

MERCURY INFORMATION CLEARINGHOUSE



Quarter 9 – Mercury Information Clearinghouse Final Report

December 2005



Canadian Electricity Association
Association canadienne de l'électricité



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QUARTER 9 – MERCURY INFORMATION CLEARINGHOUSE FINAL REPORT

ACKNOWLEDGMENT AND DISCLAIMERS

This report was prepared under contract with the Canadian Electricity Association (CEA) and supported by funding from that organization, the Canadian Council of Ministers of the Environment, the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) Cooperative Agreement No. DE-FC26-98FT40321, and the Center for Air Toxic Metals[®] (CATM[®]) Program at the Energy & Environmental Research Center (EERC). However, any opinions, findings, conclusions, or recommendations expressed herein are the author(s) and do not necessarily reflect the views of any of the above-mentioned organizations.

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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:

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
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).

MERCURY INFORMATION CLEARINGHOUSE

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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:

- 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.

QUARTER 9 FOCUS: MERCURY INFORMATION CLEARINGHOUSE FINAL REPORT

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

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/kg¹	Chloride, mg/kg (dry)	Chlorine, 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
SaskPower²									
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.

since the effort began 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 $\mu\text{g}/\text{Rm}^3$. NSPI's Point Aconi (only continuous fluidized-bed combustor tested) measured a stack gas mercury concentration of 0.32 $\mu\text{g}/\text{Rm}^3$ (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 $\mu\text{g}/\text{Rm}^3$ 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 $\mu\text{g}/\text{Rm}^3$) 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 cobenefit of the February 2005 Clean Air Interstate Rule

Table 2. CEA Mercury Program Ash Data

Power Plant	MW	Coal Type	Blend Ratio	Bottom Ash: Fly Ash Ratio	BOTTOM ASH ANALYSIS				FLY ASH ANALYSIS				
					Moisture, %	Carbon, % (dry)	Mercury ¹ , mg/kg (dry)	Mercury, Min/Max. mg/kg*	Moisture, %	Carbon, % (dry)	Mercury, mg/kg (dry)	Mercury, Min/Max. mg/kg*	
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

Power Plant	MW/Coal Type	Method Used	Coal Mercury, mg/kg (dry)	Bottom Ash Mercury, mg/kg (dry)	Fly Ash Mercury, mg/kg (dry)	Total Hg Emissions		Speciation of Mercury Emissions		
						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.

(CAIR), which requires that a number of utilities in the eastern states install wet FGD systems for SO₂ 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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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, SO₃, 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

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

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

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 ft²/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

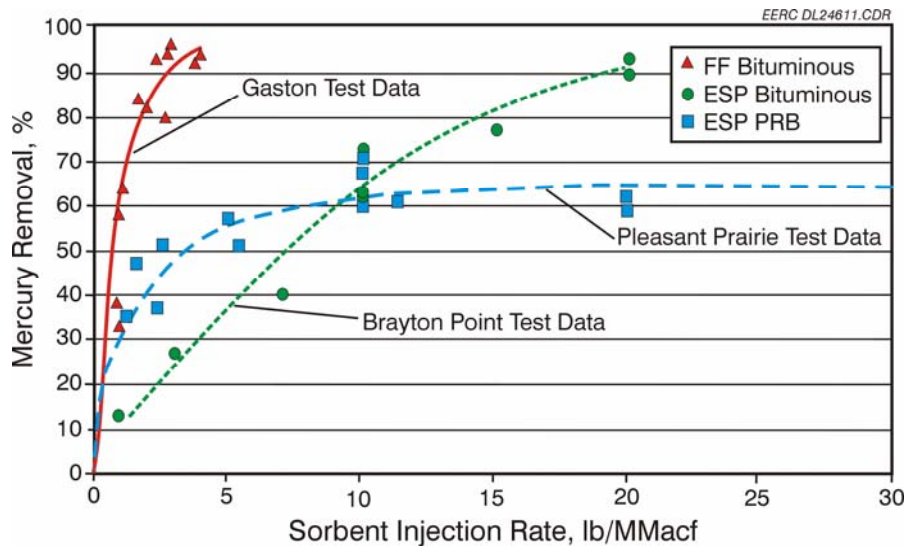


Figure 1. Mercury removal as a function of ACI rate at three sites.

did appear to be increased arcing across the ESP. However, longer-term tests need to be completed before final conclusions can be made.

