm. However, less than 10% of the Hg they consume comes from fish. The pilot whale meat they eat is quite high in Hg and accounts for more than 90% of their mercury exposure. Averaged daily consumption of ~12-g portions of pilot whale muscle meat is much lower than that of fish, but whale meat is most often consumed in intermittent feasts with relatively large meal portions. With total Hg contents of 3.3 ppm (~50 times higher than the Hg of the fish they eat), pilot whale meat provides the bulk of Hg exposure in this population. The level of mercury-dependent harm found in Faroese children that have been prenatally exposed to Hg has been quite subtle, but distinct.

This is in contrast to the results of the Seychelles Study where no adverse associations have been noted, even though the absolute Hg exposure appears similar. A critical difference is that in the Seychelles, ~100% of the Hg exposure comes from fish consumption. The Seychelles population consumes large quantities of fish with relatively low Hg levels (12), resulting in a Hg exposure that is ~10–20 times as great as typically occurs in North American diets. In the Seychelles measurements of neurodevelopmental outcomes, fish consumption by Seychellois mothers during pregnancy was not associated with harmful effect but, in some cases, was associated with beneficial effects on their children, possibly as a result of improved nutrition (selenium and omega-3 fatty acid).

One explanation of the contrasting observations of the Faroe Islands and the Seychelles studies may be that they are observing dose-dependent differences that arise from intermittent exposures to high concentrations of Hg (characteristic of whale meat) as opposed to persistent low-level Hg exposures (characteristic of fish meat consumption). Another possibility that needs to be considered is that there are distinctions in the molar ratios of Hg and Se present in the foods consumed by their study populations.

Figure 8 shows the relative molar concentrations of Hg and Se present in fish and whale meats. The data displayed in Figure 8 were converted into molar concentrations in order to accurately compare Hg and Se contents in samples. Since 1 nmol Hg/g = 200.59 ppb; 1 ppm Hg =~5 nmol Hg/g; 1 nmol Se/g = 78.96 ppb, thus 1 ppm Se = ~12.6 nmol Se/g). Aside from pilot whale (13) and swordfish (14), data depicted in this figure originate from Hall et al. (15).

As is apparent in Figure 9, mercury is present at a ~fourfold excess in whale meat, but its relative abundance in fish is substantially less. Greater risks of maternal consumption causing neurodevelopmental harm in a developing fetus are associated with mercury occurring at molar ratios in excess of 1:1. Data shown were calculated from data displayed in Figure 8.

Fish samples collected from Minamata Bay contained as much as 40 ppm CH_3Hg. Although Se contents were not measured in these fish, conservative estimates indicate the Hg:Se molar ratio in these fish would have been between 10 and 40 moles of Hg for every mole of Se. Children exposed in utero to Hg from these highly contaminated fish showed severe neurodevelopmental impairment, even though the mothers experienced minimal or no clinical symptoms (16).

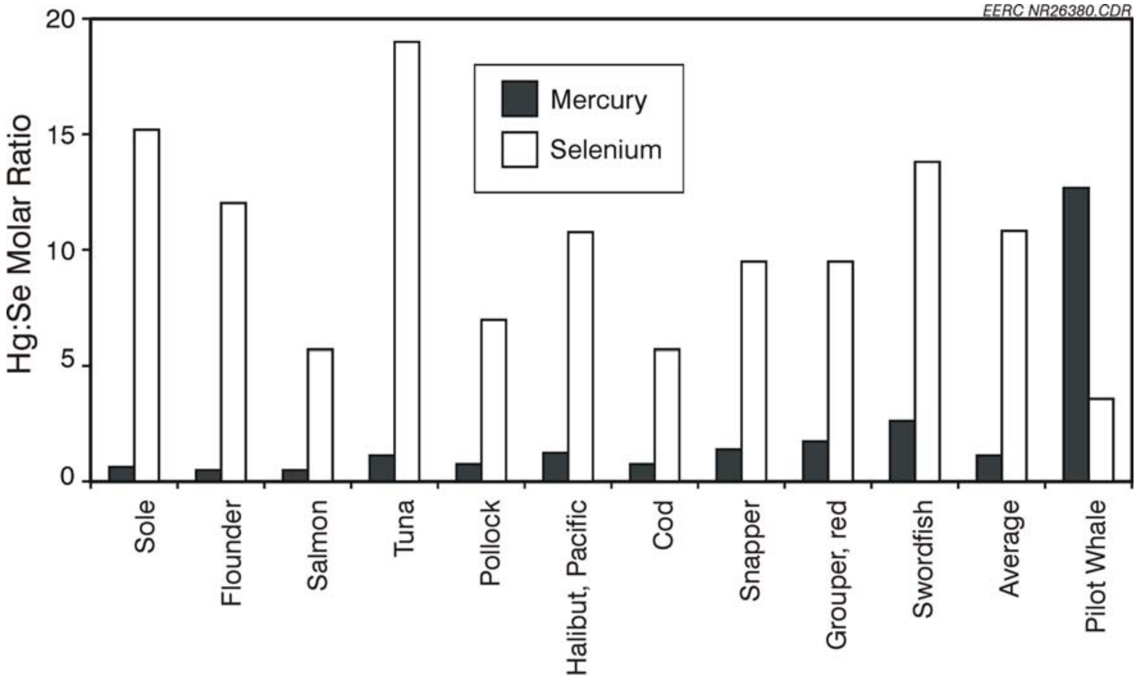

Figure 8. Molar relationships between mercury and selenium concentrations in seafood.

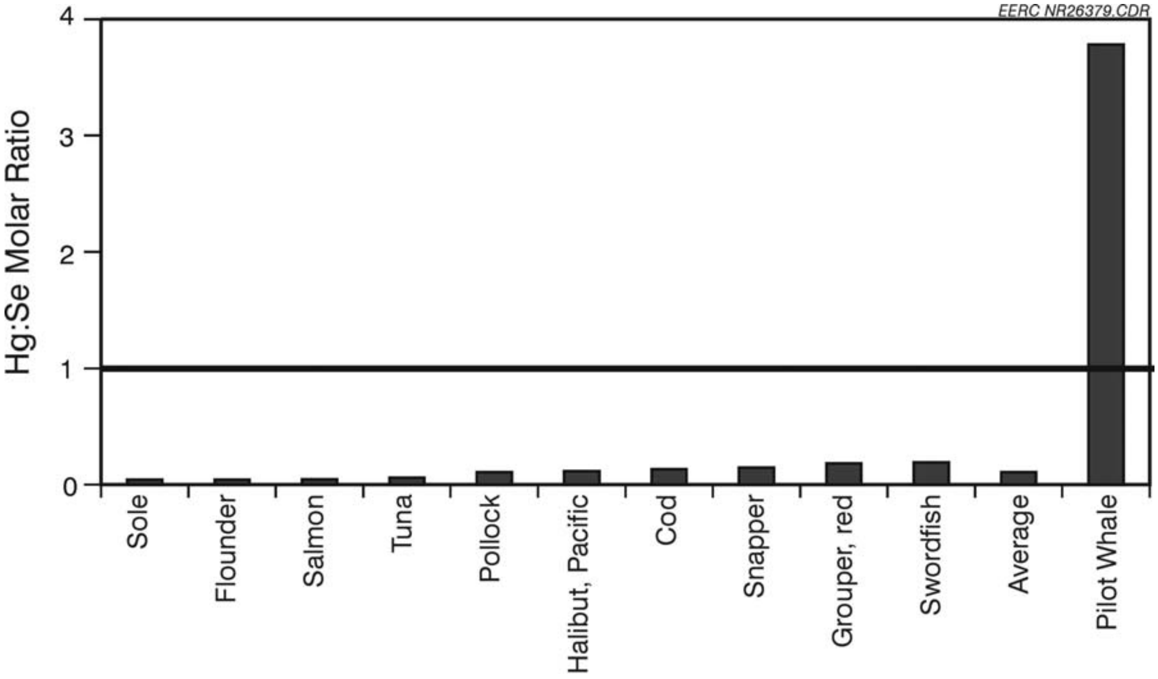

Figure 9. Molar ratio of mercury:selenium concentrations in seafood.

The data shown in Figure 10 were calculated from data displayed in Figure 8. As is apparent in Figure 10, selenium is highly available in fish meat but very poorly available from whale meat. Selenium's protective effects against Hg would be among the benefits associated with Se-rich dietary intakes from fish consumption.

The first panel in Figure 11 reflects the relative effects of mercury exposure from pilot whale vs. fish consumption in the Faroes. Since the concentration of mercury in pilot whale meat is ~50 times as great as that of the cod consumed in the Faroes, the slopes of the dose response curves of blood mercury levels are quite different. Blood MeHg rises quite rapidly for each meal of whale meat and is equaled only after many meals on fish. The graph reflects the approximated differences in exposure from whale feasts vs. normal fish meals. Because of the much greater time interval required to consume a similar quantity of MeHg, the natural depuration effects of exfoliation and hair growth diminish the intensity of the peak exposure from a similar mass quantity of MeHg from fish. Meanwhile, the second panel in Figure 11 depicts the relative effects of fish consumption vs. whale consumption on selenium status of the exposed individual. Each whale meal diminishes the selenium status of the consumer, meanwhile selenium status improves with each fish meal.

Recent work indicates the problem of excessive Hg exposure from whale meat consumption is not limited to the Faroes. Concentrations of MeHg in 160 samples of red meat products from small cetaceans sold for human consumption in markets throughout Japan from 2000–2003 all exceeded the provisional permitted levels in fish and shellfish set by the Japanese Government, 0.3 µg MeHg/wet g (17). The average MeHg level in the most contaminated species (false killer whale) was

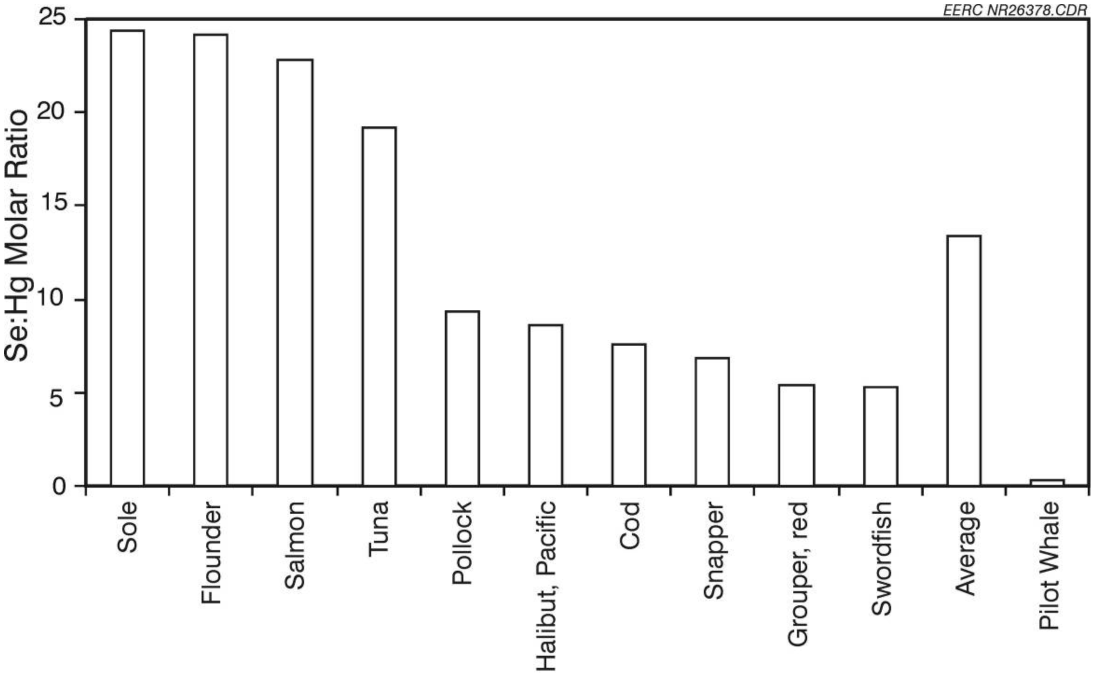

Figure 10. Molar ratio of selenium:mercury concentrations in seafood.

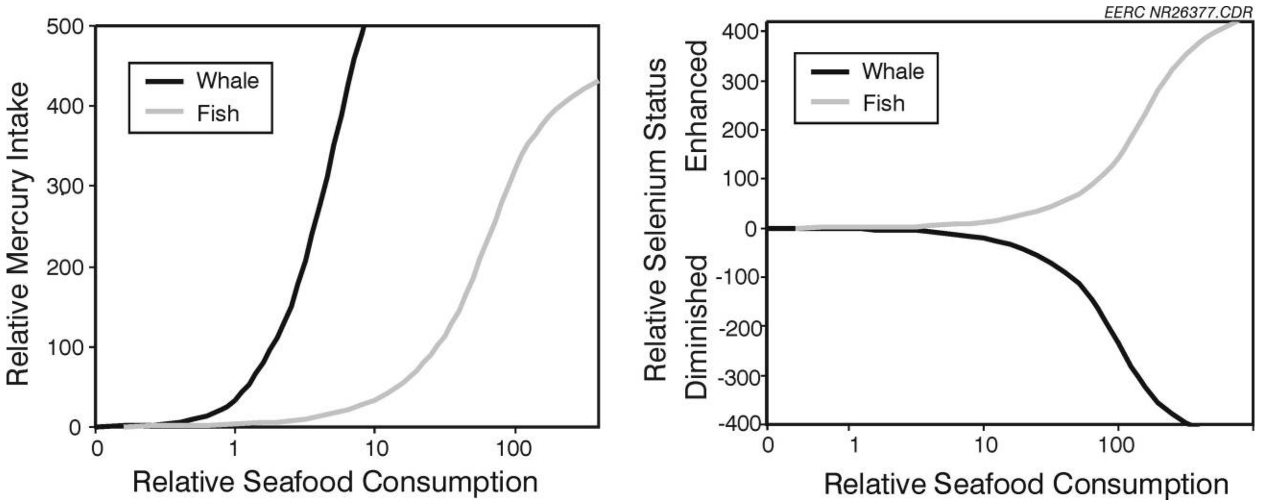

Figure 11. Relative effects of whale vs. fish consumption.

11.5 μg MeHg/wet g. The molar ratio of total Hg to Se was substantially greater than 1. It is, therefore, believed that consumption of red meat products from small cetaceans could pose a health problem for not only pregnant women but also for the general population.

It is clear that the Se naturally present in all foods and abundant in ocean fish and other seafoods can provide significant protection against Hg toxicity. However, it is becoming apparent that instead of merely being a protective "tonic," Se is instead a potential "target" of Hg toxicity since the loss of Se-dependent enzymes undoubtedly contributes to Hg's pathologic effects. As research on this issue accrues, it is apparent the tonic-to-target paradigm shift will foster new understanding of apparent discrepancies in results of various studies. Efforts to define interactions between Se and Hg continue to move forward as increasing numbers of research groups are investigating this emerging perspective of the Hg issue.

Environmental Hg

Progress is being made in understanding how to deal with environmental Hg, and new practices may lead to ways of reducing Hg contamination of fish in freshwater lakes. Flooding of terrestrial areas stimulates MeHg production and leads to increased bioaccumulation in fish (18). Burning greatly reduced plant and soil retention of total and methylmercury, diminishing the amounts available for bioaccumulation in fish. Although this approach contributes to the global atmospheric pool of elemental Hg, it may be valuable to apply to reduce the Hg contamination in fish that often occurs in reservoirs and other areas where dry–wet cycling happens.

The Guizhou Province in the southwest of China has areas of extremely high soil selenium and also has many areas with high accumulations of Hg. Elemental analysis of a coal sample from this province indicated Hg concentrations of 55 ppm, which is ~200 times the average Hg concentration in North American coals (19). Atmospheric emissions of Hg from mining, ore processing, chemical industry wastewaters, and coal burning for electricity production in Guizhou Province amount to ~12% of the world's total anthropogenic emissions (20). As a result, even foods that are not normally known for mercury accumulation develop substantial and potentially hazardous burdens. The concentration of Hg in rice grains can reach up to 569 µg/kg of total Hg of which 145 µg/kg was in MeHg form. The percentage of Hg as MeHg varied from 5% to 83%. Although this area is rich in Se, it is not known if the inorganic Hg in the rice is in the less available HgSe form or not.

Physical factors controlling total Hg and MeHg concentrations in lakes and streams of the northeastern United States were assessed using multiple regression models using watershed characteristics and climatic variables (21). These factors explained 38% or less of the variance in mercury values. Methylation efficiency (MeHg/total Hg) was modeled well (r^2 of 0.78) when a seasonal term was incorporated. Their physical models explained 18% of the variance in fish Hg concentrations in 134 lakes and 55% in 20 reservoirs.

The role of Se in reducing bioaccumulation of Hg in fish has been reported (22–24), and inverse relationships between fish tissue Hg and the abundance of Se present in the ecosystem have been noted (25, 26). Selenium supplementation of lake waters in Sweden resulted in a 75%–85% reduction in Hg levels of fish over a 3-year period (27), and loss of Se can have the opposite effect. When Se-rich discharges of fly ash to an artificial lake were removed, researchers noted a steady increase in Hg concentrations (28, 29). Studies such as these indicate the importance of Se-dependent Hg retirement in aquatic ecosystems, possibly through formation of insoluble Hg:Se complexes that deposit in sediments. Several studies of the relationships between Hg and Se are currently ongoing in Canada and elsewhere in the world.

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COMMERCIALIZATION ASPECTS OF SORBENT INJECTION TECHNOLOGIES IN CANADA (QUARTER 8 REPORT)

The CAMR in the United States and the acceptance in principle of a draft of the CWS for mercury illustrate the need for cost-effective mercury control strategies for coal-fired electric utilities. Recent demonstration activities have shown effective mercury capture with sorbent injection at full-scale systems. Out of this effort, concerns have been raised regarding the availability of carbon, sorbents, additives, and the related capital equipment if there were widespread adoption of ACI technology.

Issues that relate to the state of commercialization of sorbent injection technologies include the following:

- Policy and regulatory issues that impact commercialization of mercury sorbent technologies
- Sorbents most likely to be used based on coal type and plant configurations
- Capital investment requirements and the availability of necessary equipment and labor
- Availability of sorbents and/or additives
- Status of mercury measurement technology for compliance purposes
- Balance-of-plant impacts

Projections by the activated carbon industry do not suggest that either the availability of activated carbon or equipment will be a significant issue, although existing shortages in labor and construction materials are likely to continue, causing delays in capital improvements in Canada. Over the long term, there are several areas of concern that need to be addressed before widespread commercial implementation of sorbent injection technology can occur. These include the following:

- Environmental and economic impacts of lost fly ash utilization (greenhouse gas credits)
- The impact of ACI on FF and ESP performance
- Environmental impacts of treated carbon
- Longer-term leaching potential of disposed ash

A disadvantage of ACI is the impact the added carbon may have on ash salability. There are a large number of utilities in Canada and the United States that sell at least a portion of the ash collected to the concrete industry. In Canada, almost all the utilities burning lignite or subbituminous coal (SaskPower, TransAlta, EPCOR, and ATCO POWER) have facilities selling their ash for use as an admixture in place of portland cement at varying concentrations up to as high as 50%. A review of the impacts of mercury on by-product utilization was addressed in Quarter 4, Rerelease of Mercury from Coal Combustion By-Products, Therefore, any mercury control technology that prevents the sale of ash would have financial as well as environmental penalties. Increased ash to the landfill, forgone revenue from by-product sales, and increased energy consumption to manufacture portland cement not replaced with fly ash all directly result from activated carbon in fly ash. In some cases, as little as 1% carbon in the ash may result in rejection of the ash by the cement industry especially when from ACI. One method of preventing activated carbon from entering the bulk of the fly ash is to add a small baghouse after the ESP with ACI between the two particulate control units.

The downside is the added capital cost associated with installing a baghouse and the additional operating cost of replacing bags and the pressure drop.

The long-term effect of ACI injection on particulate control devices is currently being investigated. Long-term demonstration activities in Canada and the United States are being funded that will provide data over periods of up to 1 year. Data from these activities should help quantify many balance-of-plant effects, including both effects on particulate control devices and fate of halogens and other enhancement additives used to improve mercury capture.

Research is also ongoing to evaluate the long-term leaching potential of mercury from combustion by-products. Limited testing to date has indicated that mercury is stable on the ash; however, results from testing over periods of many months will be necessary to illustrate that stability.

CONCLUSIONS

With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC developed comprehensive quarterly information updates that provide a detailed assessment of developments in the various areas of mercury monitoring, control, policy, and research. A total of eight topical reports were completed and are summarized and updated in this final CEA quarterly report. Original text for each of these reports are provided in Appendix A.

In addition to a comprehensive update of previous mercury-related topics, a review of results from the CEA Mercury Program is provided. Members of Canada's coal-fired electricity generation sector (ATCO Power, EPCOR, Manitoba Hydro, New Brunswick Power, Nova Scotia Power Inc., Ontario Power Generation, SaskPower, and TransAlta) and CEA, compiled an extensive database of information from stack-, coal-, and ash-sampling activities. Data from this effort are also available at the CEA Web site and have provided critical information for establishing and reviewing a mercury standard for Canada that is protective of environment and public health and is cost-effective.

CEA members committed to a program of quarterly sampling and reporting of mercury in coal, residue, and stack emissions. Over the past 2 years, a large data set of approximately 35,000 data points has been generated that characterizes the range and variability of mercury present in the coal and the resulting variability of mercury present in by-products and stack emissions. Quarterly reports from each of the member companies provide detailed data on coal characteristics, ash, and stack gas measurements and can be viewed at www.ceamercuryprogram.ca. Through this sample and analysis effort, CEA met their goal to improve emission inventories to support mercury management strategies and provide member utilities experience with mercury measurement methods. The findings of this effort have helped to reduce the uncertainty around mercury emissions and concentrations in coal and combustion by-products and provided critical information for establishing and reviewing a mercury standard for Canada.

In conjunction with quarterly sampling, a laboratory quality assurance and quality control program was conducted. In general the goal of improving and validating laboratory proficiency in mercury analysis was achieved through the laboratory round-robin. Through this effort, quality assurance of lab procedures and methods was achieved, and a database of coal characteristics from across Canada was enhanced.

Finally, through the compilation of this report and the previous eight quarterly information clearinghouse reports, the goal of creating and maintaining a database of global mercury research has been achieved.

REFERENCES

References can be found in each individual section.

UPCOMING EVENTS

Power-Gen International 2005 Conference & Exhibition
December 6–8, 2005, Sands Expo & Convention Center, Las Vegas, NV
http://pgi05.events.pennnet.com

Pittcon 2006
March 12–17, 2006, Orlando, FL
www.pittcon.org

231st ACS National Meeting & Exposition
March 26–30, 2006, Atlanta, GA
www.chemistry.org

Coal Ash Professionals Training Course
April 19–21, 2006, Memphis, TN
www.undeerc.org

A&WMA Annual Conference & Exhibition
June 20–23, 2006, New Orleans, LA
www.awma.org

Eighth International Conference on Mercury as a Global Pollutant
August 6–11, 2006, Madison, WI
www.mercury2006.org/Default.aspx?tabid+1393

The Mega Meeting: Power Plant Air Pollutant Control Symposium (formerly The Mega-Symposium)
August 28–31, 2006, Baltimore, MD
www.megasymposium.org

Pittcon 2007
March 11–16, 2007, New Orleans, LA
www.pittcon.org

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APPENDIX A

QUARTERS 1–8

MERCURY INFORMATION CLEARINGHOUSE

Quarterly 1 - Sorbent Injection Technologies for Mercury Control

Canadian Electricity Association
Association canadienne de l'électricité

EERC
Energy & Environmental Research Center

Center for Air Toxic Metals

MERCURY INFORMATION CLEARINGHOUSE

QUARTERLY 1 – SORBENT INJECTION TECHNOLOGIES FOR MERCURY CONTROL

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U.S. GOVERNMENT DISCLAIMER

REPORT AVAILABILITY

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650 and the CEA mercury program Web site (www.ceamercuryprogram.ca).

MERCURY INFORMATION CLEARINGHOUSE

QUARTERLY 1 – MERCURY MEASUREMENT

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MERCURY INFORMATION CLEARINGHOUSE

QUARTERLY 1 – SORBENT INJECTION TECHNOLOGIES FOR MERCURY CONTROL

EXECUTIVE SUMMARY

Mercury is an immediate concern for the Canadian and U.S. electric power industries because of pending regulation of mercury emissions. Canada has established a consultative process to develop Canadawide Standards (CWS) for mercury emissions from coal-fired electricity generation. Although the process has not been completed, an estimate of the reduction in mercury emissions within Canada is likely to be in the range of 60%–90% and aligned with U.S. standards.

Options for mercury control in existing coal-fired power plants consist of the enhancement of existing air pollution control systems and the addition of new multipollutant control options. Enhancement of existing air pollution control devices includes sorbent injection with and without sorbent enhancement agents upstream of existing particulate control systems and mercury oxidation upstream of wet and dry scrubbers. This report focuses on the injection of sorbents, specifically activated carbon.

The use of sorbent and/or activated carbon injection as a means of removing mercury from coal combustion flue gas is widely accepted as the most developed and commercially viable method. Application of sorbent injection in coal-fired utility boilers is very challenging because of lower concentrations of mercury and the range of mercury forms in coal combustion flue gases. The level of mercury in flue gases is typically 10 micrograms/normal cubic meter, and the mercury is in three forms: elemental, oxidized, and particulate. The distribution of mercury in the various forms is dependent upon coal composition. Typically, lower-rank subbituminous and lignitic coals with low chlorine levels produce flue gases where the mercury is dominated by the elemental form. Higher-rank bituminous coals that contain over 200 ppm chlorine produce flue gases where the mercury is in the oxidized or particulate form. The oxidized and particulate forms of mercury are more easily controlled by existing air pollution control devices than the elemental form. Flue gases that contain high levels of elemental mercury require the addition of a sorbent enhancement agent in order to increase the capture efficiency of mercury.

Activated carbon sorbent injection to achieve a required level of removal must be maintained at a minimum amount in order avoid adverse impacts on air pollution control devices or ash disposal and utilization. The ability of the activated carbon sorbent to control mercury depends upon flue gas composition and temperature as well as the sorbent particle size, reactivity, and capacity. Research and demonstration projects for mercury control technologies are currently ongoing at laboratory, pilot, and field scales. Activated carbons show promise; however, their effectiveness depends on coal type and power plant configuration.

MERCURY INFORMATION CLEARINGHOUSE

QUARTERLY 1 – SORBENT INJECTION TECHNOLOGIES FOR MERCURY CONTROL

INTRODUCTION

In response to the need identified by the Canadian Electricity Association (CEA), the Energy & Environmental Research Center (EERC) was contracted to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of CEA, Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of developments in mercury monitoring, control, policy, and related research advances.

Recent developments in the area of mercury regulations from coal-fired power plants in both Canada in the form of Canadawide Standards (CWS) and the United States in the U.S. Environmental Protection Agency's (EPA's) Proposed Utility Mercury Reduction Rule illustrate the need for effective mercury control strategies for coal-fired electric utilities. Sorbent injection upstream of a particulate control device is the retrofit technology that has demonstrated the widest application for mercury control in plants not equipped with flue gas desulfurization (FGD) scrubbers and is discussed in detail in this quarterly report.

In order to adequately address topics and provide the detail necessary for the various stakeholders to make informed decisions, selected topics will be discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that will be addressed in subsequent quarterly reports include, but are not limited to, the following:

- Mercury Policy
  - Upcoming events and news releases
  - Regulation, policy, compliance strategies, and health developments

- Mercury Measurement
  - Continuous mercury monitors
  - Advanced mercury-sampling systems
  - Wet-chemistry mercury measurement techniques
  - Baseline mercury levels and emissions

- Mercury Control
  - Sorbent technologies and control in unscrubbed systems
  - Advanced and developmental mercury control technologies
  - Summary of large-scale test activities and associated economics
  - Mercury oxidation and control for scrubbed systems
  - Multipollutant control strategies
  - Impact of mercury control on combustion by-products/fate of captured mercury

- Summary of mercury-related economics for commercial systems

Mercury Chemistry and Transformations

- Mercury chemistry fundamentals, modeling, prediction, and speciation
- Mercury fate and transport – Impacts on health

One objective of this quarterly report is to provide timely information on developments in the field of mercury. In order to address timely issues as well as provide necessary detail on selected topics, additional subject headings will be provided to summarize recent developments not related to the quarterly topic. In this manner, updated information can be provided on topics previously covered or in advance of topics not yet discussed.

The primary subject areas for this first quarterly report include an introduction to policy regarding regulations for mercury control as well as a detailed discussion on mercury control using sorbent injection. In the second quarterly report to be submitted in April 2004, mercury measurement will be covered in detail as well as CWS developments and a review of EPA's Proposed Utility Mercury Reduction Rule.

MERCURY POLICY – BRIEF OVERVIEW OF CURRENT REGULATIONS

Mercury is an immediate concern for the Canadian and U.S. electric power industries because of pending regulation of mercury emissions. Canada has established a consultative process to develop CWS for mercury emissions from coal-fired electricity generation. A process is well under way to evaluate and discuss, in conjunction with a multistakeholder advisory group, options for achieving cost-effective reductions in mercury emissions. Recently, the Canadian Council of Ministers of the Environment (CCME) agreed that consultation should continue with regard to setting CWS in 2005 (1). CCME is committed to developing mercury standards by 2005. The most common discussion points for this standard are to achieve significant (>50%) emission reductions by 2010, with ongoing review to address the emerging science in the United States and elsewhere on mercury control. Standards within Canada are likely to be in the range of 60%–90% and to align with U.S. standards.

In December 2000, EPA decided that regulation of mercury from coal-fired electric utility steam-generating units is appropriate and necessary under Section 112 of the Clean Air Act (2). 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* (1997) (3) and the *Utility Hazardous Air Pollutant Report to Congress* (1998) (4) 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. On December 15, 2003, EPA published the proposed Utility Mercury Reduction Rule in order to solicit comments on two approaches for mercury emission control. The proposed EPA rule is being reviewed extensively by many organizations and is summarized here; however, a more comprehensive evaluation of the proposed rule will be provided in the next quarterly report. Under one approach, coal-fired power plants in the United States would be required to install currently available control devices defined as maximum achievable control technologies (MACT) under Section 112 of the Clean Air Act. This approach requires utilities to comply by the end of 2007 and is expected to result in mercury emission reduction of 14 tons (29%). The second approach, proposed under Section 111 of the Clear Air Act would create a market-based “cap-and-trade” program. This alternative would apply to both new and existing sources and takes advantage of co-pollutant mercury control associated with SO_2 and NO_x reductions required by the Interstate Air Quality Rule that was also proposed by EPA in December 2003. Under this approach, a mandatory declining cap would be set for total mercury emissions from all U.S. coal-fired power plants. Emissions trading would be allowed, and a mercury cap of 34 tpy would be enforced in 2010 and a lower cap of 15 tpy would be enforced in 2018, resulting in a total mercury emission reduction of nearly 70%. Implementation of this alternative would require EPA to revise its December 2000 finding that it is appropriate and necessary to regulate utility hazardous air emissions under the MACT standard of the Clear Air Act.

In light of these proposed regulations, it is important to note that there are no commercially available mercury removal technologies that can be universally applied to coal-fired boilers because of the array of coals and plant configurations present in North American coal-fired electric generating facilities. It is critical, therefore, to maintain an accurate and timely review of the issues associated with both control technologies and measurement in the context of changing environmental policies. Further development of sampling and measurement methods are necessary to improve accuracy and reduce the costs currently associated with mercury monitoring and future compliance. This is especially important with respect to the CWS effort and as U.S. and Canadian stakeholders develop commercially viable control methods.

QUARTERLY 1 FOCUS: SORBENT INJECTION TECHNOLOGIES FOR MERCURY CONTROL

The use of sorbent and/or activated carbon injection as a means of removing mercury from coal combustion flue gas is widely accepted as the most developed and commercially viable alternative. Many other technologies are being investigated, but the demonstrated performance of activated carbon in the municipal waste combustor industry has generated much interest for application in the coal-fired utility industry. However, application of sorbent injection in coal-fired utility boilers is far more challenging, owing to the lower concentrations of mercury that must be treated, the lower equilibrium capacities and mass-transfer rates associated with these lower concentrations, the wide range of concentrations of acid gases and chlorine species present, and the shorter gas residence time upstream of the particulate control device.

Sorbent Injection Background and Fundamentals

A detailed review of sorbent injection technologies has been conducted by the EERC and was published by Elsevier in *Fuel Processing Technology* in 2003 (5). This report provides a summary of the key findings in that review and a comprehensive look at the issues related to mercury control using sorbent injection. This report covers the following general topics: 1) mercury control requirements to be met, 2) laboratory studies on variables affecting sorbent capacity, 3) pilot-scale tests on capture performance for different coals, 4) research on sorbent properties to identify improved sorbents, and 5) full-scale demonstration results. The review provided goes beyond the presentation of descriptive information and attempts to explain cause-and-effect relationships; thus the interpretation may need to be revised as the understanding of mercury chemistry advances.

Requirement

Sorbent injection can be used as an effective control technology, provided a required level of mercury removal is achieved with a minimum amount of activated carbon while avoiding adverse impacts on air pollution control devices or on ash disposal and utilization. At the present time, activated carbon at typically 50 cents per pound represents a cost factor of about 0.4 mils/kWh at an injection ratio of C/Hg of 10,000:1 for coal containing 0.1 ppm mercury. Injection at this level results in approximately 1%–2% in fly ash loading in a coal combustion system. This carbon content in the ash adversely impacts the use of fly ash for cement replacement in concrete. Therefore, low carbon injection rates or sorbents other than carbon are desired to minimize the impact on ash marketability and reduce sorbent costs.

Equilibrium Sorption Capacities Determined in the Laboratory

Numerous bench-scale, fixed-bed tests have been conducted (6–11) to evaluate the mercury adsorption capacity of sorbents, including a range of carbons such as iodine- and sulfur-impregnated carbons and inorganic compounds. The capacities have been measured in nitrogen, air, or simulated flue gas of varying compositions. The testing conducted in simulated flue gas is the most relevant to actual conditions to which a sorbent is exposed. Some of the key factors that influence sorption capacity include temperature, oxidation state of the mercury, and composition of flue gas.

Lignite-derived DARCO™ FGD activated carbon has been studied as a mercury sorbent for coal-fired systems more extensively than any other sorbent. FGD activated carbon has a bulk density of 0.51 g/cm^3 and a surface area of 600 m^2/g. Baseline tests conducted at Radian (6, 10) and the EERC (7, 11) were performed in a simulated flue gas atmosphere typically containing 6% O_2, 12% CO_2, 8% H_2O, 1600 ppm SO_2, 50 ppm HCl, and 20–80 µg/Nm^3 Hg^0 or $HgCl_2$. The variables investigated included mercury concentration; concentration of the acid gases SO_2, HCl, and NO_x (NO and NO_2); water vapor concentration; and mercury oxidation. Tables 1 and 2 present details on carbon properties and test conditions (6). Important findings for DARCO™ FGD activated carbon are presented in Figures 1A–1I and in the discussion that follows:

- Increasing temperature (Figure 1A [10]) results in decreased equilibrium adsorption capacity.

- Equilibrium adsorption capacity using baseline simulated flue gas composition and a bed temperature of 135°C was found to increase linearly with increasing inlet levels of either Hg^0 or $HgCl_2$, as shown in Figure 1B (6). This is consistent with a physical adsorption mechanism. It is also believed that chemisorption of an oxidized species to a basic site on the carbon is the binding site on the carbon.

Table 1. Properties of DARCO™ FGD Powdered-Activated Carbon (5)

Carbon Property	Lab Data	Norit America's Datasheet
General Properties		
Bulk Density, g/mL	–	0.51
Surface Area, m^2/g	–	600
Molasses Decolorizing Efficiency	–	90
Iodine Number	–	600
Particle Size		
% Passing 325 mesh	94	95 minimum
Avg. Size from SEM Analysis, µm	15	–
Avg. Size from Microtrac Analysis, µm	14	–
Pore-Size Distribution, mg/g		
Micro, <20 Å	–	0.18
Meso, 20–50 Å	–	0.25
Macro, 50–150,000 Å	–	1.06
Chemical Composition, wt%		
Oxygen	28	–
Carbon	22	–
Silicon	14	–
Calcium	13	–
Iron	7.4	–
Aluminum	7.1	–
Sulfur	3.7	1.8
Magnesium	2.9	–

Table 2. Bench-Scale Test Sorption Capacity Experiments for DARCO™ FGD PAC (5)

Parameter	Baseline Value	Range Tested
Gas Rate (1/min at 75 °F)	1	–
Gas Composition		
$HgCl_2$, µg/N m^3	40–80	10–130
Hg^0, µg/N m^3	40–80	–
SO_2, ppmd	1600	0–3000
HCl, ppmd	50	1–100
O_2, %	6	–
CO_2, %	12	–
H_2O, %	7	–
Adsorption Temperature, °F	275	225–400

- Sorbent particle size determines the minimum sorbent requirement needed to effect mass transfer from the bulk gas to sorbent particles (12, 13). Based on the mass transfer calculations, 90% removal in 2 seconds at a C/Hg ratio of 10,000 for a flue gas stream that contains 10 µg Hg/Nm^3 in flue gas requires a mean particle size of about 4 µm for a typical size distribution. The capacity of the sorbent would be 100 µg Hg/g C at an exiting mercury concentration of 1 µg Hg/Nm^3. In-flight mercury capture using DARCO™ FGD may be limited by mass transfer.

- Water vapor in flue gas increases the equilibrium sorption capture for mercuric chloride and Hg^0 (6).

- HCl increases the equilibrium adsorption capacity of the DARCO™ FGD for Hg^0 as shown in Figure 1D (6).

- SO_2 in the absence of NO_x, as shown in Figure 1E (6), reduces the equilibrium adsorption capacity dramatically for Hg^0 and mercuric chloride. The effect of a combination of SO_2 and NO_2 reduces the capture of Hg^0 even more severely (Figure 1F), with significant reductions in sorption capacity noted at concentrations as low as 100 ppm SO_2 and 2.5 ppm NO_2 (8, 11, 14).

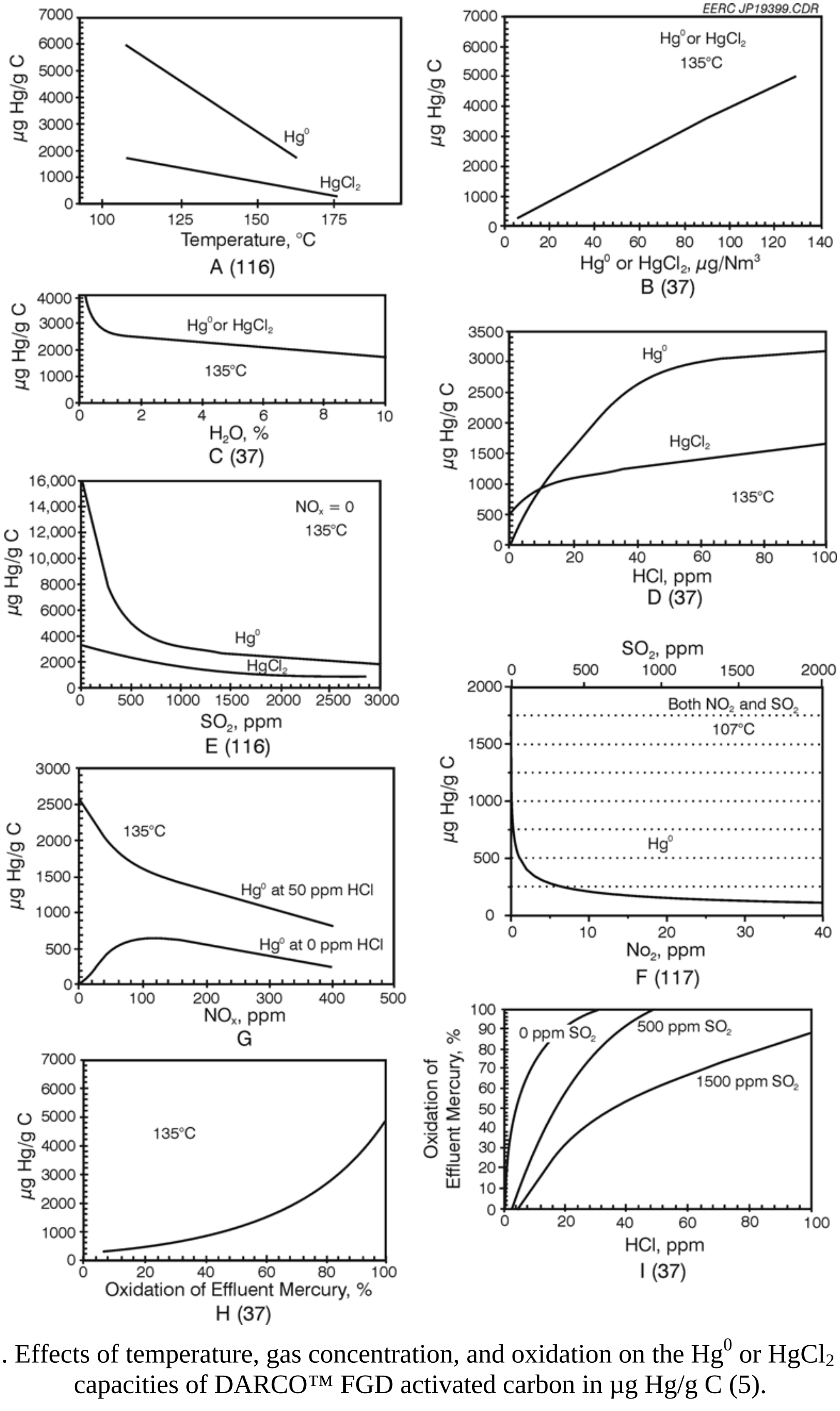
- NO_x (10% NO_2 and 90% NO) has an impact on Hg^0 capacity in the presence of SO_2 and HCl, as shown in Figure 1G (6). The equilibrium sorption capacity of Hg^0 is minimal in the absence of both NO_x and HCl, and it increases as NO_x alone increases. In the presence of HCl, the capacity for Hg^0 drops as NO_x increases. The combined effect of NO_2 and SO_2 is discussed in detail elsewhere (8, 11, 14). The capacity effects suggest that HCl and NO_x/NO_2 can promote the oxidation and capture of Hg^0 and no chemisorption capture appears to occur in the absence of mercury oxidation.

- The equilibrium sorption capacity for Hg^0 increases with increasing levels of oxidation occurring across the carbon test bed, as determined by changing the concentrations of HCl and SO_2, as shown in Figure 1H (6). This indicates that mercury oxidation is an essential step in capturing mercury on sorbents, as shown in Figure 1I.

Mercury Capture on Activated Carbon in Pilot-Scale Tests

DARCO™ FGD activated carbon was tested in pilot-scale facilities to capture mercury through injection upstream of a fabric filter (FF). Figure 2 shows trends in mercury removal across FF systems burning Powder River Basin (PRB) subbituminous coal and low-sulfur eastern bituminous coal as a function of injection rate. These coals contained similar levels of mercury but quite different concentrations of chlorine, sulfur, iron, and calcium. Overall, the results for the PRB coal indicate 1) significant mercury capture on fly ash without sorbent injection in both electrostatic precipitator (ESP) and FF systems, 2) lower removals in the ESP as compared to the FF, and 3) moderate increases in removal associated with either increased carbon injection or lower temperatures.

Very different trends were observed when DARCO™ FGD activated carbon was injected into pilot FF systems burning two eastern bituminous coals: low-sulfur Evergreen coal tested at the DOE National Energy Technology Laboratory (NETL) (15) and Blacksville coal tested at the EERC (7). Overall results for the bituminous coals indicate 1) for the Evergreen coal, increasing the injection rate from a C/Hg ratio of 2500–10,000 resulted in an increase in removal from 30% to 85% and extrapolation to C/Hg = 0, which suggests that very little removal occurred on fly ash without carbon injection (Figure 2); 2) for Blacksville bituminous coal, increasing the injection rate over a range of C/Hg ratios between 3500 and 13,000 resulted in little if any increase in removal at any given temperature (7), and removals increased from 10% to 95% at a constant C/Hg ratio of 3800 when the flue gas was cooled from 175° to 100°C, as shown in Figure 3, and 3) temperature on mercury removal is less pronounced for the Evergreen bituminous coal and is still less for the Belle Ayr PRB coal (Figure 3).



A (116)

B (37)

C (37)

D (37)

E (116)

F (117)

G

H (37)

I (37)

Figure 1. Effects of temperature, gas concentration, and oxidation on the Hg^0 or HgCl$_2$ sorption capacities of DARCO™ FGD activated carbon in μg Hg/g C (5).

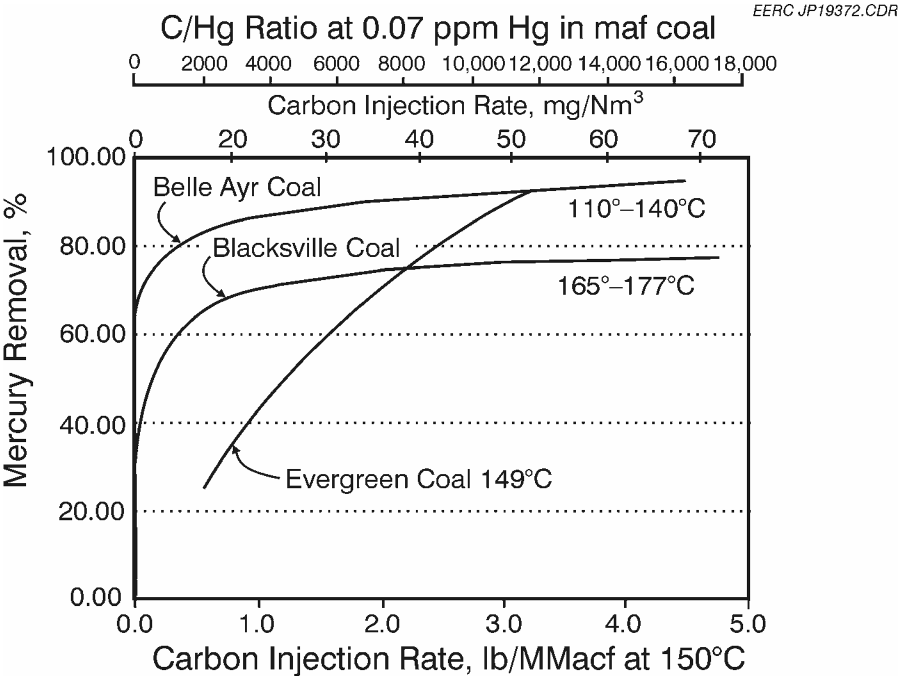


Figure 2. Effect of carbon injection rate on mercury removal in pilot system FF burning Belle Ayr, Wyoming, subbituminous coal and Evergreen bituminous coal (5).

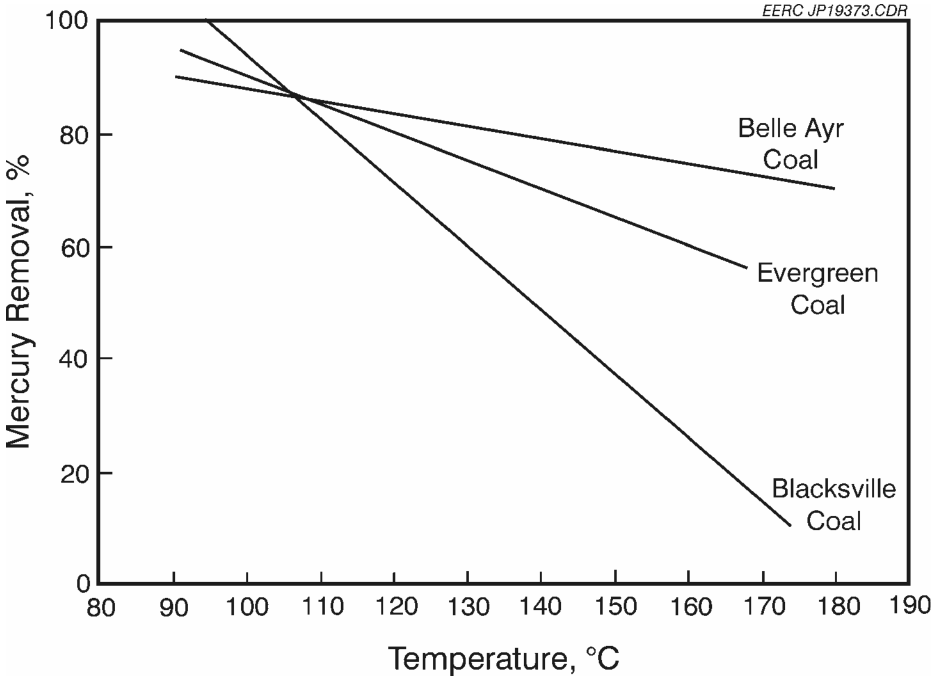


Figure 3. Effect of temperature on mercury removal showing sensitivity to coal type: Evergreen, Blacksville, and Belle Ayr coals (5).

An analysis of mass-transfer control for the three test coals based on selected experimental data points relating mercury capture at 150°C to carbon injection ratios (C/Hg) between 3760 and 6400 is summarized in Table 3. Results of mass-transfer calculations presented in Table 3 were used to predict removal levels for the three test coals at a C/Hg ratio between 0 and 10,000 and also the C/Hg ratio estimated to be required to achieve 90% removal. The removals calculated for the Belle Ayr and Evergreen test coals agree with the observed trend presented in Figure 2. It is predicted that C/Hg ratios of 12,872 and 15,822, respectively, would be required to achieve 90% removal.

Observed Hg removals were independent of injection rate above a C/Hg ratio of 3760 for Blacksville coal. This indicates that other factors besides mass transfer need to be considered. The dramatic increase in removal from 10% to 95% observed for Blacksville coal when the flue gas was cooled from 175° to 100°C at a constant C/Hg injection ratio of 3800 suggests an increase in the effective sorption capacity at the lower temperature. Therefore, it is proposed that the effective sorption capacity of Blacksville coal available in the 5-second residence time was increased dramatically because of the combined effects of decreasing temperature and heterogeneous catalytic oxidation promoted by maghemite.

Effects of Sorbent Properties

Carbon sorbents of different types have been tested to identify methods to improve performance and reduce cost. Four types of activated carbon, including lignite-derived, bituminous coal-derived, iodine-impregnated, and sulfur-impregnated carbons, are listed in Table 4. The properties of the sorbents and Hg^0 sorption capacities are presented.

In general, the sorption capacities for activated carbons derived from lignite and bituminous coal are similar. Table 4 shows that the carbons differ significantly with respect to surface area, pore diameter, porosity, and particle size. Overall, there is no conclusive evidence at this time that the precursor coal is a critical factor in selecting an activated carbon for sorbent injection.

Carbons that had been treated with different chemical agents to increase their mercury capture performance are compared in Table 4. Iodine-impregnated activated carbon exhibited capacities between 507 and 8530 µg Hg/g C, depending on Hg^0 concentration and flue gas temperature. These capacities are comparable to those shown for untreated coal-based carbons at similar conditions. The iodine-impregnated carbon performed better than either lignite- or bituminous coal-derived activated carbons in pilot-scale injection tests (7). Sulfur-impregnated carbons have higher sorption capacities than their untreated precursors (16–21).

Catalytic carbons derived from bituminous coal-derived activated carbons (e.g., Calgon F 400) by impregnating with nitrogen compounds and recarbonizing were shown to have mercury sorption capacities in air similar to those of lignite-derived FGD carbon (22, 23). Treatment with calcium chloride has been shown to produce a significant increase in capacity (20), and $Ca(OH)_2$-based sorbents (alone and admixed with fly ash) have been reported to provide superior capture of mercuric chloride but not Hg^0 (24).

Impregnated carbons may offer a practical advantage over the coal-derived activated carbons but need more testing. Currently, the differences observed in equilibrium capacity do not

Table 3. Comparison of Activated Carbon Injection for Pilot Test Using Norit FGD Carbon (5)

	Belle Ayr Wyoming PRB Subbituminous	Blacksville Pittsburgh No. 8 Bituminous	Evergreen Low-Sulfur Bituminous
Coal Analysis, mf			
Hg, ppm	0.07	0.069	0.09
Cl, ppm	50	650	1247
S, ppm	5000	24,000	10,000
Fe, ppm	2600	14,000	NA
Ca, ppm	14,000	3100	NA
Flue Gas Conditions			
Hg Equivalent to Coal Hg, μg/N m^3	7.54	6.4	8.57
Characteristic Mercury Oxidation, % Hg(II)[a]	36 [55]	75	81
HCl Equivalent to Coal Cl, ppm	3	37	71
NO$_x$, ppm	750	550	600
SO$_2$, ppm	260	1670	770
Selected Experimental Results on Mercury Capture at 150 ℃			
C/Hg Ratio Tested	4000	3760	6400
Carbon Concentration, g/N m^3	0.03	0.024	0.055
Total Mercury Removal at Designated C/Hg, %	74	37	62
Removal on Fly Ash w/o Carbon Injection, %	60	6 [55]	6 (est)
Analysis of Mass Transfer Control Assuming Fast Reaction 35 on Carbon and Slow Reaction on Ash[b]			
Total Removal at Designated C/Hg, %	74	37	62
Removal on Fly Ash with Carbon Injection, %	39	4	2.4
Adjusted Removal on Carbon, %	35	33	60
Carbon Particle Size Required, μm	15.1	14	14
Hg on Injected Carbon, μg Hg/g C	88	88	93
Nominal Capacity at 150 °C	250	500	500
Percent of Capacity Utilized	35	18	19
Removal Versus Injection Rate, %			
C/Hg			
0	60	6	6
2000	68	24	29
4000	74	39	47
10,000	86	68	77
12,872	90		
15,822			90
21,038		90	

[a] Reported oxidation levels ahead of a FF baghouse, not necessarily at the same temperature.

[b] This assumption causes the injected carbon to be initially exposed to a gaseous Hg concentration corresponding to the mercury content of the coal, which is consistent with the reported conclusion that capture on fly ash occurs via a slow surface reaction.

Table 4. Selected Properties of Activated Carbons (5)

Sorbent Type	Sorbent Identification	Ash, wt%	Surface Area, m^2/g	Pore Volume, cm^3/g	Avg. Pore Diameter, nm	Porosity, %	Mass Mean Particle Size, μm	Impregnation Treatment			Carrier Gas	Elemental Mercury Capacity		
								Reagent	Amt., %	Temp., °C		Hg^0 Conc., μg/N m^3	Temp., °C	Capacity, μg/g
Lignite Activated Carbon														
Norit Americas	DARCO™ FGD	32.1	546	0.611	3.8	57.9	15				Simulated flue gas w/o NO_x	45	135	2590
Norit Americas	DARCO™ FGD		500–700				9					54	135	3627
												52	163	2460
Bituminous Coal-Derived Carbon														
Norit Americas	PC-100		900		1.8		<30				Simulated flue gas w/o NO_x	330	100	1780[a]
Prepared by the Illinois State Geological Survey from Illinois Bituminous Coal	AC-36	18.9	680									54	135	2091
	AC-C	18.8	688	0.382		46.2	8					76	135	2188
Iodine-Impregnated Carbon														
Barnebey & Sutcliffe			750				3.5	Iodine			Simulated flue gas w/o NO_x	60	107	8530
												60	135	1929
												60	163	892
												20	135	1697
												20	163	507
Sulfur-Impregnated Carbons														
Calgon, Bituminous Coal-Derived Activated Carbon Treated with Sulfur	BPL		1007				210	None	0.6					
	BPL-S-4/1-250		168					Sulfur	37.4	250	Nitrogen	55	140	550[b]
	BPL-S-4/1-400		632					Sulfur	10.5	400		55	140	1450[b]
	BPL-S-4/1-600		835					Sulfur	10.1	600		55	140	2200[b]
	BPLH-0.25		570					H_2S	12.7	150		55	140	200[b]
			27				3–8	Sulfur	5.5		Simulated flue gas w/o NO_x	50		1500[b]
								Sulfur	33	400		50		13,831
								Sulfur	33	400		50		3260

[a] The value of 1780 μg/g was for 24-h exposure at 100 °C to gas containing 330 μg/N m^3 Hg^0 (24). Hsi et al. (18) reported a capacity of 230 μg/g at 4 h, 140 °C, and 40 μg/N m^3.

[b] These capacity values were estimated by graphical integration with extrapolation to breakthrough and may be quite approximate.

appear to be important since most of the capacity values are adequate at C/Hg ratios well below 10,000. The minimum C/Hg ratio of 5000 to 10,000 is anticipated to be required based on diffusion control. The final criteria is sorbent cost. Impregnated sorbents require additional processing, resulting in higher costs. Finally, the limits on carbon in fly ash and the loss of revenue due to the inability to sell fly ash also need to be considered in the economics of mercury control.

Large-Scale Demonstrations of Sorbent Control Technologies

An overview of full-scale test results shows that the effectiveness of sorbent injection is highly variable for various particulate control devices and coal rank (25). Results from Phase I field tests performed by ADA-ES under a cooperative agreement with NETL for a unit burning bituminous coals show very high removals, greater than 90%, at low injection rates of 3 lb/MMacf for a COHPAC™ FF installed in series with a hot-side ESP (EPRI's TOXECON™ control technology)[1]. Much lower removals were observed at similar injection rates for a cold-side ESP where capture trended linearly toward 90% only at high injection rates of 20 lb/MMacf.(25–28). Retrofit ESP–FF technology can be applied for multipollutant control to improve particulate collection efficiency and remove mercury separately without affecting the marketability of a majority of the fly ash. Hot-side ESPs alone, operating at 450°–750°F, do not effectively capture mercury. Mercury capture from a PRB coal-burning unit equipped with a cold-side ESP reached 50%–60% at low injection rates of 5 lb/MMacf but leveled off between 60%–65% at higher rates up to 30 lb/MMacf. These data suggest that high injection rates alone do not ensure high capture in ESPs for low-rank coals having both low chlorine content and low unburned carbon in ash. Mercury capture in this PRB test was not improved, with decreased temperature achieved by spray cooling the flue gas from 300° to 250°F. However, raising the flue gas temperature from 300° to 350°F in the ESP case burning bituminous coal reduced mercury capture from 90% to only 45% at 20 lb/MMacf, indicating that cooling may be required where flue gas temperatures exceed 340°F (26).

Full-scale testing of five different activated carbons chosen on the basis of laboratory adsorption capacity demonstrated similar trends in removal versus injection rate when tested at 300°F. These results indicated that all had sufficient capacity and reactivity to capture mercury from bituminous flue gas in an ESP. Comparison of in-duct capture with total removal across the ESP showed that the majority of the capture and almost all of the capture at high injection rates of 15–20 lb/MMacf occurred in less than a half-second of residence time in the duct (29). In bench-scale tests, equilibrium absorption capacities have been evaluated for several sorbents and compared to that of Norit FGD carbon (30). Oil-based activated carbons tested under PRB simulated flue gas conditions demonstrated an elemental mercury absorption capacity ranging from 1168 to 2267 µg/g, which was similar to Norit FGD carbon at 2070 µg/g under the same conditions. A number of activated carbons derived from vehicle tire rubber char have also been tested and have been shown to oxidize 95%–99% of the inlet elemental mercury and possess absorption capacities ranging from 444 to 2310 µg/g when tested with PRB simulated flue gas. In lignite flue gas in which chloride concentrations are very low, many activated carbons have not performed well. However, in tests of iodated carbons in a lignite simulated flue gas, mercury absorption capacities ranged from 1430 to 1930 µg/g, compared to only 1140 µg/g for the Norit

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[1] 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^{TM} for controlling mercury in power plants.

FGD carbon. In these tests, absorption capacity appeared to increase with iodine content as well as surface area of the carbon. Initial testing of carbon nanotube and fixed-structure carbon materials have demonstrated promise; however, adsorption capacity values are still much lower than more commercially available activated carbon.

Lignites like subbituminous coals typically have low chlorine content, high calcium content, and very low levels of unburned carbon in fly ash. Comparing carbon injection results for lignite from EERC field tests with the ADA–NETL tests discussed above, mercury removals for lignite using a cold-side ESP followed by a FF approached 90% at an injection rate of 7 lb/MMacf, approximately twice the injection rate needed for bituminous coal (31). Field results for lignite using a cold-side ESP alone showed the same level of removal at high injection rates as for PRB coal, except that capture for lignite peaked at 40%–50% instead of 50%–60%. Results of recent pilot-scale tests performed to optimize capture for lignite using various particulate control devices were reported for northern Great Plains test lignites that typically generate 85% elemental mercury at the inlet to particulate control devices (31). Mercury removals for cold-side ESP and ESP–FF configurations (EPRI's TOXECON™ and the EERC's *Advanced Hybrid*™ filter) were in general agreement with results of earlier field tests, with some difference observed for different lignites. Increasing temperature from 300° to 400°F required only a modest increase in injection rates (e.g., 14%) to achieve the same removals observed at 300°F in an ESP or ESP–FF configuration, respectively. However, a 70% increase in injection rate was required for a FF alone, possibly because of increased frequency of pulse cleaning at the higher temperature. Reducing the particle size of the activated carbon from a mean diameter of 20 to 5 microns increased mercury removals for a Popler River lignite test from a range of 30%–40% to a range of 30%–75% in the interval of 8–18 lb/MMacf. A similar size reduction had no significant effect for another lignite, possibly because of particle agglomeration or coal-specific differences in the oxidants present. The addition of HCl to flue gas at two different temperatures (1700° and 300°F) to improve downstream sorbent effectiveness did not significantly improve mercury removal. However, the addition of NaCl to the lignite feed substantially improved mercury capture to levels approaching or exceeding 90% for three configurations tested: ESP–FF, *Advanced Hybrid*™, and ESP alone.

The EERC's *Advanced Hybrid*™ particulate filter combines the best features of ESPs and FFs in a unique configuration that provides multipollutant control capability for ultrahigh collection of fine particulate and additional advantages as an excellent gas–solid contactor for mercury control (32). The *Advanced Hybrid*™ technology has demonstrated over 90% mercury control at a low carbon (DARCO™ FGD) injection rate of 1.5 lb/MMacf in tests on a 2.5-MW test unit operated on a slipstream from a cyclone-fired boiler burning PRB coal along with 4% supplemental fuel that included tire-derived fuel (TDF). Without supplemental TDF fuel, mercury removals at 1.5 lb/MMacf were 54%–74% in field tests and 50%–60% in smaller pilot-scale tests, which are levels comparable to the 60% removals observed for lignite in EERC field tests with the ESP–FF at 1–3 lb/MMacf (31). The effect of firing TDF based on a comparison of field- and pilot-scale data was to increase the level of unburned carbon from 0.2% to the range of 0.5%–1.9% and the level of HCl in the flue gas from 1–2 ppm to about 5 ppm (compared to 50–100 ppm for most bituminous coals), resulting in a large decrease in the inlet percentage of elemental mercury from 67% to 6%. Without TDF, injection of 10 ppm HCl upstream of the *Advanced Hybrid*™ filter had no appreciable effect on mercury capture. When operating without high-voltage power, the *Advanced Hybrid*™ filter distributes flue gas and sorbent evenly among all of the filter bags to make optimum use of sorbent capacity. With power on, most of the sorbent is collected on the charged plates. Under this condition, mass transfer between the gas and the sorbent particles in-flight may be relatively more important than the sorbent capacity in limiting mercury removal. However, nearly identical removals of 93.8% and 94.8% were measured with the power on and off, indicating that gas–solid contact and residence time were adequate to achieve very high removals at the low carbon injection rate of 1.5 lb/MMacf in either case. Increasing the air to cloth ratio (A/C) from 5 to 10 ft/min at a constant injection rate of 1.5 lb/MMacf reduced mercury removals only marginally from the range of 94%–97% to 91%–92%, whereas increasing A/C from 6 to 14 ft/min at a constant sorbent rate, effectively reducing the volumetric injection rate from 2.51 to 1.07 lb/MMacf, lowered mercury removal from 94% to 77%. Carbon injection in the *Advanced Hybrid*™ filter had no adverse effect on particulate filtration, bag-cleaning interval, or pressure drop.

