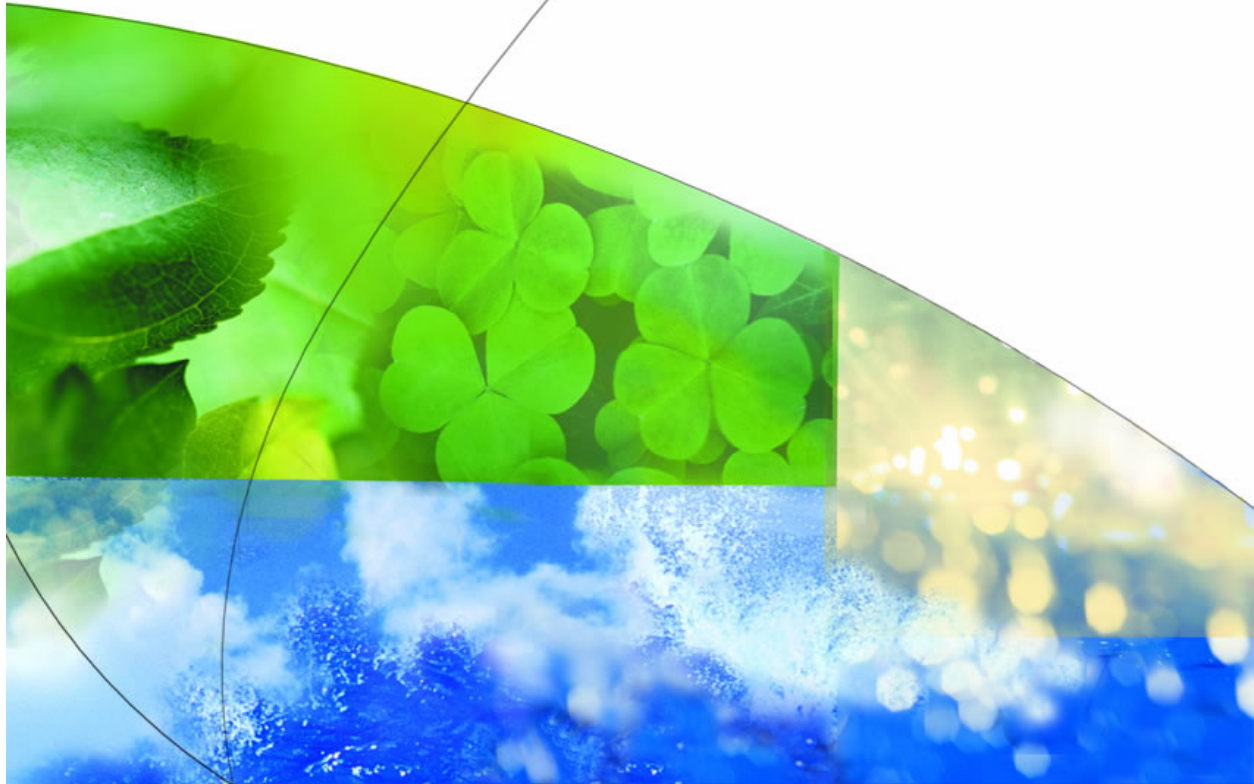


MERCURY INFORMATION **CLEARINGHOUSE**



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

October 2004



MERCURY INFORMATION CLEARINGHOUSE

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

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REPORT AVAILABILITY

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

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MERCURY INFORMATION CLEARINGHOUSE

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

EXECUTIVE SUMMARY

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

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

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

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

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

The data assembled and summarized here indicate that mercury associated with CCBs is stable and highly unlikely to be released under most management conditions, including utilization and disposal. Therefore, existing CCB management options are expected to be

environmentally sound options for CCBs from systems with mercury control technologies installed.

MERCURY INFORMATION CLEARINGHOUSE

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

INTRODUCTION

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

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

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

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

- Quarterly 3 – Advanced and Developmental Mercury Control Technologies

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

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

- Mercury policy – updated each quarter based on available information
 - Upcoming events and news releases
 - Regulation, policy, compliance strategies, and health developments
- Baseline mercury levels and emissions
- Mercury control
 - Summary of large-scale test activities and associated economics
 - Mercury oxidation and control for scrubbed systems
 - Multipollutant control strategies
 - Summary of mercury-related economics for commercial systems
- Mercury chemistry and transformations
 - Mercury chemistry fundamentals, modeling, prediction, and speciation
 - Mercury fate and transport – impacts on health

MERCURY POLICY

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

Another component of the CEA Mercury Program is the Laboratory Round Robin, a review of analytical laboratories. Developed by CEA member companies and funded by CCME,

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

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

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

- 1) Concentrate on the protection of children and pregnant women.
- 2) Stimulate and encourage early implementation of new technology.
- 3) Leverage the \$50 billion investment of the Clean Air Interstate Rule to reduce total mercury emissions.
- 4) Take into account the need to maintain America's competitiveness worldwide.
- 5) Be one component of many efforts to reduce mercury emissions.