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 powdered 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)
<i>Alberta</i>			
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
<i>Manitoba</i>			
Brandon	95	1	0.30–0.59
<i>New Brunswick</i>			
Belldune	450	1	0 ²
<i>Nova Scotia</i>			
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
<i>Saskatchewan</i>			
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:

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

RD ≤ 10% for Hg concentration > 1 μg / m³

or

RD ≤ 20% for Hg concentration ≤ 1 μg / m³

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 (Hg⁰) and oxidized mercury (Hg²⁺) 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 Hg⁰ gas cylinders and mercury gas generators, such as those provided by the PS Analytical and Tekran systems, for delivering Hg⁰. 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 CO₂ 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 known 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 MWe 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 SO₂ 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 NO₂ and is removed in the scrubber (the other 10% remains unoxidized). Less than 10% of the SO₂ in the gas is oxidized to form SO₃, which eventually forms sulfuric acid (H₂SO₄). 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 cases 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*TM 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

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 ($\mu\text{g/g}$) Reported	Leaching Method	Number of Samples in Sample Set	Range of Mercury Leachate Concentrations Hg, $\mu\text{g/L}$
EERC (3)	Fly ash without Hg control	40	<0.01–2.03	Batch DI H ₂ O	72	<0.01–0.32
EERC (3)	Fly ash with Hg control	28	0.15–120	Batch DI H ₂ O	43	<0.01–0.07
EERC (3)	FGD material without Hg control	10	<0.01–0.22	Batch DI H ₂ O	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 ₂ O/ HAc/ Na ₂ CO ₃ / SP/ H ₂ SO 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 ₂ O/ HAc/ Na ₂ CO ₃ / SP/ H ₂ SO 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 ₂ O	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 ₂ O	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 ₂ O	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 ₂ O	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 ₂ O	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

without and 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.

Leaching¹

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 Release²

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

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 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 $\mu\text{g/g}$ and 0.785 $\mu\text{g/g}$. The FGD material had a mercury content of 0.218 $\mu\text{g/g}$ 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 than 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/m³ (the FGD + bottom ash and mill rejects) to 1.456 ng/m³ (above FGD + mill rejects). Samples collected above natural grassland upwind from the associated power plant had 0.640 ng/m³ of mercury. For organomercury, the sample collected above the natural grassland gave a reading of 0.017 ng/m³. Samples collected above various disposal sites ranged from 0.006 ng/m³ (FGD + pyrite) to

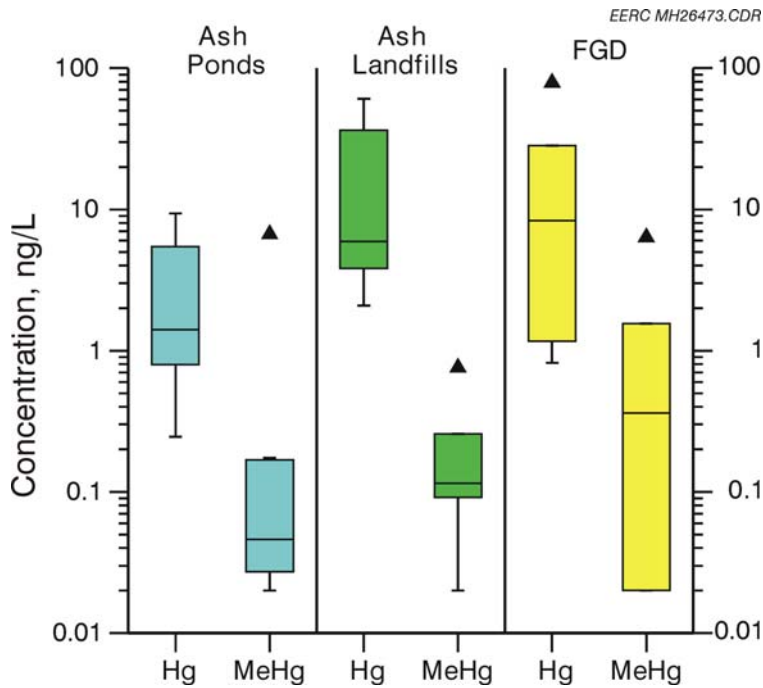


Figure 2. Field leachate – mercury speciation (15).

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

0.354 ng/m³ (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

Curing Interval	Mass Release Rate, ng/day/kg			
	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 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 $\text{Hg}(\text{II})$, 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.