The activated carbon used in most pilot- and full-scale ACI tests has been DARCO™ FGD made by Norit Americas Inc., which has become the benchmark. In general, only slight differences in performance have been noted between these or other untreated commercial carbons. The criteria for selecting an activated carbon or other sorbent are minimum cost, including transportation, handling, feeding, and disposal, and ability to maintain marketability of fly ash. An extensive evaluation funded by NETL with technical support from EPRI was performed to identify cost-effective alternatives to commercially available activated carbons, starting with a broad screening and narrowing the selection by performing injection tests on boiler slipstreams (33). Overall results showed that there are alternatives that could be commercially developed to provide higher performance at lower cost but that not all sorbents will perform universally (e.g., for all coals). The initial screening was based on laboratory sorbent capacities at a mercury concentration of 50 µg/Nm^3, testing 47 sorbents in simulated low-sulfur eastern bituminous flue gas and 27 in simulated PRB flue gas. Seventeen low-cost candidates were chosen for subsequent injection testing on a slipstream from a pulverized-fuel-fired boiler burning 85% bituminous coal and 15% petroleum coke, and five were chosen for similar testing on a cyclone-fired boiler burning PRB coal. DARCO™ FGD was tested as a reference carbon. Small-scale injection tests were performed to simulate two configurations: 1) in-flight capture in 2–4 seconds representative of the first section of an ESP and 2) capture for sorbent injection downstream of an ESP and ahead of a FF. The 10-acfm test unit used in this evaluation has been shown to provide results comparable to those measured in the field tests on the TOXECON™ technology (28).

In the injection tests performed on carbons selected for bituminous coal application, five of the 17 and the FGD reference carbon all demonstrated greater than 90% capture in the ESP–FF configuration. Parametric tests in this configuration identified two, a corn char and a treated activated carbon, that achieved higher removals at lower injection rates than FGD carbon over the range of 1–2 lb/MMacf with removals 5%–10% higher at 350° than at 315°F. In-flight tests showed that a soot-derived carbon having a significantly smaller particle size (d_{50}) of 6.2 µm provided higher removals than corn char carbon with a particle size of 15 µm. In-flight mercury capture generally increased with residence time and injection rate, but maximum removals were all less than 70% in the range of 2.5–15 lb/MMacf.

In the injection tests for PRB coal, three of five test carbons and the FGD carbon demonstrated similar performance of 80%–86% removal in the ESP–FF configuration at an injection rate of 1.5 lb/MMacf, including carbons derived from corn, soot, and German brown coal. Parametric tests resulted in similar removals for FGD carbon and the corn- and brown coal-derived test carbons trending upward from 65% to 95% over the range of 0.5–5 lb/MMacf, with no appreciable difference in removals between 300° and 350°F. In time-of-flight tests at 300°F, all removals were less than 50% for both soot- and corn-derived carbons in the range of 2.5–5 lb/MMacf, with the smaller particle size of the soot-derived carbon again providing somewhat higher removals. A commercial iodine-impregnated carbon demonstrated much higher removals in this configuration and greater improvement between 2- and 4-second residence time, suggesting that the small amount of HCl present in the PRB flue gas was not adequate to provide in situ conditioning of the untreated sorbents at the high injection rates required in an ESP.

Bench- and pilot-scale testing of a non-carbon-based sorbent have shown promising results for mercury capture at high temperatures, typical for a combined physisorption and chemisorption process. The sorbent is currently marketed as a specialty mineral additive for concrete applications, positively affecting compressive strength and pozzolanity. Fixed-bed testing suggested mercury capture could reach 75% with increasing temperature up to 1100°F. However, at temperatures below 600°F, no mercury sorption was observed. Pilot-scale tests were conducted at Southern Research Institute's 1.75-MW Combustion Research Facility burning Choctaw bituminous coal. Mercury capture was measured at near 50% at the baghouse inlet, approximately 4 seconds downstream of the sorbent injection point, at a rate of 22lb/MMacf. For this test, the temperature of the injection point was 1600°F, and at the baghouse inlet, 320°F. Mercury measurements at the baghouse outlet illustrated a general downward trend in mercury concentration over 8 hours of intermittent sorbent injection, ending in a maximum removal of near 90% at the conclusion of testing (34).

The effect of sorbent injection on mercury capture can be substantially impacted by the dispersion of sorbent within the flue gas (34). In an effort to quantify the mercury capture that occurs as a result of sorbent injection relative to residence time and turbulent mixing, bench-scale tests have been conducted using Norit FGD carbon, a nitrogen carrier gas, and a batch-mixing chamber. By monitoring mercury concentration at the various stages of injection, mixing, and residence time, the relative effects of each stage on mercury capture was determined. On average, 80% of the capture occurred immediately after sorbent injection. Additional residence times of 5 and 30 seconds under turbulent mixing conditions, made up less than 5% of the 30% mercury capture measured. Results from this research indicate that the way sorbent is injected into full-scale ductwork can impact mercury capture. Additional in-duct residence time may not be sufficient to ensure maximum efficiency, especially when applying sorbent injection technologies to ESP configurations where in-flight mass transfer is of primary importance.

Lessons Learned in Conducting the EPA Information Collection Request

In 1998, EPA issued an Information Collection Request (ICR) for calendar year 1999 to obtain mercury and chlorine analyses on coal and mercury speciation and emission data for 84 U.S. generating units representing different plant configurations burning various coals. Based on these data, it was estimated that, on average, 60% of the 75 tons of mercury in coal burned in utility boilers during 1999 was emitted into the atmosphere. Statistical correlations of percentage emissions, varying from under 10% to over 90%, were obtained to identify the most significant differences based on coal type and plant design. However, correlation and interpretation of the ICR data were limited by what are now recognized as deficiencies in data collection. Following is a summary of issues identified that can be addressed in future data-gathering efforts:

- Mercury speciation and capture in air pollution control devices downstream of the boiler are now known to be influenced by other elements in the coal and ash besides chlorine, which was analyzed as part of the ICR. At a minimum, future studies should include analyses for sulfur in coal, unburned carbon in ash, and the elements Ca, Mg, Na, K, and Fe. In addition, samples of coal and fly ash should be retained under suitable laboratory storage conditions to facilitate future analysis, as needed.

- Several different methods were used to analyze mercury and chlorine concentration in the coal during the ICR. The current methods of choice for mercury analysis are acid leaching (American Society for Testing and Materials [ASTM] D 6414) microwave digestion and direct combustion (ASTM 6722). The methods used for analyzing coal for chlorine were quite imprecise below 100 ppm. Improvements in analysis, including the use of ASTM D 6721-03, have decreased the lower limit of quantification to approximately 10 ppm. The Ontario Hydro wet chemical method used for measuring total and speciated mercury in the ICR tests on power plant flue gas is still the method of choice for research quality studies at plant sites. However, rigorous quality assurance and control, which appeared to be lacking in some ICR results, are required to ensure reliable results.

UPCOMING EVENTS

Winter International Activated Carbon Conference
March 1–2, 2004, Mexico City, Mexico
http://members.aol.com/hnpacs/conferences/IACC11techSum.htm

227th American Chemical Society National Meeting – Spring 2004
March 28–April 1, 2004, Anaheim, California

Electric Power 2004
March 30–April 1, 2004, Baltimore, Maryland
Mercury Session March 29, 2004, 1:30–4:30 p.m.
http://www.electricpowerexpo.com/conference_program.asp

Symposium on Air Quality Measurement Methods and Technology
April 19–22, 2004, Research Triangle Park, North Carolina
http://www.awma.org/events/confs/Measurements/default1.asp

Principles, Applications, and Opportunities with Activated Carbons
Professional Analytical and Consulting Services – Dr. Nowicki will provide a
2-day short course for $950
June 17–18, 2004, Toronto, Ontario, Canada
http://members.aol.com/hnpacs/news/MercurySorbentOpp.htm

International Conference on Mercury as a Global Pollutant
June 7–July 2, 2004, Ljubljana, Slovenia
http://congress.cd-cc.si/icmgp04/?menu_item=welcome&menu_level=2

Air & Waste Management Association 97th Annual Conference and Exhibition
June 22–25, 2004, Indianapolis, Indiana
http://www.awma.org/ACE2004/

228th ACS National Meeting – Fall 2004
August 22–26, 2004, Philadelphia, Pennsylvania

EPRI–EPA–DOE–A&WMA Power Plant Air Pollutant Control “Mega” Symposium August 30–
September 2, 2004, Washington, D.C.
Sign-up deadline April 15, and final presentations due July 23, 2004
http://www.awma.org/events/mega.pdf

14th International Activated Carbon Conference
October 7–8, 2004, Pittsburgh, Pennsylvania
http://members.aol.com/hnpacs/conferences/IACC11techSum.htm

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MERCURY INFORMATION
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Quarter 2 - Mercury Measurement

April 2004

Canadian Electricity Association
Association canadienne de l'électricité

EERC
Energy & Environmental Research Center

Center for Air Toxic Metals

MERCURY INFORMATION CLEARINGHOUSE

QUARTERLY 2 – MERCURY MEASUREMENT

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REPORT AVAILABILITY

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650 and the CEA mercury program Web site (www.ceamercuryprogram.ca).

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QUARTERLY 2 – MERCURY MEASUREMENT

EXECUTIVE SUMMARY

Mercury is an immediate concern for the Canadian and U.S. electric power industries as a result of pending regulation of mercury emissions. Canada has established a consultative process to develop Canadawide Standards (CWS) for mercury emissions from coal-fired electricity generation. In the United States, the Proposed Utility Mercury Reduction Rule comment period has been extended until June 29, 2004, at which time the U.S. Environmental Protection Agency (EPA) will be reviewing input from industry and environmental groups and developing a final rule.

With mercury regulations pending and with the early stages of full-scale demonstration of control technologies, measurement of mercury in combustion flue gas is of critical importance to demonstrate compliance and to allow evaluation of mercury control technologies. However, collecting a representative flue gas sample for mercury analysis presents many challenges owing to complex flue gas chemistry, high temperatures, mercury reactivity, and particulate loading. Given these challenges, many methods and instruments are available under varying degrees of development and are addressed in this quarterly report.

The most common approach for measuring mercury emissions from anthropogenic point sources consists of sampling train methods. Several common impinger-based methods include EPA Method 29, the tris buffer method, the Research Triangle Institute (RTI) method, and the Ontario Hydro method. Each of these methods relies upon an isokinetic nozzle and filter to collect a flue gas sample which is transported through a variety of liquid and solid sorbents to separate and preconcentrate gaseous mercury species. Quantification of the collected mercury species is then conducted using cold-vapor atomic absorption spectroscopy (CVAAS), cold-vapor atomic fluorescence spectroscopy (CVAFS), or energy-dispersive x-ray fluorescence (EDXRF).

A similar sample collection approach can also be applied to capture mercury species on a solid sampling medium through adsorption, amalgamation, diffusion, or ion exchange. These methods offer advantages in easier handling and greater stability; however, they are limited to time-averaging applications.

Real-time data collection can only be obtained through mercury continuous emission monitors (Hg CEMs). A large variety of Hg CEMs are available utilizing a variety of flue gas conditioning approaches; however, all commercially available instruments measure elemental mercury and are based on one of the following methods: preconcentration by gold amalgamation with CVAAS, Zeeman-modulated CVAAS, or preconcentration by gold amalgamation with CVAFS detection. Development work is ongoing for instruments that use atomic emission spectroscopy (AES) and laser technologies. As they are currently configured, Hg CEMs possess several challenges to long-term, low-maintenance operation, the most significant of which include sample collection and flue gas conditioning. Mercury species reactivity and particulate

loading make transporting a representative gas sample to the instrument a challenge and require heated sample lines and particulate removal techniques which prevent the buildup of a filter cake. Flue gas conditioning is an area where the greatest development is needed. Wet chemistry methods have typically been used to convert mercury to the elemental form that the analyzer can detect. These solutions are corrosive or caustic chemicals and challenges associated with their use are considered the limiting factor in Hg CEM reliability. Efforts to develop dry conversion units are beginning to produce results and focus on high-temperature catalysts and thermal reduction to convert oxidized mercury to the elemental form for analysis. It is anticipated that developments in this area will be the critical factor in ensuring real-time mercury measurements can be conducted reliably under steady-state operation.

MERCURY INFORMATION CLEARINGHOUSE

QUARTERLY 2 – MERCURY MEASUREMENT

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of developments in mercury monitoring, control, policy, and related research advances.

Recent developments in the area of mercury regulations from coal-fired power plants in Canada in the form of Canadawide Standards (CWS) and the United States in the U.S. Environmental Protection Agency's (EPA's) Proposed Utility Mercury Reduction Rule illustrate the need for effective mercury control strategies for coal-fired electric utilities as well as standard and reliable means of measuring mercury emissions. Currently, there is a variety of measurement methods and instruments that are commercially available or under development. A detailed review of these measurement alternatives is provided in this quarterly report.

In order to adequately address the many topics and provide the detail necessary for the various stakeholders to make informed decisions, selected topics will be discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that will be addressed in subsequent quarterly reports include, but are not limited to, the following:

- Mercury policy
  - Upcoming events and news releases
  - Regulation, policy, compliance strategies, and health developments

- Mercury measurement
  - Continuous mercury monitors
  - Advanced mercury-sampling systems
  - Wet-chemistry mercury measurement techniques

- Baseline mercury levels and emissions

- Mercury control
  - Sorbent technologies and control in unscrubbed systems
  - Advanced and developmental mercury control technologies
  - Summary of large-scale test activities and associated economics
  - Mercury oxidation and control for scrubbed systems
  - Multipollutant control strategies

  - Impact of mercury control on combustion by-products/fate of captured mercury
  - Summary of mercury-related economics for commercial systems

- Mercury chemistry and transformations
  - Mercury chemistry fundamentals, modeling, prediction, and speciation
  - Mercury fate and transport – impacts on health

One objective of this quarterly report is to provide timely information on developments in the broad field of mercury. In order to address timely issues as well as provide necessary detail on selected topics, additional subject headings will be provided to summarize recent developments not related to the quarterly topic. In this manner, updated information can be provided on topics previously covered or in advance of topics not yet discussed. The primary subject area for this quarterly report is a comprehensive review of available and developing mercury measurement methods and technologies.

MERCURY POLICY

The CWS Uniform Data Collection Program is ongoing and will support standard development expected by 2005. In the United States, EPA extended the comment period for the Utility Mercury Reduction Rule until June 29, 2004, to allow interested parties 90 days to review the document and submit formal comment. Upon completion of the comment period, a more detailed review of the rule will be provided to CEA.

On December 15, 2003, EPA proposed a rule to permanently cap and reduce mercury emissions from coal-fired utilities. EPA is proposing two alternatives for controlling emissions of mercury from coal-fired utilities. The first strategy is Maximum Achievable Control Technology (MACT), and the second establishes standards of performance limiting mercury emissions from new and existing utilities. The second proposal would establish a market-based cap-and-trade program. Under the MACT provisions of the Clean Air Act, sources are given 3 years to comply with emission reduction requirements. For the power generation industry, the MACT approach raises concerns about how quickly new control technologies could be put into place. Currently, no adequately demonstrated control technologies are specifically designed to reduce mercury emissions from coal-fired utilities. Also, the short compliance window would preclude the effective use of developing technologies. Under the cap-and-trade approach, EPA would allocate allowances for mercury emissions to each state which would then allocate them to utilities. The utilities would then be allowed to trade or bank any allowances above those required to cover their emissions each year. With the cap-and-trade program, emissions monitoring and reporting requirements will be stringent. However, this will allow for flexibility in trading which will create financial incentives for utilities to look for new and low-cost ways to reduce mercury emissions. Relative to the cap-and-trade system, MACT would restrict the options and incentives for power plants to achieve low-cost reductions. These higher costs could lead to increased electricity prices.

QUARTERLY 2 FOCUS: MERCURY MEASUREMENT

With mercury regulations pending and control technologies in the full-scale demonstration stage, measurement of mercury in combustion flue gas is of critical importance. The ability to accurately and reliably measure mercury is fundamental to demonstrating compliance when regulations are promulgated and, in the mean time, to ensuring adequate quantification of mercury removal during the full-scale demonstration and commercialization of the various mercury control technologies. Collecting a representative flue gas sample for mercury analysis from coal combustion flue gas produces many challenges. The complexity of flue gas chemistry, relatively high temperatures, reactivity of mercury species, and particulate loading must be addressed to ensure that the flue gas sample that reaches the mercury-measuring device is representative of the gas stream within the duct. In addition to measuring total mercury accurately, the identification and quantification of individual physicochemical forms (i.e., species) of mercury are imperative for addressing questions concerning mercury toxicity, bioaccumulation, emission control, and atmospheric fate and transport because each has distinctive physical, chemical, and biological properties. Mercury emissions from anthropogenic sources occur in three forms: solid particulate-associated mercury Hg(p); gaseous divalent mercury, Hg^{2+}; and gaseous elemental mercury, Hg^0.

Sampling Train Methods

The most common approach for measuring mercury emissions from anthropogenic point sources, such as coal-fired utilities, is to extract a representative sample of the flue gas using a sampling train. Sampling trains generally consist of an isokinetic nozzle and a filter to collect a representative fly ash sample and a liquid or solid sorption system to collect a particulate-free gaseous sample. A variety of liquid and solid sorbents can be used to separate and preconcentrate gaseous mercury species. Four primary impinger-based methods have been proposed over the past 15 years to speciate mercury: EPA Method 29, the tris buffer method, the RTI (Research Triangle Institute) method, and the Ontario Hydro method. Each of these methods uses solutions intended to selectively capture the oxidized and elemental forms of mercury. EPA Method 101A is also used but was designed specifically for determining only the total emission of mercury and does not offer speciation. Cold-vapor atomic absorption spectroscopy (CVAAS), cold-vapor atomic fluorescence spectroscopy (CVAFS), or energy-dispersive x-ray fluorescence (EDXRF) is used to quantify the collected mercury species. These analytical techniques are much more standardized than the equipment and procedures to collect the mercury from the flue gas stream. Uncertainties in the selectivity and collection efficiencies of the sampling media contribute to the inaccuracy of species determinations. The sampling methods generally require extensive analyte recovery and preparation steps that may introduce contamination or result in the loss of mercury. All impinger-based methods proposed for determining mercury speciation are configured based on an EPA Method 5 or 17 template.

EPA Method 29

EPA Method 29, also known as the multiple metals stack emission measurement method, was developed for measuring the solid particulate and gaseous emissions of mercury and 16 other trace elements (antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, phosphorus, selenium, silver, thallium, and zinc). A schematic of the

EPA Method 29 sampling train is presented in Figure 1. The EPA Method 29 sampling train consists of seven impingers. Following an optional moisture knockout impinger, gaseous mercury species are collected in two pairs of impingers connected in series containing different absorption solutions. A portion of the gaseous mercury is captured in the first pair of impingers containing aqueous solutions of 5% nitric acid (HNO_3) and 10% hydrogen peroxide (H_2O_2), while the remainder is captured in a second pair of impingers containing aqueous solutions of 4% potassium permanganate ($KMnO_4$) and 10% sulfuric acid (H_2SO_4). An empty impinger is located between the two sets of impingers to reduce the potential for blowback of $KMnO_4$ into the second HNO_3–H_2O_2 impinger during leak checks. The last impinger in both sampling trains contains silica gel to prevent contamination and entrap moisture that may otherwise travel downstream and damage the dry-gas meter and pump.

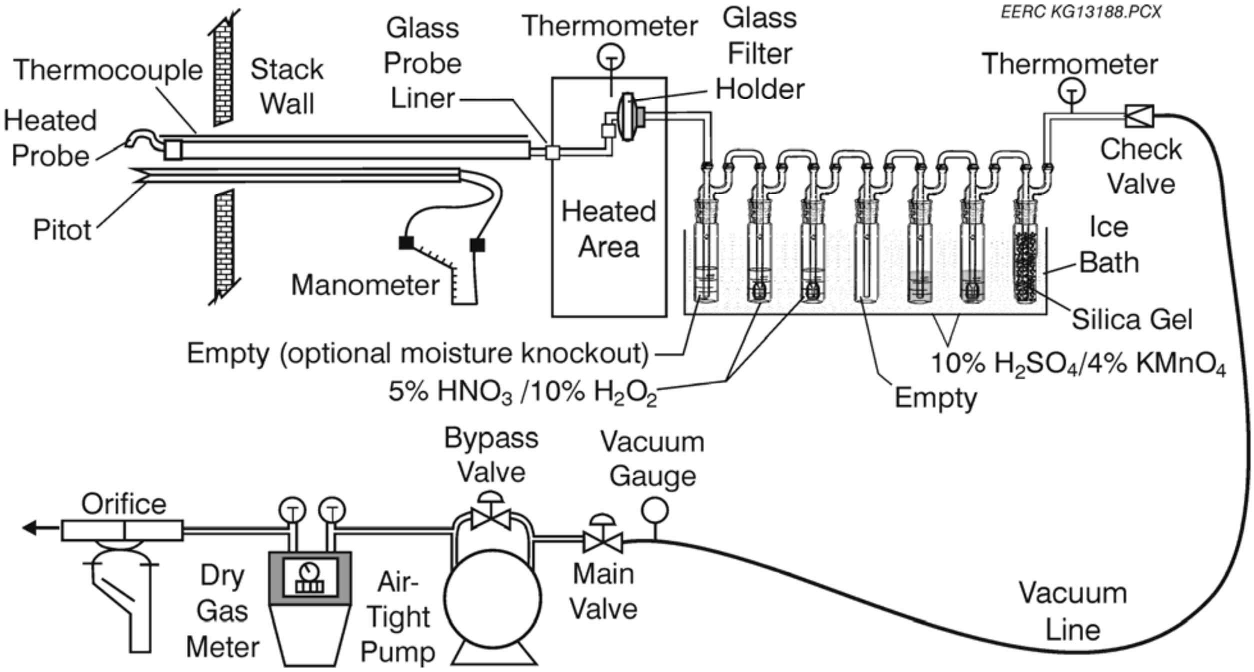

Figure 1. A schematic of the EPA Method 29 sampling train.

Although the EPA Method 29 sampling train was not originally designed for mercury speciation analysis, various research groups looked at the possibility of using the method for mercury speciation. Researchers surmised from the physical and chemical properties of mercury species that Hg^{2+} and Hg^0 would be selectively absorbed in the separate acidified hydrogen peroxide (HNO_3–H_2O_2) and acidified permanganate (H_2SO_4–$KMnO_4$) solutions, respectively, used in the EPA Method 29 impinger train. However, investigation proved these assumptions are incorrect. Data from the validation tests indicated that the two different impinger solutions employed were not effective for reliably separating the Hg^{2+} and Hg^0 forms in a chemically complex flue gas (1). As a consequence, several groups proposed modifications to the impinger solutions used in EPA Method 29. Modifications of EPA Method 29 that were tested at the EERC included the Ontario Hydro, tris buffer, and RTI methods.

Tris Buffer Method

The tris buffer method was developed by Radian International (now URS) with the support of EPRI's Environmental Control Technology Center (ECTC). A tris(hydroxymethyl) aminomethane buffer solution (abbreviated tris) is substituted for the $HNO_3–H_2O_2$ solutions in the first set of impingers of EPA Method 29 (2). It had previously been demonstrated that tris forms trigonal complexes with Hg^{2+} in alkaline and neutral media. Testing by Radian International indicated that the addition of an ethylenediaminetetraacetic acid (EDTA) chelating agent to tris was required to effectively retain mercury chloride ($HgCl_2$) (1). This method was validated using EPA Method 301 (1). A negative aspect of this modification, however, is the solution must be at a pH of 6 or higher to be effective; therefore, depending on the SO_2 concentration in the flue gas, the sampling time often must be reduced to less than an hour. If the mercury or mercury species concentration is low, this may result in nondetects. In addition, recovery of mercury from the tris solution is difficult and complex. During addition of HNO_3 and H_2O_2 to preserve the mercury in solution, carbon dioxide is evolved rapidly, so great care must be exercised to prevent loss of the mercury-containing tris solution.

RTI Method

The RTI method modified EPA Method 29 by replacing the first $HNO_3–H_2O_2$ impinger solution with deionized (DI) water. This method was never validated and is not used for mercury measurement.

Ontario Hydro Method

The Ontario Hydro method was developed by Dr. Keith Curtis and other researchers at Ontario Hydro Technologies, Toronto, Ontario, Canada, in late 1994. Since testing with EPA Method 29 appeared to show that some of the Hg^0 was captured in the $HNO_3–H_2O_2$ impingers, an attempt was made to more selectively capture the Hg^{2+} by substituting three aqueous 1 N potassium chloride (KCl) impinger solutions for one of the $HNO_3–H_2O_2$ solutions. A schematic of the impinger train is shown in Figure 2. In the first tests using this concept, no acidified peroxide impingers were in the sampling train. However, it was discovered that when the sulfur dioxide (SO_2) concentration in the flue gas was greater than approximately 750 ppm, the allowable sampling time was very short because the SO_2 reacted with the $KMnO_4$ and neutralized it. To avoid this problem, an impinger of acidified peroxide solution was used directly following the two KCl impingers. The purpose of the H_2O_2 was to absorb the SO_2, thus protecting the acidified permanganate solutions. It is assumed that any mercury collected in the acidified peroxide solution was Hg^0, since the KCl solutions would collect all of the Hg^{2+}. Early testing also showed a substantial portion of the mercury was lost from the solutions (3). This was later verified in the EERC pilot-scale testing. To counter this, acidified permanganate, dichromate, or acidified peroxide solution is added to the KCl solution immediately following sampling.

Formal evaluation of the Ontario Hydro method was completed with dynamic spiking of Hg^0 and $HgCl_2$ into a flue gas stream, and the method was validated at the EERC according to EPA Method 301 (3). The Ontario Hydro method is now ASTM Method D6784-02. It has also undergone field validation at a midwestern plant burning a high-sulfur eastern bituminous coal

(4). Based on the results from the validation testing, the relative standard deviation for gaseous elemental mercury and oxidized mercury was found to be less than 11% for mercury concentrations greater than 3 $\mu g/Nm^3$ and less than 34% for mercury concentrations less than 3 $\mu g/Nm^3$. In all cases, the laboratory bias for these tests based on a calculated correction factor was not statistically significant. These values were within the acceptable range, based on the criteria established in EPA Method 301 (% relative standard deviation [RSD] less than 50%).

In the test completed for the field validation, the quadtrain sampling resulted in a maximum variability (%RSD) of 22%. The sample recovery and analysis were done on-site, but the variability was higher than expected. However, the process variability was also high based on the plant SO_2 data and mercury CEM data. Regardless, the OH method passed the statistical criteria established in EPA Method 301 (5).

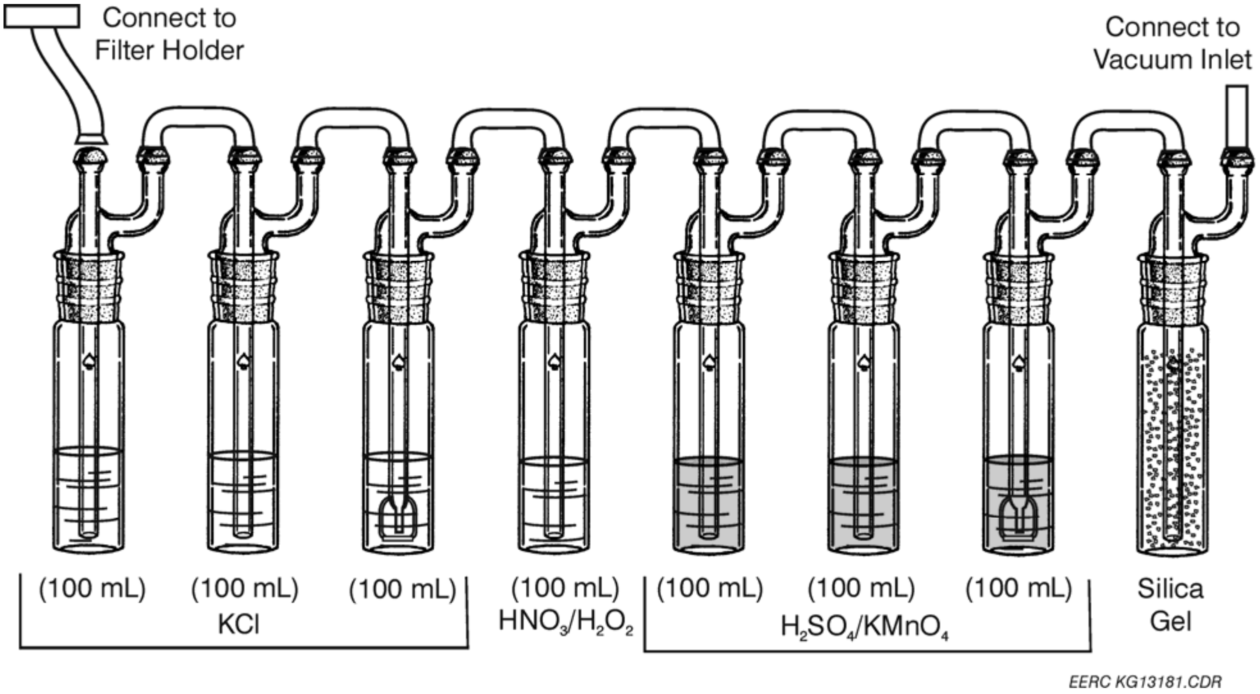

Figure 2. A schematic of the American Society for Testing and Materials (ASTM) Method D6784-02 (Ontario Hydro) sampling train.

Factors to Consider in Sampling Train Methods

The precision of particle-bound, oxidized, and elemental mercury-sampling method data is influenced by many factors: flue gas concentration, source, procedural, and equipment variables. Strict adherence to the method is necessary to reduce the effect of these variables. To ensure precise results are achieved, it is necessary that the system be leak free; all indicated system components accurately calibrated; proper sampling locations selected; glassware thoroughly cleaned; and prescribed sample recovery, preparation, and analysis procedures followed.

It should be noted that these methods were designed to be used after a plant's particulate control device. Therefore, when used with a filter in a high-dust situation (i.e., the inlet to the ESP or baghouse), reactive particulate matter can bias the speciation. This bias can be either shown as artificially high Hg^{2+} or high Hg(p).

Gaseous mercury species in flue gases that are capable of interacting with fly ash particles collected in the front half of the sampling train can produce a positive particle-bound mercury bias. Particle-bound mercury existing in the flue gas may vaporize after collection in the front half of the sampling train because of continued exposure to the flue gas sample stream and reduced pressures during the sampling period. Such vaporization would result in a negative particle-bound mercury bias.

Some of the practical limitations of the impinger-based methods originate from the problems and difficulties of using complex sample trains that are composed of relatively large amounts of glassware and tubing in the field. In addition, the glass impingers contain strongly oxidizing and acidic reagents requiring complex sample recovery and analytical procedures.

Dry Sorbent-Based Methods

In addition to impinger-based sampling trains, gaseous mercury species, Hg^{2+} and Hg^0, can be selectively captured on solid sampling medium through adsorption, amalgamation, diffusion, and ion exchange processes. Solid sorbents offer several advantages relative to liquid sorbents, including greater stability and easier handling and the mercury collected can be analyzed directly using sensitive techniques such as atomic fluorescence. These advantages provide the impetus for the development of solid sorption methods. However, the dry sorbent- based methods only provide a time-averaged mercury concentration, and the sorbents must be sent to a lab for an analysis. Based on these limitations, the dry sorbent methods will not be adequate for use in a mercury emissions control loop.

Currently, two dry sorbent methods are available for mercury measurement: the flue gas mercury sorbent speciation (FMSS) method or the Quick SEM™ (QSEM) method. Both methods rely on capturing mercury on dry sorbents. The FMSS method will speciate, but the QSEM method only measures the total mercury concentration in a flue gas stream. The FMSS method was developed by Frontier Geosciences based on earlier research with the mercury speciation adsorption method for measuring total gaseous mercury in a flue gas stream. The FMSS method pulls a semi-isokinetic sample from a flue gas duct through a miniparticulate filter and a heated solid sorbent sample train. The filter and the sorbent train are analyzed to determine Hg(p), Hg^{2+}, and Hg^0 (Figure 3). The diameter of the inlet nozzle is sized to provide isokinetic flow based on the nominal duct velocity. The miniparticulate filter consisting of a small quartz fiber filter disk is inserted into a quartz tube on a pure nickel support screen to collect fly ash for Hg(p) determination (6). The FMSS method sorbent train consists of dual dry sorbent traps for the gas-phase Hg species. The first trap contains dry KCl-coated quartz chips and is used to capture the Hg^{2+}. The second trap containing tri-iodine-impregnated activated carbon is used to capture the Hg^0 in the flue gas stream. After sample collection, the entire sample train trap is sent to a laboratory for analysis. Analysis of the sorbent traps is conducted by CVAFS, following strong acid digestion, BrCl oxidation, aqueous $SnCl_2$ reduction, and dual gold amalgamation (EPA Method 1631B, modified). The analysis of the Hg(p) on the fly ash is done by thermal desorption at 800°C, passing through a heated MnO converter, gold preconcentration, and CVAFS detection.

FMSS Method

The FMSS method was validated at the EERC according to a modified EPA Method 301 (7). The mean relative percent difference (RPD) was ±22% for Hg^0, ±8% for Hg^{2+}, ±10% for total Hg, and ±6.5% for Hg(p). The FMSS exhibited good agreement with Ontario Hydro methods, and accuracy was better than ±20% for all species for the range of conditions in the validation study, including ruggedness tests. The mean accuracy of the duplicates and the triplicates for the FMSS method was better than 97% for Hg^{2+}, total Hg, and Hg^{2+}.

EERC MH23084.CDR

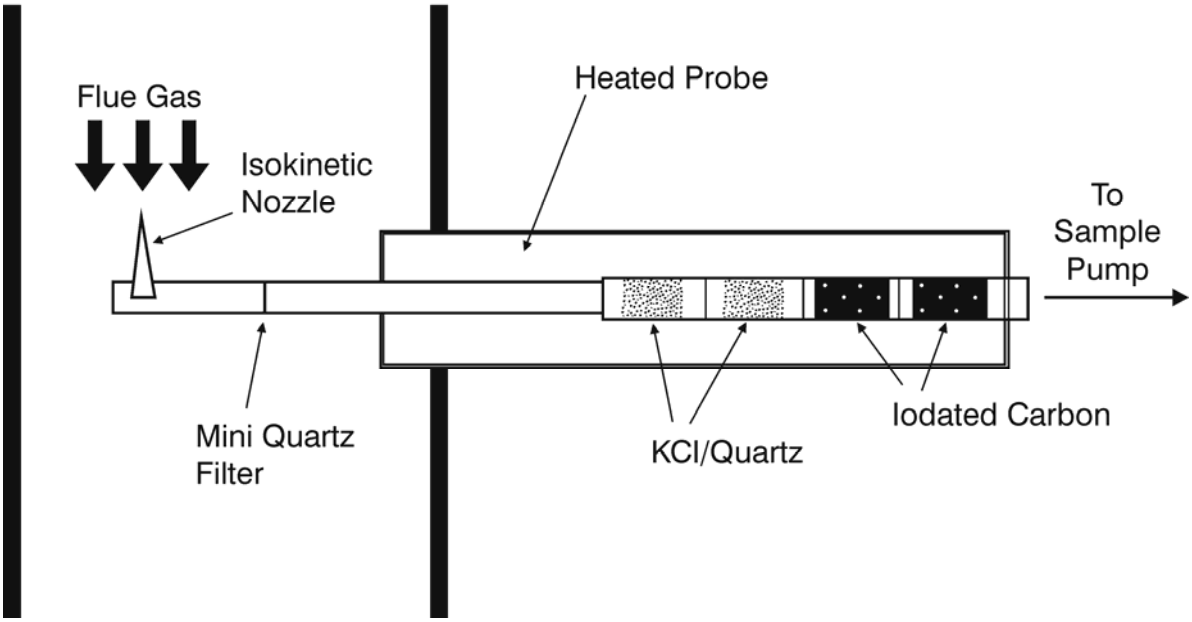

Figure 3. A schematic of the FMSS sampling train.

QSEM Method

The QSEM method was developed by EPRI, ADA Environmental Solutions, and Frontier Geosciences to measure total vapor-phase mercury mass concentration, which represents the sum of elemental and oxidized forms of mercury in a flue gas stream. A schematic of the sampling train is illustrated in Figure 4. The method is designed for use in low-dust applications with mercury concentrations ranging from 0.03 to 100 µg/dNm^3. Known volumes of flue gas are extracted from a duct through a single or paired iodine-impregnated carbon traps. Sample recovery consists of an acid leaching of the exposed traps and the leachate analyzed by CVAFS detection. Analysis of the leachate can also be performed using CVAAS detection. Where this method is used to collect data to demonstrate compliance with a regulation, it must be performed

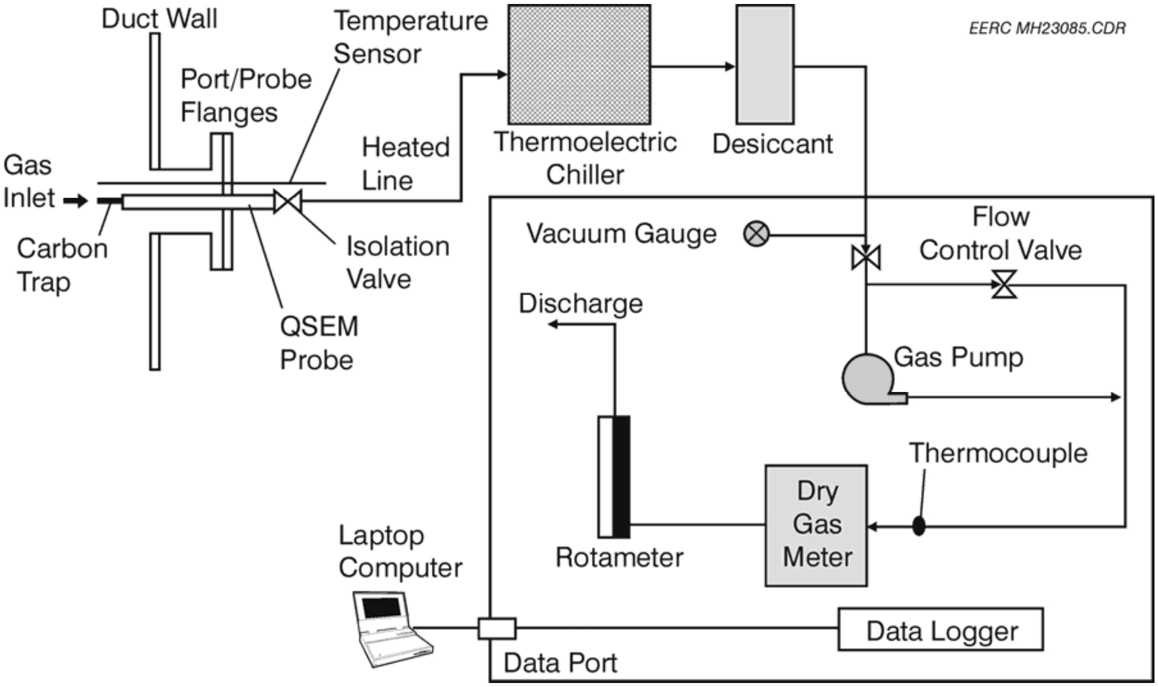

Figure 4. A schematic of the Quick SEM™ sampling train.

with paired sorbent trap equipment. The precision and accuracy of this method have not been reported, but it is inferred they are roughly the same as for the other dry sorbent method. This method is being proposed as EPA Method 324 (8).

Mercury Continuous Emission Monitors (Hg CEMS)

The Ontario Hydro wet chemistry method and dry sorbent methods provide good results for total and speciated mercury measurements; however, these methods can fail to provide the real-time data often necessary for research and compliance. Hg CEMs are similar to other combustion system CEMs in that a sample is extracted from the gas stream, conditioned, and sent to a remote analyzer for detection. However, as stated earlier, mercury is present in three different forms (Hg[p], Hg^{2+}, and Hg^0), which greatly complicates the measurement process. Although online emission analyzers can be costly to purchase, install, and maintain, they offer several benefits, including the following:

- Real- or near-real-time emission data
- Evaluation of control strategies
- Operational data for process control
- Greater understanding of process variability and operation
- Greater public assurance

As they are currently configured and utilized, Hg CEMs possess several challenges to long-term, low-maintenance continuous operation for flue gas mercury monitoring. The two main challenges include the areas of sample collection and flue gas conditioning. Collecting a representative flue gas sample for mercury analysis from coal combustion flue gas is very difficult. The complexity of flue gas chemistry, high temperatures, reactivity of mercury species, and particulate loading must be addressed to ensure that the flue gas sample that reaches the mercury-measuring device is representative of the gas stream within the duct. To a great extent, heated sample lines, gas conditioning systems, and material of construction have addressed many of these issues; however, monitoring dirty locations remains difficult, especially when reactive ash is present and traditional probe filters are used. Additionally, further development/ demonstration of gas conditioning systems will be required to ensure simple, reliable, and representative flue gas monitoring can be achieved.

Hg CEMs are currently used in Europe for compliance purposes. However, a typical German power plant is equipped with two electrostatic precipitators (ESPs), two scrubbers, a spray dryer, a carbon adsorber, a catalytic oxidizer, and a baghouse to control emissions. The effects of potential interferants in the flue gas such as carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), hydrochloric acid (HCl), ammonia (NH_3), chlorine (Cl_2), and particulate are almost entirely eliminated. After passing through these pollution control devices, most, if not all, of the remaining mercury is in the elemental phase (9). Measuring Hg^0 with all of the interfering gases removed is much easier than measuring all forms of mercury in a raw flue gas stream. Therefore, it is difficult to extrapolate European Hg CEM performance to U.S. applications. In order for Hg CEMs to be considered for regulatory compliance assurance, acceptable performance will need to be demonstrated. It is this lack of demonstrated performance that caused EPA's Office of Solid Waste to propose the use of total Hg CEMs for compliance assurance only as an option in the Phase I MACT Rule for Hazardous Waste Combustors (10). Currently the EPA has proposed a new performance standard which would outline the requirement for mercury measurement using continuous emission monitors. This Performance Specification 12A (PS-12A) titled "Specification and Test Methods for Total Vapor-Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources" would be included in the U.S. Code of Federal Regulations (CFR) (40 CFR Part 60, Appendix B). However, due to the challenges identified previously with Hg CEMs, an additional sorbent based mercury measurement method, EPA Method 324, has also been proposed for inclusion in the CFR titled "Determination of Vapor Phase Gas mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling" (40 CFR Part 63, Appendix A: Method 324). A detailed discussion of PS-12A will be provided in a future quarterly report, however a summary of criteria are included here as they are pertinent to defining the requirements of Hg CEMs.

- The Hg CEMs must be capable of measuring the total concentration in $\mu g/m^3$ (regardless of speciation) of vapor-phase Hg and recording that concentration on a dry basis, corrected to 20°C and 7% CO_2.

- Particulate-bound Hg is not included.

- The CEMs must include a diluent (CO_2) monitor and an automatic sampling system.

- Calibration techniques and auxiliary procedures are not specified.

- Procedures for measuring Hg CEM relative accuracy, measurement error, and drift are outlined.

- Hg CEM installation and measurement location specifications and data reduction procedures are included.

- Procedures for comparison with reference methods are outlined.

The basic steps that all Hg CEMs must accomplish in order to effectively measure mercury in a flue gas stream are:

- Filter particulate matter from the sample gas while minimizing flue gas fly ash contact.

- Either transport the sample gas to a conditioning system or condition the sample at the port and transport the conditioned sample to the instrument.

- Condition the sample by reducing all forms of mercury in the sample gas to Hg^0 and remove moisture form the sample gas.

- Measure the mercury in the flue gas sample.

Mercury analyzers can be distinguished by their measurement detection principle. Methods used include preconcentration by gold amalgamation with CVAAS detection, Zeeman-modulated CVAAS, preconcentration, and gold amalgamation with CVAFS detection. Instruments are also being developed based on AES and laser technologies.

CVAAS Method

The CVAAS method determines the mercury concentration in the gas by measuring the attenuation of the light produced by a mercury vapor lamp as it passes through a cell that contains the sample gas. The mercury atoms in the cell absorb mercury at their characteristic wavelength of 253.7 nm. Other flue gas constituents such as SO_2 absorb light across a wide spectrum including the 243.7 wavelength, thus acting as an interferant. Water vapor and particulate are also broadband absorbers that must be dealt with in CVAAS measurement. One method to remove the interferants is to preconcentrate the mercury on a gold trap for a known period of time at a known flow rate. The gold trap is then heated, and the mercury is swept into the detection cell with an inert gas. A second method is to use a powerful magnet to slightly shift the wavelength of the mercury vapor lamp (Zeeman modulation). The broadband absorbers will attenuate the signal at both wavelengths, and the difference between the signals is attributed to the mercury concentration. A third method is to use two detection cells. The sample gas first passes through a cell, and the signal attenuation is measured. The sample gas then passes through a trap to remove the mercury and finally through a second cell to measure the attenuation caused by the interferants. Similar to the Zeeman-modulated method, the difference in signals is attributed to the mercury concentration.

CVAFS Method

Typically, the CVAFS method uses gold amalgamation to preconcentrate the mercury. After the mercury is desorbed from the trap, it is swept into the detection cell by an argon carrier gas. The mercury atoms in the cell are excited to fluorescence by a pulsed mercury discharge lamp, which is measured by a photomultiplier tube. The fluorescence results in increased selectivity since only the mercury atoms will fluoresce. The fluorescence can be quenched through collision of excited mercury atoms with other components of the sample gas, particularly oxygen and nitrogen. In cases where the mercury concentration is high, nitrogen may be used as the carrier gas to suppress the fluorescence signal.

AES Method

The AES method is currently being developed by Envimetrics for mercury measurement. The method is based on the emission of light from mercury atoms induced by a high energy source such as a plasma. The light is emitted at the characteristic 253.7-nm wavelength. The advantage of this method is that the electron energy can be optimized to produce more radiation from the mercury in the sample gas than any other constituent. The AES method also has the potential to be used as a multimetal monitor.

Flue Gas Conditioning

Both CVAFS- and CVAAS-type mercury analyzers can only measure elemental mercury. Therefore, to measure the total mercury concentration in a sample gas stream, the oxidized forms must be reduced to elemental mercury in a conversion system. The most common method of reducing oxidized forms of mercury to elemental is using a liquid reducing agent such as $SnCl_2$ (stannous chloride). This method is used extensively, but has proven to be problematic. The wet-chemistry conversion systems are considered to be the limiting factor in reliability of Hg CEMs. The wet-chemistry systems use corrosive or caustic chemical solutions in large quantities. The spent reagents must be treated as hazardous waste which generates disposal concerns. In addition, all of the interactions between different flue gas constituents, the different mercury species, and the reducing reagents are not yet clearly understood.

Efforts to develop “dry” conversion units are beginning to produce results. These techniques center around using high-temperature catalysts or thermal reduction units to convert the oxidized mercury fraction to elemental mercury. These units also condition the sample gas by removing moisture and other interferants before the sample gas is sent to the analyzer. Although labeled as dry systems, most use chillers and gas–liquid separators to remove moisture from the sample gas stream. Demonstration of different dry units is ongoing, with early results looking favorable. There is some concern about the life and cost of catalysts used to reduce the oxidized forms of mercury to elemental mercury. Also, with the relative immaturity of this technology, it is likely that not all interferants and interactions with flue gas and the catalysts have been identified. Once proven, these units could greatly reduce the operational maintenance requirements.

Particulate Removal

Particulate-bound mercury captured on a filter can be reduced to Hg^0, but because of particulate matter transport issues, it is impractical. Also, EPA Draft Performance Specification 12A only requires CEMs to measure "the total concentration (regardless of speciation) of vapor phase mercury (11)." Therefore, it is important to remove any particulate matter from the sample gas stream in a manner that ensures it does not interfere with the operation of the analyzer or impart a bias to the mercury data. Conventional filtration methods will not work because as the particulate matter forms a dust cake on the filter media, it has a greater chance to interact with the flue gas and the mercury. The total mercury concentration could be biased low if the particulate matter is reactive and captures mercury. Although not important for measuring total mercury, the particulate matter on the filter could potentially bias the speciation of the measured mercury by oxidizing elemental mercury across the filter media. In an effort to greatly reduce or eliminate this problem, most CEM systems are either equipped with an inertial separation probe or a blowback filter of some type. In wet stack applications, downstream of a wet scrubber, water droplets in the stack make representative sample collection difficult. Mercury in the oxidized form could likely be associated with water droplets and not captured in isokinetic sampling. The EERC currently uses long heated probes upstream of a filter. The assumption is that mercury downstream of the scrubber would be elemental and, therefore, not significant in the water condensing in the stack.

Calibration

Regardless of measurement technique or conversion system, all instruments must be calibrated. All of the instruments available are easily zeroed by passing a filtered mercury-free sample gas through the analyzer. There are basically four ways to span a Hg CEM. First is manual injection of a known quantity of mercury. Since the vapor pressure of mercury is a well-known function of temperature, only the volume injected and the temperature of the vapor need be known in order to determine the amount injected. This is considered a primary standard for calibration. Second would be the use of a calibrated permeation source which may be internal or external to the instrument. These permeation devices can also be used to spike a sample at the inlet to the sampling probe to demonstrate the integrity of the sampling system. Third is the use of a calibration gas from a certified cylinder. The problem with cylinders is the high cost and low volume of gas in each cylinder. The last option (mainly for a CVAAS instrument using Zeeman modulation) involves using a small sealed cell with a known volume that contains a bead of elemental mercury. Again, the concentration in the cell is a function of the temperature of the cell. The cell is placed in the light path of the instrument, and the concentration is known based on the temperature of the cell.

Commercially Available CEMs

Table 1 provides a list of the commercially available Hg CEMs. A short description of each instrument is also provided. These descriptions are not meant to provide a detailed description, but simply an overview. The Web site for each vendor is provided.

Durag HM-1400 TR

Web site: http://www.durag.net/em/mercury/hm1400.html

The Durag HM-1400 TR is a dual-beam nonconcentrating CVAAS instrument that uses a thermocatalytic converter to reduce oxidized mercury to elemental mercury. A heated sample probe (SP-2000) and heated sample line are used to transport the sample gas to a chiller where the moisture is removed. The ionic forms of mercury are then reduced in the thermocatalytic converter. The catalyst in the converter will also remove some of the SO_2 from the sample gas stream. The mercury in the sample gas is measured in one cell of the instrument then passes through a mercury scrubber before passing through a second cell which is used to determine the compensation for the SO_2 and NO_2 interferences. The required sample flow rate is 100–120 N L/hr. The measurement cycle time is listed as less than 3 minutes, with a measurement range of 0–45 $\mu g/Nm^3$ and a lower detection limit of <1 $\mu g/Nm^3$. The measurement range can be expanded by diluting the sample gas stream. The sensitivity is listed as 0.2 $\mu g/Nm^3$, with a total accuracy of ±1% full scale or ±5%, depending on which specification sheet you look at. Zero drift is less than ±1.4% full scale, and the span drift is less than 2% full scale after 6 months. Durag claims a 6–8-month maintenance cycle for the unit. Flue gas sampling was previously listed as an appropriate application for this instrument. However, the Durag Web site no longer lists flue gas sampling as an appropriate application.

EcoChem Analytics Hg-MK II

Web site: http://www.ecochem.biz/Mercury/AnalyzersHGMKII.htm

The EcoChem HG-MK II uses CVAAS to detect elemental mercury in the gaseous phase. In order to measure total mercury, which includes mercuric chloride, the HG-MK II uses a patented dry thermocatalytic reactor to reduce oxidized forms of mercury to elemental mercury. No wet chemical reactors are used, and this greatly decreases complexity and maintenance requirements. After reduction, the sample stream is passed through a gold trap amalgamation unit where elemental mercury is absorbed. Subsequently, the mercury is desorbed from the gold trap into a stream of pure nitrogen and measured in a ultraviolet (UV) atomic absorption photometer operating at 253.7 nm.

Table 1. Commercially Available Hg CEMs

Vendor	Product	Analysis Method	Pretreatment/ Conversion	Speciating
Durag	HM-1400 TR	Atomic absorption	Thermal catalytic	$Hg^{total}(g)$
EcoChem Analytics	Hg-MK II	Atomic absorption	Thermal catalytic	$Hg^{total}(g)$
Envimetrics	Argus-Hg 1000	Atomic emission	Thermal catalytic	$Hg^{total}(g)$
Nippon	DM-6	Atomic absorption	Thermal catalytic	No
Nippon	DM-6A/MS-1A	Atomic absorption	Wet chemistry and thermal catalytic	Yes
Nippon	DM-6B	Atomic absorption	Thermal catalytic	Yes
Nippon	AM-2 or AM-3	Atomic absorption	Wet chemistry	$Hg^{total}(g)$
Ohio Lumex	RA-915+	Atomic absorption	None available	No
Opsis AB	HG200	Atomic absorption	Dilution system	Yes
PS Analytical	Sir Galahad	Atomic fluorescence	Wet/dry chemistry (2004 or 2005)	Yes
Semtech Metallurgy AB	Hg 2010	Atomic absorption	wet chemistry	$Hg^{total}(g)$
Sick UPA GmbH	MERCEM	Atomic absorption	Wet chemistry	$Hg^{total}(g)$
ST2 Technologies	SM-3	Atomic absorption	Thermal catalytic	Yes
Tekran, Inc.	3300	Atomic fluorescence	Dilution system	Yes

EcoChem claims that there are no interferences or cross sensitivities caused by exposure to flue gas. “The EcoChem HG-MK II uses a Gold Trap Amalgamation unit to capture the mercury present in flue gas, then transfer that mercury into a stream of pure nitrogen. Then when presented to the UV photometer, the measurement can be performed very accurately with interferences completely eliminated.” “By varying the collection time associated with the gold trap, it is possible to change the measuring ranges of the instrument. Thus for a hazardous or municipal waste incinerator, the EcoChem HG-MK II can operate in the range of 0 to 50 $\mu g/m^3$. While for a coal-fired utility application, the collection time can be increased, and the measuring range may be 0 to 10 $\mu g/m^3$ or even 0 to 1 $\mu g/m^3$.” The advertised resolution is 0.1 $\mu g/m^3$.

All fittings and tubing in the instrument are made of Teflon, quartz, or glass. Areas where metal must be used incorporate "heated special alloys." All surfaces coming in contact with oxidized mercury are held at elevated temperatures.

The system is controlled by a microprocessor, with all inputs made through a water-resistant front panel keyboard with user-programmable keys ("soft keys"). A large thin-film transistor (TFT) color screen displays all system variables and measured values. The most important components are housed in two 19-in. rack-mounted units each three units high. Other components can be accessed from the back plate of the housing.

The EcoChem HG-MK II executes an automatic zero-point and a reference-point procedure at preset intervals. Important process variables like flow rate, temperature, and instrument drift are continuously monitored. In case of excessive deviations from set values, a status signal is activated to alarm the operator.

The basic components of the HG-MK II include a probe with a heated line to transport the sample to the analyzer. The sample probe extracts 2 to 3 liters a minute and transports it through a heated sampling line at 200°C. In order to prevent loss of mercury in the sampling line, it is recommended that the line not exceed 150 feet. A thermocatalytic converter reduces oxidized mercury compounds to elemental mercury vapor. The amalgamation unit consists of an integrated valve assembly, a gold trap, and a calibration source for elemental mercury vapor. The valve assembly can be switched to "continuous mode operation" in case of high mercury concentrations. The gold trap amalgamation unit offers the ability to reduce the detection threshold by modifying the collection time. The UV photometer consists of a fixed-wavelength atomic absorption spectrometer at a 253.7-nm wavelength. The photometer has a reference beam for lamp control and an electrodeless low-pressure lamp with long service life (>20,000 hours).

EcoChem claims no interference from SO_2, NO_x, volatile organic compounds, and other compounds through the use of the gold trap. However, it does not mention if HCl causes interferences with the gold trap. Manufacturers of other instruments that use gold amalgamation acknowledge interference in the presence of HCl and NO_x.

The instrument is zeroed automatically but also has manual correction for the zero point. The instrument is spanned either automatically or manually using permeation device.

Envimetrics Argus-Hg 1000

Web site: http://www.envimetrics.com/Env_Products.htm

The Argus-Hg 1000 uses atomic emission spectroscopy to measure total mercury in a flue gas stream. The particulate in the sample gas is removed by a ceramic blowback filter before it passes through a thermo catalytic converter which reduces all mercury in the sample gas to elemental mercury. A Peltier chiller is used to remove moisture from the gas before it is transported to the analyzer. In the analyzer, the sample gas first passes through an absorber which collects the mercury. When the absorber is heated, the mercury is swept into the detector with an argon carrier gas. The instrument will only consume one (200-ft^3) tank of argon a year. Microwave energy is used to excite electrons in a plasma. The high-energy electrons then collide with the mercury atoms in the sample gas causing them to radiate both visible and UV light. The electron energy has been optimized to produce a large amount of UV light from mercury and a minimal amount of UV light from all other species in flue gas, thus eliminating the effects of any interferants. Calibration of the analyzer is achieved with an internal permeation device, and there is no need for zero adjustment. The lower detection limit is advertised as 0.03 $\mu g/m^3$ with a 3-minute cycle time. Envimetrics participated in the second round of the EPA Environmental Technology Verification (ETV) Program (12).

Nippon DM-6

Web site: http://www.hg-nic.com/dmseries.html

Nippon has four different analyzers for sampling flue gas from a coal-fired utility. The DM-6 is considered a “dry” system. In the pretreatment unit, DM-6P, the sample gas is drawn from the stack and passes through a filter to remove dust. The mercury compounds are then reduced to elemental mercury by contacting with the solid-state reduction catalyst which is housed in the probe. The sample gas with the reduced elemental mercury then passes through a chiller to remove the moisture (condensate is continuously pumped back into the stack) and then transported to the detector via Teflon tubing to be continuously measured by CVAAS. A liquid crystal display shows the mercury concentration which is updated every second. The detector unit has outputs for either an external computer and/or a data logger. The response time is less than 1 minute, and the sensitivity is listed as 0.1 $\mu g/m^3$.

Horiba Instruments, Inc., of Irvine, California, has entered into a long-term agreement with Nippon Instruments Corp. (NIC) headquartered in Osaka, Japan, to exclusively sell and service the NIC Continuous Mercury Emissions Monitor in the United States. NIC has been designing and selling instruments to measure mercury in the environment for the last 25 years.

Nippon participated in the first two rounds of EPA ETV Program to evaluate Hg CEMs (12).

Nippon DM-6A/MS-1A

Web site: http://www.hg-nic.com/dmseries.html

The DM-6A/MS-1A is similar to the DM-6, but it has the added capability of speciating the mercury in the sample gas stream. First, the sample gas is mixed with a solution that captures the oxidized forms of mercury. The sample then passes through a gas–liquid separator. A potassium hydroxide (KOH) scrubber is used to remove interference gases such as SO_2. The gas portion of the sample then passes through a chiller to remove moisture and then through the detector to give a measurement of gaseous elemental mercury in the flue gas stream. The solution containing the Hg^{2+} is mixed with a reducing solution ($SnCl_2$) to reduced the oxidized mercury to gaseous elemental mercury. This sample stream then passes through a gas–liquid separator. This sample gas stream then passes through a KOH scrubber to remove interference gases. After dehumidification, the sample passes through the detector to give a measurement of oxidized mercury in the flue gas stream. The DM-6 and DM-6A both have a nominal range of

0.1–1000 $\mu g/m^3$. Both are calibrated with an internal permeation device and have an automatic zero adjust.

Nippon DM-6B

The DM-6B is essentially two DM-6 units running in parallel. The first unit operates as a DM-6 to give a measurement of total gaseous mercury. The second unit passes the flue gas through a chiller before passing through the catalyst. By doing this, the oxidized mercury is removed with the condensate, and the result is a measurement of the gaseous elemental mercury in the sample gas stream. This instrument is currently being evaluated by the EERC.

Nippon AM-2 or AM-3

Web site: http://www.smglink.com/nic/

The AM-2/3 instrument uses gold amalgamation concentration techniques with CVAAS detection to measure mercury in a gas stream. In some areas, the AM-2/3 is still listed as appropriate for sampling mercury in a flue gas stream, but it appears it has been replaced by the DM-6 series instruments. The AM-2 was also evaluated during the first round of the EPA ETV Program (12).

Ohio Lumex RA-915+

Web site: http://www.ohiolumex.com/

The Ohio Lumex RA-915+ is a real-time continuous monitor for total and elemental mercury measurement. The instrument is based on differential Zeeman atomic absorption spectroscopy using high-frequency modulation of light polarization. A mercury lamp is placed in a permanent magnetic field which has the ability to slightly change the wavelength of the mercury light. This allows for background correction for such broadband absorbers as SO_2, moisture, and particulate matter. The Lumex has a multipass cell which provides an effective path length of 10 meters. The instrument does not use gold amalgamation preconcentration which allows for a faster response time. In ambient air, a lower detection limit of 2 ng/m^3 can be achieved according to the manufacturer. Ohio Lumex provides a cell for thermal reduction of oxidized mercury to elemental mercury. No catalyst is used in the thermal decomposition cell. Further testing needs to be completed with this system to ensure recombination of the oxidized mercury does not take place.

The Lumex needs an external mercury supply such as a permeation device or a gas cylinder for calibration. The instrument does come with a small cell of fixed volume that contains saturated mercury vapor which can be used to check the calibration.

An earlier version of the Ohio Lumex instrument was evaluated during the first round of the EPA ETV Program (12).

Opsis Hg-200

Web site: http://www.opsis.se/monitoring/cemproducts.asp?Id=6

The Hg-200 uses a dilution extraction system to provide a flue gas sample to the analyzer. Four ¼-inch Teflon lines are used to connect the stack probe to the analyzer. One line carries dilution air to the probe, another transports diluted sample from the probe to the instrument, the third sends calibration gas from the analyzer to the probe, and the fourth is a vacuum sensor line for verifying that the sampling system is working. The sample gas is filtered before critical orifices are used to mix and dilute the sample gas. The nominal dilution rate is 100:1 which prevents condensation during transport to the analyzer. A pump is used to supply 2 L/min of sample gas to the analyzer. A thermocatalytic converter is used to reduce all of the mercury to the elemental form. The catalyst can be run hot or cold to give measurements of total or elemental mercury, respectively. The cycle time is normally 5 minutes. The analyzer portion of this system uses CVAAS and a double-beam photometer. The mercury is preconcentrated on a gold trap. An internal permeation device is used for span calibration of the instrument along with an automatic-zero adjustment. The lower detection limit of the instrument is listed as 0.05 ng/m^3, with a nominal measurement range of 0.5–1000 μg/m^3. The Opsis Hg-200 was evaluated in the first round of the EPA ETV Program (12).

PS Analytical Sir Galahad 10.665

Web site: http://www.psanalytical.com/

The Sir Galahad analyzer utilizes a completely integrated sampling, conditioning, and analysis system to determine the mercury concentration in a flue gas stream. The sample gas is extracted from the duct using a heated inertial separation probe. The sample is then transported to a wet chemical system where the sample stream is split into two streams. The first stream is mixed with a KCl solution to remove the oxidized mercury from the sample gas stream. The gas passes through a chilled gas–liquid separator to remove moisture. It is then sent to the Sir Galahad analyzer for determination of mercury concentration. The second gas stream is mixed with a reducing solution which reduces all of the mercury in the sample gas stream to elemental mercury. It also passes through a chilled gas–liquid separator to remove moisture before being sent to the analyzer. A switching box is used upstream of the analyzer to select between sampling total Hg or Hg^0 and sending either zero gas or a span gas to the probe tip. The span gas is generated by the CavKit which is similar to a permeation device. The Sir Galahad analyzer utilizes gold amalgamation and CVAFS to determine the mercury concentration in the sample gas stream. A source of compressed mercury-free argon and clean, dry air is required for operation of the analyzer. If the mercury concentrations are high, mercury-free nitrogen can be substituted for the argon. Calibration of the system is done using Hg^0 as the primary standard. It is contained in a closed vial held in a thermostatic bath. The temperature of the mercury is monitored, and the amount of mercury is calculated using vapor pressure calculations. Typically, the calibration of the unit has proven to be stable over a 24-hr period. The sample cycle time is typically 6 minutes, and the nominal measurement range is 0.001–2500 μg/m^3. PS Analytical has participated in both rounds of the EPA ETV Program (12).