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

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

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

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

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

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

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

BACKGROUND

Mercury and CCBs

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

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

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

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

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

Anticipated Impacts of Proposed Mercury Control Technologies on CCBs

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

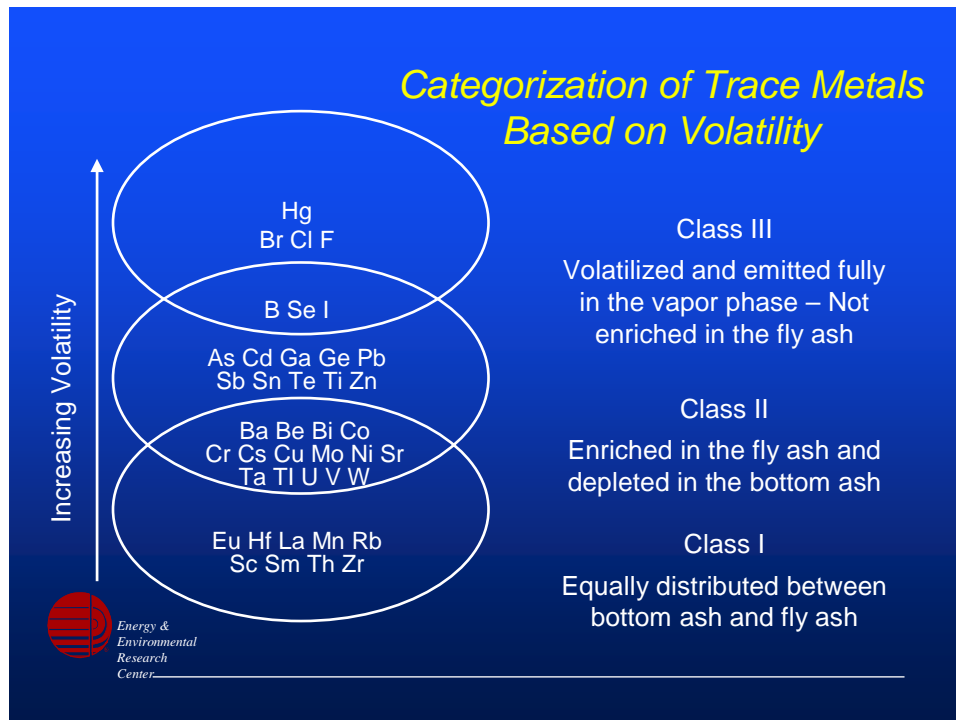


Figure 1. Categorization of trace elements based on volatility.

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

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

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

Another potential impact to CCBs from mercury control technologies is in the area of calcium-based FGD materials. It has been shown in field tests (26–28) that WFGD is successful

at removing a high percentage of oxidized mercury from the flue gas stream. Elemental mercury is not removed by WFGD, but existing WFGD systems capture approximately 90% of the mercury (II) at essentially no cost to the utility. Studies to enhance the capture of mercury in WFGD systems, generally by enhancing the oxidized mercury in the flue gas, are under way (29–38). Studies are also being performed on removing elemental mercury in WFGD systems as well as on increasing the percentage of oxidized mercury that is removed. The use of WFGD systems for mercury control has the potential to facilitate multipollutant control and may provide some impetus for utilities to consider WFGD systems over other SO₂ controls for DOE Phase II (39) and new fine-particulate control standards. It has been shown that FGD material generated from wet systems can be oxidized to produce gypsum and that mercury present in the WFGD material is partitioned into the gypsum, implying that the mercury is not readily leached from the gypsum (40). The primary effort in the area of mercury emission control using FGD systems has been performed using wet systems, although other types of calcium-based FGD systems also are expected to remove oxidized mercury from flue gas at varying efficiency levels.

STABILITY OF MERCURY ON CCBs

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

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

The total concentration of mercury on CCBs or sorbents cannot be used as an indicator of stability. The stability of mercury on CCBs or sorbents can only be evaluated by subjecting the

sample to a variety of laboratory tests that expose the material to conditions that simulate those in field settings for realistic management options for the material in question.

Leaching¹

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

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

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

¹ The authors of the various references have reported data in several different formats. The following concentrations are equivalent: ppm (parts per million) = $\mu\text{g/g}$; ppb (parts per billion) = $\mu\text{g/kg}$, ng/g , $\mu\text{g/L}$; 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. $\mu\text{g/L}$ and ng/L have been used for concentrations in liquids such as leachate concentrations.

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

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

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

¹ Sorbent injected downstream of the old ESP.

² Not applicable.

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

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

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

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

^a Replicated measurements.

^b Not detected.