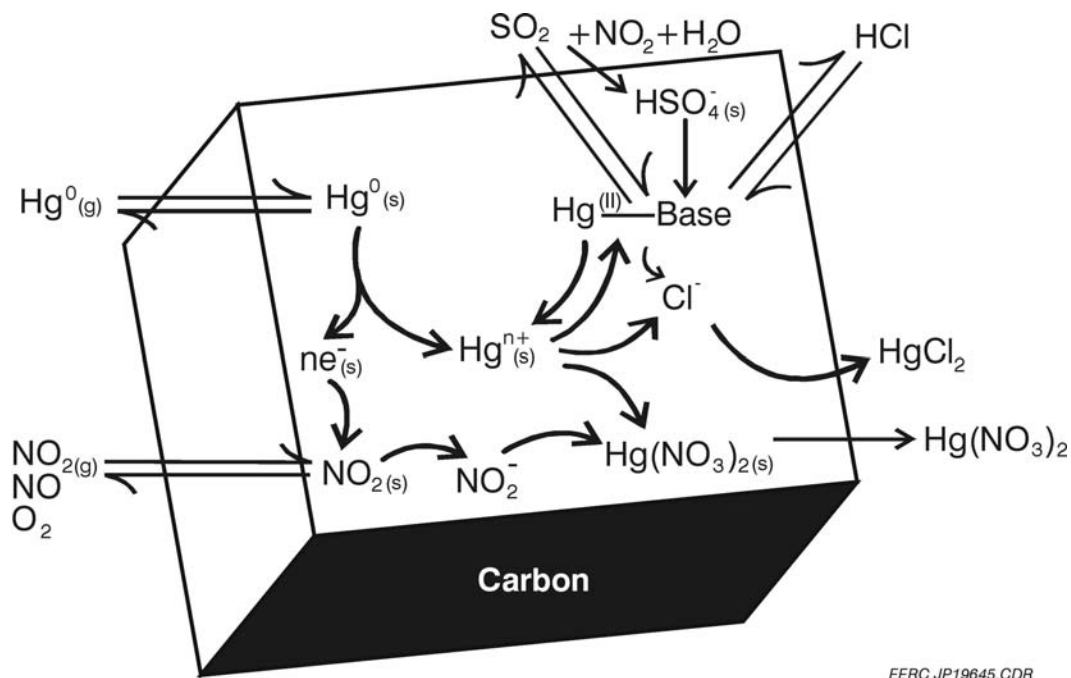
There are several facts and ideas that have been developed in the last few years that are critical to understanding how the capture of mercury takes place on a carbon sorbent in a flue gas stream. Several unequivocal pieces of evidence demonstrated that the sorption at elevated temperatures occurs via 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 $\text{Hg}(\text{II})$ 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



EERC JP19645.CDR

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

increased with decreasing particle size for the three ashes. 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 SO₂ 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, H₂SO₄, and Hg(II) compete, as shown on the left side of the figure, forming a positive carbenium ion intermediate in each case.

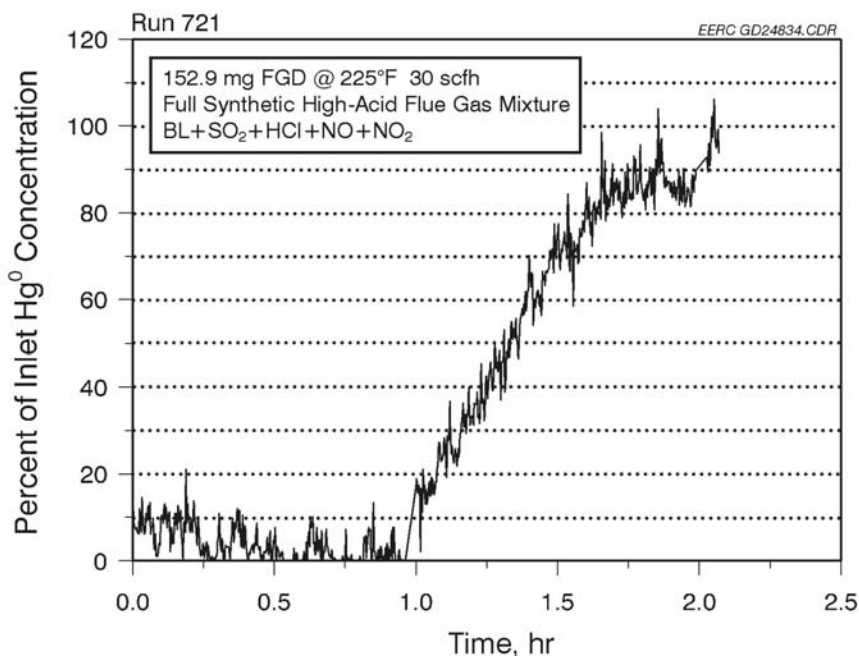


Figure 4. Breakthrough curves for high and low acid gas.