Semtech Metallurgy AB Hg 2010

The Semtech analyzer uses CVAAS with background Zeeman correction to determine the mercury concentration in a sample gas stream. Semtech offers a wet-chemistry conversion system to reduce oxidized mercury to elemental mercury. However, the conversion system only works if there is no SO_2 present in the sample gas. The lower detection limit can be changed by increasing the path length. Several sample cells are available, with the longest providing a 500-mm path length. With the 500-mm cell, the lower detection limit is 0.3 $\mu g/m^3$ and the upper limit is 160 $\mu g/m^3$. The instrument automatically zeros every hour by pulling room air through a carbon filter and then through the detection cell. The span can be checked with a sealed cell of known volume which contains saturated mercury vapor. The concentration in the cell is only a function of the temperature of the cell. There are no set flow rate requirements for the Semtech. The Semtech Hg 2010 has been certified by TÜV Rheinland for determining compliance with the German legal limit of 50 $\mu g/Nm^3$ for total mercury emissions from waste incinerators.

SICK UPA GmbH MERCEM

Web site: http://www.maihak.de/sickmaihak_de/en.html

The TÜV-certified SICK MERCEM instrument uses CVAAS to detect elemental mercury in the gaseous phase. The MERCEM employs a sample probe containing two sintered metal filters to extract a particulate-free flue gas sample. A heated (185 °C) sample line is used to transport the sample gas to the conditioner and analysis units. A tin(II) chloride ($SnCl_2$) solution is injected into the sample line and transported concurrently with the sample gas to a reactor for converting oxidized mercury to elemental mercury. The concentration of $SnCl_2$ reducing solution is kept constant by refilling from a reservoir with a peristaltic pump.

After passing through a peltier cooler to remove moisture, the dry sample gas enters a gold trap for amalgamation. In the amalgamation procedure, a precisely defined volume of the sample gas is passed through a gold trap, and the elemental mercury forms an amalgam with the gold. At the end of this collection phase, the gold trap is heated electrically and the mercury is released and transported through the cell of the photometer by an inert carrier gas stream. Following the purging cycle, the gold trap is cooled and is then ready for the next collection period. By varying the collection period, the measurement range or the detection limit can be varied over a wide range to meet individual requirements. The recommended range is 0–100 $\mu g/m^3$, with a detection limit of <0.5 $\mu g/m^3$, depending on sampling time. Therefore, mercury can be accurately measured for a wide range of sources from hazardous waste incinerators to coal-fired power plants.

The amalgamation procedure features an additional major advantage, i.e., that the Hg analyzer is never in direct contact with the stack gas. Thus interferences caused by other components in the stack gas are eliminated. However, compared to other CVAAS systems, the response time is longer by approximately 180 s.

Although a relatively large unit, the MERCEM comprises a system cabinet containing the sample gas transfer lines, analyzer unit with sample gas preparation assembly, and control unit. All components inside the cabinet can be easily accessed for maintenance purposes when the front door is open. The reservoir for the reductant solution is located directly behind the front door, making it very easy to replace.

The MERCEM is designed for continuous operation and contains all control units and self-check functions required for automatic operation. The temperature and flow rate of the sampling system are constantly monitored. The unit has an automatic zeroing system but calibration using elemental mercury is accomplished using an external source.

ST2 Technologies SM-3

Web site: http://www.mercury-instruments.de

U.S. Distributor: ST2 Service Technologies, Inc., http://www.st2-service.com

The TÜV-certified Mercury Instruments SM-3 uses CVAAS to detect elemental mercury in the gaseous phase. A probe with a heated line and filter is used to transport the sample to the analyzer. In order to measure total mercury, which includes mercuric chloride, the SM-3 uses a patented dry thermocatalytic reactor to reduce oxidized forms of mercury to elemental mercury. No wet chemical reactors are used, and this greatly decreases complexity and maintenance requirements. After all the mercury in the flue gas has been reduced, the gas is passed to a peltier cooler and the water is condensed out. The dry gas is then fed to the mercury detector where the mercury concentration is measured using a UV atomic absorption photometer operating at 253.7 nm.

To prevent recombination and any adsorptional loss of mercury, all surfaces coming into contact with the sample gas are heated to temperatures >180°C. The SM-3 does not use any gold collector for mercury preconcentration, thus giving a very fast response and providing results continuously and in real time. Possible problems connected with "poisoning" of the gold surface are thus eliminated.

The instrument has three operating ranges, 0–45, 0–75, 0–500 $\mu g/m^3$, and a stated detection limit of <1% of measuring range. The response time is <60 seconds, compared to up to 6 minutes for systems using a gold trap. The zero drift is <1%, and the instrument comes with an auto-zero feature. The instrument must be externally calibrated using a permeation tube or other such device. However, Mercury Instruments does sell an external calibration system (MC 3000) that works directly with the SM-3.

The system is controlled by a microprocessor, with all inputs made through a water-resistant keyboard. A large TFT color screen displays all system variables and measured values. The unit is housed in a single, relatively small unit (550 × 1000 × 700 mm).

Tekran®, Inc., 3300

Web site: http://tekran.com/phpcode/index.php

The Tekran® Series 3300 speciating mercury continuous emissions monitor uses a CVAFS analyzer in conjunction with a dry conversion system and sampling probe to measure speciated mercury in a flue gas stream. The sample gas is pulled through a stack-mounted high- flow-rate inertial probe to minimize mercury measurement artifacts due to filtering. The sample is then diluted and transported through a heated line to a conditioning module. The diluted sample is split into two streams. In the first stream, a thermal conditioner unit reduces all of the mercury forms present in the sample to elemental mercury. Recombination is avoided by the quantitative removal of HCl and other gases by a patented thermal conditioner/scrubber system. The second pathway removes ionic (water-soluble) mercury, leaving only the elemental mercury to pass through to the converter. This stream is then subjected to additional conditioning to remove acid gases and excess humidity from the sample. Ionic mercury is determined by difference. This conversion unit has the advantage of not using chemical reagents or solid sorbents.

The probe is capable of performing automated filter blowback, multipoint calibrations, and standard additions of elemental mercury into the sample matrix. Probe temperatures, flow rates and pressures are monitored and telemetered to the system controller via a datacom link.

The two conditioned streams are analyzed using a Tekran Model 2537A mercury vapor analyzer. This analyzer is in wide use all over the world and has demonstrated its accuracy, stability, and reliability under the most remote and rugged conditions imaginable. The analyzer uses gold preconcentration combined with atomic fluorescence detection. The advertised minimum detection limit for the analyzer is less than 0.05 $\mu g/m^3$. A source of compressed mercury-free argon is required for operation of the instrument.

A calibration source allows both multipoint calibrations and standard additions to be automatically initiated. Both these operations are performed through the entire CEM path, including all probe filters. The calibration unit generates concentrations of mercury by using a National Institute of Standards and Technology-traceable temperature-controlled saturated mercury vapor source. Precision mass flow controllers are used to dilute the output of this source to the desired value. The unit is capable of continuously generating large flow rates of calibration gas at no ongoing cost – unlike expensive mercury calibration gas cylinders.

The computer provides full control of each module within the system. Industry standard protocol is used to monitor and control each unit. All temperatures, flows, and pressures are displayed by the application program and may be set by authorized users. The system features remote operation and problem diagnosis, either via a modem and telephone line or through the Internet.

SUMMARY

Hg CEMs are necessary and useful tools for measuring mercury for both research and compliance applications, and a variety of instruments are available, each with unique advantages and drawbacks. Measurement of mercury in a flue gas stream generated by coal combustion is much more challenging than measuring from other sources. Sources such as incinerators typically have more pollution control equipment such as scrubbers in conjunction with fabric filters and sorbent beds which all help to clean up the flue gas before it reaches a mercury measurement system. However, development is ongoing to address the challenges to providing long-term operation for flue gas monitoring with a minimal amount of maintenance. All of the analyzers mentioned will measure mercury in a relatively clean sample gas stream. The main challenge facing mercury CEM manufacturers is providing a “clean” sample gas to the mercury analyzer. The sample conditioning methods currently available are:

- Wet chemistry – These systems provide speciated mercury data by using wet chemistry methods to either remove or reduce oxidized mercury from the sample gas as well as remove interferant gases from the sample gas stream. To date these have been the most frequently used systems for research and there has been a great deal of data collected while using them. The reliability of these systems has been improved through several design iterations, but they still require more maintenance than is acceptable for long term monitoring. Because these systems are wet chemistry based they require large amounts of chemicals and generate a large amount of waste (up to 8 liters per day). The wet chemistry systems have worked well in plants burning either lignite or subbituminous coal. However, in plants burning bituminous coal with high sulfur and chlorine, there have been problems with the chemistry of the system. Some plants with high SO_2 also generate high SO_3 concentrations. The SO_3 can pass through the wet chemistry portion of the system as an aerosol and deposit on backup filters and sample lines. This can cause problems with mercury capture and changes to speciation. The wet chemistry systems can be used with any type of mercury analyzer.

- Thermal Catalytic Reduction – These systems can provide speciated mercury data. The oxidized forms of mercury are reduced to elemental mercury across a catalyst bed. A dry sorbent or wet chemistry system may be used to remove oxidized mercury from the sample gas stream. These systems may include additional wet chemistry systems for removing interferants from the gas stream before sending the gas to the analyzer. The volume of wet chemicals consumed in these systems is much smaller than the all wet systems (on the order of a liter per week). Limited long-term data has been generated using these systems. However, there appears to be problems with the life of the catalysts particularly in high acid gas situations. The catalysts are expensive and may need frequent regeneration and or replacement. The thermal catalytic systems have yet to demonstrate long-term reliability. It is most likely that not all of the interferants and interactions with different flue gas components have been identified. Thermal catalytic reduction is best used with the CVAAS analyzers because the interferant gases for CVAFS are not necessarily removed.

- Dilution and Thermal Catalytic Reduction – This is a relatively new method for conditioning the sample gas for mercury analysis. These systems dilute the sample gas at or near the probe before sending it to a sample conditioner. The theory is that the diluted sample is easier to transport, and condition. The lower concentrations of interferant gases are also less likely to poison the catalyst used for reducing oxidized mercury to elemental mercury. Speciating the mercury is accomplished by scruubing the oxidized mercury from the sample gas with a small amount of de-ionized water or a dry trap. Again, it is most likely that not all of the interferants and interactions with different flue gas components have been identified. Because of dilution and the resulting low mercury concentrations, a CVAFS analyzer must be used. These systems are the latest iteration of conditioning systems and not much data have been generated with them, but they have the potential to be very reliable with low maintenance requirements.

At this time there does not appear to be one instrument or measurement technology that will work best in all applications. However, the latest iteration of systems becoming available this summer show promise. The most advanced systems are those that integrate all of the components necessary to accurately and reliably measure mercury emissions from a utility boiler. These components include:

- Particulate removal system-It must continuously remove particulate matter before it can interact with the sample gas.
- Sample transport-Integrated with sample probe
- Sample conditioning system-Must provide “clean” dry sample gas to the mercury analyzer.
- Mercury analyzer
- Calibration/spiking system-Easy, preferably automatic calibration checks. Spiking of at least elemental mercury at the probe. Dynamic spiking of elemental mercury into the flue gas matrix at the probe is a plus.

As instrument improvements occur, updated reviews of their performance in demonstration tests will be provided in future quarterly reports to provide the reader with the information necessary to identify instruments best suited for their application and needs.

UPCOMING EVENTS

Emission Monitoring 2004 – A seminar providing independent and objective perspectives for meeting emission monitoring and testing challenges
June 2–4, 2004, Durham, North Carolina
http://www.emissionmonitoring.com

Principles, Applications, and Opportunities with Activated Carbons
Professional Analytical and Consulting Services – Dr. Nowicki will provide a 2-day short course for $950
June 17–18, 2004, Toronto, Ontario, Canada
http://members.aol.com/hnpacs/news/MercurySorbentOpp.htm

International Conference on Mercury as a Global Pollutant
June 7–July 2, 2004, Ljubljana, Slovenia
http://congress.cd-cc.si/icmgp04/?menu_item=welcome&menu_level=2
Air & Waste Management Association 97th Annual Conference and Exhibition
June 22–25, 2004, Indianapolis, Indiana
http://www.awma.org/ACE2004/

228th ACS National Meeting – Fall 2004
August 22–26, 2004, Philadelphia, Pennsylvania
http://oasys.acs.org/oasys.htm

EPRI–EPA–DOE–A&WMA Power Plant Air Pollutant Control “Mega” Symposium August 30–September 2, 2004, Washington, D.C.
Sign-up deadline April 15, and final presentations due July 23, 2004
http://www.awma.org/events/mega.pdf

14th International Activated Carbon Conference
October 7–8, 2004, Pittsburgh, Pennsylvania
http://members.aol.com/hnpacs/conferences/IACC11techSum.htm

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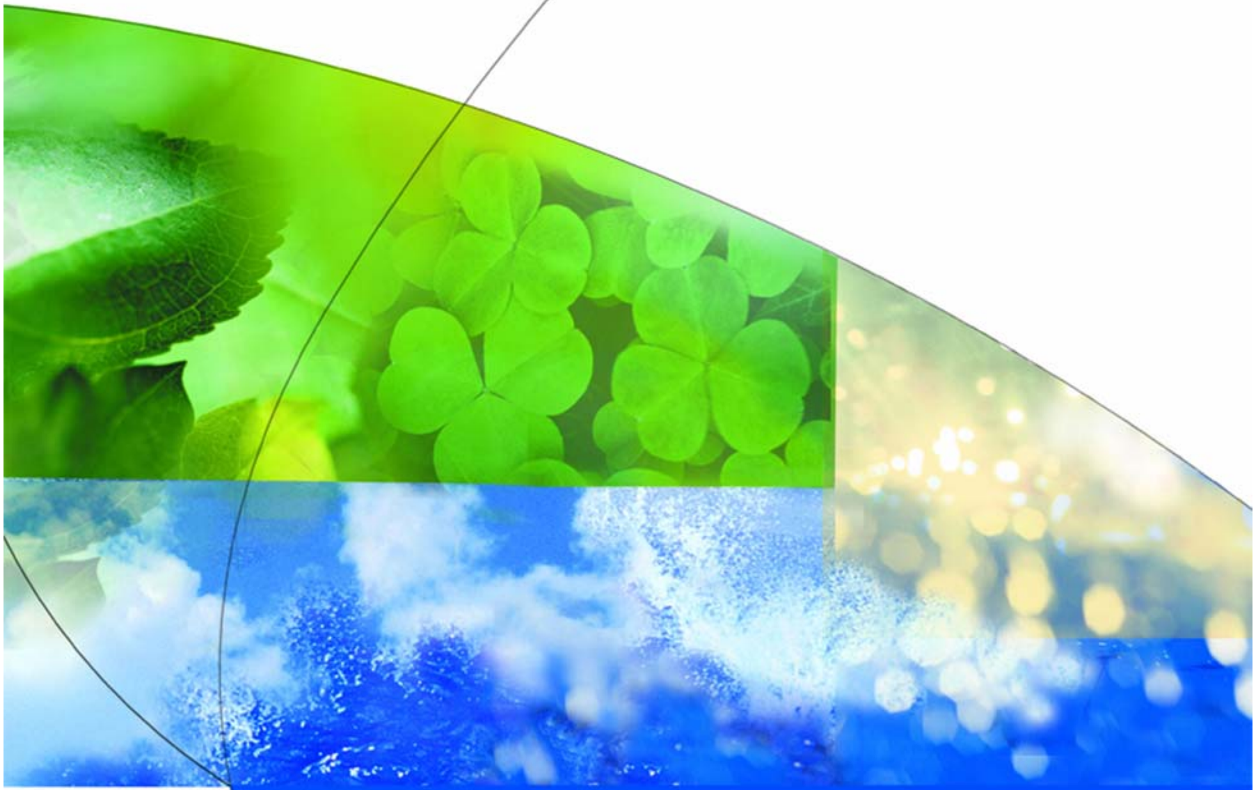

Quarter 3 – Advanced and Developmental Mercury Control Technologies

July 2004

Canadian Electricity Association
Association canadienne de l'électricité

EERC®
Energy & Environmental Research Center

Center for Air Toxic Metals®

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 3 – ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

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REPORT AVAILABILITY

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650 and the CEA mercury program Web site (www.ceamercuryprogram.ca).

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EXECUTIVE SUMMARY

The topic for this third quarterly report is Advanced and Developmental Mercury Control Technologies. A wide variety of approaches from combustion modification to multipollutant mercury control are under development. A number of unique mercury control technologies have passed the bench- and pilot-scale developmental phases and are now being tested at full scale.

For the near term, from 50% to 80% control may meet regulatory requirements. However, 90% control is a better research and development target for a technology to be considered attractive to meet longer-term needs. Further vendor guarantees of near 95% may be necessary to ensure compliance targets can be consistently achieved. Since the amount of mercury in coal is very small (typically about 0.1 μg/g), the total amount of mercury input (and potential emissions) for a 500-MW plant in a year is only about 300 lb and, as liquid mercury, would occupy a volume of only about one-third of a cubic foot. This suggests that there is potential for generating a minimum amount of waste material if the mercury can be effectively captured and concentrated. On the other hand, if the captured mercury is highly dispersed in waste material or by-product, the mercury must be proven to be in a stable form so that there is little possibility of reemission into the atmosphere. Until this question is fully answered, any mercury control technology that produces a large amount of mercury-containing waste material or by-product is not attractive as a long-term mercury control technology.

Many of the developing technologies appear to potentially be capable of achieving >90% control, but in most cases, this level of control has not been demonstrated over the longer term at a large scale. Concentration and sequestering of the collected mercury are also possible for many of the technologies, but this step has not been demonstrated, even at the bench-scale level, for most approaches.

Removal of the mercury from the fuel prior to combustion is a mercury control approach that has been considered for many years, and in current practice, “washed” eastern U.S. bituminous coal has resulted in some mercury removal. Now a commercial process is being developed at a large scale that improves fuel quality and removes a significant fraction of the mercury for lignite and subbituminous coal. Another alternative to back-end mercury control is combustion modification to produce an ash material that has mercury adsorbent properties. Recent developments related to combustion modifications and in situ generation of sorbents for mercury control are discussed in this report.

Several new developments in sorbent composition and use as well as new multipollutant approaches are also discussed. Another attractive approach is the insertion of mercury capture structures into the flue gas downstream from particulate control and scrubbers. Recently issued mercury control patents and published pending patent applications are also discussed.

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 3 – ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emission from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of developments in mercury monitoring, control, policy, and related research advances.

Recent developments in the area of mercury regulations from coal-fired power plants in Canada in the form of Canadawide Standards (CWS) and the United States in the U.S. Environmental Protection Agency's (EPA's) Proposed Utility Mercury Reduction Rule illustrate the need for effective mercury control strategies for coal-fired electric utilities. In the first quarterly report, sorbent injection technologies were reviewed in detail. However, many other technologies, at varying stages of development, are being investigated to achieve targeted mercury removal. A review of these technologies is provided in this quarterly report. In the second quarterly report, mercury measurement technologies were reviewed. Since that submittal, no significant advancements have been identified.

In order to adequately address the many topics pertinent to mercury research and development and provide the detail necessary for the various stakeholders to make informed decisions, selected topics will be discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that will be addressed in subsequent quarterly reports include, but are not limited to, the following:

- Mercury policy
  - Upcoming events and news releases
  - Regulation, policy, compliance strategies, and health developments

- Mercury measurement
  - Continuous mercury monitors
  - Advanced mercury-sampling systems
  - Wet-chemistry mercury measurement techniques

- Baseline mercury levels and emissions

- Mercury control
  - Sorbent technologies and control in unscrubbed systems

  - Advanced and developmental mercury control technologies
  - Summary of large-scale test activities and associated economics
  - Mercury oxidation and control for scrubbed systems
  - Multipollutant control strategies
  - Impact of mercury control on combustion by-products/fate of captured mercury
  - Summary of mercury-related economics for commercial systems

- Mercury chemistry and transformations
  - Mercury chemistry fundamentals, modeling, prediction, and speciation
  - Mercury fate and transport – impacts on health

One objective of this quarterly report is to provide timely information on developments within the broad field of mercury. In order to address timely issues as well as provide necessary detail on selected topics, additional subject headings will be provided to summarize recent developments not related to the quarterly topic. In this manner, updated information can be provided on topics previously covered or in advance of topics not yet discussed. The primary subject area for this quarterly report is a review of advanced and developmental mercury control technologies.

MERCURY POLICY

The Government of Canada is working closely with provincial and territorial partners to put in place a CWS for mercury emissions from coal-fired power plants that will prevent the release of 60%–90% of the mercury in coal by 2010. Canadian coal-fired generating companies have embarked on a multiyear program to improve the information base around mercury measurement and control that will aid in the development of the CWS. A key component of the CEA Mercury Program is the Coal, Residue, and Flue Gas Sampling and Analysis Program that companies have undertaken. This program has generated a rich database that is being analyzed to provide valuable information around mercury emission inventories and management to this decision-making process. The data can be accessed on the program Web site: www. ceamercuryprogram.ca.

On December 15, 2003, EPA proposed a rule to permanently cap and reduce mercury emissions from coal-fired utilities. EPA is proposing two alternatives for controlling emission of mercury from coal-fired utilities. The first strategy is Maximum Achievable Control Technology (MACT), and the second establishes standards of performance limiting mercury emissions from new and existing utilities. The second proposal would establish a market-based cap-and-trade program. Under the MACT provisions of the Clean Air Act, sources are given 3 years to comply with emission reduction requirements. For the power generation industry, the MACT approach raises concerns about how quickly new control technologies could be put into place. Under the cap-and-trade approach, EPA would allocate allowances for mercury emissions to each state which would then allocate them to utilities. The utilities would then be allowed to trade or bank any allowances above those required to cover their emissions each year. With the cap-and-trade program, emission monitoring and reporting requirements will be stringent. However, this will allow for flexibility in trading which will create financial incentives for utilities to look for new and low-cost ways to reduce mercury emissions. Under both alternatives, a two-step implementation process has been proposed in which more stringent mercury emission limits would be required over time. This stepwise emission control requirement could significantly impact implementation strategies which would need to address short-term requirements while allowing the flexibility to meet more stringent requirements at a later time.

In the United States, EPA extended the comment period for the Utility Mercury Reduction Rule until June 29, 2004, to allow interested parties 90 days to review the document and submit formal comment. In a submission to EPA issued in April 2004, Environment Canada stated its support of U.S. efforts to limit mercury emissions, as mercury reductions in the United States will likely have impacts on air quality for both countries. Environment Canada’s comment to EPA goes on to state that its modeling has indicated that as much as 10% of the mercury deposited in Canada and 38% of the mercury in the Great Lakes region each year comes from U.S. sources. This shared impact of air quality illustrates the benefit of collaborative efforts between Canada and the United States, which have, in the past, led to substantial reductions in acid rain pollutants in the 1980s and 1990s and more recently through the 2000 Ozone Annex, which is reducing smog pollutants.

Two specific recommendations to EPA include consideration of a more stringent MACT standard for mercury, resulting in a 60%–90% reduction in mercury from coal combustion.

Alternately, under a cap-and-trade option presented by EPA, Environment Canada recommends implementing a lower Phase I cap, which would result in national capture of mercury from coal combustion in the range of 60%–90%.

In Europe, the European Commission recently issued a consultation document on mercury which evaluated mercury emissions, production, trade, and use and also reviewed health and environmental impacts. The consultation period closed in May, and the Commission will present a proposal to the Council later this year. Specific details of that proposal will be presented in a quarterly report when the document becomes available.

QUARTER 3 FOCUS: ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

The topic for this third quarterly report is “Advanced and Developmental Mercury Control Technologies” and is intended to serve as a review of technologies not currently commercially available. Control technologies presented in this summary are at various stages of development and, in most cases, have been tested under only limited operational conditions. The objective of this technology review is to present claims and available results of the various advanced and developmental technologies being investigated. Additional research and development work will be needed to adequately address the balance of plant impacts, cost-competitiveness, and technical feasibility of these mercury control approaches. The most commercially available control technology was presented in the first quarterly report entitled “Sorbent Injection Technologies for Mercury Control.” It is anticipated that “Mercury Control for Scrubbed Systems” and “Multipollutant Control” will be addressed separately in future quarterly reports. The intent for this quarterly report is to focus on control technologies not covered in the other quarterly reports.

Removal of mercury from the fuel prior to combustion is a mercury control approach that has been considered for many years. Coal washing of bituminous fuels for the removal of pyrites and other mineral matter also results in the removal of some of the mercury, however, not to the extent that would be needed to meet future control requirements. Coal washing for ash reduction has proven to be effective primarily for bituminous fuels with large mineral grains. With subbituminous and lignite fuels, conventional coal washing is not effective because of the way the inorganic material is distributed within the coal. For subbituminous coals, deep cleaning or pretreatment of the coal, such as with K-fuel process, has the potential to remove a significant fraction of the mercury. A review of the K-fuel developments is presented in this report. Another fuel-upgrading project, conducted by Great River Energy with funding from DOE, is to evaluate the drying of a high-moisture North Dakota lignite at the large-scale level. The process does not claim to remove mercury from the lignite but upgrades the fuel with waste heat, resulting in overall plant efficiency improvement, with some subsequent reduction in mercury emissions. However, even with mild thermal processing of a raw fuel, there is potential for removing some of the mercury along with the moisture by increasing the drying tempature.

Another alternative to back-end mercury control is combustion modification to produce an ash material that has mercury-adsorbent properties. Mercury control may occur as a result of combustion modifications for NO_x control, but deliberate combustion modifications to achieve mercury control are also being considered. A related interesting process is the DOE-developed and -patented Thief process whereby a fraction of the fuel is extracted from the combustion zone to maximize mercury sorption properties and then is reinjected back into the flue gas as a mercury sorbent. Recent developments related to combustion modifications for mercury control are discussed later in this report.

Mercury control with conventional wet and dry scrubbers and sorbent injection upstream of electrostatic precipitators (ESPs) or fabric filters are not included in this quarterly report. However, in many cases, there is significant overlap among the various control approaches.

Technologies that utilize sorbents in new and innovative ways as well as new multipollutant approaches are discussed. In addition, a brief review of recently issued mercury control patents and published pending patent applications is presented.

Evaluation Criteria

For effective mercury control from coal-fired boilers, several important considerations are:

- For the near-term, from 50% to 80% control may meet regulatory requirements. However, for a technology to be considered viable for longer-term control, at least 90% control should be demonstrated in R&D (research and development) demonstrations while vendor guarantees may require 90%–95% removal to ensure long-term compliance.
- Since the amount of mercury in coal is very small (typically about 0.1 μg/g), the total amount of mercury input (and potential emissions) for a 500-MW plant in a year is only about 300 lb and, as liquid mercury, would occupy a volume of only about one-third of a cubic foot. This suggests that there is potential for generating a minimum amount of waste material if the mercury can be effectively captured and concentrated.
- If the captured mercury is highly dispersed such as in fly ash, spent sorbent, or scrubber waste, the mercury must be proven to be in a stable form so that there is little possibility of reemission into the atmosphere. Until this question is fully answered, any mercury control technology that produces a large amount of mercury-containing waste material or by-product may not be attractive as a long-term mercury control technology.

K-Fuel or K-Fuel Plus

Company Profile

KFx Inc. (KFx), founded in 1981, is headquartered in Denver, Colorado. KFx has been developing K-Fuel Plus for over 20 years and has spent nearly $120 million advancing and refining the K-Fuel Plus technology and process. KFx's K-Fuel Plus technology uses a combination of heat and pressure to transform low-energy coal into high-energy premium fuel containing low levels of sulfur, ash, and mercury.

KFx and Lurgi South Africa (Pty) Ltd. have an exclusive worldwide agreement to combine the K-Fuel Plus technology with Lurgi's technical services and equipment to upgrade low-energy, high-moisture coal into a premium K-Fuel Plus product. The Lurgi equipment that is to be used in the K-Fuel Plus plants is proven equipment technology that has been in use for over 70 years. KFx announced in June 2004 that it will be locating its first commercial plant at the Fort Union site near Gillette, Wyoming. KFx recently purchased the Fort Union Mine site. The location includes approximately 1000 acres of land, a rail loop with load-out facilities, a coal crusher, related buildings, water disposal wells, and remaining coal reserves. The plan is for the initial plant to produce 750,000 tons per year of K-Fuel®, with raw coal input purchased from adjacent mines.

For further expansion, an agreement was reached with Arch Coal, Inc., wherein Arch has invested $2 million in the purchase of KFx stock and KFx and Arch will evaluate the potential joint development of an 8-million-ton/year K-Fuel® plant at Arch's Coal Creek Mine near Gillette, Wyoming.

K-Fuel Process

K-Fuel® precombustion technology applies heat and pressure to boost the heating value of subbituminous coal and lignite by up to 30%, in the process removing more than 70% of the mercury and up to 30% of the sulfur dioxide and nitrogen oxide (1, 2). These reductions are achieved from coal that is already low in mercury and sulfur, and because these constituents are removed prior to combustion, the need for postcombustion controls may be reduced.

The K-Fuel® process employs both mechanical and thermal means to increase the quality of subbituminous coal and lignite by removing moisture, sulfur, nitrogen, mercury, and other heavy metals.

To begin the process, raw coal is delivered to the K-Fuel® processing plant from the mine. The coal enters the first-stage separator, developed using conventional coal-cleaning technology, where it is crushed and screened to remove the large rock and rock material. The processed coal is then passed on to an intermediate storage facility prior to being sent to the next stage in the process.

From the intermediate storage facility, the coal is sent via a distribution system to the K-Fuel® thermal process. This process essentially operates like a giant pressure cooker, utilizing Lurgi Mark IV vessels under high pressure and temperature to place thermal stress on the coal. The coal passes through pressure locks into the processors, and then steam at 460°F and 485 psi is injected into the processors. While the coal is maintained at these conditions, the mineral inclusions are fractured under the thermal stress, removing both the included rock (which contains some mercury) and sulfur-forming pyrites. The inherent moisture of the coal is liberated as well.

After it has been treated for a sufficient time in the main processor, the coal is discharged into a second pressurized lock, which is sealed off from the primary reactor. After sealing, the processor pressure is vented into a water condenser to return the processor to atmospheric pressure and to flash-cool the coal to approximately 200°F. The coal is then discharged onto a belt and further cooled by convection and indirect cooling. After cooling, the coal is sent to a second-stage separator for additional screening to remove sulfur- and mercury-containing mineral matter that has been liberated by the thermal process.

The water liberated from the coal is removed at various points in the process. This water, along with some condensed process steam, is either sent directly to treatment or is reused within the process. The water treatment system removes coal fines and hydrocarbon compounds liberated from the coal in the processor and uses carbon filtering to remove mercury and other heavy metals that were liberated from the coal and rock. The waste products (carbon, mercury, and heavy metals) from the filtering process are sent to a qualified, permitted disposal site for final disposition.

The claimed environmental benefits for the K-Fuel® include:

- Reduces the mercury content of already-low mercury subbituminous and lignite coals by 70%, as high as 90% in some cases.
- Removes up to 30% of sulfur from parent coals, which are already low in sulfur compared to midwestern bituminous coals.
- Reduces fuel nitrogen by up to 30%.
- Controls mercury while it is in a more concentrated and contained form, permitting significant savings in waste disposal volumes and costs.

Advantages

- K-Fuel® is reported to achieve >70% with up to 90% mercury removal.
- Mercury is removed before the fuel reaches a plant, so there would be no concern over mercury in the fly ash or other combustion by-products. This greatly facilitates fly ash disposal as well as fly ash utilization. It would also be a major advantage to a plant burning the K-Fuel® if the mercury would be low enough so that there was no concern over the level of mercury emissions from the plant. Very likely, the higher Btu fuel would result in hotter combustion conditions which potentially could affect NO_x emissions and the amount of unburned carbon in the ash unless the appropriate low-NO_x burners were implemented.
- The captured mercury can be isolated and concentrated for disposal or permanent sequestering of the captured mercury with minimum volume of material.
- K-Fuel® has potential as a long-term mercury control solution.

Status and Development Issues

- The concept has been under development for many years and has been tested at a large scale. The investment and plans for building a full-scale plant are progressing. The actual level of Hg reduction in the final fuel product as well as the fate of the removed mercury within the process will need to be demonstrated.
- The work to date has focused mainly on the upgrading of the fuel and reductions in moisture and sulfur. Within the process, the potential for optimizing removal of mercury to achieve >90% also makes this a potentially attractive long-term mercury control approach.

- Powder River Basin (PRB) coals already account for about one-third of U.S. production and represent most of the growth in U.S. production in the last 10 years. Whether a significant portion of that production could eventually be upgraded as K-Fuel® or similar products is primarily an economic one and highly dependent on tighter regulations. The current upward trend in world oil prices and focus on CO_2 emission reduction would both appear to make K-Fuel® more attractive in the marketplace. Even a small reduction in CO_2 emissions resulting from improved plant efficiency could make the fuel desirable over conventional coal. However, even with a highly attractive market, the building of new plant capacity to meet increased demand would be a slow process.

Combustion Modification and in Situ Generation of Sorbents

An attractive approach to mercury control is to enhance the capture of mercury by modification of the combustion process to produce fly ash or unburned carbon that results in better mercury retention. One of the challenges is a lack of a good understanding of the fundamental chemistry of mercury capture and retention in fly ash. Subsequently, the exact characteristics of the ash matter that result in optimum mercury capture are unknown. In general, the thought is that either increased carbon in the ash or generation of carbon in the ash with the appropriate characteristics will enhance mercury capture. Since low-NO_x burner (LNB) technology is already known to produce more carbon in the ash, a logical extension of LNB burner approaches is to specifically modify the process for enhanced mercury control, such as is being investigated in a DOE-funded project by General Electric Energy and Environmental Research Corporation (GE EER). Another interesting approach is extracting a portion of the coal from the combustion zone and then quenching it prior to complete combustion to produce a material with good mercury sorption characteristics. This approach is know as the Thief process and is being developed in-house at DOE's National Energy Technology Laboratory (NETL). Another somewhat similar approach is detailed in two EPRI patents that describe a method for in situ activation of carbon-based sorbents by injecting carbonaceous material at the appropriate location in a boiler. A summary of these three approaches follows.

Process and System to Reduce Mercury Emission by Combustion Modification (GE EER)

GE EER is conducting a DOE-funded 2-year field evaluation using a combination of overfire air (OFA) and coal reburn to achieve multipollutant control of both NO_x and mercury. The field testing is at Western Kentucky Energy's R.D. Green Station, which burns a blend of Illinois bituminous coal and petroleum coke. Field measurements of fly ash properties and mercury removal across the ESP will be taken on Unit No. 1 after installation of an OFA and coal reburn system for NO_x control. Data from the Unit No. 1 field testing will be used to optimize the design of the NO_x control system for mercury removal using a 300-kW pilot-scale combustor at GE EER's test facility. Results from the pilot-scale testing will be used for the design of the OFA and coal reburn system to be installed on R.D. Green Unit No. 2. Mercury removal performance will then be tested on Unit No. 2 after installation of the optimized NO_x control system. Results of pilot-scale testing were recently reported (3, 4) to achieve 60% removal with a 5% to 10% loss-on-ignition (LOI) fly ash produced.

In the patented process (5), a method to decrease emission of mercury is described where a factor is selected to control a combustion process to generate a flue gas comprising fly ash with enhanced unburned carbon. The combustion process is controlled according to a factor selected from reburning fuel, flue gas temperature, OFA injection, coal particle size, LNB flow, LNB design, combustion zone air, stoichiometric ratio of fuel, fuel/air mixing in a primary combustion zone, and fuel/air mixing in a secondary combustion zone to produce the flue gas comprising fly ash with enhanced unburned carbon and to vaporize mercury. In pilot-scale testing, the flue gas is allowed to cool, similar to typical particulate control device temperatures, where fly ash is removed containing the enhanced unburned carbon and absorbed mercury.

Thief Process for the Removal of Mercury from Flue Gas (DOE NETL)

The Thief process has been tested in DOE facilities with a 500-lb/hr coal-fired combustor with both bituminous and subbituminous coals. Results reported to date indicate that up to 90% mercury control is possible and that the mercury capacity of the generated sorbents approaches the capacity of commercially available sorbents (6).

A U.S. patent (7) describes the approach where mercury removal is by adsorption onto a thermally activated sorbent produced in situ at the power plant. To obtain the thermally activated sorbent, a lance (thief) is inserted into a location within the combustion zone of the combustion chamber to extract a mixture of semicombusted coal and gas. The semicombusted coal has adsorptive properties suitable for the removal of elemental and oxidized mercury. The mixture of semicombusted coal and gas is separated into a stream of gas and semicombusted coal that has been converted to a stream of thermally activated sorbent. The separated stream of gas is recycled to the combustion chamber. The thermally activated sorbent is injected into the duct work of the power plant at a location downstream from the boiler. Mercury within the flue gas contacts and adsorbs onto the thermally activated sorbent. The sorbent–mercury combination is removed from the plant by a particulate collection system.

The in situ mercury removal system operates by extracting a stream of partially combusted and/or pyrolized coal and gases from the combustion zone. The high temperatures of the combustion chamber activate the coal and impart an alteration within the coal. Mercury's affinity to adsorb onto the coal is increased by this alteration so that the coal can be described as a thermally activated sorbent. The size of the extracted coal particles can be similar to the size of coal that was injected into the boiler. A hollow lance, a thief, is inserted into the combustion zone, and suction is applied through the lance to draw the partially combusted coal and gas mixture out of the combustion chamber and through a gas–solid separator such as a cyclone separator. The thief may use a cooling device when located in the combustion chamber in order to reduce further oxidation of the solids. The thief could also be designed to concentrate the solids in the gas stream before removal from the combustion zone in order to further reduce the heat rate penalty and optimize the cost of operation. Additionally, a small flow of inert gas may be injected into the thief to help quench the oxidation of the sampled solids.

As an option, the thermally activated sorbent may also be chemically or physically treated to enhance its reactivity with mercury. Examples of chemical treatment include washing the sorbent with hydrochloric acid or depositing sulfur on the surface of the sorbent. An example of physical treatment is grinding.

The sorbent, whether chemically treated or untreated, is injected into the duct work of the power plant, preferably where the temperature is 400°F or less. Similar to activated carbon, the sorbent will remove elemental and oxidized mercury from the flue gas which will then be collected in the plant’s particulate collection system and removed from the plant along with the fly ash collected by the particulate collection system. In another variation, the sorbent could be injected after the plant's particulate collection system, and a separate particulate collection system just for the sorbent could eliminate sorbent contamination of the fly ash collected in the plant's particulate collection system and increase the sorbent’s utilization with respect to mercury capture by recycling of the sorbent. Additionally, in the event that a wet scrubber is installed in the power plant for flue gas desulfurization, the sorbent may be injected into the flue gas either before or after the scrubbing process.

Method for Removal of Vapor-Phase Contaminants from a Gas Stream by in Situ Activation of Carbon-Based Sorbents (EPRI)

Two EPRI patents by Chang et al. describe the process in detail (8, 9). This is a somewhat similar technology to the Thief process in that a sorbent material is generated within the process. However, the process is different than the Thief process because it includes the separate injection of a carbonaceous material at a strategic location in the system, while the Thief process utilizes the feed coal and then extracts from the combustion zone a fraction of the coal before it has undergone complete combustion.

The Chang process has several variations, including the use of a separate combustion system to activate the injected material as well as an option for extraction of a portion of the flue gas to activate a fixed carbon bed. Testing or development of the Chang process has not been reported.

The Chang patents describe the process for removing vapor-phase contaminants from a gas stream, which includes the step of adding a raw carbonaceous starting material into a gas stream having an activation temperature sufficient to convert the raw carbonaceous starting material into an activated material in situ. The raw carbonaceous starting material can be either a solid-, liquid-, or vapor-phase material. The activated material then adsorbs the vapor-phase contaminants, and the activation material containing the vapor-phase contaminants is removed from the gas stream using a particulate collection device. The process is particularly suited for the removal of vapor-phase air toxics, such as mercury, from the flue gas of a combustion process.

In another aspect of the invention, a gas stream source directs a gas stream to an activation region. The gas stream has an activation temperature at the activation region. A raw carbonaceous starting material is positioned at the activation region, such that the gas stream activates the raw carbonaceous starting material into an activated carbonaceous material. The activated carbonaceous material is then positioned in the exhaust stream of a combustion process to adsorb vapor-phase contaminants.

Advantages

- The largest single advantage for all three control technologies is that mercury capture could potentially be achieved with the coal alone (the EPRI/Chang process also includes using coal as one of the options).

- All three techniques could potentially offer a very low-cost approach.

- All three have potential for widespread application, especially for mercury control requirements for less than 90% control.

- The EER process possesses the advantage of very simple implementation.

- With the EER combustion modification process, some NO_x control would also be seen.

Status and Development Issues

- For all three processes, the resulting chemistry of the produced sorbent materials and the preferred process for optimizing mercury capture have not been reported.

- The EER process is the furthest along and is being tested at full scale. A major goal will be to determine the level of control that can be achieved in a full-scale boiler. Another key issue is the extent to which the mercury removal depends on coal type. Of the three processes, this is also the simplest and would appear to be most likely implemented in the near future. One of the main concerns is that the process depends on incomplete combustion and the presence of significant unburned carbon in the ash. This makes fly ash utilization and disposal more challenging.

- The Thief process appears to offer more flexibility in achieving a much higher-capacity carbon than the other two combustion modification and in situ technologies but with significant additional complexibility. Since the Thief process can include injection downstream of a primary particulate control device, it also offers an opportunity for separating the fly ash from the spent carbon. However similar techniques can be implemented with many sorbent injection technologies.

- The EPRI process defined in its patent offers flexibility with the raw feed materials which may offer an opportunity to generate a very highly reactive, high-capacity sorbent. Since the generated sorbent material does not have to be collected and reinjected, the process may offer an opportunity to generate a very fine particle-size material. If so, in-flight capture would be enhanced making it an attractive application for ESP controlled units. This process, however, has not been tested yet, so near-term development is unlikely.

New Sorbent Developments

Since sorbent technology was the focus of the first quarterly report, extensive discussion of sorbent developments will not be given in this report. However, two significant sorbent developments that warrant discussion are the development of Amended Silicates™ and activated carbon impregnated with bromine. Both approaches have been previously tested and now will be demonstrated at the full scale as part of the DOE-funded large-scale mercury control demonstration program.

Amended Silicates

ADA Technologies, Inc., has been developing a non-carbon-based sorbent for several years (10–12). The Amended Silicates™ material will be tested under the DOE-funded large-scale mercury demonstration program. Amended Silicates, LLC (a joint venture of ADA Technologies, Inc., and CH2M Hill), Littleton, Colorado, will test the material at Cinergy's 175-MW Miami Fort Unit 6 that burns bituminous coal. The research team also includes the University of North Dakota EERC, Western Kentucky University, and Boral Materials Technologies.

Amended Silicates™ sorbents use silicate materials as substrate particles on which chemicals with a strong affinity for heavy metals (e.g., mercury and mercury compounds) are impregnated. Because of their physical structure, the silicates present extend surface area on each particle with an easily generated particle size of a few micrometers. This configuration promotes maximum exposure of the chemical amendment to the mercury vapor present in the coal-fired flue gas stream.

According to the recently issued patent awarded for the material and process (13), the Amended Silicates™ material is a high-capacity regenerable sorbent for removal of mercury from flue gas. A phyllosilicate substrate, for example, vermiculite or montmorillonite, acts as an inexpensive support to a thin layer for a polyvalent metal sulfide, ensuring that more of the metal sulfide is engaged in the sorption process. The sorbent is prepared by ion exchange between the silicate substrate material and a solution containing one or more of a group of polyvalent metals including tin (both Sn[II] and Sn[IV]), iron (both Fe[II] and Fe[III]), titanium, manganese, zirconium, and molybdenum, dissolved as salts, to produce an exchanged substrate. Controlled addition of sulfide ions to the exchanged silicate substrate produces the sorbent. The sorbent is used to absorb elemental mercury or oxidized mercury species such as mercuric chloride from flue gas-containing acid gases (e.g., SO_2, NO_x, and HCl) and other gases over a wide range of temperature.

ADA Technologies has run pilot tests at the Comanche Station, which burns western subbituminous coal, for three different Amended Silicates™ sorbent formulations (11). One variant produced superior results, and a second showed promise, as it easily matched the performance of carbon. Tests were conducted in several campaigns between November 2002 and March 2003. For these tests, total mercury concentrations in the flue gas stream ranged from about 4 to 8 $\mu g/Nm_3$, with the particulate-bound fraction well under 20%. The baseline data showed mercury removal across the pilot baghouse by the native fly ash of about 24%. At an injection rate of 1.6 lb per million actual cubic feet of flue gas, the mercury removal increased to 60%–70%. The removal was 92% at a rate of 3.8lb/MMacf and 96.7% for the injection of 9.1 lb/MMacf. When fly ash plus spent sorbent samples were subjected to toxicity characteristic leaching procedure (TCLP) tests, no measurable mercury was found in the leachate. More extensive leachability studies are being initiated through a recent DOE solicitation and will be addressed in a quarterly report focusing on by-product utilization.

Amended Silicates™ formulations have also been tested at elevated temperatures and pressures as a possible mercury control technology for next-generation coal gasifiers. Laboratory experiments have shown one variant to effectively capture mercury at a temperature of 770°F and 200 psig, with sorbent mercury capacity in excess of 3% by weight. This is a strong indication that Amended Silicates™ technology could offer significant cost advantages in future coal gasification systems. In this application, the Amended Silicates™ sorbent can be disposable or used in a pressure-swing mode where a significant fraction of the captured mercury is liberated when the pressure is released at operating temperature.

ADA Technologies, Inc., has in place an alliance agreement with CH2M Hill (Denver, Colorado), a major environmental engineering firm, to commercialize the Amended Silicates™ technology through the creation of a new joint venture company to manufacture and sell sorbent. CH2M Hill brings to the joint venture broad expertise in the design and construction of chemical process facilities as well as experience in the delivery of environmental control technologies to a wide range of commercial, industrial, and government clients.

Advantages

- The Amended Silicates™ technology has the potential to achieve >90% mercury removal.
- A sorbent that is non-carbon-based is highly attractive because of the potential for ash utilization without concern over additional carbon in the ash. Based on material properties and test results to date, no impact of the material on the fly ash utilization is expected.
- With regeneration, the mercury can be isolated for disposal, and since the mercury can be concentrated, permanent sequestering of the captured mercury is possible with minimum volume of material.
- Cost appears to be reasonable and with further development may approach the cost of activated carbon.

Status and Development Issues

- The concept has moved beyond the bench-scale level and has been tested at the pilot level at a coal-fired power station. The current DOE-funded project will take the evaluation to the full-scale demonstration level.
- Critical developmental questions concern the level of control that can be demonstrated compared to existing and new activated carbons and the stability of the mercury in the ash.

The ability to manufacture large amounts of the material at a reasonable cost also needs to be demonstrated.

- While regeneration ability is desirable, this does not appear to be a near-term requirement if the mercury is stable and ash utilization is not impaired. Demonstrating that impacts to ash utilization are negligible will be an important factor for further commercialization of the process.

Bromine-Impregnated Activated Carbon

Sorbent Technologies Corporation (STC) has been working to develop better-performing and lower-cost technology to control mercury stack emissions for a number of years. The company's efforts have concentrated on testing inexpensive, novel sorbent materials on both elemental mercury, Hg^0, and oxidized mercury, Hg^{2+}, on both simulated and real coal-fired boiler flue gases, in both fixed-bed fabric filter simulations, and with actual duct-injection into ESPs. Over this period, STC has developed a number of advanced mercury sorbent materials specifically designed for the conditions found at coal-fired power plants.

Results from the testing with these sorbent materials have previously been reported (14, 15), but the formulation has only been recently disclosed (16–18).

According to a recently published patent application summary (18), the process includes a method for removing mercury and mercury-containing compounds from a combustion gas in an exhaust gas system. The steps involve providing a mercury sorbent, injecting it into a stream of mercury-containing combustion gas for a sufficient time to allow at least an effective amount of the mercury and mercury-containing compounds in the combustion gas to adsorb onto the mercury sorbent, and collecting and removing the mercury sorbent from the combustion gas stream. The mercury sorbent is prepared by treating a carbonaceous substrate with an effective amount of a bromine-containing gas, especially one containing elemental bromine or hydrogen bromide, for a time sufficient to increase the ability of the carbonaceous substrate to adsorb mercury and mercury-containing compounds. The points of injecting, collecting, and removing the mercury sorbent may be varied, depending upon the exact configuration of the exhaust gas system.

According to the application, the mercury sequestration claims have five essential elements. The first three are that 1) a carbon-based adsorbent, such as powdered activated carbon (PAC), is used 2) to capture and concentrate vaporous mercury species from 3) a hot, flowing gas stream of combustion products. The fourth requirement is that the adsorbent material be 4) injected into the flowing gas to intimately mix with it and be separated from the gas in a particulate collector. The fifth and final essential element of the invention is that, at some time before it is mixed with the mercury-containing combustion gas, the carbon material must be exposed to a bromine-containing treatment gas, possibly producing surface complexes that are particularly reactive to gaseous mercury species.

In January 2003, STC field-tested the Type A sorbents at the 18-MW scale (60,000 acfm) at the Lausche Plant of Ohio University (15). This stoker plant burns a high-sulfur bituminous coal and has a cold-side ESP for emission control. Baseline Ontario Hydro method sampling indicated no intrinsic mercury removal across the ESP at temperatures from 300°–350°F. For comparison, NORIT DARCO flue gas desulfurization (FGD) PAC did not remove much mercury at Lausche. At an injection rate of almost 18 lb/MMacf, it captured less than 20% of the flue gas mercury. This plant's unusually high SO_3 in the flue gas of about 20 ppm, which competes for active adsorption sites on the PAC, may have been responsible for this poor performance. The STC Type A sorbents, on the other hand, performed very well on the difficult Lausche flue gas, achieving about 60% Hg removal at 3 lb/MMacf and almost 70% removal at 4 lb/MMacf. An important feature of the advanced Type A sorbents is that their mercury performance is largely independent of temperature up to over 600°F.

Because of the higher-temperature performance, there is also potential for some level of mercury control with hot-side ESPs. Recently reported results (17) from the Duke Power Cliffside Plant, which burns a low-sulfur bituminous coal, showed that from 40% to 80% mercury control was possible with a hot-side ESP.

The STC sorbents do not appear to leach their captured mercury (15). TCLP testing has not detected any Hg leaching from the Type A sorbents. In one example, a well-saturated fixed-bed sample of Type A sorbent was mixed with ash to 0.9 µg Hg/g fly ash, a representative amount, and sent to EA Group Laboratories for analysis. An additional fly ash blank and a sample with dry FGD were included for comparative purposes. The TCLP results were all below the laboratory's mercury detection limits. Mercury volatilization from saturated Type A sorbents has also been examined and, so far, has not been found to be a concern. Additional leachate and volatilization measurements, however, will need to be performed to be certain, particularly long-term leachate analyses at field pHs.

The STC sorbents will also be tested under the DOE-funded large-scale mercury demonstration program. The project will test a novel sorbent (assumed to be a bromine-impregnated carbon-based sorbent) at Duke Energy's Buck Station or Allen Station, which are both equipped with an ESP and burn bituminous coal, and also at Detroit Edison's St. Clair Station, which burns a mixture of bituminous and subbituminous coal. Joining STC, Duke Power, and Detroit Edison are Fuel Tech, Western Kentucky University's Combustion Laboratory, PS Analytical, Spectra Gases, and Stock Equipment Company.

Direct Bromine Injection

With the reported success of the bromine sorbents, a logical question is whether direct bromine injection into the flue gas might enhance mercury capture by the fly ash or other sorbent materials. Another patent application published within the last year (19) includes this option. The patent application summary discloses a method of treating a coal combustion flue gas, which includes injecting a molecular halogen or thermolabile molecular halogen precursor able to decompose to form molecular halogen at flue gas temperature. The claims specifically list bromine, in addition to chlorine and iodine, as possible molecular halogen and/or thermolabile molecular halogen precursors. The molecular halogen converts elemental mercury to mercuric halide absorbable by alkaline solids such as subbituminous or lignite coal ash; alkali-fused bituminous coal ash capturable in whole or part by ESPs, baghouses, dry flue gas, or desulfurization solids; and with or without subsequent adsorption by a liquid such as a flue gas desulfurization scrubbing liquor.

Advantages

- Direct bromine injection has the potential to achieve >90% mercury removal
- The use of bromine to enhance mercury control appears to be a unique welcome advancement in the attempts to make better carbon-based sorbents.
- The reasonable level of control with ESPs (hot side as well as cold side) has the potential to make this approach very attractive when compared to reported results to date with commercially available sorbents.
- Cost appears to be reasonable because only a small amount of injected halogen compound may be necessary.
- This technology has potential as a long-term mercury control solution with widespread application.

Status and Development Issues

- The concept has moved beyond the bench-scale level and has been tested at the pilot level at coal-fired power stations. The current DOE-funded project will take the evaluation to the full-scale demonstration level.
- Critical developmental questions are the level of control that can be demonstrated compared to other newly developed activated carbons or non-carbon-based sorbents. The long-term stability of the mercury in the ash also needs to be more fully addressed. The ability to manufacture large amounts of the material at a reasonable cost or pretreat the carbon on-site does not appear to be a significant developmental issue.
- Improved performance and reduced injection rates of these sorbents will need to be sufficient to offset any increase in cost over that of commercially available activated carbon.
- Fate and transport of bromine will need to be evaluated to ensure there are no adverse impacts to by-product utilization, disposal, or human health.

MerCAP™

The general MerCAP™ (Mercury Control via Adsorption Process) concept is to place fixed structures into a flue gas stream to adsorb mercury and then periodically regenerate them and recover the captured mercury (20, 21). While a variety of regenerable sorbent materials could be used, most of the development work has focused on the use of gold-coated substrates in the form of parallel plates spaced about 0.5 to 1 in. apart. Previous work has shown that the level of control is impaired in an unscrubbed flue gas environment (22). Subsequently, current development efforts seek to achieve high levels of mercury removal in scrubbed flue gases, either downstream from a spray dryer scrubber or a wet scrubber.

DOE NETL is currently funding a demonstration of MerCAP™. In this project, URS Group will test EPRI's MerCAP™ technology for controlling mercury emissions from coal-fired power plants (23–25). The MerCAP™ sorbent structures will be retrofitted into a single compartment in the outlet plenum of the Unit 10 baghouse at Great River Energy's Stanton Station, which burns North Dakota lignite, and will treat 6 MW_e equivalence of flue gas. At Southern Company Services' Plant Yates, which burns eastern bituminous coal, gold-coated plates will be configured as a mist eliminator (ME) located downstream of a 1-MW_e pilot wet absorber, which receives flue gas from Unit 1. The results of this study will provide data required for assessing the feasibility and estimating the costs of a full-scale MerCAP™ process for flue gas mercury removal. It will provide information about optimal operating conditions for different flue gas conditions, the effectiveness of sorbent regeneration, and the ability of the gold sorbent to hold up to flue gas over an extended period. In addition, if successful, the novel approach of incorporating MerCAP™ structures in existing baghouse compartments will demonstrate a cost-effective means for achieving mercury control using existing baghouse technologies. Testing will occur over a 6-month period at Great River Energy's lignite-fired Stanton Station and at Southern Company Services' bituminous-fired Plant Yates.

Advantages

- The MerCAP™ process by itself has the potential to achieve >90% mercury removal when installed downstream of a scrubber. However, any upstream removal of oxidized mercury by the scrubber makes the total mercury removal of >90% even more likely.

- Captured mercury will not be mixed with the fly ash. This facilitates fly ash disposal as well as fly ash utilization as a by-product.

- With regeneration, the mercury can be isolated for disposal, and since the mercury can be concentrated, permanent sequestering of the captured mercury is possible with a minimum volume of material.

- The fact that good mercury removal up to 2000 hr has been demonstrated indicates that with further advancements an annual replacement and maintenance schedule could be achieved.

- The process has potential as a long-term mercury control solution with widespread application.

Status and Development Issues

- The concept has moved beyond the bench-scale level and has been tested with a small slipstream device at a number of coal-fired power stations. The current DOE-funded project will take the evaluation to the next level and will attempt to answer a number of critical development questions.

- Since the concept depends on the amalgamation of mercury with gold, a key concern is the absorption ability of the gold as well as the regeneration ability and lifespan of the material. Reported results indicate that the process does not work well in unscrubbed flue gas, but the specific components causing the poor absorption were not disclosed. The scrubbers are expected to remove most of the SO_2, most or all of the HCl, and little of the NO or NO_2. It is well known from continuous mercury monitor (CMM) development work that the gold traps used in many mercury analyzers are poisoned by HCl or a combination of HCl and NO_x. This suggests that HCl may be the main component that impairs absorption. A very critical developmental question is how sensitive the material is to small concentrations of HCl or other gases that affect the absorption of mercury.

- The work to date has focused on the capture of mercury from the flue gas and not the regeneration of the plates or sequestering of the mercury. A viable regeneration process along with a method to concentrate the mercury is a major development step that has not yet been addressed.

W.L. Gore & Associates, Inc.,-Promoted Felt Filter Bag Inserts

W.L. Gore & Associates, Inc., has developed an innovative technology for control of mercury emissions in flue gas streams. Specifically, the configuration involves a mercury control filter placed inside the existing particulate control filter bag, essentially a bag-within-a-bag concept. This concept is similar to the MerCAP™ technology in that both attempt to achieve mercury capture by placing an adsorbent material in a convenient location within the system and then periodically (e.g., every 6 months) removing the components for regeneration and/or mercury concentration. Reported high measured mercury capacities of over 75 mg Hg/g of adsorbent material make this approach feasible (26).

The Gore Mercury Filter System has not been tested as extensively at the MerCAP™ system, but the concept has been tested at the small pilot-scale level both at EPA facilities and at the EERC. Operationally, the mercury filter elements did not appear to impair the pulse cleaning of the bags. Results showed that, initially, nearly 100% mercury removal could be achieved. This is an encouraging result because it indicates that there was good contact with the flue gas and filter elements and there was no mass-transfer limitation. For the materials tested, breakthrough occurred under some process conditions, but one of the purposes of the testing was to gain a better understanding of how the process conditions affected the level of mercury removal.

Details of the process are disclosed in U.S. Patent Application 20040074391, which was published April 22, 2004 (27). The application claims include compositions for the adsorbent material as well as fabrication of a filter system whereby the mercury adsorbent elements are installed as inserts on the inside of conventional pulse-jet filter bags. The inserts have a permeability such that the forward filtration and pulse cleaning of the filter bags are not obstructed.

The adsorbent component of the invention has a unique chemical composition which is capable of capturing mercury under the operating conditions of the filter system employed. A stated goal is to achieve a mercury capture capacity exceeding 20 mg Hg/g of initial dry weight of adsorbent. Stated possible mercury-binding agents may include anions or salts selected from halides, thiocyanates, sulfides, polysulfides, selenium, tellurium, and phosphorus compounds. Particularly, the binding agent could comprise at least one binding compound having a component selected from the group consisting of an anion of a halide, an anion of a thiocyanate, an anion of a sulfide, an anion of a polysulfide, an anion of selenium, an oxyanion of selenium, an anion of tellurium, an oxyanion of tellurium, an anion of phosphorus, and an oxyanion of phosphorus. Preferred binding agents are selected from the group of potassium iodide, copper iodide, zinc iodide, and copper thiocyanate.

A promoter is added to increase adsorption, to reduce volatility of binding agents, and to generate anchoring sites on the high surface area support for bonding to the mercury-binding agent complex. Suitable promoters include compounds having at least one of a multivalent metallic cation and a multivalent metalloid cation that is not spontaneously reduced by iodide. Preferred promoters comprise carboxylate salts of Zn(II) or Mg(II). A particularly preferred combination of binding agent and promoter comprises potassium iodide as the binding agent and zinc acetate hydrate as the promoter. Trivalent or quadrivalent metallic or metalloid cations that meet the reduction potential criterion above are suitable for use. After exposure to heating during preparation or use of the mercury-trapping filter, the nature of the binding agent or the promoter compounds may be altered. The acceptable or optimal ratios of binding agent to promoter vary depending on the specific combinations of ingredients used.

The adsorbent insert of the invention may be flexible or rigid. Examples of flexible inserts include woven or felted materials imbibed with activated carbon particles having the mercury-binding agent/promoter thereon or even activated carbon fibers woven or felted into a flexible sheet having the mercury-binding agent/promoter thereon. The insert may have any desired geometry such as a flat disk or panel, a sleeve or tube, a hub-and-spoke geometry, a canister, or the like, provided the insert fits into the filter element or is somehow attached to the downstream side of the filter element.

Advantages

- The insert has the potential to achieve nearly 100% mercury removal, depending on how often it would need to be changed

- Captured mercury will not be mixed with the fly ash. This facilitates fly ash disposal as well as fly ash utilization as a by-product.

- With regeneration, the mercury can be isolated for disposal since the mercury can be concentrated; permanent sequestering of the captured mercury is possible with a minimum volume of material.

- The insert could be retrofit into existing filter systems.

- The insert has potential as a long-term mercury control solution with widespread application.

Status and Development Issues

- The concept has been tested at the small-scale pilot level. Longer-term endurance testing would be a logical next step toward development.

- A better understanding of how specific flue gas components affect the capacity needs to be determined.

- The work to date has focused on the capture of mercury from the flue gas and not the regeneration or sequestering of the mercury.

- The process appears to have potential, but currently there are no known testing programs outside of Gore to further develop this technology.

EnviroScrub Pahlman Process

A multipollutant control technology that is truly unique is being developed by EnviroScrub (28–30). In 2000, EnviroScrub Technologies Corporation ("EnviroScrub") acquired the dry Pahlman™ scrubbing technology, which can simultaneously remove SO_x, NO_x , and Hg.

Since June 2003, the company has been granted two U.S. patents, consisting of 104 claims, on its Pahlman™ process technology. Pahlman™ process technology consists of a single-stage, dry system, which can essentially replace three separate emission reduction technology (ERT) systems: wet FGD for SO_x scrubbing, selective catalytic reduction (SCR) for NO_x scrubbing, and activated carbon injection for mercury reduction. High capture percentages coupled with the single-stage capabilities of the system make the technology attractive compared to the standard alternatives of wet FGD, SCR, and activated carbon systems.

A conceptual process diagram is shown in Figure 1.

Manganese is the twelfth most abundant element on earth, constituting about 0.1% of the earth's crust. As an oxide, it occurs in nature in at least 30 known forms, including over 14 minerals of economic significance, and in numerous synthetic forms. Manganese oxides are used commercially as desulfurizers and alloy metal in steel production, as decolorizers in glass manufacturing, in ceramic glaze, and extensively as depolarizers in dry-cell batteries. Extensive technical literature is available on the subject of manganese oxides. The Pahlman™ process uses a sorbent composed of oxides of manganese. These specialized sorbents have been generically named Pahlmanite™ sorbent in honor of the late Dr. John E. (Jack) Pahlman who led the early research and development work on the process.

The manganese may exist in six different valence (oxidation) states. For purposes of the Pahlman™ process, valence states of interest are 2+, 3+, and 4+. These states correspond to the oxides MnO, Mn_2O_3, and MnO_2. The oxide Mn_3O_4 is likely a solid solution of manganese in the 2+ and 3+ states.