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

Coal	Activated Carbon	Injection Rate, g/hr	Fly Ash (leachate) Mercury, ppm (ppb)		
			ESP	FF	Advanced Hybrid™ Filter
Poplar River	NA ^a	NA	0.030 (<0.01)	NA	NA
Poplar River	Luscar char	40–150	0.218 (0.032)	NA	NA
Poplar River	Luscar char	10–50	0.011 (<0.01)	8.66 (<0.01)	NA
Poplar River	Luscar char	20–120	NA	NA	1.15 (<0.01)
Freedom	Fine Luscar char	15–115	0.198 (<0.01)	NA	NA
Freedom	DARCO FGD	10–40	Not analyzed	17.8 (0.057)	NA
Freedom	Luscar char	10–40	0.040 (<0.01)	5.73 (<0.01)	NA
Freedom	Luscar char	10–40	NA	NA	0.865 (<0.01)

^a Not applicable.

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

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

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

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

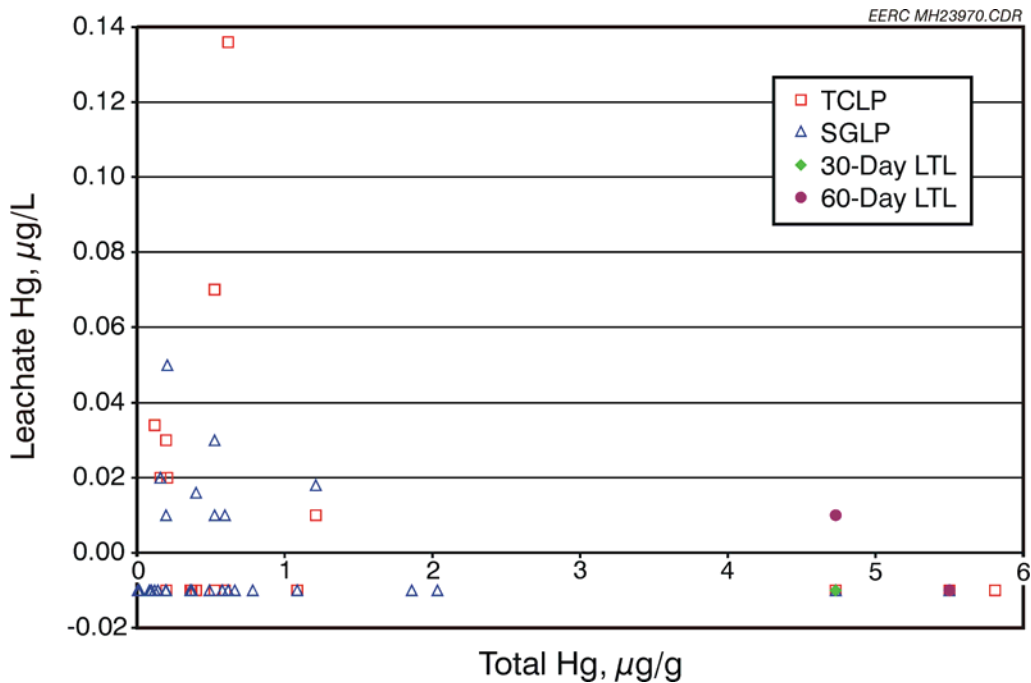


Figure 2. Leachate vs. total Hg; nondetects are shown as negative values.

Table 4. Mercury and Sulfur in Ash (50)

Run No.	Coal Type	Injection Condition	Na ₂ S ₄ in Flue Gas, ppmv	Total Hg in Ash, ppb	TCLP Hg, µg/L
6	Bit. ^a	Baseline condition	0	1.28	20.6
7	Bit.		13.5	1.94	76.8
8	Bit.	Raised flue gas temperature	13.5	1.94	76.8
9	Bit.	Lowered flue gas temperature	13.5	1.94	76.8
10	Bit.	Normal temperature	6.8	NA ^b	NA
11	Bit.	Repeat condition 2	13.5	NA	NA
12	Bit.	Inject chlorine through burner	13.5	NA	NA
13	Bit.	Half chlorine injection	13.5	2.20	69.9
14	Bit.	Maintain chlorine injection, turn off Na ₂ S ₄ injection	0	1.84 ± 0.28	70.4
15	PRB	Baseline	0	1.76	65.7
16	PRB		12.2	1.93	0.342
17	PRB		6.1	1.93	0.342
18	PRB	Return to baseline	0	1.93	0.342
19	PRB	Residual effect	2.9	1.93	0.342
20	PRB	Start fresh	2.9	NA	NA
21	PRB		6.1	NA	NA
22	PRB	Increased air injection temperature	6.1	1.29	30.5

^a Bituminous coal.

^b Not applicable.

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

Vapor Release²

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

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

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

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

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

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

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

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

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

Microbiological Vapor-Phase Release

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

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

INTERPRETATION AND CONCLUSIONS

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

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

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

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

UPCOMING EVENTS

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

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

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

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

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

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

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

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

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

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

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