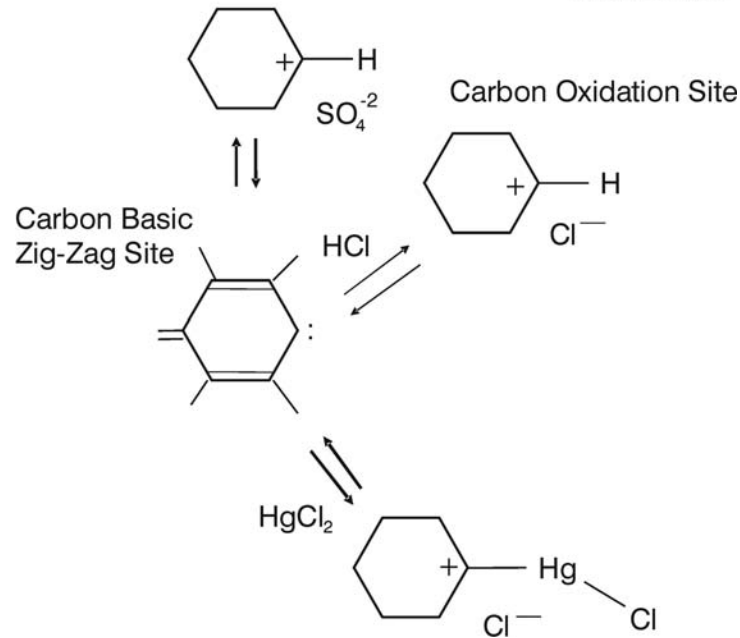


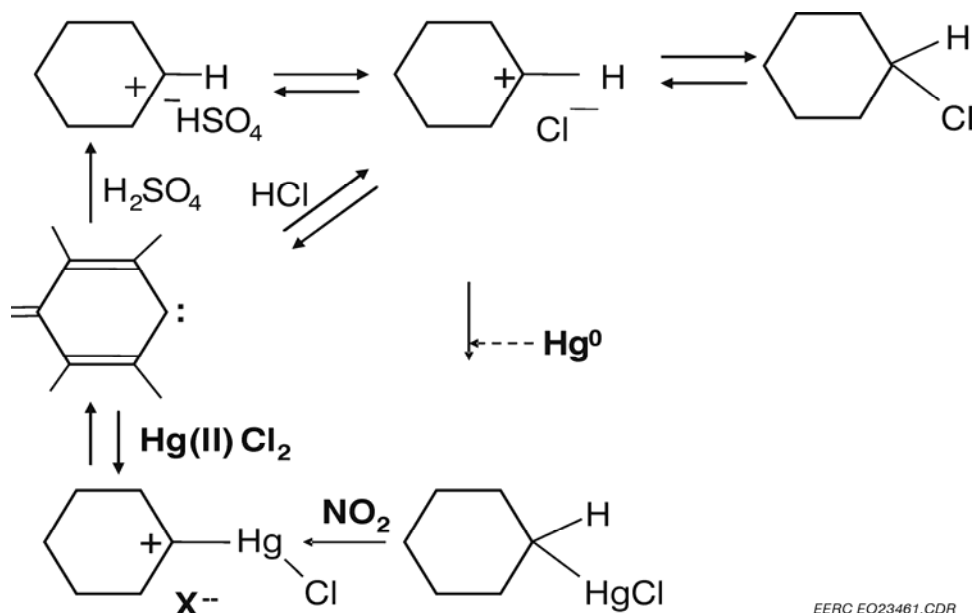
Figure 5. Mercury and acid gas-binding mechanism at carbon edge.

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 $\text{Hg}(\text{II})$ 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 ($\text{HI} > \text{HBr} > \text{HCl}$) 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,



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Figure 6. Oxidation mechanism – carbenium ion oxidant.

but 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 Hg⁰, 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 Hg⁰.