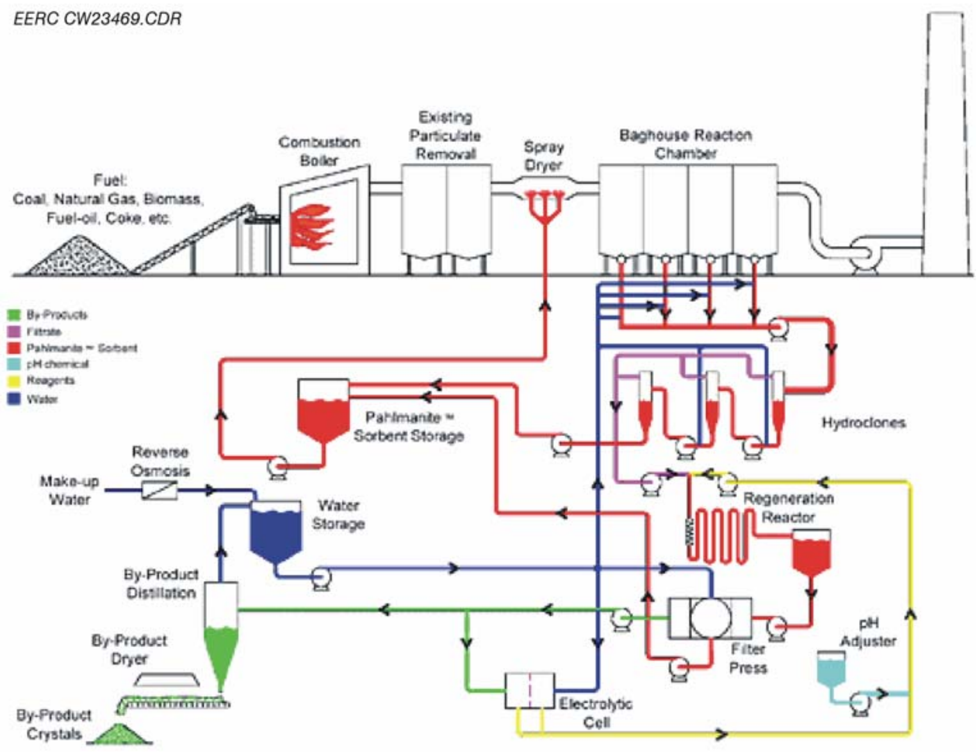

Figure 1. Conceptual layout for the Pahlman™ process (from EnviroScrub Web site).

A characteristic of most oxides of manganese species is nonstoichiometry; that is, most oxides of manganese molecules contain, on average, less than the theoretical number of two oxygen atoms (typically, the average number of oxygen atoms ranges from 1.5 to 2.0). This nonstoichiometry is thought to result from solid–solution mixtures of two or more oxide species and exists in all but the beta (β), or pyrolusite, form of manganese dioxide. The most active types of Pahlmanite™ sorbent usually have the formula $MnO_{1.7 \text{ to } 1.95}$, which translates into manganese valence states of 3.4+ to 3.9+, as opposed to the theoretical 4.0+ state. It is unusual for average valence states above about 3.9 to exist in most forms of oxides of manganese. The formula MnO_2 symbolically represents all varieties of manganese dioxide.

Some manganese oxides have the ability to absorb oxygen from gas. Manganous oxide (MnO) will oxidize to MnO_2 in the presence of air, for example. Additionally, the dioxides are themselves oxidizers; they readily exchange oxygen in chemical reactions; and they are known to have catalytic properties. This oxygen exchange ability may be related to proton mobility and lattice defects common within most MnO_2 crystal structures. These characteristics are important to the Pahlman™ process's, since removal of NO_x and SO_2 gases and Hg requires oxidation of the species to be removed prior to reaction with Pahlmanite™ sorbent to form manganese sulfates, nitrates, and mercury compounds. It is important to understand and optimize such desirable properties during manufacture of Pahlmanite™ sorbent.

Manganese compounds are soluble in water in the 2+ valence state, but not in the 4+ state. Therefore Mn^{2+} compounds are readily soluble, as opposed to MnO_2. This property is used in the Pahlman™ process's sorbent capture and regeneration procedure, in that Pahlmanite™ sorbent is reduced from about the 4+ state to the 2+ state during formation of manganese nitrates and sulfates. These species are water-soluble, allowing the sulfate, nitrate, and Mn^{2+} ions to be dissociated and the Mn^{2+} to be oxidized again to about Mn^{4+}.

Chemical reactivity ("activity") appears to be controlled by a variety of MnO_2 characteristics, including bound water, crystal structure and crystal lattice defects, surface area, particle size, valence state, and presence of other elements within the crystal lattice. Much of the MnO_2 literature deals with electrochemical activity for applications in electric batteries. This type of activity is not always similar to or useful for Pahlman™ process gas removal applications. Part of the chemical activity associated with gas removal appears related to catalytic properties of MnO_2. These properties are still being investigated at present, but appear to affect oxidation of nitrous oxide (NO) to nitrogen dioxide (NO_2) (and, possibly, sulfur dioxide [(SO_2)] to sulfur trioxide [(SO_3)]) as intermediate steps, in the formation of manganese nitrates and sulfates on the surface of Pahlmanite™ sorbent and in the formation of mercury compounds.

EnviroScrub has developed patented and proprietary processes for producing and regenerating hybrid types of manganese-based sorbents, which are very effective for NO_x, SO_2, and Hg removal applications and have possibilities for other applications. Their sorbents are effective for gas removal because of a combination of properties not found in commercially available oxides of manganese. These properties include high gas permeability, low bulk density, high valence state, extremely high specific surface area, cryptomelanelike crystal structure, and a high degree of hydration.

Advantages

- Very high levels of SO_2, NO_x, and mercury removal have been reported. A significant advantage is the potential to achieve >90% mercury removal (28).

- This is truly a unique multipollutant control approach that is not based on the combining of several existing approaches.

- As presented, the technology would be placed downstream of a particulate control device so that the captured mercury will not be mixed with the fly ash. This facilitates fly ash disposal as well as fly ash utilization as a by-product.

- Since it includes a regeneration process, there is potential for the mercury to be isolated for disposal and permanent sequestering of the captured mercury with a minimum volume of material.

- The technology has potential as a long-term mercury control solution with widespread application when installed as a multipollutant control technology as an alternative to SCR and FGD technologies.

Status and Development Issues

- The concept has moved beyond the bench-scale level and has been tested with a 1000-acfm trailer-mounted slipstream device at a number of coal-fired power stations. However, only the collection step has been demonstrated. The fairly complex regeneration and recycling steps have not been tested.

- According to the process diagram, the preferred approach would be to spray the material into a reactor; however, specific operational conditions have not been presented. Most of the testing to date has been with dry injection of the adsorbent materials. Whether the same removal levels for SO_2, NO_x, and Hg would be seen with spray injection is unknown.

- How the mercury would be separated and sequestered has not been reported. Adapting the process to separate the mercury is a major development step.

- Much longer-term and larger-scale testing needs to be completed to address all aspects of the process.

- The chemistry of the sorbent materials and the preferred recipe of the materials are proprietary and have not been reported.

Combined Oxidation of NO_x and Mercury

Oxidation technologies to enhance mercury capture in conventional wet scrubbers will be addressed in a later quarterly report. However, two processes that oxidize mercury along with NO_x for capture in an ammonia-based wet scrubber are unique. Both the BOC LoTox™ and ECO™/Powerspan are NO_x control approaches whereby the NO_x is oxidized to a soluble form to allow capture in a wet scrubber. Even though the oxidation approaches for the two processes are different, both of these processes claim that elemental mercury is also oxidized to HgO and subsequently captured in the wet scrubber along with SO_2 and NO_x. Both of the processes are coupled with an ammonia-based wet scrubber.

LoTOx™

The BOC LoTOx™ system is based on the patented Low-Temperature Oxidation (LTO) Process for Removal of NO_x Emissions, exclusively licensed to BOC Gases by Cannon Technology (31, 32). Marsulex Inc. and the BOC Group have signed a joint marketing agreement that will enable each company to offer electric utilities an integrated multipollutant control solution that provides maximum compliance for emissions of sulfur dioxide, sulfur trioxide, nitrous oxides, mercury, and other heavy metals in conjunction with ammonia-based wet scrubbing. The mercury removal is achieved by oxidizing elemental mercury with ozone to produce soluble HgO, which is captured in a downstream wet scrubber.

The LoTOx™ System is a NO_x removal system that injects ozone into the flue gas stream to oxidize insoluble NO_x to soluble oxidized compounds. Ozone is produced on-site and on demand by passing oxygen through an ozone generator. LoTOx™ is a low-temperature system;

therefore, it does not require heat input to maintain operational efficiency or to prevent the "slip" of treatment chemicals, such as ammonia, as is common with SCR and selective noncatalytic reduction (SNCR) systems.

Ozone is produced in response to the amount of NO_x present in the flue gas generated by the process. The low operating temperature allows stable and consistent control regardless of variation in flow, load, or NO_x content. There are no adverse effects of acid gases or particles on the LoTOx™ system, and some particles may even enhance the reaction by producing sites for nucleation of moisture and by catalyzing the oxidation reaction.

Ozone rapidly reacts with insoluble NO and NO_2 molecules to form soluble N_2O_5. The species N_2O_5 is highly soluble and will rapidly react with moisture in the gas stream to form nitric acid. The conversion of NO_x into the aqueous phase in the scrubber is rapid and irreversible, allowing nearly complete removal of NO_x. The nitric acid, along with unreacted N_2O_5 and nitrous acid formed by reaction of NO_2 with water, can be easily scrubbed out of the gas stream in a wet scrubber with water or neutralized with a caustic solution.

The rapid reaction rate of ozone with NO_x makes ozone highly selective for treatment of NO_x in the presence of other compounds such as CO and SO_x, resulting in a high ozone utilization efficiency for NO_x removal with no wasteful consumption of ozone by CO and SO_x.

ECO™/Powerspan

Powerspan Corp. is the primary researcher and proprietary owner for the ECO™ process (33–35). However, Powerspan has entered into an alliance with Wheelabrator Air Pollution Control, Inc., to commercialize the system. Powerspan and First Energy jointly funded the latest pilot plant. In addition, DOE awarded a grant to Powerspan to optimize the mercury removal capability of the technology on a 50-MW demonstration facility at the R.E. Burger Plant. These tests are currently being conducted, but results are not yet available.

In the ECO™ process, flue gas exiting the ESP or fabric filter is routed to the ECO™ reactor where it is exposed to a high-voltage discharge, which generates high-energy electrons. These high-energy electrons initiate chemical reactions that lead to the formation of oxygen and hydroxyl radicals. These radicals then oxidize the pollutants in the flue gas, leading to the formation of particulate matter and aerosol mist. These components are removed downstream in an ammonium salt wet scrubber and wet ESP forming the ammonium sulfate and ammonium nitrate by-products. Approximately 90% of the NO in the flue gas is oxidized to NO_2 and is removed in the scrubber (the other 10% remains unoxidized). Less than 10% of the SO_2 in the gas is oxidized to form SO_3, which eventually forms sulfuric acid (H_2SO_4). Elemental mercury vapor is oxidized to form mercuric acid (HgO), which is removed by the wet scrubber/wet ESP.

Advantages

- For both processes, combining NO_x, SO_2, and mercury control within one process makes the approach attractive.

- High mercury removals of >90% should be possible.

- With removal of the mercury from the scrubber liquor, there is potential for mercury concentration and long-term sequestration.

Status and Development Issues

- The concepts are being tested at a large scale so near-term commercialization is viable.

- The level of mercury control that can be achieved has not been demonstrated yet. The fate of the mercury within the scrubber is also unknown, and how the mercury can be removed for disposal is unproven.

Mercury Control with the *Advanced Hybrid*™ Filter

Since 1995, DOE has supported development of a new concept in particulate control, called the advanced hybrid particulate collector (AHPC) (36). The AHPC is licensed to W.L. Gore & Associates, Inc., and is being marketed as the *Advanced Hybrid*™ filter. The *Advanced Hybrid*™ filter combines the best features of ESPs and baghouses in a unique configuration, providing major synergism between the two collection methods, both in the particulate collection step and in the transfer of dust to the hopper. The *Advanced Hybrid*™ filter provides ultrahigh collection efficiency, overcoming the problem of excessive fine-particle emissions with conventional ESPs, and it solves the problem of reentrainment and re-collection of dust in conventional baghouses. The *Advanced Hybrid*™ filter also appears to have unique advantages for mercury control over baghouses or ESPs as an excellent gas–solid contactor. Since most of the sorbent material will collect on the perforated plates, there will be minimal effect on the pressure drop across the filter bags. In addition, better gas–solid contact is achieved than in conventional ESPs because the distance that gas must cross streamlines to reach sorbent particles is much smaller than in ESPs.

The objective of this current DOE-funded project is to demonstrate 90% total mercury control with commercially available sorbents in the *Advanced Hybrid*™ filter. The approach included field demonstration pilot-scale testing with a 2.5-MW *Advanced Hybrid*™ filter at the Big Stone Power Plant, which burns subbituminous coal from several different PRB mines.

Over 90% mercury control was demonstrated at low carbon addition rates upstream of the *Advanced Hybrid*™ filter with commercially available Norit FGD activated carbon. However, the level of control was dependent on other flue gas components. One of the very interesting findings was the discovery that when the plant cofired a small amount of tire-derived fuel, the level of mercury captured in the fly ash, the fraction of oxidized mercury in the inlet flue gas, and the level of total mercury removal with activated carbon all were significantly increased likely due to the increased chlorine content from tire-derived fuel. Another significant result was that the injection of activated carbon for mercury control had no effect on bag-cleaning interval or pressure drop. The perforated plate geometry of the *Advanced Hybrid*™ filter allows sufficient gas–solid contact to achieve over 90% mercury removal at low carbon addition rates, even though most of the carbon is collected on the perforated plates.

Good mercury control was demonstrated at A/C ratios up to 14 ft/min, but the highest mercury removal (94%) was seen with a combination of a lower A/C ratio and somewhat increased carbon injection rate (6 ft/min and 2.5 lb of carbon/million Btu)

Advantages

- The *Advanced Hybrid*™ filter has the potential to achieve >90% mercury removal for both bituminous and subbituminous fuels.

- Even better mercury removal might be achieved with very low addition rates of new, more advanced sorbents.

- At very low addition rates of carbon, fly ash utilization for some applications may still be possible based on the total amount of carbon in the ash. However, the use of fly ash for cement application may be subject to other tests such as the anti-foaming index

- Cost appears to be reasonable because from 70% to 90% control was demonstrated with a low carbon rate (1.5 lb/million But) of low-cost Norit FGD carbon

- The *Advanced Hybrid*™ filter has potential as a combined long-term mercury control solution along with ultrahigh collection (99.99% removal) of fine particles.

Status and Development Issues

- The concept for mercury control has moved beyond the bench scale and has been tested at the 2.5-MW pilot level at a coal-fired power station. However, there are currently no plans for a full-scale demonstration to evaluate mercury control effectiveness.

- The availability of the approach depends on the commercial success of the *Advanced Hybrid*™ filter for particulate control. A full-scale evaluation of the *Advanced Hybrid*™ filter technology is being demonstrated at the Big Stone Power Station; however, this demonstration does not include an evaluation of mercury removal capabilities. Subsequent installations will depend on the results from the Big Stone demonstration.

SUMMARY

A variety of approaches for mercury control are under development, ranging from combustion modification to multipollutant technologies. Many of these unique technologies have passed the bench- and pilot-scale developmental phases and are now being tested at full scale.

For the near-term, it appears that 50%–80% control may meet regulatory requirements. However, 90% control is a better target for a technology to be considered attractive to meet longer-term needs. Since the amount of mercury in coal is very small (typically about 0.1 µg/g), the total amount of mercury input (and potential emissions) for a 500-MW plant in a year is only about 300 lb. This suggests that there is potential for generating a minimum amount of waste material if the mercury can be effectively captured and concentrated. On the other hand, if the captured mercury is highly dispersed in waste material or by-product, the mercury must be proven to be in a stable form so that there is little possibility of reemission into the atmosphere. This will be a significant factor in the development of new technologies for long-term mercury control.

Many of the developing technologies appear to be capable of achieving >90% control, but in most cases, this level of control has not been demonstrated over the longer term at a large scale. Concentration and sequestering of the collected mercury is also possible for many of the technologies, but this step has not been demonstrated, even at the bench-scale level for most approaches.

Removal of the mercury from the fuel prior to combustion is a mercury control approach that has been considered and practiced for many years, but now a commercial process, K-Fuel®, is being developed at a large scale that removes a significant fraction of the mercury for lignite and subbituminous coal. Another alternative to back-end mercury control is combustion modification to produce an ash material that has mercury adsorbent properties. Recent developments related to combustion modifications and in situ generation of sorbents for mercury control show positive results in testing conducted to date; however, large-scale demonstrations and balance of plant issues will need to be addressed.

Attractive alternatives are being developed that focus on multipollutant technology and mercury capture devices downstream of particulate control and/or scrubbers. Development of these technologies and data from full-scale demonstrations will be reviewed as they become available and summarized in subsequent quarterly reports to CEA.

UPCOMING EVENTS

POWER-GEN International
November 30–December 2, 2004, Orlando, Florida
http://pgi04.events.pennnet.com

229th ACS National Meeting ACS
March 13–17, 2005, San Diego, California
http://oasys.acs.org/acs/229nm/topics.html

30th International Conference on Coal Utilization & Fuel Systems (formerly Clearwater Coal Conference)
April 17–21, 2005
http://www.coaltechnologies.com

A&WMA 98th Annual Conference and Exhibition
June 21–24, 2005, Minneapolis, Minnesota
http://www.awma.org

230th ACS National Meeting ACS
August 28–September 1, 2005, Washington, DC
http://oasys.acs.org/acs/230nm/topics.html

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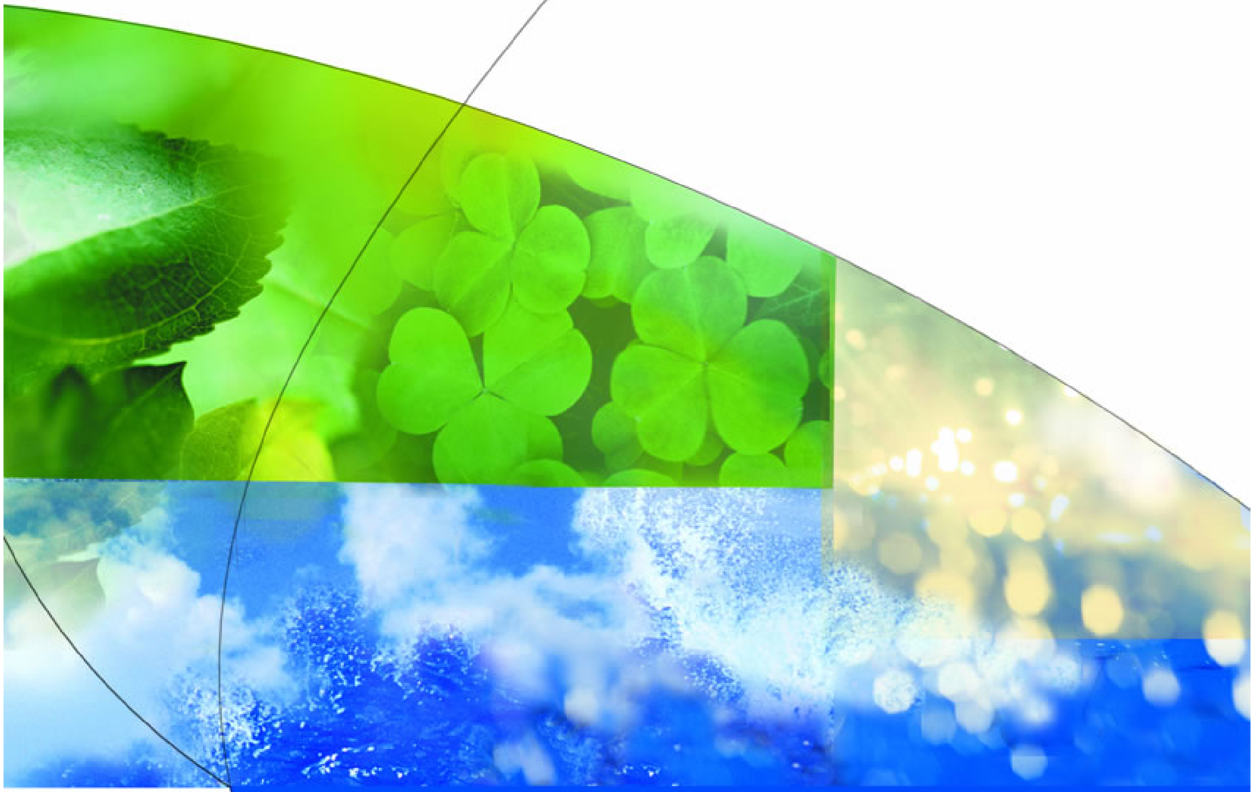

Quarter 4 – Rerelease of Mercury from Coal Combustion By-Products

October 2004

Canadian Electricity Association
Association canadienne de l'électricité

EERC
Energy & Environmental Research Center

Center for Air Toxic Metals

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 4 – RERELEASE OF MERCURY FROM COAL COMBUSTION BY-PRODUCTS

ACKNOWLEDGMENT AND DISCLAIMERS

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QUARTER 4 – RERELEASE OF MERCURY FROM COAL COMBUSTION BY-PRODUCTS

EXECUTIVE SUMMARY

The topic for this fourth quarterly report is Rerelease of Mercury from Coal Combustion By-Products (CCBs). The stability of mercury associated with CCBs is an issue that has only recently been under investigation, but it has become a more significant issue as the utility industry begins to develop, test and, eventually, install mercury emission controls that may increase the mercury associated with CCBs. The reasons for evaluating the rerelease of mercury from CCBs are 1) to determine the stability of mercury captured on CCBs and 2) to aid utilities in determining and understanding changes in CCBs associated with mercury control and associated CCB management.

Mercury can be present in quantifiable levels in CCBs, and the mechanisms that allow mercury to be removed with CCBs have become the focus for many developing mercury control technologies. Mercury is most likely to be found in fly ash and flue gas desulfurization (FGD) materials and not in bottom ash and boiler slag because of the relatively high temperatures at which bottom ash and boiler slag are formed and removed from coal combustion systems. As a result of improved mercury removal, especially through particulate control devices and FGD systems, increased mercury concentrations are likely to be observed in respective CCBs.

Potential rerelease mechanisms for mercury from CCBs are identified as 1) direct leachability, 2) vapor-phase release at ambient and elevated temperatures, and 3) biologically induced leachability and vapor-phase release.

Currently, the incorporation of sorbents into the fly ash stream, resulting from injection of sorbent into the flue gas, poses the highest potential impact on CCBs. At this time, the most likely sorbent candidate is activated carbon. The second most likely impact to CCBs from mercury control technologies is in the area of FGD materials, especially in materials generated from wet FGD systems.

Existing data indicate that the mercury content of fly ash and FGD materials collected during tests of mercury control technologies can be significantly increased over the mercury content currently being generated without mercury emission controls in place. Since many mercury control systems currently under development are using carbon sorbents to remove mercury from the flue gas, it is important to note that the unburned carbon associated with some currently generated fly ash has similar sorbent properties as activated carbon used for mercury removal. Both samples of fly ash with unburned carbon and fly ash with activated carbon sorbent have shown good performance in evaluations of mercury stability.

The data assembled and summarized here indicate that mercury associated with CCBs is stable and highly unlikely to be released under most management conditions, including

utilization and disposal. Therefore, existing CCB management options are expected to be environmentally sound options for CCBs from systems with mercury control technologies installed.

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 4 – RERELEASE OF MERCURY FROM COAL COMBUSTION BY-PRODUCTS

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of the CEA, the Center for Air Toxic Metals® Affiliates, the U.S. Department of Energy (DOE), and the Canadian Council of Ministers of the Environment (CCME), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of developments in mercury monitoring, control, policy, and related research advances.

Ongoing developments in the area of mercury regulations for coal-fired power plants in Canada in the form of Canadawide Standards (CWS) and the United States in the U.S. Environmental Protection Agency's (EPA's) Proposed Utility Mercury Reduction Rule illustrate the need for effective mercury control strategies for coal-fired electric utilities. In previous quarterly reports, various mercury control technologies were reviewed in detail. Additionally, a review of the state of technology for mercury measurement was provided in the second quarterly report. As more emphasis is placed on mercury removal from flue gas, increased mercury concentrations may be found in the various coal combustion by-products (CCBs) which are valuable raw materials in the concrete and wallboard industries among others. The fate of these by-products and the mercury contained within them is of significant interest if mercury from coal combustion is going to be eliminated from the global pool. It is of vital importance that mercury removed from coal combustion flue gas and present in CCBs is stable and not hazardous to the environment or human health. If mercury concentrations of these CCBs is significantly increased over that of currently produced CCBs, utilities, CCB users, regulators, and others may need to modify management options to ensure the environmentally sound management of these materials. Therefore, significant research has been conducted to evaluate the mechanisms by which mercury is associated with fly ash and scrubber effluents. A review of the fate of mercury in CCBs is provided in this quarterly report.

In order to adequately address the many topics pertinent to mercury research and development and provide the detail necessary for the various stakeholders to make informed decisions, selected topics will be discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that have been addressed in previous quarterly reports include the following:

- Quarterly 1 – Sorbent Control Technologies for Mercury Control
- Quarterly 2 – Mercury Measurement

- Quarterly 3 – Advanced and Developmental Mercury Control Technologies

As advancements are made in these previously covered topics, updates will be provided as a secondary topic of the quarterly report. However, to date no significant advancements in technology development or measurement control have been identified.

Topics that will be addressed in upcoming quarterly reports include, but are not limited to, the following:

- Mercury policy – updated each quarter based on available information
  - Upcoming events and news releases
  - Regulation, policy, compliance strategies, and health developments

- Baseline mercury levels and emissions

- Mercury control
  - Summary of large-scale test activities and associated economics
  - Mercury oxidation and control for scrubbed systems
  - Multipollutant control strategies
  - Summary of mercury-related economics for commercial systems

- Mercury chemistry and transformations
  - Mercury chemistry fundamentals, modeling, prediction, and speciation
  - Mercury fate and transport – impacts on health

MERCURY POLICY

The CCME has been in the process of developing CWS for mercury since 1998 for several significant mercury-emitting sectors and products. Standards have been completed for base metal smelters, incinerators, mercury-containing lamps, and dental amalgam wastes. A CWS for mercury emissions from coal-fired electric power-generating plants is currently under development. Canadian coal-fired generating companies have embarked on a multiyear program to improve the information base around mercury measurement and control that will aid in the development of the CWS. A key component of the CEA Mercury Program is the Coal, Residue, and Flue Gas Sampling and Analysis Program that companies have undertaken. This program has generated a rich database around mercury emission inventories and management to inform this decision-making process. To date, data have been collected from 16 different power plants operated by ATCO Power, EPCOR, Manitoba Hydro, New Brunswick Power, Nova Scotia Power, Ontario Power Generation, SaskPower, and TransAlta. The preliminary data can be accessed on the program Web site: http://www.ceamercuryprogram.ca. The data is currently undergoing verification and analysis by the CCME and the coal-fired generating companies to ensure the data set is robust for consideration in the 2005 CWS development process.

Another componenet of the CEA Mercury Program is the Laboratory Round Robin, a review of analytical laboratories. Developed by CEA member companies and funded by CCME, this program consisted of a two-phased analysis and quality assurance program. Mercury concentrations in fuel, by-products, and stack gas samples tend to exist at very low levels; therefore, accurate laboratory analysis is critical to ensuring an effective mercury inventory program. Phase I of this program has been completed and focused on assessing participating laboratories by analyzing standard samples over a 6-month period. Phase II of the Laboratory Round Robin provided ongoing quality assurance for the data collection program and benchmarked several common Canadian coals for mercury and other coal-specific properties. Laboratories participating in the program tended to do very well. For more information regarding the Laboratory Round Robin, go to http://www.ceamercuryprogram.ca.

In the United States, EPA has received 586,000 comments on the Proposed Utility Mercury Reduction Rule after it extended the comment period to June 29, 2004. From this record number of comments, including 4800 unique comments, approximately 200 comments contained substantial content and ranged in length from five to ten pages.

In his address to the 2004 annual Air and Waste Management Mega Symposium, EPA Administrator Mike Leavitt stated that EPA is in the process of reviewing the comments which will be summarized in a comment response document in advance of the March 15 deadline for the final rule. Additionally, he laid out five guiding principles that EPA is using in devising the final mercury rule. The rule will:

1) Concentrate on the protection of children and pregnant women.

2) Stimulate and encourage early implementation of new technology.

3) Leverage the $50 billion investment of the Clean Air Interstate Rule to reduce total mercury emissions.

4) Take into account the need to maintain America’s competitiveness worldwide.

5) Be one component of many efforts to reduce mercury emissions.

Once the EPA comment response document becomes available, a summary will be provided in the following quarterly report.

In Europe, the European Commission recently issued a consultation document on mercury which evaluated mercury emissions, production, trade, and use and reviewed the health and environmental impacts of mercury. The original focus of the effort was Europe’s chlor-alkali industry, which is the largest user of mercury in Europe; however, it is in the process of phasing out its use. A copy of the Commission’s document is available at the following Web site: http://europa.eu.int/comm/environment/chemicals/mercury/pdf/consultation.pdf.

Currently, coal combustion in power plants is the largest single source of mercury emissions in Europe. However, the issue of mercury emissions is complicated by two opposing trends. In response to concerns over mercury, emission standards are tightening. However, unlike many other parts of the world, mercury emissions and environmental concentrations in Europe appear to be falling according to data collected between 1990 and 2000 and summarized at the aforementioned Web site. Based on this data, it is unclear what strategy the Commission will take regarding mercury emissions, and unlike the United States, it is not certain that Europe will introduce mercury controls at an early stage.

QUARTER 4 FOCUS: RERELEASE OF MERCURY FROM COAL COMBUSTION BY-PRODUCTS

Mercury and other air toxic elements can be present in fly ash, flue gas desulfurization (FGD) material and, to a lesser extent, bottom ash and boiler slag. The mercury that can associate with CCBs is a function of the mercury content of the coal used, the coal properties, the combustion technology, and the emission control technologies at the plant. Generally speaking, mercury released from the combustion of coal remains in the gaseous state until cooling to temperatures typical of back-end emission control equipment, at which point it either reacts with components of the flue gas and is removed from the system as particulate-bound mercury in the ash, a sulfur compound with FGD control, or is emitted out the stack.

Mercury emission control technologies are being developed to remove mercury from the flue gases and, in many cases, these technologies are designed to incorporate the mercury removed from the flue gas into the fly ash or FGD material. The stability of mercury associated with CCBs is an issue that has only recently come under investigation, but it has become a prominent question as the industry strives to develop and test mercury emission controls that may consequently increase the mercury associated with CCBs. The primary reason for evaluating the rerelease of mercury from CCBs is to aid utilities in determining and understanding changes in CCBs associated with mercury control and how these changes may impact CCB management.

The rerelease mechanisms for mercury from CCBs are 1) direct leachability and 2) vapor-phase release at ambient and elevated temperatures. Both leachability and vapor-phase transport can be impacted by microbiological action on the CCBs.

BACKGROUND

Mercury and CCBs

Mercury can be present in quantifiable levels in CCBs. It is most likely to be found in fly ash and FGD materials and not in bottom ash and boiler slag because of the relatively high temperatures at which bottom ash and boiler slag are formed and removed from coal combustion systems.

Historically, data on mercury concentrations in fly ashes have varied widely, but leachability of mercury has generally fallen below detection limits (1–4). Hassett et al. (5–7) reported mercury concentrations ranging from <0.01 to 2.41 ppm in samples of fly ash from all ranks of coal from both the eastern and western United States. Consistent with what is known about the chemistry of mercury in combustion systems, the average mercury content of fly ash is higher than that for bottom ash or slag and increases with the carbon content of the ash (8, 9). The mercury contents of FGD scrubber materials are, in turn, higher on average than those of fly ash (10). Concentrations of 39 and 70 ppm were reported by DeVito and Rosenhoover (11) and DeVito (12) for two FGD materials.

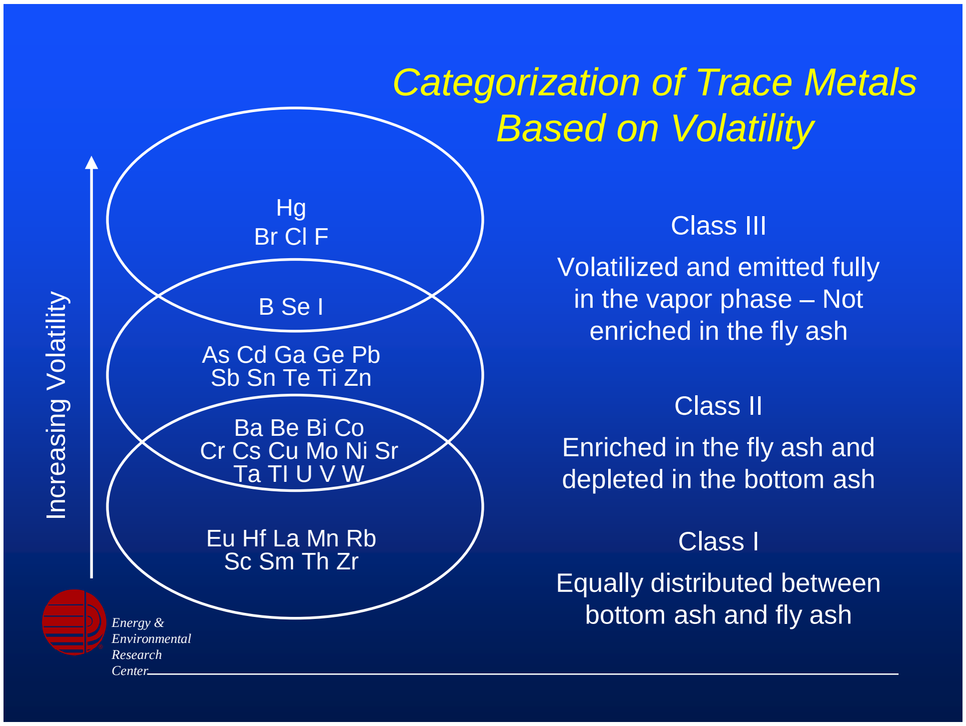
Nearly 100% of the mercury present in coal exits the boiler with the flue gas. The speciation of that mercury however is highly influenced by the composition of the flue gas (12). Data from the EPA Information Collection Request (ICR) allowed for some generalizations to be made regarding the potential for various CCBs to capture mercury. Hot-side electrostatic precipitators (ESPs) do not allow capture of mercury on the fly ash because the temperature is too high, but cold-side ESPs and fabric filters operate at temperatures that do allow some mercury to be removed from the flue gas. Fabric filters tend to remove significant percentages of both elemental and oxidized mercury because of the excellent gas–solids contact as the flue gas moves through the dust cake on the filter. Wet FGD (WFGD) systems and spray dryer absorbers have been shown to be effective in removing oxidized mercury from flue gas. Additional information on the results collected in the EPA ICR can be found in other sources (13–16). CEA has a program in place with eight coal-fired power generation companies in Canada designed to develop information associated with mercury emissions from coal-fired generation and to find cost-effective and efficient management options for mercury emissions (more information is available at the following Web site: http://www.ceamercuryprogram.ca/EN/program_overview.html). The CEA program collected information on the mercury content of CCBs, and the data assembled are under review.

The EPA ICR data did not include information on the concentrations of mercury on the CCBs generated at the test facilities, so it is an inference that the noted mercury reductions indicate an associated mercury capture on the CCBs. It is logical to conclude that at least some mercury can be captured by fly ash and/or FGD material. It is known that the mercury can be present in the flue gas as either elemental and/or oxidized species and that both elemental and oxidized mercury can be sorbed on carbon. Mercury can be physically or chemically sorbed on carbon, so it can be assumed that unburned carbon present in fly ash can sorb mercury by either or both of these mechanisms. While elemental mercury can be sorbed on carbon, it is actually transformed to oxidized mercury (17), implying that its stability on the carbon will be similar to that of oxidized mercury. The mechanism of mercury capture on unburned carbon is expected to be equivalent to that of activated carbon introduced into the flue gas as a means of mercury removal and control. However, insufficient data exist to extrapolate that assumption to include modified activated carbons such as halogenated or sulfuric-impregnated carbon or other modified carbon sorbents under development. In many cases, the quantities of carbon sorbent needed for mercury control are not expected to be higher than the level of unburned carbon already found in some fly ashes. The activation of the carbon sorbent, however, is anticipated to be problematic for use of these fly ashes as a mineral admixture in concrete because the activated carbon has been shown to sorb standard air-entraining admixtures and limit the function of the admixture to produce an air-entrained concrete, which is needed for numerous applications.

The EPA ICR data strongly imply that certain coal fly ashes may exercise a catalytic effect on the oxidation of elemental mercury. Inorganic compounds such as manganese oxide, iron-containing compounds, and chromium and nickel oxides have been shown to catalyze mercury oxidation (18, 19), but various tests with the addition of some of these compounds to simulated flue gas did not produce the anticipated oxidation of mercury (20, 21). The mechanism of sorption of mercury on fly ash is extremely complicated and has not yet been fully investigated.

Anticipated Impacts of Proposed Mercury Control Technologies on CCBs

Proposed mercury emission controls have the potential to impact fly ash and FGD materials because mercury is highly volatile and should leave the combustion zone in the flue gas. As noted in Figure 1, mercury should be volatilized and emitted fully in the vapor phase in combustion systems. Mercury in the vapor phase in the flue gas has the potential to be sorbed onto the fly ash, carbon (either unburned carbon or sorbent), other sorbents, and the FGD reagent, or it may be emitted. The highest potential for mercury controls to impact CCBs is through the use of sorbent injection technologies that will incorporate the sorbent into the fly ash stream. The most likely sorbent candidate is activated carbon, even though other sorbents have been and are being tested. Testing at four full-scale boilers that measured mercury across particulate control devices gives some insight to the importance of particulate control in mercury removal and indicates that increased carbon relates to increased mercury removal. Even though no sorbent injection or other add-on mercury control technology was in place during these tests, the unburned carbon present in the fly ash provided significant mercury removals. Mercury removals ranged from a low of 28% for an ESP to between 61% and 99% for units equipped with reverse-gas baghouses (22). The highest mercury removals were observed where there was a high level of unburned carbon in the fly ash (high loss on ignition [LOI]). Pilot tests reinjecting power plant fly ashes ahead of a reverse-gas baghouse indicated removals between 13% and 80% at temperatures in the range of 135°–160°C (275°–320°F), and again, removals increased with increased LOI. It must be noted that LOI is not equivalent to carbon content of ash.



Categorization of Trace Metals Based on Volatility

Increasing Volatility

Hg
Br Cl F

B Se I

As Cd Ga Ge Pb
Sb Sn Te Ti Zn

Ba Be Bi Co
Cr Cs Cu Mo Ni Sr
Ta Tl U V W

Eu Hf La Mn Rb
Sc Sm Th Zr

Class III

Volatilized and emitted fully in the vapor phase – Not enriched in the fly ash

Class II

Enriched in the fly ash and depleted in the bottom ash

Class I

Equally distributed between bottom ash and fly ash

Energy & Environmental Research Center

Figure 1. Categorization of trace elements based on volatility.

At tests performed at Wisconsin Electric’s Pleasant Prairie Power Plant, Unit 2, in 2001 (23), activated carbon injection (ACI) resulted in mercury removals of 40%–70%, with increased removals correlating to increased carbon injection. The LOI of the fly ash produced without sorbent injection at Pleasant Prairie was approximately 0.5% but was increased to as high as 3.5%. More noteworthy than the LOI increase was the impact of that increase on the performance of the fly ash–sorbent mixture in the Foam Index Test, which provides an indication of the appropriateness of the fly ash to be used with an air-entraining agent (AEA). The fly ash–sorbent mixture not only failed the Foam Index Test, but the fly ash from Unit 2 continued to fail the test for 5 weeks after the conclusion of the sorbent injection tests. The presence of carbon in fly ash has been reported to impact the use of fly ash in concrete. The impact relates to air entrainment in concrete. AEAs are used to facilitate the incorporation of very small air bubbles into the concrete mix. The presence of these air voids provides improved freeze-thaw durability of the concrete. For commonly used AEAs, the presence of carbon interferes with the formation of the air voids by sorbing the AEA. Early in the development of specifications for fly ash for use as a mineral admixture in concrete, an upper limit of 6.0% LOI was set for fly ash in order to address this technical issue associated with unburned carbon in fly ash. The potential addition of activated carbon is expected to exacerbate the problem associated with carbon in fly ash and its use in concrete. Preliminary results, such as those from the Pleasant Prairie tests, indicate that the long-standing limit of 6.0% LOI will not be adequate to determine the appropriateness of fly ash activated carbon mixtures for use in concrete. Work addressing this issue is under way by various academic and industrial groups and includes development of AEAs which will perform adequately even with higher carbon content fly ash, admixtures that deactivate the carbon and allow successful use of standard AEA, and carbon removal systems. High carbon fly ash is also used as a feedstock component for cement clinker production which is a high-temperature process. The chemistry of mercury suggests that mercury associated with fly ash (or the carbon in fly ash) will be released as vapor. Since there is evidence that noncarbon sorbents sorb mercury, research needs to be undertaken to determine the fate of mercury in a cement kiln and the associated emission control systems.

Senior et al. (23) also reported on activated carbon sorbent injection tests at Alabama Power’s Gaston Station, which has a hot-side ESP and a COHPAC (compact hybrid particulate collector), which provides a second particulate collection after the ESP for polishing purposes. This system allows the injection of sorbent after the bulk of the fly ash has been collected and separate collection of any remaining fly ash in the flue gas stream along with the mercury-loaded sorbent.

Noncarbon sorbents have been tested for their mercury removal potential, with the intent of identifying sorbents that would capture and hold mercury and have a reduced impact on the fly ash for potential utilization especially in concrete (24, 25). One fly ash from a western subbituminous coal was shown to have a significant mercury sorption capacity after heating to remove all carbon (22), and mercury capture was improved by spray cooling to reduce the gas temperature to 110°C (230°F).

Another potential impact to CCBs from mercury control technologies is in the area of calcium-based FGD materials. It has been shown in field tests (26–28) that WFGD is successful at removing a high percentage of oxidized mercury from the flue gas stream. Elemental mercury is not removed by WFGD, but existing WFGD systems capture approximately 90% of the mercury (II) at essentially no cost to the utility. Studies to enhance the capture of mercury in WFGD systems, generally by enhancing the oxidized mercury in the flue gas, are under way (29–38). Studies are also being performed on removing elemental mercury in WFGD systems as well as on increasing the percentage of oxidized mercury that is removed. The use of WFGD systems for mercury control has the potential to facilitate multipollutant control and may provide some impetus for utilities to consider WFGD systems over other SO_2 controls for DOE Phase II (39) and new fine-particulate control standards. It has been shown that FGD material generated from wet systems can be oxidized to produce gypsum and that mercury present in the WFGD material is partitioned into the gypsum, implying that the mercury is not readily leached from the gypsum (40). The primary effort in the area of mercury emission control using FGD systems has been performed using wet systems, although other types of calcium-based FGD systems also are expected to remove oxidized mercury from flue gas at varying efficiency levels.

STABILITY OF MERCURY ON CCBs

As previously noted, data on mercury concentrations in fly ashes are varied. CEA data (http://www.ceamercuryprogram.ca/EN/program_overview.html) indicates mercury concentrations ranging from <0.002 to 1.221 ppm in fly ash and from 0.001 to 0.342 ppm in bottom ash. Hassett et al. (5–7) reported mercury concentrations ranging from <0.01 to 2.41 ppm in samples of fly ash from full-scale coal-fired power plants from all ranks of U.S. coal. Concentrations of 39 and 70 ppm were reported by DeVito and Rosenhoover (11) and DeVito (12) for two FGD materials. The mercury content of FGD material is higher on average than the mercury content of fly ash which is consistently higher than the concentrations found in bottom ash or boiler slag (10). The mercury concentration of fly ash tends to increase with the carbon content of the ash (8–9). Recently, the EERC reported that the mercury content of fly ash and FGD collected during tests of mercury control technologies can be significantly increased with samples containing a total mercury concentration as high as 120 ppm reported. However, of 21 samples collected from mercury control demonstrations, only 6 had mercury concentrations greater than those noted for samples from systems without mercury control. Those six samples had mercury concentrations ranging from 4.7 to 120 ppm.

Limited data on fly ash–carbon sorbent mixtures (eight total samples) indicate a range of 0.2–5.5 ppm total mercury content, with only two samples from one location providing data indicating mercury content greater than 1 ppm mercury. The limited data do not provide adequate evidence that mercury contents of fly ash–carbon sorbent mixtures will be consistently higher than fly ash produced without mercury emission controls installed. Senior and Bustard (23) reported mercury concentrations in the range of 10–100 ppm in spent sorbent from test runs using the COHPAC system. These data points should be considered separately from samples of fly ash or FGD material that may be impacted by mercury emission controls.

The total concentration of mercury on CCBs or sorbents cannot be used as an indicator of stability. The stability of mercury on CCBs or sorbents can only be evaluated by subjecting the sample to a variety of laboratory tests that expose the material to conditions that simulate those in field settings for realistic management options for the material in question.

Leaching[1]

Various leaching methods are available to evaluate CCBs and other materials for environmental performance, but current data on the leachability of mercury from CCBs has been generated primarily by use of the TCLP (toxicity characteristic leaching procedure) and the SGLP–LTL (synthetic groundwater leaching procedure–long-term leaching). The TCLP, frequently applied to CCBs, involves the extraction of contaminants from a 100-g size-reduced sample of waste material with an appropriate extraction fluid. A 20:1 liquid-to-solid (L/S) ratio (mass/mass, m/m) is employed, and the mixture is rotated for 18 ± 2 hr at 30 rpm using a rotary agitation apparatus. The extraction fluid used for the extraction depends on the alkalinity of the waste material. Very alkaline waste materials are leached with a fixed amount of acetic acid without buffering the system (pH 2.88 ± 0.05), while other waste materials are leached with acetic acid buffered at pH 4.93 ± 0.05 with 1-N sodium hydroxide. After rotation, the final pH is measured, and the mixture is filtered using a glass fiber filter. The filtrate is collected in an appropriate container, and preservative may be added if needed. The filtrate is analyzed for a number of constituents. EPA now recognizes that the TCLP is an inappropriate test for use with CCBs. The SGLP–LTL is a procedure developed at the EERC. The SGLP–LTL was designed to use a synthetic groundwater for the leachate to more closely simulate environmental conditions and to include longer-term leaching time frames for reactive CCBs. In many cases, the SGLP–LTL uses distilled, deionized water because specific site information for the management options to be applied to the CCB is unavailable. The complete SGLP–LTL usually includes leaching times of 18 hours, 30 days, and 60 days. However, LTL is only necessary for alkaline samples (pH >10), because CCB samples with pH values below 10 do not undergo long-term hydration reactions that impact leachate characteristics.

The amount of mercury leached from currently produced CCBs is extremely low and generally does not represent an environmental or rerelease hazard. Concentrations of mercury in leachates from fly ashes and FGD material using either the TCLP or the SGLP are generally below detection limits (0.005 to 0.05 µg/L) (5, 11, 12, 24, 30, 31, 33).

Mercury leachate concentrations from various types of leaching tests (both batch and column) for CCBs resulting from the use of mercury control technologies have been reported. In addition to TCLP and SGLP, the synthetic precipitation leaching procedure (SPLP) and synthetic acid leaching (SAL) batch tests have been used as short-term methods. LTL, a component of the SGLP, has also been performed using 30- and 60-day equilibration periods.

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[1] The authors of the various references have reported data in several different formats. The following concentrations are equivalent: ppm (parts per million) = µg/g; ppb (parts per billion) = µg/kg, ng/g, µg/L; and ppt (parts per trillion) = pg/g, ng/L. The EERC has used ppm, ppb, and ppt to express concentrations associated with solid materials and vapor-phase releases. µg/L and ng/L have been used for concentrations in liquids such as leachate concentrations.

Senior et al. (23, 41) reported that little or no detectable Hg was leached by TCLP or SGLP from fly ash samples resulting from powdered activated carbon (PAC) injection demonstrations at four coal-fired power plants. As shown in Table 1, baseline fly ash, fly ash + sorbent, and COHPAC samples all gave similar leaching results, illustrating very low concentrations.

Table 1. Leaching Results (leached by the EERC) (23, 41)

Plant	Location	Injection Rate, lb/MMacf	Hg in, µg/L TCLP	SGLP
Salem Harbor	ESP Row A (control)	0	0.034	<0.01
Salem Harbor	ESP Row A	10	<0.01	<0.01
Salem Harbor	ESP Row A	10	<0.01	<0.01
Brayton Point	New ESP	0	<0.01	0.01
Brayton Point	Old ESP[1]	0	0.02	0.05
Brayton Point	New ESP	10	0.07	0.03
Brayton Point	Old ESP[1]	10	0.03	0.01
Brayton Point	New ESP[1]	20	<0.01	0.01
Brayton Point	Old ESP	20	0.02	0.02
Gaston	COHPAC B-side	1.5	0.01	<0.01
Gaston	COHPAC B-side	1.5	NA[2]	<0.01
Gaston	COHPAC B-side	1.5	<0.01	<0.01
Pleasant Prairie	ESP hopper composite	10	<0.01	<0.01
Pleasant Prairie	ESP hopper composite	10	<0.01	<0.01
Pleasant Prairie	ESP hopper composite	10	<0.01	NA

[1] Sorbent injected downstream of the old ESP.

[2] Not applicable.

Gustin et al. (42, 43) and Ladwig (44) also reported on the leachability of Hg from the Pleasant Prairie and Brayton Point PAC injection tests using SPLP (see Table 2). An increase in the Hg leachate concentration was noted between the baseline and PAC injection samples by Gustin et al. for the Pleasant Prairie samples, which were all collected from the same ESP. The Brayton Point baseline and test samples were collected at different points, so a direct comparison cannot be made.

Fly ash samples from pilot-scale test burns using ACI and the *Advanced Hybrid*™ filter were leached using SGLP and LTL (45). The SGLP and 30-day LTL leachate results were below the limit of quantification (i.e., <0.01 ppb); however, the 60-day LTL leachates indicated a small release of mercury (Table 3). Pavlish et al. (45) reported that the results indicate that the fabric filter and *Advanced Hybrid*™ filter were more effective in capturing particulate Hg relative to the ESP.

Table 2. Total Hg Concentrations in Fly Ash and Hg Concentrations in SPLP Extracts (adopted from Gustin et al. [43])

Sample	Total Hg, ppb	Leached Hg, ng/L
S2A-1 (base)	247	0.65
S2A-1[a]		0.8
S2A-1[a]		0.6
S2A-1[a]		0.2
S2A-2 (ACI)	2300	ND[b]
S2A-2[a]		ND
S2A-2[a]		2.9
S2A-3 (ACI)	1040	3
S2A-3[a]		6.9
S2A-3[a]		10.7
B7A-1 (base)	670	2.6
B7A-1[a]		2.6
B7A-2 (ACI)	752	ND
B7A-2[a]		ND
B7A-3 (ACI)	670	ND

[a] Replicated measurements.

[b] Not detected.

Table 3. Coal Fly Ash and Leachate (60-day) Mercury Contents (adapted from Pavlish et al. [45])

			Fly Ash (leachate) Mercury, ppm (ppb)		
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	15–115	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.

In early work at the EERC, 22 samples from full-scale power plants operating without any mercury controls were subjected to SGLP, and all resulting leachate mercury concentrations were <0.01 µg/L, with one exception where the leachate concentration was 0.018 µg/L (46). More recently, the EERC reported that SGLP leachate concentrations of mercury ranged from <0.01 to 0.05 µg/L and TCLP leachate concentrations of mercury ranged from <0.01 to 0.14 µg/L (47). These data, which included evaluations of fly ash from systems with and without mercury controls in place, are shown in Figure 2. EERC researchers concluded from the data presented that there was no correlation between total mercury content and leachable mercury.

Results of column leaching performed by Kazonich et al. (48) indicated that mercury leached at extremely low levels when subjected to leaching by solutions ranging from acidic to alkaline. Results of continuing work at DOE's National Energy Technology Laboratory (NETL) using the column leaching procedure and multiple leaching solutions indicated that release of mercury from CCBs by leaching was not related to the total concentration of mercury in the sample (49). The NETL data also indicated that higher leachate concentrations were observed with the acetic acid leachate; however, NETL concluded that it was unlikely that leachate concentrations of mercury would exceed drinking water standards.

The use of sodium tetrasulfide (Na_2S_4) injection as a mercury control technology is being explored in pilot-scale facilities at Southern Research Institute (50). A bituminous and a subbituminous coal were tested and associated ash samples subsequently leached using TCLP. Leachate concentrations of mercury are shown in Table 4. An increase in total Hg content in the ash was noted for both coals with Na_2S_4 injection; however, on comparison to leachates from baseline ash, an increased mercury leachate concentration was only noted for the bituminous ash while the subbituminous ash had a lower mercury leachate concentration.

The effect of FGD used for Hg control has been reported by Richardson (51) and Golden (52). Associated TCLP leaching results for forced oxidation limestone processes were all <0.06 µg/L, while the single FGD material from a system using inhibited oxidation gave a mercury leachate concentration of 0.34 µg/L. Withum et al. (53, 54) leached a variety of Hg control technology CCBs with both TCLP and American Society for Testing and Materials (ASTM) D3987 tests. All samples had Hg leachate concentrations of <1.0 µg/L.

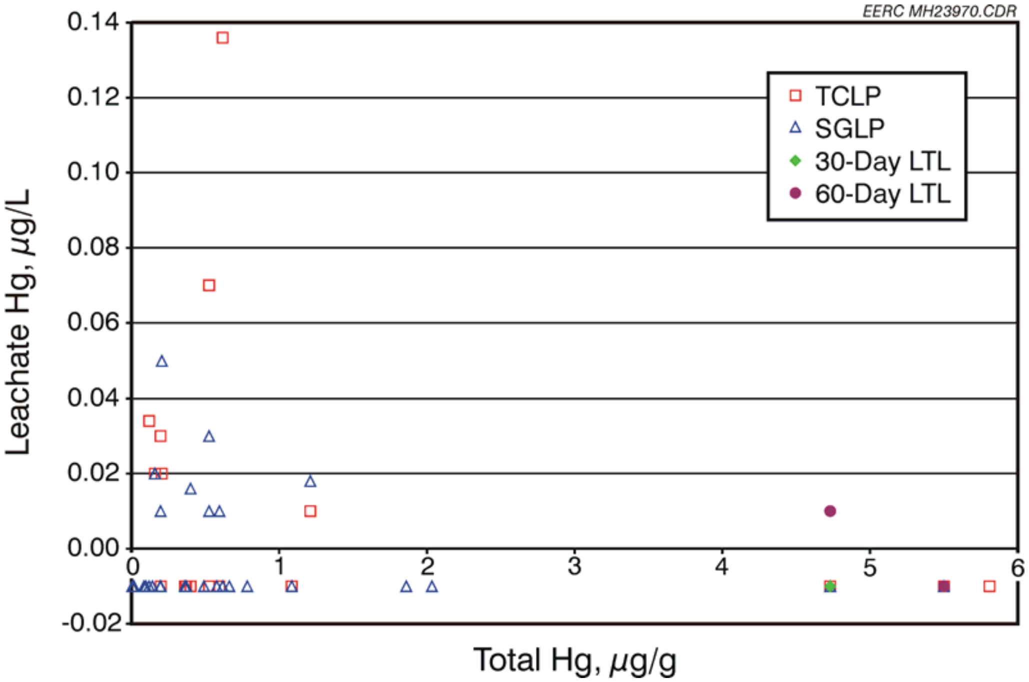

Figure 2. Leachate vs. total Hg; nondetects are shown as negative values.

Table 4. Mercury and Sulfur in Ash (50)

Run No.	Coal Type	Injection Condition	Na_2S_4 in Flue Gas, ppmv	Total Hg in Ash, ppb	TCLP Hg, µg/L
6	Bit.[a]	Baseline condition	0	1.28	20.6
7	Bit.		13.5	1.94	76.8
8	Bit.	Raised flue gas temperature	13.5	1.94	76.8
9	Bit.	Lowered flue gas temperature	13.5	1.94	76.8
10	Bit.	Normal temperature	6.8	NA[b]	NA
11	Bit.	Repeat condition 2	13.5	NA	NA
12	Bit.	Inject chlorine through burner	13.5	NA	NA
13	Bit.	Half chlorine injection	13.5	2.20	69.9
14	Bit.	Maintain chlorine injection, turn off Na_2S_4 injection	0	1.84 ± 0.28	70.4
15	PRB	Baseline	0	1.76	65.7
16	PRB		12.2	1.93	0.342
17	PRB		6.1	1.93	0.342
18	PRB	Return to baseline	0	1.93	0.342
19	PRB	Residual effect	2.9	1.93	0.342
20	PRB	Start fresh	2.9	NA	NA
21	PRB		6.1	NA	NA
22	PRB	Increased air injection temperature	6.1	1.29	30.5

[a] Bituminous coal.
[b] Not applicable.

Leaching tests on four carbon sorbents were performed using TCLP. Detectable levels of mercury in the leachate were observed for only one sorbent (55). These preliminary results suggest that mercury is not readily leached from sorbents, which implies that the rerelease of mercury from spent sorbents such as those reported by Senior and Bustard (23) may not pose a significant management issue relative to leaching.

Vapor Release[2]

The release of mercury vapor from CCBs resulting from the use of Hg control technologies has been evaluated on a limited basis. Methods of determining the release include measuring the Hg in the air, capturing the Hg released over extended time periods, and evaluating the Hg content of the CCBs at varying time periods, which generally require very sensitive analytical techniques. Hassett and Heebink performed long-term ambient-temperature desorption experiments, and results indicated that five of the six CCBs analyzed acted as mercury sinks (56).

Butz and Smith (57) compared the total Hg content of CCBs initially and after 8 months in open and closed containers to determine offgassing. The results reported suggest that the Hg bound to the ash and/or activated carbon is fairly stable.

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[2] The authors of the various references have reported data in several formats. The following concentrations are equivalent: ppm (parts per million) = µg/g; ppb (parts per billion) = µg/kg, ng/g, µg/L; and ppt (parts per trillion) = pg/g, ng/L.

Fly ash volatilization studies performed by Schwalb et al. (54) compared total mercury contents of several ash samples as-received and after exposure to elevated temperatures (100° and 140°F [37.7° and 60°C]) for 6 months with total mercury concentration measured at 3 and 6 months. Results are shown in Table 5.

Table 5. Fly Ash Volatilization Results – Hg Concentration, ppm (54)

		3 month		6 month	
Plant ID	As-Received	100°F	140°F	100°F	140°F
3	0.09 ± 0.02	0.09	0.10	0.12	0.17
6	0.29 ± 0.05	0.34	0.32	0.38	0.34
6	0.19 ± 0.04	0.22	0.25	0.28	0.24
6	0.69 ± 0.11	0.72	0.69	0.69	0.69
4	0.08 ± 0.02	0.11	0.12	0.13	0.12
4	0.08 ± 0.02	0.09	0.10	0.11	0.13

Gustin et al. (42, 43) and Ladwig (44) evaluated the Hg flux for CCBs. Results indicated that both baseline fly ash samples and those with activated carbon exhibited a net deposition of Hg on the fly ash. Deposition was greatest on the samples with activated carbon, leading Gustin et al. (42) to conclude that it was possible that the higher carbon in the ash facilitated atmospheric Hg uptake.

Gustin et al. (43) also evaluated Hg flux from fresh samples and samples exposed to air for 9 months in order to determine the potential for reemission of deposited atmospheric Hg from ash. Experiments included the addition of water to the samples exposed to air which resulted in a difference in the Hg flux noted. Mercury deposited on dry ash, as previously noted, but results indicated that mercury was emitted from the wet ash. Gustin et al. (43) reported that the emission rate for the wet ash declined over time and returned to deposition. The addition of water to the fresh samples resulted in less of a difference in flux, indicating that Hg released after the addition of water was deposited atmospheric Hg and that the fresh ash did not have loosely bound, readily released Hg.

Limited information has been reported on the stability of mercury captured on sorbents (55). Results of thermal desorption tests indicate that mercury is thermally released from sorbents at temperatures considerably below the peak temperatures observed for fly ashes. Significant percentages of the mercury captured on the saturated sorbents were released upon heating above 135°C (275°F) in nitrogen, carbon dioxide, or flue gas; and 30%–50% of the original mercury capture capacity of the sorbent was regenerated after one or two regeneration cycles. Ambient release of mercury into a low flow rate of air was determined by collecting desorbed mercury on a sorbent. After correcting for blank determinations, essentially no mercury was released at ambient temperature (24°C [75°F]) from either of the sorbents tested. These data may be valuable in assessing the potential for rerelease of mercury from spent sorbents.

Microbiological Vapor-Phase Release

EERC researchers have reported on the microbiologically induced release of mercury vapor from CCBs (58) under aerobic and anaerobic conditions. Results of these preliminary experiments indicated that both elemental and organomercury were released. The experimental matrix consisted of eight flasks under aerobic conditions (using breathing-quality air) and eight flasks under anaerobic conditions (using argon). In each set of eight flasks, two contained only buffer, three contained a slurry of the CCB with buffer, and three contained a slurry of the CCB with buffer and glucose. An 80-g aliquot of CCB was placed in the flasks, and 100 mL of a phosphate buffer (with or without glucose) was added to create a neutral pH. The CCB-containing flasks also had 100 µL of mixed bacterial culture added. Vapor traps collected the organo- and elemental mercury released from the system, and leachates were collected at the conclusion of the 30-day experiment.

At the 2004 Combined Power Plant Air Pollutant Control Mega Symposium, the EERC reported that oganomercury species were detected at very low levels both in the vapor and leachate generated from the microbiologically mediated release experiments (58). The EERC reported speciation of these organomercury compounds in leachates to be dimethyl and diethyl mercury but present at levels <5 ng/L (ppt).

INTERPRETATION AND CONCLUSIONS

The data currently available on CCB mercury content and stability are limited because demonstration of mercury control technologies has only recently been initiated. Data on fly ash and FGD materials that have been generated at full-scale coal-fired power plants without mercury emission controls in place indicate that the concentration of mercury is relatively low for most samples, with total mercury concentrations ranging from <0.01 to 2.41 ppm. It has also been reported that the mercury content of fly ash and FGD collected during tests of mercury control technologies can be significantly increased with samples with a total mercury concentration as high as 120 ppm reported; however, of 21 samples collected from mercury control demonstrations, only six had mercury concentrations greater than those noted for samples from systems without mercury control. These data represent a very limited number of samples, types of mercury control, and combustion systems, but in 2004–2006, several tests of mercury emission control technologies at full-scale facilities will be performed, and a concerted effort is planned by DOE to fully evaluate the stability of mercury associated with the CCBs produced from these tests.

Carbon sorbents are expected to be used in many systems as part of the mercury control technologies, so it is important to note that normal activated carbon sorbents are not expected to perform differently than unburned carbon associated with fly ash, and samples of fly ash with unburned carbon have shown similar performance in evaluations of mercury stability. The stability of the mercury associated with these materials is similar to that of materials generated without mercury emission controls. Work on release of Hg from modified activated carbon sorbents is ongoing, and results are not available to assess the Hg behavior associated with these sorbents.

Existing data indicate that the stability of mercury on fly ash and FGD material is similar for samples collected at sites without mercury controls and during tests of mercury control technologies. Data assembled and summarized in this document indicate that mercury associated with CCBs is environmentally stable under most management conditions, including utilization and disposal. The exception to this is exposure to high temperatures such as those that may be achieved in cement production.

Evaluations of CCBs that are collected from full-scale demonstration of mercury control are needed to confirm the data available in the literature. The data do not sufficiently represent all of the variables that may be associated with CCBs generated when mercury controls are in place. Existing data indicate that present CCB management options are expected to be environmentally sound for CCBs from systems with mercury control technologies installed, but information that should become available in the next few years is expected to allow conclusions to be drawn from a broader and more representative sample set.