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 Cl₂. 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 SO₂ 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 Cl₂, 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.

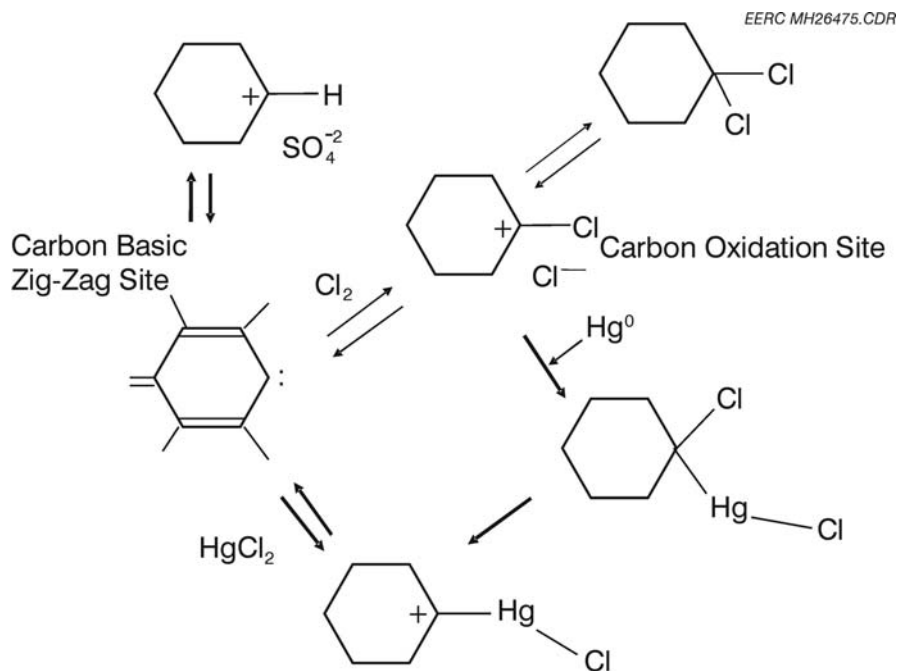


Figure 7. Mercury oxidation mechanism for chlorinated carbon.

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 (CH₃Hg) 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 CH₃Hg 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 CH₃Hg than those fed Se-adequate diets. This mechanism would also explain why maternal exposure to CH₃Hg 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 CH₃Hg 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 $1 \text{ nmol Hg/g} = 200.59 \text{ ppb}$; $1 \text{ ppm Hg} \approx 5 \text{ nmol Hg/g}$; $1 \text{ nmol Se/g} = 78.96 \text{ ppb}$, thus $1 \text{ ppm Se} \approx 12.6 \text{ nmol Se/g}$. 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).