UPCOMING EVENTS

By-Product Beneficial Use Summit
November 8, 2004, Kansas City, Missouri
http://www.byproductsummit.com/papers.html

Coal Combustion Products Partnership Workshop
November 16, 2004, Atlanta, Georgia, contact William Aljoe (412) 386-6569
http://fossil.energy.gov/news/events/

POWER-GEN International
November 30–December 2, 2004, Orlando, Florida
http://pgi04.events.pennnet.com

229th ACS National Meeting
March 13–17, 2005, San Diego, California
http://oasys.acs.org/acs/229nm/topics.html

World of Coal Ash
April 11–15, 2005, Lexington, Kentucky
http://www.acaa-usa.org/ASP/EventCalendar.ASP?YEAR=2005

30th International Conference on Coal Utilization & Fuel Systems (formerly Clearwater Coal Conference)
April 17–21, 2005, Clearwater, Florida
http://www.coaltechnologies.com

International Conference on Clean Coal Technologies for Our Future
May 10–12 2005, Sardinia, Italy, contact Rodney Anderson (304) 285-4709
http://fossil.energy.gov/news/events/

A&WMA 98th Annual Conference and Exhibition
June 21–24, 2005, Minneapolis, Minnesota
http://www.awma.org

230th ACS National Meeting
August 28–September 1, 2005, Washington, D.C.
http://oasys.acs.org/acs/230nm/topics.html

Air Quality V: Mercury, Trace Elements, and Particulate Matter Conference
September 18–21, 2005, Washington, D.C.
http://www.undeerc.org

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MERCURY INFORMATION
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Quarter 5 – Mercury Fundamentals

January 2005

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MERCURY INFORMATION CLEARINGHOUSE

QUARTER 5 – MERCURY FUNDAMENTALS

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EXECUTIVE SUMMARY

Understanding fundamental chemical principles of mercury in coal combustion flue gas is critically important in the ongoing efforts to capture and measure mercury from coal-fired power plants. Homogeneous gas-phase reactions of mercury with halogen oxidants, which are presented first, are vital in determining the oxidation state of the mercury in the flue gas. Next is a description of our current chemical understanding of activated-carbon sorbents for mercury capture in coal combustion flue gas. For low-chlorine coals, much of the mercury in the flue gas is elemental (Hg^0) and only a small amount is oxidized (Hg^{2+}), but finely powdered sorbent injection upstream of a particulate collection device has the potential to capture both elemental and oxidized mercury present in the flue gas. Additional capture of Hg^0 can occur under some flue gas conditions, however Hg^0 is not as readily removed by activated carbon as Hg^{2+}.

There are several facts and ideas that have been developed in the last 2 years that are critical to understanding how the capture of mercury takes place on a carbon sorbent in a flue gas stream. Several unequivocal pieces of evidence demonstrated that the sorption occurs via an oxidation mechanism (chemisorption) rather than physisorption. Acid gases in the flue gas, such as HCl, promote this oxidation. In a bench-scale system using a gas stream with low HCl, it takes a few minutes to promote the sites on the carbon surface to their active state, resulting in an induction period which limits Hg removal effectiveness to fabric filter applications where carbon is present in the gas stream for a sufficient time period. In high-HCl streams or on sorbents that have been pretreated with HCl or certain other acids, the induction period is eliminated. The oxidation has nothing to do with formation of atomic halogen species. Thus, a current model suggests that the oxidation occurs at a positive site on the carbon that is able to accept electrons from the mercury (Lewis acid site), and this site is generated by adding a hydrogen ion (or halogen from Cl_2 or Br_2) to the carbon structure. An actual chemical structure on the carbon edge is described in the text. Recent unpublished evidence indicates that the kinetics of the oxidation are determined by the number of active sites generated, the temperature (higher is better), the nature of the anions present, and the concentrations of NO_2, NO, and O_2 in the gas phase that can accept electrons from the carbon.

The breakthrough curves for tests conducted in a variety of gas compositions and the X-ray photoelectron spectra of sorbents exposed to various combinations of gases for various lengths of time showed that the capacity of the carbon is determined by the sulfuric acid (H_2SO_4)that accumulates via oxidation of SO_2. The primary oxidant for the SO_2 is the NO_2 in the flue gas, but moisture is also required. Thus, H_2SO_4, HCl, and Hg^{2+} compete at the basic binding sites on the carbon, with H_2SO_4 eventually dominating the sites at the time of breakthrough. Therefore, the capacity has little to do with the mercury, but rather the sulfuric acid concentration. Further, the negative temperature effect for mercury capacity is determined by the rate of SO_2 oxidation. This insight resolves old, confusing questions about mercury capture. Binding of $HgCl_2$ in the flue gas occurs at basic sites on either the carbon structure or the mineral content of a sorbent, but an

additional factor is involved. In the absence of NO_2, a gradual reduction of $HgCl_2$ to Hg^0 is observed. This reduction is caused by SO_2 and occurs gradually as the concentration of acid builds up and catalyzes the reduction.

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 5 – MERCURY FUNDAMENTALS

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of the CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, the U.S. Department of Energy (DOE), and the Canadian Council of Ministers of the Environment (CCME), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of advances in mercury monitoring, control, policy, and related research progress.

Ongoing developments in the area of mercury regulations for coal-fired power plants in Canada in the form of Canadawide Standards (CWS) and the United States in the U.S. Environmental Protection Agency’s (EPA’s) Proposed Utility Mercury Reduction Rule illustrate the need for a solid understanding of mercury chemistry and effective mercury control strategies for coal-fired electric utilities.

In previous quarterly reports, various mercury control technologies and the impact of mercury on coal combustion by-products were reviewed in detail. Additionally, a review of the state of technology for mercury measurement was provided in the second quarterly report. As more emphasis is placed on mercury removal from flue gas, a better understanding of mercury chemistry in combustion flue gas is necessary. Significant research is ongoing to characterize the interactions of mercury within various flue gas compositions, temperatures, and control devices. This quarterly report summarizes what has been learned, as well as recent developments in understanding mercury fundamentals. Also included in this report is a short summary on the current understanding of mercury in biological systems and related health effects.

In order to adequately address the many topics pertinent to mercury research and development and provide the detail necessary for the various stakeholders to make informed decisions, selected topics will be discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that have been addressed in previous quarterly reports include:

Quarter 1 – Sorbent Control Technologies for Mercury Control

Quarter 2 – Mercury Measurement

Quarter 3 – Advanced and Developmental Mercury Control Technologies

Quarter 4 – Rerelease of Mercury from Coal Combustion By-Products

Topics that will be addressed in upcoming quarterly reports include, but are not limited to, the following:

- Mercury policy – updated each quarter based on available information
  - Upcoming events and news releases
  - Regulation, policy, compliance strategies, and health developments

- Baseline mercury levels and emissions

- Mercury control
  - Summary of large-scale test activities and associated economics
  - Mercury oxidation and control for scrubbed systems
  - Multipollutant control strategies
  - Summary of mercury-related economics for commercial systems

- Mercury chemistry and transformations
  - Mercury fate and transport – impacts on health

MERCURY POLICY

The CCME has been developing CWS for mercury since 1998 for several significant mercury-emitting sectors and products. Standards have been completed for base-metal smelters, incinerators, mercury-containing lamps, and dental amalgam wastes. A CWS for mercury emissions from coal-fired electric power-generating plants is under development. Canadian coal-fired generating companies have embarked on a multiyear program to improve the information base around mercury measurement and control that will aid in the development of the CWS. Data from this effort are still in verification and analysis by the CCME; however, preliminary results can be accessed in the program Web site: www.ceamercuryprogram.ca.

Recently, Alberta Environment commissioned a study to review and report on the various proposed and final legislative and regulatory initiatives of Canadian federal and provincial jurisdictions and U.S. federal and state jurisdictions relevant to mercury emissions from coal-fired power plants. A draft report entitled “Summary Report on Canadian and U.S. Legislative and Regulatory Initiatives to Manage Mercury Emissions from Coal-Fired Thermal Electric Facilities” is being reviewed. In it, Linda Duncan summarizes the myriad efforts that are under way to reduce mercury emissions from coal-fired utilities and outlines the various strategies each Canadian province has to achieve that goal. Once the final report has been submitted to Alberta Environment, information on how to access the document will be provided in a quarterly report.

Another component of the CEA Mercury Program is the Laboratory Round, which consists of a review of analytical laboratories. This program was developed by CEA member companies and funded by CCME. Laboratories participating in the program tended to do very well. For more information regarding the laboratory round robin, go to www.ceamercuryprogram.ca.

In the United States, EPA published a Notice of Data Availability (NODA) in the Federal Register (Vol. 69, No. 230, pp 69864-69878) on December 1, 2004. The NODA summarizes the comments received by EPA (January 2004), and solicits further comment to help EPA evaluate which regulatory approach will best reduce mercury emissions from power plants. The EPA received over 680,000 comments on the Proposed Utility Mercury Reduction Rule and the related supplemental proposal issued in March 2004. The NODA is part of the EPA process to deliver a final mercury rule by March 15, 2005. EPA will take comment on this action for 30 days after publication in the Federal Register. For more information on the NODA, visit http://www.epa.gov/mercury/control_emissions/noda.htm.

In Mexico, mercury emissions from combustion sources account for only 7%, or approximately 2.2 ton/year, of the nation's total estimated anthropogenic mercury emissions, according to estimates published in 1999 (http://www.epa.gov/ttn/chief/conference/ei12/index.html#ses-11), of which only 0.87 ton/year come from coal combustion. The primary sources of Mexico's estimated mercury emissions result from gold and mercury mining and refining activities and account for nearly 21 ton/year of atmospheric mercury emissions. Currently, Mexico is approaching the end of a three-phase emission inventory that will quantify a variety of point-source emissions. However, limited data are available pertaining to Mexico's policy development for mercury emissions from coal-fired power plants.

QUARTER 5 FOCUS: MERCURY FUNDAMEMTALS

BACKGROUND

As the date for promulgation of mercury emission regulations at utilities approaches, it is important to review the fundamental chemistry of mercury control technologies with a view toward arriving at a better understanding of the issues that determine how, when, and why mercury is captured in flue gas streams and correcting misunderstandings about mercury capture by sorbents. This review focuses on descriptions of the homogeneous and heterogeneous reactions of mercury in flue gas, with an emphasis on the chemical understanding of the control technology associated with the use of activated carbon sorbents for mercury capture in coal combustion flue gas. Finely powdered sorbent injection upstream of a particulate collection device has the potential to capture both elemental (Hg^0) and oxidized mercury (Hg^{2+}) present in the flue gas. An intensive study of carbon sorbents at the bench scale led to an acceptable scientific explanation of mercury capture. The approach in this review is to ask questions about the factors that are important to examine, how the experiments were conducted, what we learn from the experiments, and how this leads to a viable model for mercury capture.

GAS PHASE REACTIONS

What factors strongly influence the behavior of mercury in coal combustion flue gas and coal-derived fuel gas?

The most important factor in determining the emission of mercury in coal combustion flue gas is the oxidation state of the mercury. This is often referred to as the speciation of the mercury, and mainly the distinction is between three forms: Hg^0 and Hg^{2+} compounds in the gas phase and in the solid phase (particulates). Which Hg^{2+} compounds are present (that is, the definitive speciation) is important because the behaviors of Hg^{2+} compounds are quite different with respect to volatility, thermal stability, and propensity to be captured by a sorbent. Not enough is known about the definitive speciation of oxidized mercury in flue gas, owing to the difficulty of analysis of the tiny amounts present. An important fact is that Hg^{2+} compounds may be easily converted to other species on a solid surface or in the gas phase. Thus other reactive compounds present in the flue gas exert an important influence not only on the relative amounts of Hg^0 and Hg^{2+}, but also which Hg^{2+} species exist in any gas composition or temperature condition.

Hg^0 is highly volatile and relatively stable toward most compounds. Thus it does not stick well to solid surfaces. In the high furnace temperatures, all the mercury in the coal is converted to Hg^0, but as it cools in the heat exchangers, ducts, or particulate collection devices, it is oxidized to Hg^{2+} compounds. The degree of oxidation varies with gas composition and, therefore, with coal and combustion particulars, as described in detail below. The oxidation may occur in the gas phase between the mercury atoms and the gas molecules (homogeneous reactions) or on the surface of particulates or sorbents (heterogeneous reactions), in many cases by a complex mechanism.

Hg^{2+} compounds exhibit a wide variety of thermal stabilities and volatilities, but in general, Hg^{2+} compounds are much stickier than Hg^0, owing to lower vapor pressures and greater reactivity. Many reactions occur, including acid-base reactions, substitution reactions, and redox reactions in gas, solution, and surface reactions. The outcomes of these reactions are determined by relative bond strengths and other factors, such as the ability to form complex ions with more than two bonds. For example, mercury chloride ($HgCl_2$) has a high bond strength between the mercury and chlorine and will form from a species with weaker bond strength such as mercuric nitrate ($Hg[NO_3]_2$) with the addition of hydrochloric acid (HCl) or chloride. $HgCl_2$ not only is thermally stable, but also has a high enough vapor pressure so that it can desorb from many surfaces. On the other hand, both $HgCl_2$ and $Hg(NO_3)_2$ will undergo acid–base reactions resulting in a variety of less volatile compounds with enhanced stickiness. This type of mercury compound is a Lewis acid because it can accept electrons and bond to a base. Thus $HgCl_2$ from a gas phase may collect on an ash particle by reaction with a basic component on the ash and thereby convert to particulate mercury. The actual product may be a low-volatility basic mercury chloride complex.

Halogen species play vital roles in mercury transformation in coal combustion flue gas. Owing to its relatively high concentration in many coals, chlorine is the most important determinant for Hmercury speciation in the flue gas, which then determines how easily mercury is captured on a sorbent or ash or flue gas desulfurization (FGD) system. Typically higher chlorine gives more oxidized mercury in the flue gas. Chlorine and bromine (1, 2) compounds have been added to fuels or to exhaust gases (3–5) to increase dramatically the proportion of oxidized Hg, which is more easily captured in the ash or on a sorbent, but utilities are concerned about the corrosion that results from increased halogen concentrations. Not only do halogens (Cl_2 and Br_2) and hydrohalide acids (HCl, HBr) attack metal systems, but they also may damage bag filter fabrics.

Which homogeneous reactions of Hg^0 are important in flue gas?

The chlorine in the coals is converted in the furnace to the atomic form, but being highly reactive, subsequently reacts with flue gas components and itself to form the molecular form (Cl_2). Reactions of atomic chlorine generated in the furnace heavily depend on temperature–time profile during passage through the ducts and control devices. The issue is how much atomic chlorine is still present, if any, and what other chlorine compounds or radicals are effective for oxidation of Hg^0 in the gas phase. Horne et al. (6) determined rate constants for Hg + Cl atom by measuring the formation of HgCl using a spectroscopic (279 nm) method for this product. The second-order rate constant for this Hg(I) species was about $1\text{-}3 \times 10^{-11}$ cm^3 $molecules^{-1}sec^{-1}$. This fast reaction could be followed by a second reaction to form $HgCl_2$. Using indirect methods, Ariya et al. (7) determined second-order rate constants for Hg^0 with halogen species as shown in Table 1.

Table 1. Halogen Reactivity to Hg^0

Halogen Species	Rate Constant
Cl atom	1.0×10^{-11} cm^3 $molecules^{-1}sec^{-1}$
Br atom	3.2×10^{-12} cm^3 $molecules^{-1}sec^{-1}$
Br_2	9×10^{-17} cm^3 $molecules^{-1}sec^{-1}$
Cl_2	2.6×10^{-18} cm^3 $molecules^{-1}sec^{-1}$

Thus the atomic Cl rate constant is about 4 million times higher than Cl_2. However, under a typical temperature profile of a coal-fired utility plant, the atomic Cl generated in the combustion zone has already reacted with other flue gas constituents or itself before it could oxidize Hg^0 at the required temperature. Reactions with water vapor, SO_2, and other components are likely, and, of course, heterogeneous reactions with particulates may be occurring.

Because halogen reactivity with mercury is key factor in control, research in this area is being conducted by many investigators. Mamani-Paco and Helble (8) studied the oxidation of Hg with HCl and Cl_2 using a quenching system comprised of a gradient temperature reaction tube from which samples could be withdrawn for analysis. No oxidation occurred using realistic quench rates with 100 ppm HCl. This is expected: HCl is not an oxidizing agent since it is already in a highly reduced form. Using a composition containing 50 ppm Cl_2 gave only 10% oxidation of Hg^0. Procaccini et al. (9) investigated the fast quenching of combustion products from chlorocarbon fuels. Cl_2 formed from the recombination of atomic chlorine during cooling, but at fast quenching rates ($>10^3$ K/s), a small percentage of atomic chlorine could persist. No acidic flue gas components, except HCl, were present in these studies. Sliger et al. (10) injected HCl and Hg^{2+} acetate into a natural gas flame, and obtained oxidation data consistent with the reaction of Hg^0 with a superequilibrium concentration of atomic chlorine at 400° to 700°C. Using a very fast (10×) fast quench, Niksa and Fujiwara (11) reported up to 40% oxidation at 300 ppm Cl (11). Thus, these data showed that high concentrations of Cl atom are needed for homogeneous oxidation, but these are not usually available in utility exhaust systems. Recently, Zhuang et al. (12) reported a fast quenching experiment in a small coal combustion apparatus which showed that with HCl injection most of the mercury was deposited on the ash, and only 6% of the total mercury was elemental. This experiment implies that atomic chlorine generated in the hot zone was still available at lower temperatures, owing to the fast quench rate, and thus oxidized the mercury at a lower temperature where Hg–Cl reactions are most effective. While most of the mercury was on the ash, it was not clear whether oxidation occurred in the gas phase or solid phase, or where on the solid phase. The product of the atomic chlorine reaction with Hg is HgCl, which would readily collect on ash, carbon, or sorbent particulates or react with other species or itself.

What is clear is that because of its high reactivity, it is difficult to preserve atomic chlorine generated in the furnace so that it will be available for reaction with Hg^0 at lower temperatures, where the resulting $HgCl_2$ will be stable. The reactivity of the halogenated species resulting from the early reactions of atomic chlorine with SO_2, H_2O, and NO may be important and is under investigation. For example, the reaction of SO_2Cl_2 with Hg^0 occurs at 150°C (sealed glass tube) to give $HgCl_2 + SO_2$, probably by a free-radical chain reaction, but how fast the reaction occurs in the gas phase is unknown.

What can we do to increase effectiveness of halogens in flue gas?

Halide compounds have been added to fuels to increase the concentrations of atomic halogens formed and subsequently the X_2 and other reactive halogen species in the flue gas (1–5). This method produced excellent capture efficiencies. But again, the reactions with mercury may be heterogeneous. Cl species attached to the fly ash, unburned carbon, and/or sorbent, if used, can form reactive sites that can oxidize and capture mercury on the surface. The role played by the halogens with respect to promoting the activity of the carbons is discussed in detail below. Based on earlier research (7), we expect atomic Cl to be more reactive to Hg than atomic Br, but also it may be more reactive to other gas components and particulates, resulting in lower concentrations.

MERCURY SORBENTS

How are sorbents evaluated and what are the effects of gas compositions, temperatures, and other variables?

Initial screening of activated carbons for mercury control is typically conducted on a bench-scale unit; at the same time, these evaluations produce a more thorough understanding of mercury reactions on activated carbon surfaces under a variety of conditions. Synthetic mixtures of the components flue gases were used so that precise amounts of these components could be added and the effects of varying components determined. In fact, the results were highly reproducible. A second benefit of bench-scale testing is that the effects of heterogeneous reactions on the ash particulates can be eliminated. A comparative study of synthetic and real flue gases with the same sorbent and equipment showed a close correspondence.

Two related types of bench scale experiments were utilized in groundbreaking papers in 1998 reporting mercury sorption studies in flue gas. One of these (13) used a thin bed (150 mg) of fine carbon sorbent supported on a quartz filter in a stream of synthetic flue gas at a temperature appropriate for a utility control system (125° to 150°C). However, the gas flow (30 scfh) was much higher than that in a utility duct in order to distinguish those sorbents that could perform most efficiently. The velocity/sorbent mass ratio was therefore approximately 100 L/min/g. The second experiment utilized a small amount of sorbent (20 mg) that was diluted with a large amount of sand (14). This experiment was conducted with a realistic flow rate of 2.1 scfh corresponding to 50 L/min/g, so that valid evaluations of sorbent effectiveness could be made. Gas mixtures containing Hg^0 or $HgCl_2$ are passed through the carbon bed. A continuous mercury monitor (CMM) is usually employed to determine the Hg concentrations in the inlet and outlet. Both Hg^0 and total Hg can be determined; the latter is determined after a unit that converts all mercury to Hg^0. The percentage emissions (100 × outlet Hg/inlet Hg) are plotted against time to obtain a breakthrough curve that shows when the capacity has been exceeded for those conditions.

How are reactivity's and capacities of sorbents determined?

The typical S-shaped curve for an experiment conducted in synthetic flue gas is shown in Figure 1. The breakthrough part of the curve when the emitted total mercury rises to 100% of the inlet is indicative of the capacity of the carbon sorbent operated over the time period of the experiment. This 100% breakthrough point corresponds to a state where the sites that bind the mercury have been filled. Integration of the area above the curve until the time of 100% emission gives an effective sorption capacity in mg Hg, which can be divided by the sorbent weight to give a capacity in mg Hg/g sorbent. It would not be correct to call this an equilibrium capacity, as some have done, because it is not actually mercury that is filling most of the binding sites, but rather other flue gas constituents and derivatives that poison the sites and prevent mercury from binding. Often, the curve goes higher (120%) than the inlet concentration, indicating that the mercury that was previously captured at these sites is being displaced by other species. Obviously, this condition would not be desirable in a utility boiler.

Although the breakthrough curve appears to be a capacity experiment, the initial part of the curve indicates the kinetics of the mercury oxidation and capture and is therefore extremely important in determining the effectiveness of the sorbent in the seconds after injection into a duct and before it has been, in the case of the ESP, removed from the gas flow. In the early part of the sorption experiment, little mercury and poisoning agents have collected on the sorbent, so the amount of mercury adsorbed is a function of the number of oxidation sites times the reactivity of these sites. Considerable variation in the initial percentage of emission has been observed, depending

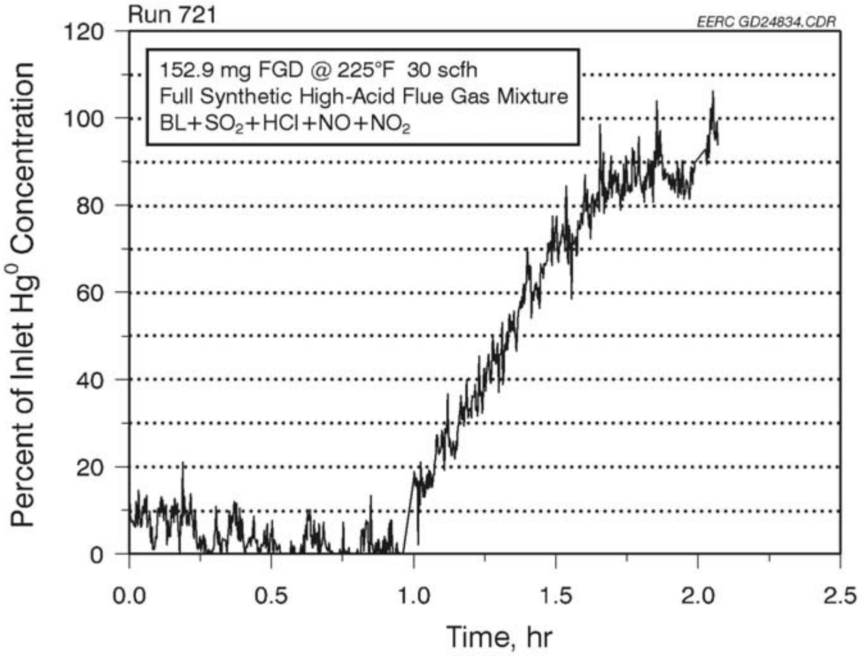


Figure 1. Breakthrough curve for FGD carbon using an EERC bench-scale test unit with Hg^0 and all four acid gases present.

not only on the sorbent, but also on the composition of the gases in the experiment. This initial measurement is related to the space velocity: either reducing the bed size or increasing the flow rate gives less reaction velocity and, therefore, a higher emission level. Since we continue to see variations in the space velocity for a wide range of sorbents with similar sizes and porosities, the experiments are not mass-transfer limited. Whether mass transfer limits carbon reactivities in full-scale utility injections will be addressed later.

The S-shaped breakthrough curves for Hg^0 in flue gas differ significantly from those conducted in nitrogen or air, where typically the curves increase from the start, and also from those conducted in flue gases containing very low HCl, where the curves decrease from the start and then increase. The rapid rise in emitted mercury is undoubtedly the result of a low number of reaction sites on the carbon that are able to function in nitrogen or air, so they fill rapidly. The curve in low HCl gas is indicative of a promotion phenomenon, where the low concentration of HCl accumulates slowly and steadily increases the number of active reaction sites on the carbon. This phenomenon will be discussed in detail later. Typically, the breakthrough curves for inorganic sorbents resemble the carbon curves in air.

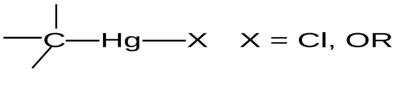
How is Hg^0 in flue gas captured on the carbon sorbent? Physical adsorption versus chemisorption.

In several early reports on mercury capture in air or inert gas and in one of the early reports on the capture of mercury in flue gas on activated carbon (14), the authors suggested that elemental mercury is physically adsorbed to carbon. The term physical adsorption or physisorption implies a weak bond involving van der Waals or induced dipole forces between the mercury atom and the carbon surface. This means that the outer 6s electrons in the mercury atom, which are shielded from the nucleus by a lot of inner electrons, become polarized by dipole charges on the carbon surface so that they set up their own dipole moment, resulting in a dipole attraction to the carbon surface. Thus in this sorption model, the mercury is not oxidized, but still an elemental form. Later, we will discuss the misinterpretations that led to this conclusion.

It is now understood that chemisorption is the primary mechanism for adsorption in flue gas and other gases at moderate temperatures. In the chemisorption model for mercury capture on carbon, Hg^0 becomes oxidized on the carbon and binds as a Hg^{2+} compound. Both spectroscopic and reactivity data provide compelling evidence for a chemisorption mechanism for mercury capture on carbons in flue gas at moderate temperatures. An early paper on mercury sorption on a nonimpregnated Saran carbon (15) showed immediate and complete breakthrough of mercury at 150°C in an air stream corresponding to a velocity/sorbent ration of 2.5 L/sec/g, indicating that physical adsorption cannot occur at this temperature. Later, using a stopped-flow reactor with activated carbons at temperatures in the range of 100°–300°C, Hall showed that the reaction rate for Hg^0 sorption is ½ order in molecular oxygen (16). Thus the carbons are catalyzing the oxidation of mercury with oxygen as the primary oxidant. In a flow-through experiment with an unimpregnated bituminous carbon at 140°C in air at a slow flow rate (0.19 L/sec), Krishnan et al. (17) observed early breakthrough, but a gradual decrease in capacity. Since there did not appear to be any effect of Hg^0 concentration on the capture of mercury, the reaction, the reaction was zero order with respect to Hg^0 concentration. Thus, the limiting factor was the low number of active sites in the activated carbon. But why did Singha (15) not see any sorption? In more recent flow through experiments at the EERC with granular carbon (Calgon F400 or NORIT GAC1240) beds at 150°C, we showed that at slow flow rates, the breakthrough time in nitrogen was instantaneous, but was significantly longer in air (18). With F400 at fast flow rates, breakthrough was instantaneous for both gases, thus there is clearly a space velocity factor in these experiments. Therefore, only at very slow flow rates can one see sorption occurring in air.

Further evidence for the formation of oxidized mercury on the carbon was obtained from desorption experiments. Heating the spent-sorbent beds from a variety of experiments to temperatures over 200° C resulted in release of mercury. Sometimes temperatures of 750°C were needed to eliminate the mercury from the sorbent. Although the released mercury in these thermal experiments was mostly elemental, it is unlikely that any Hg^0 existed on the carbon, since Hg^0 volatilized easily at ambient temperatures in an air stream. When heated in a 10% hydrogen stream, the spent sorbents released mercury at 125° C as Hg^0. This is the reported temperature for reduction of Hg^{2+} compounds.

Some of the most conclusive evidence for chemisorption comes from an examination of the chemical form of mercury on the spent carbons using x-ray atomic florescence spectroscopy (XAFS). This is a powerful spectroscopic technique that can distinguish elemental and some of the oxidized mercury forms in a solid sample on the basis of the inflection point differences (IPD) in the energy absorbance curve. Huggins et al. (19) showed that the mercury IPD of sorbents exposed to flue gas was not consistent with that of elemental mercury or with mercury bonded to oxygen. Rather, the IPD varied with gas composition and was consistent with a Hg^{2+} species bonded to a soft element such as chlorine, carbon, or reduced sulfur. This fact also rules out mercury compounds such as HgO, $HgSO_4$, or $Hg(NO_3)_2$, as well as bonds between mercury and surface oxygen groups, including phenoxide, lactone, or ketone groups previously suggested as binding sites for mercury, and also most mineral surfaces, such as iron or other metal oxides, silicates, and carbonates. Organic and inorganic sulfides are rapidly oxidized to sulfonates and sulfates, respectively (20, 21) and these are also ruled out by the spectroscopic data (19), since they bind via the oxygen rather than the sulfur VI. When a sorption experiment was carried out with moisture present, but no flue gas, the IPD data for the mercury line indicated that the mercury was bonded to at least one oxygen (22), so there is more than one structure resulting from chemisorption, depending on the conditions. Thus the carbon site may have been the same for both experiments, but different heteroatoms (chlorine versus oxygen) could also be bonded to mercury, depending on which is present, as illustrated below.



[Eq. 1]

What are the interactions between flue gas constituents, carbon sorbent, and mercury?

As discussed above, noncatalytic activated carbons have little affinity for mercury in air, but the sorption properties of the same carbons change drastically in flue gas. Mercury sorption testing must be conducted in flue gas or simulated flue gas conditions to have any validity for utility mercury control. This increases the complexity of the experiments and requires extreme care that both total and elemental mercury are accurately measured at inlet and outlet to the experiment, and that it does not stick to surfaces in transit to detection. Thus the CMMs must eliminate the interference caused by molecular SO_2 and other species by using adequate trapping techniques or optical methods. Only a few laboratories conform to these exacting specifications and produce reliable data and valid models based on these data.

Two studies published in 1998 pointed out some important effects of flue gas components on mercury sorption; however, many of these effects were not understood until the interactions were later investigated. A large factorial series of tests using powdered activated carbon (NORIT FGD) was conducted at the EERC in a bench-scale system consisting of a thin fixed-bed reactor in gas streams (100° to 150°C) containing 11 to 15 $\mu g/m^3$ of Hg^0 in various simulated flue gas compositions consisting of acidic SO_2, NO_2, and HCl gases plus a base mixture of N_2, O_2, NO, CO_2, and H_2O (23). The results of these experiments (breakthrough curves) showed that NO_2 or the combination of HCl plus O_2 is required for effective Hg^0 capture, so these represent the primary oxidants or electron acceptors for mercury oxidation. But increasing NO_2 concentration gave shorter breakthrough times. In contrast, when SO_2 was omitted, no breakthrough occurred. But increasing SO_2 gave shorter breakthrough times, as with the NO_2. For each NO_2 concentration, a series of breakthrough curves was obtained when the SO_2 was varied. The higher the NO_2 concentrations, the shorter the SO_2 breakthrough times in the series. Thus, understanding of a very important interaction between NO_2, SO_2 and the Hg sorption began to develop. This strong interaction indicated that the NO_2 was oxidizing the SO_2 as well as the mercury on the carbon surface, and the resulting sulfur VI was inhibiting the mercury capture and causing the breakthrough. This effect was consistent with previous studies on the carbon-catalyzed oxidation of SO_2. The water in the flue gas was also needed for breakthrough to occur, which could be attributed to a requirement for the formation of sulfur VI.

Carey et al. (14) showed that increasing the inlet Hg concentration resulted in increasing the capacity of the carbon. This was suggested to be characteristic of a physical adsorption mechanism, but their other data clearly indicated an oxidative capture mechanism, so they were unable to resolve their dilemma. What was not understood was that the capacity had really nothing at all to do with the mercury concentration. Only the sulfur VI formation determines the capacity, and this occurs at the same rate no matter what the mercury concentration is. So the more inlet mercury there is, the more is captured until the binding sites are filled with sulfur VI. The EERC work also established that the Hg emitted after breakthrough is mostly oxidized and can exceed inlet Hg concentration immediately following breakthrough. We also showed that Hg emitted after breakthrough in absence of HCl was $Hg(NO_3)_2$ (24), although in high HCl (50 ppm) the emitted oxidized form is undoubtedly $HgCl_2$. This does not mean that either of these two compounds has collected in the carbon prior to breakthrough, however. In fact, both forms easily desorb from a solid surface at 150 °C, so they are not likely to be present on the carbon prior to breakthrough.

How do the mercury capture and interactions with flue gas occur?

Based on these parametric studies and recognition that all the mercury is still converted to Hg^{2+} after breakthrough, an initial model was presented (25) that described the chemisorption mechanism as oxidation and competitive binding of the oxidized mercury with a catalytic carbon site or sites. Oxidation of Hg^0 to form a bound Hg^{2+} species occurs with the electrons donated to an electron accepting (i.e., Lewis acid) site on the carbon and eventually to NO_2 or O_2. But following oxidation, the binding site for Hg^{2+} must be basic in nature, since the Hg^{2+} is a Lewis acid. The breakthrough was dominated by the competition for binding sites between the Hg^{2+} and acid components, mainly H_2SO_4 that is known to be generated from the oxidation of SO_2 on the carbon. When the basic binding sites are completely occupied by acidic species derived from the flue gas, Hg^{2+} salts are displaced from the binding sites. But oxidation still occurs even after complete breakthrough. Thus, loss of capacity must not be the result of pore plugging by species resulting from acid gases, since this would inhibit both reactions. The extensive mineral matter (35%) of the NORIT FGD sorbent could contribute basic sites for Hg binding, but a sequential removal of the inorganic matter from the FGD sorbent did not significantly affect the breakthrough behavior (26). Basic mineral groups, such as CaO present in the FGD sorbent, therefore played no role in the mercury–flue gas interactions that determine the breakthrough capacity. Actually several activated carbons prepared from pure carbon precursors were perfectly good sorbents. Thus, the binding site was postulated to be a Lewis basic site residing on the carbon surface. This suggests that the bound Hg is actually an organometallic complex. Sorption of $HgCl_2$ from a flue gas may not exhibit this exclusivity however, since an oxidation site is not needed and any basic site on the sorbent may work.

The nature of the mercury–flue gas–sorbent interactions in synthetic flue gas representative of high Cl coals was further elucidated in x-ray photoelectron spectroscopy (XPS) experiments performed with two activated carbon sorbents, NORIT FGD and the EERC lignite-derived AC, exposed to various simulated flue gas compositions containing Hg^0 with various levels of SO_2, NO_2, HCl, and H_2O for time periods before and after breakthrough of mercury (20, 21). Because of the interference caused by silicon, XPS data could not be obtained for the mercury species present in the exposed sorbents. These studies verified that sulfur VI (sulfate, bisulfate, sulfonate, or sulfuric acid) is the major sulfur species on all the exposed sorbent samples, and the longer the exposure to SO_2, the more sulfate is found in the sample. When NO_2 or H_2O was omitted from the flue gas, less sulfate was accumulated. Thus, adsorbed SO_2 is clearly oxidized on the sorbent surface to sulfur VI species in a process facilitated by NO_2 and H_2O. The XPS data also indicate that two types of chlorine are present: ionic and covalent, and that both chlorine forms disappeared from the sample at breakthrough. That chlorine is present as both chloride ion and covalent (organic) chlorine indicates that the HCl in the flue gas can donate a hydrogen ion to a basic site, as well as add both hydrogen and chlorine to a basic site to form the organochlorine product. The accumulation of chlorine in the absence of SO_2 as well as the disappearance of chlorine after continued exposure in SO_2 is explained by competition of HCl with bisulfate or sulfuric acid. As more bisulfate is generated from SO_2 at the carbon surface, it displaces the HCl, owing to the high volatility of HCl. Since disappearance of chlorine is coincident with mercury breakthrough, it is clear that Hg^{2+} is also in competition at the same basic site.

How does HCl promote the reactivity of the carbons?

In tests conducted at relatively high HCl concentrations (50 ppm), the capture of mercury at the start was always very high (less than 5% of inlet concentration), but in very low HCl concentrations such as those obtained when low-Cl coals are burned (1 ppm), the initial capture efficiency was low (50%–60% emission) (27), followed by an increase in capture efficiency to the 5%–10% emission level (90%–95% capture). The higher HCl concentration thus eliminated this induction period where poor capture is obtained. It is clear that HCl is not an oxidizing reagent, since it's already in the most reduced state. This is therefore a promotional effect of the HCl on the activity of the carbon in catalyzing the oxidation of mercury. A similar promotional effect was reported by Ghorishi et al. (28) when adding aqueous HCl to the sorbent.

What is the effect of Hg concentration on the sorption?

In the Carey et al. paper (14) on sorbent properties, it was noted that the sorption capacity increased with mercury concentration. The authors attributed this to a physisorption mechanism, which was inconsistent with their other data, and the issue was not resolved in that paper or subsequent reviews. It is now clear that the sulfur VI accumulation at the active sites is the factor that determines the capacity and not the Hg concentration in the gas phase or on the sorbent. So what happens with a good sorbent in flue gas containing appreciable HCl is that all the mercury is initially captured no matter what its concentration, owing to the large number of promoted sites. Thus the more Hg in the gas phase, the more is captured, until breakthrough when sulfuric acid has poisoned the sites and no additional mercury is captured. In effect, the capacity appears larger for the higher concentration, but it has nothing to do with adsorbtion and desorption of Hg^0, as in the physisorption model.

How do the Hg^0 oxidation and interactions occur?

Several features of the oxidation site were inferred from the HCl promotion and bonding effects (18) that led to development of a model of the chemical mechanism of mercury capture. This mechanism uses a single carbon site for oxidation and binding but in two different forms and thus offers more detail on the nature of the bonding site and its interaction with flue gases and mercury (29). The model, shown in Figure 2, uses the concept of zigzag carbene edge structures recently proposed by Radovic and Brockrath (30). The zigzag carbon flanked by the aromatic rings has an electron pair and is the basic binding site for which the HCl, H_2SO_4, and the Hg^{2+} compete, as shown on the left side of the figure, forming a positive carbenium ion intermediate in each case.

The model (Figure 2) thus provides a detailed mechanism for the catalytic role of acids, such as HCl, in the oxidation step. The conversion of carbene to carbenium ion by HCl and other acids generates the oxidation site (Lewis acid). The mechanistic model shows Hg^0 oxidation by the carbenium cation to the organomercury intermediate and subsequent oxidation by NO_2 to the bound Hg^{2+} species. At the breakthrough point, $HgCl_2$ is continuously released as sulfuric acid drives the formation of the carbenium sulfate. Comparative testing of a large number of acid-promoted AC showed that they exhibit a specific acid-catalysis, not a general acid catalysis. That is, those acids with polarizable counterions (HI>HBr>HCl) show faster initial rates compared with strong and weak oxyacids and fluoroacids (31). This finding is consistent with a mechanism where the halide ion proximate to the cation actually can assist in the oxidation mechanism by stabilizing the incipient mercurinium ion forming in the transition state.

Is atomic halogen formed on the carbon surface as a result of flue gas interactions on the carbon?

Recently, we showed that for HCl-promoted AC, Hg oxidation was not impeded by the presence of free radical scavengers, indicating that an alternative mechanism involving Cl atoms is not likely (31). Furthermore, the addition of olefins (cyclohexene and styrene) to an HCl-treated carbon gave no substitution products which would have resulted from abstraction of hydrogen by any Cl atoms present (32). In contrast, the addition of HCl to the styrene occurred exclusively via the Markownikoff regioselectivity, indicating a cation mechanism. Thus, all four experiments indicated the absence of a radical or halogen atom pathway.

Are carbons with added halogens more effective than nonhalogenated sorbents?

It has been known since 1934, when the first patent for mercury sorption was granted, that adding molecular halogens, such as chlorine (Cl_2), bromine (Br_2), or iodine (I_2) to carbons results in effective sorbents for Hg^0 capture in air (33). The first application used iodine as the halogen,

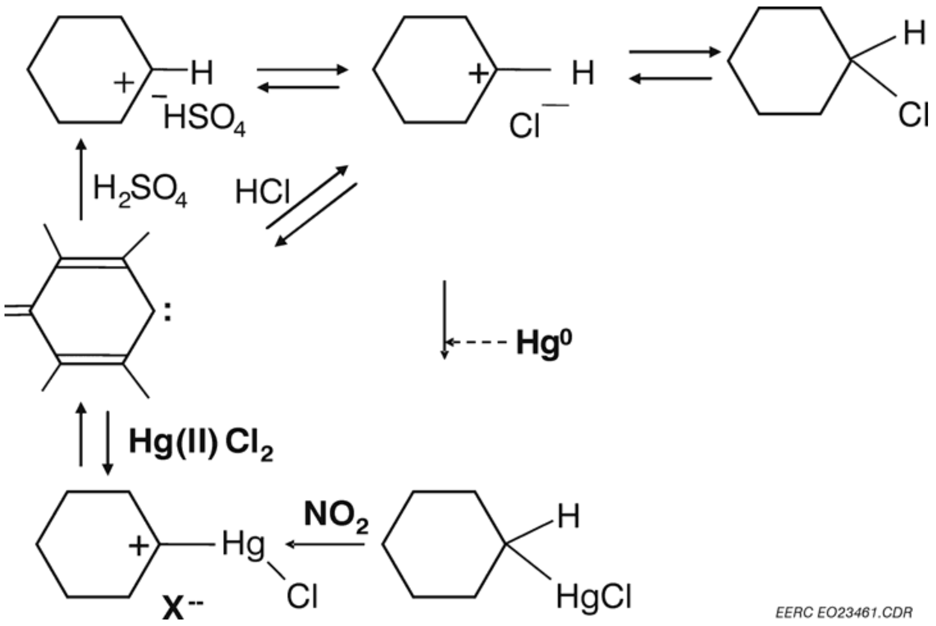


Figure 2. Oxidation mechanism – carbenium ion oxidant.

but later applications used chlorine (34) and bromine (35) or a mixed halogen compound (36). Originally, the model for this type of sorbent was that the halogens on the carbon were responsible for reactions with the Hg^0, but a considerable amount of chemical evidence (37) showed that the halogens that are impregnated into carbon react with the carbon and are strongly bound to the carbon. So it is more likely that the halogens promote the reactivity of the carbon, as we have demonstrated for HCl, rather than react as such with the Hg^0. More work is needed and ongoing to clarify this mechanism with the halogenated carbons. Nonetheless, owing to the high reactivity of the halogenated carbons, full scale testing of these sorbents is being conducted.

What is the effect of temperature on Hg^0 sorption?

Early research (14) determined that mercury capacity was inversely related to temperature, and was incorrectly attributed to physisorption. A better explanation for the lower capacity at higher temperature is that the rate of oxidation of SO_2 to sulfuric acid increases with temperature, so that the build up of poisoning H_2SO_4 on the sorbent occurs at a faster rate. Thus the temperature effect on capacity has nothing to do with the Hg directly or with physisorption. The question of temperature dependence of the initial carbon reactivity was only recently answered. Comparisons of the initial capture efficiency (where kinetic rather than capacity effects predominate) in low-Cl gas at high and low temperature showed that Hg^0 was captured more effectively at the higher temperature. Since the rate increases with temperature, the oxidation step is rate controlling and the physisorption reverse reaction is not of importance in controlling the rate. The implications of this finding for control technology are that when contact time is very short and reactivity is important, then higher temperatures will give faster oxidation rates, whereas for sorbents collected on a filter bag and in contact with the flue gas for a long time, the capacity will be greater at a lower temperature.

How can we measure the kinetics of oxidation of Hg?

Current work involves decoupling the oxidation from the binding steps so that effects on the oxidation step can be determined, and rate constants derived. These experiments utilize a sorbent bed that has broken through so that 100% of the inlet Hg^0 is oxidized by the bed in the flue gas, but no mercury is captured. Then, by measuring the Hg^0 and total Hg in the effluent gas simultaneously for a matrix of experiments in which one, two, three, and four components are deleted or reduced, rates of oxidation and changes in binding chemistry can be determined for each condition. Thus removal of NO_2 resulted in a significant decrease in the oxidation rate, but oxidation was still able to occur (pseudo 1st-order k = 1.4 L/sec/g sorbent) with O_2 and NO present. Removal of HCl from the gas composition decreased the oxidation rate, consistent with the specific acid catalysis mechanism, but, since oxidation still occurred, the oxidation can evidently occur via the sulfate-bound carbenium ion.

There are several issues of mercury sorption in air that have not been addressed. Further studies are needed to elucidate how these less reactive systems are able to capture mercury.

Which inorganic sorbents are effective for elemental mercury capture?

A variety of inorganic sorbents have been investigated for capture of elemental mercury. Of course the idea of using fly ash to capture mercury is appealing, but most attempts to use fly ash in an injection device or a bed have failed to produce much capture. As described in a subsequent section, lime and calcium silicate can capture Hg^{2+}, but they are ineffective for elemental, because they cannot oxidize the Hg^0 to a nonvolatile form (38). Addition of oxidizing agents was reported to assist in the capture, but in tests conducted at the EERC, the results could not be verified, perhaps because of the instability of the oxidant. The use of manganese dioxide and other transition metal oxides for mercury sorption in air was reported by Cavallaro et al. (39). Later, its use for mercury control in flue gas was patented both for fixed bed and injected particle applications (40, 41). The University of North Dakota investigated a large number of transition metal oxides in air and in synthetic flue gas, but the reaction rates and capacities were inferior to those of carbon sorbents. The reactions in inert gases are feasible because the metal oxide sorbent is itself the oxidant, rather than a flue gas component. The metal oxide sorbents are effective up to about 200°C, but flow rates must not be too high, owing to the slower kinetics.

Can mercury emissions in reducing gases be captured?

Mercury capture in a fuel gas resulting from coal gasification is likely to be more difficult. All the mercury in the fuel gas is the elemental species. Current gasifier technology requires cooling the gas to effect capture. Capture at elevated temperatures is desired so that the hot fuel gas would not require cooling and subsequent reheating in a subsequent reactor or turbine. But hydrogen and perhaps CO can reduce Hg^{2+} to Hg^0 or prevent formation of Hg^{2+} from Hg^0. The reduction of a number of Hg^{2+} compounds with H_2 occurs at 125°C. These are mainly the chloride, oxide and similar oxygen bonded compounds. So it is really impossible to capture Hg^0 as any of these compounds at temperatures above this.

To capture Hg^0 at 300°C and higher, formation of very stable Hg^{2+} compounds is required. Stability testing results at the EERC showed that sulfides and selenides have stabilities at these temperatures (42). Sorbents based on incorporation of these elements are currently being explored.

Which sorbents capture mercury (II) in flue gas effectively?

When the chlorine content of a coal is high, a substantial portion of the mercury in the flue gas is in the oxidized (probably $HgCl_2$) form. The capture of oxidized mercury in flue gas occurs readily in an aqueous solution, such as a wet scrubber , or on a basic solid sorbent. The gases forms of Hg^{2+} are mainly the halide and nitrate salts, and these are also very soluble in water and will readily pass through the gas-liquid interface. If the aqueous solution is acidic and also contains sulfite or SO_2, the Hg^{2+} is reduced to Hg^0 (43) and then is released back to the gas phase and emitted from the wet scrubber system. However, if the aqueous phase is basic, the Hg^{2+} is stable and converts to stable complex mixed-oxide forms with low solubility and no volatility.

Capture on the basic solid sorbent occurs because the volatile Hg^{2+} compounds are Lewis acids and chemisorb to the basic surface. Lancia et al. (44) reported $Ca(OH)_2$ for sorption of

$HgCl_2$ with an efficiency of 95%. This result for lime-based sorbents was verified by Ghorishi and Gullet (45), who also demonstrated that SO_2 inhibits the sorbent. Since SO_2 and HCl compete for basic sites on the sorbent, they are the limiting parameters for capacity. Thus, as with the carbon sorbents, a negative temperature effect and apparent increase in sorption with Hg concentration was observed, which has nothing to do with physical adsorption. So a low temperature and baghouse collection of the sorbent will remove Hg^{2+}. Similar basic lime sorbents (lime-treated fly ash and calcium silicate) are effective.

Does activated carbon capture $HgCl_2$ like it does Hg^0?

An extensive matrix of tests was performed at the EERC with FGD carbon using $HgCl_2$ in a wide variety of synthetic flue gas compositions at 300°F (46). The baseline composition included O_2 (6%), CO_2 (12%) and H_2O (8%). With SO_2 and NO_2 present in the gas composition, essentially no breakthrough occurred and no Hg^0 appeared in the effluent gas. However, with SO_2 but not the NO_2 or HCl, the mercury broke through slowly and gradually. The breakthrough curve was not like that of Hg^0 on the same sorbent. Importantly, the mercury in the effluent was elemental, not oxidized. Thus the SO_2 appeared to be reducing the $HgCl_2$ to Hg^0 when NO_2 was absent, but not when it was present. Addition of NO to the gas composition did not prevent the SO_2 reduction from occurring. Since the amount of reduction increased gradually with time, the reduction was occurring on the sorbent surface, and it is possible that the sorbent was catalyzing the reduction, but not necessitated. It is also likely that the $HgCl_2$ binds not only to the basic groups on the carbon structure, but also to the substantial amount of basic inorganic matter (such as CaO) in the FGD sorbent.

What causes the reduction of Hg^{2+} on the sorbent?

What we know about the reaction of Hg with SO_2 or bisulfite is that the reaction proceeds only under acid conditions. Thus the increase of reduction in these experiments could be attributed to acid building up on the sorbent during its exposure to flue gas, whether or not the $HgCl_2$ is bound to carbon or inorganic matter. How the NO_2 prevents the reduction is less clear. Is it by continuously oxidizing the bound SO_2 or is it by continuously reoxidizing the carbon surface so that it cannot donate electrons to the mercury?

What are the consequences of using carbon for oxidized Hg?

Unless removed by selective catalytic reduction (SCR) or another process, NO_2 would be present in the flue gas, and would therefore reverse the reductive process involving SO_2 that would otherwise render the carbon ineffective for capturing $HgCl_2$ in flue gas over a long period. Thus using sorbents in an SCR system could present difficulties with respect to low capacities. It is also feasible that the reduction can be prevented by stabilizing the Hg^{2+} using a sorbent with impregnated sulfide. Karatza et al. reported the improved capture of $HgCl_2$ with sulfide-impregnated sorbents (47), but the breakthrough still occurred relatively quickly. Perhaps the sulfide-impregnated sorbent should only be used in an SCR system, so that the sulfur is not oxidized and would be effective for capture and stabilization of Hg^{2+}. In Karatza et al. (47), the species of mercury emitted after breakthrough was not determined. But, since capture was improved, it is clear that chemisorption of $HgCl_2$ is important in the capture mechanism.

What is the value of the understanding the fundamental mechanisms?

A better understanding of the interactions and effects of flue gas constituents and conditions will result in an improved mechanistic model and the development of more effective sorbents for mercury capture and control. We can actually derive and compare rate constants for the oxidation reactions. Ultimately, the refined model will have the potential to be used to describe carbon–Hg-flue gas rates and equilibria for various kinds of carbons and to predict capture rates under a variety of conditions.

What is the potential for successful capture?

We have developed not only reliable methods for mercury analysis and experimentation, but also an extensive experience in mercury behavior in flue gas and on carbon surfaces. We provided intuitive solutions to understanding mercury behavior under these conditions in the form of detailed chemical mechanistic model that the EERC and others can further use for understanding. Many problems remain to be solved, but with the described expertise we are positioned to solve these problems.

ATMOSPHERIC REACTIONS

What is the fate of the fraction of mercury that is not captured by the various pollution control devices?

Recently published studies have shown a rapid decrease in the fraction of oxidized mercury when measured in the plume of a power plant. Two projects performed by EPRI and the EERC consisted of mercury measurements at the power plant duct and within the plume using an aircraft equipped with gas measurement equipment. Results from the first study suggested that some reduction of Hg^{2+} to Hg^0 may be occurring in the plume, however, the fraction of Hg^{2+} at the stack was very small leaving little room for further reduction upon exiting the stack. In the most recent study, conducted at a facility burning a low-sulfur PRB fuel, Hg^{2+} measured at the stack was much higher than the previous study. The fraction of oxidized mercury measured at the stack was approximately 34%. Immediately downwind of the stack, the fraction of oxidized mercury had dropped to 16%, and 5 miles downwind of the stack the fraction was as low as 10%, illustrating a significant decrease the fraction of Hg^{2+} as the plume traveled downwind of the stack. Results from this study were measured from only one facility operating a cold-side ESP and SCR on half of the flue-gas from the stack and does not necessarily represent atmospheric reactions from all coal combustion derived mercury emissions. Additional study will be necessary to determine if mercury emissions, once exhausted to the atmosphere tend toward the Hg^0 or Hg^{2+} species and therefore contribute more to local or global deposition. The results from the studies discussed to not support regional “hot spots” of mercury resulting from coal combustion at power plants, however, additional study is required since only two power plants have been investigated.

BIOLOGICAL SYSTEMS

How does mercury bioaccumulate in fish?

The fate of mercury precipitates will partially depend upon whether they have fallen onto land or water surfaces. In both cases, sunlight-dependent photoreduction can result in reformation of Hg^0 that is emitted back into air to rejoin the global pool. A variable portion remains in the oxidized form and is retained where it falls. Certain quantities of retained Hg^{+2} form stable complexes that are biologically unavailable while the rest is accumulated by organisms, particularly in aquatic environments. When Hg accumulation rates exceed the capacity of natural mechanisms to release it back into the atmosphere or geologically retire it from active cycling, Hg concentrations build up in aquatic biota. Certain bacteria employ a biochemical pathway (methylation) that creates methylmercury (CH_3Hg), the predominant form of Hg that bioaccumulates in organisms of the food web. CH_3Hg typically constitutes the bulk of the total Hg in an organism, although as discussed below, biologically inert forms of mercury can also accumulate in tissues.

Creatures accumulate CH_3Hg and Hg^{+2} from their food sources, biomagnifying the total Hg concentrations from prey to predator. This begins at the bottom of the food web. Mercury present in bacteria and plankton is consumed by microinvertebrates. These invertebrates are consumed by predatory invertebrates that are consumed by fish that are, in turn, consumed by even larger fish. As a result of these amplification steps, fish at the top of the food web can harbor tissue Hg concentrations $>10^6$-fold higher than that of the water in which they swim (48). Aspects of the aquatic environment that influence biota production rates will also affect Hg bioaccumulation. Multiple factors such as sulfate and selenium (Se) availability exert both direct and indirect concentration-dependent effects on Hg bioaccumulation (49).

How does selenium inhibit Hg-bioaccumulation in fish?

Several studies suggest an important role of Se in the reducing bioaccumulation of Hg in fish (50–52) and inverse relationships between fish tissue Hg and the abundance of Se present in the ecosystem have been noted (53, 54). Selenium supplementation of lake waters in Sweden resulted in a 75%–85% reduction in Hg levels of fish over a 3-year period (55) and loss of Se can have the opposite effect. When Se-rich discharges of fly ash to an artificial lake were removed, researchers noted a steady increase in Hg concentrations (56, 57). Studies such as these indicate the importance of Se-dependent Hg retirement in aquatic ecosystems, possibly through formation of insoluble Hg:Se complexes that deposit in sediments (Figure 3).

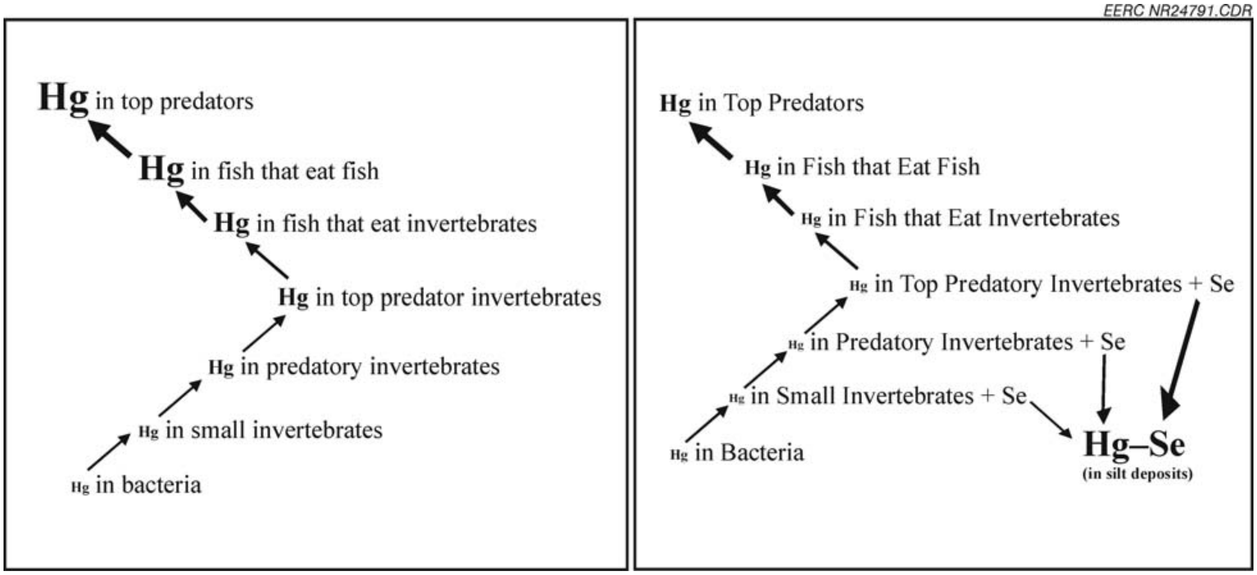


Figure 3. Mercury bioaccumulation in fish without selenium vs. in presence of selenium.

Chemically similar to sulfur, Se is a nutritionally essential element required to support the activity of enzymes that are normally present in all cells of all creatures (58). Researchers are currently aware of 25 selenoproteins, many of which are enzymes whose activities appear to be especially important in the brain, pituitary, and thyroid since these tissues are virtually impossible to deplete of Se (58). It is particularly important to note that the selenide formed during each cycle of selenocysteine synthesis has an exceptionally high affinity constant for Hg: 10^{45}; a millionfold higher than Hg's affinity for sulfide 10^{39} (59). Furthermore, since synthesis of selenoproteins is a continual process, the availability of selenide for forming potential complexes with mercury appears to be much greater than that of sulfide. Mercury selenide precipitates have extremely low solubility, ranging from 10^{58} to 10^{65} and are thought to be metabolically inert (60). Since these complexes are so insoluble, they are more likely to not be absorbed as they pass through the digestive tracts of creatures of the food web. Since Hg in the form of Hg:Se is less likely to be absorbed and accumulate, diminished Hg bioaccumulation in ecosystems with adequate Se resources may be the result of Hg:Se formation.

Why is the issue of determining a Hg threshold troubled by continued uncertainty?

Although sustained exposure to high concentrations of CH_3Hg has caused neurotoxic effects in exposed adults in Japan (61) and Iraq (62), mercury advisories have mainly arisen because of concern regarding CH_3Hg's effects during fetal development. Episodes of fetal CH_3Hg poisoning confirm that the developing brain is especially susceptible to Hg toxicity (63–66). Minamata Disease, or CH_3Hg poisoning, was first recognized in 1956 around Minamata Bay (61) and occurred again in 1965 in the Agano River Basin in Niigata, Japan (67). Minamata Disease was caused by the consumption of Hg-contaminated fish and shellfish obtained from these waters.

Typical ocean fish contain less than 0.5 ppm CH_3Hg; however, fish samples collected from Minamata Bay contained as much as 40 ppm CH_3Hg. Children exposed in utero to these high concentrations of Hg showed severe neurodevelopmental impairment, even though the mothers experienced minimal or no clinical symptoms (68). Although the dangers of acute exposures to high doses of Hg have been clearly recognized, controversy over fish consumption and the risks of CH_3Hg ingestion continue. Actual threshold levels for toxic effects of chronic exposure to low-dose Hmercury have not been agreed upon since no biochemical marker of risk has been established. However, recent insights regarding physiological mechanisms affected by mercury poisoning have the potential to reconcile these differences.

The contrasting observations reported by studies of mercury exposure performed in fish eating populations of the Seychelles and the Faroe Islands may be related to differences in the patterns of Hg exposure of their respective study populations. In the Seychelles, no adverse associations have been noted among a population consuming large quantities of fish with typically low Hg levels (69). In certain measurements of neurodevelopmental outcomes, fish consumption by Seychellois mothers during pregnancy were associated with beneficial effects on their children, possibly as a result of improved nutritional status.

These results contrast with those found in the Faroe Islands (70, 71), which reported adverse associations from prenatal CH_3Hg exposure. Although adult Faroe Islanders consume ~72 g of fish per day, the fish they consume have relatively low Hg contents; ~0.07 ppm. Only ~10% of the mercury they consume comes from fish. Averaged daily consumption of ~12 g portions of pilot whale muscle meat with mercury contents of 3.3 ppm and intermittent consumption of pilot whale organ meats with mercury contents that can be more than 10-fold higher provide the bulk of Hg exposure in this population. Thus more than 90% of mercury exposure in the Faroe Islands arises from consuming whale meat.

One potential explanation of these contradictory observations is that the studies in the Faroe Islands and the Seychelles may be observing differences in the dangers of intermittent exposures to high concentrations of mercury in whale meat vs. consistent low-level mercury exposures that accompany fish consumption. Se-dependent protective effects against mercury toxicity appear likely to also be very important considerations.

What are Se-dependent protective effects against Hg toxicity?

The ability of selenium compounds to decrease the toxic action of mercury has been established in all investigated species of mammals, birds, and fish (72, 73). The Hg–Se interaction has previously been assumed to be a “protective effect” whereby supplemental Se complexes with Hg and prevents toxic effects in animals fed otherwise debilitating amounts of Hg (74–76). Since 1967, when the first report on the protective effect of Se against Hg toxicity appeared (77), numerous studies have shown that Se counteracts the negative impacts of Hg exposure. However it is clear that the role of Se in diminishing Hg toxicity goes beyond simple sequestration.

While Hg sequestration by Se clearly has an effect on Hg's bioavailability, it is equally clear that Se sequestration by Hg would have an effect on Se bioavailability. It is possible that instead of Se acting to immobilize Hg, Hg-dependent sequestration of Se could inhibit formation of selenium-dependent proteins. These proteins are normally present in all cells of all creatures. Since these enzymes are essential to support normal enzyme metabolic functions, especially in brain tissues, excessive exposure to Hg would be expected to disrupt selenium-dependent processes that occur in the brain. Mercury-dependent sequestration of Se that leads to inhibition of selenium dependent enzyme functions may explain why selenium-deficient rodents are more susceptible to prenatal toxicity of CH_3Hg than those fed Se-adequate diets. This mechanism would also explain why maternal exposure to CH_3Hg reduced Se-dependent enzyme activity in the brains of fetal/neonatal rats (78).

In Figure 4, the normal cycle of selenoprotein synthesis is depicted on the left. Putative disruption of this cycle by mercury is depicted on the right. Selenide freed during selenoprotein breakdown from food or cellular proteins becomes available to bind with mercury. Formation of insoluble mercury selenides may reduce the bioavailability of selenium for protein synthesis.

It is clear that the Se naturally present in all foods and abundant in ocean fish and other seafoods can provide significant protection against Hg toxicity. However, it is becoming apparent that instead of merely being a protective "tonic," Se is instead a "target" of Hg toxicity since the loss of Se dependent enzymes undoubtedly contributes to Hg's pathologic effects. As research on this issue accrues, it is apparent the tonic to target paradigm shift will foster new understanding of apparent discrepancies in results of various studies. Efforts to define interactions between Se and Hg are moving forward rapidly as increasing numbers of research groups are investigating this emerging perspective on the Hg issue.

INTERPRETATION AND CONCLUSIONS

Understanding fundamental chemical principles of mercury in coal combustion flue gas is critically important to the ongoing efforts to capture and measure mercury from coal fired power

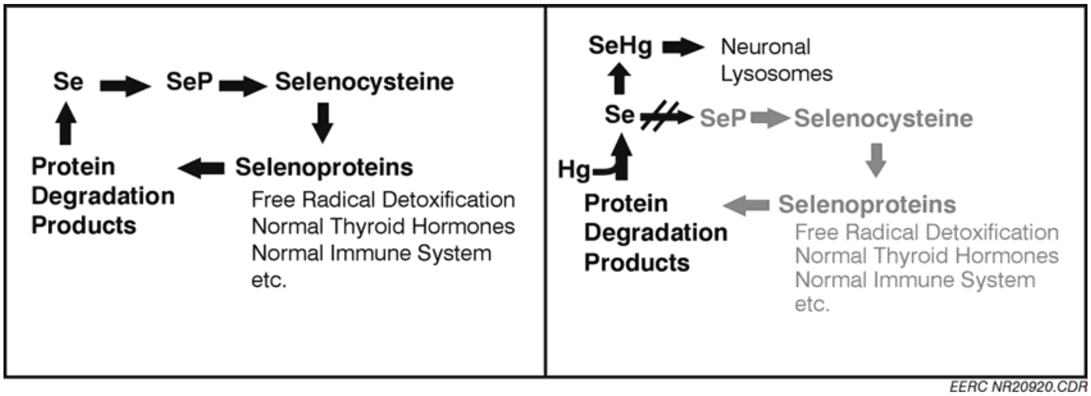


Figure 4. Normal selenoenzyme synthesis vs. interruption of the cycle by mercury.

plants. Homogeneous gas-phase reactions of mercury with halogen oxidants are important in determining the species in the flue gas which in turn impacts interactions with activated carbon sorbents. For low chlorine coals, much of the mercury in the flue gas is Hg^0 and only a small amount is Hg^{2+}, but finely powdered sorbent injection upstream of a particulate collection device has the potential to capture both Hg^{2+} present in the flue gas. Additional capture of Hg^0 can occur under some flue gas conditions, however, Hg^0 is not as readily removed by activated carbon as Hg^{2+}.

Recent research has improved understanding of how the capture of mercury takes place on a carbon sorbent in a flue gas stream indicating that sorption occurs via an oxidation mechanism (chemisorption) rather than physisorption. Acid gases in the flue gas, such as HCl, promote this oxidation and oxidation has nothing to do with formation of atomic halogen species. A current model suggests that the oxidation occurs at a positive site on the carbon that is able to accept electrons from the mercury (Lewis acid site), and this site is generated by addition of a hydrogen ion (or halogen from Cl_2 or Br_2) to the carbon structure. Recent, unpublished evidence indicates that the kinetics of the oxidation are determined by the number of active sites generated, the temperature (higher is better), the nature of the anions present, and the concentrations of NO_2, NO, and O_2 in the gas phase that can accept electrons from the carbon.

The capacity of the carbon is determined by the sulfuric acid that accumulates via oxidation of SO_2. The primary oxidant for the SO_2 is the NO_2 in the flue gas, but moisture is also required therefore H_2SO_4, HCl, and Hg^{2+} compete for carbon sites. The carbon capacity has little to do with the mercury and more to do with the sulfuric acid concentration in the flue gas.

In biological systems, CH_3Hg accumulation can pose significant health problems and has precipitated much of the current interest in mercury regulation and control. However, selenium may play an important role in minimizing some of the risks mercury poses to environmental and human health.

UPCOMING EVENTS

229th ACS National Meeting
March 13–17, 2005, San Diego, California
http://oasys.acs.org/acs/229nm/topics.html

World of Coal Ash
April 11–15, 2005, Lexington, Kentucky
http://www.acaa-usa.org/ASP/EventCalendar.ASP?YEAR=2005

14th International Emission Inventory Conference "Transforming Emission Inventories – Meeting Future Challenges Today"
April 11-14, 2005, Las Vegas, Nevada
http://www.epa.gov/ttnchie1/conference/ei14/index.html

30th International Conference on Coal Utilization & Fuel Systems (formerly Clearwater Coal Conference)
April 17–21, 2005, Clearwater, Florida
http://www.coaltechnologies.com

International Conference on Clean Coal Technologies for Our Future
May 10–12 2005, Sardinia, Italy, contact Rodney Anderson (304) 285-4709
http://fossil.energy.gov/news/events/

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Air Quality V: Mercury, Trace Elements, and Particulate Matter Conference
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MERCURY INFORMATION
CLEARINGHOUSE

Quarter 6 – Mercury Control Field Demonstrations

April 2005

Canadian Electricity Association
Association canadienne de l'électricité

EERC
Energy & Environmental Research Center

Center for Air Toxic Metals

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 6 – MERCURY CONTROL FIELD DEMONSTRATIONS

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QUARTER 6 – MERCURY CONTROL FIELD DEMONSTRATIONS

EXECUTIVE SUMMARY

Introduction

The Canadian Electricity Association (CEA) identified a need and contracted the University of North Dakota (UND) Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of the CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, the U.S. Department of Energy (DOE), and the Canadian Council of Ministers of the Environment (CCME), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of advances in mercury monitoring, control, policy, and related research progress.

In order to adequately address the many topics pertinent to mercury research and development and provide the detail necessary for the various stakeholders to make informed decisions, selected topics are discussed in detail in each quarterly report. Specific topics that have been addressed in previous quarterly reports include the following:

Quarter 1 – Sorbent Control Technologies for Mercury Control

Quarter 2 – Mercury Measurement

Quarter 3 – Advanced and Developmental Mercury Control Technologies

Quarter 4 – Rerelease of Mercury from Coal Combustion By-Products

Quarter 5 – Mercury Fundamentals

Mercury Policy

The CCME has been in the process of developing Canada-Wide Standards (CWS) for mercury since 1998 for several significant mercury-emitting sectors and products. Standards have been completed for base metal smelters, incinerators, mercury-containing lamps, and dental amalgam wastes. A CWS announcement is scheduled sometime in 2005 for mercury emissions from coal-fired electric power-generating plants, with implementations to begin in 2010.

In the United States, the Environmental Protection Agency (EPA) issued the first Clean Air Mercury Rule (CAMR) on March 15, 2005, to permanently cap and reduce mercury emissions from coal-fired power plants (a power plant is defined as an electrical generating facility that provides >25 MW_e). The CAMR is a two-phase market-based cap-and-trade program that will build on to EPA's Clean Air Interstate Rule (CAIR), which was implemented to permanently cap emission of sulfur dioxide (SO_2) and nitrogen oxide (NO_x) in the eastern 28 states and the District of Columbia. The first phase of CAMR begins in 2010 and will cap Hg emissions at 38 tons, a 21% reduction from current emissions (48 tons). Phase 2 will be implemented in 2018, setting the final cap at 15 tons with an overall reduction of 69%. Although the initial phase of CAMR is expected to be met as a cobenefit of wet scrubber and selective catalytic reduction (SCR) system installations to meet the CAIR, the Phase II cap of 15 tons will require additional mercury-specific controls at many power plants.

For trading purposes, EPA has established allocations for each state, the District of Columbia, and Indian Reservations based on their share of the total heat input from coal. These were then adjusted to reflect coal rank and existing air pollution control equipment. For allocation purposes, coal-firing units were subcategorized as bituminous, subbituminous, lignite, integrated gasification combined cycle (IGCC), and coal refuse. Each state will be free to decide if it wishes to participate in the trading program.

In addition to the cap-and-trade program, new coal-fired sources will have additional mercury requirements as part of the New Source Performance Standards. The requirements have been subcategorized as follows.

- Bituminous units – 21×10^{-6} lb/MWhr
- Subbituminous units
  - Wet flue gas desulfurization (FGD) – 42×10^{-6} lb/MWh
  - Dry FGD – 78×10^{-6} lb/MWh
- Lignite units – 145×10^{-6} lb/MWh
- IGCC units – 20×10^{-6} lb/MWh
- Coal refuse units – 1.4×10^{-6} lb/MWh

Quarter 6 Focus: Mercury Control Field Demonstrations

In 1999, DOE National Energy Technology Laboratory (NETL) issued a request for proposal (RFP) to test mercury control technologies at the full scale. The near-term goal of the RFP was to evaluate technologies that could achieve 50%–70% mercury removal at a cost of less than three-quarters of the estimated cost of $50,000–$70,000/lb (Can$136,000–Can$191,000/kg) mercury removed. The longer-term goal was to develop technologies that could provide up to 90% control at a cost of half to three-quarters of activated carbon injection technology by the year 2010. During 2003 and 2004, NETL issued three more RFPs to evaluate mercury control technologies through its Office of Fossil Energy’s Innovation Program and through the Clean Coal Initiative. This quarterly report focuses on the results of the large-scale mercury control projects that have been recently completed or are ongoing and identifies planned future projects.

Table ES-1 summarizes 41 large-scale mercury control projects. This information identifies the lead contractor for each project, demonstration site, boiler type and size, fuel type, air pollution control device (APCD) employed, Hg control technology being evaluated, and project status. The demonstration sites represent utility boilers across the United States and one in Canada. Boiler types representing the major North American boiler manufacturers are included. Fuel types represented include U.S. northern plains and Gulf Coast lignite, Powder River Basin subbituminous coal, high- and low-sulfur bituminous coal, and a Canadian lignite. Air pollution control technologies represented include cold- and hot-side electrostatic precipitators (c-ESP and h-ESP), various types of wet FGD systems, and spray dryer absorbers–fabric filter (SDA–FFs). All of these projects involve the evaluation of some type of additive, reagent, or sorbent for its potential to control Hg emissions in conjunction with existing air pollution control technology or modify Hg speciation in the flue gas to facilitate Hg control. Most of the projects involve the injection of some form of activated carbon into the flue gas stream. Several projects involve the use of additives to wet FGD systems to improve Hg emission control. Other approaches include coal blending or the addition of fuel additives to affect Hg speciation and control. Although several projects have been completed, most projects are ongoing, with a significant number scheduled to begin in 2005 or 2006.

Table ES-1 – Mercury Control Demonstration Projects Funded by the U.S. Department of Energy

Lead Contractor	Demonstration Site	Boiler Type/Size	Fuel Type	APCD	Hg Control Technology	Status
UND EERC	Leland Olds Station Unit 1 Basin Electric Power Cooperative	B&W wall-fired 220 MW	ND lignite	c-ESP	ACI with SEA	Complete
ADA-ES Inc.	Coal Creek Station Unit 1 Great River Energy	CE t-fired 546 MW	ND lignite	c-ESP Wet FGD	TOXECON II™	Complete
B&W	Endicott Station Michigan South Central Power Agency	B&W Stirling Boiler 55 MW	Bituminous	c-ESP Wet FGD	FGD reagent additive	Complete
B&W	Zimmer Station Cinergy	B&W Carolina boiler 1300 MW	Bituminous	c-ESP Wet FGD	FGD reagent additive	Complete
Mobotec USA	Cape Fear Station Unit 5 Progress Energy	CE t-fired 154 MW	Low-sulfur bituminous	c-ESP	Sorbent injection ROFA™/ROTAMIX™	Complete
Southern Company	E.C. Gaston Station Unit 3 Alabama Power	CE t-fired 270 MW	Low-sulfur bituminous	h-ESP COHPAC™	ACI	Ongoing
URS	Plant Yates Unit 1 Georgia Power	CE t-fired 100 MW	Low-sulfur bituminous	c-ESP	ACI	Ongoing
URS	Plant Yates Unit 2 Georgia Power	CE t-fired 100 MW	Low-sulfur bituminous	c-ESP Wet FGD	ACI	Ongoing
Sorbent Technologies Corporation	St. Clair Station Unit 1 DTE Energy	B&W wall-fired 160 MW	PRB PRB–bit. blend	c-ESP	Brominated ACI	Ongoing
Sorbent Technologies Corporation	Buck Station Duke Energy	NA	Low-sulfur bituminous	h-ESP	Brominated ACI	Ongoing
ADA-ES Inc.	Holcomb Station Sunflower Electric Power Corporation	B&W Carolina Boiler 360 MW	PRB PRB/W-bit.	SDA–FF	ACI Coal blending	Ongoing
URS	Stanton Station Unit 1 Great River Energy	FW wall-fired 150 MW	PRB	c-ESP	ACI	Ongoing
URS	Stanton Station Unit 10 Great River Energy	CE t-fired 60 MW	ND lignite	SDA–FF	ACI	Ongoing
SaskPower and UND EERC	Poplar River Power Station Units 1 and 2 SaskPower	NA 300 MW	Poplar River lignite	c-ESP	ACI Pilot-scale slipstream	Ongoing
ADA-ES Inc.	Meramec Station AmerenEU	NA 140 MW	PRB	c-ESP	ACI	Ongoing
UND EERC	Stanton Station Unit 1 Great River Energy	FW wall-fired 150 MW	PRB	c-ESP	ACI	2005
UND EERC	Antelope Valley Station Unit 1 Basin Electric Power Cooperative	CE t-fired 440 MW	ND lignite	SDA–FF	ACI ACI with SEA	2005

Continued . . .

Table ES-1 – Mercury Control Demonstration Projects Funded by the U.S. Department of Energy (continued)

Lead Contractor	Demonstration Site	Boiler Type/Size	Fuel Type	APCD	Hg Control Technology	Status
UND EERC	Milton R. Young Station Unit 2 Minnkota Power Cooperative	B&W cyclone-fired 450 MW	ND lignite	c-ESP Wet FGD	Mercury oxidation fuel/FG additives	2005
UND EERC	Monticello Station Unit 3 Texas Utilities Company	B&W wall-fired 750 MW	Texas lignite	c-ESP Wet FGD	Mercury oxidation fuel/FG additives	2005
UND EERC	Big Brown Station Texas Utilities Company	CE t-fired 600 MW	Texas lignite Lignite–PRB	c-ESP	ACI	2005
URS	Monticello Station Unit 3 Texas Utilities Company	B&W wall-fired 750 MW	Texas lignite	c-ESP Wet FGD	Wet FGD additives	2005
URS	Plant Yates Unit 2 Georgia Power	CE t-fired 100 MW	Low-sulfur bituminous	c-ESP Wet FGD	Wet FGD additive	2005
URS	Conesville Station American Electric Power	NA 400 MW	Bituminous	c-ESP Wet FGD	Wet FGD additive	2005
ADA-ES Inc.	Conesville Station American Electric Power	NA 400 MW	Bituminous	c-ESP Wet FGD	ACI	2005
ADA-ES Inc.	Laramie River Station Unit 3 Missouri Basin Power Project	B&W 550 MW	PRB	SDA–ESP	ACI	2005
ADA-ES Inc.	Monroe Station Unit 4 Detroit Edison	B&W 785 MW	PRB–bit. blend	c-ESP	ACI	2005
ADA-ES Inc.	Louisa Station Unit 1 MidAmerican	B&W 650 MW	PRB	h-ESP	Sorbent injection	2005
ADA-ES Inc.	Independence Station Unit 1 Entergy	CE 840 MW	PRB	c-ESP	TOXECON II™	TBD
ADA-ES Inc.	Gavin Station American Electric Power	B&W 1300 MW	Bituminous	c-ESP	TOXECON II™	TBD
ADA-ES Inc.	Council Bluff Unit 2 MidAmerican	NA	PRB	h-ESP	Sorbent injection	TBD
ALSTOM Power, Inc.	Dave Johnston Station PacificCorp	NA	PRB	c-ESP	ACI with additives	2005
ALSTOM Power, Inc.	Leland Olds Station Unit 1 Basin Electric Power Cooperative	B&W 440 MW	ND lignite	c-ESP	ACI with additives	2006
ALSTOM Power, Inc.	Portland Station Reliant Energy	NA	Bituminous	c-ESP	ACI with additives	2006
GE EER	John Sevier Station Tennessee Valley Authority	NA	Bituminous	NA	Combined Hg and NO_x Control	2005

Continued . . .

Table ES-1 – Mercury Control Demonstration Projects Funded by the U.S. Department of Energy (continued)

Lead Contractor	Demonstration Site	Boiler Type/Size	Fuel Type	APCD	Hg Control Technology	Status
GE EER	Lee Station Unit 3 Progress Energy	NA	Bituminous	c-ESP	Combined Hg and NO_x control	2005
Sorbent Technologies Corporation	Lee Station Unit 1 Progress Energy	NA	Bituminous	c-ESP	Brominated ACI	2005
Sorbent Technologies Corporation	Crawford Station Unit 7 Midwest Generation	NA	PRB	c-ESP	Brominated ACI	2006
Sorbent Technologies Corporation	Will County Station Midwest Generation	NA	PRB	h-ESP	Brominated ACI	TBD
Mobotec USA	Whitewater Station Richmond Power and Light	NA	NA	NA	Sorbent injection ROFA™/ROTAMIX™	2005
ADA-ES Inc.	Presque Isle Station WE Energy	NA	NA	NA	TOXECON II™	2005
Amended Silicates, LLC	Miami Fort Station Unit 6 Cinergy	NA 175 MW	Bituminous	c-ESP	Amended Silicates™	2005

ACI – activated carbon injection
ADA-ES Inc. – ADA Environmental Solutions Inc.
B&W – Babcock & Wilcox Company
CE – Combustion Engineering
COHPAC – compact hybrid particulate collector
c-ESP – cold-side electrostatic precipitator
FGD – flue gas desulfurization
FW – Foster Wheeler
GE EER – GE Energy and Environmental Research
h-ESP – hot-side electrostatic precipitator
NA – not available
PRB – Powder River Basin subbituminous coal
ROFA™ – Rotating Opposed-Fire Air
ROTAMIX™ – Rotating Mixing
SDA–FF – spray dryer absorber–fabric filter
SEA – sorbent enhancement additive
TBD – to be determined
t-fired – tangentially fired
UND EERC – University of North Dakota Energy & Environmental Research Center
URS – URS
W-bit. – western bituminous coal

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 6 – MERCURY CONTROL FIELD DEMONSTRATIONS

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of the CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, the U.S. Department of Energy (DOE), and the Canadian Council of Ministers of the Environment (CCME), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of advances in mercury monitoring, control, policy, and related research progress.

Ongoing developments in mercury regulations for coal-fired power plants in Canada in the form of Canada-Wide Standards (CWS) and the United States in the recently published U.S. Environmental Protection Agency's (EPA's) mercury rule illustrate the need for a solid understanding of mercury chemistry and effective mercury control strategies for coal-fired electric utilities.

In order to adequately address the many topics pertinent to mercury research and development and provide the detail necessary for the various stakeholders to make informed decisions, selected topics will be discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include measurement, control, policy, and transformations. The discussion in this quarterly report will focus on the status and results of the many large-scale mercury control projects that are ongoing or recently completed. Specific topics that have been addressed in previous quarterly reports include the following:

Quarter 1 – Sorbent Control Technologies for Mercury Control

Quarter 2 – Mercury Measurement

Quarter 3 – Advanced and Developmental Mercury Control Technologies

Quarter 4 – Rerelease of Mercury from Coal Combustion By-Products

Quarter 5 – Mercury Fundamentals

Topics that will be addressed in upcoming quarterly reports include, but are not limited to, the following:

- Quarter 7 will provide a summary of the status of mercury regulations in the various states, provinces, and federal entities. Specifically, a review of the EPA final Utility

Clean Air Mercury Rule (CAMR) will be reviewed and presented in this quarterly. It will also include a summary of possible compliance strategies for utilities in the United States and impacts on state regulations and litigation.

- Quarter 8 will review commercialization aspects of mercury control technologies including warranties, phase-in, material supply, balance-of-plant impacts, and operational issues.

- Quarter 9 will be the final report and will summarize pertinent updates in areas presented in earlier quarterly reports. Additionally, it will summarize the status of the CEA mercury program, including data summaries from stack sampling, coal and ash analysis, and the laboratory round-robin. These results will be compared against program objectives.

MERCURY POLICY

The CCME has been developing a CWS for mercury since 1998 for several significant mercury-emitting sectors and products. Standards have been completed for base-metal smelters, incinerators, mercury-containing lamps, and dental amalgam wastes. A CWS announcement is scheduled in 2005 for mercury emissions from coal-fired electric power-generating plants, with implementations to begin in 2010. In anticipation of the 2005 CWS announcement, the Canadian coal-fired generating companies have embarked on a multiyear program to improve the mercury measurement and control information base. Data from this effort are still in verification and analysis by the CCME; however, preliminary results can be accessed in the program Web site: www.ceamercuryprogram.ca.

EPA issued the first CAMR on March 15, 2005, to permanently cap and reduce mercury emissions from coal-fired power plants (a power plant is defined as an electrical generating facility that provides >25 MWe). The CAMR is a two-phase market-based cap-and-trade program that will build on EPA's Clean Air Interstate Rule (CAIR), which was implemented to permanently cap emission of sulfur dioxide (SO_2) and nitrogen oxide (NO_x) in the eastern 28 states and the District of Columbia. The first phase of CAMR begins in 2010 and will cap Hg emissions at 38 tons per year from the current 48 tons, a 21% reduction. Phase 2 will be implemented in 2018 and will set the final cap at 15 tons, a reduction of 69%. It is expected that the initial phase of CAMR will be met as a cobenefit by the additional wet scrubbers and selective catalytic reduction (SCR) systems that will be installed to meet the CAIR. However, a cap of 15 tons will require additional mercury-specific controls at many power plants.

For trading purposes, EPA has established allocations for each state, the District of Columbia, and Indian reservations based on their share of the total heat input from coal. These were adjusted to reflect coal rank and existing air pollution control equipment. Mercury emission limit subcategorizations were developed for bituminous coal, subbituminous coal, lignite coal, coal refuse, as well as integrated gasification combined-cycle (IGCC) configurations and wet and dry scrubber systems when used at facilities burning subbituminous fuel. The total

2010–2017 state allocations are 38 tons of mercury emission, and from 2018 and thereafter, the state allocations are 15 tons of mercury emission. Each state will be free to decide if it wishes to participate in the trading program.

In addition to the cap-and-trade program, new coal-fired sources will have additional mercury requirements as part of the New Source Performance Standards. The requirements have been subcategorized as follows:

- Bituminous units – 21×10^{-6} lb/MWh
- Subbituminous units
  - Wet flue gas desulfurization (WFGD) – 42×10^{-6} lb/MWh
  - Dry FGD – 78×10^{-6} lb/MWh
- Lignite units – 145×10^{-6} lb/MWh
- IGCC units – 20×10^{-6} lb/MWh
- Coal refuse units – 1.4×10^{-6} lb/MWh

In addition to the CAMR, several states are in various stages of establishing state-specific regulations for mercury to further reduce mercury emissions. A more comprehensive review of the CAMR and of the status of state regulatory activities will be provided in the Quarter 7 report.

QUARTER 6 FOCUS: MERCURY CONTROL FIELD DEMONSTRATIONS

FIELD DEMONSTRATIONS COMPLETED

In 1999, the DOE National Energy Technology Laboratory (NETL) issued a request for proposal (RFP) to test mercury control technologies at the full scale. The near-term goal of the RFP was to evaluate technologies that could achieve 50%–70% mercury removal at a cost of less than three-quarters of the estimated cost of $50,000–$70,000/lb (Can$136,000–Can$191,000/kg) mercury removed. The longer-term goal was to develop technologies that could provide up to 90% control at a cost of half to three-quarters of activated carbon injection (ACI) technology by the year 2010. In September 2000, NETL announced an award to a team headed by ADA-ES to do full-scale testing of ACI at four power plants (1). A brief description of the plants and the month tested is provided in Table 1.

Table 1. Description of the Power Plant Tests by ADA-ES Using ACI

Company	Plant	Coal Rank	Configuration	Test Completed
Alabama Power	E.C. Gaston	Low-sulfur bit.	h-ESP[1] and COHPAC™	April 2001
WE Energies	Pleasant Prairie	PRB[2]	c-ESP[3]	November 2001
PG&E	Brayton Point	Low-sulfur bit.	c-ESP	August 2001
PG&E	Salem Harbor	Low-sulfur bit.	c-ESP SNCR[4]	November 2002

[1] Hot-side electrostatic precipitator (h-ESP).
[2] Powder River Basin.
[3] Cold-side ESP.
[4] Selective noncatalytic reduction.

The testing at each of these facilities included parametric testing using several different commercially available powdered activated carbons (PACs) followed by a 1- to 2-week test using one of the PACs based on the parametric testing. The results of the tests are shown in Figure 1. As expected, the use of a fabric filter (FF) (high air-to-cloth ratio, COHPAC™) with ACI at the E.C. Gaston Station provided the best mercury removal at the lowest ACI rate, 87%–90% removal at an ACI rate of 1.5 lb/Macf. However, as a result of increased particulate loading to the COHPAC FF, the cleaning frequency increased significantly. For the same type of coal (low-sulfur bituminous), an ACI rate of 20 lb/Macf was needed at the Brayton Point Station (ESP alone) to obtain 90% mercury removal. At an ACI rate of 1.5 lb/Macf, only about 15% mercury removal was achieved at the Brayton Station. For the PRB coal with a c-ESP (Pleasant Prairie Station), the maximum mercury removal was 66% regardless of the ACI rate. However, at an ACI rate of 1.5 lb/Macf, mercury removal was ~40%.

The effect of temperature, unburned carbon (loss-on-ignition [LOI]), and an SNCR with and without ACI was evaluated at the Salem Harbor Station (2). With the SNCR online, an ESP inlet temperature of 295°F, and the plant at full load (86 MW), the LOI was 25%–35%, and the baseline mercury removal range was 87%–94%. When the SNCR was taken off-line, the

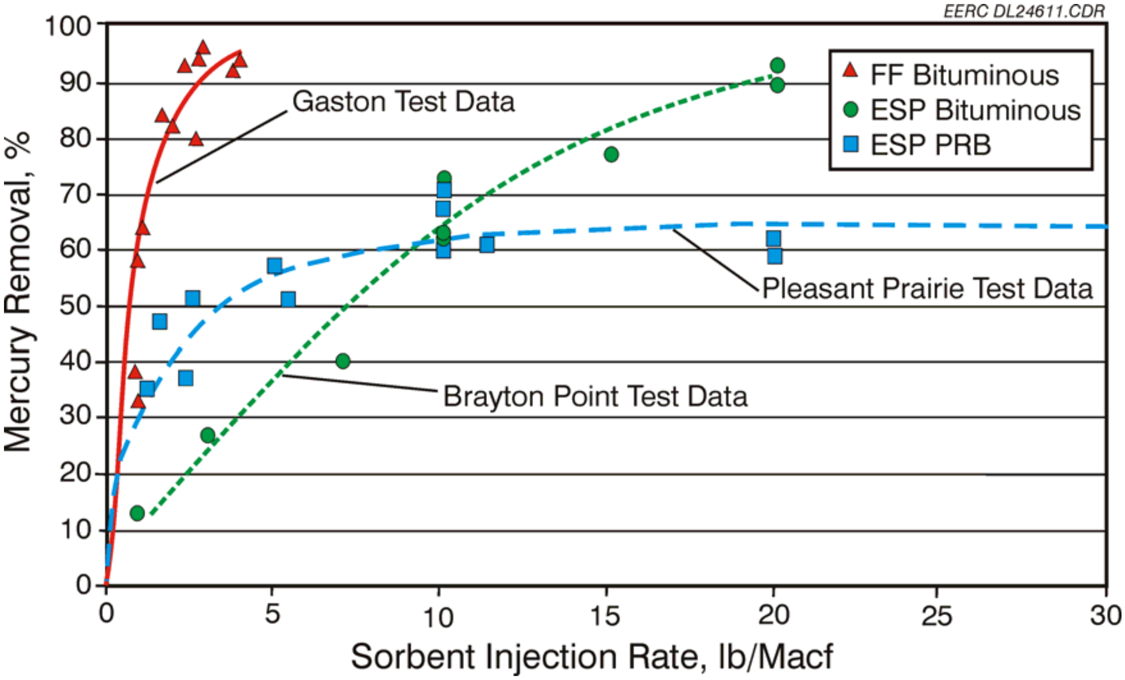

Figure 1. Mercury removal (%) vs. sorbent injection rate (lb/Macf) for tests at three sites.

baseline mercury removal was essentially unchanged, but the data were more variable. The results were similar when the LOI was decreased to 15%–20% by reducing the load to 65 MW. However, when the temperature at the ESP inlet was increased to 350°F, the baseline mercury removal decreased to only 5%–20%.

Prior to the tests with ACI, the Salem Harbor facility had switched to a lower-sulfur coal resulting in a lower baseline removal efficiency of about 47% at an ESP inlet temperature of 298°–306°F and less than 10% at 343°–347°F. At an ACI rate of 10 lb/Macf, the mercury removal increased to 82% for the lower temperature range compared to 65% at the higher temperatures.

With new requirements for additional SO_2 and NO_x control on existing power plants, it is expected in the next 5–10 years that a number of plants will be installing SCRs and WFGD systems. Based on field mercury measurements (3), it is possible that for these systems, 90% mercury control will be achieved without any sorbent or additional mercury controls. However, this appears to be true only when an eastern bituminous coal is fired. Mercury control is more problematic for western lower-rank fuels: lignites and subbituminous coals. In general, lignites and subbituminous coals contain significantly lower levels of chlorine and have a much higher concentration of alkali components compared to bituminous coals. As a result, most of the mercury generated is in the form of elemental mercury (Hg^0), which is more difficult to remove. Therefore, the focus for mercury control research and testing in the last several years has been to develop mercury control technologies for low-rank fuels.

As a result, in 2003 and 2004, NETL issued three more RFPs to evaluate mercury control technologies through its Office of Fossil Energy's Innovation Program and through the Clean Coal Initiative with a focus on low-rank coals. A total of 11 projects were selected that involved ACI either as a primary control option or as a comparison for a novel control technology. The balance of this section summarizes additional demonstration projects that have been completed. Subsequent sections of this document summarize ongoing demonstration projects as well as projects that will begin in 2005.

Leland Olds Station – Basin Electric Power Cooperative

The EERC, in conjunction with Basin Electric Power Cooperative and NETL, completed a sorbent injection project in 2004 at the Leland Olds Station (LOS). LOS Unit 1 is a 220-MW Babcock and Wilcox (B&W) pulverized-coal wall-fired system. Twenty low-NO_x burners with overfire air are supported by ten feeders and pulverizers. The primary fuel is lignite coal from the Freedom Mine (North Dakota) with occasional blending with 30% PRB coal from the Dry Fork Mine (Wyoming). Particulate control is accomplished using two parallel ESPs manufactured by Joy. The specific collection area (SCA) for each ESP is 320 ft^2/1000 acfm supported by four rows of hoppers with eight hoppers per row.

The testing completed at the LOS involved three phases: baseline, parametric, and monthlong testing. Specific activities focused on sorbent injection into one full-scale ESP. The sorbents used during this field demonstration included PAC as well as PAC with sorbent enhancement additives (SEA). ACI was upstream of the ESP, and the SEAs were added with the fuel. Project results were documented in a symposium paper entitled "Enhancing Carbon Reactivity for Mercury Control: Field Test Results from Leland Olds" and a symposium presentation entitled "Developing Mercury Control Options for Utilities Firing Western Fuels," respectively (4, 5).

The baseline testing showed that mercury removal across the ESP was 18%. The goal of the parametric testing was to obtain a minimum mercury removal rate of 55% with ACI and an SEA. After the optimization tests were completed and the mercury removal objective achieved, the monthlong test was initiated. The average mercury removal for the monthlong test was reported to be 63% based on an ACI rate of 3 lb/Macf and an SEA injection rate of 5 lb chlorine/Macf. In this case, the SEA was calcium chloride. The average flue gas mercury concentrations over the monthlong test were extrapolated to calculate a theoretical mercury emission rate of 2.04 lb/TBtu for the 220-MW unit. Based on the monthlong test, there were no significant impacts on plant operations. Special air-cooled corrosion probes, placed in the flue gas stream in the economizer and the inlet and outlet of the secondary airheater for 4 weeks showed no signs of abnormal deposition or corrosion as a result of the calcium chloride added with the fuel. Subsequent short-duration testing with a second SEA (unidentified) and an ACI rate of 3 lb/Macf demonstrated mercury removal rates as high as 80%. We are evaluating potential long-term impacts on plant operations, and a yearlong demonstration is under consideration.

Coal Creek Station – Great River Energy

ADA-ES Inc., in conjunction with Great River Energy, and EPRI completed an ACI project at Great River Energy's Coal Creek Station (CCS) near Underwood, North Dakota. Work was conducted on Unit 1 firing a North Dakota lignite. CCS Unit 1 is a 546-MW Combustion Engineering pulverized-coal (pc), tangentially fired system. Unit 1 particulate control is accomplished with a c-ESP manufactured by Wheelabrator-Frye Inc. The calculated SCA for the ESP is 599 ft^2/1000 acfm. The ESP design includes six electrical fields, with an individual field length of approximately 12.5 feet in the direction of gas flow. Flue gas temperature at the ESP inlet ranges from 330° to 360°F, depending on boiler load. A WFGD system manufactured by Combustion Engineering is employed to control SO_2 emissions.

The TOXECON II™ concept involves injecting PAC within an ESP. For this project, PAC was injected between the third and fourth collecting fields of the ESP. The rationale for this approach was to permit the collection of a large percentage of the fly ash from the ESP hoppers prior to ACI to avoid carbon contamination of fly ash that can be marketed as a salable by-product. Mercury sampling occurred at the inlet and outlet of the ESP. Testing on Unit 1 at CCS was carried out in two phases, baseline and parametric testing. Two activated carbons were used during the parametric testing, DARCO FGD™ (NORIT) and CB 200xF™ (an iodine-impregnated sorbent derived from coconut shell, Calgon/Barnebey Sutcliffe). Baseline and parametric test results were documented in a symposium paper entitled "Full-Scale Evaluation of TOXECON II on a Lignite-Fired Boiler" and a separate symposium presentation entitled "Full-Scale Evaluations of Mercury Control Options for Western Fuels," respectively (6, 7).

Baseline results over 2 days of testing averaged 7% mercury removal, with a range of 5%–20%. During 3 days of parametric testing with the DARCO FGD activated carbon, injection rates ranged from 1 to 15 lb/Macf. At injection rates of 1 and 3 lb/Macf, average mercury removal was 46% and 58%, respectively. Increasing the DARCO FGD injection rate to >5 lb/Macf resulted in a mercury removal rate of 70%. However, injection rates of 10 lb/Macf and higher did not appear to increase mercury removal.

Based on previous experience, the CB 200xF AC was expected to perform better than the DARCO FGD activated carbon. However, during a single day of parametric testing, the CB 200xF AC did not perform as well as the DARCO FGD AC for specific injection rates of 1, 3, and 10 lb/Macf. Two explanations were offered for the CB 200xF AC not performing up to expectations. First, the flue gas temperature regime for this project was higher, 350° to 360°F versus <225°F for previous SDA–FF tests. Therefore, the iodine likely volatilized from the carbon surface upon carbon particle injection and heating. Another potential contributing factor was particle size. Characterization of the DARCO FGD AC showed an average particle size of 19 µm versus 87 µm for the CB 200xF activated carbon. This difference in particle size dramatically impacts the number of particles and equivalent available surface area injected per unit mass.

Because of the short duration of these tests, balance-of-plant issues could not be practically evaluated. However, a number of observations were made. Although no increase in average stack opacity was observed during ACI tests with only 25% of the flue gas being treated, a 10% to 30% increase in rapping spike opacity was observed. Carbon was evident on the surface of the scrubber slurry during ACI tests, indicating that some activated carbon was passing through the ESP. Particulate sampling at the outlet of the ESP during baseline and ACI tests showed a 100% increase in the outlet mass loading when carbon was injected. An electrical short was experienced in the fifth field of the ESP after a period of ACI was completed. However, ACI was not occurring when the field tripped. Although the exact cause is uncertain, it may have resulted from carbon injection and tracking on the insulators. The use of purge blowers could effectively solve tracking problems if they were found to be persistent during long-term testing. Finally, LOI analyses of fly ash samples collected from the fourth field of the ESP during baseline and ACI tests showed that LOI values increased from 0.14 to 3.79 wt% as a result of ACI. In order to determine the commercial potential of the TOXECON II concept, further parametric testing will be necessary along with long-term testing to verify performance as well as potential balance-of-plant issues.

Endicott Station – Michigan South Central Power Agency

B&W, in conjunction with McDermott Technology, Inc. (MTI), Michigan South Central Power Agency (MSCPA), the Ohio Coal Development Office, and NETL, completed a WFGD mercury control project at MSCPA's Endicott Station located in Litchfield, Michigan. The project objective was 90% overall mercury removal at a 50% to 75% cost advantage when compared to ACI technology. Activities focused on evaluation of B&W–MTI's proprietary enhanced mercury removal concept for FGD systems. The concept employs a reagent additive to increase mercury removal across the FGD system and reduce reemission of mercury once it is captured in the FGD system. Project results were documented in a final project report entitled "Full-Scale Testing of Enhanced Mercury Control Technologies for Wet FGD Systems" (8).

Endicott Station is a single-unit, nominally 55-MW B&W Stirling boiler firing an Ohio bituminous coal. Particulate control is accomplished with a c-ESP manufactured by Belco, with a reported particulate removal efficiency of >98%. SO_2 control is accomplished using a single absorber B&W limestone wet scrubber. The SO_2 concentration at the inlet of the FGD system was reported to be nominally 3600 ppm. The liquid-to-gas ratio and slurry pH were reported to be 78 gal/1000 acf and 5.4–5.6, respectively. SO_2 removal is typically 92%. In situ forced oxidation is employed to produce a gypsum by-product for cement applications.

Work completed at the Endicott Station involved three phases: parametric, verification, and monthlong testing. Parametric testing was used to determine optimum process conditions followed by 2 weeks of verification testing to confirm the performance of the optimum process conditions selected. Long-term testing involved operation at optimum process conditions for a 4-month period to document mercury removal and demonstrate that there were no detrimental impacts on SO_2 removal, FGD system materials of construction, or by-product utilization.

Verification test results at the Endicott Station demonstrated an average total mercury removal rate of 76% across the FGD system, with an oxidized mercury removal rate of 96%. During the long-term test, average mercury removal across the FGD system increased to 79%. Results from both test periods demonstrated that most of the oxidized mercury present in the flue gas was removed in the WFGD system. In addition, sampling data showed no increase in flue gas elemental mercury concentration at the FGD system outlet sample location, demonstrating that mercury reemission was prevented.

Characterization of WFGD solids generated at the Endicott Station during this project determined that the captured mercury was associated with the fines in a stable form. This is a significant observation because the fines can be separated from the gypsum crystals using commercially available technology. Once separated, the mercury-containing fines can be placed in a standard landfill, and concerns with respect to mercury concentration in gypsum by-products, marketed in this case for cement applications, can be mitigated.

A cost comparison of the B&W–MTI proprietary process with ACI was presented for a 500-MW plant employing a c-ESP for particulate control and a combination of low- and high-sulfur fuels. For an existing plant with a WFGD system, a significant annual levelized cost (ALC) advantage was reported for the B&W–MTI process (0.18 mil/kWh) versus ACI (0.85 mil/kWh for 60% Hg removal). In the case of an existing plant without a WFGD system, an advantage was reported for the ACI technology (1.65 mil/kWh for 70% Hg removal) versus the B&W–MTI process (4.23 mil/kWh, including the cost of FGD technology). Reducing the mercury removal target to 60% results in a greater advantage for the ACI technology (0.85 mil/kWh) versus the B&W–MTI process (4.23 mil/kWh including the cost of FGD technology). A comparison of the B&W–MTI FGD technology (4.23 mil/kWh) versus the ACI SDA–FF technology (4.59 mil/kWh) shows an ALC advantage for the B&W–MTI FGD technology for 80% mercury removal.

Specific plans for future work were not discussed. However, the report stated that B&W was committed to the development and commercial application of mercury control technology for WFGD systems.

Zimmer Station – Cinergy

B&W, in conjunction with MTI, Cinergy, the Ohio Coal Development Office, and NETL, completed a WFGD mercury control project at Cinergy's Zimmer Station located in Moscow, Ohio. The project objective was 90% overall mercury removal at a 50% to 75% cost advantage when compared to ACI technology. Activities focused on evaluation of B&W–MTI's proprietary enhanced mercury removal concept for FGD systems. The concept employs a reagent additive to increase mercury removal across the FGD system and reduce reemission of mercury once it is captured in the FGD system. Project results were documented in a final project report entitled "Full-Scale Testing of Enhanced Mercury Control Technologies for Wet FGD Systems" (8).

Zimmer Station is a single-unit, nominally 1300-MW B&W Carolina-type universal pressure boiler firing an Ohio bituminous coal. Particulate control is accomplished with two c-ESPs manufactured by Flakt, with a reported particulate removal efficiency of 99.9%. SO_2

control is accomplished using six B&W absorber modules employing Thiosorbic®, a magnesium-enhanced lime slurry reagent. The SO_2 concentration at the inlet of the FGD system was reported to be nominally 3300 ppm. Liquid-to-gas ratio and slurry pH were reported to be 21 gal/1000 acf and 5.8–6.0, respectively. SO_2 removal is typically 92%, but 95% can be achieved with five absorber modules. Ex situ forced oxidation is employed to produce a gypsum by-product for wallboard applications.

Work completed at the Zimmer Station only involved 2 weeks of verification testing to confirm the performance of the process conditions selected. The FGD slurry reagent additive was added to all operating absorber modules simultaneously. Verification test results at the Zimmer Station demonstrated an average total mercury removal rate of 51% across the FGD system, with an oxidized mercury removal rate of 87%. In addition, sampling data showed an increase in flue gas elemental mercury concentration at the FGD system outlet location, demonstrating that mercury reemission was not prevented. Increasing the reagent addition rate by 50% provided no improvement in mercury removal. Overall, these data demonstrate a lower level of performance when compared to the Endicott Station results.

Characterization of WFGD solids generated at the Zimmer Station during this project determined that the captured mercury was associated with the fines in a stable form, consistent with the Endicott Station observation. This is significant because the fines are separated from the gypsum crystals as a result of the ex situ oxidation at the Zimmer Station. Once separated, the mercury-containing fines can be placed in a standard landfill, and concerns with respect to mercury concentration in gypsum by-products, marketed in this case for wallboard applications, can be mitigated.

A cost comparison of the B&W–MTI proprietary process with ACI was presented for a 500-MW plant employing a c-ESP for particulate control and a combination of low and high-sulfur fuels. For an existing plant with a WFGD system, a significant advantage was reported for the B&W–MTI process (0.18 mil/kWh) versus ACI (0.85 mil/kWh for 60% Hg removal). In the case of an existing plant without a WFGD system, an advantage was reported for the ACI technology (1.65 mil/kWh for 70% Hg removal) versus the B&W–MTI process (4.23 mil/kWh including the cost of FGD technology). Reducing the mercury removal target to 60% results in a greater advantage for the ACI technology (0.85 mil/kWh) versus the B&W–MTI process (4.23 mil/kWh, including the cost of FGD technology). A comparison of the B&W–MTI FGD technology (4.23 mil/kWh) versus the ACI SDA–FF technology (4.59 mil/kWh) shows an advantage for the B&W–MTI FGD technology for 80% mercury removal.

E.C. Gaston Station – Alabama Power

Southern Company, in conjunction with Alabama Power, ADA-ES, Inc., EPRI, and NETL, completed a mercury control project at the E.C. Gaston Station using ACI in combination with a COHPAC system. The E.C. Gaston Station, located in Wilsonville, Alabama, has four 270-MW B&W balanced-draft coal-fired boilers and one Combustion Engineering 880-MW forced-draft coal-fired boiler. All units fire a variety of low-sulfur, washed, eastern bituminous coals. The primary particulate control equipment on all units is h-ESPs. Units 1 and 2 and Units 3 and 4 share common stacks. In 1996, Alabama Power contracted with Hamon Research-Cottrell to install a COHPAC system downstream of the h-ESP (274 ft^2/1000 acfm, Research-Cottrell) on Unit 3. This COHPAC system was designed to maintain Unit 3 and 4's stack opacity levels below 5% on a 6-minute average.

The COHPAC system is a hybrid pulse-jet baghouse, designed in this case to treat flue gas volumes of 1,070,000 acfm at 290°F (gross air-to-cloth ratio of 8.5 ft/min with online cleaning). This COHPAC baghouse consists of four isolatable compartments—two compartments per air preheater identified as either A- or B-side. Each compartment consists of two bag bundles, each bundle consisting of 544 bags for a total of 1088 bags per compartment, or 2176 bags per casing. The bags were 23-foot-long polyphenylene sulfide (PPS) felt filter bags, 18-oz/yd^2 nominal weights. The ACI evaluation was conducted on one-half of the gas stream, nominally 135 MW. The B-side was chosen for testing. The A-side was monitored as the control.

The work plan for the E.C. Gaston Station included baseline, optimization, and long-term testing. Baseline testing documented baseline mercury removal rates. Optimization testing established a carbon injection scheme that achieved the highest mercury removal rate within the operational limits of the system. Long-term testing was split into two 6-month periods: one 6-month period with old bags and a second 6-month period with new bags. Project results were documented in two symposium papers entitled "Field Test Program for Long-Term Operation of a COHPAC System for Removing Mercury from Coal-Fired Flue Gas" and "Long-Term Operation of a COHPAC System for Removing Mercury from Coal-Fired Flue Gas," respectively (9, 10).

The baseline testing indicated that the COHPAC bag-cleaning frequency was much higher than expected, exceeding the targeted maximum allowable cleaning frequency of 1.5 pulses/bag/hour (p/b/h) that was used during a 2-week test in 2001. There were times when the COHPAC bags were cleaning continuously at 4.4 p/b/h. The baseline mercury removal rates ranged from 0% to 90% depending on inlet particulate mass loading. The reason given for the large range was that the particulate mass loading entering the COHPAC system greatly exceeded design capacity.

Because of the frequent bag cleaning observed during baseline tests, ACI rates during the optimization tests were severely limited in order to avoid cleaning frequency problems and still achieve reasonable mercury removal. Based on the optimization tests, the following ACI rates were selected: 1) when the COHPAC baghouse inlet mass loading was <0.07 gr/acf, the carbon injection rate was set to either 16 or 20 lb/h (0.52 or 0.66 lb/Macf); 2) when inlet mass loading was higher, between 0.07 and 0.14 gr/acf, the carbon injection rate was reduced to 10 lb/h (0.35 lb/Macf); and 3) when the inlet mass loading was >0.14 gr/acf, the COHPAC baghouse was often in a state of continuous cleaning, and ACI was discontinued.

Long-term testing with the old bags (2.7 denier) was conducted for 6 months using the ACI optimization parameters previously discussed. During this period, the average mercury removal rate was 86% for full-load operation. Average inlet and outlet mercury concentrations for the 6-month period were 14.3 and 2.1 $\mu g/Nm^3$, respectively. Nominal daily average inlet and outlet mercury concentrations varied from 5.1 to 25.6 $\mu g/Nm^3$ and 0.24–6.2 $\mu g/Nm^3$, respectively. Reducing boiler load by 28% and the corresponding flue gas flow rate and COHPAC baghouse air-to-cloth ratio resulted in 95% mercury removal for an ACI rate of 45 lb/hr, or 2.0 lb/Macf.

Following installation of new bags (7 denier), baseline and optimization tests were repeated. The symposium papers referenced for this work did not contain final results for the second 6-month test period. However, preliminary results were reported. Preliminary data demonstrated that an ACI rate of 45 lb/hr (1.3 lb/Macf) resulted in an average of 92% mercury removal. Maximum and minimum hourly values were 98% and 80%, respectively.

The only significant balance-of-plant issue identified was bag-cleaning frequency. Specifically, the older bags had to be cleaned more frequently than the newer bags. Eight carbon types were selected for testing in June–August 2004, including carbon from CARBOCHEM, Superior Adsorbent, General Technologies, Donau, NORIT, and RWE. Final data from these tests and the second 6-month test period were expected to be available in 2004, but were not available for inclusion in this summary.

Cape Fear Station – Progress Energy Carolinas

Mobotec USA, in conjunction with Progress Energy Carolinas, NETL, and other organizations, completed a multipollutant (including mercury) control project at the Cape Fear Station. The approach involved a combination of furnace sorbent injection (FSI) with rotating opposed fire air (ROFA™) and rotating mixing (ROTAMIX™) systems. The Cape Fear Station, located in Moncure, North Carolina, has two Combustion Engineering tangentially fired boilers: Unit 5, nominally 154 MW, and Unit 6, nominally 174 MW. Both units fire a low-sulfur bituminous coal. The primary particulate control equipment on both units is a c-ESP originally manufactured by Buell with a nominal SCA of 300 ft^2/1000 acfm. Unit 5 operated at 75% load, nominally 100 MW, during the sorbent injection tests.

The purpose for installing the ROFA and ROTAMIX systems in conjunction with FSI was multipollutant control, specifically SO_2, NO_x, HCl, and mercury. The sorbents used included limestone and trona. ROFA is a combustion air distribution and mixing technology intended to improve combustion and reduce NO_x emissions. ROTAMIX combines SNCR chemistry with FSI, making use of the ROFA air distribution system. The test plan for work at the Cape Fear Station included baseline, some optimization, and short-term performance tests. Project results were documented in a symposium paper entitled "Full-Scale Evaluation of a Multi-Pollutant Reduction Technology: SO_2, Hg, and NO_x" (11).

Baseline sampling documented SO_2, SO_3, NO_x, HCl, and mercury concentrations at the stack. Total mercury concentrations ranged from 10.54 to 11.31 $\mu g/Nm^3$. Speciation data indicated that particulate, oxidized, and elemental mercury concentrations were 0.01 to 0.10 $\mu g/Nm^3$, 7.95 to 8.16 $\mu g/Nm^3$, and 2.50 to 3.14 $\mu g/Nm^3$, respectively. Optimization tests were conducted by injecting each sorbent material at multiple elevations during an 8-hr period to determine the best location. Subsequent short-term (4-hr) performance tests involved injecting each sorbent at selected locations using alkali-to-sulfur molar ratios of 2:1 and 3:1. During the short-term performance tests, sampling documented SO_2, SO_3, and mercury emissions at the stack for comparison with the baseline data.

During the short-term limestone and trona injection tests, total mercury concentrations at the stack were reduced by nearly 90% and 67%, respectively. Total mercury concentrations in the stack during the limestone injection tests ranged from 1.12 to 1.18 $\mu g/Nm^3$, with particulate, oxidized, and elemental mercury concentrations of 0.01–0.18 $\mu g/Nm^3$, 0.90–1.04 $\mu g/Nm^3$, and 0.07–0.09 $\mu g/Nm^3$, respectively. Total mercury concentrations in the stack during the trona injection tests ranged from 3.54 to 3.65 $\mu g/Nm^3$, with particulate, oxidized, and elemental mercury concentrations of 0.04–0.11 $\mu g/Nm^3$, 2.07–2.15 $\mu g/Nm^3$, and 1.28–1.54 $\mu g/Nm^3$, respectively. Although the paper did not discuss a rationale for the mercury removal reported, the mercury speciation data indicate that oxidized and elemental mercury observed at the stack during baseline sampling were converted to particulate mercury and captured in the ESP.

The only significant balance-of-plant issue identified was severe slagging in the superheater, requiring Unit 5 to be shut down for slag removal. The severe slagging was attributed to the injection of limestone as an initiator, with trona injection compounding the problem. Because of the short duration of these injection tests, the degree of slagging observed is a serious operational problem. After the test was concluded, one key sootblower on Unit 5 was found to be inoperative. In addition to sootblowing, in order to mitigate the slagging problem observed, it is likely that sorbent injection must be moved to a lower-temperature regime in the furnace.

Future demonstration tests with the ROFA and ROTAMIX technology systems employing FSI are anticipated. Near-term plans include a demonstration test at the Richmond Power and Light Whitewater Station beginning in March 2005 (12).

FIELD DEMONSTRATIONS IN PROGRESS

Plant Yates – Georgia Power

URS, in conjunction with Southern Company, Georgia Power, ADA-ES, Inc., EPRI, and NETL, is conducting a mercury control project at Plant Yates, located in Newnan, Georgia. Sorbent injection tests have been conducted on both Units 1 and 2. Plant Yates Units 1 and 2 are 100-MW Combustion Engineering wet-bottom tangentially fired systems. Both units fire a low-sulfur bituminous coal and employ ESPs for particulate control. Unit 2 also employs dual flue gas conditioning (sulfur trioxide and ammonia injection) to enhance ESP performance. Unit 1 is equipped with a Chiyoda Thoroughbred-121 FGD system with a single-jet bubbling reactor (JBR) downstream of the ESP for SO_2 control. Unit 2 is not equipped with an SO_2 control system.

The testing completed at Plant Yates involved injection of three different sorbent types on each unit, DARCO FGD, Super HOK™, and NH carbon. Project results were documented in a symposium paper entitled “Sorbent Injection for Mercury Control Upstream of Small-SCA ESPs” (13).

Unit 1 baseline results (without sorbent injection) were 34% mercury removal for an average ESP inlet mercury concentration of 4.02 μg/Nm^3 and an average ESP outlet concentration of 2.64 μg/Nm^3 (corrected to 3% O_2). Unit 2 baseline results were similar, 36% mercury removal for average ESP inlet and outlet mercury concentrations of 6.04 μg/Nm^3 and 3.89 μg/Nm^3, respectively. The fly ash had a high LOI content, typically in the 9–13 wt% range for both units.

Similar mercury removal trends were observed for all three sorbent types when injected into Unit 1. Specifically, the mercury removal rate leveled off between 50% and 70% for sorbent injection rates >6 lb/Macf. Graphical depictions of the data showed that the NH carbon and the DARCO FGD data sets were nearly identical and the HOK curve was slightly lower. For the Unit 2 sorbent injection tests, the mercury removal levels out near 70% for sorbent injection rates of 6 lb/Macf and above. When the DARCO FGD sorbent was injected, a maximum mercury removal rate of 70% was observed at a sorbent injection rate of 2 lb/Macf. Increasing the DARCO FGD sorbent injection rate to 13 lb/Macf did not result in an increase in mercury removal.

Based on the tests completed, sorbent injection did not significantly affect the operation of the ESPs; however, results from longer-term testing have not yet been reported.

St. Clair Station – DTE Energy

DTE Energy, in conjunction with Sorbent Technologies Corporation and NETL, conducted a sorbent injection project at the St. Clair Station. The St. Clair Station has six boilers, four nearly identical 160-MW B&W wall-fired units and two Combustion Engineering tangentially fired boilers rated at nominally 350 MW and 540 MW, respectively. The flue gas from each of the four wall-fired boilers splits into two ducts to pass through one of eight parallel Wheelabrator-Frye c-ESPs. The sorbent injection tests were conducted on Unit No. 1 upstream of an 80-MW-equivalent ESP. The ESP used in support of this project has six fields and an SCA of 700 ft^2/1000 acfm. However, in practice, the first field is not energized. Flue gas temperature at the sorbent injection point was about 335°F at full load. Vapor-phase mercury species in the flue gas, both total and elemental, were continuously measured upstream of the sorbent injection point and downstream of the ESP. Although the St. Clair Station typically fires a blend of 85% subbituminous coal and 15% bituminous coal, some testing while firing 100% subbituminous coal was planned.

Testing conducted at the St. Clair Station was carried out in three phases: baseline, parametric, and long-term testing using B-PAC™ activated carbon. This activated carbon is bromine-impregnated and intended to be compatible with fly ash use in concrete. Baseline and parametric testing results were documented in a symposium paper entitled “Full-Scale Mercury Sorbent Injection Testing at DTE Energy’s St. Clair Station” (14). Long-term testing, defined as

24 hr per day for a 30-day period, has been completed but results were not reported in the symposium paper.

Results of the baseline testing indicated that the mercury removal across the ESP varied between 0% and 40%. Preliminary parametric test results indicated that a sorbent injection rate of 2 lb/Macf resulted in a 50% reduction in total mercury emissions beyond the baseline observations. Therefore, overall mercury removal (baseline + sorbent injection) was 60%. Although testing at the St. Clair Station has been completed, final results for the parametric and long-term testing activities were not available for inclusion in this discussion. In addition, information concerning balance-of-plant issues was not available.

Following completion of the sorbent injection testing at the St. Clair Station, Sorbent Technologies Corporation planned to move the test equipment to Duke Energy's Buck Station in North Carolina for additional full-scale sorbent injection trials. Buck Station fires low-sulfur bituminous coal. Particulate control for the unit selected employs a h-ESP that operates at 700°F. Testing at the Buck Station was scheduled for the winter of 2004–2005.

Holcomb Station – Sunflower Electric Power Corporation

ADA Environmental Solutions Inc., in conjunction with Sunflower Electric Power Corporation, NETL, and EPRI, is conducting an ACI project at Sunflower Electric Power Corporation's Holcomb Station. The Holcomb Station is located near Garden City, Kansas. The unit being used in support of this project is a load-following, subcritical, 360-MW pc-fired system. The B&W opposed-fired Carolina-type radiant boiler was designed to burn PRB coal. SO_2 and particulate emission control is accomplished with three SDA modules supplied by Niro Joy Western, followed by two very low-A/C ratio reverse-air FFs, supplied by Joy Western.

The project at the Holcomb Station involved five phases: 1) baseline testing, 2) coal blending, 3) sorbent screening, 4) parametric testing, and 5) long-term tests. As many as five different coals were expected to be fired during the test program. However, Jacobs Ranch (mine located near Gillette, Wyoming) and Black Thunder (mine located near Wright, Wyoming) were fired during the baseline, coal blending, and parametric tests. Project results were documented in two symposium papers with the same titles, "Full-Scale Evaluation of Mercury Control by Injecting Activated Carbon Upstream of a Spray Dryer and Fabric Filter," and different primary authors (15, 16).

Baseline tests were conducted firing 100% PRB. Resulting mercury removal rates varied from −3% to 23% across the SDA–FF. Coal-blending tests involved blending a western bituminous coal from the West Elk Mine with a PRB subbituminous coal in an attempt to improve upon the baseline mercury removal observed. Graphical data presented in the paper indicated that an unspecified (1.5x) blend ratio of bituminous to subbituminous coal resulted in 50% mercury removal. Increasing the unspecified blend ratio to 3x resulted in 76% mercury removal. Sorbent screening tests evaluated 20 sorbents from ten vendors. Based on the screening tests, three activated carbons were selected for parametric testing.

The three activated carbons selected for parametric testing were identified as FGD-E3 (NORIT), 208CP (Calgon), and DARCO FGD (NORIT). Each of the activated carbons was tested for a period of 4 to 7 hr. Data showed that the 208CP and DARCO FGD activated carbons resulted in similar levels of mercury removal, 50% and 54%, respectively, for a sorbent injection rate of 1.0 lb/Macf. The activated carbon identified as FGD-E3 demonstrated the best performance, resulting in 77% mercury removal at an injection rate of 0.7 lb/Macf.

A proprietary chemical additive, ALSTOM's KNX, was added to the coal at the crusher house to increase the halogen concentration in the flue gas in an attempt to improve mercury capture. Application of the additive to the coal for a 48-hr period significantly changed the speciation of the mercury at the outlet of the air preheater. Specifically, the percentage of elemental mercury was reduced from 70%–90% to 20%–30%. However, no change in mercury removal across the SDA–FF system was observed. Also, at the FF outlet, the percentage of elemental mercury was 80%, only marginally lower than the 90% elemental mercury observed during baseline sampling. Two potential explanations were offered concerning these results: 1) the chemical additive resulted in a sampling artifact at the air preheater outlet or 2) oxidized mercury was reduced to elemental mercury across the SDA–FF system. The EERC believes the potential for the chemical additive to result in a sampling artifact is more likely than the reduction of oxidized mercury across the SDA–FF system. Although the reduction of mercury species has been widely shown in WFGD systems, it is not commonly expected in dry systems.

Simultaneous injection of the DARCO FGD activated carbon upstream of the SDA–FF system and addition of the KNX chemical additive to the coal resulted in 86% mercury removal compared to 54% mercury removal with DARCO FGD injection alone. These data indicate that the use of a fuel additive to increase the flue gas halogen concentration in conjunction with ACI can significantly increase mercury removal rates.

Based on the results from parametric testing, the FGD-E3 activated carbon was selected for use during 30 days of continuous injection. Results from this long-term testing showed an average mercury removal of 93% for an ACI rate of 1.2 lb/Macf. The corresponding outlet flue gas mercury concentration was 1.13 $\mu g/Nm^3$. Balance of plant issues were not discussed in the references cited. Sample and data analysis are ongoing for this site demonstration.

Plans for subsequent work include four additional sites: 1) AmerenEU's Meramec Station, 2) Missouri Basin Power Project's Laramie River Station, 3) Detroit Edison's Monroe Station, and 4) American Electric Power's Conesville Station. Brief summaries concerning these site demonstrations are included later in this report.

Meramec Station – AmerenEU

ADA Environmental Solutions, Inc., in conjunction with AmerenEU, NETL, EPRI, and other organizations, is conducting an ACI project at AmerenEU Meramec Station Unit 2 at St. Louis, Missouri. Unit 2 is a load-following, 140-MW pc-fired system. The boiler fires 100% PRB coal from multiple mines for compliance with SO_2 emission limits. Particulate emission control is accomplished with a c-ESP manufactured by American Air Filter with an SCA of

320 ft^2/1000 acfm. The demonstration test was conducted on a flue gas volume representing a nominal capacity of 70 MW. Project results through December 31, 2004, were documented in a Quarterly Technical Report entitled "Evaluation of Sorbent Injection for Mercury Control" (17).

The project at the Meramec Station involved three phases: baseline, parametric, and long-term testing. Baseline tests were conducted firing 100% PRB from several sources. Initial mercury sampling data showed average ESP inlet and outlet mercury concentrations were 8.5 and 6.8 $\mu g/dNm^3$, respectively, indicating 20% mercury removal. Generally, baseline mercury removal rates ranged from 15% to 18% across the ESP.

Two activated carbons were selected for parametric testing, DARCO Hg (previously referred to as DARCO FGD) (NORIT) and DARCO Hg-LH (previously referred to as DARCO FGD-E3) (NORIT), as well as the use of a fuel additive. Data showed that the DARCO Hg activated carbon resulted in 72% mercury removal for an injection rate of 5 lb/Macf. No improvement in mercury removal was observed for increased carbon injection rates as high as 20 lb/Macf. Similar to other tests involving low-rank fuels, increasing the carbon injection rate beyond a certain value does not result in further mercury removal because of the limited halogen concentration in the fuel.

DARCO Hg-LH is a brominated activated carbon. Chemically treated carbons have been shown to increase mercury removal when compared to untreated carbons. Data from the parametric testing showed that the DARCO Hg-LH carbon resulted in at least 91% mercury removal at an injection rate of 3.2 lb/Macf. This represents a nominal 26% increase in mercury removal for the DARCO Hg-LH versus DARCO Hg carbon at a 36% lower carbon injection rate.

KNX was added to the coal to increase the halogen concentration in the flue gas in an attempt to improve mercury capture with and without carbon injection. Because of changes in mill operation, LOI values were higher during these tests and likely increased the observed mercury removal somewhat. However, the addition of the KNX to the fuel increased mercury removal from 22%–34% to 57%–64% without any carbon addition. When KNX additive was injected with the fuel and the DARCO Hg carbon at the inlet of the ESP, vapor-phase mercury removal was 87%. Indirectly accounting for particulate mercury indicated total mercury removal was 95% for a DARCO Hg carbon injection rate of 5 lb/Macf. These data indicate that the use of a fuel additive to increase the flue gas halogen concentration with and without the injection of an activated carbon can significantly increase mercury removal rates.