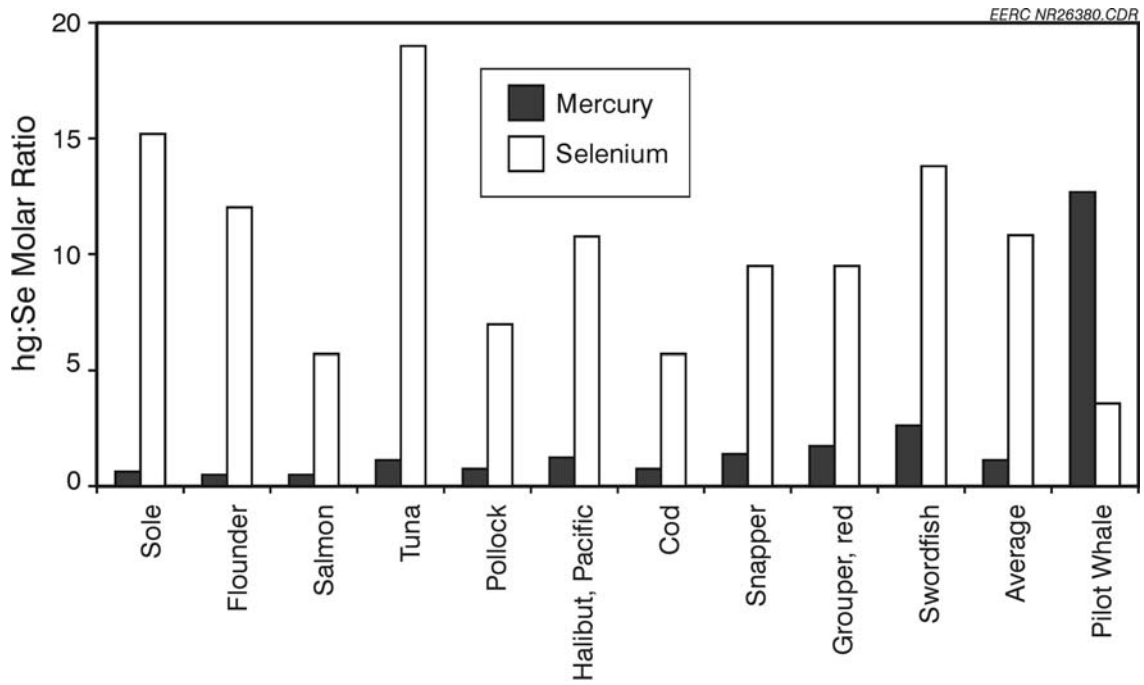


Figure 8. Molar relationships between mercury and selenium concentrations in seafood.

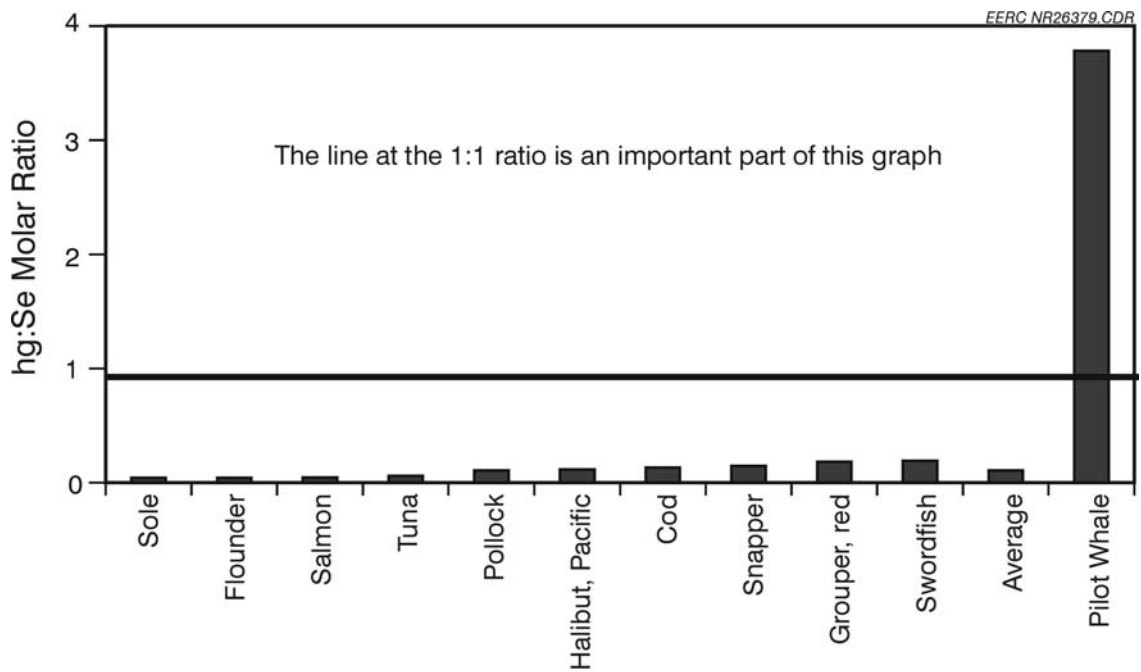


Figure 9. Molar ratio of mercury:selenium concentrations in seafood.