Based on the results from parametric testing, the DARCO Hg-LH activated carbon was selected for use during long-term testing. The long-term testing aimed to demonstrate 60%–70% mercury removal with no impact on ash sales and show 85%–95% mercury removal. Data from a 5-day test demonstrated that a carbon injection rate of nominally 1.0 lb/Macf resulted in 60%–70% vapor-phase mercury removal across the ESP.

Injection of the DARCO Hg-LH activated carbon during a 30-day period demonstrated >90% mercury removal across the ESP. A carbon injection rate of 4.5 lb/Macf was initially required to achieve 90% vapor-phase mercury removal across the ESP. However, after 4 days, the injection rate was reduced to 3 lb/Macf while maintaining the mercury removal objective. Based on mercury continuous emission monitor (CEM) data, vapor-phase mercury removal averaged 93% for an average carbon injection rate of 3.3 lb/Macf. ESP inlet and outlet mercury concentrations averaged 5.98 and 0.44 lb/Tbtu, respectively. Ontario Hydro sampling supported the CEM data.

The high overall mercury removal observed during this demonstration project may have been influenced to some degree by site-specific characteristics. Specifically, the 30% particulate-phase mercury observed at the ESP inlet was higher than typically observed for a PRB coal-fired system. This was attributed to the higher-than-expected LOI carbon in the ash and the high-surface-area tubular air preheater.

Balance-of-plant issues were discussed with respect to ESP performance and ash sales. No increase in stack opacity was observed during the 35 days of carbon injection at the inlet of the Unit 2 ESP. However, problems with ESP data acquisition during the long-term testing made it difficult to determine the impact of carbon injection on ESP operating parameters. Longer-duration testing was recommended for an ESP with a smaller SCA to conclusively document potential impacts on ESP performance.

Although carbon injection at a low rate (1 lb/Macf) resulted in a small increase in the ash carbon content (0.4%), previous work has shown that ash quality for concrete applications is negatively impacted by even trace amounts of activated carbon. Therefore, the ash is not expected to be salable for cement applications even at the low carbon injection rates. Segregation of the injected carbon and ash would be required to maintain ash sales. Segregation options identified for consideration included TOXECON and TOXECON II.

Sample and data analysis are ongoing for this site demonstration. Final results are expected to be addressed in a site report to be completed in September 2005. Plans for subsequent work include three additional sites: 1) Missouri Basin Power Project's Laramie River Station, 2) Detroit Edison's Monroe Station, and 3) American Electric Power's Conesville Station.

Laramie River Station – Missouri Basin Power Project

ADA-ES, Inc., in conjunction with Missouri Basin Power Project, NETL, and other organizations, will be conducting a sorbent injection project at Missouri Basin Power Project's Laramie River Station during the first quarter of 2005. Work will be conducted on Unit 3 firing a PRB coal. Laramie River Station Unit 3 is a nominal 550-MW B&W boiler. SO_2 and particulate control is accomplished with a B&W SDA–ESP combination. The ESP has an SCA of 599 ft^2/1000 acfm. The demonstration test will be conducted on a flue gas volume representing a nominal capacity of 140 MW.

The test plan for work at the Laramie River Station involves short-term parametric tests. Specifically, two carbon-based sorbents will be injected into the flue gas at the inlet of the SDA. The sorbents selected were DARCO Hg and DARCO Hg-LH. Test plans also include coal blending (PRB and western bituminous coal) tests and the use of KNX. Plans for this project were briefly addressed in a Quarterly Technical Report entitled “Evaluation of Sorbent Injection for Mercury Control” (17).

Stanton Station – Great River Energy

URS, in conjunction with Apogee Scientific, Great River Energy, ADA-ES, Inc., NETL, and EPRI, is conducting an ACI project at Great River Energy’s Stanton Station. Work is being conducted on both Unit 1 firing subbituminous coal and Unit 10 firing North Dakota lignite. Stanton Station Unit 1 is a 150-MW Foster Wheeler pc wall-fired system with low-NO_x burners. Unit 1 particulate control is accomplished with a Research-Cottrell c-ESP, and no FGD technology is employed. Unit 10 is a 60-MW Combustion Engineering pulverized coal tangentially fired system with low-NO_x burners. Particulate and SO_2 emissions are controlled using a Research-Cottrell SDA–FF.

The work plan for the Stanton Station included three phases: baseline, parametric, and monthlong testing. Specifically, activated carbon sorbents were to be injected into the flue gas stream at the inlet of the ESP on Unit 1 and the inlet of the SDA–FF on Unit 10. Project results for Unit 10 were documented in a symposium paper entitled “Full-Scale ACI for Mercury Control in Flue Gas Derived from North Dakota Lignite” (18).

Unit 10 baseline test results showed total vapor-phase mercury concentration ranging from 7.5 to 13 $\mu g/Nm^3$. Speciation data indicated that <10% of the total mercury was in an oxidized form. Consistent with the speciation data, mercury removal across the SDA–FF was <10% during baseline test periods.

Unit 10 parametric testing included evaluation of six sorbents: 1) DARCO FGD ($0.50/lb), 2) CB 200xF BS IAC (iodated coconut shell, $7.71/lb), 3) FGD-E1 (chemically treated, $0.60/lb), 4) FGD-E3 (halogenated, $0.65/lb), 5) 208CP BS SAC (superactivated coconut shell, $0.85/lb), and 6) ST BAC (brominated, $0.50–1.00/lb). The flue gas temperature range for the SDA–FF system was 175° to 184°F. Results from the parametric testing demonstrated that the NORIT DARCO FGD AC achieved 75% mercury removal at an injection rate of 6.0 lb/Macf, while the Barnebey Sutcliffe 208CP BS SAC achieved almost 60% mercury removal at an injection rate of 1.5 lb/Macf. Chemically treated carbons performed significantly better than the nonchemically treated carbons. Specifically, at an injection rate of 1.0 lb/Macf, both the DARCO Hg-LH and Sorbent Technologies ST BAC demonstrated mercury removal rates of >85%. At an ACI rate of 1.5 lb/Macf, mercury removal rates of >90% were observed for the FGD-E3 and ST BAC materials. The Barnebey Sutcliffe CB 200xF BS IAC AC did not produce 90+% mercury removal as anticipated based on previous experience. The reason for the CB 200xF BS IAC not performing up to expectations is believed to be related to particle size. Characterization of samples of the CB 200xF BS IAC used in support of this project indicated an average particle size of 87 versus 47 µm for a sample retained from tests completed previously.

Based on the parametric testing results, extended testing was completed with the NORIT FGD-E3 activated carbon for a duration of 24 days. The performance objective for the testing was 60%–75% mercury removal across the SDA–FF. Results demonstrated that an ACI rate of

1.0 lb/Macf was needed to achieve 65%–75% mercury removal. The lower mercury removal rate observed during the extended testing is believed to be related to the higher sulfur concentration when compared to parametric tests.

Based on the testing completed on Unit 10, neither the sorbent injection rate nor the sorbent type affected the FF cleaning frequency. Also, no noticeable differences were observed in the operation of the spray dryer system during the baseline tests or the ACI tests. Future activities will focus on completion of planned project testing on Unit 1 firing a subbituminous coal.

Poplar River Power Station – SaskPower

The EERC, in conjunction with SaskPower, NETL, EPRI, the North Dakota Industrial Commission, ALSTOM, and a consortium of lignite-burning utilities and mining companies in Canada and the United States, is conducting a sorbent injection project at SaskPower's Poplar River Power Station. Work is being conducted on a pilot-scale slipstream system connected to Poplar River Power Station Units 1 and 2, which fire Poplar River lignite. Units 1 and 2 are nominally 300 MW. Unit 1 is a Combustion Engineering tangentially fired boiler with six mills. Unit 2 is a B&W opposed wall-fired pc boiler with six mills. Particulate control is accomplished with c-ESPs. Unit 1 was manufactured by Lodge-Cottrell, with an SCA of 412 ft^2/1000 acfm and a design efficiency of 99.6%. Unit 2 was manufactured by American Air Filter, with an SCA of 400 ft^2/1000 acfm and a design efficiency of 99.5%.

The slipstream system includes two FFs in series. The purpose of the first FF is to remove fly ash from the flue gas stream prior to the second FF if desired. The second FF can operate at air-to-cloth ratios of 2 to 8 ft/min and flue gas temperatures of 212° to 392°F. Piping arrangements allow the first FF to be partially or completely bypassed, and the flue gas source can be selected from one of four locations: 1) Unit 1 furnace, 2) Unit 1 secondary air heater, 3) Unit 1 secondary air heater ESP, or 4) Unit 2 secondary air heater ESP. A water-based gas cooler is also available to control flue gas temperature at the inlet of the second FF. A loss-in-weight feeder supports a pneumatic conveying system for sorbent injection at the inlet of the second FF. Two CEMs were installed to permit simultaneous sampling upstream of the sorbent injection location and downstream of the second FF.

Luscar char was one of several activated carbons selected for use during the slipstream system tests. The basis for the Luscar char selection as the initial sorbent was a series of bench-scale and pilot-scale tests completed at the EERC prior to initiating the work at Poplar River Power Station (19). Particulate control device configurations included c-ESP, FF, ESP–FF (referred to as COHPAC in the United States and TOXECON when a sorbent is added between the two), and the *Advanced Hybrid*™ filter.

Variables evaluated in the previous bench- and pilot-scale tests included the following:

- Two lignites, one from the Freedom Mine in North Dakota and the other from the Poplar River Mine in Saskatchewan.

- Two carbon-based sorbents, activated Luscar char (Bienfait) and DARCO FGD. These were selected based on sorbent-screening results (reactivity and capacity), physical properties (particle size and surface area), cost, and consensus among project sponsors. The Luscar char was thermally activated at the EERC at 1472°C.

- ACI temperature, 300° and 400°F.

- PAC particle size, standard and fine (mass median diameters of 20 and 5 µm).

Results from the previous bench- and pilot-scale tests demonstrated the following:

- Based on bench-scale test results, activated Luscar char and DARCO FGD were much more effective in capturing mercury compared to other sorbents tested.

- The mercury speciation data for the two test fuels, Poplar River and Freedom lignite, were nearly identical, 85% Hg^0, 15% Hg^{2+}, and <1% particulate-bound mercury.

- Total flue gas mercury concentration was higher when the Poplar River lignite was fired, as expected, based on the mercury concentration in the coals, 0.077 mg/kg for the Freedom lignite and 0.153 mg/kg for the Poplar River lignite. Chloride concentration was very low in both fuels, <20 ppm.

- In all four control devices tested, increasing activated Luscar char and DARCO FGD injection rates and decreasing flue gas temperatures significantly improved mercury removal for both the Poplar River and Freedom fuels.

- Generally, the activated Luscar char and DARCO FGD were slightly more effective at capturing mercury when Freedom lignite was fired relative to the Poplar River lignite.

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

- Four control technologies were tested with ACI: 1) ESP–FF (TOXECON in the United States), 2) the *Advanced Hybrid* filter, 3) FF, and 4) ESP, with the performance varying somewhat depending on fuel and sorbent injection method.

- The pilot-scale results for lignite firing showed that higher ACI rates were required to achieve similar mercury removal levels when compared to full-scale data for eastern bituminous coals.

Slipstream system project activities will include evaluation of several sorbent materials (carbons with enhanced activity and lower-cost activated carbons) at various injection rates, flue gas temperature effects, carbon injection between an ESP and an FF, carbon injection between two FFs, FF air-to-cloth ratio effects, fly ash-loading effects, carbon regeneration and recycle, and process modifications to improve carbon utilization (20). Slipstream pilot-scale tests are currently under way at SaskPower's Poplar River Power Station, and some results are expected to be available by the second quarter of 2005. Based on the pilot-scale data, including plans for long-term testing (up to 1 year), estimates of full-scale technology costs and performance will be developed.

FUTURE FIELD DEMONSTRATIONS

Stanton Station – Great River Energy

The EERC, in conjunction with Great River Energy and NETL, will be conducting a sorbent injection project in 2005 at Great River Energy's Stanton Station. Work will be conducted on Unit 1 firing a subbituminous coal. Stanton Station Unit 1 is a 150-MW Foster Wheeler pc wall-fired system with low-NO_x burners. Unit 1 particulate control is accomplished with a Research-Cottrell c-ESP, and no flue gas desulfurization technology is employed.

The work plan for the Stanton Station includes three phases: baseline, parametric, and long-term testing. Specifically, impregnated and activated carbon sorbents will be injected into the flue gas at the inlet of the ESP. Plans for this project were briefly addressed in a symposium presentation entitled "Developing Mercury Control Options for Utilities Firing Western Fuels," a symposium paper entitled "Full-Scale ACI for Mercury Control in Flue Gas Derived from North Dakota Lignite," and on a NETL Web site, respectively (5, 18, 21).

Antelope Valley Station – Basin Electric Power Cooperative

The EERC, in conjunction with Basin Electric Power Cooperative and NETL, will be conducting a sorbent injection with enhancement additives project in 2005 at Basin Electric Power Cooperative's Antelope Valley Station. Work will be conducted on Unit 1 firing a North Dakota lignite. Antelope Valley Station Unit 1 is a 440-MW Combustion Engineering pc tangentially fired system with low-NO_x burners. SO_2 and particulate emission control is accomplished with SDA modules, supplied by Niro Joy Western, followed by low-air-to-cloth-ratio reverse-air FFs, supplied by Joy Western.

The work plan for the Antelope Valley Station includes three phases: baseline, parametric, and long-term testing. Specifically, activated carbon sorbents will be injected into the flue gas stream at the inlet of a SDA module. Plans for this project were briefly addressed in a symposium presentation entitled "Developing Mercury Control Options for Utilities Firing Western Fuels" and on a NETL Web site, respectively (5, 21).

Milton R. Young Station – Minnkota Power Cooperative

The EERC, in conjunction with Minnkota Power Cooperative and NETL, will be conducting a mercury oxidation project in 2005 at Minnkota Power Cooperative's Milton R. Young Station. Work will be conducted on Unit 2 firing North Dakota lignite. Milton R. Young Station Unit 2 is a 450-MW B&W cyclone-fired system. Unit 2 particulate control is accomplished with a Wheelabrator-Frye c-ESP. SO_2 control is accomplished with a WFGD system.

The work plan for the Milton R. Young Station includes three phases: baseline, parametric, and long-term testing. Specifically, fuel and flue gas additives will be used in an attempt to shift mercury speciation from largely elemental to largely oxidized. Plans for this project were briefly addressed in a symposium presentation entitled "Developing Mercury Control Options for Utilities Firing Western Fuels" and on a NETL Web site, respectively (5, 21).

Monticello Station – Texas Utilities Company

The EERC, in conjunction with Texas Utilities Company and NETL, will be conducting a mercury oxidation project in 2005 at Texas Utilities Company's Monticello Station. Work will be conducted on Unit 3 firing Texas lignite. Monticello Station Unit 3 is a 750-MW B&W pc wall-fired system. Unit 3 particulate control is accomplished with a Walther c-ESP. SO_2 control is accomplished with a WFGD system.

The work plan for the Monticello Station includes three phases: baseline, parametric, and extended testing. Specifically, fuel and flue gas additives will be used in an attempt to shift mercury speciation from largely elemental to largely oxidized to allow subsequent capture in the wet scrubber. Plans for this project were briefly addressed in a symposium presentation entitled "Developing Mercury Control Options for Utilities Firing Western Fuels" and on a NETL Web site, respectively (5, 21).

Big Brown Station – Texas Utilities Company

The EERC, in conjunction with Texas Utilities Company, NETL, EPRI, ADA-ES, Inc., B&W, and several Texas state agencies and a consortium of Texas and North Dakota utilities, will be conducting a 24-month project entitled "Field Testing of ACI Options for Mercury Control at TXU's Big Brown Station" beginning in 2005. Texas Utilities Company's Big Brown Station is located near Fairfield, Texas. Work will be conducted on one of two units firing a Texas Basin lignite or a lignite–subbituminous coal blend. Big Brown Station Units 1 and 2 are 600-MW Combustion Engineering pc tangentially fired systems. Particulate control is accomplished with Research-Cottrell c-ESPs.

The test plan for work at the Big Brown Station includes three phases: baseline, parametric, and long-term testing. Specifically, activated carbon sorbents will be injected into the flue gas stream at the inlet of a c-ESP. Plans for this project were briefly addressed in a symposium presentation entitled "Developing Mercury Control Options for Utilities Firing Western Fuels" and on a NETL Web site, respectively (5, 21).

Monroe Station – Detroit Edison

ADA-ES, Inc., in conjunction with Detroit Edison, NETL, and other organizations, will be conducting a sorbent injection project at Detroit Edison's Monroe Station during the second quarter of 2005. Work will be conducted on Unit 4 firing a PRB–eastern bituminous coal compliance fuel blend for SO_2 emissions. Monroe Station Unit 4 is a nominal 785-MW B&W boiler with an SCR system for NO_x control. Particulate control is accomplished with a Research-Cottrell c-ESP having an SCA of 258 ft^2/1000 acfm. The demonstration test will be conducted on a flue gas volume representing a nominal capacity of 196 MW.

The test plan being developed for work at the Monroe Station includes three phases: baseline, parametric, and long-term testing. Specifically, carbon-based sorbents (not yet selected) will be injected into the flue gas stream at the inlet of the ESP. Plans for this project were briefly addressed in a quarterly technical report entitled "Evaluation of Sorbent Injection for Mercury Control" and on a NETL Web site, respectively (17, 21).

Conesville Station – American Electric Power

ADA-ES, Inc., in conjunction with American Electric Power (AEP), NETL, and other organizations, will be conducting a sorbent injection project at AEP's Conesville Station during the third quarter of 2005. Work will be conducted on Unit 5 or 6 firing an eastern bituminous–PRB coal blend. Conesville Station Units 5 and 6 are nominal 400-MW Combustion Engineering boilers. Particulate control is accomplished with a Research-Cottrell c-ESP having an SCA of 301 ft^2/1000 acfm. The ESP is followed by a WFGD system for control of SO_2 emissions.

The work plan being developed for the Conesville Station includes three phases: baseline, parametric, and long-term testing. Specifically, carbon-based sorbents (not yet selected) will be injected into the flue gas stream at the inlet of the ESP. Plans for this project were briefly addressed in a quarterly technical report entitled "Evaluation of Sorbent Injection for Mercury Control" and on a NETL Web site, respectively (17, 21).

URS

URS, in conjunction with Texas Utilities Company, Georgia Power, American Electric Power, NETL, EPRI, Southern Company, and Degussa Corporation, will be conducting a 12-month project entitled "Field Testing of Additive to Remove Mercury from FGD Systems and Prevent Re-emissions" beginning in 2005. The project will evaluate the use of an additive in wet lime and limestone FGD systems to prevent mercury reemissions in coal-fired power plants. The additive is intended to prevent oxidized mercury captured in an FGD system from being reduced and subsequently reemitted into the flue gas stream as elemental mercury. In addition, the additive assists in the removal of mercury from by-products and its separate disposal. Field sites selected for this demonstration project include 1) Texas Utilities Company's Monticello Station at Mt. Pleasant, Texas; 2) Georgia Power's Plant Yates at Newnan, Georgia; and 3) AEP Conesville Station at Conesville, Ohio. Some information concerning the project is summarized on a DOE NETL Web site (21).

ADA-Environmental Solutions, Inc.

ADA-ES, Inc., in conjunction with EPRI, Dynegy, NETL, and Olgethorpe Power, will be conducting a project entitled "Testing TOXECON II and Unique Sorbent Injection into h-ESPs" beginning in 2005. TOXECON II technology involves ACI directly into the downstream collecting fields of an ESP. With the majority of the fly ash collected in the upstream fields, only a small portion of the fly ash is contaminated with carbon. The second technology to be tested involves the injection of novel sorbents for mercury removal on units with h-ESPs. Field sites identified included Mid America Energy's Louisa Station and Council Bluffs Station, AEP's Gavin Station, and Entergy's Independence Station. Some information concerning the project is summarized on a NETL Web site (21).

ALSTOM Power, Inc.

ALSTOM Power, Inc., in conjunction with PacificCorp, Basin Electric Power Cooperative, Reliant Energy, NETL, the EERC, the North Dakota Industrial Commission, and Minnkota Power Cooperative, will be conducting a 30-month project entitled "Testing Proprietary Activated-Carbon-Based Sorbents and Additives" beginning in 2005. The activated carbon-based sorbent, prepared with chemical additives, is intended to promote oxidation and capture of mercury. Field sites selected for this demonstration project include the following: 1) PacificCorp's Dave Johnston Station at Glenrock, Wyoming, firing a subbituminous coal; 2) Basin Electric's LOS at Stanton, North Dakota, firing a North Dakota lignite; and 3) Reliant Energy's Portland Station at Portland, Pennsylvania, firing a bituminous coal. Some information concerning the project is summarized on a NETL Web site (21).

GE Energy

GE Energy, in conjunction with Tennessee Valley Authority (TVA) and NETL, will be conducting an 18-month project entitled "Testing Technology for Concurrent Control of Hg and NO_x Emissions" beginning in 2005. GE Energy has developed a cost-effective technology combining mercury and NO_x control with a mercury removal objective of at least 90%. The field site selected for this demonstration is TVA's John Sevier Station in Rogersville, Tennessee, firing a bituminous coal. Some information concerning the project is summarized on a NETL Web site (21).

Sorbent Technologies Corporation

Sorbent Technologies Corporation, in conjunction with Midwest Generation, Progress Energy, Headwaters/ISG Resources, NETL, Fuel Tech, Inc., Western Kentucky University, and Acticarb Tailored Products LLC, will be conducting a 24-month project entitled "Testing B-PAC™ Technology for Mercury Control," beginning in 2005. This project will demonstrate how the injection of brominated powdered activated carbon (B-PAC™) and a concrete-safe version of the carbon can cost-effectively control mercury emissions from coal-fired power plants operating both c- and h-ESPs. Specific demonstration sites were identified as Midwest Generation's Will County and Crawford Stations and Progress Energy's Lee Station. Some information concerning the project is summarized on a NETL Web site (21).

Amended Silicates

ADA Technologies has developed a new class of clay-based adsorbents for mercury and other metals, called Amended Silicates™ (22, 23). These materials use inexpensive silicate substrates, impregnated with chemicals that possess a strong affinity for the target metal. The sorbent is prepared by ion exchange between the silicate substrate and a solution containing one or more of a group of polyvalent metals including tin (both Sn[II] and Sn[IV]), iron (both Fe[II] and Fe[III]), titanium, manganese, zirconium, and molybdenum, dissolved as salts, to produce an exchanged substrate. Controlled addition of sulfide ions to the exchanged silicate substrate produces the sorbent.

Bench-scale testing with the best formulations confirmed that the Amended Silicates exhibit mercury capacities greater than that of activated carbon. The primary advantage of these materials is their silicate structure; Amended Silicates do not appear to adversely impact the use of fly ash as a pozzolan material. Amended Silicates also are less sensitive to moisture, temperature, and acid gas concentration than carbon. These are detrimental factors in the use of activated carbon for mercury control, as excess carbon in fly ash could force a utility to pay for ash disposal rather than collecting revenue from its sale. Handling and injection of Amended Silicates are similar to that of activated carbon. The silicates are easily collected in an ESP or FF. Following the extensive laboratory tests, pilot-scale tests were done using a nominal 500–1000-acfm slipstream at Xcel Energy's Comanche Station, which burns a PRB coal. Both the pilot- and full-scale plant were equipped with a reverse-gas FF. The temperature of the pilot unit ranged from 200° to 325°F (94° to 163°C). Two Amended Silicates sorbents were tested at rates that were varied from 1.6 to 9 lb/Macf. For comparison, ACI also was tested at an add rate of 4.2 lb/Macf. The results are shown in Figure 2. As can be seen, the Amended Silicates provided performance similar to activated carbon with the advantage of lower unit cost and little, if any, impact on the fly ash. It is expected that the cost of the Amended Silicates will be \$0.30–\$0.40/lb compared to \$0.50 for DARCO FGD. The same equipment used for ACI can be used to inject Amended Silicates; therefore, capital costs will be the same.

For those power plants that sell their fly ash, the use of Amended Silicates may be an option. However, long-term testing is necessary to conclusively prove the technology. Full-scale demonstration tests are being planned at Xcel Energy's Arapahoe Station and at Cinergy's 175-MW Miami Fort Station. The Arapahoe Station is similar to the Comanche Station, as it burns a PRB coal and has an FF for particulate control. Testing is expected to begin early in 2005. Testing at Cinergy's 175-MW Miami Fort Station will be done as part of NETL's full-

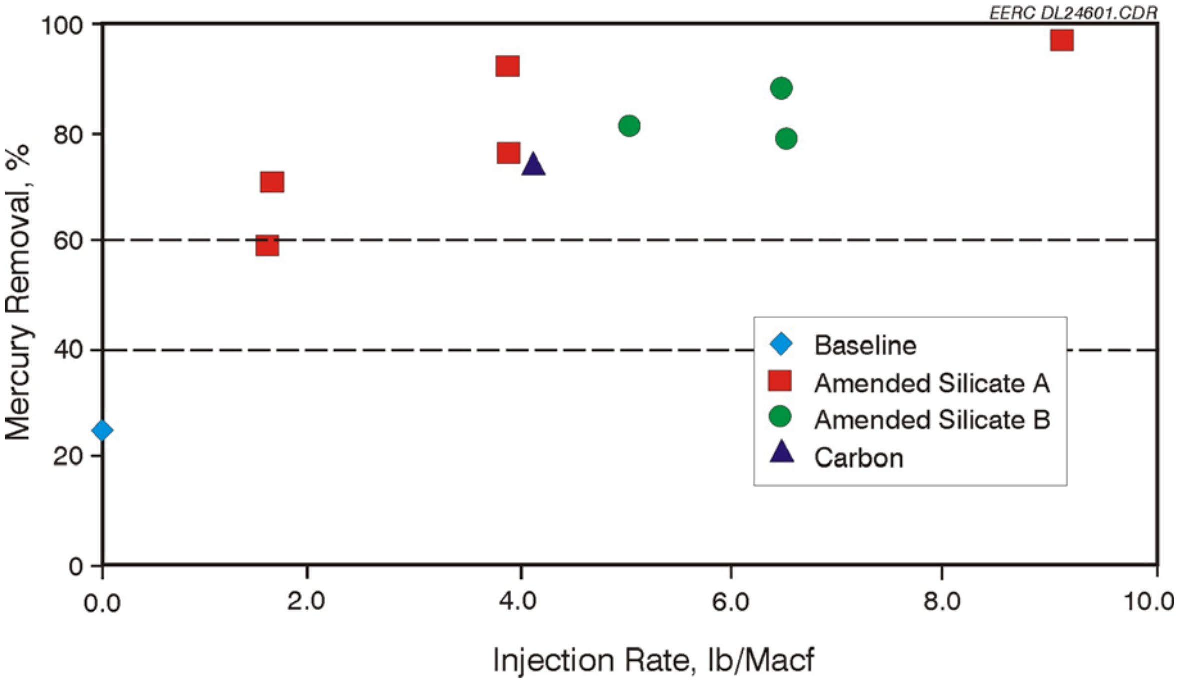

Figure 2. Mercury removal rates from pilot slipstream tests.

scale demonstration program. The unit upon which the test will be conducted at the Miami Fort Station has an ESP and burns an Ohio bituminous coal. Testing at this facility is also expected to begin in the spring of 2005. In a commercial partnership with CH2M Hill, the sorbent-manufacturing process is being scaled up to manufacture quantities of Amended Silicate sorbents to meet projected needs of the demonstration tests with the anticipation of increasing production for a permanent, full-scale operation.

UPDATES ON PREVIOUS QUARTERLIES

Quarter 1 was a general overview of the topic “Sorbent Control Technologies for Mercury Control.” The specific technologies are described in the current quarterly as they relate to specific field demonstrations.

Quarter 2 was on the topic of “Mercury Measurement”; there have been a number of developments since April 2004 (see Appendix A).

Quarter 3 was on the topic of “Advanced and Developmental Mercury Control Technologies”; the updates are in Appendix B.

Quarter 4 has no updated information on the rerelease of mercury from coal combustion by-products.

Quarter 5 has no updated information on mercury fundamentals.

UPCOMING EVENTS

International Conference on Clean Coal Technologies for Our Future
May 10–12 2005, Sardinia, Italy
Contact Rodney Anderson (304) 285-4709
http://fossil.energy.gov/news/events/

IGCC Symposium: Examine Technology Risk, Costs, Financing, Environmental Performance, and IGCC's Future in the Power Industry
June 2–3, 2005, Pittsburgh, Pennsylvania
http://www.events.platts.com

A&WMA 98th Annual Conference and Exhibition
June 21–24, 2005, Minneapolis, Minnesota
http://www.awma.org

230th ACS National Meeting
August 28–September 1, 2005, Washington, D.C.
http://oasys.acs.org/acs/230nm/topics.html

Air Quality V: Mercury, Trace Elements, and Particulate Matter Conference
September 18–21, 2005, Washington, D.C.
http://www.undeerc.org

Eighth International Conference on Mercury as a Global Pollutant
August 6–11, 2006, Madison, Wisconsin
http://www.mercury2006.org/Default.aspx?tabid+1393

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APPENDIX A

UPDATE OF QUARTER 2 MERCURY MEASUREMENT

UPDATE OF QUARTER 2 MERCURY MEASUREMENT

Since April 2004, when the Mercury Information Clearinghouse second quarterly report was released, there have been a number of developments in mercury measurement, including the following:

- On March 15, 2005, the Clean Air Mercury Rule was announced by the U.S. Environmental Protection Agency (EPA), regulating mercury from U.S. coal-fired power plants for the first time.
- New mercury measurement techniques have been developed.
- Additional experience was gained with next-generation continuous mercury monitors (CMMs).

Clean Air Mercury Rule (http://www.epa.gov/mercuryrule)

The new regulations for mercury emissions from U.S. coal-fired boilers were announced under Section 111 of the Clean Air Act Amendments and, as such, will be cap-and-trade rules. Some form of CMM will be required. EPA has announced that two measurement methods will be accepted: the sorbent trap method previously referred to as Proposed EPA Method 324 and/or QuickCEMs™, now officially named 40 CFR, Part 75, Appendix K, and CMMs. It is expected that most U.S. utilities will use the sorbent trap method; however, this could change as more robust CMMs become available. For both of these methods, EPA has established performance specifications (PS 12A), which relate to the setup, certification, and quality assurance/quality control (QA/QC) for each method. A summary of these specifications is provided; for details, go to www.epa.gov/mercuryrule.

40 CFR, Part 75, Appendix K Specifications

Each sorbent trap is to be configured with three distinct but identical sections connected in series such that each can be analyzed separately. The first section is to be the primary trap for the gas-phase mercury. The second section is to be a backup to prevent mercury breakthrough. The third section is designated for QA/QC and is, therefore, spiked with a known amount of gaseous elemental mercury (Hg^0) prior to the trap. Also, paired traps must be used, with the mercury results averaged. The specific sorbent and analysis types are not specified; however, the method used must pass the QA/QC requirements as shown in Table A-1. The sampling flow rate must maintain proportional sampling (the ratio of stack flow rate to sample flow rate is constant). Also, a continuous monitoring system must be used to determine the moisture in the stack gas.

Table A-1. Sorbent Trapping QA/QC Specifications

QA/QC Specifications	Acceptance Criteria	Frequency	Consequences if Not Met
Pretest Leak Check	≤4% of target sampling rate	Prior to sampling	Sampling cannot begin
Posttest Leak Check	≤4% of target sampling rate	After sampling	Sampling invalidated
Proportional Sampling Rate	Maintain within 25% of initial from first hour of collection	Every hour	Case-by-case evaluation
Sorbent Trap Sec. 2 Breakthrough	<5% of Sec.1 Hg mass	Every sample	Sample invalidated
Paired Sample Trap Agreement	<10% relative deviation	Every sample	Sample invalidated
Spike Recovery Study	±15% for each of three Hg conc. levels	Prior to analyzing field samples and prior to using a new sorbent	Field samples cannot be analyzed until criteria are met
Multipoint Analyzer Calibration	10% of true value and $r^2 \geq 0.99$	Each day prior to analysis of field samples	Recalibrate until criteria are met
Analysis of Standard Sample	10% of true value	Each day prior to analysis of field samples	Repeat until criteria are met
Spike Recovery (Sec. 3 of trap)	±25% of spiked concentration	Every sample	Paired sample trap invalidated
RATA (paired OH trains)	RA≤20.0% or mean diff. of ≤1 µg/dscm	For initial certification, then annually	Cannot begin sampling until RATA is passed
Dry gas meter calibration (initially at 3 setting and 1 setting thereafter)	Calibration factor (Y) within 5% of average value from initial 3 point calibration	Prior to initial use, quarterly thereafter	Recalibrate the meter at three orifice settings to determine a new Y
Temperature Sensor Calibration	Absolute temperature measured by sensor within ±1.5% of ref. sensor	Prior to initial use, quarterly thereafter	Recalibrate; sensor may not be used until specifications are met
Barometer Calibration	Absolute pressure measured by instrument within ±10 mm Hg reading with a Hg barometer	Prior to initial use, quarterly thereafter	Recalibrate; instrument may not be used until specifications are met

CMMs

The requirements for the use of CMMs are essentially the same as previously stipulated in PS 12A when the proposed mercury rule was released for public comment in January 2004. The primary difference is that for calibration and system checks, either elemental or oxidized mercury (Hg^{2+}) calibration gases can be used. A summary of the requirements is presented below.

For initial certification, EPA requires the following tests for CMMs:

- A 7-day calibration error test using Hg^0 calibration gas standards or a National Institute of Standards and Technology (NIST) traceable source of Hg^{2+} may be used. The monitor must meet a performance specification of 5.0% of span on each day of the test (for span values of 10 µg/scm) or an alternate specification of 1.0 µg/scm absolute difference between reference gas and the CMMs.

- A three-point linearity check, using Hg^0 calibration gas standards. The monitor must meet a performance specification of 10.0% of the reference concentration at each gas level or an alternate specification of 1.0 µg/scm absolute difference between reference gas and the CMMs.

- A cycle time test. The maximum allowable cycle time would be 15 minutes.

- A RATA using paired Ontario Hydro (OH) method trains. The results must agree within 10% of the relative standard deviation, and the results should be averaged.

- A bias test, using data from the RATA, to ensure that the CMMs is not biased low with respect to the reference method.

- A three-point system integrity check, using mercuric chloride ($HgCl_2$) standards. The monitor would be required to meet a performance specification of 5.0 % of span at each gas level.

For ongoing QA/QC, the following QA/QC tests are required:

- Daily two-point calibration error checks, using Hg^0 gas standards or a NIST traceable source of Hg^{2+}. The monitor would be required to meet a performance specification of 7.5% of span or an alternate specification of 1.5 µg/scm absolute difference between reference gas and CMMs.

- If daily calibrations are done using Hg gas standards, a weekly system integrity check at a single point must also be completed using a NIST traceable source of Hg^{2+}. The weekly test is not required if daily calibrations are performed with a NIST traceable source of oxidized Hg.

- Quarterly three-point linearity checks, using Hg^0 gas standards. The performance specifications would be the same as for initial certification. Quarterly three-level system integrity checks (using a NIST traceable source of Hg^{2+} may be performed in lieu of the quarterly linearity checks with Hg^0.

- Annual RATA and bias tests. The performance specifications would be the same as for initial certification.

New Mercury Measurement Methods

Two new mercury measurement methods, the E.ON Engineering sorbent trap method and the Cooper Environmental Services LLC filter tape XACT method, were presented at the U.S. Department of Energy National Energy Technology Laboratory- and EPRI-sponsored Mercury Measurements Workshop, July 2004. The presentation about the two methods can be obtained at the following Web site: www.netl.doe.gov/publications/proceedings/04/HgWorkshop.

The E.ON method is similar to other sorbent trap methods such as the flue gas mercury speciation (FAMS) method that was described in the Quarterly 2 report. The only real difference is that in place of the solid KCl trap, an adsorber resin is used to remove the Hg^{2+}. The adsorber resin is a Dowex 1 × 8 resin that chemisorbs Hg^{2+}. A schematic of the train is shown in Figure A-1.

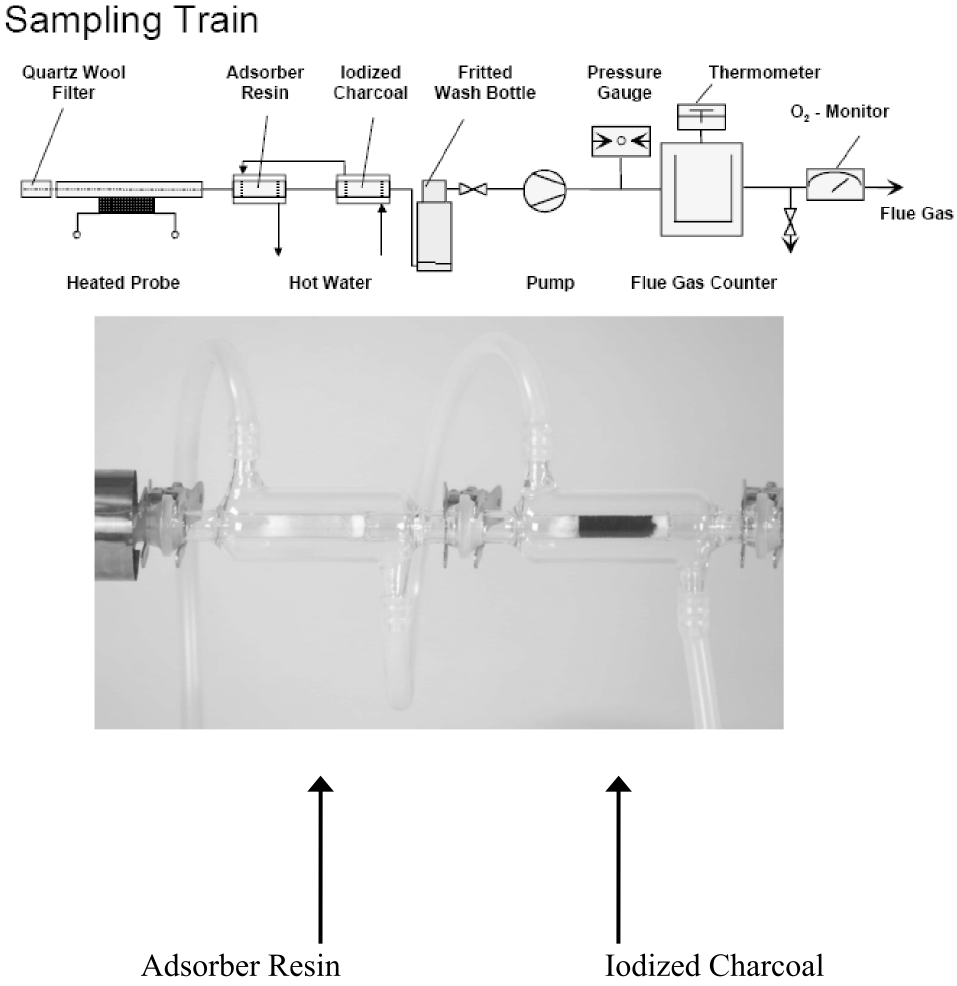

Figure A-1. Diagram of E.ON Engineering mercury speciation sampling train.

The detection limit is stated by E.ON as 0.05 μg/m^3, assuming a 1-m^3 sampling volume. Table A-2 presents the blank test results for this method.

Because this method was developed in Germany, there has only been limited testing in the United States. This method must be compared to the Ontario Hydro (OH) method and validated. At this time, only E.ON is using the method, so its availability is limited. In addition, little is known about the QA/QC procedures that are outlined in the Clean Air Mercury Rule for 40 CFR, Part 75, Appendix K as they relate to the E.ON method.

Table A-2. Specification for the E.ON Mercury Speciation Method

Trap	Average Value, µg/m^3	Std. Dev., µg/m^3	Detection Limit*, µg/m^3
Digestion Blank	0.004	0.002	0.010
Dowex Resin Blank	0.007	0.003	0.015
Iodized Charcoal Blank	0.012	0.006	0.030

*Detection limit defined as 5 × std. dev.

The filter tape XACT method is a semicontinous multimetals analyzer that uses an intermittently moving tape containing an adsorbent that is sequentially exposed to flue gas. Once a deposit forms on the tape, it is analyzed for mercury and other metals using x-ray fluorescence x-ray fluorescence (XRF). The result is a total mercury concentration (particulate-bound and gaseous forms). The only conditioning required is the addition of dilution gas to cool the sample. XRF is a nondestructive technique so the sample filters may be archived for future analysis. This system can be used to measure 25 elements in stack gas emissions. The sample time can be varied from about 15 minutes per analysis to over 1 hour, depending on how long the tape is exposed to the flue gas. The detection limit is defined by the period of time that each section of the tape is exposed to the flue gas. For very low mercury concentrations, longer periods of time are needed compared to locations with higher mercury concentrations. For a typical coal boiler (10 µg/Nm^3), 1 hr would provide a detection limit of 0.1 µg/Nm^3.

In many ways, the QA/QC for the method is similar to those for other continuous/ semicontinuous mercury monitors and may well fit under the PS-12A specifications listed in the new mercury rule. However, the 15-minute cycle time may be a problem. Currently, Cooper Environmental is doing system calibrations using NIST thin-film standards and confirming the calibration factors with a quantitative aerosol generator (QAG). These QAG tests have demonstrated that the XACT method has a precision of about 2% and accuracies better than 5% for the five metals, Cr, As, Cd, Hg, and Pb.

An updated CMM vendor list is shown in Table A-3. Several of the monitors listed previously are not considered commercially available for measuring mercury in combustion flue gases. In addition, several companies, including Ohio Lumex and PS Analytical, are developing new pretreatment/conversion systems that should be commercially available by the fall of 2005.

Comparisons of Wet-Chemistry and Dry Pretreatment/Conversion Systems

A conditioning/conversion system is arguably the most important part of a mercury measurement system. This is the point where the unknown sample gas is conditioned by removing interfering flue gas components or reducing their impact by dilution. Flue gas composition varies widely based on coal type and plant configuration, presenting numerous challenges for the measurement systems. Wet-chemistry systems have been used extensively, and many of their limitations have been identified. These systems remove interfering constituents by bubbling the sample gas through reactive solutions. The main concerns with the wet systems include the following:

- The amount of chemicals used and the volume of waste generated

- Capture of an unknown amount of CO_2, which affects the sample volume
- Mercury "hang-up" in the system, which changes with changing equilibrium
- Condensation of flue gas constituents such as SO_3 and selenium
- Potential for unidentified chemical reactions

A model to predict CO_2 capture by the NaOH solution is under development. Mercury hang-up changes in flue gas and the mercury concentration spikes, indicating a release of mercury from the sampling system. The spikes are attributed to changes in the equilibrium of the mercury in the sample gas with the small amount of mercury captured in the sampling system. Changes in the acid gas concentrations can cause mercury to desorb from surfaces where it has accumulated over time. When condensation of flue gas constituents is observed, the system temperatures are increased to eliminate it.

As the use of dry pretreatment/conversion systems becomes more common, new issues are emerging. All dry systems use thermal treatment to convert all the mercury in the flue gas to elemental mercury. Some monitors (Ohio Lumex and the Thermo Electron system under development) use direct thermal treatment. The entire system remains hot to prevent recombination. More commonly, a catalyst is used to allow thermal decomposition of mercury at lower temperatures. Examples of such systems include the Horiba/NIC DM-6B and Durag HM-1400 TR. For a monitor that uses the more sensitive cold-vapor atomic fluorescence method (i.e., Tekran 3300), dilution thermal systems can be used.

In addition to converting the mercury, the unit must also deliver mercury to the analyzer without any interfering gases. Most of these systems are not completely dry; they often use small amounts of chemicals or water to remove potential contaminants from the sample gas stream. In addition to being susceptible to the same problems as wet-chemistry conditioning/conversion systems, they have had issues with catalyst life. Catalysts have either failed or exhibited a short life when challenged with sample streams containing high concentrations of acid gases. For example, in tests using the Horiba/NIC system at a plant with high levels (>50 ppm) of SO_3, the catalyst lasted less than 24 hours. In some plants, selenium precipitates out in the conversion system, reducing measured mercury. This can usually be rectified by ensuring there are no cold spots in the system. In some cases, it is necessary to use a small amount of basic solution to remove selenium prior to the catalyst.

The dry systems that utilize dilution to eliminate the effects of interfering gases have not been used for any period of time in high-acid gas environments; therefore, it is unknown how they will perform under these conditions. However, at a facility firing a Powder River Basin coal (low sulfur and chlorides), the dry Tekran system has been in continuous operation for more than 1 year with no reported problems. The Energy & Environmental Research Center has been measuring the mercury concentration at the inlet and outlet of a slipstream at a lignite facility (again, relatively low in sulfur and chlorides) since September 2004 using two Tekran dry systems. The only issue that has been identified is fine particulate matter penetrating the inertial separation probe. Potentially, particulate matter could build up in the critical orifice in the conversion unit used to control the sample gas flow rate. Another challenge is that if something goes wrong with the analyzer, it is impossible to verify the dilution rate in the field. Because of the system design, the instrument must be returned to Tekran for a dilution rate check.

Table A-3. Commercially Available CMMs

Vendor	Product	Analysis Method	Pretreatment/ Conversion	Speciating[1]	Web Site
Cooper Environmental Services[2]	XACT	XRF	Dilution for cooling	Hg^{total}(g, p)	www.cooperenvironmental.com
Durag	HM-1400 TR	CVAA	Thermal catalytic	No	www.durag.net
EcoChem Analytics[3]	Hg-MK II	CVAA	Thermal catalytic	Yes	www.ecochem.biz
Envimetrics	Argus-Hg 1000	Atomic emission	Thermal catalytic	No	www.envimetrics.com
Horiba/NIC	DM-6B	CVAA	Thermal catalytic	Yes	www.environ.hii.horiba.com
OhioLumex	RA-915+	CVAA	Direct Thermal	No	www.ohiolumex.com
Opsis AB	HG200	CVAA	Dilution system	Yes	www.opsis.se
PS Analytical	Sir Galahad	CVAF	Wet/dry chemistry (2005)	Yes	www.psanalytical.com
Semtech Metallurgy AB	Hg 2010	CVAA	Wet chemistry	No	www.semtech.se
Sick UPA GmbH	MERCEM	CVAA	Wet chemistry	No	www.cemsi.on.ca
ST^2 Technologies	SM-3	CVAA	Thermal catalytic	Yes	www.st2-service.com
Tekran, Inc.	3300	CVAF	Dilution system	Yes	www.tekran.com

[1] The analyzers that speciate mercury measure total gas-phase mercury and elemental mercury and determine oxidized mercury by difference.
[2] The Cooper Environmental XACT analyzer is a multimetal unit that measures both particulate-bound mercury and total gas-phase mercury.
[3] The EcoChem Hg-MK II can be purchased as a speciating dual analyzer or as single, total gas-phase mercury analyzer.

APPENDIX B

UPDATE OF QUARTER 3
ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

UPDATE OF QUARTER 3 ADVANCED AND DEVELOPMENTAL MERCURY CONTROL TECHNOLOGIES

MerCAP™

Results from initial testing at the Stanton Station were presented at the most recent Mega Symposium, held in Washington, D.C., August 30–September 2, 2004 (1). While plans are to evaluate the technology on a full baghouse compartment (6-MW scale), the only results reported were from a much smaller 140-acfm test probe. The reported results with several configurations showed rapid deterioration of mercury removal from a starting value of 80% to less than 20% within 15–20 hours of operation. This is in stark contrast to the previously reported 2000 hr of operation with only moderate deterioration. These latest results indicate that a better understanding is needed of how the presence of specific flue gas components can lead to rapid deactivation of the substrate surfaces.

EnviroScrub Pahlman Process

Recent mercury control results from slipstream testing at the Minnesota Power Boswell plant were presented at the last Mega symposium (2) and in an Energy & Environmental Research Center report to the U.S. Department of Energy National Energy Technology Laboratory (3), which cofunded the work. The best mercury removal seen was 99% (elemental) and 94% (total) for a batch test in which testing was started immediately following sorbent loading. However, when sampling was started 2 hr after different levels of sorbent loading, total mercury removal was 76% in one case and 91% for the second case. At longer exposure times, the level of mercury control further declined even though the SO_2 removal remained over 90%. This suggests that the process may need to be optimized for the highest level of mercury control independent of the level of SO_2 control. These batch tests may not be indicative of the process in continuous mode. Mercury control with the continuous process has not been demonstrated.

Mercury Control with the *Advanced Hybrid*™ Filter

The perforated-plate geometry of the *Advanced Hybrid*™ filter is intended to provide sufficient gas–solid contact to achieve over 90% mercury removal at low carbon addition rates, even though most of the carbon is collected on the perforated plates rather than on the bags. To prove this, recent tests measured the amount of mercury collected by the perforated plates in the *Advanced Hybrid*™ filter apart from any mercury control on the filter bags (4). Results showed that at a relatively small carbon injection rate with an enhanced sorbent, 90% mercury control was seen across the plates. This is important because it shows that efficient mercury control can be achieved by collecting the carbon on the perforated plates alone. To achieve good mercury control, the carbon need not be collected on the filter bags, which can lead to pressure drop problems. These results are consistent with pilot-scale and field data that have always shown that carbon injected upstream of the *Advanced Hybrid*™ filter for mercury control has little or no effect on pressure drop.

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MERCURY INFORMATION
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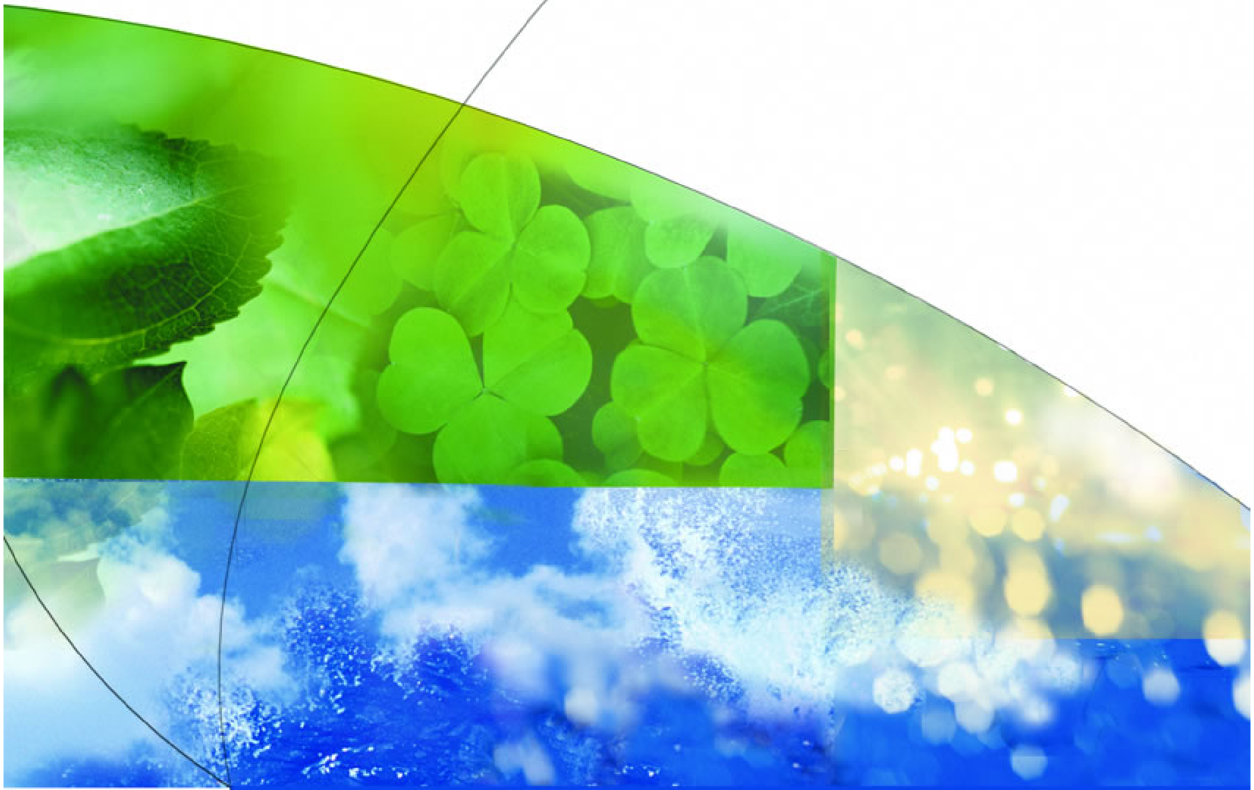

Quarter 7 – Mercury Regulations in the United States: Federal and State

July 2005

Canadian Electricity Association
Association canadienne de l'électricité

EERC
Energy & Environmental Research Center

Center for Air Toxic Metals

DEPARTMENT OF ENERGY
UNITED STATES OF AMERICA

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 7 – MERCURY REGULATIONS IN THE UNITED STATES: FEDERAL AND STATE

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REPORT AVAILABILITY

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650 and the CEA Mercury Program Web site (www.ceamercuryprogram.ca).

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EXECUTIVE SUMMARY

On March 15, 2005, the U.S. Environmental Protection Agency (EPA) announced the new Clean Air Mercury Rule for coal-fired power plants. The rule makes the United States the first country in the world to regulate mercury emissions from coal-fired power plants. It was the decision of the EPA to regulate mercury under Section 111 rather than Section 112 of the Clean Air Act. Under Section 111, a cap-and-trade rule was established. The Clean Air Mercury Rule is viewed by EPA to function in conjunction with the Clean Air Interstate Rule (CAIR) to reduce mercury emissions nationwide. It is expected that the additional wet flue gas desulfurization (FGD) and selective catalytic reduction (SCR) systems that will be installed to comply with the CAIR SO_2 and NO_x requirements in 28 eastern states will provide a substantial mercury cobenefit.

Based on the 1997 Information Collection Request (ICR) data, it has been established that current U.S. mercury emissions from coal-fired electric utilities total 48 tons a year. The cap-and-trade provision of the new rule would reduce that to 38 tons of mercury a year in 2010, a reduction of 20.8%. It is fully expected that the addition of new wet FGD and SCR systems to reduce SO_2 and NO_x under CAIR will allow the states to meet the 2010 mercury reduction requirements without additional mercury controls. By 2018, coal-fired power plants will be required to make further reductions to 15 tons a year, a total reduction of 68.8% from 1997 emissions. To ensure the required mercury reduction is met and to facilitate trading, EPA has established emission budgets for each state based on the baseline heat input adjusted for the coal burned for each plant in a given state.

The new Clean Air Mercury Rule has proven to be very controversial, as ten state attorneys general have filed suit against EPA and the mercury rule. Three of these states, New Jersey, Massachusetts, and Connecticut, have promulgated much more restrictive regulations. The state of Wisconsin also passed a mercury reduction rule; however, it has been superseded by the federal Clean Air Mercury Rule. A summary of the requirements for the three states with regulations are shown in Table ES-1.

Table ES-1. Summary of State Mercury Regulations

State	Date	Emission Limit	Nominal Removal	Date	Emission Limit	Nominal Removal
Massachusetts	01/01/2008	0.0075 lb/GWh	85%	10/01/2012	0.0025 lb/GWh	95%
New Jersey	12/15/2007	3 mg/MWh	90%	–	–	–
Connecticut	07/01/2008	0.6 lb/10^{12} Btu	90%	–	–	–

In addition to the states that have passed legislation, several other states have had legislative activity, although it is not expected that legislation will pass in any of those states this year.

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 7 – MERCURY REGULATIONS IN THE UNITED STATES: FEDERAL AND STATE

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of developments in mercury monitoring, control, policy, and research.

Recent developments in the area of mercury regulations for coal-fired power plants in Canada in the form of Canada-Wide Standards (CWS) and the United States in the U.S. Environmental Protection Agency's (EPA's) Clean Air Mercury Rule (CAMR) illustrate the need for effective mercury control strategies for coal-fired electric utilities as well as standard and reliable means of measuring mercury emissions. A review of mercury regulations in the United States at both the federal and state levels are provided in this quarterly report.

In order to adequately address the many topics and provide the detail necessary for the various stakeholders to make informed decisions, selected topics are discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that have been addressed in previous quarterly reports include the following:

- Quarterly 1 – Sorbent Control Technologies for Mercury Control
- Quarterly 2 – Mercury Measurement
- Quarterly 3 – Advanced and Developmental Mercury Control Technologies
- Quarterly 4 – Rerelease of Mercury from Coal Combustion By-Products
- Quarterly 5 – Mercury Fundamentals
- Quarterly 6 – Mercury Control Field Demonstrations

Specific topics that will be addressed in future quarterly reports include, but are not limited to, the following:

- Mercury policy
  - Upcoming events and news releases
  - Regulation, policy, compliance strategies, and health developments

- Mercury measurement
  - Continuous mercury monitors
  - Advanced mercury-sampling systems
  - Wet-chemistry mercury measurement techniques

- Baseline mercury levels and emissions

- Mercury control
  - Sorbent technologies and control in unscrubbed systems
  - Advanced and developmental mercury control technologies
  - Summary of large-scale test activities and associated economics
  - Mercury oxidation and control for scrubbed systems
  - Multipollutant control strategies
  - Impact of mercury control on combustion by-products/fate of captured mercury
  - Summary of mercury-related economics for commercial systems

- Mercury chemistry and transformations
  - Mercury chemistry fundamentals, modeling, prediction, and speciation
  - Mercury fate and transport – impacts on health

One objective of the quarterly reports is to provide timely information on developments in the broad field of mercury. In order to address timely issues as well as provide necessary detail on selected topics, additional subject headings will be provided as necessary to summarize recent developments not related to the quarterly topic. In this manner, updated information can be provided on topics previously covered or in advance of topics not yet discussed. The primary subject area for this quarterly report is a review of the mercury regulations in the United States at both the federal and state levels.

MERCURY POLICY

The primary subject area for this quarterly is a review of mercury policy in the United States. In Canada, a Draft Canada-Wide Standard for Mercury Emissions from Coal-Fired Electric Power Generation Plants was recently released that will result in a reduction of mercury emissions by 58% by 2010 based on estimated emissions. These estimated emissions were based on data obtained between 2002 and 2004 through a utility-monitoring program. Significant data have been compiled from coal, ash, and stack testing at facilities across Canada. Results from these activities can be viewed on the CEA Web site at www.ceamercuryprogram.ca/index.html.

The draft CWS, which is available at www.ccme.ca/assets/pdf/canada_wide_standards_hgepg.pdf, provides provincial caps on mercury emissions from existing coal-fired electric power generation (EPG) plants to result in 65% capture of mercury, Canada-wide, from coal burned. In the second phase, the CWS may explore additional capture from EPGs of more than 80% from coal burned beginning in 2018. A summary of estimated mercury emissions resulting from coal firing and proposed caps for each province is summarized in Table 1.

Requirements for new coal-fired EPG units will include 85% capture from burning bituminous and blended coals and 75% capture for subbituminous and lignite fuels.

Following review of this draft rule in the fall of 2005, final endorsement by the Canadian Council of Ministers of the Environment would occur in November 2005.

Table 1. Province Mercury Emission Estimates and Proposed Caps for 2010

Province	Estimated Emission, kg/yr[a]	2010 Cap, kg/yr
Alberta	1180[b]	590
Saskatchewan	710	430[c]
Manitoba	20	20
Ontario	495	0
New Brunswick	140	25
Nova Scotia	150	65
Total	2695	1130

[a] Based on 2002 to 2004 utility-monitoring program results.

[b] Alberta’s commitment is through the implementation of the Clean Air Strategic Alliance Electricity Project Team recommendations. Alberta emissions are based on a 90% capacity factor.

[c] Saskatchewan’s early actions, between 2004 and 2009, will be used to meet its provincial caps for the years 2010 to 2013. Examples of early actions include a mercury switch collection program and early mercury controls at the Poplar River Power Station.

QUARTER 7 FOCUS: MERCURY REGULATIONS IN THE UNITED STATES: FEDERAL AND STATE

U.S. FEDERAL MERCURY REGULATIONS

In December 2000, EPA decided that regulation of mercury from coal-fired electric utility steam-generating units was appropriate and necessary under Section 112 of the Clean Air Act (1). 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* (1997) (2) and the *Utility Hazardous Air Pollutant Report to Congress* (1998) (3) 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. On January 30, 2004, EPA published the proposed Utility Mercury Reduction Rule 40 CFR 60 and 63 (4) in order to solicit comments for two approaches for mercury emission control. Under one approach, coal-fired power plants in the United States would be required to install currently available control devices defined as maximum achievable control technologies (MACT) under Section 112 of the Clean Air Act. The second approach, proposed under Section 111 of the Clear Air Act, would create a market-based "cap-and-trade" program. This alternative would apply to both new and existing sources and take advantage of copollutant mercury control associated with SO_2 and NO_x reductions required by the Interstate Air Quality Rule that was also proposed by EPA on January 30, 2004, in 40 CFR 51, 72, 75, and 96 (5). Under this approach, a mandatory declining cap would be set for total mercury emissions from all U.S. coal-fired power plants. Implementation of this alternative would require EPA to revise its December 2000 finding that it is appropriate and necessary to regulate utility hazardous air emissions under the MACT standard of the Clear Air Act.

The EPA received over 680,000 comments on the Proposed Utility Mercury Reduction Rule and the related supplemental proposal issued in March 2004. As follow-up, EPA published a Notice of Data Availability (NODA) in the Federal Register (Vol. 69, No. 230, pp 69864–69878) on December 1, 2004. The NODA summarized the comments received by EPA (January 2004) and solicited further comment to help EPA evaluate what regulatory approach would best reduce mercury emissions from power plants.

On March 15, 2005, EPA announced the new CAMR for coal-fired power plants (6). The rule makes the United States the first country in the world to regulate mercury emissions from coal-fired power plants. It was the decision of EPA to regulate mercury under Section 111 rather than Section 112 of the Clean Air Act. As such, it was required that EPA rescind its December 2000 finding that it was appropriate and necessary to regulate mercury under Section 112(d), which would have necessitated the MACT standard. Under Section 111, a cap-and-trade rule was established. The CAMR is viewed by EPA to function in conjunction with the Clean Air Interstate Rule (CAIR) to reduce mercury emissions nationwide (7). It is expected that the additional wet flue gas desulfurization (FGD) and selective catalytic reduction (SCR) systems that will be installed to comply with the CAIR SO_2 and NO_x requirements in 28 eastern states will provide a substantial mercury cobenefit. Following is a brief overview of the CAMR. The actual rule and the preamble can be found at www.epa.gov/air/mercuryrule/rule.htm and the CAIR rule at www.epa.gov/CAIR/rule.html.

For purposes of the CAMR rule, an affected utility is defined as a fossil fuel-fired combustion unit that serves a generator that produces electricity for sale that is >25 MW_e in size. A cogeneration facility that produces at least one-third of its electricity for sale during any portion of the year and is >25 MW_e in size is also considered a utility.

Based on the 1997 Information Collection Request (ICR) data, it has been established that current U.S. mercury emissions from coal-fired electric utilities total 48 tons a year. The cap-and-trade provision of the new rule would reduce that to 38 tons of mercury a year in 2010, a reduction of 20.8%. It is fully expected that the addition of new wet FGD and SCR systems to reduce SO_2 and NO_x (under CAIR) will allow the states to meet the 2010 mercury reduction requirements without additional mercury controls. EPA is of the opinion that full-scale mercury control technologies cannot be developed and widely implemented within the next 5 years but will be available by 2018. Therefore, the rule will require further reductions to 15 tons by 2018, a total reduction of 68.8% from 1997 emissions. By 2018, it is expected that a number of plants will have employed mercury control strategies.