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,

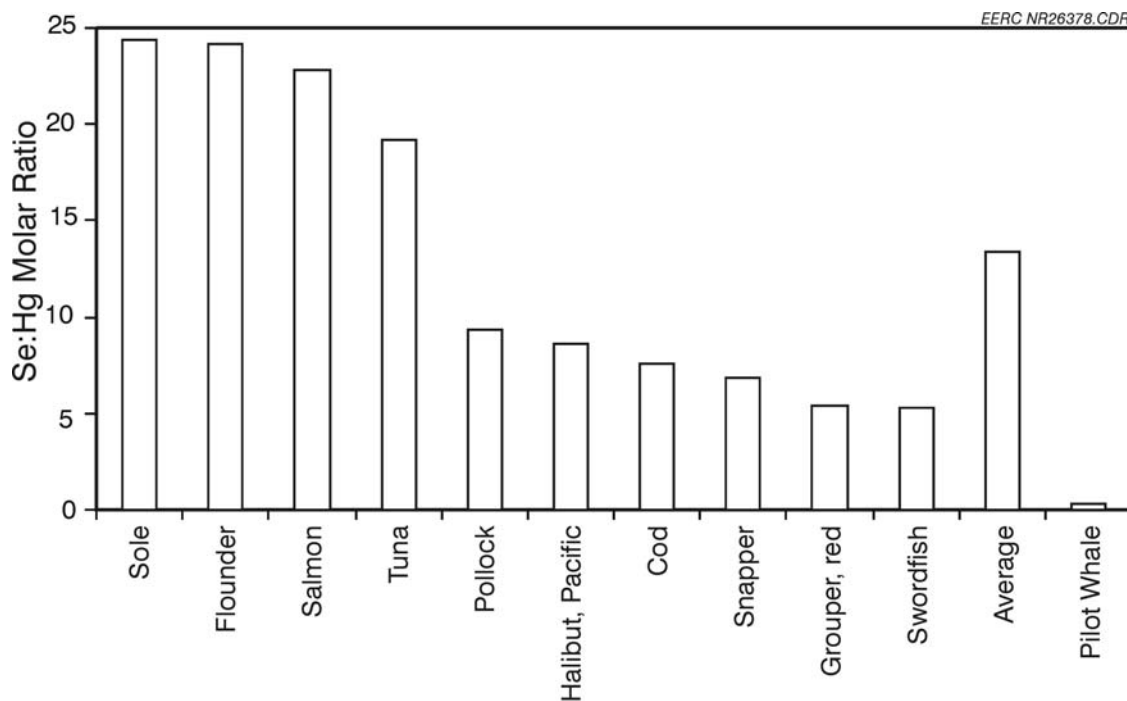


Figure 10. Molar ratio of selenium:mercury concentrations in seafood.

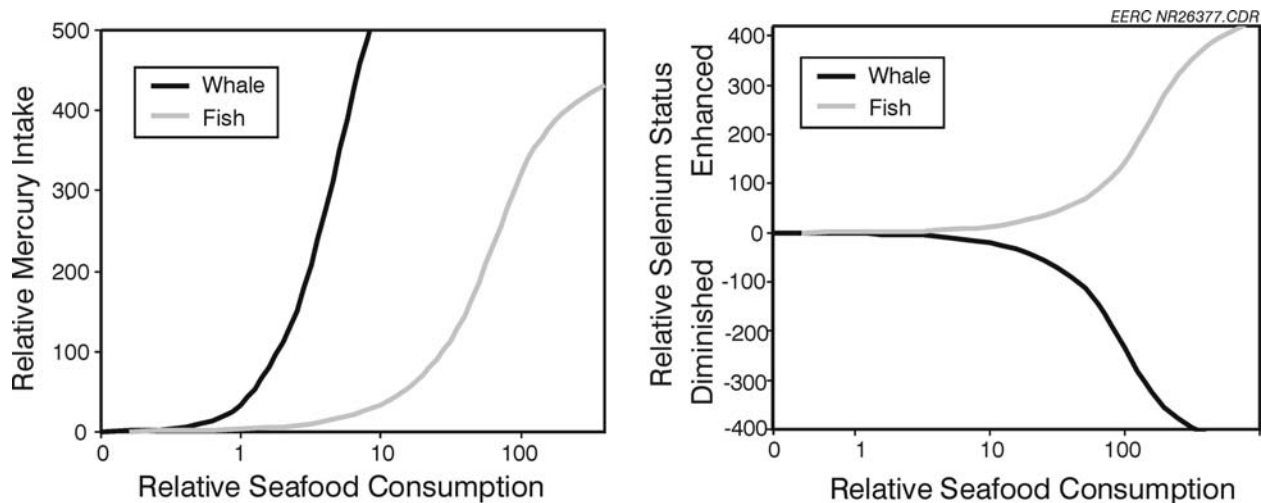


Figure 11. Relative effects of whale vs. fish consumption.

0.3 μg MeHg/wet g (17). The average MeHg level in the most contaminated species (false killer whale) was 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.

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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