To ensure the required mercury reduction is met and to facilitate trading, EPA has established emission budgets for each state based on the baseline heat input adjusted for the coal burned by each plant in a given state. The adjustment factors were 1 for bituminous, 1.25 for subbituminous, and 3 for lignite coals. Table 2 shows the emission budget for each state for both phases of the rule. The ten states with the lowest emission budgets are highlighted; this reflects those states that have the least coal-fired electrical generation. Each state has the right to promulgate stricter mercury standards and/or decline to participate in the trading program. If a state declines to participate in trading, the caps shown in Table 2 become hard emission limits for that state for the targeted years. If the state participates in the trading program, it must submit a model trading plan to EPA.

Similar to the existing SO_2 trading program, the banking of mercury allowances (1 allowance = 1 ounce mercury) will be allowed at the beginning of the cap-and-trade program. Although EPA admits that early banking of allowances will most likely lead to less reduction in later years, it is expected that it will allow for greater reductions prior to 2010.

Under the CAMR, new coal-fired generation sources (built after January 30, 2004) must also meet a new source emission standard. The requirements for new sources have been subcategorized according to coal rank and, in the case of subbituminous coal, for the type of SO_2 control technology employed. These emission standards are shown in Table 3.

The new rule also provides detailed information on how and when mercury is to be measured and what record keeping is needed in order to comply with the trading rules. Two

Table 2. State Mercury Emission Budgets

State	2010–2017, tons Hg/yr	After 2018, tons Hg/yr
Alabama	1.289	0.509
Alaska	0.005	0.005
Arizona	0.454	0.179
Arkansas	0.516	0.204
California	0.041	0.016
Colorado	0.706	0.279
Connecticut	0.053	0.021
Delaware	0.072	0.028
Florida	1.233	0.487
Georgia	1.227	0.484
Hawaii	0.024	0.009
Idaho	0	0
Illinois	1.594	0.629
Indiana	2.098	0.828
Iowa	0.727	0.287
Kansas	0.723	0.285
Kentucky	1.525	0.602
Louisiana	0.601	0.237
Maine	0.001	0.001
Maryland	0.490	0.193
Massachusetts	0.172	0.068
Michigan	1.303	0.514
Minnesota	0.695	0.274
Mississippi	0.291	0.115
Missouri	1.393	0.550
Montana	0.378	0.149
Nebraska	0.421	0.166
Nevada	0.285	0.112
New Hampshire	0.063	0.025
New Jersey	0.153	0.060
New Mexico	0.299	0.118
New York	0.393	0.155
North Carolina	1.133	0.447
North Dakota	1.564	0.617
Ohio	2.057	0.812
Oklahoma	0.721	0.285
Oregon	0.076	0.030
Pennsylvania	1.780	0.702
Rhode Island	0	0
South Carolina	0.580	0.229
South Dakota	0.072	0.029
Tennessee	0.944	0.373
Texas	4.657	1.838
Utah	0.506	0.200
Vermont	0	0
Virginia	0.592	0.234
Washington	0.198	0.078
West Virginia	1.394	0.550
Wisconsin	0.890	0.351
Wyoming	0.952	0.376

Table 3. New Source Mercury Emission Standards

Unit	ng/J	lb/10^6 MWh
Bituminous Units	0.00260	21.0
Subbituminous Units		
Wet FGD	0.00530	42.0
Dry FGD	0.00980	78.0
Lignite Units	0.01830	145.0
Coal Refuse Units	0.00018	1.4
IGCC*	0.00250	20

* Integrated gasification combined cycle.

mercury measurement methods are allowed; the first is 40 CFR, Part 60, Appendix K (previously proposed EPA Method 324 or the sorbent trap method). The second method is to use continuous mercury monitors (CMMs). Although no specifics are provided such as what sorbent or monitors are to be used, very detailed initial certification procedures are listed as well as specifications for quality assurance/quality control (QA/QC).

It is the expectation of EPA that compliance with SO_x and NO_x requirements of the CAIR will provide substantial cobenefit for mercury capture and result in compliance with the CAMR Phase I mercury budgets by 2010. As such, very little specific mercury control technology implementation will be required in the near term to meet federal requirements. Where mercury control is necessary, activated carbon injection may be implemented for additional mercury capture. A significant amount of work has been done through industry, utility, and DOE efforts to demonstrate the effectiveness of carbon injection, the results of which have been presented in previous CEA reports, including Quarterly 1 and 6. Phase II mercury budgets will require additional mercury control technology by 2018; however, advancements in control technologies over the next several years will have a significant impact on utility plans to meet their mercury emission limits.

Although mercury control is not likely to be required for compliance with Phase I federal regulations, several states have developed mercury emission requirements more stringent than the federal CAMR and, as such, will require near-term implementation of control technologies. Specific activities to control mercury are presented in subsequent sections.

The new CAMR has proven to be very controversial, and several environmental organization as well as ten state attorneys general have filed suit in the U.S. District of Columbia Court of Appeals against EPA and the mercury rule. The ten states are as follows (four of the states are highlighted in Table 2, and with the exception of Wisconsin, all are on the lower end of the annual mercury allocation):

- New Jersey
- New Hampshire
- Maine
- New York
- California

- New Mexico
- Connecticut
- Wisconsin
- Vermont
- Massachusetts

The states are challenging EPA's authority to remove power plants from the list of pollution sources subject to Section 112 requiring MACT, and secondly, they are challenging the cap-and-trade system, asserting that it is not protective of public health. These states are alleging that under a cap-and-trade system, some plants will actually increase mercury emissions, thereby creating "hot spots" of mercury deposition and contamination.

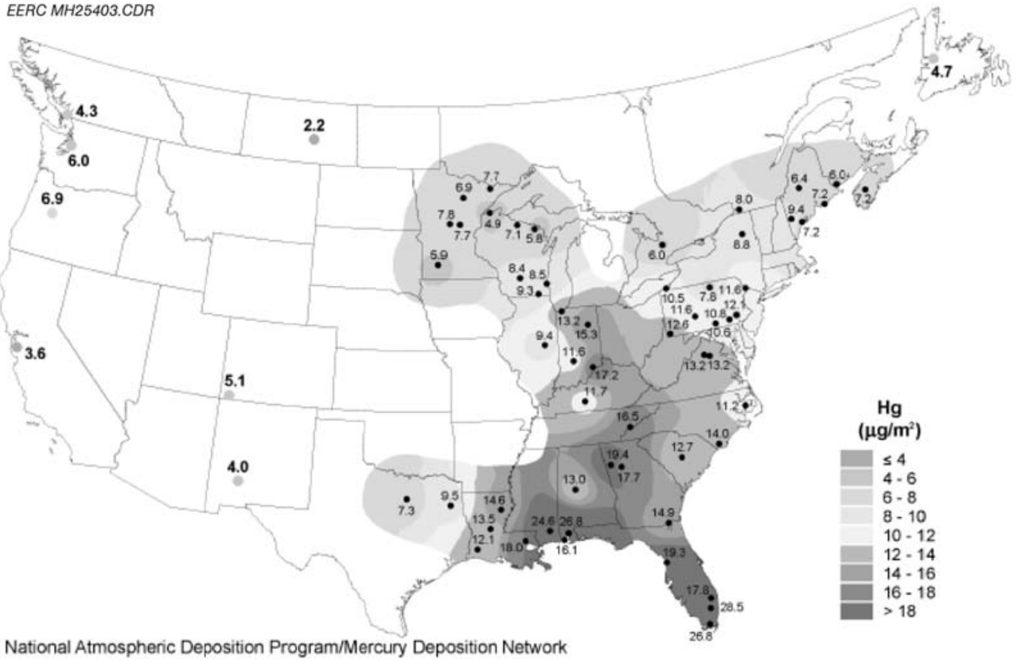
All of the states filing suit, with the exception of California, New Mexico, and Wisconsin, are in the northeastern part of the United States. Even though these states do not have many coal-fired electric utilities, their concern is that substantial deposition occurs within their boundaries from plants outside their states. For example, a mercury task force in New Jersey determined wet deposition to be 14–18 $\mu g/m^2/yr$ (8). Somewhat less deposition (10–12 $\mu g/m^2/yr$) was reported in a 2003 study by the Mercury Deposition Network (MDN) (9). For comparison purposes, the MDN results indicated wet deposition in the northeastern part of the United States to be 4–12 $\mu g/m^2/yr$; 20–30 $\mu g/m^2/yr$ in parts of Florida, Georgia, Alabama, and Louisiana; and, although the database is not extensive, 2–6 $\mu g/m^2/yr$ in the western portion of the United States. A map of mercury wet disposition is shown in Figure 1. It has also been estimated that dry deposition may be 40%–45% of wet deposition (10).

STATE REGULATIONS

Under the Clean Air Amendments of 1990, each state is free to promulgate stricter emission regulations than are provided for by the federal rule-making process. To date, three states, Massachusetts, Connecticut, and New Jersey, have imposed mercury emission limits more restrictive than the CAMR. In New Hampshire, a bill limiting emissions has been introduced and is currently in committee. Wisconsin has also issued a mercury rule; however, the rule contained a clause that would not allow it to be more restrictive than the federal rule. Therefore, some provisions of the Wisconsin rule will have to be amended. The state regulations that are currently in place or under consideration are discussed below.

Massachusetts

On May 26, 2004, the Executive Office of Environmental Affairs and the Massachusetts Department of Environmental Protection (DEP) announced the adoption of new regulations that limit mercury emissions from coal-fired power plants in Massachusetts. These regulations took effect on June 4, 2004. Massachusetts has four affected facilities, shown in Table 4. The rule in Massachusetts requires that by January 1, 2008, or 15 months after complying with existing SO_2 and NO_x regulations, mercury emissions from the four plants must be less than 0.0075 lb/GWh



National Atmospheric Deposition Program/Mercury Deposition Network

Figure 1. Mercury wet deposition map.

(2.20 lb/10^{12} Btu), or the average total mercury removal efficiency must be 85% or greater. The removal efficiency, based on CMMs, is to be calculated based on the average historic mercury inlet concentration and is determined on a rolling 12-month basis. Effective October 1, 2012, mercury emissions must be reduced to 0.0025 lb/GWh (0.73 lb/10^{12} Btu), or the average total mercury removal efficiency must be greater than 95%. Two Massachusetts plants have multiple units: Salem Harbor and Brayton Point. Mercury testing for these facilities can be conducted at one location, representative of full-load operation and applied to the entire facility. Beginning January 1, 2008, the affected plants must have installed certified CMMs. Prior to this date, other compliance methods can be used (as approved by the Massachusetts DEP), but triplicate measurements must be made on a quarterly basis. The rule allows for variances when testing new technologies, and trading will be allowed on a very limited basis. If a plant terminates operations before January 1, 2010, it must demonstrate compliance by using early or off-site reductions. Also, any plant that emits less than 5 lb of mercury on an annual basis may demonstrate compliance by using early or off-site reductions through September 30, 2012. A summary of the expected emission reduction in Massachusetts is shown in Figure 2.

Although testing using activated carbon has been done at Salem Harbor and Brayton Point (11) it is expected that the addition of SCRs and wet scrubbers that is being mandated for SO_2 and NO_x control, along with the natural mercury capture in the fly ash, will allow the Massachusetts plants to meet state regulations without additional mercury controls for the first phase. However, additional controls may be required to meet the second phase.

Table 4. Power Plants Affected by the Massachusetts Mercury Rule

Plant	No. of Affected Units	Coal	Total MW
Brayton Point	3	Bituminous	1132
Salem Harbor	3	Bituminous	325
Mount Tom	1	Bituminous	146
Sommerset	1	Bituminous	112

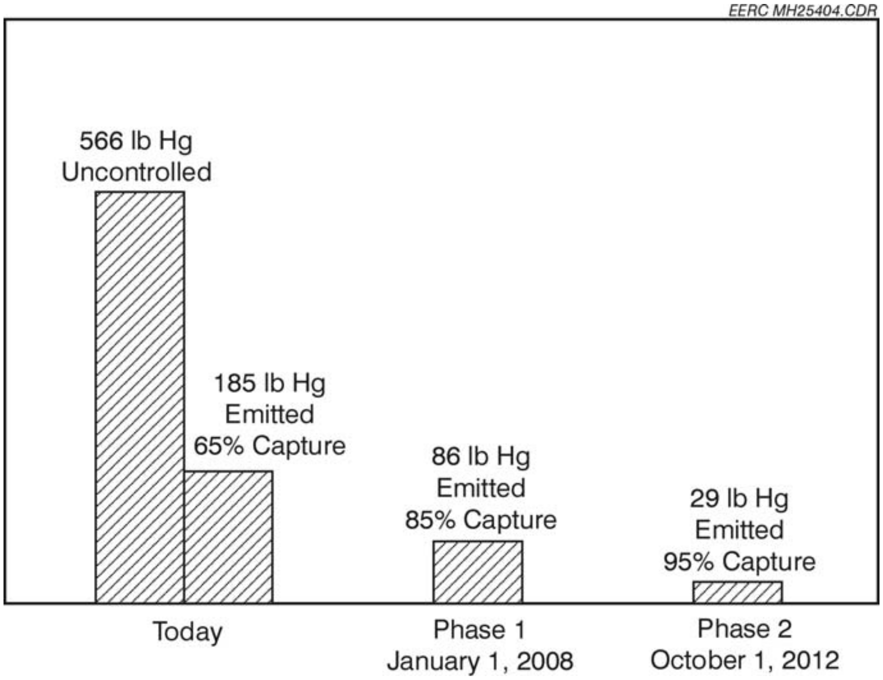


Figure 2. Anticipated mercury emissions for Massachusetts.

New Jersey

On December 6, 2004, a mercury rule was established in New Jersey applicable to coal-fired boilers. A total of seven facilities (ten units) are impacted by the rule and are listed in Table 5. The rule will require the facilities to meet a 3-mg/MWh (1.94-lb/10^{12} Btu) annual emission limit or achieve a minimum 90% mercury removal efficiency (annual basis). This must be accomplished by December 15, 2007.

Alternately, a multipollutant strategy that meets the state's approval can be implemented by December 15, 2012. PSEG Fossil recently reached a settlement with the New Jersey Department of Environmental Protection and the EPA to resolve allegations of noncompliance with federal and New Jersey New Source Review (NSR) regulations. The NSR provisions of the Clean Air Act are designed to ensure that power plants and other sources of air emissions install best available emissions control technologies when they undergo major expansions or refurbishments that significantly increase emissions. As part of the settlement, PSEG Fossil is

Table 5. Power Plants Affected by the New Jersey Mercury Rule*

Plant	No. of Affected Units	Coal	Total MW
Logan	1	Bituminous	230
Mercer	2	Bituminous	653
Carneys Point	2	Bituminous	590
B.L. England	2	Bituminous	300
Deepwater	1	Bituminous	74
Hudson	1	Bituminous	660
Vineland	1	Bituminous	25

* It is expected that the B.L. England and Vineland facilities will be shut down prior to December 15, 2007.

expected to spend $340 million over the next 10 years to reduce emissions of NO_x, SO_2, and mercury at the Hudson and Mercer Generating Stations. These emission reductions will be achieved by installing SCR and dry scrubber technology at Hudson and Mercer Generating Stations. In addition, a baghouse will be installed at Hudson. PSEG Fossil is expecting a 90% reduction in mercury emissions at these plants through the cobenefits of these control technologies. However, it may be necessary to add small amounts of activated carbon to ensure compliance with the New Jersey mercury rule.

At Carneys Point Power Plant, a dry scrubber and fabric filter are already installed, resulting in a natural mercury capture of > 65%. It is expected that additional mercury controls will be needed to meet the New Jersey regulations. Mercury testing has been conducted by Consol at Carneys Point using activated carbon, and >90% mercury control has been achieved (12).

The New Jersey Mercury Rule does not allow trading or averaging between sites; however, the rule does allow averaging mercury from multiple coal-fired boilers at a site for compliance purposes. It is expected that the rule will reduce current mercury emissions from coal-fired power plants from 700 ± 300 lb/yr to less than 75 lb/year.

Stack testing will be required for each unit at both the inlet of the first pollution control device and at the stack. The tests must be conducted using an approved method on a quarterly basis. If a facility maintains compliance for eight consecutive quarters, the frequency of sampling may be reduced to once every fourth quarter. The state of New Jersey is also strongly recommending the use of CMMs once they become commercially available and can meet the performance specifications published by EPA in the CAMR.

Connecticut

In March 2003, environmental organizations including Clean Water Action, the Connecticut Coalition for Clean Air, and the Clean Air Task Force along with electric utility PSEG Power Connecticut (owner of the 375-MW Bridgeport Harbor coal-fired power plant) issued a joint recommendation to the Connecticut General Assembly for legislation establishing stringent new mercury emission standards for the state's coal-fired power plants. The joint proposal, unanimously adopted and signed into law in June 2003, requires coal-fired power plants in Connecticut to achieve either a mercury emission standard of 0.6 lb/10^{12} Btu or a 90% mercury removal efficiency. The requirements become effective in July 2008. There are two affected plants in the state of Connecticut, as shown in Table 6.

Table 6. **Power Plants Affected by the Connecticut Mercury Rule**

Plant	No. of Affected Units	Coal	Total MW
Bridgeport Harbor	1	Bituminous	375
Thames*	1	Bituminous	200

* The Thames unit is a circulating fluid bed.

If the owner or operator of any affected unit properly installs and operates mercury control technology designed to achieve the required mercury removal and fails to achieve that desired performance, the owner of the plant must notify the Connecticut Commissioner of Environmental Protection by February 1, 2009. Quarterly stack sampling will need to be performed and reported for evaluation and establishment of an alternative emission limit for that unit based upon the optimized performance of the properly installed and operated control technology. The Commissioner of Environmental Protection will establish an alternative emission limit for that unit no later than April 1, 2010.

Any stack test used to demonstrate compliance with the mercury emission rate requirement is to be based on an average of stack tests conducted during the two most recent calendar quarters. The method to be used for measuring mercury is EPA Method 29; however, an alternative method may be used if approved by the Commissioner of Environmental Protection.

If the Commissioner of Environmental Protection determines that CMMs are commercially available and can perform in accordance with the specification as published in the CAMR, the plant must install the monitors but will not need to conduct stack testing except as required by the CMM QA/QC specifications written in the federal mercury rule.

In addition to establishing the new mercury emission limits in 2008, the law also directs the Connecticut Department of Environmental Protection in 2012 to review all stationary sources of mercury emissions in the state. As part of this review, the Department of Environmental Protection will consider new emission standards based on available technology, the cost of achieving additional reductions, and public health and environmental benefits associated with further reductions from each source reviewed.

New Hampshire

In New Hampshire, a bill has been introduced that would provide a multipollutant reduction program that limits emission of mercury, SO_2, NO_x, and CO_2. Two coal-fired power plants in New Hampshire (shown in Table 7) would be affected by these regulations.

Table 7. Power Plants Affected by the Proposed New Hampshire Mercury Rule

Plant	No. of Affected Units	Coal	Total MW
Merrimack*	2	Bituminous	510
Schiller	3	Bituminous	180

* The two Merrimack boilers are wet-bottom cyclone units.

It is estimated that the plants in New Hampshire are currently emitting mercury at a rate of 129 lb/yr. This legislation would cap mercury emissions at 50 lb/yr beginning July 1, 2009, and then 24 lb/yr beginning July 1, 2013. In the initial bill, a modified cap-and-trade program within the state was proposed; however, the trading portion of the bill was eliminated in the senate.

The baseline theoretical inlet mercury concentration for each plant would be determined through coal analysis on a monthly basis. Stack testing would be required to determine removal from the theoretical inlet concentration. Stack testing would be conducted at both units at Merrimack and one unit at Schiller.

Wisconsin

In June 2003, the Wisconsin Natural Resources Board approved new regulations that would require the state's coal-fired utilities to reduce mercury emissions. The intent of the rule was to reduce mercury emission by 40% by January 1, 2010, and 75% by January 1, 2015, for all coal-fired power plants >25 MW. However, included in the rule was section NR 446.029, “Adoption of Federal Mercury Standard,” which states the following:

> *If a federal emission standard limiting mercury emissions from a major utility is promulgated under Sections 111 or 112 of the federal Clean Air Act, the department shall adopt a similar standard, including administrative requirements that are consistent with federal administrative requirements. The standard adopted by the department may not be more restrictive in terms of emission limitations than the federal standard.*

The result is that the Wisconsin mercury rule has been superseded by the federal CAMR, and no specific mercury removal technology is being planned in Wisconsin.

STATES WITH INTRODUCED LEGISLATION

Legislation has been introduced recently in seven other states as well:

- Minnesota
- Indiana
- Maryland
- Montana
- New York
- Ohio
- Virginia

The legislation being considered by these states is preliminary and provides for a wide range of emission requirements and compliance strategies. It is unclear at this time what type of mercury control will be required in these states.

STATES WITH NONLEGISLATIVE ACTIVITIES

In states where legislation is not in place nor been introduced, other activities, including air permitting, investigations by state environmental departments, and voluntary programs, have been ongoing to address the concerns of mercury emissions from coal combustion. The following describes these activities in Iowa, North Carolina, Minnesota, and Delaware.

Iowa

In June 2003, the Iowa Department of Natural Resources issued a permit to MidAmerican Energy Company for construction of a 765-MW coal-fired boiler at the Council Bluffs Energy Center that will require mercury control. It is expected that the unit will begin operation early in 2007 and will fire a Powder River Basin (PRB) subbituminous coal. Based on the permit, the unit will require best available control technology (BACT) for a range of pollutants. The BACT emission limits for this boiler are shown in Table 8. The allowed mercury emission rate (highlighted) would require 80%–85% removal based on the average mercury content of PRB

Table 8. BACT Emission Limits for the New Boiler at the Council Bluffs Energy Center

Pollutant	tons/yr[1]	Limits, lb/10^6 Btu (unless otherwise noted)
Particulate Matter (PM)	NA[2]	0.027
PM_{10}	NA	0.025
Opacity	NA	5%
Sulfur Dioxide (SO_2)	3362	0.1
Nitrogen Oxides (NO_x)	2353	0.07
Volatile Organic Compounds	121	0.0036
Carbon Monoxide	5177	0.154
Lead	NA	0.000026
Fluorides	NA	0.0009
Sulfuric Acid Mist (SO_3 and H_2SO_4)	NA	0.00421
Mercury	NA	1.7×10^{-6}
Hydrogen Chloride (HCl)	NA	0.0029
Total Selected Metals[3]	NA	1.04×10^{-4}

[1] Twelve-month rolling average.
[2] Not applicable.
[3] Total selected metals are arsenic, beryllium, cadmium, chromium, lead, manganese, nickel, and selenium.

coal. To meet the requirements shown in Table 8, the unit will have the following pollution control systems:

- Spray dryer
- Baghouse
- Low-NO_x burners with overfire air
- SCR
- Activated carbon injection

Activated carbon injection for mercury control is specifically identified in the permit. A minimum activated carbon feed rate of 10 lb/10^6acf or a rate specified by optimization trials is required. Optimization testing (maximum of 9 months) is to begin immediately after start-up to determine the level of activated carbon needed to ensure that emission limits are achieved. During each test period, in addition to stack testing, the mercury is to be measured in the coal and the bottom ash. Also, the coal feed rate and bottom ash generation rates are to be determined.

Compliance is to be ensured through stack testing consisting of an average of three stack tests using the ASTM D6784-02 method (the Ontario Hydro method) on an annual basis. In addition, EPA Method 29 will be required to measure trace elements. There are no requirements in the permit for continuous monitoring for mercury.

North Carolina

In North Carolina, the Clean Smokestacks Act requires new controls for NO_x and SO_2 and is expected to provide a cobenefit of 55% mercury reduction. Also, the North Carolina State Department of Environmental and Natural Resources is required to submit a report to the legislature in 2005 on whether mercury-specific controls should be adopted after implementation of the SO_2 and NO_x controls.

Minnesota

In 1999, Minnesota passed a law requiring the Minnesota Pollution Control Agency to solicit voluntary reduction agreements from all sources that emit more than 50 lb of mercury annually. The law set a goal of reducing mercury releases in the state by 70% from 1990 levels by 2006. A 2002 progress report indicated very little reductions had occurred under the voluntary initiative. Progress is to be assessed again in 2005, and a report is expected to be issued in October 2006. In response to the slow rate of voluntary mercury reduction, a bill was submitted to the Minnesota legislature in March 2005 that would cut mercury emissions by 90% by 2009 or 2011, depending on the plant configuration.

Delaware

The governor of Delaware has asked the Delaware Department of Natural Resources and Environmental Control to begin a process to reduce mercury from the two power plants located in Delaware (Indian River and Edge Moor). A formal rule-making process is expected to begin in fall 2005.

UPCOMING EVENTS

230th ACS National Meeting
August 28–September 1, 2005, Washington, D.C.
http://oasys.acs.org/acs/230nm/topics.html

International Pittsburgh Coal Conference
September 11–15, 2005, Pittsburgh, PA
www.engrng.pitt.edu/pcc/

Mercury Measurement in Combustion Flue Gases Short Course
September 12–14 and September 14–16, 2005, Grand Forks, ND
www.undeerc.org

Air Quality V: Mercury, Trace Elements, SO_3, and Particulate Matter Conference
September 18–21, 2005, Washington, D.C.
www.undeerc.org

Pittcon 2006
March 12–17, 2006, Orlando, FL
www.pittcon.org

Coal Ash Professionals Training Course
April 19–21, 2006, Memphis, TN
www.undeerc.org

A&WMA Annual Conference & Exhibition
June 20–23, 2006, New Orleans, LA
www.awma.org

Eighth International Conference on Mercury as a Global Pollutant
August 6–11, 2006, Madison, WI
www.mercury2006.org/Default.aspx?tabid+1393

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MERCURY INFORMATION
CLEARINGHOUSE

Quarter 8 – Commercialization Aspects of Sorbent Injection Technologies in Canada

October 2005

Canadian Electricity Association
Association canadienne de l'électricité

EERC
Energy & Environmental Research Center

Center for Air Toxic Metals

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 8 – COMMERCIALIZATION ASPECTS OF SORBENT INJECTION TECHNOLOGIES IN CANADA

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REPORT AVAILABILITY

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650 and the CEA Mercury Program Web site (www.ceamercuryprogram.ca).

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EXECUTIVE SUMMARY

The primary objective of this quarterly report is to provide information on the state of commercialization of sorbent injection technologies. The quarterly includes the following topics:

- Policy and regulatory issues that impact commercialization of mercury sorbent technologies.

- Sorbents most likely to be used based on coal type and plant configurations.

- Capital investment requirements and the availability of necessary equipment and labor.

- Availability of sorbents and/or additives.

- Status of mercury measurement technology for compliance purposes.

- Balance of plant impacts.

The Clean Air Mercury Rule in the United States and the acceptance in principle of a draft of the Canada-Wide Standards for mercury illustrate the need for cost-effective mercury control strategies for coal-fired electric utilities. Recent demonstration activities have shown effective mercury capture with sorbent injection at full-scale systems. Out of this effort, concerns have been raised regarding the availability of carbon, sorbents, additives, and the related capital equipment if there was widespread adoption of activated carbon injection (ACI) technology. Projections by the activated carbon industry do not suggest that either the availability of activated carbon or equipment will be an issue. However, there are several areas of concern that still need to be addressed in the long term. These include the following:

- Environmental and economic impacts of lost fly ash utilization
- The impact of ACI on fabric filter (FF) and electrostatic precipitator (ESP) performance
- Longer-term leaching potential of disposed ash

Clearly, the salability of fly ash is a major concern as it does not take much carbon in the ash to render it unacceptable to the concrete industry. This would result in a substantial financial penalty for those plants currently selling ash as well as an increase in ash in landfills and an increase in demand for portland cement and associated energy and emissions from its manufacture. To maintain fly ash sales, plants may have to consider the installation of a FF specifically for mercury capture, downstream of an existing ESP.

If the fly ash is to be disposed of, a concern has been that ACI is only converting one environmental problem into another. Short-term leaching tests indicated that once mercury is captured by the ash or carbon, it is very stable and does not leach to any significant degree. However, long-term leaching testing has not been widely conducted and will be necessary to verify the stability of mercury on carbon.

The impact of ACI on particulate control devices has not yet been determined. The short duration—less than 2 months—of most of the large-scale test activities has not shown significant detriment to either ESP performance or FF pressure drop. However, there are data for specific plants that indicate problems could arise if ACI were conducted for longer periods. In the coming year, longer-term tests of 3- to 12-month duration will be conducted which should provide more conclusive information regarding the impact of ACI on ESP performance and help determine if long-term carbon use will increase pressure drop across FFs. These long-term data will be critical to support vendors' ability to provide performance guarantees on systems designed to maintain mercury emission compliance.

MERCURY INFORMATION CLEARINGHOUSE

QUARTER 8 – COMMERCIALIZATION ASPECTS OF SORBENT INJECTION TECHNOLOGIES IN CANADA

INTRODUCTION

The Canadian Electricity Association (CEA) identified a need and contracted the Energy & Environmental Research Center (EERC) to create and maintain an information clearinghouse on global research and development activities related to mercury emissions from coal-fired electric utilities. With the support of CEA, the Center for Air Toxic Metals® (CATM®) Affiliates, and the U.S. Department of Energy (DOE), the EERC is developing comprehensive quarterly information updates to provide a detailed assessment of developments in mercury monitoring, control, policy, and research.

In order to adequately address the many topics and provide the detail necessary for the various stakeholders to make informed decisions, selected topics are discussed in detail in each quarterly report. Issues related to mercury from coal-fired utilities include the general areas of measurement, control, policy, and transformations. Specific topics that have been addressed in previous quarterly reports include the following:

- Quarterly 1 – Sorbent Control Technologies for Mercury Control
- Quarterly 2 – Mercury Measurement
- Quarterly 3 – Advanced and Developmental Mercury Control Technologies
- Quarterly 4 – Rerelease of Mercury from Coal Combustion By-Products
- Quarterly 5 – Mercury Fundamentals
- Quarterly 6 – Mercury Control Field Demonstrations
- Quarterly 7 – Mercury Regulations in the United States: Federal and State

Recent promulgation of mercury regulations from coal-fired power plants in the United States, the Clean Air Mercury Rule (CAMR), and the acceptance in principle of a draft of the Canada-wide Standards (CWS) illustrate the need for cost-effective mercury control strategies for coal-fired electric utilities. Full-scale tests conducted across North America have demonstrated very good mercury capture using sorbent injection or activated carbon injection (ACI), and it appears that this technology will receive widespread implementation as coal-fired utilities work to meet the new regulations. A review of commercialization aspects of widespread sorbent injection technologies for mercury control is provided in this quarterly report and includes the following:

- Policy and regulatory issues that impact commercialization of mercury sorbent technologies.

- Sorbents most likely to be used based on coal type and plant configurations.

- Capital investment requirements and the availability of necessary equipment and labor.

- Availability of sorbents and/or additives.
- Status of mercury measurement technology for compliance purposes.
- Balance-of-plant impacts.

MERCURY POLICY

In March, 2005, the U.S. Environmental Protection Agency (EPA) issued the first-ever mercury regulation entitled the CAMR. At Air Quality V, Robert Weyland of EPA said the rationale for the rule was the EPA's desire to allow electric generating utilities as much flexibility as possible and still protect public health. As a result, EPA issued the rule under Section 111 rather than Section 112 of the Clean Air Act Amendments (CAAA), thereby providing a cap-and-trade mechanism. The rule is designed to be implemented in two phases. The first phase would cap mercury emissions from coal-fired power plants at 38 tons/year by 2010 (about 48 tons/year is currently being emitted), and the second phase would permanently cap emissions at 15 tons/year by 2018. It is EPA's position that the first phase will be accomplished as a cobenefit of the February 2005 Clean Air Interstate Rule (CAIR), which requires that a number of utilities in the eastern states install wet flue gas desulfurization (FGD) systems for SO_2 control and selective catalytic reduction (SCR) for NO_x control. Mitchell Baer of DOE added that, although the second phase of the rule will require addition mercury controls, it is expected that a number of mature economical technologies will be available to meet CAMR requirements.

The CAMR provides individual states the right to establish their own rules, provided that they meet the state-specific caps established under the CAMR. As outlined by Joyce Epps of the Pennsylvania Department of Environmental Protection, several northeastern states are evaluating options as a response to the CAMR, which may include lawsuits against EPA (14 states and several environmental groups have currently filed) or instituting more restrictive legislation. Of particular concern to many states and organizations is the delisting of mercury from Section 112 of the CAAA which provides for maximum achievable control technology and the decision to regulate mercury under Section 111, providing for a cap-and-trade structure. As a result of these suits and petitions from states, tribes, and environmental groups, EPA opened a reconsideration process on June 24, 2005, for parts of Section 112 to ensure sufficient public comment. However, the reconsideration process will not stay the rule. Although, several states are developing more stringent rules and most likely there will be several early adapters, the United States will not directly compete with Canadian utilities for mercury sorbents and/or additives until 2012 or later.

The government of Canada, working closely with provincial and territorial partners, has accepted in principle a draft of the CWS for mercury emissions from coal-fired power plants (www.ccme.ca/initiatives/standards.html). Later this year, the draft will be reviewed by the Air Management Committee, Environmental Planning and Protection Committee, and Deputy Ministers Committee and a finalized version developed. In November, the final CWS is expected to be endorsed by the Canadian Council of Ministers of the Environment (CCME). Based on the provincial caps provided for under the CWS, mercury emissions would be reduced from the current 2695 kg/yr to 1130 kg/yr (58% reduction) by 2010 based on best achievable control technology economically available (BATEA). Therefore, the coal-fired utilities will need to install mercury technologies that can provide 50%–60% control. In addition, as part of the CWS, a review process will be implemented to evaluate requiring much higher levels of control, up to 80% by 2018. For new facilities, use of best available control technologies (BACT) for mercury will be required upon start-up. Based on current estimates, BACT levels would be 85% control for bituminous coals and blends (emission rates of 3 kg/TWh) and 75% control for lignites (15 kg/TWh) and subbituminous fuel (8 kg/TWh).

QUARTER 8 FOCUS: COMMERCIALIZATION ASPECTS OF SORBENT INJECTION TECHNOLOGIES IN CANADA

SORBENTS MOST LIKELY TO BE USED BASED ON COAL TYPE AND PLANT CONFIGURATIONS

In March 2005, the EERC issued a report to the CCME entitled “Technical Review of Mercury Technology Options for Canadian Utilities”(1). It was determined the most likely near-term candidate to obtain 50% to 60% mercury control for all Canadian utilities would be ACI. The estimated ACI rates based on U.S. full-scale test data (shown in Figure 1) are provided in Table 1.

Results are now being reported (2) from large-scale test activities conducted under the DOE Phase II mercury control program. Data that have shown that using halogenated carbons, manufactured by Sorbent Technologies (B-PAC) and NORIT Americas Inc. (DARCO Hg-LH), may be a cost-effective mercury control option particularly for low-rank fuels (lignites and subbituminous coals). It may be possible to achieve 50% to 60% mercury control at ACI rates of <2 lb/Macf, even for facilities with only a cold-side electrostatic precipitator (ESP). Results have also shown that with a fabric filter (FF) only 1 lb/Macf or less of the halogenated carbon may be needed. Data also indicate that putting in low-cost proprietary additives, such as the EERC sorbent enhancement additive (SEA)2 or Alstom’s KNX, ACI rates may even be lower (3, 4). These tests are ongoing, and additional data are needed before final conclusions can be drawn. DOE recently issued a request for proposals for its Phase III program, and announcements of awards should be made in February 2006. It is expected that these projects will provide much more definitive results along with balance-of-plant impact information over longer operating periods and data related to how halogenated injection may impact plant operation, emissions, and by-products.

Although research is being conducted, it is not expected that noncarbon sorbents will be commercially available for mercury control prior to implementation of the CWS.

CAPITAL INVESTMENT

There are essentially three scenarios for mercury control that would require capital investment by the power industry. The first scenario is that only activated carbon (treated or untreated) is used. The second includes an additive along with activated carbon. The final and most costly scenario, from a capital investment point of view, is the installation of a FF downstream of an existing ESP with ACI between the ESP and FF.

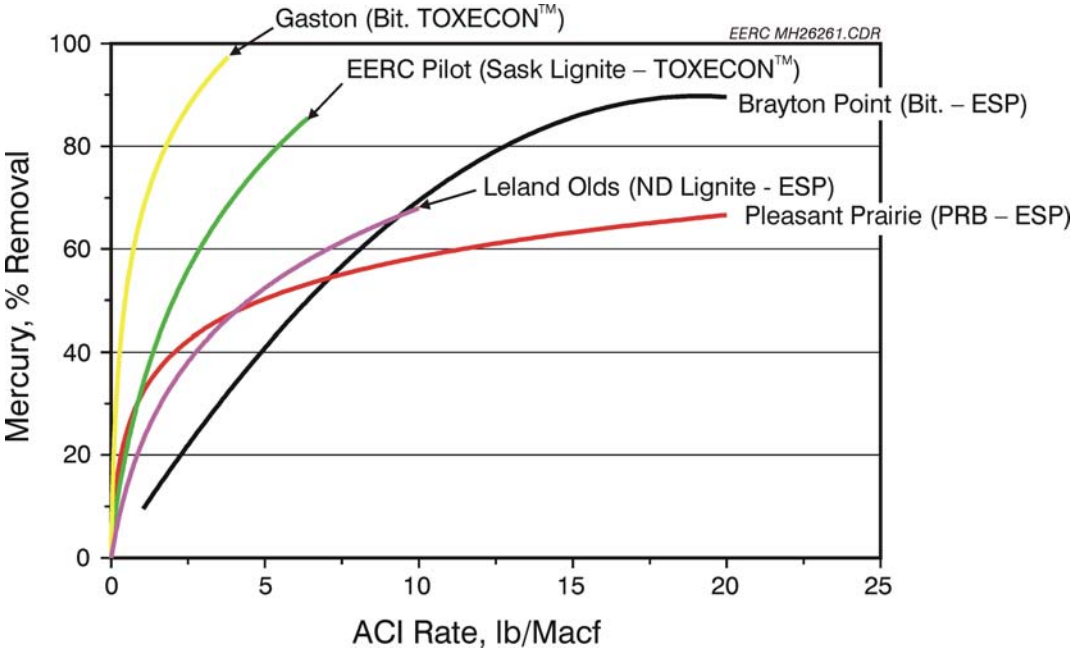

Figure 1. U.S. field test experience with ACI.

Table 1. Estimated ACI Rates Based on U.S. Full-Scale Testing Experience and Select Pilot-Scale Test Results

Coal Type	ACI–ESP[1] lb/Macf	ESP–ACI–FF lb/Macf
Blend (bit.–sub.–petcoke)	4–8	2–4
Bituminous	4–8	2–4
Subbituminous	5–10	3–5
Lignite	5–20	3–6

[1] Cold-side ESP.

Capital Cost of ACI and/or Additives

Based on an economic study done by Hoffman and Ratafia-Brown for DOE (5), it was estimated that the capital cost for ACI equipment for a 500-MW plant would be US$3–US$4/kW. For smaller systems, the cost can be as high as US$8/kW. Typically, capital costs for an ACI system include the following:

- Equipment transportation costs
- Equipment installation costs including concrete pads and injection ports
- Activated carbon storage silo
- A feeder skid that includes blowers, variable-screw feeders, and control system
- Injection lances including piping and distribution manifolds

With the exception of the injection lances and piping, the equipment is off-the-shelf and has been used for a number of years in the waste-to-energy industry to control mercury. The injection lances will need to be sized based on the duct dimension and, most likely, a modeling effort will be needed to ensure adequate sorbent distribution. The injection skids can be purchased directly from vendors such as NORIT Americas, or a contractor can be hired to assemble the skid on-site. Figure 2 is a photograph of an ACI skid. Based on discussion with Norit Americas, the availability of injection skids will not be a factor limiting the adoption of ACI.

When additives are used to enhance activated carbon activity, they are either added as spray onto the coal as it exits the mill or as solid near the top of the boiler. Somewhat similar injection equipment is needed for the additives as for activated carbon, but the system will be considerably smaller and, therefore, less costly. Based on field tests, it is expected that the total capital cost for the additive injection equipment will be less than US$100,000. Figure 3 is a picture of the additive injection equipment.

The third and most expensive option is to install a FF downstream of the ESP with ACI occurring between the ESP and FF. This has three primary advantages. The first is to provide a better contactor for the activated carbon, resulting in higher mercury removal. The second benefit is that the majority of the fly ash is not contaminated with the activated carbon and can be sold to the concrete industry. This issue will be discussed more fully later in this report. Finally, installation of a FF has the potential to improve overall particulate control. The capital cost for installing a FF is estimated to be US$55–US$70/kW, depending on the size of the plant and the air-to-cloth ratio needed to maintain a reasonable pressure drop and cleaning cycle. The cost items are as follows:

- Major equipment (35%)
- Auxiliary or accessory equipment (15%)
- Field installation (20%)
- Project management and engineering (13%)
- Freight, taxes, subcontractor, etc. (17%)
- Start-up cost, working capital, and other capitalized costs (15%–20%)

It should be noted that these costs represent vendor prices, and do not necessarily include additional costs incurred by the facility. Additional time and expense can be borne by the utility to install foundations, modify ductwork and controls, and additional fan capacity. Under some scenarios the added cost to the utility can be as much as 2 times greater than the quoted vendor costs.

Figure 2. Photograph of an ACI skid.

Figure 3. Photograph of a skid used to spray additives onto the coal.

Availability of Equipment

A typical FF installation will require 3 to 4 months, with an additional 4 to 7 weeks to hook up the baghouse to the boiler unit. The amount of time depends on the size of the plant, overall configuration, size of the baghouse, and general complexity of the design. Taking into account design, lead times, project planning, and system shakedown, project completion could required up to 2 years. There are 32 units in Canada that have cold-side ESPs and would potentially benefit from adding a FF as part of their overall mercury control strategy (excluding those that are scheduled for shutdown, which includes all of those in Ontario). If 10 units were to install FFs prior to 2010, the primary concerns include availability of steel, labor, and heavy-lifting cranes. In the United States, it has been estimated that the additional wet FGD and SCR units that would be installed as a result of the Clear Skies Initiative or CAIR would only increase the demand for steel in the United States by 0.1% (6). The addition of 10 baghouse in Canada over 3 years would have little impact on steel demand. Although the high demand for raw materials and construction materials has resulted in delays and price increases as suppliers work to meet increased demand globally. Of more concern would be the availability of cranes. Although EPA does not consider it an issue, utilities have stated that the unavailability of cranes in the United States could delay installation of SCRs.

Labor requirements for the installation of the air pollution control technologies are split between two categories, general construction labor and high-skilled labor (boiler makers, pipe fitters, electricians, etc.). The following statements are based on the report “Labour Requirements for Canada and Provinces from 2005 to 2013” (7):

- In general, labor markets will be somewhat tight with potential shortages of skilled labor.

- There will be pressure for specialty trades serving the industrial sector and also on construction engineering.

- Specialty labor that would impact the utility industry, including crane operators, pipe and gas fitters, electricians, and boiler makers, are expected to have very strong markets in the next 5–10 years.

Although skilled labor may be at a premium during the next decade, it is unknown how much of an impact the installation of 10–15 FF and 20–25 ACI skids over the next 5 years would have on the overall labor market. Currently, a shortage of labor has been experienced, especially in western Canada where increased oil and gas work has led to very low unemployment. As Canadian utilities begin to bring mercury control technologies online beginning in 2008, a strong labor market is expected to exist. The continued demand for labor to support the energy industry in Canada is likely to continue well into the projected implementation period for mercury control technology.

AVAILABILITY OF SORBENTS AND ADDITIVES

Adoption of the CWS for mercury will have more stringent mercury control requirements than the U.S. CAMR, at least until CAMR Phase II occurs in 2018. Although several states are adopting more stringent controls and there will be some early adopters, it is not expected that there will be much pressure on the availability of activated carbon or chemical additives by U.S. utilities until at least 2012–2015.

Availability of Activated Carbon

There are a number of major producers of powdered activated carbon (PAC) in the United States, Canada, Europe, and China. Several of the more important ones are the following:

- NORIT Americas
- Calgon Carbon Corporation
- Nucon International, Inc.
- Luscar Ltd.
- Barneby & Sutcliffe Corp.
- RWE Rheinbraun
- Ningxia Huahui

NORIT Americas has stated (8) it currently has the capacity to provide 20–30 power plants with all the carbon they would need and not impact their current business. In addition, within several years, NORIT said, it could greatly increase its capacity if needed. Table 2 presents the PAC requirements need to achieve 50%–60% mercury removal for each power plant in Canada (1). The table does not list those plants that are scheduled to be decommissioned in the next decade or coal-fired power plants in Ontario that are expected to be shut down by 2009. It can be seen from Table 2 that the maximum PAC requirement for Canadian plants would be about 13,000 metric tons (tonne)/yr. The current worldwide installed capacity for PAC is approximately 726,000 tonne/yr of which 50% is produced in United States and China. Therefore, the maximum Canadian utility demand would be less than 2% of the overall capacity. This level of usage is not expected to put pressure on the overall market.

The availability of treated carbons is also not expected to be a concern. Both NORIT (DARCO Hg-LH) and Sorbent Technologies (B-PAC) have indicated that today they could provide brominated carbons to treat 8–10 300-MW boilers, and this capacity could easily be expanded to treat 30–50 plants within 2 years (8, 9). As was stated earlier, these treated carbons and/or halogenated additives may be the low-cost option for plants burning low-chloride lignites and subbituminous coals. Halogenated additives are usually chloride or bromide salts and are readily available from bulk chemical suppliers in the quantities required by power plants.

OPERATION AND MAINTENANCE (O&M) COSTS ASSOCIATED WITH MERCURY CONTROL

Using the report generated by Hoffman and Ratafia-Brown for DOE (5), the following are variable O&M costs associated with ACI:

- Sorbent
- Activated carbon disposal
- Power
- Operating labor
- ACI equipment maintenance
- Water (for spraying additives if used)
- Cost of money (inflation and interest)

Table 2. Potential Activated Carbon Usage in Canada Based on a Requirement of 50%–60% Mercury Removal (1)

Power Station	Net Capacity, MW	Capacity Factor	Units	ACI, lb/Macf	ACI Rate kg/hr	Total PAC tonne/yr
Alberta						
Battle River	675	88.30%	3	5–10	400–800	3100–6200
Sheerness	766	88.60%	2	5–10	440–880	3420–6840
Genesee	1212	92.30%	3	5–10	700–1400	5600–11,200
Keephills	720	89.10%	2	5–10	480–960	3750–7500
Sundance	2020	83.20%	6	5–10	1250–2480	9110–18,220
Manitoba						
Brandon	95	48.90%	1	5–10	65–130	280–560
New Brunswick						
Belldune[1]	450	92.70%	1	0	0	0
Nova Scotia						
Lingan	600	84.60%	4	4–8	260–520	1930–3860
Point Aconi[2]	165	84.00%	1	0	0	0
Point Tupper	150	91.20%	1	4–8	65–130	520–1040
Trenton	310	76.60%	2	4–8	130–260	870–1750
Saskatchewan						
Boundary Dam	814	78.60%	6	5–20	540–2220	3720–14,880
Poplar River	562	81.50%	2	5–20	360–1460	2570–10,280
Shand	279	82.80%	1	5–20	190–740	1380–5520
Total	***8834***		***35***			***36,190–87,850***

[1] Belldune is already achieving 70% mercury removal.

[2] Point Aconi is already achieving 90% mercury removal.

In addition to these items, another potential cost would be the loss of revenue from selling fly ash and the resultant increased disposal costs. If a FF were installed to prevent this loss, there would be costs associated with pressure drop (increased power requirements), general maintenance of the cost of the baghouse, and bag replacement.

Table 3 presents the total O&M cost for each plant in Canada based on the carbon usage presented in Table 2. Table 3 assumes that there is no loss of income as a result of selling the fly ash; however, the table includes the added cost of disposal. The cost of the sorbent is 93%–94% of the total O&M cost. Therefore, any technology that reduces PAC usage will have a substantial impact on O&M costs.

Table 3. Additional O&M Costs for Canadian Power Plants as a Result of Adding ACI

Power Station	Net Capacity, MW	Units	Total O&M[1] for all Units, Million US$/yr
Alberta			
Battle River	675	3	8.95–12.41
Sheerness	766	2	6.44–8.00
Genesee	1182	3	6.46–12.61
Keephills	766	2	4.44–8.66
Sundance	2020	6	11.50–22.40
Manitoba			
Brandon	95	1	0.30–0.59
New Brunswick			
Belldune	450	1	0[2]
Nova Scotia			
Lingan	600	4	1.32–4.92
Point Aconi	165	1	0[3]
Point Tupper	150	1	0.60–1.16
Trenton	310	2	1.23–2.37
Saskatchewan			
Boundary Dam	814	6	5.11–19.86
Poplar River	562	2	3.38–13.08
Shand	279	1	1.71–6.60

[1] O&M Costs are based on a report to DOE (5).
[2] Belldune is already achieving 70% mercury control (w-FGD).
[3] Point Aconi is already achieving 90% mercury control (circulating fluid bed).

MERCURY MEASUREMENT

The U.S. CAMR will require continuous mercury monitoring at each stack of coal-fired units by January 1, 2009. There are two allowable mercury measurement methods in the CAMR.

The first is to install continuous mercury monitors (CMMs), and the second is to use mercury sorbent traps. Protocols for measurement and reporting under the CWS for mercury have not yet been established, but, based on conversations with Environment Canada, these protocols will be available to the public by early spring of 2006. Although there has been some discussion that coal and hopper ash mercury concentrations can be used instead of actual stack measurements, it is possible that some form of direct mercury measurement will be required at the stack. There are essentially three direct mercury measurements methods:

- Wet chemistry methods such as the Ontario Hydro (OH) mercury speciation method (ASTM International [ASTM] D6784-02).

- Sorbent trap method (40 CFR, Part 75, Appendix K)

- CMMs (Tekran, PS Analytical, Horiba/NIC, etc.).

All three of these methods were discussed in detail in CEA Quarterly 2 – Mercury Measurement and updated in CEA Quarterly 6. Each of these methods has advantages and disadvantages.

OH Method

There are many groups in both the United States and Canada that can conduct OH method testing. However, depending on the number of samples required and the duration, testing can be expensive, and a high level of quality assurance/quality control (QA/QC) is needed. The OH method is not a continuous method and, therefore, not allowed under CAMR. However, it is the only acceptable reference method for conducting relative accuracy test assessments (RATAs).

Sorbent Trap Method (Appendix K)

Although the sorbent trap methods are relatively easy to use, there have been some problems. EPA requires that the traps be configured with three distinct, but identical, sections connected in series (the sections must be connected such that they can be analyzed separately). The first section is the primary trap for capturing the gas-phase mercury. The second section is a backup in case of mercury breakthrough. The third section is designated for QA/QC purposes and is, therefore, spiked with a known amount of elemental mercury (Hg^0). Paired traps must be used, with the mercury results averaged. It is the spiked third section that has been a source of problems. To date, the spiking of this section has not been consistent enough to ensure good recoveries (10).

The cost of the sorbent trap method is currently quite high. This is a result of limited competition in making the traps and doing the analysis. The cost for obtaining two spiked traps and doing the analyses is approximately US$1800, or about US$60,000–US$80,000/yr. This cost does not include the equipment shown in Figure 4, which is a schematic of the method (current equipment cost is US$25,000–US$30,000) or the labor required to replace the traps, about

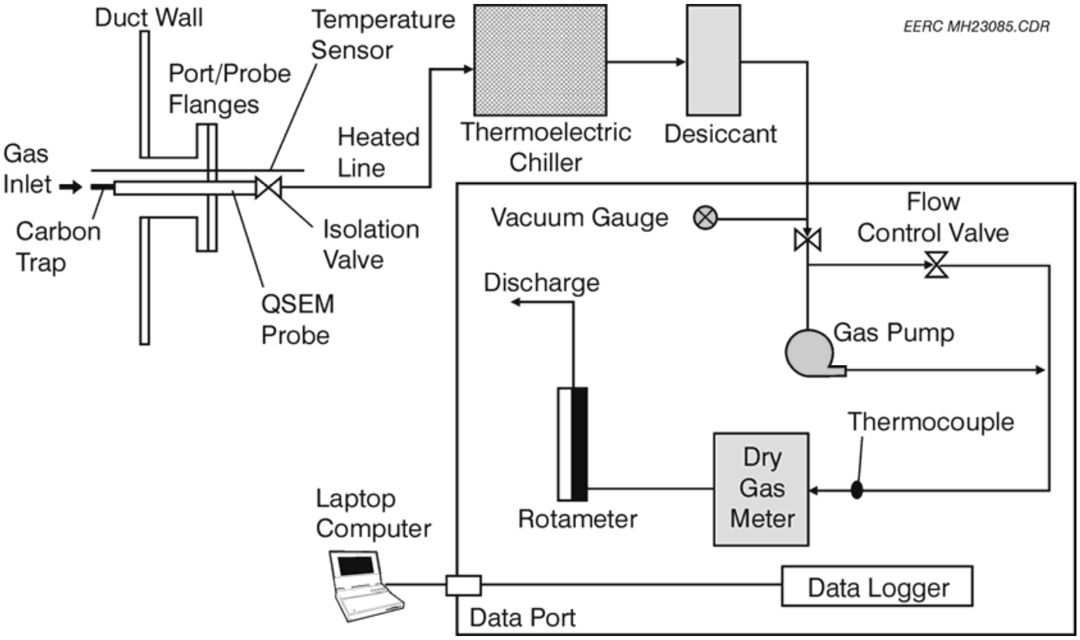

Figure 4. Schematic of the sorbent trap method.

4 hours a week. It is expected that during the next 1–2 years, costs will be reduced considerably with increased competition and the development of more cost-effective spiking and analytical methods.

Included in the CAMR protocols for the sorbent trap method is the requirement that a RATA be done each year. This requires a minimum of nine valid (as discussed in 40 CFR, Part 75, Appendix A and K) dual OH trains be completed. The U.S. utility industry is strongly urging EPA to produce a protocol that would lead to the development of an instrumental reference method to replace the OH method.

Continuous Mercury Monitors

Most facilities in the United States will opt to install CMMs. Over the past 3 years, there has been significant improvement in CMM technology. The most important improvements have been 1) the development of dry pretreatment/conversion systems, 2) the use of inertial filtration, and 3) the development of automated calibration methods. It is expected that over the next several years the technology will continue to improve as a result of performance specifications (PS 12A) being established by EPA. EPA has been conducting RATAs at two sites. To date, only three CMMs have finished the RATA, the Tekran Model 3310, Thermo Electron Mercury Freedom system, and the Horiba/NIC DM-6B. The Tekran has passed at both sites, the Thermo Electron passed at the first site (it did not finish the testing at the second site), and the Horiba/NIC failed at both sites. However, in the next 2–3 years it is expected that all three of these instruments as well as a PS Analytical system will be able to meet the PS 12A specifications. The capital cost for the complete Tekran or PS Analytical systems is about

US$200,000 and for the Thermo-Electron or Horiba/NIC, about US$180,000. Also, there are operating costs that include supplies, training, and maintenance. These cost have not yet been established as there are few long-term operating data. The Tekran analyzer has been located at Ontario Power Generation's Nanticoke Station for 18 months and has been operating quite well. This CMM is being monitored and maintained by Tekran personnel. Also two Tekrans have been operated at the slipstream test facility at SaskPower's Poplar River Station for several months with good success.

It is anticipated that in the United States during the next 3 years, 500–800 of these monitors will be ordered. With the exception of Thermo Electron and Horriba, the companies that manufacture these analyzers are small, and although many have now associated themselves with larger companies, there may be challenges in large-volume production in the near term.

BALANCE-OF-PLANT IMPACTS AS A RESULT OF MERCURY CONTROL TECHNOLOGY

If ACI is to be the primary method for reducing emissions in Canada, there are four potential impacts on plant operation, which include the following:

- Inability to sell ash to the concrete industry
- Decrease in ESP effectiveness
- Increased pressure drop in FFs
- Leaching of mercury from the ash after disposal

There are a large number of utilities in Canada and the United States that sell at least a portion of the ash collected to the concrete industry. In Canada, almost all the utilities burning lignite or subbituminous coal (SaskPower, TransAlta, EPCOR, and ATCO) have facilities selling their ash for use as an admixture in place of portland cement at varying concentrations up to as high as 50%. A review of the impacts of mercury on by-product utilization was addressed in Quarter 4, Rerelease of Mercury from Coal Combustion By-Products, which is available on CEA's Web site: www.ceamercuryprogram.ca. Therefore, any mercury control technology that prevents the sale of ash would have financial as well as environmental penalties. Increased ash to the landfill, forgone revenue from by-product sales, and increased energy consumption to manufacture portland cement not replaced with fly ash all directly result from activated carbon in fly ash. Typically, a power plant can receive US$4–US$7/tonne of ash. Ash disposal costs are US$14–US$16/tonne; a difference of US$18–US$23/tonne.

Very low levels of PAC addition to the flue gas have the potential to prevent ash use in the concrete industry. ASTM C618 puts a limit on carbon content in the concrete of 6%. However, the foam index test has failed at carbon concentrations as low as 1% when that carbon is from the injection of activated carbon. For reference, a prediction of the additional carbon that could be present in the ash for a 500-MW plant at several ACI rates is presented in Table 4. In the foam index test, set amounts of cement, fly ash, and water are placed in a jar and shaken. Drops of a concrete air-entraining admixture are added in small increments and shaken after each addition. The number of drops necessary to produce a stable foam on the surface of the cement–ash mixture is the foam index. The salable limit is 25 drops. Foam index results with ash collected from a slipstream pilot baghouse during ACI tests at WE Energy's Pleasant Prairie Station are shown in Table 5. As can be seen, even 1% carbon in the ash may not meet requirements. PAC, more than unburned carbon generated during combustion, appears to have a more detrimental impact on the foam index test. This may be a result of the higher surface area and the more extensive pore structure of PAC.

Table 4. Additional Carbon from ACI in the Ash for a 500-MW Plant

Injection Concentration, lb/Macf	Injection Rate, lb/hr	Additional Carbon in the Ash, %
10	340	4.3
5	170	2.2
2	70	0.9
1.1	40	0.5

Table 5. Carbon in Ash Foam Index Results

Injection Concentration, lb/Macf	Unburned Carbon in Ash, %	Foam Index, Drops	Comments
0	0.55	15	Acceptable
1	1.1	>72	Maxed out
3	1.6	>72	Maxed out
10	3.6	>72	Maxed out

An option for mercury control, while maintaining a marketable fly ash product, is to add a FF after the ESP. The PAC is then added between the ESP and baghouse. The bulk of the fly ash is captured in the ESP and can be used for concrete, without problematic ACI; the FF provides mercury capture and overall particulate capture improves for the plant. Initially, it was thought that a very small-footprint baghouse (air-to-cloth ratios of 8–12 ft/sec) could be used; however, because of bag blinding and pressure drop, more moderately sized baghouses (air-to-cloth ratios of 4–6 ft/sec) are now favored for these configurations.

Other potential solutions include the use of noncarbon-type sorbents, such as the amended silicates being developed by ADA Technologies or the cement-friendly carbon materials being developed by Sorbent Technologies. However, these materials are less commercially available than PAC.

For those plants that dispose of their ash in landfills, some concern exists that captured mercury will leach from the ash and enter the environment. Bench-scale tests conducted to date show that the captured mercury is very stable and does not leach from the solids (11, 12).

Following standard leaching tests, the mercury concentrations in the solution are measured in the parts-per-trillion range. As ACI is still a relatively new technology, long-term landfill leaching tests have not been done.

A long-term concern is the impact of ACI on ESP performance. Carbon is an insulator and has the potential to degrade ESP performance by limiting the power that can be applied to the electrodes without arcing. The results to date have been mixed. In short-term tests (5–10 days), there has not been any apparent impact on ESP performance as a result of carbon injection (13). However, in other short-term tests when PAC was injected prior to a small ESP (surface collection area of about 200) there was increased arcing but no detrimental effects on particulate emissions or opacity (14). The only longer-term data (1 month) reported were for the tests being conducted at the Yates Plant (15). From this test, it was concluded that carbon injection caused an increase in the arc rate of the ESP at low-load conditions, compared to arcing that occurs without ACI. There was no observed physical damage to the ESP after 1 month, but it is unclear as to the effect that the increased arcing will have on the mechanical integrity of the ESP over longer time periods. Over the next several years, a number of longer-term tests, up to 6 months, will have been conducted, and the results should clarify whether ACI will affect ESP performance. Those long-term data will be critical to support vendors' ability to provide performance guarantees on systems designed to maintain mercury emission compliance.

CONCLUSIONS

The U.S. CAMR and the acceptance in principle of a draft of the CWS for mercury illustrate the need for cost-effective mercury control strategies for coal-fired electric utilities. Recent demonstrations have shown effective mercury capture with sorbent injection at full-scale systems. Out of this effort, concerns have been raised regarding the availability of carbon, sorbents, additives, and the related capital equipment if there were widespread adoption of ACI technology. Projections by the activated carbon industry do not suggest that either the availability of activated carbon or equipment will be an issue. However, there are several areas of concern that still need to be addressed in the long term. These include the following:

- Salability of the fly ash
- The impact of ACI on ESP performance
- Longer-term leaching potential of disposed ash

Clearly, the salability of fly ash is a major concern as it does not take much carbon in the ash to render it unacceptable to the concrete industry. This would result in a substantial financial penalty for those plants currently selling ash. Further, to maintain fly ash sales, those plants may have to consider the installation of a FF specifically for mercury capture downstream of an existing ESP.

If the fly ash is to be disposed of, a concern has been that ACI is only converting one environmental problem into another. Short-term leaching tests indicated that once mercury is captured by the ash or carbon, it is very stable and does not leach to any significant degree.

However, only long-term leaching testing has not been widely conducted and will be necessary to verify the stability of mercury on carbon.

The impact of ACI on ESP performance has not yet been determined. The short duration—less than 2 months—of most of the large-scale test activities has shown no significant detriment. However, there are data for specific plants that indicate problems could arise if ACI were conducted for longer periods. In the coming year, longer-term tests of 3–12-month duration will be conducted, which should provide more conclusive information regarding the impact of ACI on ESP performance.

Currently the following conclusions can be drawn with the respect to the adoption of ACI in by Canadian utilities to meet the provincial caps as stated in the draft CWS for mercury:

- Because of the differences between the U.S. CAMR and CWS for mercury, it is not expected that U.S. utilities will be in direct competition with Canadian utilities for PAC or ACI injection until 2012 or later.
- There will not be a shortage of PAC or treated carbons or ACI equipment if Canadian utilities adopt ACI to reduce mercury emissions by 50%–60%.
- It is possible there could be a shortage of skilled labor in Canada in the next decade; especially in western Canada.
- It is clear the adoption of ACI will negatively impact the salability of the fly ash and may result in the installation of FFs.
- There is a potential for ACI to have a negative impact on ESP performance, but longer-term tests must be completed before any conclusions can be drawn.
- CMMs may be in short supply and long delivery times may occur as U.S. utilities will be required to continuously monitor mercury by January 1, 2009.
- Short-term leaching data show that the potential for mercury leaching from combustion by-products is very low; however, longer-term leaching measurements from landfills need to done.

UPCOMING EVENTS

Power-Gen International 2005 Conference & Exhibition
December 6–8, 2005, Sands Expo & Convention Center, Las Vegas, NV
http://pgi05.events.pennnet.com

Pittcon 2006
March 12–17, 2006, Orlando, FL
www.pittcon.org

231st ACS National Meeting & Exposition
March 26–30, 2006, Atlanta, GA
www.chemistry.org

Coal Ash Professionals Training Course
April 19–21, 2006, Memphis, TN
www.undeerc.org

Air & Waste Management Association Annual Conference & Exhibition
June 20–23, 2006, New Orleans, LA
www.awma.org

Eighth International Conference on Mercury as a Global Pollutant
August 6–11, 2006, Madison, WI
www.mercury2006.org/Default.aspx?tabid+1393

The Mega Meeting: Power Plant Air Pollutant Control Symposium (formerly The Mega-Symposium)
August 28–31, 2006, Baltimore, MD
www.megasymposium.org

Pittcon 2007
March 11–16, 2007, New Orleans, LA
www.pittcon.org

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